

Note

Electrochemical reduction of $\text{Ru}(\eta^6\text{-arene})(\kappa^3\text{-tris(pyrazolyl)methane})$ dicationic complexes

William M. Volcheck ^a, Derek A. Tocher ^b, William E. Geiger ^{a,*}

^a Department of Chemistry, University of Vermont, Burlington, VT 05405, USA

^b Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

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Abstract

One-electron reduction of $[\text{Ru}(\eta^6\text{-arene})(\kappa^3\text{-HCPz}_3)]^{2+}$ complexes (arene = *p*-xylene, *p*-cymene, or hexamethylbenzene, Pz = pyrazolyl) was observed at approximately -1.4 V vs. ferrocene in nonaqueous media. Cyclic voltammetry data showed no direct evidence of a hapticity change for either the arene or the tris(pyrazolyl)methane (TPM) ligand in the electron-transfer step. The resulting 19-electron radicals underwent reactions at the arene, giving persistent cyclohexadienyl ruthenium complexes which could be oxidized back to the original complex in an overall chemically reversible process. The dominant reaction for the hexamethylbenzene-containing radical was shown to be an arene-based dimerization ($k_{\text{dim}} = 4 (\pm 3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) which occurs in competition with an H-atom capture, most likely from solvent. The behavior of the 19-electron radicals is similar to that of their all-carbocyclic mixed-sandwich analogues $\text{Ru}(\text{arene})(\text{C}_5\text{R}_5)$ [O.V. Gusev, M.A. Ievlev, T.A. Peganova, M.G. Peterleitner, P.V. Petrovskii, Y.F. Oprunenko, N.A. Ustyryuk, *J. Organomet. Chem.* 551 (1998) 93].

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1. Introduction

Since changes in ligand hapticity are among the most important factors influencing the reactivity of organometallic complexes, the structural consequences of their redox reactions remain under study [1]. Arenes and tris(pyrazolyl)borates are two families of ligands known to be capable of redox-induced hapticity changes. Complexes of the former may undergo η^6 to η^4 arene–metal rearrangements in response to changes in the electron count at the metal center [1b], whereas those of the latter are capable of redox-induced κ^3 to κ^2 hapticity changes [2]. With these facts in mind, we were interested in probing the reduction of mixed-sandwich ruthenium complexes of the type $[\text{Ru}(\eta^6\text{-arene})(\kappa^3\text{-HCPz}_3)]^{2+}$ (Pz = pyrazolyl). The neutral tris(pyrazolyl)methane (TPM) ligand was chosen in place

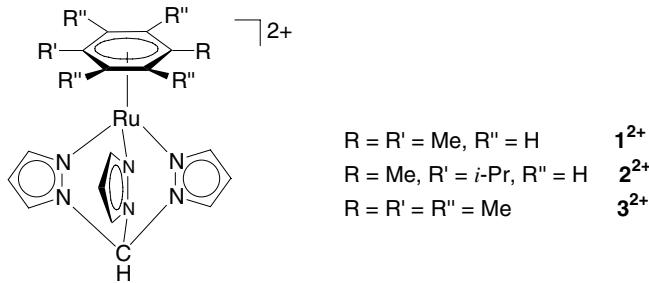
of the analogous borate anion so that the charge on the 18-electron system was the same as that of $[\text{Ru}(\eta^6\text{-C}_6\text{R}_6)_2]^{2+}$. This symmetrical sandwich complex undergoes folding of an arene with loss of two Ru–C bonds when reduced to neutral $\text{Ru}(\eta^6\text{-C}_6\text{R}_6)(\eta^4\text{-C}_6\text{R}_6)$ (R = Me) [3]. We reasoned that cathodic reduction of $[\text{Ru}(\eta^6\text{-arene})(\kappa^3\text{-HCPz}_3)]^{2+}$ [4] might give rise to a hypervalent complex stabilized by lowering of the hapticity of either the arene or the tris-pyrazolyl methane ligand. Although electrochemistry is not itself a structure tool, its results may be highly suggestive about the occurrence of redox-induced structural changes, especially if the thermodynamic and kinetic properties of successive one-electron reactions are known [1c,1d,5].

