

# Reduction of iridocenium salts $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-L})]^+$ ( $\text{L} = \text{C}_5\text{H}_5$ , $\text{C}_5\text{Me}_5$ , $\text{C}_9\text{H}_7$ ); ligand-to-ligand dimerisation induced by electron transfer

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Received 7 June 1996; revised 25 July 1996

## Abstract

Redox properties of iridium complexes  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-L})]^+$  ( $1^+$ ,  $\text{L} = \text{C}_5\text{H}_5$ ;  $2^+$ ,  $\text{L} = \text{C}_5\text{Me}_5$ ;  $3^+$ ,  $\text{L} = \text{C}_9\text{H}_7$ ) were studied by cyclic voltammetry (CV). All three complexes can be reduced to 19-electron radicals 1–3. The stability and reactivity of these radicals depend on the electronic and steric properties of the ligands. The mixture of dimers  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^4\text{-}\eta^5\text{-C}_5\text{H}_5\text{C}_5\text{Me}_5)\text{Ir}(\eta^5\text{-C}_5\text{H}_5)]$  (**4a**) and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\mu\text{-}\eta^4\text{-}\eta^5\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5)\text{Ir}(\eta^5\text{-C}_5\text{H}_5)]$  (**4b**) was formed as a result of reduction of  $1^+$  with Na/Hg in THF. Both chemical and electrochemical reduction of  $2^+$  gave the dimer  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^4\text{-}\eta^5\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)]$  (**5**) in low yield. Reduction of  $3^+$  gave the tetranuclear complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^4\text{-}\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\mu\text{-}\eta^4\text{-}\eta^5\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^4\text{-}\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)]$  (**6**).

**Keywords:** Iridium; Cyclopentadienyl; Cyclic voltammetry; Electrochemistry; Electron transfer; Metallocenes

## 1. Introduction

19-Electron metallocenes of rhodium, palladium and platinum were recently studied by our groups [1–4]. These 19-electron radicals were found to be essentially more reactive than their cobalt and nickel analogues [1–4]. The stability of radicals depends considerably on ligand nature [1]. Iridium(II) sandwiches are much less studied in comparison with cobalt(II) and rhodium(II) metallocenes. The reduction of  $[\text{Ir}(\eta^5\text{-C}_5\text{H}_5)_2]^+$  with sodium [5] and ESR spectroscopy data for  $[\text{Ir}(\eta^5\text{-C}_5\text{H}_5)_2]$  [6] were only reported. Electrochemical investigations of iridocene derivatives were not carried out at all. We report here the electrochemical study and preparative reduction of iridocenium cations  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-L})]^+$  ( $1^+$ ,  $\text{L} = \text{C}_5\text{H}_5$ ;  $2^+$ ,  $\text{L} = \text{C}_5\text{Me}_5$ ;  $3^+$ ,  $\text{L} = \text{C}_9\text{H}_7$ ).

## 2. Results and discussion

### 2.1. CV investigation of $1^+ \text{--} 3^+$

CV data show that all three complexes  $1^+ \text{--} 3^+$  are reduced in a one-electron process. This is confirmed by the similarity in height of the cathodic peaks to those for ferricenium (at the same concentration as internal reference). First reduction peaks of  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_5)]^+$  ( $1^+$ ) and  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+$  ( $2^+$ ) are observed at more negative potentials ( $\Delta E \sim 0.4 \text{ V}$ ) compared with the first reduction peaks of rhodium analogues (Table 1). Reduction peaks of  $1^+$  and  $2^+$  are irreversible at temperatures as low as  $-60^\circ\text{C}$  (Fig. 1), unlike peaks of penta- and decamethylrhodocenium which are quasi-reversible at room temperature and reversible at  $-35^\circ\text{C}$  [1]. Irreversibility of the peaks shows that iridium 19-electron radicals are less stable than their rhodium analogues. The higher reactivity of 19-electron metallocenes of the third transition metal row compared with analogous second transition metal row complexes was shown in the case of platinum and palladium decamethylmetallocenes [2–4]. The second reduction peak was

