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Bis(arene) complexes of Ru^{II}. Synthesis, crystal structure and electrochemical behavior of [bis(η^6 -*p*-isopropyltoluene)Ru][BF₄]₂

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Abstract

Cleavage of the chloro-bridged Ru^{II} dimer, [(*p*-isopropyltoluene)Ru(Cl)₂]₂ with AgBF₄ in acetone and refluxing the product in trifluoroacetic acid with an excess of *p*-isopropyltoluene leads to the formation of the dicationic bis(arene) Ru^{II} complex, [(*p*-isopropyltoluene)₂Ru][BF₄]₂, in nearly quantitative yield. Strong upfield shifts are observed in the ¹³C NMR spectrum of the arene carbon atoms of *p*-isopropyltoluene following coordination and an investigation of the electrochemistry of this complex shows that it undergoes an irreversible reduction in nitromethane solvent at -0.78 V versus an Ag/AgCl reference electrode. An X-ray crystal structure determination of the complex shows that the complex consists of a Ru^{II} center located between two *p*-isopropyltoluene ligands that are coordinated in an η^6 manner. The arene rings are separated by a distance of 3.450 Å and are essentially coplanar with a dihedral angle of 178.4°. The crystals are monoclinic, space group *P*2₁/*n* with lattice constants *a* = 10.094(2) Å, *b* = 12.996(3) Å, *c* = 17.371(3) Å, β = 94.90(1)° and *V* = 2270.4(8) Å³. Convergence to conventional *R* values of *R* = 0.0711 and *R*_w = 0.0854 with a goodness-of-fit of 1.15 was obtained for 280 variable parameters and 2976 reflections with *I* > 0σ(*I*).

1. Introduction

There has long been considerable interest in the structures and properties of transition metal arene complexes. Much of this work has focused on cyclopentadienyl transition metal complexes, but more recently, has been extended to include η^6 -arenes and various other arenes such as cyclophanes and polycyclic benzenoid aromatics. Of particular interest are arene complexes of the platinum group metals such as ruthenium and osmium [1]. Such complexes are finding increasing applications in areas that include catalyst precursors, organometallic reagents for constructing conducting molecular charge-transfer complexes, as well as precursor materials with potential applications as conducting polymers [2–6]. Much of the pioneering work in the area has been carried out by E.O. Fischer who first devised a general route for the preparation of (η^6 -arene)Ru^{II} complexes [7]. Since then a number of workers have developed synthetic routes useful in the

preparation of a number of Ru^{II} complexes containing a wide variety of aromatic ligands [7–15].

Despite the fact that many η^6 -arene complexes of Ru^{II} are surprisingly stable, information concerning this interesting class of compounds remains scarce. As a result, in many instances the structures and packing motifs have not been established, and the chemical reactivities of these novel complexes have not been explored. Furthermore, a number of important questions of a more fundamental nature remain poorly understood. These include the extent to which coordination to a transition metal results in bond localization and various distortions to the π -electron system of the arene, as well as the surprisingly high up-field shifts observed in the ¹H NMR spectra of some naphthalene derivatives of Cr⁰, a precise explanation for which still remains to be developed [16]. The structure of a bis(arene)Ru^{II} complex in which one of the phenyl rings of a triphenylphosphine ligand is bound in an η^6 -manner has been described [17]. More recently, the structures of symmetric bis(arene)Ru^{II} complexes containing benzene [18], mesitylene and hexamethylbenzene ligands have also been reported [2,3].

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Owing to our interest in the preparation of new bis(arene)Ru^{II} complexes useful as precursor materials in the preparation of organometallic Ru^{II} polymers, we undertook the preparation of a new series of bis(arene) complexes containing labile *p*-isopropyltoluene ligands. In this paper, we report the synthesis, characterization, electrochemical properties and X-ray crystal structure of the Ru^{II} *p*-isopropyltoluene sandwich complex, [bis(η^6 -*p*-isopropyltoluene)Ru][BF₄]₂.

2. Results and discussion

Cleavage of the chloro-bridged Ru^{II} arene dimer, [bis(η^6 -*p*-isopropyltoluene)Ru(Cl)₂]₂, using a silver salt such as AgBF₄ in acetone yields the monomeric complex containing three easily displaced molecules of acetone. Refluxing this complex in a small amount of trifluoroacetic acid with a slight excess of *p*-isopropyltoluene leads to the formation of the symmetric [bis(*p*-isopropyltoluene)Ru^{II}]²⁺ dication in good yield as the BF₄⁻ salt. The crystals appear colorless, but exhibit a strong broad absorbance with a λ_{max} at 259 nm.