The electrochemical reductions of three complexes of the type $[\text{Ru}(\eta^6\text{-arene})(\kappa^3\text{-HCPz}_3)]^{2+}$ (arene = *p*-xylene, 1^{2+} , *p*-cymene, 2^{2+} , and hexamethylbenzene, 3^{2+}) were investigated with these goals in mind. Owing to the fact that their $[\text{PF}_6]^-$ salts had inconveniently low solubilities

* Corresponding author.

E-mail address: william.geiger@uvm.edu (W.E. Geiger).

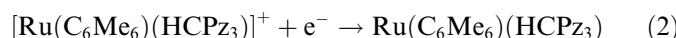
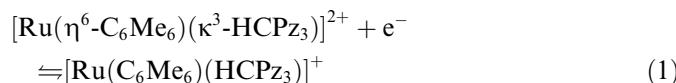
(less than 5×10^{-4} M) in most nonaqueous solvents, complexes **1**²⁺ and **2**²⁺ were given a relatively cursory study, with **3**²⁺ being subjected to a more in-depth investigation.



2. Results and discussion

2.1. General overview

These complexes generally undergo two one-electron cathodic processes having a fairly large separation of about 0.5 V between the first and second processes (Eqs. (1) and (2)). The chemical reversibility of the first reduction, which occurred



at about -1.4 V to -1.5 V vs. ferrocene, varied with compound and solvent, but the 19-electron cation $[\text{Ru}(\text{arene})(\text{HCPz}_3)]^+$ is at least voltammetrically observed for each compound using cyclic voltammetry at scan rates as low as 0.2 V s $^{-1}$. The one-electron nature of the first reduction was confirmed both by coulometry (*vide infra*) and by comparison of the voltammetric currents under the same conditions with those of the previously studied [6] one-electron reduction of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{Me}_5\text{H})]^{2+}$ [7]. Some ‘electrode history’ problems were observed with compounds **1**²⁺ and **2**²⁺, so that frequent re-polishing of the electrode was required for reproducible data, which were much more readily obtained for **3**²⁺. A diffusion coefficient of 7.5×10^{-6} cm 2 s $^{-1}$ was measured for **3**[PF₆]₂ in acetone/0.1 M [NBu₄][PF₆] by chronoamperometry [8]. The CV peak separations, ΔE_p , for the **3**^{2+/+} couple were larger

than those expected for a Nernstian charge transfer (e.g., 136 mV at 0.4 V s $^{-1}$), and the increases of non-ohmic origin (the oxidation of ferrocene gave 72 mV, for example, at the same scan rate) were used along with the literature procedure [9] to calculate the standard heterogeneous rate constant for the process **3**^{2+/+} as $k_s = 7 \times 10^{-3}$ cm s $^{-1}$. A charge transfer coefficient (α value) of 0.5 was assumed based on the symmetric shapes of the CV waves.

The second cathodic wave, apparently due to the reduction of $[\text{Ru}(\eta^6\text{-arene})(\kappa^3\text{-HCPz}_3)]^+$ to the corresponding neutral complex, was irreversible in all cases. This cathodic wave increased in prominence at higher CV scan rates which outran the follow-up reaction of the monocation. The relevant potentials for both processes are collected in Table 1. Two different types of supporting electrolytes were employed: [NBu₄][PF₆] for most of the work, and K[PF₆] for experiments involving ¹H NMR monitoring of crude electrolysis solutions. In the NMR experiments, *d*₆-acetone was used as the electrolysis solvent.

The first reduction of **1**²⁺ and **2**²⁺ displayed limited chemical reversibility, with a reverse-to-forward current ratio of 0.6–0.7 at a CV scan rate of 0.2 V s $^{-1}$, showing that the radicals **1**⁺ and **2**⁺ have half-lives only of the order of seconds [10]. Bulk electrolyses confirmed that the reductions of **1**²⁺ and **2**²⁺ were one-electron processes (1.0–1.1 F/equiv).

