Reduction of ruthenium arenecyclopentadienyl complexes Reactions induced by electron transfer

Oleg V. Gusev *, Mikhail A. Ievlev, Mikhail G. Peterleitner, Svetlana M. Peregudova, Larisa I. Denisovich, Pavel V. Petrovskii, Nikolai A. Ustynyuk

A.N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of Russia, Vavilov St. 28, 117813 Moscow, Russia

Abstract

Ruthenium arenecyclopentadienyl complexes $[Ru(\eta^5-C_5R_5)(\eta^6-arene)]^+$ (1, R = H, arene = C_6H_6; 2, R = Me, arene = C_6H_6; 3, R = H; arene = $C_6H_3Me_3$; 4, R = Me, arene = $C_6H_3Me_3$; 5, R = H, arene = C_6Me_6; 6, R = Me, arene = C_6Me_6; 7, R = Me, arene = $C_{10}H_8$) and $[Ru(\eta^5-C_9H_7)(\eta^6-C_6H_6)]^+$ (8) have been studied by cyclic voltammetry; the complexes are capable of both reduction and oxidation. The reduction peak potential values for 1–6 become more negative by about 31 mV for each Me-group at the arene ring and 61 mV for each Me-group at the cyclopentadienyl ring. Reduction of naphthalene complex 7 proceeds by two one-electron processes; the first one is reversible and the second one is irreversible. Two reversible reduction peaks were observed for indenyl complex 8. The following reactions occur on reduction of benzene complexes 1, 2 and 8 with sodium amalgam in tetrahydrofuran (THF): hydrogen atom addition to and decoordination of benzene ligand as well as dimerization of ligand-to-ligand type. Mesitylene compounds 3 and 4 form dimers $[(\eta^5-C_5R_5)Ru(\mu-\eta^5:\eta^5-Me_3H_3C_6C_6H_3Me_3)Ru(\eta^5-C_5R_5)]$ (14, R = H; 15, R = Me) in both chemical and electrochemical reduction processes. Reaction of $[Ru(\eta^5-C_5H_5)(\eta^6-C_6Me_6)]^+$ (5) with sodium amalgam in THF leads to the dimer $[(\eta^5-C_5H_5)Ru(\mu-\eta^5:\eta^5-Me_6C_6C_6Me_6)Ru(\eta^5-C_5H_5)]$ (16) as the major product; products of H-atom addition to both hexamethylbenzene and cyclopentadienyl ligands, $[Ru(\eta^5-C_5H_5)(\eta^5-C_6Me_6H)]$ (17) and $[Ru(\eta^4-C_5H_6)(\eta^6-C_6Me_6)]$ (18), are also formed in low yields. In the case of permethylated 6 only H-atom addition to hexamethylbenzene was observed and the mixture of endo-H and exo-H isomers $[Ru(\eta^5-C_5H_5)(\eta^5-C_6Me_6H)]$ (19a,b) was isolated. Reduction of 7 gives $[Ru(\eta^5-C_5Me_5)(\eta^5-C_{10}H_9)]$ (20). The modes of reaction of 19-electron radicals formed by reduction of 1–8 depend on electronic and steric properties of ligands.

Keywords: Ruthenium; Cyclopentadienyl; Arene; Cyclic voltammetry

1. Introduction

The methods of generation of platinum metal 19-electron sandwich complexes and their reactivity were recently investigated in our laboratory [1–3]. In contrast to relatively stable and well-known first row transition metals 19-electron complexes [4–6] the analogous second- and third-row transition metals complexes are highly reactive [1–3,7,8]. The electronic and steric nature of cyclopentadienyl ligands was shown to exert essential influence on the reactivity of 19-electron metallocenes for rhodocenes [1]. We report here on the chemical and electrochemical reduction of cationic

ruthenium arenecyclopentadienyl complexes and on the influence of arene and cyclopentadienyl ligands on the stability and reactivity of neutral 19-electron radicals formed in these processes.

Ruthenium neutral arenecyclopentadienyl complexes are poorly studied unlike their iron analogues $[Fe(\eta^5-Cp)(\eta^6-arene)]$ [4]. Ruthenium cationic arene complexes $[Ru(\eta^5-Cp)(\eta^6-arene)]^+$ were believed to be irreducible up to high negative potentials [9,10]. The reduction potential was determined only for one complex, $[Ru(\eta^5-C_5H_5)(\eta^6-C_6H_6)]^+$ [11]. The reduction of the latter was carried out by sodium amalgam and gave the cyclohexadienyl compound $[Ru(\eta^5-C_5H_5)(\eta^5-C_6H_7)]$ [12]. More recently, reduction of mono- and binuclear complexes bearing polyaromatic ligands as well as complexes with polyfluorenated arenes have been studied by cyclic voltammetry (CV) [13,14].

* Corresponding author. Tel.: (+7) 095 1359337; fax: (+7) 095 1355085; e-mail: shu@ineos.ac.ru.

2. Results and discussion

2.1. CV study of cationic complexes 1–8

A series of ruthenium arenecyclopentadienyl complexes was studied by CV. Acetonitrile was used as a solvent which provided solubility of all complexes in a concentration 2×10^{-3} $mol\,l^{-1}$. Although acetonitrile is known to be able to replace arenes in ruthenium complexes [15] this process did not take place in CV experiments as a decrease in the concentrations of complexes under study and formation of well-known $[Ru(\eta^5-C_5R_5)(NCCH_3)_3]^+$ were not observed. The measurements were carried out in the potential range -2.9 to $+2.5\,V$ on a carbonglass electrode. Peak potentials are listed in Table 1.

2.1.1. $[Ru(\eta^5-C_5H_5)(\eta^6-C_6H_{6-n}Me_n)]^+$ (1, n = 0; 3, n = 3; 5, n = 6) and $[Ru(\eta^5-C_5Me_5)(\eta^6-C_6H_{6-n}Me_n)]^+$ (2, n = 0; 4, n = 3; 6, n = 6)

Reduction processes are one-electron and irreversible for 1–6, indicating the high reactivity of reduction products formed. The fact that these processes are one-electron is confirmed by the similarity of the heights of the cathodic peaks to those for ferricenium used as the internal reference at the same concentration. A typical example of a cyclic voltammogram is given in Fig. 1. Except for 1, cyclic voltammograms of all complexes have the same pattern and differ only by quantitative characteristics. Values of reduction potentials are shifted to a more negative area with increasing number of methyl groups at either cyclopentadienyl or arene rings. Each methyl group at arenes induces a potential shift by 31 mV. This shift is close to that (28 mV) found for a representative set of arene transition metals complexes [16]. The comparison of three couples of cyclopentadienyl and pentamethylcyclopentadienyl complexes with the same arene ring (1 and 2, 3 and 4, 5 and 6) gives the potential shift of 61 mV with respect to one methyl

group. The similar values for other transition metal complexes are from 45 to 95 mV [1,6,17].

The oxidation peak was not found up to $+2.5\,V$ for $[Ru(\eta^5-C_5H_5)(\eta^6-C_6H_6)]^+$ (1), which is consistent with literature data [9,10]. Values of irreversible oxidation peak potentials for all other complexes (2–8) were determined. Oxidation peaks for 2–6 observed at $+1.9$ to $+2.2\,V$ (Table 1) slightly depend on the number of methyl groups in the π-ligands.