The proton decoupled ¹³C NMR data for this complex displays seven sharp resonances. Small chemical shifts are observed in the ¹³C NMR spectrum for the C atoms of the methyl and isopropyl groups relative to the spectrum of the free (uncomplexed) *p*-isopropyltoluene molecule, and all six carbon atoms of the arene ring are observed shifted upfield between 20 and 25 ppm.

The room temperature ¹H NMR spectrum for this complex displays well-resolved peaks. The methyl and isopropyl protons are shifted downfield in the complex, whereas the arene ring protons are shifted upfield slightly. The central proton of the arene isopropyl group exhibits a well-resolved septet and a 6.90 Hz coupling to the protons on the methyl groups. Similar chemical shifts in the ¹H NMR spectrum have been observed in other Ru^{II} complexes containing these ligand groups [18]. The splitting pattern does not suggest any substantial degree of hindered rotation at room temperature, however, a more detailed variable-temperature investigation would be needed in order to firmly establish this point.

The X-ray crystal structure of the complex confirms the proposed binding mode of the *p*-isopropyltoluene ligands. In this structure, we find the Ru^{II} center to be sandwiched essentially equidistant between the two *p*-isopropyltoluene ligands. Bonds from the carbon atoms of the arene ligands to the transition metal center range from a minimum of 2.207(9) Å to a maximum of 2.261(11) Å. For both rings, Ru(1) is not located symmetrically with respect to the centroid de-

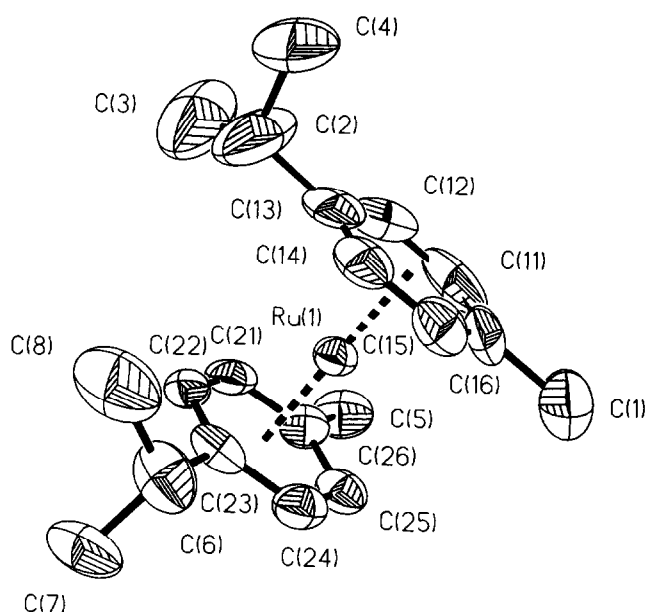


Fig. 1. View of the structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. The two BF₄ counterions are not shown and H atoms have been omitted for clarity.

fined by the six carbon atoms of the arene ring but is, in fact, shifted towards that portion of each ring bearing the methyl group and away from the isopropyl groups.

The arene ligands in this complex are twisted with respect to each other by an angle of 73.3° and are almost perfectly coplanar with a dihedral angle of 178.4°. The separation between rings measures 3.450 Å and both rings are essentially planar with only minimal deviations from the least-squares plane exhibited by any of the arene-ring carbon atoms. For both rings, the carbon-carbon bond lengths range from a minimum of 1.353(16) Å to a maximum of 1.462(13) Å. A closer inspection of the C-C bond lengths, however, reveals a pattern in which the C-C bond lengths alternate in a regular manner. Coordination to a transition metal center results in some distortion to the π -electron framework, a principal consequence of which is the introduction of some degree of bond localization within the arene ring.

The electrochemical behavior of this complex shows that it undergoes an irreversible reduction in nitromethane at -0.78 V *vs.* Ag/AgCl (-0.74 V *vs.* SCE). Electrochemical data for [η^6 -(C₆Me₆)₂-Ru]²⁺, [η^6 -(*p*-xylene)(η^6 -C₆Me₆)Ru]²⁺ and [η^6 -(durene) η^6 -(C₆Me₆)Ru]²⁺ has been reported [19], and in the case of [η^6 -(C₆Me₆)₂Ru]²⁺, the reduction occurs in the form of two well-resolved one-electron steps [23].