2.2. Reduction of **3**²⁺

Representative CV scans for **3**²⁺ are shown in Figs. 1 and 2. The former shows the two cathodic waves described above, and the latter shows the anodic product waves that are observed after scanning through the two cathodic waves. The product wave labeled A is not observed unless the second reduction is included in the scan. Waves B and C, however, at $E_{pa} = 0.15$ V and 0.45 V, respectively, show up not only in CV scans through the first cathodic wave, but also as the dominant product peaks after one-electron bulk reduction of **3**²⁺. Exhaustive cathodic electrolyses were conducted on **3**²⁺ in acetone/[NBu₄][PF₆] at $E_{app} = -1.75$ V. The coulomb counts were in the range of 1.0–1.3 F/equiv as the solutions underwent only slight darkening of their original light yellow color. No cathodic peaks were observed, indicating the absence of both the starting material and easily reduced products. Anodic peaks due

Table 1
Potentials (Volt vs. ferrocene) of $[\text{Ru}(\eta^6\text{-arene})(\kappa^3\text{-HCPz}_3)]^{2+}$ compounds studied in this work

Arene	Compound	Solvent	Supporting electrolyte	$E_{1/2}^a$	E_{pc}^b
<i>p</i> -Xylene	1 ²⁺	CH ₂ Cl ₂	0.1 M [NBu ₄][PF ₆]	-1.37	
<i>p</i> -Xylene	1 ²⁺	CH ₃ CN	0.1 M [NBu ₄][PF ₆]	-1.43	
<i>p</i> -Xylene	1 ²⁺	THF	0.1 M [NBu ₄][PF ₆]	-1.42	-1.87
<i>p</i> -Xylene	1 ²⁺	Acetone	0.1 M [NBu ₄][PF ₆]	-1.39	-1.96
<i>p</i> -Cymene	2 ²⁺	Acetone	0.1 M [NBu ₄][PF ₆]	-1.49	-2.01
Hexamethylbenzene	3 ²⁺	Acetone	0.1 M [NBu ₄][PF ₆]	-1.46	-1.96
Hexamethylbenzene	3 ²⁺	Acetone	0.1 M K[PF ₆]	-1.45	-1.95

^a First reduction process (reduction of dication to monocation).

^b Second wave; irreversible process with cathodic peak potential ($v = 0.1$ V s $^{-1}$) listed.

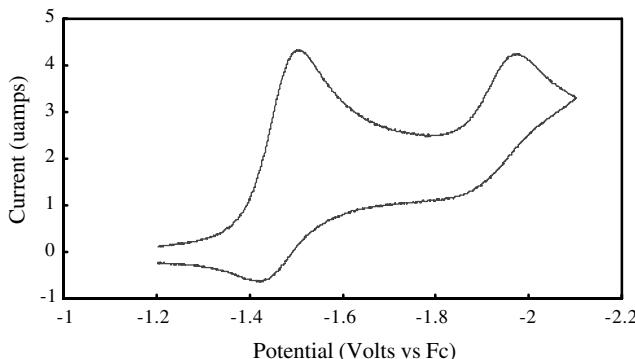


Fig. 1. Cyclic voltammogram of 0.5 mM $[3][\text{PF}_6]_2$ in acetone/0.1 M $[\text{NBu}_4][\text{PF}_6]$ at Au electrode ($d = 1$ mm), scan rate 0.2 V s^{-1} .