2.1.2. $[Ru(\eta^5-C_5Me_5)(\eta^6-C_{10}H_8)]^+$ (7)

The complex 7 is reduced in dichloromethane or propylene carbonate in a one-electron reversible process [13,14]. An additional one-electron irreversible reduction peak was found at $-2.78\,V$ along with a reversible peak at $-1.71\,V$ (Fig. 2) in acetonitrile as a solvent allowing expansion of the range of measurements. The second reduction peak corresponds to the second electron transition; the resulting 20-electron anion is unstable. It is noteworthy that the first reduction peak was observed at less negative potential values than reduction peaks for 1–6. The 0.31 V anodic displacement of the $[Ru(\eta^5-C_5Me_5)(\eta^6-C_{10}H_8)]^+$ (7) reduction potential vs. that of the $[Ru(\eta^5-C_5Me_5)(\eta^6-C_6H_6)]^+$ (2) is comparable with the same shift for iron analogues [18]. The difference between the first and the second reduction peak potentials of 7 is quite characteristic (1.07 V) for Group VIII metal sandwiches [1,3,4,8].

An irreversible oxidation peak of 7 was observed at $+1.71\,V$ (Table 1, Fig. 2), i.e. at the less positive potential compared to that for 2. The analogous changes of oxidation peak potential on passing from naphthalene to benzene complexes were also found for chromium complexes [19].

2.1.3. $[Ru(\eta^5-C_9H_7)(\eta^6-C_6H_6)]^+$ (8)

Cyclic voltammetry of complex 8 showed two one-electron reduction peaks at -1.68 and $-1.93\,V$ (Fig. 3). The first cathodic peak of 7 is shifted to less negative values ($\Delta E = 0.34\,V$) vs. that for cyclopentadienyl complex 1. The reduction potentials of rhodium [1] and cobalt [20] indenyl complexes exhibit the same tendency to change.

The difference between the first and the second reduction peak potentials is too small (0.25 V) in comparison with that for other complexes (for example, 1.07 V for 7). The closely spaced reduction peaks could indicate that the reduction process is followed by structural changes [16,21–27]. It could be proposed that the indenyl ligand is responsible for the structural changes because an analogous situation was not observed for 1–7. A decrease of indenyl ligand hapticity ($\eta^5 \rightarrow \eta^3$) is the most probable process in this case (Scheme 1), as it was shown for manganese complexes [21,23]. The data obtained do not allow one to conclude whether the

Table 1
Cyclic voltammetry data for complexes 1–8 ($c = 2 \times 10^{-3}$ $mol\,l^{-1}$; CH_3CN, 0.1 M Bu_4NBF_4; $v = 200\,mV\,s^{-1}$; reference electrode SCE)

Complex		E_{pc} (V)	E_{pa} (V)
$[Ru(\eta^5-C_5H_5)(\eta^6-C_6H_6)]^+$	(1)	-2.02	—
$[Ru(\eta^5-C_5Me_5)(\eta^6-C_6H_6)]^+$	(2)	-2.32	$+2.11$
$[Ru(\eta^5-C_5H_5)(\eta^6-C_6H_3Me_3)]^+$	(3)	-2.13	$+2.25$
$[Ru(\eta^5-C_5Me_5)(\eta^6-C_6H_3Me_3)]^+$	(4)	-2.41	$+2.12$
$[Ru(\eta^5-C_5H_5)(\eta^6-C_6Me_6)]^+$	(5)	-2.18	$+2.00$
$[Ru(\eta^5-C_5Me_5)(\eta^6-C_6Me_6)]^+$	(6)	-2.51	$+2.13$
$[Ru(\eta^5-C_5Me_5)(\eta^6-C_{10}H_8)]^+$	(7)	-1.71	$+1.71$
		-2.78	
$[Ru(\eta^5-C_9H_7)(\eta^6-C_6H_6)]^-$	(8)	-1.68	$+1.75$
		-1.93	
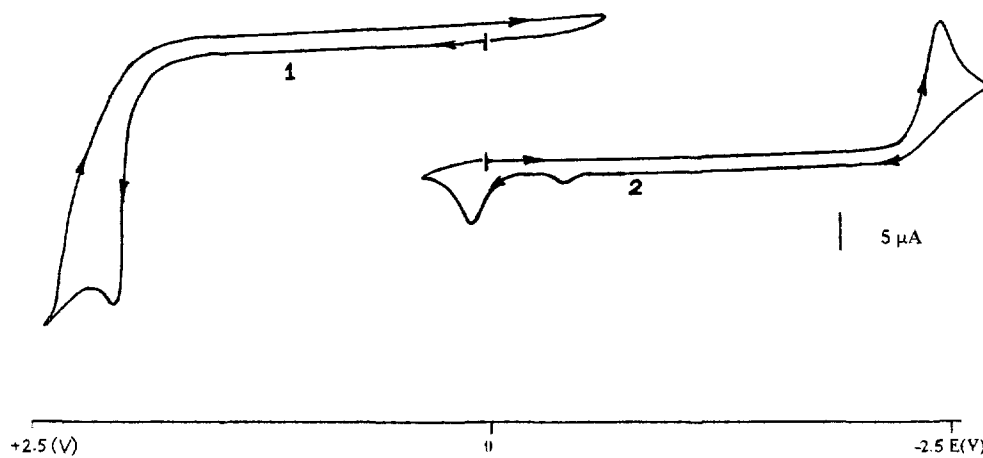
Fig. 1. Cyclic voltammogram of [Ru(η^5-C$_5$Me$_5$)(η^6-C$_6$Me$_6$)]$^+$ PF$_6^-$ (6) in H$_3$CCN (v = 200 mV s^{-1}); (1) oxidation, (2) reduction.
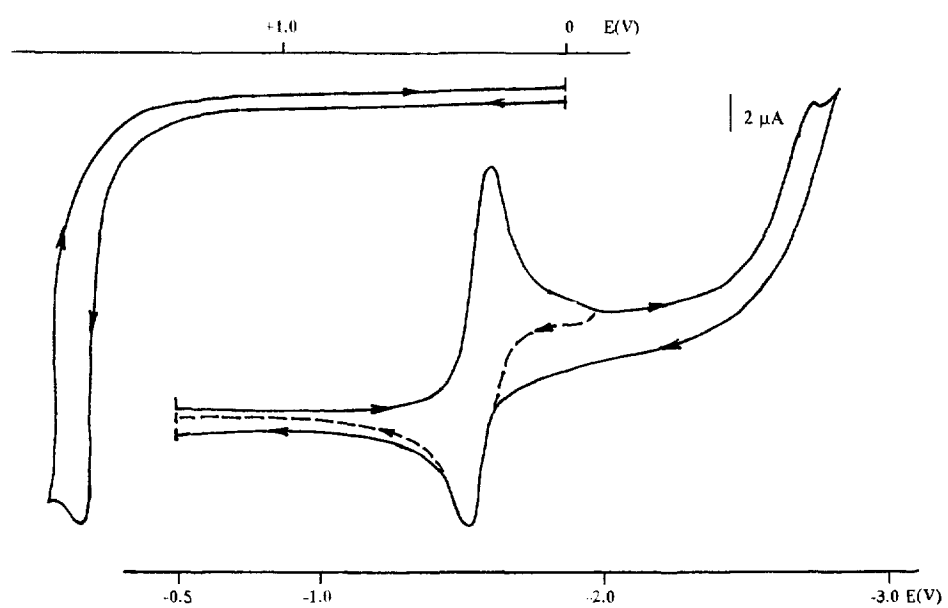
Fig. 2. Cyclic voltammogram of [Ru(η^5-C$_5$Me$_5$)(η^6-C$_{10}$H$_8$)]$^+$ PF$_6^-$ (7) in H$_3$CCN (v = 200 mV s^{-1}).
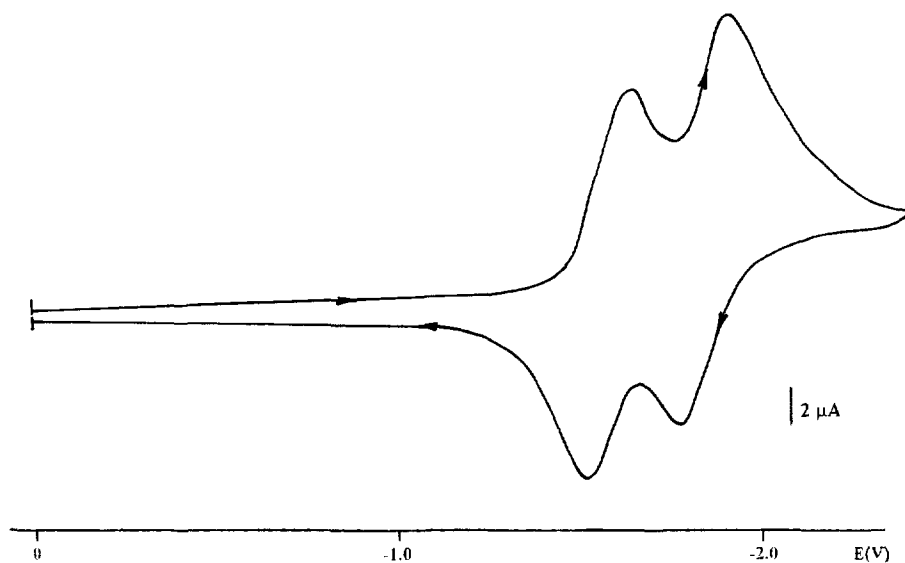
Fig. 3. Cyclic voltammogram of [Ru(η^5-C$_9$H$_7$)(η^6-C$_6$H$_6$)]$^+$ PF$_6^-$ (8) in H$_3$CCN (v = 200 mV s^{-1}).
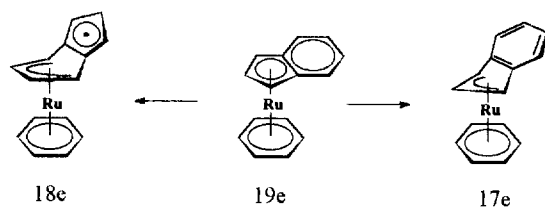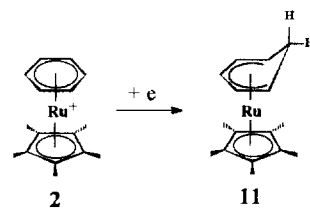
Scheme 1.