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}^a
Ru(1)	7493(1)	2625(1)	5742(1)	42(1)
F(1)	7989(17)	173(12)	1525(13)	362(13)
F(2)	6749(25)	917(13)	2178(8)	368(15)
F(3)	6096(13)	148(11)	1134(7)	232(7)
F(4)	7206(9)	1539(7)	1148(6)	171(5)
F(5)	3809(9)	1231(8)	4682(5)	177(5)
F(6)	3015(11)	1191(7)	3559(4)	169(5)
F(7)	3449(10)	2666(6)	4048(10)	224(8)
F(8)	1793(8)	1739(9)	4385(7)	190(6)
B(1)	7088(20)	705(12)	1522(10)	106(7)
B(2)	2996(11)	1759(9)	4213(7)	72(4)
C(1)	8037(17)	5213(9)	5644(9)	157(8)
C(2)	5414(15)	1711(12)	7059(8)	142(7)
C(3)	4780(17)	936(12)	6639(8)	174(9)
C(4)	4612(17)	2182(11)	7684(8)	154(8)
C(5)	6671(10)	2505(7)	3798(5)	77(4)
C(6)	10108(9)	1071(8)	6510(5)	74(3)
C(7)	10935(9)	259(8)	6170(6)	89(4)
C(8)	9410(12)	648(11)	7197(6)	117(6)
C(11)	6132(13)	3925(9)	5638(6)	91(5)
C(12)	5442(9)	3065(10)	5972(7)	88(4)
C(13)	6012(11)	2591(7)	6647(6)	76(4)
C(14)	7227(9)	3001(7)	6965(4)	63(3)
C(15)	7830(9)	3826(7)	6635(5)	68(3)
C(16)	7285(11)	4297(6)	5983(6)	71(4)
C(21)	7144(8)	1309(6)	4943(4)	56(3)
C(22)	7960(7)	975(5)	5594(4)	47(3)
C(23)	9128(7)	1464(6)	5835(4)	56(3)
C(24)	9523(8)	2319(6)	5396(5)	55(3)
C(25)	8731(8)	2666(6)	4741(5)	55(3)
C(26)	7519(8)	2136(6)	4498(4)	51(3)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

It is well established that changes in hapticity are important in catalysis involving transition metal complexes containing various polyolefin ligands. While the oxidation state of the reduced species in this investigation remains to be firmly established, changes in hapticity are required if the complex is to maintain an 18-electron configuration. Changes in hapticity have indeed been documented for various Rh-arene systems [21,23]. For cyclophane complexes of Ru^{II}, both the ease of reduction and the electrochemical reversibility have been shown to be highly dependent on the nature of the cyclophane ligand, and related to the ease with which the cyclophane can adopt an η^4 configuration [24]. Similar patterns of behavior would be anticipated for Ru^{II} complexes containing large polycyclic benzenoid aromatic ligands. We are in the progress of exploring the electrochemical properties of such complexes, and will be reporting the results of these investigations shortly.

TABLE 2

Bond lengths (\AA)			
Ru(1)–C(11)	2.175(12)	Ru(1)–C(12)	2.217(10)
Ru(1)–C(13)	2.261(11)	Ru(1)–C(14)	2.219(8)
Ru(1)–C(15)	2.207(9)	Ru(1)–C(16)	2.227(8)
Ru(1)–C(21)	2.212(8)	Ru(1)–C(22)	2.215(7)
Ru(1)–C(23)	2.232(8)	Ru(1)–C(24)	2.220(8)
Ru(1)–C(25)	2.227(9)	Ru(1)–C(26)	2.255(7)
F(1)–B(1)	1.142(25)	F(2)–B(1)	1.249(24)
F(3)–B(1)	1.365(22)	F(4)–B(1)	1.275(18)
F(5)–B(2)	1.302(15)	F(6)–B(2)	1.355(15)
F(7)–B(2)	1.306(15)	F(8)–B(2)	1.275(14)
C(1)–C(16)	1.553(17)	C(2)–C(3)	1.369(21)
C(2)–C(4)	1.535(22)	C(2)–C(13)	1.502(18)
C(5)–C(26)	1.504(11)	C(6)–C(7)	1.498(14)
C(6)–C(8)	1.538(15)	C(6)–C(23)	1.554(12)
C(11)–C(12)	1.462(17)	C(11)–C(16)	1.353(16)
C(12)–C(13)	1.404(15)	C(13)–C(14)	1.407(13)
C(14)–C(15)	1.382(13)	C(15)–C(16)	1.361(13)
C(21)–C(22)	1.410(10)	C(21)–C(26)	1.396(11)
C(22)–C(23)	1.373(10)	C(23)–C(24)	1.424(11)
C(24)–C(25)	1.408(11)	C(25)–C(26)	1.435(11)
Bond angles ($^\circ$)			
F(1)–B(1)–F(2)	114.1(20)	F(1)–B(1)–F(3)	103.4(15)
F(2)–B(1)–F(3)	108.7(18)	F(1)–B(1)–F(4)	114.0(19)
F(2)–B(1)–F(4)	108.9(14)	F(3)–B(1)–F(4)	107.2(14)
F(5)–B(2)–F(6)	100.6(10)	F(5)–B(2)–F(7)	113.5(11)
F(6)–B(2)–F(7)	106.1(12)	F(5)–B(2)–F(8)	113.8(11)
F(6)–B(2)–F(8)	105.5(10)	F(7)–B(2)–F(8)	115.4(11)
C(3)–C(2)–C(4)	114.8(14)	C(3)–C(2)–C(13)	119.6(13)
C(4)–C(2)–C(13)	106.9(11)	C(7)–C(6)–C(8)	111.2(9)
C(7)–C(6)–C(23)	105.9(7)	C(8)–C(6)–C(23)	113.5(8)
C(12)–C(11)–C(16)	121.2(9)	C(11)–C(12)–C(13)	119.5(9)
C(2)–C(13)–C(12)	125.4(10)	C(2)–C(13)–C(14)	118.3(10)
C(12)–C(13)–C(14)	116.3(9)	C(13)–C(14)–C(15)	122.1(8)
C(14)–C(15)–C(16)	122.2(8)	C(1)–C(16)–C(11)	122.4(10)
C(1)–C(16)–C(15)	118.9(10)	C(11)–C(16)–C(15)	118.6(9)
C(22)–C(21)–C(26)	121.0(7)	C(21)–C(22)–C(23)	122.0(7)
C(6)–C(23)–C(22)	123.5(7)	C(6)–C(23)–C(24)	118.1(7)
C(22)–C(23)–C(24)	118.1(7)	C(23)–C(24)–C(25)	121.2(7)
C(24)–C(25)–C(26)	119.7(7)	C(5)–C(26)–C(21)	122.0(7)
C(5)–C(26)–C(25)	119.8(7)	C(21)–C(26)–C(25)	118.1(7)