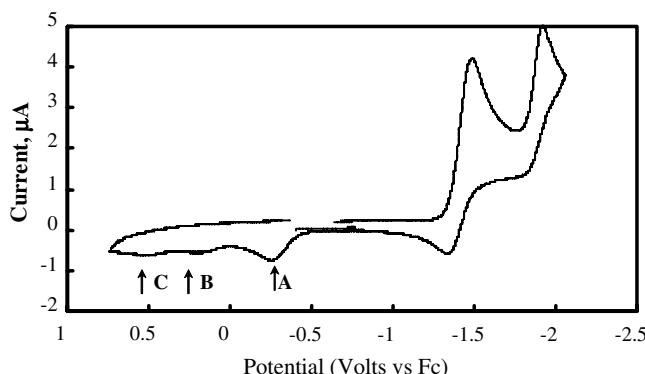
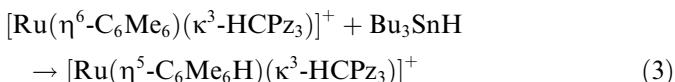


Fig. 2. Cyclic voltammogram of 1.6 mM $[3][\text{PF}_6]_2$ in acetone/0.1 M $[\text{NBu}_4][\text{PF}_6]$ scanning through second cathodic wave. Negative-going scan originated at -0.4 V ; scan rate 0.2 V s^{-1} .

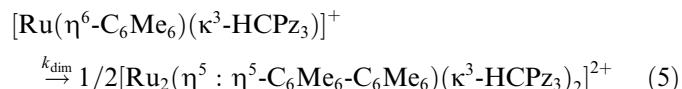
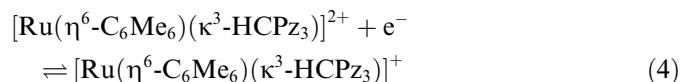
to products were observed, however, at the positions of waves B and C, the currents for which, taken together, were equal to that originally measured for the starting material 3^{2+} . Peak B was larger than that of peak C, showing it to be responsible for the major product. If the solution was anodically re-electrolyzed positive of waves B and C (at $E_{\text{appl}} = 0.7 \text{ V}$), the original cathodic features of 3^{2+} were quantitatively restored. Thus, the one-electron reduction of 3^{2+} and the re-oxidation of the products responsible for waves B and C constitute chemically reversible processes.

Two additional voltammetric experiments aided the analysis of the follow-up reactions. In one of these, the H-atom donor Bu_3SnH was added to a solution of 3^{2+} , causing the chemical reversibility of the $3^{2+/+}$ couple to vanish and the size of product wave C to increase dramatically. On this basis, the product responsible for wave C was concluded to be the cyclohexadienyl system $[\text{Ru}(\eta^5\text{-C}_6\text{Me}_6\text{H})(\kappa^3\text{-HCPz}_3)]^+$, 4^+ , formed by H-atom abstraction by the 19-electron radical (Eq. (3)):



In a second series of experiments, the chemical reversibility of the $3^{2+/+}$ couple was probed as the concentration of 3^{2+}

was varied over the range of $0.1\text{--}2.0 \text{ mM}$. At increased concentrations the reduction became less chemically reversible and the size of product wave B increased, suggesting that dimerization of the 19-electron radical was responsible for product wave B. For example, at a CV scan rate of 0.2 V s^{-1} , i_a/i_c , measured by the Nicholson method [11] decreased from 0.86 at $0.3 \text{ mM } 3^{2+}$ to 0.67 at $2 \text{ mM } 3^{2+}$. The dominant redox process for the reduction of 3^{2+} was thus ascribed to the EC_{dim} process of Eqs. (4) and (5). The reasons for assigning the dimer as having two η^5 -cyclohexadienyl ligands are discussed below. Based on a set of eight data



points obtained at varying analyte concentrations and CV scan rates, the dimerization rate constant was determined using the working curves of Lasia [12] as $k_{\text{dim}} = 4(\pm 3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