Scheme 3.

first or the second electron transfer process induces structural changes; both opportunities have been discussed in the literature [16,21–27].

Another possibility is the haptotropic shift of the [Ru(η^6-C$_6$H$_6$)] moiety from a five- to a six-membered ring of the indenyl ligand and formation of 18-electron η^4:η^6-bis(arene) complexes bearing unpaired electron density at the uncoordinated ring (Scheme 1). Haptotropic rearrangements are low barrier processes for 19-electron indenyl and fluorenyl complexes [28].

The oxidation peak potential of [Ru(η^5-C$_9$H$_7$)(η^6-C$_6$H$_6$)]$^+$ (**8**) was found at less positive values than that for [Ru(η^5-C$_5$Me$_5$)(η^6-C$_6$H$_6$)]$^+$ (**2**), as was observed for the couple [Ru(η^5-C$_9$H$_7$)(η^5-C$_5$H$_5$)]/[Ru(η^5-C$_5$Me$_5$)(η^5-C$_5$H$_5$)] earlier [29]. The similar influence of the indenyl ligand on the oxidation potentials was discussed [29,30].

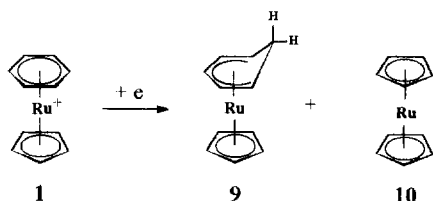### 2.2. Reduction of ruthenium arenecyclopentadienyl complexes

2.2.1. Reduction of [Ru(η^5-C$_5$R$_5$)(η^6-C$_6$H$_6$)]$^+$ (1, R = H; 2, R = Me) and [Ru(η^5-C$_9$H$_7$)(η^6-C$_6$H$_6$)]$^+$ (8)

Reduction of **1** with sodium amalgam in THF or pentane–water was reported to afford cyclohexadienyl complex **9** in low yield [12]. Our attempts to repeat such a reduction of **1** (sodium amalgam, THF) have led to the mixture of **9** and ruthenocene **10** in ratio 2:1 (^{1}H NMR data) (Scheme 2).

Presumably a 19-electron radical initially formed in the reaction is unstable similarly to an iron analogue [Fe(η^5-C$_5$H$_5$)(η^6-C$_6$H$_6$)] [31,32]. Partial decomposition of these radicals generates a cyclopentadienyl anion which reacts further with [Ru(η^5-C$_5$H$_5$)(η^6-C$_6$H$_6$)] radical to give **10** via benzene ligand substitution by analogy with the same process for an iron complex [33].

Reduction of **2** under the same conditions led to formation of cyclohexadienyl complex **11** as a sole

product in 58% yield. The formation of [Ru(η^5-C$_5$Me$_5$)$_2$] and products of decomposition was not observed in this case probably due to the higher stability of the pentamethylcyclopentadienylruthenium–benzene bond in comparison with the cyclopentadienylruthenium–benzene bond as was found for iron analogues [31,32] (Scheme 3).

Electrochemical reduction of [Ru(η^5-C$_9$H$_7$)(η^6-C$_6$H$_6$)]$^+$ (**8**) was carried out at −2.4 V, which is more negative than the second reduction peak potential of **8** (Table 1, Fig. 3). After one electron was passed through the solution a current decreased from 18 to 2 mA, cyclic voltammetry showed the absence of peaks of **8** and the electrolysis was stopped. The resulting solution was evaporated and the residue was crystallized from benzene–hexane. The crystalline product isolated is a dimer **12**; the mother liquor contains a mixture of **12** and mononuclear cyclohexadienyl complex **13**. Both **12** and **13** result from the initially formed one-electron reduction product in accordance with coulometry data. Apparently, the radical [Ru(η^5-C$_9$H$_7$)(η^6-C$_6$H$_6$)] is stable on the CV time scale but it undergoes chemical transformation rather than accepting the second electron during electrolysis.