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Table 1

CV data for  $[M(\eta^5-C_5Me_5)(\eta^5-L)]^+ BF_4^-$  ( $M = Rh$  or  $Ir$ ) ( $c = 2 \times 10^{-3} \text{ M L}^{-1}$ , THF, 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>,  $v = 200 \text{ mV s}^{-1}$ ; vs. SCE)

Compound	$-E_{pc}^1$ (V vs. SCE)	$-E_{pc}^2$ (V vs. SCE)
$[Ir(\eta^5-C_5H_5)(\eta^5-C_5Me_5)]^+ (1^+)$	2.03	2.53
$[Rh(\eta^5-C_5H_5)(\eta^5-C_5Me_5)]^+ [1]$	1.51	2.50
$[Ir(\eta^5-C_5Me_5)_2]^+ (2^+)$	2.27	
$[Rh(\eta^5-C_5Me_5)_2]^+ [1]$	1.82	2.78
$[Ir(\eta^5-C_9H_7)(\eta^5-C_5Me_5)]^+ (3^+)$	1.50	1.65
$[Rh(\eta^5-C_9H_7)(\eta^5-C_5Me_5)]^+ [1]$	1.14	1.96

observed for  $1^+$  at  $-2.53 \text{ V}$  (Fig. 1), but it could not be stated that it corresponds to 19/20-valence electron change, because the first electron transfer process is irreversible.

The reduction of  $3^+$  differs essentially from the reduction of  $1^+$  or  $2^+$ , as well as from the reduction of analogous rhodium complex  $[Rh(\eta^5-C_5Me_5)(\eta^5-C_9H_7)]^+ [1]$ . Two closely located reduction peaks (first peak reversible  $i_{pa}/i_{pc} = 1.0$ , second peak irreversible) are observed in the cyclic voltammery curve of  $3^+$  (Table 1, Fig. 2). The first reduction peak is observed at a less negative potential versus those of  $1^+$  ( $\Delta E = 0.53 \text{ V}$ ) and  $2^+$  ( $\Delta E = 0.77 \text{ V}$ ) as well as at a more negative potential versus  $[Rh(\eta^5-C_5Me_5)(\eta^5-C_9H_7)]^+$  ( $\Delta E = 0.36 \text{ V}$ ). The difference between the first and second reduction peak potentials for  $3^+$  is too small (0.15 V) in comparison with the same values for the rhodium analogue (0.82 V). As a rule such a small separation of the two reduction peaks is observed in the case of some structural changes (for example ligand

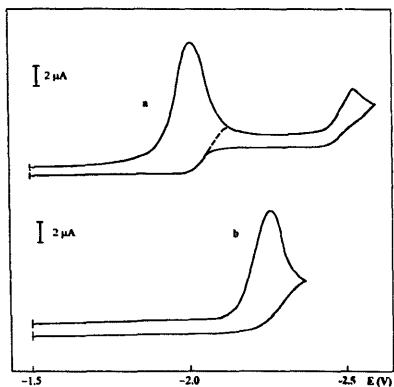


Fig. 1. Cyclic voltammogram of (a)  $[Ir(\eta^5-C_5H_5)(\eta^5-C_5Me_5)]^+$  ( $1^+$ ) and (b)  $[Ir(\eta^5-C_5Me_5)_2]^+$  ( $2^+$ ) in THF ( $v = 200 \text{ mV s}^{-1}$ ).

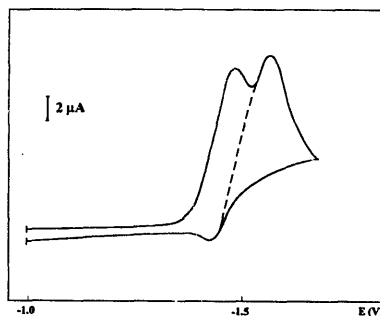


Fig. 2. Cyclic voltammogram of  $[Ir(\eta^5-C_9H_7)(\eta^5-C_5Me_5)]^+$  ( $3^+$ ) in THF ( $v = 200 \text{ mV s}^{-1}$ ).

hapticity changes) rather than valence electron changes [7].

