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# Synthesis and Electrochemical Behavior of Ruthenium(II) Arene Complexes. X-ray Crystal Structure of ($\eta^6$-4-Methylisopropylbenzene)($\eta^6$-fluorene)ruthenium(II)

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Cleavage of the chloro-bridged Ru(II) dimer, $[(\text{4-methylisopropylbenzene})\text{Ru(Cl)}_2]_2$ with $AgBF_4$ in acetone yields the solvated [4-methylisopropylbenzene]$Ru^{II}$ dication monomer which reacts with naphthalene, anthracene, phenanthrene, 9,10-dihydroanthracene, fluorene, *cis*-stilbene, *trans*-stilbene, and coronene to form stable Ru(II) sandwich complexes in good yield. The compounds were characterized by $^{13}C$ and $^1H$ NMR spectroscopy, and an investigation of their electrochemical properties showed that all could be reduced in nitromethane solvent. An X-ray crystal structure determination of the [$\eta^6$-4-methylisopropylbenzene]($\eta^6$-fluorene)$Ru^{II}$ complex verifies the $\eta^6$-binding of the arene ligands. The Ru atom is positioned midway between the two arene rings which are separated by 3.450 Å. The crystals are triclinic, space group $P\bar{1}$, with lattice constants $a = 10.304(2)$ Å, $b = 10.355(3)$ Å, $c = 12.210(2)$ Å, $\alpha = 101.47°$, $\beta = 98.91(1)°$, $\gamma = 111.05(2)°$, and $V = 1154.5(4)$ Å$^3$. Convergence to conventional $R$ values of $R = 0.0373$ and $R_w = 0.0563$ with a goodness-of-fit of 1.07 was obtained for 333 variable parameters and 3035 reflections with $I > 0\sigma(I)$.

## Introduction

Transition metal complexes containing arene ligands continue to play an important role in organotransition metal chemistry. One of the earliest observations was that coordination of unsaturated organics to a transition metal activates the coordinated olefin with respect to nucleophilic addition reactions, and this has frequently been the basis for arene functionalization. Transition metal(arene) complexes, particularly those of the platinum group metals, have also been shown to be useful as catalyst precursors for the hydrogenation of olefins[1a] and it is likely that slippage of the arene ring is an important component of the mechanism.[1b] Quite recently, several Ru(II) arene complexes have found application in the preparation of conducting charge-transfer materials.[2] Cyclophane complexes containing one or more Ru(II) transition metal ions have also been prepared.[2d,3] These latter complexes constitute interesting examples of systems by which to explore electron transfer reactions between two transition metals mediated by an extensively delocalized network of electrons.[3] Reduction, either chemically or electrochemically, requires changes in the bonding of the arene to the transition metal, and structural investigations have documented changes in hapticity in instances where the cyclophane ring can bond.[3e]

Polycyclic benzenoid aromatics, by virtue of the fact that they possess multiple ring sites and $\pi$-orbital electrons, can also form a number of interesting transition metal complexes. Investigations involving Cr(0), for example, have established that both discrete and polymeric ($\eta^6$-$\eta^6$-naphthalene)$_2$Cr(0) complexes can be prepared.[4] Complexes of this latter type are particularly interesting: theoretical considerations indicate that there is a special stability associated with 34 electron systems of this type,[5] and band structure calculations suggest that such systems should behave as electrical conductors in an oxidized state.[5a]

In a preliminary communication we described the synthesis and electrochemical behavior of the symmetrical [4-methylisopropylbenzene]ruthenium(II) sandwich complex.[6] 4-(Methylisopropyl)benzene (also referred to as cymene) was used in the synthesis of this complex, as well as those described in this paper, because the presence of alkyl substituents on the arene facilitates substitution reactions. As such, it is potentially useful as a starting material in the preparation of a variety of new Ru(arene) complexes. A crystal structure determination verified the structure of the complex, and electrochemical investigations showed that it underwent an irreversible reduction in nitromethane solvent at room temperature.

Our interest in the structures and electrochemical properties of transition metal complexes of this type led us to prepare a new series of complexes containing other arene ligands, including those containing two or more fused

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rings. Complexes in which two transition metals are coordinated will be the subject of a subsequent publication. In this paper we present the results of our investigations concerning 1:1 complexes obtained by following the reaction of [4-methylisopropylbenzene]Ru$^{II}$ dication with a variety of arene systems.

## Experimental Section

**General Considerations.** All manipulations were carried out using standard Schlenk techniques under oxygen-free nitrogen or in an inert atmosphere glovebox. Solvents were distilled from suitable drying agents prior to use. DMSO was dried over 4-Å molecular sieves. $\alpha$-Terpinene (1-isopropyl-4-methyl-1,4-cyclohexadiene), naphthalene, phenanthrene, anthracene, 9,10-dihydroanthracene, fluorene, *cis*-stilbene, *trans*-stilbene, and coronene were purchased from Aldrich Chemical Co., Inc., and used as received. Ruthenium(III) chloride hydrate was obtained from the Engelhard Corp. NMR spectra were recorded on a Bruker AM-250 spectrometer using either nitromethane-$d_3$ or DMSO-$d_6$ dried over molecular sieves and referenced to TMS. Crystallographic data were collected on a Siemens R3m/V diffractometer and electrochemical investigations were carried out using a Bioanalytical systems CV-27 voltammograph. Peak reduction potentials were determined using cyclic voltammetry in 5.0 mL of a 0.1 M solution of [NBu$_4$][PF$_6$] in nitromethane to which was added 2.0 mL of a 0.05 M solution of the appropriate complex, also in nitromethane. The cell consisted of a platinum working electrode and a platinum counter electrode. Measured cell potentials were referred to a Ag/AgCl reference electrode. All elemental analyses were performed by Texas Analytical Laboratories, Inc.