The same products **12** and **13** were obtained when **8** was reduced by sodium amalgam in THF (Scheme 4).

Increased stability of [Ru(η^5-C$_9$H$_7$)(η^6-C$_6$H$_6$)] radical in comparison with [Ru(η^5-C$_5$R$_5$)(η^6-C$_6$H$_6$)] (R = H, Me) radicals is probably caused by the ability of indenyl ligand to delocalize electron density. This could be the reason why the dimerization is more preferable in this case than H-atom abstraction from solvent.

The complexes obtained **9**, **11**, **12** and **13** were characterized by NMR spectroscopy. The resonances of *exo*-H and *endo*-H atoms bonded to the sp^3-hybridized
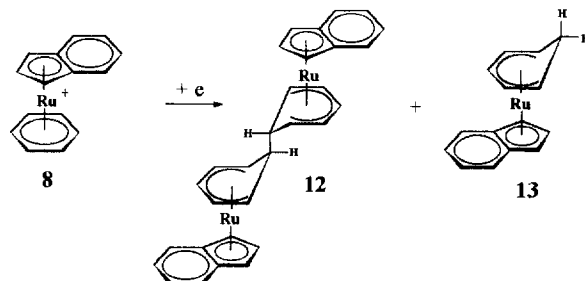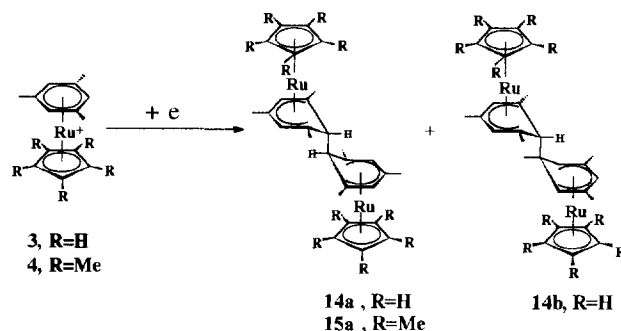

Scheme 2.

Scheme 4.

carbon atom appear as multiplets at 1.6–3.0 ppm for complexes **9**, **11**, and **13** while the *endo*-H atom in dimer **12** gives a singlet at 3.0 ppm. The ^{13}C NMR spectra for complexes **9** and **11** show signals of sp^3-carbon atom at 22.6 ppm and 29.8 ppm respectively and at 50.4 ppm for complex **12**. Signals of the other atoms of cyclohexadienyl fragments are similar for all four complexes **9**, **11–13** and observed at 2.5–2.7 and 30–33 ppm, 4.0–4.5 and 70–80 ppm, and 5.0–5.8 and 78–88 ppm in ^{1}H and ^{13}C NMR spectra respectively (Tables 2 and 3). The signals of η^5-ligands (C_5H_5, C_5Me_5 and C_9H_7) in compounds **9** and **11–13** have expected shifts and spin–spin coupling constants.

2.2.2. Reduction of [Ru(η^5-C$_5$R$_5$)(η^6-C$_6$H$_3$Me$_3$)]$^+$ (3, R = H; 4, R = Me)

Chemical reduction of [Ru(η^5-C$_5$H$_5$)(η^6-C$_6$H$_3$Me$_3$)]$^+$ (**3**) (sodium amalgam, THF) and preparative electrochemical reduction of [Ru(η^5-C$_5$Me$_5$)(η^6-C$_6$H$_3$Me$_3$)]$^+$ (**4**) (−2.5 V, THF) gave a mixture of dimers in each case. The predominant isomers **14a** and **15a** contain mesitylenes linked through unsubstituted carbon atoms. An additional asymmetric isomer **14b** was also found in the mother liquor on reduction of **3**; the yield of **14b** is approximately 5%. The asymmetric isomer **15b** as well as dimers containing mesitylene ligands linked through two methyl-substituted carbon atoms were not observed (Scheme 5).

The ^{1}H and ^{13}C NMR spectra of symmetric dimers **14a**, **15a** are quite similar except for the signals of the C_5H_5- and C_5Me_5-rings and negligible differences of the resonances of μ-η^5:η^5-C$_6$Me$_3$H$_3$C$_6$Me$_3$H$_3$ ligands

(Tables 2 and 3). The bis-cyclohexadienyl ligands are observed as four singlets at 1.78; 1.98; 2.31 and 4.24 ppm (**14a**); 1.63; 1.86; 2.10 and 3.60 ppm (**15a**) in the ratio 6:1:3:1 respectively in ^{1}H NMR spectra. The ^{13}C NMR spectra of **14a** and **15a** exhibit resonances of sp^3-carbon atoms of μ-η^5:η^5-C$_6$Me$_3$H$_3$C$_6$Me$_3$H$_3$ ligand at 59.0 (**14a**) and 58.4 ppm (**15a**); the CMe-groups show signals at 21.3, 27.1, 40.9 and 90.5 ppm (**14a**) and 19.2, 24.2, 41.4 and 86.7 ppm (**15a**). The two signals of the C_5H_5-rings at 4.52 and 4.59 ppm with a 1:1 ratio are observed in the ^{1}H NMR spectrum of **14b**. The μ-η^5:η^5-C$_6$Me$_3$H$_3$C$_6$Me$_3$H$_3$ ligand is represented by eight singlets 1.29, 1.47, 1.81, 1.83, 2.27, 2.37, 4.33 and 5.72 in the ratio of 3:1:6:6:3:2:2:1, indicating the non-symmetric structure of the ligand.

Reduction-induced dimerization of 19-electron manganese η^6-mesitylene radical [Mn(η^6-C$_6$H$_3$Me$_3$)(CO)$_3$] was reported to proceed as coupling of two mesitylene ligands so that either two methyl-substituted ring car-

Scheme 5.