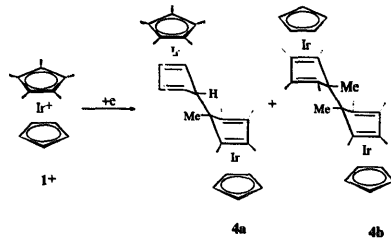
The oxidation peaks of  $1^+ - 3^+$  were not observed up to  $+1.8 \text{ V}$ .

## 2.2. Reduction of $1^+ - 3^+$

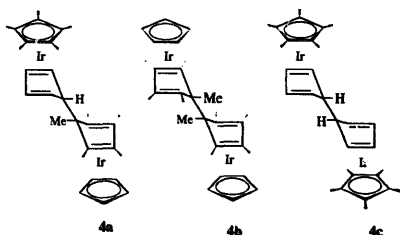
### 2.2.1. Reduction of pentamethyliridocenium $1^+$ to give $[(\eta^5-C_5Me_5)Ir(\mu-\eta^4:\eta^4-C_5H_5C_5Me_5)Ir(\eta^5-C_5H_5)]$ (**4a**) and $[(\eta^5-C_5H_5)Ir(\mu-\eta^4:\eta^4-C_5Me_5C_5Me_5)Ir(\eta^5-C_5H_5)]$ (**4b**)

Reduction of pentamethyliridocenium  $1^+$  by 1% Na-Hg in THF led to the formation of dimers **4a,b** in the ratio 2:1 in high yield (Scheme 1).

A mixture of **4a,b** was characterized by microanalysis and spectroscopically.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra showed two sets of signals corresponding to isomers **4a,b**. Resonances of  $\eta^5$ -bonded rings for the asymmetrical dimer **4a** were observed at 2.08 ( $C_5Me_5$ ) and 4.84 ( $C_5H_5$ ) ppm in the  $^1\text{H}$  NMR spectrum and at 11.2, 88.4 ( $C_5Me_5$ ) and 77.9 ( $C_5H_5$ ) ppm in the  $^{13}\text{C}$  NMR spectrum. The  $\mu-\eta^4:\eta^4-C_5H_5C_5Me_5$  ligand was indicated



Scheme 1.



Scheme 2.

by the methyl singlets at 1.48, 1.60 and 2.33 and by ring proton resonances at 2.76, 3.07 and 4.45 ppm in the  $^1\text{H}$  NMR spectrum, the  $^{13}\text{C}$  NMR spectrum showing signals at 13.3, 17.5 and 26.1 (Me), 31.7, 63.2 and 68.5 (CH), 44.6, 71.0 and 80.0 (CMe) ppm.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the symmetrical dimer **4b** showed the presence of  $\eta^5\text{-C}_5\text{H}_5$  rings (signals at 4.88 and 76.8 ppm respectively). Resonances of methyl groups of the  $\mu\text{-}\eta^1\text{-}\eta^1\text{-C}_5\text{Me}_2\text{C}_2\text{H}_2$  ligand were observed at 1.45, 2.02, 2.38 and 13.0, 15.3, 23.0 ppm in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra respectively. Quaternary CMe atoms gave three signals at 48.0, 69.6 and 80.2 ppm.

The ratio 2:1 of **4a**:**4b** is reproducible. Both isomers **4a**,**b** are thermally stable and the ratio remains unchanged after 12 h refluxing in hexane.

It should be outlined that the reduction of pentamethylrhodocenium gave the asymmetrical dimer  $[(\eta^5\text{-C}_5\text{Me}_2)\text{Rh}(\mu\text{-}\eta^1\text{-}\eta^1\text{-C}_5\text{H}_2\text{C}_2\text{Me}_2)\text{Rh}(\eta^5\text{-C}_5\text{H}_5)]$  as the only product in high yield [1]. The formation of the third possible isomer **4c** (Scheme 2) was not observed in the reduction of both pentamethylrhodocenium and pentamethyliridocenium.

The formation of asymmetric isomers as a dominant or sole product of  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_2)]^+$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) reduction cannot be explained in terms of interaction of two 19-electron radicals. If the unpaired electron density is suggested to be equally distributed between  $\text{C}_5\text{H}_5$  and  $\text{C}_5\text{Me}_2$  rings in the  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_2)]$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) radicals then the formation of a statistical set of all three dimers **4a–c** should be expected to occur with a slight prevalence of **4c** due to steric reasons. If the electron density is mainly located on one ring the formation of symmetric dimers (**4b** or **4c** in our case) should be observed. The latter case resembles the dimerisation of iron arenecyclopentadienyl radicals containing ligands of different nature which proceeds through arene ligands only [8].