**Preparation of [(acetone)$_3$[$\eta^6$-4-methylisopropylbenzene]-Ru$^{II}$][BF$_4$]$_2$.** The chloro-bridged Ru(II) dimer, [[4-methylisopropylbenzene]Ru(Cl)$_2$]$_2$, was prepared using the literature procedure.[7] AgBF$_4$ was used to abstract the halide ions in acetone solvent, producing the tris(acetone)[4-methylisopropylbenzene]-ruthenium(II) dication. In a typical synthesis, 250 mg (1.3 mmol) of AgBF$_4$ was added to 0.20 g (0.33 mmol) of the chloro-bridged Ru(II) dimer in 5.0 mL of acetone. The reaction mixture was stirred vigorously for 15 min at room temperature, and the AgCl precipitate was separated by filtration. Removal of the solvent under vacuum resulted in the formation of a yellow oil which was used immediately.

**Preparation of [[$\eta^6$-4-methylisopropylbenzene]($\eta^6$-naphthalene)Ru$^{II}$][BF$_4$]$_2$ (1).** The solvated ruthenium(II) dication was prepared using 0.762 g (3.8 mmol) of the chloro-bridged ruthenium(II) starting material and reacted with naphthalene (0.60 g, 4.7 mmol) in 18 mL of trifluoroacetic acid. The reaction mixture was heated at 90 °C for 5 min and cooled to room temperature, and the solvent was removed under reduced pressure. A small of quantity of diethyl ether (4.0 mL) was added to triturate the product which was isolated by filtration and washed with 10.0 mL of methanol. A 0.55-g (1.0-mmol) amount of yellow powder decomposing at 217 °C was isolated in 53% yield. Anal. Calc for C$_{20}$H$_{22}$B$_2$F$_8$Ru: C, 44.68; H, 4.09. Found: C, 44.49; 4.13, H.

**Preparation [[$\eta^6$-4-methylisopropylbenzene]($\eta^6$-phenanthrene)Ru$^{II}$][BF$_4$]$_2$ (2).** A 0.31-g (1.7-mmol) sample of phenanthrene was refluxed in a Schlenk flask containing 5.0 mL of trifluoroacetic acid and the Ru(II) dication obtained from 0.20 g (0.33 mmol) of the dimeric ruthenium(II) starting material. The reaction mixture was refluxed for 5 min at 90 °C, producing a yellow oil upon workup. Addition of 3.0 mL of diethyl ether resulted in the formation of a pale yellow solid in 48.8% yield (189 mg, 0.322 mmol) that decomposed at 220 °C. Anal. Calc for C$_{24}$H$_{24}$B$_2$F$_8$Ru: Ru, 17.21; C, 49.05; H, 4.09. Found: Ru, 17.13; C, 49.01; H, 4.2.

**Preparation of [[$\eta^6$-4-methylisopropylbenzene]($\eta^6$-anthracene)Ru$^{II}$][BF$_4$]$_2$ (3).** A 0.2-g (0.33-mmol) amount of the chloro-bridged Ru(II) dimer was used to prepare the Ru(II) dication, and this was reacted immediately with 0.23 g (1.3 mmol) of anthracene in 5.0 mL of trifluoroacetic acid. The reaction mixture was heated at 90 °C for 5 min and cooled, and the solvent was removed under vacuum. Addition of 3.0 mL of diethyl ether resulted in the formation of an off-white precipitate which was isolated by filtration. The product was washed with an additional 5.0-mL aliquot of ether to remove any excess anthracene, followed by 5.0 mL of freshly distilled methanol. A total of 85 mg (0.145 mmol) of product that began to decompose at 191 °C was isolated 21.9% yield. Anal. Calc for C$_{24}$H$_{24}$B$_2$F$_8$Ru: C, 49.05; H, 4.09. Found: C, 48.96; H, 4.11.

**Preparation of [[$\eta^6$-4-methylisopropylbenzene]($\eta^6$-9,10-dihydroanthracene)Ru$^{II}$][BF$_4$]$_2$ (4).** The Ru(arene) dication was prepared using 0.60 g (0.98 mmol) of the chloro-bridged ruthenium(II) starting material and reacted with 0.60 g (3.3 mmol) of 9,10-dihydroanthracene (0.60 g, 3.3 mmol) in 7.0 mL of CHCl$_3$. Heating the reaction mixture at reflux for 10 h resulted in the formation of a pale yellow material which was washed with 5.0 mL of diethyl ether, followed by 5.0 mL of freshly distilled methanol. A change in color from yellow to a pale pink was seen and 180 mg (0.425 mmol, 64.3% yield) of a solid material decomposing at 197 °C was isolated. Anal. Calc for C$_{24}$H$_{26}$B$_2$F$_8$-Ru: C, 48.80; H, 4.40. Found: C, 48.80; H, 4.35.

**Preparation of [[$\eta^6$-4-methylisopropylbenzene]($\eta^6$-fluorene)Ru$^{II}$][BF$_4$]$_2$ (5).** A 0.20-g (0.33-mmol) sample of [[4-methylisopropylbenzene]Ru(Cl)$_2$]$_2$ was used in the preparation of the dication, and this was reacted with excess fluorene (0.23 g, 1.3 mmol) in 5.0 mL of trifluoroacetic acid. The reaction mixture was refluxed for 5 min and the solvent removed under reduced pressure. Addition of 3.0 mL of anhydrous diethyl ether resulted in the formation of an off-white solid that was isolated by filtration. The product was washed with 3.0 mL of anhydrous diethyl ether to remove any remaining free fluorene and 5.0 mL of methanol. A 300-mg (0.522-mmol) amount of an off-white solid decomposing at 206 °C was isolated in 79.1% yield. Crystals suitable for an X-ray crystal structure were obtained by crystallization from a methanol/DMSO solution. Anal. Calc for C$_{23}$H$_{24}$B$_2$F$_8$Ru: C, 47.98; H, 4.17. Found: C, 47.76; H, 4.21.