Table 2
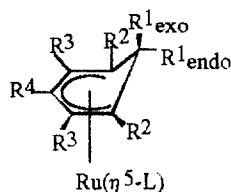^{1}H NMR data for reduction products of 1–6.8 (C_6D_6, δ (Hz), reference to TMS)

Ru(η^5-L)
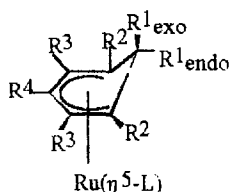
Complex	R^1_{exo}, R^1_{endo}	R^2	R^3	R^4	L
9	2.55–2.75 m 1H, 2.85–3.00 m 1H	2.55–2.75 m 2H	4.45 dd 2H (6; 5)	5.76 t 1H (5)	4.72 s C_5H_5
11	1.60–1.95 m 2H	2.53 m 2H	4.08 dd 2H (6; 5)	5.20 t 1H (5)	1.87 s C_5Me_5
12	3.00 s 1H	2.72 t 2H (6)	4.08 dd 2H (6; 5)	5.00 t 1H (5)	5.23 d 2H (2); 5.28 t 1H (2); 6.81 m 2H; 7.22 m 2H; C_9H_7
13	2.33 dd 1H$_{endo}$ (12; 6); 2.50 d 1H$_{exo}$ (12)	2.59 dd 2H (6; 6)	4.24 dd 2H (6; 5)	5.22 t 1H (5)	5.29 d 2H (2); 5.44 t 1H (2); 6.87 m 2H; 7.27 m 2H; C_9H_7
14a	1.98 s 2H	1.78 s 2Me	4.24 s 2H	2.31 s Me	4.50 s; C_5H_5
14b	1.29 s Me; 1.47 s 1H	1.81 s 2Me; 2.37 s 2H	1.83 s 2Me; 4.33 s 2H	2.27 s Me; 5.72 s 1H	4.52 s; C_5H_5; 4.59 s; C_5H_5
15a	1.86 s 1H	1.63 s 2Me	3.60 s 2H	2.10 s Me	1.76 s C_5Me_5
16	1.31 s Me	1.55 s 2Me	2.01 s 2Me	2.40 s Me	4.32 s C_5H_5
17	0.46 d Me (6); 2.46 q 1H (6)	1.80 s 2Me	1.98 s 2Me	2.39 s Me	4.40 c C_5H_5
19a	0.55 d Me (6); 2.22 q 1H (6)	1.53 s 2Me	1.95 s 2Me	2.10 s Me	1.70 s C_5Me_5
19b	0.82 d Me (6); 2.33 q 1H (6)	1.42 s 2Me	1.53 s 2Me	2.10 s Me	1.72 s C_5Me_5

Table 3
^{13}C NMR data for reduction products of **1–6,8** (C_6D_6, δ (Hz), reference to TMS)

Ru(η 5-L)

Complex	$CR^1_{exo}R^1_{endo}$	CR^2	CR^3	CR^4	L
9	22.6 CH_2	30.2 CH	70.5 CH	78.8 CH	75.5 C_5H_5
11	29.8 CH_2	32.9 CH	80.2 CH	88.5 CH	11.1 C_5Me_5, 79.4 C_5Me_5
12	50.5 CH	31.2 CH	69.8 CH	77.5 CH	79.0 C^1H, 109.6 C^2H, 117.6 C^q, 122.6 C^4H, 124.5 C^5H, C_9H_7
14a	59.0 CH	27.1 C*Me*, 40.9 C*Me*	79.3 CH	21.3 C*Me*, 90.5 C*Me*	77.7 C_5H_5
15a	58.4 CH	24.2 C*Me*, 41.4 C*Me*	81.9 CH	19.2 C*Me*, 86.7 C*Me*	10.2 C_5Me_5, 87.2 C_5Me_5
16	30.2 C*Me*, 52.4 C*Me*	19.0 C*Me*, 46.6 C*Me*	24.4 C*Me* 89.6 C*Me*	18.0 C*Me*, 90.2 C*Me*	79.7 C_5H_5
19a	13.8 C*Me*H, 49.6 C*Me*H	14.8 C*Me*, 39.2 C*Me*	19.7 C*Me*, 87.2 C*Me*	20.1 C*Me*, 90.5 C*Me*	9.4 C_5Me_5, 86.0 C_5Me_5

bons or C(H) and C(Me) couples were involved in the formation of the C–C-bond [34]. As the [Mn(CO)$_3$] group is a poor electron donor the inductive effect of electron-releasing methyl groups can enhance an electron density at methyl-substituted ring-carbons making them preferable for coupling. But this difference between substituted and unsubstituted carbons should be leveled in 19-electron mesitylene ruthenium radicals due to the strong electron donor ability of [Ru(η^5-C$_5$R$_5$)] (R = H, Me) moieties. Therefore the formation of **14a** and **15a** is stipulated by the fact that there is no additional steric hindrance exerted by methyl groups in these complexes.

It should be outlined that unlike benzene compounds **1** and **2**, the reduction of **3** and **4** did not give mononuclear cyclohexadienyl complexes. This could be explained by the increasing kinetic stability of 19-electron radicals with the increase of the number of methyl groups at arenes [16]. Therefore radical dimerization becomes more preferable than interaction with the solvent.

2.2.3. Reduction of [Ru(η⁵-C₅R₅)(η⁶-C₆Me₆)]⁺ (5, R = H; 6, R = Me)

The reduction of [Ru(η^5-C$_5$H$_5$)(η^6-C$_6$Me$_6$)]$^+$ (**5**) with sodium amalgam in THF leads to dimer **16** in 58% yield. The reduction of analogous iron complex [Fe(η^5-C$_5$H$_5$)(η^6-C$_6$Me$_6$)]$^+$ is known to give a stable 19-electron radical, which does not dimerize unlike the less methylated compounds [31,32]. Probably the 19-electron ruthenium complexes are more inclined to hapticity change and to electron density redistribution that is characteristic for other odd-electron compounds of second- and third-row transition metals [6,16,24–27,32] compared to the first row metals analogues.

Two minor products of H-atom addition to hexamethylbenzene and cyclopentadienyl ligands, **17** and **18**,

were found by ^{1}H NMR spectroscopy in the reaction mixture along with **16**. The content of **17** and **18** is approximately 10% and 5% respectively. The formation of **18** is a rare example of the reaction proceeding through the cyclopentadienyl ring in 19-electron arenecyclopentadienyl complexes (Scheme 6).

Four signals of methyl groups at 1.31, 1.55, 2.01 and 2.40 ppm in the ratio 1:2:2:1 and at 18.0, 19.0, 24.4 and 30.2 ppm are observed in ^{1}H and ^{13}C NMR spectra of dimer **16** respectively. Four signals of quaternary carbon atoms at 46.6, 52.4, 89.6 and 90.2 ppm belonging to the bridged cyclohexadienyl μ-η^5:η^5-C$_6$Me$_6$C$_6$Me$_6$ ligand are also observed in the ^{13}C NMR spectrum.

The signals of the CHMe-group of complex **17** appear as a doublet at 0.46 ppm (3H; $J = 6$ Hz) and corresponding quartet at 2.46 ppm (1H; $J = 6$ Hz) in the ^{1}H NMR spectrum. The signals of the other methyl groups of compound **17** are the singlets at 1.80, 1.98 and 2.39 ppm in the ratio of 2:2:1.

The intense singlet at 2.10 ppm of coordinated hexamethylbenzene is observed in the ^{1}H NMR spectrum of **18**. The CH$_2$-group of the η^5-cyclopentadiene ligand gives an AB-spectrum (δ(A) = 2.84 ppm; δ(B) = 3.76 ppm; J_{AB} = 10 Hz); the signals of the hydrogen atoms in α- and β-position to CH$_2$-group are observed as multiplets at 2.31 and 4.69 ppm.