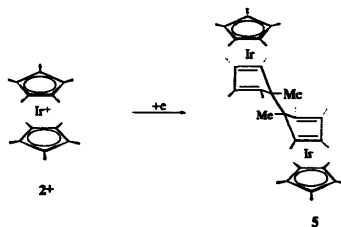
In our opinion the reason for asymmetric dimer formation is the appearance of the 19-electron neutral radicals which are strong nucleophiles [9] and attack unreacted starting cations to give intermediate dinuclear

cation radicals. Processes of such type should be very sensitive to a positive charge distribution in starting cations and to the spin electron density distribution in 19-electron radicals. If it is suggested that the spin electron density in  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_2)]$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) radicals is mainly located on the  $\text{C}_5\text{Me}_2$  rings and the positive charge in cations  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_2)]^+$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) is mainly concentrated at  $\text{C}_5\text{H}_5$  rings, then dimeric cation radicals with some degree of bonding between  $\text{C}_5\text{Me}_2$  and  $\text{C}_5\text{H}_5$  ligands should be formed. The addition of an electron to the latter should be expected to give the neutral dimer  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\mu\text{-}\eta^1\text{-}\eta^1\text{-C}_5\text{Me}_2\text{C}_2\text{H}_2)\text{M}(\eta^5\text{-C}_5\text{Me}_2)]$ . The formation of the symmetrical dimer **4b** on pentamethyliridocenium  $1^+$  reduction can be explained by more uniform delocalization of positive charge in  $1^+$  in comparison with the rhodium analogue. Some evidence for the latter assertion was found in the results of the reaction of  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_2)]^+$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) with other nucleophiles. For example, the diene complex  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_2\text{H})(\eta^5\text{-C}_5\text{H}_5)]$  was obtained as sole product in the reaction of pentamethylrhodocenium salt with  $\text{NaBH}_4$ , while similar reaction of  $1^+$  gave a mixture of isomers  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_2\text{H})(\eta^5\text{-C}_5\text{H}_5)]$  and  $[\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_2)]$  in the ratio 2:1 [10]. It should be noted that the ratio of  $\text{C}_5\text{H}_5$  and  $\text{C}_5\text{Me}_2$  ring addition products in the latter reaction is the same as the ratio of dimers **4a**:**4b** in the process discussed above.

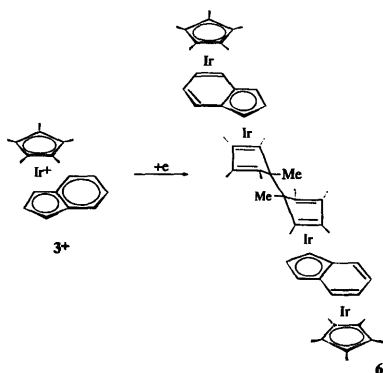
### 2.2.2. Reduction of decamethyliridocenium $2^+$ to give $[(\eta^5\text{-C}_5\text{Me}_2)\text{Ir}(\mu\text{-}\eta^1\text{-}\eta^1\text{-C}_5\text{Me}_2\text{C}_2\text{Me}_2)\text{Ir}(\eta^5\text{-C}_5\text{Me}_2)]$ (**5**)

Unlike the chemical (1% Na–Hg, THF) or electrochemical (–2.5 V, Hg electrode, THF, 0.2 M  $\text{Bu}_4\text{NPF}_6$ ) reduction of  $1^+$ , reduction of  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_2)_2]^+$  ( $2^+$ ) is accompanied by considerable decomposition. The same decomposition was observed in the case of reduction of decamethylrhodocenium [1]. The unstable neutral dimer **5** was obtained in low yield as a result of the reduction of  $2^+$  (Scheme 3).

The dimeric structure of **5** was assumed on the basis of  $^1\text{H}$  NMR spectroscopy data. Four singlets were ob-



Scheme 3.