**Preparation of [[$\eta^6$-4-methylisopropylbenzene]($\eta^6$-*trans*-stilbene)Ru$^{II}$][BF$_4$]$_2$ (6).** The Ru(II) dication was prepared in the usual way using 0.20 g (0.33 mmol) of the chloro-bridged starting materials and reacted with a slight excess (0.23 g, 1.3 mmol) of *trans*-stilbene in 5.0 mL of trifluoroacetic acid. The reaction mixture was refluxed at 90 °C for 5 min and cooled, and the solvent was removed under reduced pressure. A viscous oily product was obtained, to which was added 3.0 mL of diethyl ether. This resulted in the immediate appearance of a yellow powder which was separated out by filtration and washed with 5.0 mL of diethyl ether, followed by 5.0 mL of freshly distilled methanol. The yield was 64.3% (250 mg, 0.425 mmol) of a colorless product that decomposed at 244 °C. Anal. Calc for C$_{24}$H$_{26}$B$_2$F$_8$Ru: C, 48.88; H, 4.41. Found: C, 47.53; H, 4.58.

**Preparation of [[$\eta^6$-4-methylisopropylbenzene]($\eta^6$-*cis*-stilbene)Ru$^{II}$][BF$_4$]$_2$ (7).** The same procedures as above were used in the preparation of the *cis*-stilbene complex. The ruthenium(II) dication was prepared using 0.3 g (0.49 mmol) of the chloro-bridged dimer starting material and reacted with 4.0 mL (22.5 mmol) of *cis*-stilbene in 6.0 mL of trifluoroacetic acid. Upon workup only a small amount of product in low yield (<10%) that analyzed satisfactorily for C and H was obtained. No attempts were made to improve product yields, and this complex was not investigated further owing to the small amount of product obtained. Anal. Calc for C$_{24}$H$_{26}$B$_2$F$_8$Ru: C, 48.88; H, 4.41. Found: C, 48.83; H, 4.46.

**Preparation of [[$\eta^6$-4-methylisopropylbenzene]($\eta^6$-coronene)Ru$^{II}$][BF$_4$]$_2$ (8).** The cationic Ru(II) complex was prepared in the usual manner using 0.30 g (0.49 mmol) of the dimeric Ru(II) starting material. To this product in a Schlenk

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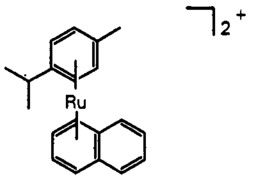
flask was added 5.0 mL of trifluoroacetic acid and 0.14 g (0.47 mmol) of coronene. The reaction mixture was refluxed at 90 °C for 5 min and then cooled and the solvent removed under reduced pressure. The product that remained, in the form of an oily residue, was washed with 3.0 mL of diethyl ether which resulted in the precipitation of an off-white solid. The precipitate was isolated by filtration and washed with a 5.0-mL aliquot of ether followed by a second 5.0-mL aliquot of methanol. A 150-mg (0.212-mmol) amount of product melting with decomposition at 210 °C was isolated in 21.6% yield. Anal. Calcd for $C_{34}H_{26}B_2F_8$-Ru: C, 57.52; H, 3.66. Found: C, 56.13; H, 3.58.

**Structure Determination of $[[\eta^6$-4-methylisopropylbenzene$](\eta^6$-fluorene$)Ru^{II}][BF_4]_2$.** Crystal data and details concerning the experimental procedures are summarized in Table 3. A regularly shaped yellow tinted crystal having approximate dimensions 0.40 × 0.24 × 0.40 mm was selected and mounted on the end of a glass fiber in a random orientation. Triclinic symmetry was suggested on the basis of the interaxial angles and confirmed by a Delaunay reduction procedure. Refined cell parameters were determined from the setting angles of 25 reflections with $15° < 2\theta < 30°$. Data collection was carried out at ambient temperature using the $\omega$-scanning technique in bisecting geometry on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo K$\alpha$ radiation. Scan rate variable, 3–15° $min^{-1}$; scan range, 1.2 deg in $\omega$. Three standards measured every 97 data showed only minor variations in intensity (<3.0%) over the period of data collection. A total of 3240 reflections ($+h,+k,+l$; $h_{max} = 11$, $k_{max} = 11$, $l_{max} = 13$) with $3.5° < 2\theta < 45°$ were obtained and corrected for Lorentz and polarization effects, including absorption. Absorption corrections were applied empirically on the basis of azimuthal scans of several strong reflections spanning a range of $2\theta$ values. Equivalent reflections were merged, resulting in 3035 unique reflections with $I > 0\sigma(I)$. Structure solution and refinement was carried out using the SHELXTL-PC collection of crystallographic software.[8] Intensity statistics favored the centrosymmetric $P\bar{1}$ space group. The position of the Ru atom was located from a sharpened Patterson map and used as an initial phasing model. All remaining non-hydrogen atoms were located using standard difference-Fourier techniques. All non-hydrogen atoms were refined anisotropically using scattering factors that included terms for anomalous dispersion.[9] Hydrogen atoms were included in idealized positions with fixed isotropic $U = 0.08$ Å$^2$. During the later stages of refinement it became apparent that the $BF_4$ anions suffered from some degree of disorder. For both anions the disorder was satisfactorily resolved by including the F atoms in alternate positions. When refined, the occupancy factors indicated a 15% disorder over two inequivalent sites for three of the four F atoms. Refinement was based on $F$ using weights of the form $w^{-1} = [\sigma^2(F) + 0.0024(F^2)]$. The maximum shift/$\sigma$ for the final cycle was 0.001 with minimum and maximum residual electron densities of +0.61 and −0.42 e Å$^{-3}$. Convergence to conventional $R$ values of $R = 0.0373$ and $R_w = 0.0565$ with a goodness-of-fit of 1.07 was obtained for 333 variable parameters and 3035 reflections with $I > 0\sigma(I)$.