Complex [Ru(η^5-C$_5$Me$_5$)(η^6-C$_6$Me$_6$)]$^+$ (**6**) was reduced electrochemically (− 2.6 V, THF, Hg-electrode)
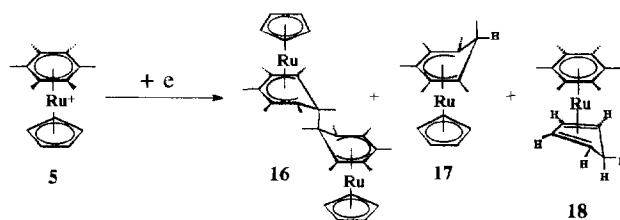
Scheme 6.
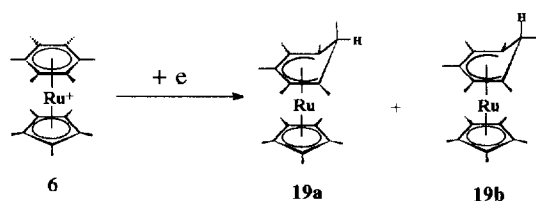
Scheme 7.

affording the mixture of hexamethylcyclohexadienyl isomers **19a,b** (Scheme 7).

Unfortunately it is impossible to determine whether the *exo*-H or *endo*-H isomer is dominant on the basis of ^{1}H NMR data. The ratio of isomers is 1:6.

The different behavior of the hexamethylbenzene complexes **5** and **6** can be explained by the very high electron density in permethylated **6** stipulating the fact that the H-atom abstraction process occurs more rapidly than dimerization.

2.2.4. Reduction of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_{10}H_8)]^+$ (7)

As mentioned above, one electron reversible reduction peak was observed on the cyclic voltammogram of **7** at a scan rate $200\,mV\,s^{-1}$. It was proposed on the basis of CV data [13] that the short living radical $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_{10}H_8)]$ undergoes decomplexation rather than other reactions. Nevertheless, reduction of **7** with sodium amalgam in THF gave $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_{10}H_9)]$ (**20**) as the product of H-atom addition to naphthalene ligand (Scheme 8).

Compound **20** was characterized by microanalysis and spectroscopically. The only set of signals observed in ^{1}H and ^{13}C NMR spectra of complex **20** indicates that the one isomer has been formed predominantly on the reduction of complex **7**. The ^{1}H NMR spectrum of **20** is similar to that reported for $[Mn(\eta^5\text{-}C_{10}H_9)(CO)_3]$ [35]. The hydrogen atoms of the coordinated ring of $\eta^5\text{-}C_{10}H_9$ ligand give five signals at 2.50, 3.07, 3.56, 4.25 and 5.67 ppm. The analysis of coupling constants allows one to suppose the isomer formed to be a product of H-addition to the 1-C-atom of coordinated naphthalene. The signals of hydrogen atoms of the non-coordinated ring of $\eta^5\text{-}C_{10}H_9$ ligand appear as multiplet in the region of 6.60–7.70 ppm. The coordinated fragment of the $\eta^5\text{-}C_{10}H_9$ ligand in the ^{13}C NMR spectrum of complex **20** is represented by resonances at
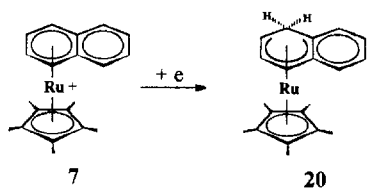
Scheme 8.

29.9 (CH_2), 34.3 (CH), 83.1 (CH), 84.6 (CH), 119.7 (C), 120.1 ppm (C); signals of the tertiary carbon atoms of the non-coordinated ring of the $\eta^5\text{-}C_{10}H_9$ ligand appear at 124.3, 125.0, 125.7 and 136.6 ppm; the C_5Me_5 ligand gives two signals at 9.9 and 74.6 ppm.

3. Conclusions

Reduction of cationic ruthenium arenecyclopentadienyl complexes generates highly reactive 19-electron radicals. Further destiny of the latter is either dimerization or H-atom abstraction from a solvent. It is a delicate balance of steric and electronic properties of η^5- and η^6-coordinated aromatic ligands that determines which reaction pathway predominates. Despite the fact that five-membered rings as a rule are formally not involved in the reactions under discussion, their electron donor effect and ability to delocalize unpaired electron density exert a strong influence on the stability and reactivity of 19-electron radicals (the stability increases in order of $C_5H_5 < C_5Me_5 < C_9H_7$). With an increase of the number of methyl groups at the arene ligand the kinetic stability of the radical increases, making dimerization through arene ligands the predominant process. In the case of permethylated complex **6** the increase of electron density due to the influence of 11 methyl groups is not counterbalanced by the ability of the other ligands to delocalize it so that the H-atom abstraction process becomes the only reaction observed.

4. Experimental details

4.1. General data

Reactions were carried out under argon using standard Schlenk-line techniques. Solvents and reagents were purified and dried by standard methods and were distilled under argon immediately prior to use. Microanalyses were performed by the Laboratory of Microanalysis of Institute of Organoelement Compounds. Cationic arenecyclopentadienyl complexes were prepared by literature methods $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$ (**1**), [9]; $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+$ (**2**), [36]; $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_3Me_3)]^+$ (**3**), [37]; $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_3Me_3)]^+$ (**4**), [36]; $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]^+$ (**5**), [37]; $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]^+$ (**6**), [36]; $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_{10}H_8)]^+$ (**7**), [13,14,38]; $[Ru(\eta^5\text{-}C_9H_7)(\eta^6\text{-}C_6H_6)]^+$ (**8**), [39].

4.2. Electrochemistry

CV data were obtained in acetonitrile solutions at room temperature under argon using a PI-50-1 potentio-

stat. A three-electrode cell was used with an SCE reference electrode, a carbonglass working electrode, and a platinum auxiliary electrode. Scan rate was $200 \, mV \, s^{-1}$ in each case. The solutions of electroactive substance were $2 \times 10^{-3} \, mol \, l^{-1}$ in 0.1 M Bu_4NPF_6 as the supporting electrolyte. Peak potentials were calibrated against the ferrocene/ferricenium (0.40 V) couple by adding ferrocene directly to the solution containing ruthenium complexes under investigation. Peak potentials are reported vs. SCE in Table 1.

4.3. Bulk electrolyses

Electrolyses were carried out in THF solutions under argon using a P-5827M potentiostat. The working stirred mercury cathode of 11 cm² area was separated from the platinum counter-electrode by a G4 frit. An aqueous SCE served as reference electrode, which had the KCl phase separated from the solution by a G4 frit. A solution of supported electrolyte had been electrolyzed at the same potential, which was chosen for the compound studied, before the ruthenium complex was dissolved. Coulometry measurements were made with an OH-404 'Radelkis'.

4.4. ^1H and ^{13}C NMR spectra

^1H and ^{13}C NMR spectra (Tables 2 and 3) were obtained with a Bruker WP-200SY and Bruker-AMX-400 spectrometers in C_6D_6 solutions. All chemical shifts are reported in parts per million (δ) with reference to TMS.