Scheme 4.

served at 1.16, 1.45, 1.80 and 1.99 (2:1:5:2 Me) ppm in the  $^1\text{H}$  NMR spectrum of **5**. Unfortunately, all attempts to prepare an analytically pure sample of **5** failed due to its low stability in solution.

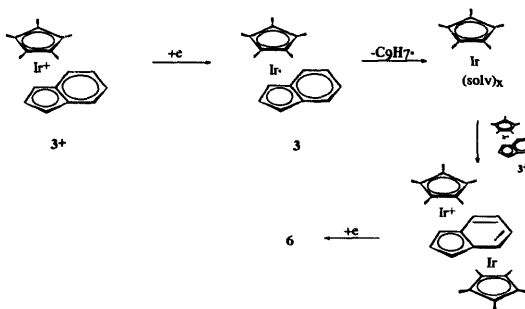
It is remarkable that the reduction of other cationic decamethylmetallocenes  $[\text{M}(\eta^5\text{-C}_5\text{Me}_5)_2]^{n+}$  ( $\text{M} = \text{Rh}$ ,  $n = 1$ ;  $\text{M} = \text{Pd}$ ,  $\text{Pt}$ ,  $n = 2$ ) [2–4] led to formation of  $\eta^4$ -pentamethylcyclopentadiene complexes  $[\text{M}(\eta^4\text{-C}_5\text{Me}_5\text{H})(\eta^5\text{-C}_5\text{Me}_5)]^{(n-1)+}$  ( $\text{M} = \text{Rh}$ ,  $n = 1$ ;  $\text{M} = \text{Pd}$ ,  $\text{Pt}$ ,  $n = 2$ ) only. The different reactivity of 19-electron decamethylmetallocenes is difficult to discuss because of low product yields on reduction of  $2^+$  and its rhodium analogue [1].

### 2.2.3. Reduction of $3^+$ to give $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^4\text{-}\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\mu\text{-}\eta^4\text{-}\eta^4\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^5\text{-}\eta^4\text{-C}_9\text{H}_7)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)]$ (**6**)

Coulometry data showed that the electrochemical reduction ( $-1.9\text{ V}$ , Hg electrode, THF,  $0.2\text{ M Bu}_4\text{NPF}_6$ )

of  $3^+$  occurred by consumption of one faraday per mol. The bulk electrolysis unexpectedly gave the tetranuclear complex **6** containing two bridged  $\eta^5$ -indenyl and one  $\mu\text{-}\eta^4\text{-}\eta^4\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5$  ligands (Scheme 4).

The complex **6** was tentatively formulated as  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\mu\text{-}\eta^4\text{-}\eta^4\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^5\text{-}\eta^4\text{-C}_9\text{H}_7)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)]$  on the basis of microanalysis and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy data. The resonances 2.01, 11.2 and 94.1 ppm showed the presence of  $\eta^5\text{-C}_5\text{Me}_5$  rings. The  $\mu\text{-}\eta^4\text{-}\eta^4\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5$  ligand was indicated by the methyl signals at 1.34, 1.51 and 2.16 ppm in the  $^1\text{H}$  NMR spectrum and at 12.8, 14.8 and 22.7 ppm in the  $^{13}\text{C}$  NMR spectrum. The signals of indenyl protons were observed at 2.61, 4.51 and 5.04 ppm in a ratio 2:1:4 in the  $^1\text{H}$  NMR spectrum of **6**. The resonance arising from H-2 indenyl hydrogen is upfield shifted by 1.4 ppm in comparison with the analogous resonance in the  $^1\text{H}$  NMR spectrum of the cation  $3^+$ , which can be explained by the different charges of these complexes. The signals of the protons of six-membered rings of **6** are strongly upfield shifted relative to the analogous signals of  $3^+$  ( $\Delta\delta = 2.4\text{ ppm}$ ), due to coordination of the six-membered rings with neutral organometallic moieties. The most significant changes were observed for the signal of H-1 and H-3 indenyl atoms, which was more upfield (2.61 ppm) than even the signal of the H-2 atom, contrary to the situation observed for  $3^+$ . The last phenomenon can probably be explained by location of these atoms in close proximity to both iridium atoms. Tertiary indenyl carbons showed seven signals (47.8, 48.0, 64.0, 73.3, 73.5, 83.8 and 83.9 ppm), six of them (with the exception of C-2 signals) forming three close pairs ( $\Delta\delta \sim 0.1\text{--}0.2\text{ ppm}$ ). Resonances of the quaternary carbons of  $\eta^5\text{-C}_5\text{Me}_5$ ,  $\mu\text{-}\eta^4\text{-}\eta^4\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5$  and  $\mu\text{-}\eta^4\text{-}\eta^5\text{-C}_9\text{H}_7$  ligands, which could not be strictly assigned, were observed as close pairs as well, which might be stipulated by restricted rotation around the C–C bond in the central  $\mu\text{-}\eta^4\text{-}\eta^4\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5$  fragment.