2.3. NMR of electrolysis products

Identification of the reduction products focused on an *in-situ* approach, owing to the fact that the organometallic products were likely to have charges identical to those of the supporting electrolyte, thereby increasing the difficulty of their separation from the electrolysis solution. In order to obtain ^1H NMR spectra directly on the electrolysis solutions, experiments were conducted in deuterated acetone, replacing $[\text{NBu}_4][\text{PF}_6]$ by $\text{K}[\text{PF}_6]$ as the supporting electrolyte. The electrolyses were conducted either at 295 K or 263 K with identical results. It was first necessary to confirm that the electrolysis products did not substantially change under the altered electrolyte conditions. This was corroborated by the finding that cathodic electrolysis of a 3 mM solution of $3[\text{PF}_6]_2$ in $d^6\text{-acetone}/0.1 \text{ M K}[\text{PF}_6]$ required 0.97 F/eq at completion and gave a solution having the major anodic product wave at $E_p = 0.15 \text{ V}$ (wave B) and a smaller wave at *ca* 0.4 V (wave C).

Although a large number of features were observed in these spectra (Fig. 3), the lines were sharp and well-defined, allowing a number of assignments to be made. A doublet at $\delta = 8.70 \text{ ppm}$ and multiplets at $\delta = 7.91(\text{t}), 7.65(\text{d}),$ and $6.42(\text{t}) \text{ ppm}$ were ascribed to the free ligand HCPz₃, and another singlet at $\delta = 2.16 \text{ ppm}$ was assigned to free hexamethylbenzene. Both of the free ligands were quantified by standard addition methods. Addition of known concentrations of free HCPz₃ to the solution determined a 13% formation of free tris(pyrazolyl)methane ligand, and a similar procedure gave 11% for hexamethylbenzene. These analyses show that about one-tenth of the electrolysis products decompose with loss of ligands.

The presence of 24 features in the range $6.4\text{--}9.4 \text{ ppm}$ (inset of Fig. 3) complicated the identification of the orga-