4.5. Reduction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (1) (general procedure)

Suspension of 1 (200 mg, 0.51 mmol) in THF (30 cm³) was stirred with an excess of 1% sodium amalgam (2 h, 25 °C). The solution was decanted, filtered and the solvent was removed in vacuo, to leave a residue which was extracted by benzene (3 × 10 cm³). Combined benzene solutions were filtered, evaporated to dryness and the residue was crystallized from hexane. Yield of 9 and 10, 69 mg (ratio 2:1). Mass-spectrum: m/z 245 (M⁺) (9), 232 (M⁺) $[Ru(\eta^5\text{-}C_5H_5)_2]$ (10); ^1H NMR (C_6D_6): δ 2.55–2.75 (m, 3H); 2.85–3.00 (m, 1H) 4.45 (dd, 2H, $J = 6$, $J = 5$ Hz); 4.72 (s, 5H, C_5H_5); 5.76 (t, 1H, $J = 5$ Hz) (9) and 4.56 s (10) ppm.

By the same procedure the following compounds were reduced.

4.5.1. $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (2)

200 mg, 0.50 mmol gives 92 mg (58%) of 11. Anal. Found: C, 62.05; H, 6.42. $C_{16}H_{22}Ru$. Calc.: C, 60.93; H, 7.03%.

4.5.2. $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_3Me_3)]^+PF_6^-$ (3)

200 mg, 0.46 mmol gives 85 mg (65%) 14a,b. Pure 14a was obtained by recrystallization of mixture 14a,b from hexane; yield of 14a, 62 mg (48%). Anal. Found: C, 58.90; H, 6.10. $C_{28}H_{34}Ru_2$. Calc.: C, 58.72; H, 5.98%. The evaporation of mother liquor results in 23 mg (17%) of 14a,b in the ratio 4:1.

4.5.3. $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_3Me_3)]^+PF_6^-$ (4)

200 mg, 0.40 mmol gives 106 mg (74%) of 15a. Anal. Found: C, 65.28; H, 8.07. $C_{38}H_{54}Ru_2$. Calc.: C, 64.01; H, 7.63%.

4.5.4. $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]^+PF_6^-$ (5)

200 mg, 0.42 mmol gives after recrystallization from hexane 81 mg (58%) 16. Anal. Found: C, 62.23; H, 7.29. $C_{34}H_{46}Ru_2$. Calc.: C, 62.17; H, 7.06%. The evaporation of mother liquor results in 21 mg of the mixture of 16, 17 and 18 in the ratio 5:2:1. ^1H NMR (C_6D_6): δ 2.10 (s, 18H, C_6Me_6); 2.31 (m, 2H, H_α); 2.84 (ddd, 1H, H_{endo}, $J = 10$, $J = J = 2$ Hz); 3.78 (d, 1H, H_{exo}, $J = 10$ Hz); 4.69 (m, 2H, H_β) (18) ppm.

4.5.5. $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_{10}H_8)]^+PF_6^-$ (7)

100 mg, 0.19 mmol gives 43 mg (62%) 20. Anal. Found: C, 64.02; H, 7.57. $C_{20}H_{24}Ru$. Calc.: C, 65.73; H, 6.62%. ^1H NMR (C_6D_6): δ 1.60 (s, 15H, C_5Me_5); 2.50 (dd, 1H, $J = J = 6$ Hz); 3.07 (dd, 1H, $J = 12$ Hz, $J = 6$ Hz); 3.56 (d, 1H, $J = 12$ Hz); 4.25 (dd, 1H, $J = 6$ Hz, $J = 5$ Hz); 5.67 (d, 1H, $J = 5$ Hz); 6.60–7.70 (m, 4H) ppm. ^{13}C NMR (C_6D_6): δ 9.9 (C_5Me_5); 29.9 (CH_2); 34.3 (CH); 74.6 (C_5Me_5); 83.1 (CH); 84.6 (CH); 119.7 (C); 120.1 (C); 124.3 (CH); 125.0 (CH); 125.7 (CH); 136.6 (CH) ppm.

4.5.6. $[Ru(\eta^5\text{-}C_9H_7)(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (8)

100 mg, 0.23 mmol gives after recrystallization from hexane 32 mg (47%) 12. Anal. Found: C, 61.32; H, 4.71. $C_{30}H_{26}Ru_2$. Calc.: C, 61.21; H, 4.45%. Evaporation of mother liquor gives 12 mg (18%) of a mixture of 12 and 13 in the ratio 2:1.

4.6. Electrochemical reduction of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_3Me_3)]^+PF_6^-$ (4)

The reduction of 4 (200 mg, 0.40 mmol) was carried out at a stirred Hg-electrode (-2.5 V) in THF (50 cm³) (0.2 N Bu_4NPF_6); after consumption of 39.1 Q ($Q_{theor} = 38.5$, $n = 1$) the current decreased from 45 to 3 mA. A cyclic voltammogram of the solution obtained showed the disappearance of reduction peak of 4 and the appearance of a new oxidation peak at -0.27 V; electrolysis was stopped. The solution was decanted and the THF was removed in vacuo, to leave a residue which was extracted by benzene (2 × 25 cm³). The combined

benzene solution was filtered and evaporated; then the residue was recrystallized from hexane; the precipitate was filtered off and dried in vacuo (yield of **15a**, 97 mg (68%)).

4.7. Electrochemical reduction of $[Ru(\eta^5-C_5Me_5)(\eta^6-C_6Me_6)]^+PF_6^-$ (6)

The reduction of **6** (170 mg, 0.32 mmol) was carried out at a stirred Hg-electrode (-2.6 V) in THF (50 cm^3) (0.2 N Bu$_4$NPF$_6$); after consumption of $32.1 Q$ ($Q_{theor} = 30.2$, $n = 1$) the current decreased from 20 to 3 mA. A cyclic voltammogram of the solution obtained showed the disappearance of the reduction peak of **6** and the appearance of two new oxidation peaks at -0.08 and $+0.45$ V; electrolysis was stopped. The solution was decanted and the THF was removed in vacuo, to leave a residue which was extracted by benzene (2×25 cm^3). The combined benzene solution was filtered and evaporated; then the residue was recrystallized from hexane; the precipitate was filtered off and dried in vacuo (yield of **19a** and **19b**, 75 mg (60%)). Anal. Found: C, 66.37; H, 8.53. C$_{22}$H$_{34}$Ru. Calc.: C, 66.13; H, 8.58%.

4.8. Electrochemical reduction of $[Ru(\eta^5-C_9H_7)(\eta^6-C_6H_6)]^+BF_4^-$ (8)

The reduction of **8** (44 mg, 0.10 mmol) was carried out at a stirred Hg-electrode (-2.4 V) in THF (50 cm^3) (0.2 Bu$_4$NPF$_6$); after consumption of $10.3 Q$ ($Q_{theor} = 9.6$, $n = 1$) the current decreased from 18 to 2 mA. A cyclic voltammogram of the solution obtained showed the disappearance of the reduction peak of **8** and the appearance of a new oxidation peak at -0.03 V; electrolysis was stopped. The solution was decanted and the THF was removed in vacuo, to leave a residue which was extracted by benzene (2×25 cm^3). The combined benzene solution was filtered and evaporated; then the residue was recrystallized from hexane; the precipitate was filtered and dried in vacuo (yield of **12**, 13 mg (44%)). Evaporation of mother liquor resulted in a mixture of **12** and **13** (6 mg) in the ratio 2:1.