Scheme 5.

Complex **6** was obtained by reduction of  $3^+$  with 1% Na–Hg in THF as well. Evidently the formation of **6** on reduction of  $3^+$  is the result of several processes. Mono-electron reduction of  $3^+$  should lead to the formation of radical species, which was confirmed by the presence of a low intensity signal ( $g_x = 2.0083$ ) in the ESR spectrum of  $3^+$  solution during electrolysis. Presumably the unstable radical **3** undergoes loss of an indenyl radical to give the solvate complex  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{thf})_2]$ . The absence of an indenyl anion oxidation peak in the electrolyzed solution of  $3^+$  confirms that it is not formed on reduction. The solvate complex  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{thf})_2]$  could further react with starting  $3^+$  to form the dinuclear cation  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^4\text{:}\eta^5\text{-C}_6\text{H}_7)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)]^+$  by analogy with the reaction of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2]$  and  $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{MeCN})_2]^+$ , which led to  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\mu\text{-}\eta^4\text{:}\eta^5\text{-C}_6\text{H}_7)\text{Ru}(\eta^5\text{-C}_5\text{H}_7)]^+$  [11]. Reduction of the cation  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^4\text{:}\eta^5\text{-C}_6\text{H}_7)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)]^+$  resulted in the formation of dimer **6** under electrolysis conditions. Oxidation of **6** regenerated  $3^+$  (Scheme 5).

### 3. Experimental

#### 3.1. 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 the Institute of Organoelement compounds.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained with Bruker WP-200SY and Bruker-AMX-400 spectrometers in  $\text{C}_6\text{D}_6$  solution. All chemical shifts are reported in parts per million ( $\delta$ ) with reference to TMS.

Iridocenium salts were prepared by literature methods:  $[\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)]^+\text{PF}_6^-$  [10],  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+\text{BF}_4^-$  [12] and  $[\text{Ir}(\eta^5\text{-C}_6\text{H}_7)(\eta^5\text{-C}_5\text{Me}_5)]^+\text{BF}_4^-$  [13].

#### 3.2. Electrochemistry

CV data were obtained in acetonitrile solutions at room temperature under argon using a potentiostat PI-50-1. A three-electrode cell was used with SCE reference electrode, a glassy carbon working electrode and a platinum auxiliary electrode. The scan rate was  $200\text{ mV s}^{-1}$  in each case. The solutions were  $0.1\text{ M}$  in  $\text{Bu}_4\text{NPF}_6$  as supporting electrolyte and  $2 \times 10^{-3}\text{ M}$  in electroactive substances. Peak potentials were calibrated against the ferrocene/ferrocenium (0.40 V) couple by adding ferrocene directly to the solution containing iridium complexes under investigation. Peak potentials are reported vs. SCE in Table 1.

#### 3.3. Bulk electrolyses

Electrolyses were carried out in THF solutions under argon using a potentiostat P-5827M. A working stirred mercury cathode of  $11\text{ cm}^2$  area was separated from the platinum counter electrode by a frit G4. An aqueous SCE served as reference electrode, with KCl phase separated from the solution by a frit G4. A solution of supporting electrolyte was electrolyzed at the same potential, which was chosen for the compound studied, before the iridium complex was dissolved. Coulometry measurements were made with an OH-404 "Radelkis".