## Results and Discussion

Halide abstraction using a silver salt provides an effective means of cleaving the chloro-bridged ruthenium(II) dimer. When carried out in acetone, a fairly air-stable product containing three coordinated molecules of acetone is produced.[10] This complex is reported to iosmerize rapidly at room temperature; two of the coordinated acetone ligands undergo an aldol type of condensation to form 4-hydroxy-4-methylpentan-2-one, and the structure of this product has been characterized crystallographically.[10] Reaction with the appropriate arene in refluxing trifluoroacetic acid results in displacement of the solvent molecules to produce the arene sandwich complexes. While not essential, the use of trifluoroacetic acid results in better product yields.

The results of the elemental analyses for all the complexes are consistent in each case with the presence of a single transition metal. In all instances the products were isolated as air-stable dications, each crystallizing with two $BF_4$ anions. Reaction yields were found to vary, ranging from less than 10% to nearly quantitative. All of the products exhibited good solubility in DMSO and nitromethane, but poor solubility in alcohols and halogenated solvents.



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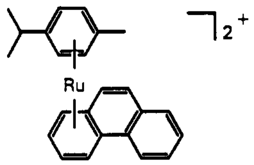

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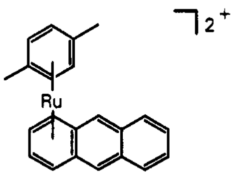

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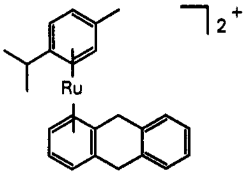

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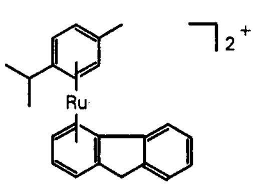

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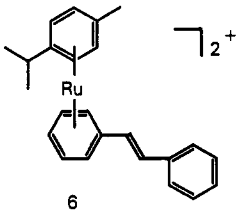

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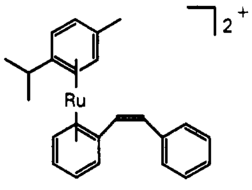

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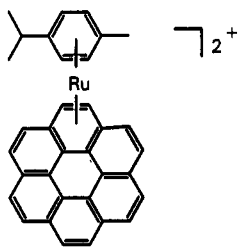

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An inspection of the chemical shifts in $^1H$ and $^{13}C$ NMR spectra of these complexes reveals a consistent pattern. In all instances the resonances of the C atoms involved in coordination to the transition metal are shifted upfield *circa* 30–40 ppm. This is accompanied by a slight downfield shift in the C atoms not coordinated to the ruthenium center in those systems having two or more fused aromatic rings. A similar behavior is observed for the protons. Those bound to the C atoms coordinated to the transition metal are also found shifted toward higher fields, typically 1–2 ppm or less, whereas the resonances for those bound to the remaining C atoms move downfield

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**Table 1. $^1$H NMR Absorptions (ppm) of Complexes**