Acknowledgements

References

[1] O.V. Gusev, L.I. Denisovich, M.G. Peterleitner, A.Z. Rubezhov, N.A. Ustynyuk and P.M. Maitlis, J. Organomet. Chem., 452 (1993) 219.

[2] (a) 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., 480 (1994) C16. (b) O.V. Gusev, L.N. Morozova, T.A. Peganova, M.G. Peterleitner, S.M. Peregudova, L.I. Denisovich, P.V. Petrovskii, Yu.F. Oprunenko and N.A. Ustynyuk, J. Organomet. Chem., 493 (1995) 181.

[3] O.V. Gusev, L.N. Morozova, M.G. Peterleitner, S.M. Peregudova, P.V. Petrovskii, N.A. Ustynyuk and P.M. Maitlis, J. Organomet. Chem., 509 (1996) 95.

[4] D. Astruc, Chem. Rev., 88 (1988) 1189.

[5] (a) U. Koelle and F. Khouzami, Angew. Chem. Int. Edn. Engl., 19 (1980) 640. (b) J.L. Robbins, N. Edelstein, B. Spencer and J.C. Smart, J. Am. Chem. Soc., 104 (1982) 1882.

[6] U. Koelle, B. Fuss, M.V. Rajasekharan, B.L. Ramakrishna, J.H. Ammeter and M.C. Bohm, J. Am. Chem. Soc., 106 (1984) 4152.

[7] (a) E.O. Fischer and H. Wawersik, J. Organomet. Chem., 5 (1966) 559. (b) H.J. Keller and H. Wawersik, J. Organomet. Chem., 8 (1967) 185. (c) N. El Murr, J.E. Sheats, W.E. Geiger and J.D.L. Holloway, Inorg. Chem., 18 (1979) 1443.

[8] J.E. Collins, M.P. Castellani, A.L. Rheingold, E.J. Miller, W.E. Geiger and A.L. Rieger, Organometallics, 14 (1995) 1232.

[9] R.A. Zelonka and M.C. Baird, J. Organomet. Chem., 44 (1972) 383.

[10] L.W. Robertson, T.A. Stephenson and D.A. Tocher, J. Organomet. Chem., 228 (1982) 171.

[11] N.A. Vol'kenau, L.S. Shul'pina, P.V. Petrovskii, L.I. Denisovich, M.G. Peterleitner and D.N. Kravtsov, The IVth All-Union Conf. on Organometallic Chemistry Abstr., Kazan, 1988, p. 79.

[12] N.A. Vol'kenau, I.N. Bolesova, L.S. Shul'pina and A.N. Kitaigorodskii, J. Organomet. Chem., 267 (1985) 313.

[13] U. Koelle and M.H. Wang, Organometallics, 9 (1990) 195.

[14] U. Koelle, A. Hornig and U. Englert, Organometallics, 13 (1994) 4064.

[15] A.M. McNair and K.R. Mann, Inorg. Chem., 25 (1986) 2519 and references cited therein.

[16] W.J. Bowyer, J.W. Merkert, W.E. Geiger and A.L. Rheingold, Organometallics, 8 (1989) 191.

[17] G.E. Herberich, U. Englert and F. Marken, J. Chem. Soc. Dalton Trans., (1993) 1979.

[18] M. Lacoste and D. Astruc, J. Chem. Soc. Chem. Commun., (1987) 667.

[19] B.F. Bush and J.J. Lagowski, J. Organomet. Chem., 386 (1990) 37.

[20] P.L. Pauson and G. Wilkinson, J. Am. Chem. Soc., 76 (1954) 2024.

[21] S. Lee, S.R. Lovelace and N.J. Cooper, Organometallics, 14 (1995) 1974.

[22] D. Astruc, M. Lacoste and L. Toupet, J. Chem. Soc. Chem. Commun., (1990) 558.

[23] A.I. Yarmolenko, S.V. Kukharenko, L.N. Novikova and V.V. Strelets, Izv. Akad. Nauk SSSR Ser. Khim., (1995) 1347.

[24] W.J. Bowyer and W.E. Geiger, J. Am. Chem. Soc., 107 (1985) 5657.

[25] R.M. Nielson and M.J. Weaver, Organometallics, 8 (1989) 1636.

[26] J. Merkert, R.M. Nielson, M.J. Weaver and W.E. Geiger, J. Am. Chem. Soc., 111 (1989) 7084.

[27] D.T. Pierce and W.E. Geiger, J. Am. Chem. Soc., 114 (1992) 6063.

[28] (a) N.A. Ustynyuk, L.I. Denisovich, M.G. Peterleitner, L.N. Novikova, N.A. Pomazanova and D.N. Kravtsov, Metalloorgan. Khim., 1 (1988) 216. (b) S.V. Kukharenko, V.V. Strelets, N.A. Ustynyuk, L.N. Novikova, L.I. Denisovich and M.G. Peterleitner, Metalloorgan. Khim., 4 (1991) 299. (c) S.V. Kukharenko, L.N. Novikova, V.V. Strelets and N.A. Ustynyuk, Izv. Akad. Nauk SSSR Ser. Khim., (1994) 48. (d) L.N. Novikova, B.A.

Mazurchik, N.A. Ustynyuk, S.V. Kukharenko and V.V. Strelets, *Izv. Akad. Nauk SSSR Ser. Khim.*, (1994) 319. (e) S.V. Kukharenko, L.N. Novikova, V.V. Strelets, N.A. Ustynyuk and A.I. Yarmolenko, *Izv. Akad. Nauk SSSR Ser. Khim.*, (1994) 1815.

[29] P.G. Gassman and C.H. Winter, *J. Am. Chem. Soc.*, *110* (1988) 6130.

[30] M.F. Ryan, A.R. Siedle, M.J. Burk and D.E. Richardson, *Organometallics*, *11* (1992) 4231.

[31] C. Moinet, E. Roman and D. Astruc, *J. Organomet. Chem.*, *128* (1977) C45.

[32] J.-R. Hamon, D. Astruc and P. Michaud, *J. Am. Chem. Soc.*, *103* (1981) 758.

[33] N.A. Ustynyuk, N.A. Pomazanova, L.N. Novikova and D.N. Kravtsov, *Metalloorgan. Khim.*, *2* (1989) 204.

[34] M.V. Gaudet, A.W. Hanson, P.S. White and M.J. Zaworotko, *Organometallics*, *8* (1989) 286.

[35] R.L. Thompson, S. Lee, A.L. Rheingold and N.J. Cooper, *Organometallics*, *10* (1991) 1657.

[36] V.S. Kaganovich, A.R. Kudinov and M.I. Rybinskaya, *Metalloorgan. Khim.*, *3* (1990) 70.

[37] T.P. Gill and K.R. Mann, *Organometallics*, *1* (1982) 485.

[38] U. Koelle and J. Kossakowski, *J. Organomet. Chem.*, *362* (1989) 383.

[39] A.R. Kudinov, L.S. Shul'pina, P.V. Petrovskii and M.I. Rybinskaya, *Izv. Akad. Nauk SSSR Ser. Khim.*, (1992) 699.