#### 3.4. Reduction of $1^+ \rightarrow 3^+$ by Na–Hg (general procedure)

A suspension of  $[\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)]^+\text{PF}_6^-$  ( $1^+$ ) (0.27 g, 0.5 mmol) in THF ( $20\text{ cm}^3$ ) was stirred with an excess of 1% Na–Hg (2 h, at  $25^\circ\text{C}$ ). The solution was decanted, filtered and the solvent was removed in vacuo, to leave a residue that was crystallized from hexane. Yield of **4a,b** 0.14 g (71%). Anal. Found: C, 46.32; H, 5.22.  $\text{C}_{30}\text{H}_{40}\text{Ir}_2$  Calc.: C, 45.90; H, 5.14.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.48 (s, 6H,  $2\text{CH}_3$ ); 1.60 (s, 3H,  $\text{CH}_3$ ); 2.08 (s, 15H,  $\text{C}_5\text{Me}_5$ ); 2.33 (s, 6H,  $2\text{CH}_3$ ); 2.76 (dd, 2H,  $J = 2.2$ ,  $J = 1.6\text{ Hz}$ ); 3.07 (t, 2H,  $J = 2.2\text{ Hz}$ ); 4.45 (dd, 2H,  $J = J = 2.2\text{ Hz}$ ); 4.84 (s, 5H,  $\text{C}_5\text{H}_5$ ) **4a**. 1.45 (s, 6H,  $2\text{CH}_3$ ); 2.02 (s, 3H,  $\text{CH}_3$ ); 2.38 (s, 6H,  $2\text{CH}_3$ ); 4.88 (s, 5H,  $\text{C}_5\text{H}_5$ ) **4b**.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  11.2 ( $\text{C}_5\text{Me}_5$ ); 13.3 ( $2\text{CMe}$ ); 17.5 ( $2\text{Me}$ ); 26.1 ( $\text{Me}$ ); 31.7 ( $2\text{CH}$ ); 44.6 ( $2\text{CMe}$ ); 63.2 ( $1\text{CH}$ ); 68.5 ( $2\text{CH}$ ); 71.0 ( $\text{CMe}$ ); 77.9 ( $\text{C}_5\text{H}_5$ ); 80.0 ( $2\text{CMe}$ ); 88.4 ( $\text{C}_5\text{Me}_5$ ) **4a**. 13.0 ( $2\text{Me}$ ); 15.3 ( $2\text{CMe}$ ); 23.0 ( $\text{Me}$ ); 48.0 ( $2\text{CMe}$ ); 69.6 ( $\text{CMe}$ ); 76.8 ( $\text{C}_5\text{H}_5$ ); 80.2 ( $2\text{CMe}$ ) **4b**.

Under similar conditions  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+\text{BF}_4^-$  ( $2^+$ ) (0.24 g, 0.5 mmol) gave  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\mu\text{-}\eta^4\text{:}\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}(\eta^5\text{-C}_5\text{H}_5)]$  (**5**) (0.03 g, 6%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.16 (s, 6H,  $2\text{CH}_3$ ); 1.45 (s, 3H,  $\text{CH}_3$ ); 1.80 (s, 15H,  $\text{C}_5\text{Me}_5$ ); 1.99 (s, 6H,  $2\text{CH}_3$ ).