| compnd no. | (solvent) | |
|---|---|---|
| $[\mathbf{1}]^{2+}$ | ($CD_3NO_2$) | 6.70 (d, 2H, *J* = 6.65 Hz), 6.51 (d, 2H, *J* = 6.61 Hz), 2.62 (sep, 1H, *J* = 6.90 Hz), 2.02 (s, 3H), 1.27 (d, 6H, *J* = 6.92 Hz) (4-methylisopropylbenzene); 8.29 (dd, 2H, $J_1$ = 6.76 Hz, $J_2$ = 6.71 Hz), 8.07 (dd, $J_1$ = 6.68 Hz, $J_2$ = 6.70 Hz, 2H), 7.88 (dd, $J_1$ = 4.66 Hz, $J_2$ = 7.16 Hz, 2H), 7.05 (dd, $J_1$ = 4.8 Hz, $J_2$ = 4.73 Hz, 2H) (naphthalene) |
| $[\mathbf{2}]^{2+}$ | (DMSO-$d_6$) | 6.66 (d, 2H, *J* = 6.39 Hz), 6.42 (d, 2H, *J* = 6.44 Hz), 2.55 (sep, 1H, *J* = 6.97 Hz), 1.71 (s, 3H), 1.15 (d, 6H, *J* = 6.97 Hz) (4-methylisopropylbenzene); 8.72 (m, 1H) 8.42 (m, 1H), 8.16 (m, 1H), 8.08 (m, 2H), 7.93 (m, 1H), 7.68 (m, 3H), 7.08 (m, 1H) (phenanthrene) |
| $[\mathbf{3}]^{+}$ | ($CD_3NO_2$) | 6.61 (d, 2H, *J* = 5.0 Hz) 6.49 (d, 2H, *J* = 5.0 Hz) 2.39 (sep, 1H, *J* = 5.1 Hz), 1.87 (s, 3H) 1.11 (d, 6H, *J* = 5.0 Hz) (4-methylisopropylbenzene); 8.80 (s, 2H), 8.19 (m, 4H), 7.86 (m, 2H) 7.08 (m, 2H) (anthracene) |
| $[\mathbf{4}]^{2+}$ | ($CD_3NO_2$) | 6.44 (d, 2H, *J* = 6.72 Hz), 6.23 (d, 2H, *J* = 6.69 Hz), 2.80 (sep, 1H, *J* = 6.91 Hz), 2.24 (s, 3H), 1.27 (d, 6H, *J* = 6.87 Hz) (4-methylisopropylbenzene); 7.53 (m, 4H), 7.12 (m, 2H), 4.15 (dd, 4H, *J* = 21.42 Hz) (9,10-dihydroanthracene) |
| $[\mathbf{5}]^{2+}$ | (DMSO-$d_6$) | 6.71 (d, 2H, *J* = 6.69 Hz), 6.52 (d, 2H, *J* = 6.68 Hz), 2.62 (sep, 1H, *J* = 7.07 Hz), 2.03 (s, 3H) 1.27 (d, 6H, *J* = 6.88 Hz) (4-methylisopropylbenzene); 8.28 (m, 2H), 8.07 (m, 2H), 7.88 (m, 2H) 7.05 (m, 2H) 4.27 (dd, 2H, *J* = 23.50 Hz) (fluorene) |
| $[\mathbf{6}]^{2+}$ | ($CD_3NO_2$) | 7.25 (d, 2H, *J* = 6.35 Hz), 7.10 (d, 2H, *J* = 6.36 Hz), 2.99 (sep, 1H, *J* = 6.82 Hz), 2.49 (s, 3H), 1.33 (d, 6H, *J* = 6.75) (4-methylisopropylbenzene); 7.87 (m, 2H), 7.76 (m, 3H), 7.10 (m, 2H), 7.02 (m, 5H) (*trans*-stilbene) |
| $[\mathbf{8}]^{2+}$ | ($CD_3NO_2$) | 5.28 (d, 2H, *J* = 6.48 Hz), 5.04 (d, 2H, *J* = 6.37 Hz), 1.57 (sep, 1H, *J* = 6.83 Hz), 1.00 (s, 3H), 0.53 (d, 6H, *J* = 6.87) (4-methylisopropylbenzene); 8.86 (d, 2H, *J* = 9.06 Hz), 8.74 (d, 2H, *J* = 8.41 Hz), 8.59 (d, 2H, *J* = 8.38 Hz), 8.45 (s, 2H), 8.21 (d, 2H, *J* = 9.05), 7.83 (s, 2H) (coronene) |

**Table 2. $^{13}$C NMR Absorptions (ppm) of Complexes**

| compnd no. | (solvent) | |
|---|---|---|
| $[\mathbf{1}]^{2+}$ | ($CD_3NO_2$) | 120.8, 111.6, 94.9, 92.2, 32.6, 22.5, 18.1 (4-methylisopropylbenzene); 139.6, 130.0, 103.3, 94.6, 94.2 (naphthalene) |
| $[\mathbf{2}]^{2+}$ | (DMSO-$d_6$) | 120.6, 111.4, 92.3, 87.9, 32.6, 22.2, 21.9, 17.3 (4-methylisopropylbenzene); 140.5, 133.2, 132.1, 131.2, 129.5, 127.5, 123.7, 123.6, 123.5, 101.8, 94.5, 94.3, 94.2, 93.4 (phenanthrene) |
| $[\mathbf{3}]^{2+}$ | ($CD_3NO_2$) | 120.1, 111.2, 94.2, 91.8, 32.9, 22.7, 18.8 (4-methylisopropylbenzene); 141.3, 133.4, 131.8, 130.3, 100.6, 94.9, 94.5 (anthracene) |
| $[\mathbf{4}]^{2+}$ | ($CD_3NO_2$) | 123.8, 114.9, 93.8, 92.8, 33.3, 22.8, 19.8 (4-methylisopropylbenzene); 133.9, 129.7, 129.3, 115.8, 93.7, 92.8, 34.5 (9,10-dihydroanthracene) |
| $[\mathbf{5}]^{2+}$ | (DMSO-$d_6$) | 119.2, 111.0, 95.4, 91.4, 30.6, 21.8, 21.6, 16.4 (4-methylisopropylbenzene); 145.7, 133.0, 128.3, 126.3, 125.1, 114.5, 113.5, 93.5, 92.3, 91.9, 91.7, 86.1, 36.6 (fluorene) |
| $[\mathbf{6}]^{2+}$ | ($CD_3NO_2$) | 121.3, 112.6, 94.7, 92.7, 31.1, 22.3, 18.7 (4-methylisopropylbenzene); 142.5, 132.4, 130.8, 129.3, 128.4, 118.9, 105.2, 95.1, 92.4, 90.4 (*trans*-stilbene) |
| $[\mathbf{8}]^{2+}$ | ($CD_3NO_2$) | 119.7, 106.3, 89.9, 87.4, 28.6, 19.3, 14.1 (4-methylisopropylbenzene); 136.7, 131.6, 130.6, 129.8, 127.9, 127.5, 125.6, 124.4, 122.3, 114.9, 95.9, 87.9 (coronene) |

slightly. In some instances the two methyl groups belonging to the isopropyl portion of the methylisopropylbenzene ligand give rise to two independent sets of resonances. We find, for example, two resonances for these methyl groups in the proton decoupled $^{13}$C spectrum of the fluorene and phenanthrene products. Similarly, a doublet of doublets for the isopropyl protons, as opposed to the usual doublet, is observed in the $^1$H NMR spectrum of these complexes. This suggests some degree of hindered rotation about the arene–carbon bond, although a more detailed variable temperature NMR investigation would be needed in order to firmly establish this point.