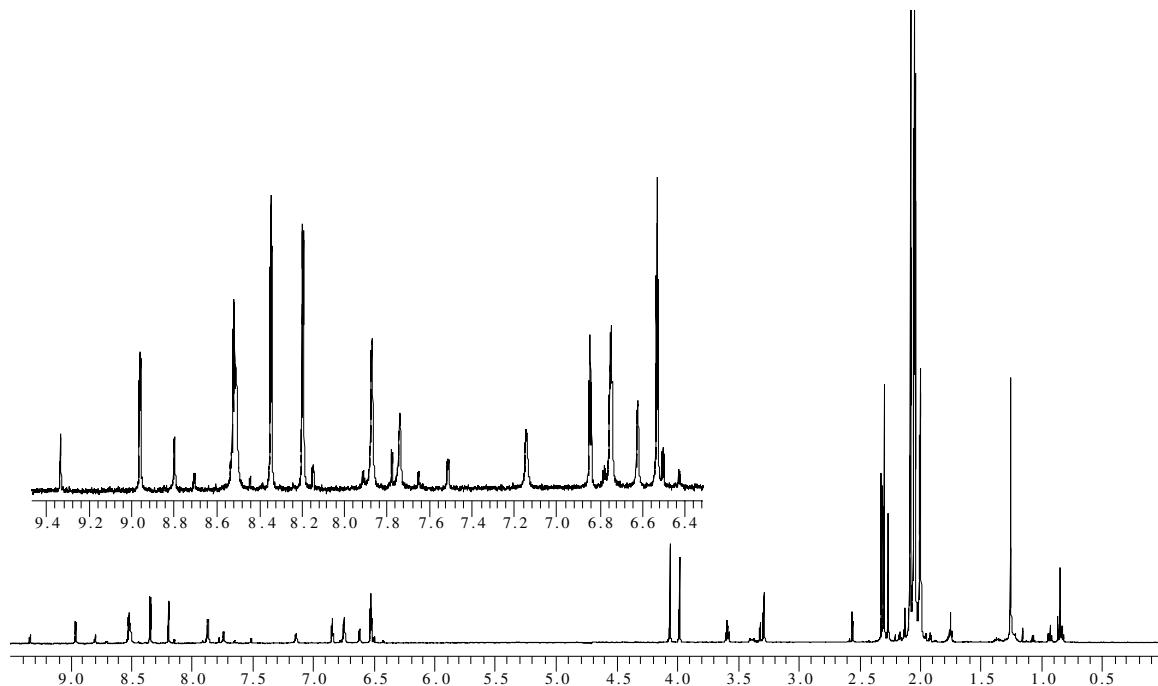


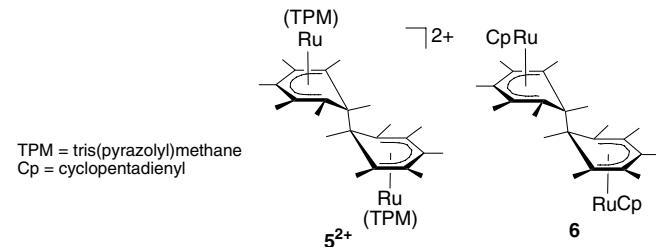
Fig. 3. ^1H NMR spectrum of solution after one-electron bulk cathodic electrolysis of 3 mM $[\mathbf{3}]\text{PF}_6$ in d_6 -acetone/0.1 M $\text{K}[\text{PF}_6]$. The inset contains the expanded TPM region.

nometallic products. Two sets of features were seen, each consistent with two equivalent and one unique metal-bonded pyrazolyl rings: (major) set one: 8.34 (d, 4H), 8.19 (d, 4H), 6.53 (t, 4H), 8.96 (d, 2H), 8.52 (d, 2H), 6.84 (t, 2H) and 8.80 (s, 0.8H); (minor) set two: 8.51 (d, 4H), 7.87 (d, 4H), 6.74 (t, 4H), 7.74 (d, 2H), 7.14 (d, 2H), 6.62 (t, 2H) and 9.33 (s, 0.6H). The two sets followed a roughly 3:1 ratio of intensities, allowing an estimate of the relative ‘yields’ of the major and minor products.

Although the presence of one unique pyrazolyl ring in the HCPz_3 ligand might be taken as evidence of κ^2 -bonding in the major reduction product, such a conclusion would be inconsistent with voltammetric data, which clearly indicates a reaction which is second-order in $\mathbf{3}^+$ being responsible for the major product. The dication $\mathbf{5}^{2+}$, which would arise from dimerization at an aryl carbon owing to partial organic radical character in 19-electron $\mathbf{3}^+$, is more consistent with the combined voltammetric and NMR results. The two metals regain their 18-electron configurations in $\mathbf{5}^{2+}$ by coordination to only five carbons per cyclohexadienyl ring. There is, in fact, good precedent for the pyrazolyl-ligand NMR features of such a system based on previous reports on mononuclear ruthenium complexes of the type $[\text{Ru}(\eta^5\text{-C}_6\text{H}_6\text{R})(\kappa^3\text{-CHPz}_3)]^+$, which showed that one of the pyrazolyl moieties may be rendered unique owing to a rotational barrier arising from interaction with the cyclohexadienyl group [13].

The NMR results in the pyrazolyl region are certainly consistent with the proposed minor product $\mathbf{4}^+$, but definitive identification of $[\text{Ru}(\eta^5\text{-C}_6\text{Me}_6\text{H})(\kappa^3\text{-HCPz}_3)]^+$ was not possible owing to the presence and overlap of resonances (including that of h -acetone) in the hexamethyl-