Similarly  $[\text{Ir}(\eta^5\text{-C}_6\text{H}_7)(\eta^5\text{-C}_5\text{Me}_5)]^+\text{BF}_4^-$  ( $3^+$ ) (0.26 g, 0.5 mmol) gave  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^4\text{:}\eta^5\text{-C}_6\text{H}_7)\text{Ir}(\mu\text{-}\eta^4\text{:}\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}(\mu\text{-}\eta^4\text{:}\eta^5\text{-C}_6\text{H}_7)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)]$  (**6**) (0.13 g, 67%). Anal. Found: C, 45.35; H, 5.30.  $\text{C}_{38}\text{H}_{74}\text{Ir}_4$  Calc.: C, 45.23; H, 4.84.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.34 (s, 6H,  $2\text{CH}_3$ ); 1.51 (s, 3H,  $\text{CH}_3$ ); 2.01 (s, 15H,  $\text{C}_5\text{Me}_5$ ); 2.16 (s, 6H,  $2\text{CH}_3$ ); 2.61 (m, 2H); 4.51 (m, 1H); 5.04 (d, 4H,  $J = 0.9\text{ Hz}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  11.2 ( $\text{C}_5\text{Me}_5$ ); 12.8 ( $4\text{Me}$ ); 14.8 ( $4\text{Me}$ ); 22.7 ( $2\text{Me}$ ); 30.1 ( $\text{CMe}$ ); 31.9 ( $\text{CMe}$ ); 47.8 ( $\text{CH}$ ); 48.0 ( $\text{CH}$ ); 60.7 ( $\text{CMe}$ ); 61.0 ( $\text{CMe}$ ); 64.0 ( $\text{CH}$ ); 67.0 ( $\text{C}$ ); 67.1 ( $\text{C}$ ); 73.3 ( $\text{CH}$ ); 73.5 ( $\text{CH}$ ); 83.8 ( $\text{CH}$ ); 83.9 ( $\text{CH}$ ); 89.5 ( $\text{CMe}$ ); 89.7 ( $\text{CMe}$ ); 94.1 ( $\text{C}_5\text{Me}_5$ ).

#### 3.5. Bulk electrolysis of $2^+$

Electrolysis of  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+\text{BF}_4^-$  ( $2^+$ ) (0.1650 g, 0.30 mmol) was carried out at  $-2.5\text{ V}$  in THF ( $50\text{ cm}^3$ ,

0.2 M  $\text{Bu}_4\text{NPF}_6$ ). After consumption of 30.5 Q ( $Q_{\text{theor}} = 29.5$ ,  $n = 1$ ) the current decreased from 15 to 2 mA. A cyclic voltammetry curve of the solution obtained showed the disappearance of the reduction peak of  $2^+$  at  $-2.27$  V and electrolysis was stopped. The solution was evaporated to dryness in vacuo, a residue was extracted with hexane ( $3 \times 20 \text{ cm}^3$ ). The combined hexane solution was filtered, concentrated to  $2 \text{ cm}^3$  and cooled to  $-78^\circ\text{C}$ . The precipitated crystals were filtered and dried in vacuo. Yield of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\mu\text{-}\eta^4\text{-}\eta^4\text{-C}_5\text{Me}_2\text{C}_5\text{Me}_2)\text{Ir}(\eta^5\text{-C}_5\text{H}_5)]$  (**5**) 0.0185 g (5%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.16 (s, 6H,  $2\text{CH}_3$ ); 1.45 (s, 3H,  $\text{CH}_3$ ); 1.80 (s, 15H,  $\text{C}_5\text{Me}_5$ ); 1.99 (s, 6H,  $2\text{CH}_3$ ).

### 3.6. Bulk electrolysis of $3^+$

The electrochemical reduction of  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_2)(\eta^5\text{-C}_9\text{H}_7)]^+\text{BF}_4^-$  ( $3^+$ ) (0.0624 g, 0.12 mmol) was carried out at  $-1.9$  V in THF ( $50 \text{ cm}^3$ , 0.2 M  $\text{Bu}_4\text{NPF}_6$ ). After consumption of 12.1 Q ( $Q_{\text{theor}} = 10.4$ ,  $n = 1$ ) the current decreased from 16 to 2 mA and electrolysis was stopped. The cyclic voltammetry curve of the solution showed the disappearance of reduction peaks of  $3^+$  at 1.50 and 1.65 V and the appearance of a new oxidation peak at  $+0.47$  V. Oxidation of the solution obtained at  $+0.6$  V occurred by consumption of two faradays per mol  $Q_{\text{exp}} = 10.0$  ( $Q_{\text{theor}} = 4.1$ ,  $n = 1$ ). The cyclic voltammetry curve of the solution showed the disappearance of the oxidation peak at  $+0.47$  V and the appearance of reduction peaks of  $3^+$  at 1.50 and 1.65 V.

### Acknowledgements

We thank the Russian Foundation of Fundamental Research and INTAS (Grant INTAS 94-393) for support and Professor Peter M. Maitlis for discussions and encouragement.

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