The presence of two or more available ring sites in several of the systems investigated affords the transition metal an opportunity to coordinate at more than one position. However, for anthracene and phenanthrene, only one product was identified. $^{13}$C NMR data for these complexes indicate that the metal binds preferentially to the outer ring, and not the center. Similarly, coordination to the inner ring is ruled out for coronene because this would lead to a highly symmetrical structure giving rise to only three resonances in the $^{13}$C spectrum, whereas twelve are actually observed. A similar interpretation has been presented for a (cyclopentadienyl)Fe$^{II}$ complex of coronene, where only one species was identified in solution.[11] A possible reason is that the outer carbons in coronene bear the highest negative charge, and this is supported by extended Huckel calculations.[12]

Interpretation of the chemical shift data in these complexes is aided by an X-ray crystal structure determination of the [$\eta^6$-methylisopropylbenzene]($\eta^6$-fluorene)Ru$^{II}$ dication which verifies both the stoichiometry and proposed $\eta^6$-binding mode of the arene ligands (Figure 1). In this complex the transition metal is located symmetrically between the two arenes at a distance of 1.73 Å from the centroid defined by the two sets of six carbon atoms to which it is attached. The two arene rings are essentially parallel to each other and the observed dihedral angle defined by their least-squares plane is 178.5°. From the room temperature NMR data it appears that the 4-(methylisopropyl)benzene ligand rotates freely in this complex; in the solid state the arene ligands adopt a configuration that minimizes repulsive interactions between the alkyl groups and fluorene.

Structural features associated with the 4-methylisopropylbenzene group compare favorably with those observed in the structure of the symmetrical sandwich complex, [[$\eta^6$-4-methylisopropylbenzene]$_2$Ru][$BF_4$]$_2$.[6] For the C atoms of the coordinated arene rings we find that the C–C bonds range from 1.395 to 1.420 Å (C–C average = 1.410 Å) and are longer, on the average by 0.030 Å compared with those in the free ring of fluorene. We find no evidence for any regular alternation in any of the

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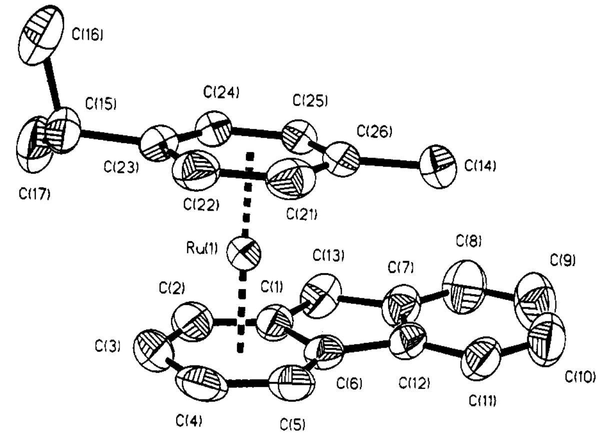

**Figure 1.** View of the structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. The two $BF_4$ counterions are not shown and H atoms have been omitted for clarity.

C–C bond lengths that would be indicative of some degree of bond localization. Both of the coordinated rings remain essentially planar, which suggests that the aromatic character of the arene rings is largely maintained.

Many of the key structural features associated with the fluorene ligand are similar to those found in the structure of free fluorene.[13] Specifically, the molecule is not planar, but is instead folded about the methylene bridge at an angle of 2.5°, compared with 1.3° for free fluorene. Similarly, C–C bond lengths and angles associated with the free arene ring in the structure of this complex are in good agreement with those published in a room-temperature X-ray crystal structure of free fluorene.[13a] It is interesting to note that fluorene can also be deprotonated, forming the planar aromatic fluorenyl anion, and the crystal structure of an iron complex containing this ligand has been described.[14]

Cyclic voltammetry was used to investigate the electrochemical properties of the complexes, and it was found that all undergo reduction in nitromethane solvent with varying degrees of reversibility. Only a reduction step was seen when dihydroanthracene, *trans*-stilbene, and coronene were examined. The naphthalene and anthracene complexes, on the other hand, showed both an anodic and cathodic wave with a ratio of $I_c$:$I_a$ approximately equal to unity at scan rates up to 2 V/s. For the phenanthrene complex, the electrochemical response depended on scan rate. An irreversible reduction was seen at low scan rates (<500 mv/s); however, increasing the scan rate to 2 V/s led to the appearance of an anodic wave with $I_c$:$I_a$ approximately equal to 0.5. Beyond that, both the anodic and cathodic currents decreased. For those systems exhibiting quasi-electrochemical reversibility, the peak cathodic and anodic potentials proved to be highly dependent on scan rate. In the absence of more detailed information concerning the electrochemical behavior of the complexes, we are unable to state with certainty whether or not the reduction step is one that involves one or two electrons. If the reduction involves two electrons, it would also be of interest to establish whether or not this process involves two discrete one electron steps or occurs as a one step process involving two electrons.[15]