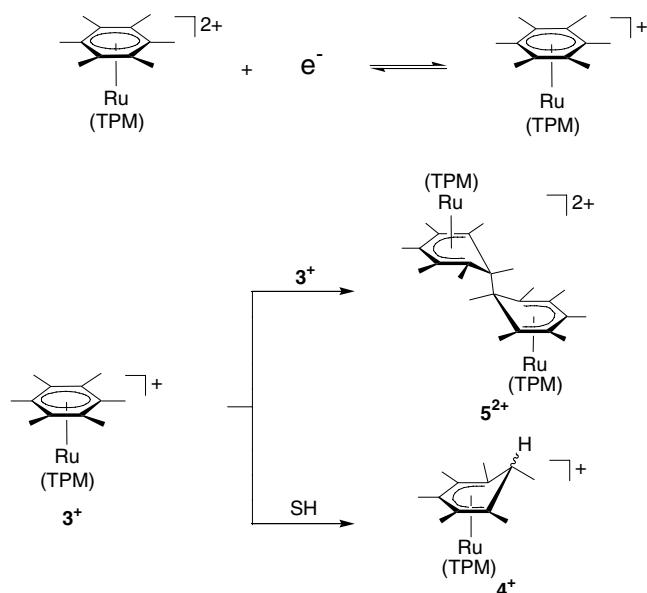
cyclohexadienyl region. The stronger argument for $\mathbf{4}^+$ comes from the voltammetry data cited above.



Literature support for the proposed mechanism is found from the fates of radicals in which the HCPz_3 ligand is replaced by a cyclopentadienyl anion. Gusev et al. have shown that one-electron reduction of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{Me}_6)]^+$ results in formation of the bis(cyclohexadienyl) dimer $\mathbf{6}$, which is analogous to $\mathbf{5}^{2+}$ [14]. Furthermore, the major reduction product in the case of the permethylated cyclopentadienyl analogue was shown to be the cyclohexadienyl complex $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_6\text{Me}_6\text{H})$, analogous to our proposed minor product $\mathbf{4}^+$, formed by reaction of the 19-electron radical $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_6\text{Me}_6)$ with an adventitious hydrogen atom donor [14].

3. Conclusions

The most significant conclusion to be made from this study is that there is no strong evidence that one-electron reduction of a $[\text{Ru}(\eta^6\text{-arene})(\kappa^3\text{-HCPz}_3)]^{2+}$ complex results in lowering of the hapticity of either ligand. One could make an argument, based on the relatively slow charge-



Scheme 1.

transfer rate of the $3^{2+/+}$ couple ($k_s = 0.007 \text{ cm s}^{-1}$) that some geometric change may accompany reduction of the 18-electron complex. A similar rate constant measured for the oxidation of $\text{Rh}(\text{CO})(\text{PCy}_3)(\kappa^2\text{-HCPz}'_3)$ ($\text{Cy} = \text{cyclohexyl}$, $\text{Pz}' = 3,5\text{-dimethylpyrazolyl}$) was, in fact, interpreted in terms of partial formation of a $\text{Rh}-\text{N}$ bond [2c]. There are two reasons why do not favor such an interpretation. One of these concerns the transfer coefficient of 0.5 observed for the $3^{2+/+}$ couple. When redox systems have α values close to 0.5, the charge-transfer step generally does not involve making and breaking of bonds [for a comparison, note that a β value ($\beta = 1 - \alpha$) of 0.33 was determined for the Rh complex] [15]. There were also some variations in electrode responses with the present system that made us less confident about attaching too great a significance to the measured k_s value [16].

Also supporting the conclusion that the metal–ligand bonding remains largely unchanged in the actual charge-transfer step $[\text{Ru}(\eta^6\text{-arene})(\kappa^3\text{-HCPz}_3)]^{2+/+}$ is the fact that the follow-up reactions of the monocation are consistent with those of a 19-electron, rather than 17-electron, system having significant radical character at the arene ligand. Supporting this conclusion is the fact that the gross reactivity of $[\text{Ru}(\text{arene})(\text{HCPz}_3)]^+$ mimics that of the isoelectronic sandwich analogue $\text{Ru}(\text{arene})(\text{C}_5\text{R}_5)$ [14] in undergoing either arene-based dimerization or H-atom abstraction to give 18-electron metal-cyclohexadienyl products. Scheme 1 shows the overall reductive behavior of $[\text{Ru}(\text{arene})(\text{HCPz}_3)]^{2+}$. The dominant outcome of ligand-based dimerization of the 19-electron complex is in keeping with a growing volume of examples of such reactions [14,17].