**Table 3. Crystal Data and Data Collection Summary**

| | |
|---|---|
| empirical Formula | $C_{23}H_{24}B_2F_8Ru$ |
| cryst size (nm) | 0.40 × 0.24 × 0.40 |
| cryst syst | triclinic |
| space group | $P\bar{1}$ |
| unit cell dimens | |
| $a$ (Å) | 10.304(2) |
| $b$ (Å) | 10.355(2) |
| $c$ (Å) | 12.210(2) |
| $\alpha$ (deg) | 101.47(2) |
| $\beta$ (deg) | 98.910(10) |
| $\gamma$ (deg) | 111.05(2) |
| vol (Å$^3$) | 1154.5(4) |
| $z$ | 2 |
| fw | 575.1 |
| density (calc) (Mg/m$^3$) | 1.654 |
| abs coeff (mm$^{-1}$) | 0.737 |
| min/max transm | 0.690/0.865 |
| $F(000)$ | 576 |
| radiation ($\lambda$ (Å)) | Mo K$\alpha$ (0.710 73) |
| temp (K) | 295 |
| $2\theta$ range (deg) | 3.5–45.0 |
| scan speed (deg/min) | variable; 3.00–15.00 in $\omega$ |
| scan range ($\omega$) (deg) | 1.80 |
| index ranges | $0 \leq h \leq 11, -11 \leq k \leq 10, -13 \leq l \leq 13$ |
| no. of reflns collcd | 3240 |
| no. of ind reflns | 3035 ($R_{int}$ = 1.02%) |
| no. of obs reflns | 3035 ($F > 0.0\sigma(F)$) |
| quantity minimized | $\sum w(F_o - F_c)^2$ |
| weighting scheme | $w^{-1} = \sigma^2(F) + 0.0024F^2$ |
| no. of params refined | 333 |
| final $R$ indices (obs data) | $R$ = 3.73%, $R_w$ = 5.63% |
| largest and mean $\Delta/\sigma$ | 0.001, 0.000 |
| largest diff peak (e/Å$^3$) | 0.61 |
| largest diff hole (e/Å$^3$) | –0.42 |

Variations in the potential at which the different complexes become reduced prompts us to consider whether or not there is any correlation between the peak reduction potential and readily identifiable electronic or structural property of the arene. Aromaticity in polyaromatics decreases in a general way with increasing size, and from the electrochemical data, we find that systems possessing two or more fused aromatic rings are the most easily reduced. Of the complexes examined, we find the anthracene complex to have the least negative peak reduction potential. On the other hand, complexes possessing arene rings separated by intervening alkyl groups (4-methylisopropylbenzene, fluorene), display reduction potentials that are shifted toward more negative potentials. Inspection of the literature shows that similar electrochemical behavior has been documented in other arene complexes bearing the (cyclopentadienyl)Ru$^{II}$ fragment.[16] (Cyclopentadienyl)ruthenium(II) complexes containing benzene or substituted benzene derivatives are not found to be reduced, even up to potentials of –2.5 V.[17] It is interesting to note that this behavior contrasts with that of (cyclopentadienyl)Fe$^{II}$ complexes, where this trend is reversed.[18]

An important question concerning the reduction of the Ru(II) center in these complexes is whether or not any structural changes are involved. Redox-induced $\eta^6$–$\eta^4$

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**Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)**

| | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Ru(1) | 1416(1) | 3256(1) | 2570(1) | 36(1) |
| F(1) | 7743(4) | 777(3) | 9406(3) | 70(2) |
| F(2) | 8011(13) | 3036(7) | 9422(6) | 185(7) |
| F(3) | 9102(7) | 2083(8) | 8482(7) | 150(5) |
| F(4) | 6928(9) | 1201(8) | 7784(6) | 195(5) |
| F(5) | −4415(5) | −3350(5) | 2657(3) | 109(3) |
| F(6) | −4082(7) | −3419(15) | 4469(5) | 211(7) |
| F(7) | −3654(9) | −4802(7) | 3263(9) | 173(5) |
| F(8) | −2196(6) | −2512(8) | 3916(7) | 160(4) |
| F(2A) | 8964(13) | 2947(15) | 9397(12) | 43(4) |
| F(3A) | 7933(19) | 1454(16) | 7778(12) | 50(4) |
| F(4A) | 6626(14) | 2041(17) | 8732(14) | 52(4) |
| F(6A) | −4148(16) | −4419(19) | 3969(17) | 52(5) |
| F(7A) | −2377(21) | −3768(23) | 3184(15) | 74(6) |
| F(8A) | −2994(33) | −2283(28) | 4285(20) | 98(8) |
| B(1) | 7837(6) | 1778(6) | 8797(4) | 53(2) |
| B(2) | −3544(7) | −3457(7) | 3538(5) | 68(3) |
| C(1) | −345(5) | 4043(4) | 2619(4) | 45(2) |
| C(2) | 685(6) | 4927(5) | 2146(4) | 57(2) |
| C(3) | 2121(6) | 5586(5) | 2761(4) | 60(2) |
| C(4) | 2551(5) | 5383(5) | 3851(4) | 59(2) |
| C(5) | 1535(5) | 4484(5) | 4321(4) | 51(2) |
| C(6) | 77(5) | 3836(4) | 3697(3) | 45(2) |
| C(7) | −2354(5) | 2396(5) | 3014(4) | 57(2) |
| C(8) | −3673(5) | 1358(7) | 2989(5) | 78(3) |
| C(9) | −3765(7) | 792(7) | 3929(6) | 89(3) |
| C(10) | −2616(6) | 1256(6) | 4864(5) | 76(3) |
| C(11) | −1307(5) | 2238(5) | 4868(4) | 58(2) |
| C(12) | −1185(5) | 2796(4) | 3950(4) | 47(2) |
| C(13) | −1930(5) | 3189(5) | 2118(4) | 59(2) |
| C(14) | −52(6) | 61(5) | 3230(4) | 65(2) |
| C(15) | 3472(5) | 3385(5) | 565(4) | 55(2) |
| C(16) | 4026(6) | 2342(7) | −82(5) | 83(3) |
| C(17) | 2735(6) | 3977(7) | −241(5) | 83(3) |
| C(21) | 2336(5) | 1732(5) | 2999(4) | 50(2) |
| C(22) | 3166(4) | 2535(5) | 2357(4) | 48(2) |
| C(23) | 2538(4) | 2580(4) | 1261(3) | 46(2) |
| C(24) | 1047(4) | 1829(4) | 843(3) | 42(2) |
| C(25) | 205(4) | 1026(4) | 1488(3) | 43(2) |
| C(26) | 856(5) | 936(4) | 2564(4) | 46(2) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table 5. Selected Bond Lengths (Å) and Angles (deg)**