4. Experimental

All experiments were carried out under a nitrogen atmosphere, using either Schlenk or drybox conditions.

Compounds **1** $^{2+}$, **2** $^{2+}$, and **3** $^{2+}$ were prepared as their $[\text{PF}_6]^-$ salts using the method previously described in the literature [4]. Solvents used for electrochemistry were prepared by first being refluxed and distilled from appropriate drying agents, followed by static bulb-to-bulb vacuum transfers from the same drying agent (CaH_2 in the cases of acetonitrile and dichloromethane, potassium in the case of THF, and anhydrous potassium carbonate in the case of acetone). d^6 -Acetone (Cambridge Isotopes) was dried over type 4 \AA molecular sieves. $[\text{NBu}_4]\text{PF}_6$ was prepared by metathesis of $[\text{NBu}_4]\text{I}$ (in acetone) and $[\text{NH}_4]\text{PF}_6$ (in water), recrystallized three times from ethanol, and dried under vacuum at 100 $^\circ\text{C}$ for at least two days. $\text{K}[\text{PF}_6]$ (Baker) was recrystallized three times from 1:1 water/isopropanol and vacuum dried at 100 $^\circ\text{C}$.

Electrochemical measurements were conducted using a PARC Model 273A potentiostat interfaced to a personal computer. A standard three-electrode cell was employed inside a Vacuum Atmospheres drybox in which the oxygen content was generally 1–5 ppm during an experiment. The temperature of the electrochemical solution was regulated by its emersion in a hydrocarbon bath cooled by a temperature controller. The experimental reference electrode was a homemade Ag/AgCl electrode, separated from the main solution by a fine frit. All the potentials reported in this paper are referenced, as recommended [18], to the ferrocene/ferrocenium couple, the potential of which was measured by addition of a small amount of ferrocene to the solution at an appropriate time in the experiment. The working electrodes were gold disks obtained from Bioanalytical Systems having nominal diameters of either 1.8 mm or 1.0 mm. The areas of these electrodes were determined to be 0.0258 cm^2 and 0.0132 cm^2 , respectively, using chronoamperometry for ferrocene in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{NBu}_4]\text{PF}_6$ and assuming a diffusion coefficient of $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for ferrocene. The electrodes were prepared for use by successive polishings with alumina, followed by washings with nanopure water and vacuum drying. For bulk electrolysis, a three-compartment “H” cell was used in which the working and auxiliary compartments were separated by two fine frits to avoid mixing of the compartments. A large Pt basket was used as the working electrode in these experiments and the electrolysis was carried out until the current was less than 1% of the original. Mechanistic criteria addressing questions of diffusion control, chemical reversibility, and Nernstian behavior followed the procedures which have been described in detail elsewhere [19].

^1H NMR spectra were recorded using either a 500 MHz or 250 MHz Bruker spectrometer.

Acknowledgements

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[7] CV scans of the first cathodic wave of 3^{2+} had a current function only 10% larger than that measured for the one-electron reduction of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{Me}_5\text{H})]^{2+}$, a compound with essentially the same size to charge ratio.

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[9] R.S. Nicholson, *Anal. Chem.* 37 (1965) 1351.

[10] If one were to assume a first-order process for the follow-up reaction, the product 1^+ or 2^+ would be calculated to have a half-life of about 5 s. As shown by concentration studies, the follow-up reaction for 3^+ is actually second-order in complex.

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[15] Transfer coefficients are defined using α for reductions and β ($=1-\alpha$) for oxidations. The oxidation of the Rh complex was determined to have a β value of 0.33 [1c]. Important to the present argument is the fact that redox couples in which bond making and breaking are concomitant with electron transfer generally do not have α values close to 0.5, which would imply a transition state structure midway between reactant and product. See Ref. [8, pp. 97–98], for a discussion of transfer coefficients.

[16] Significantly larger ΔE_p values were measured if the Au electrode was replaced by a Pt electrode. Freshly re-polished gold electrodes did, however, give reproducible results.

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