| | | | |
|---|---|---|---|
| Ru(1)–C(1) | 2.244(6) | Ru(1)–C(2) | 2.237(6) |
| Ru(1)–C(3) | 2.207(5) | Ru(1)–C(4) | 2.209(4) |
| Ru(1)–C(5) | 2.219(5) | Ru(1)–C(6) | 2.238(5) |
| Ru(1)–C(21) | 2.216(6) | Ru(1)–C(22) | 2.216(5) |
| Ru(1)–C(23) | 2.256(5) | Ru(1)–C(24) | 2.210(4) |
| Ru(1)–C(25) | 2.200(3) | Ru(1)–C(26) | 2.259(5) |
| C(1)–C(2) | 1.415(7) | C(1)–C(6) | 1.403(7) |
| C(1)–C(13) | 1.504(6) | C(2)–C(3) | 1.395(7) |
| C(3)–C(4) | 1.417(8) | C(4)–C(5) | 1.411(7) |
| C(5)–C(6) | 1.417(6) | C(6)–C(12) | 1.482(6) |
| C(7)–C(8) | 1.388(7) | C(7)–C(12) | 1.399(6) |
| C(7)–C(13) | 1.520(8) | C(8)–C(9) | 1.389(11) |
| C(9)–C(10) | 1.375(8) | C(10)–C(11) | 1.365(7) |
| C(11)–C(12) | 1.361(7) | C(14)–C(26) | 1.508(7) |
| C(15)–C(16) | 1.536(9) | C(15)–C(17) | 1.505(9) |
| C(15)–C(23) | 1.517(7) | C(21)–C(22) | 1.412(7) |
| C(21)–C(26) | 1.400(6) | C(22)–C(23) | 1.410(6) |
| C(23)–C(24) | 1.402(5) | C(24)–C(25) | 1.420(6) |
| C(25)–C(26) | 1.417(6) | | |
| C(2)–C(1)–C(6) | 120.2(4) | C(2)–C(1)–C(13) | 129.4(4) |
| C(6)–C(1)–C(13) | 110.4(4) | C(1)–C(2)–C(3) | 119.3(5) |
| C(2)–C(3)–C(4) | 120.7(5) | C(3)–C(4)–C(5) | 120.4(4) |
| C(4)–C(5)–C(6) | 118.4(4) | C(1)–C(6)–C(5) | 121.0(4) |
| C(1)–C(6)–C(12) | 109.1(3) | C(5)–C(6)–C(12) | 129.8(4) |
| C(8)–C(7)–C(12) | 119.5(5) | C(8)–C(7)–C(13) | 129.1(5) |
| C(12)–C(7)–C(13) | 111.3(4) | C(7)–C(8)–C(9) | 117.3(5) |
| C(8)–C(9)–C(10) | 122.0(5) | C(9)–C(10)–C(11) | 120.6(6) |
| C(10)–C(11)–C(12) | 118.5(5) | C(6)–C(12)–C(7) | 107.1(4) |
| C(6)–C(12)–C(11) | 130.9(4) | C(7)–C(12)–C(11) | 122.0(4) |
| C(1)–C(13)–C(7) | 102.1(4) | C(16)–C(15)–C(17) | 111.8(5) |
| C(16)–C(15)–C(23) | 106.6(4) | C(17)–C(15)–C(23) | 114.5(4) |
| C(22)–C(21)–C(26) | 121.1(4) | C(21)–C(22)–C(23) | 121.5(4) |
| C(15)–C(23)–C(22) | 120.2(4) | C(15)–C(23)–C(24) | 122.3(4) |
| C(22)–C(23)–C(24) | 117.5(4) | C(23)–C(24)–C(25) | 121.2(4) |
| C(24)–C(25)–C(26) | 120.7(4) | C(14)–C(26)–C(21) | 122.1(4) |
| C(14)–C(26)–C(25) | 120.0(4) | C(21)–C(26)–C(25) | 117.8(4) |

**Table 6. Peak Reduction Potentials for [[4-methylisopropylbenzene](L)Ru][$BF_4$] Complexes in Nitromethane[a]**

| L | $E_c$ (V) | $E_a$ (V) | ref |
|---|---|---|---|
| 9,10-dihydroanthracene | −0.82 | | |
| cymene | −0.75 | | 6 |
| *trans*-stilbene | −0.67 | | |
| fluorene | −0.69 | | |
| phenanthrene | −0.48 | −0.21 | |
| coronene | −0.44 | | |
| naphthalene | −0.38 | −0.09 | |
| anthracene | −0.27 | +0.03 | |

[a] Measured potentials are referenced to a Ag/AgCl reference electrode at 298 K. The supporting electrolyte was 0.1 M [$Bu_4N$][$PF_6$].

hapticity changes following electrochemical reduction have been documented,[19] and for ruthenium(II) cyclophane complexes, correlations have been established between the case of reduction and ligand structure, the ease of reduction decreasing from systems which can adopt hapticity changes to those which cannot.[3] It would be interesting to establish whether or not changes in hapticity occur in these polybenzenoid aromatic studies, since such a process would involve a considerable degree of $\pi$-electron localization and concomitant distortion of the arene. The reversible electrochemical behavior of the naphthalene and anthracene complexes suggests that these are the most promising systems to explore, and these investigations are currently in progress.

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**Supplementary Material Available:** A table bond lengths and angles for $BF_4$ anions, lists of atomic positional parameters for hydrogen atom coordinates, and a table of anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

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