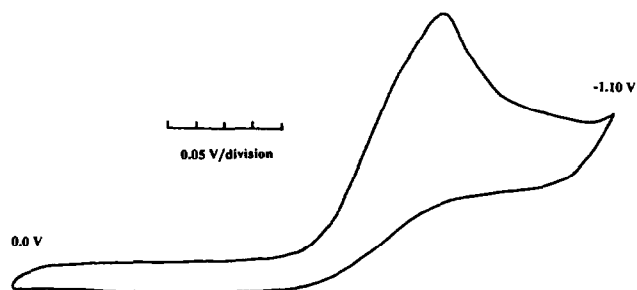


Fig. 2. Cyclic voltammetric scan at a scan rate of 2 V/s showing a reduction at -0.78 V vs. a Ag/AgCl reference electrode in nitromethane.

3. Experimental details

All manipulations were carried out using standard Schlenk techniques under oxygen-free nitrogen or an inert atmosphere glove box. Solvents were distilled from suitable drying agents prior to use. α -Terpinene (1-isopropyl-4-methyl-1,4-cyclohexadiene) was purchased from the Aldrich Chemical Company, Inc., and used as received. Ruthenium(III) chloride hydrate was obtained from the Engelhard Corporation. NMR spectra were recorded on a Bruker AM-250 spectrometer using DMSO-*d*₆ solvent dried over molecular sieves and referenced to TMS. The IR spectrum was recorded on a Perkin-Elmer FT 1600 and the crystallographic data were collected on a Siemens R3m/V diffractometer. Electrochemical investigations were carried out using a Bioanalytical systems CV-27 voltammograph and elemental analyses were performed by Texas Analytical Laboratories, Inc.

3.1. Preparation of di- μ -chloro-bis[chloro(η^6 -*p*-isopropyltoluene)Ru]

The chloro-bridged Ru^{II} dimer, [(*p*-isopropyltoluene)Ru(Cl)₂]₂, was prepared by a modification of the literature procedure [13]. Ru^{III} chloride hydrate (2.0 g, 9.6 mmol) was refluxed in 100.0 ml of freshly distilled ethanol in the presence of 10.0 ml (61.4 mmol) of 1-isopropyl-4-methyl-1,4-cyclohexadiene under N₂. After 4 h the reaction was stopped and the red-brown crystalline product was isolated by filtration. A second crop of crystals was obtained by reducing the filtrate to approximately half of its original volume and cooling it overnight at -10°C. Both fractions were combined providing 1.8 g of product with a product yield of 90% based on the amount of Ru metal in the starting material used.

3.2. Preparation of [bis(η^6 -*p*-isopropyltoluene)Ru][BF₄]₂

To a Schlenk flask containing 100 mg (0.16 mmol) of the chloro-bridged Ru^{II} *p*-isopropyltoluene dimer in acetone was added 127 mg (0.65 mmol) of AgBF₄. The reaction mixture was stirred vigorously for 15 min at room temperature after which the solution was filtered to remove the AgCl precipitate. The resulting yellow solution was taken to dryness by evaporation under reduced pressure. No attempt was made to isolate the product. The residue was treated with an excess (0.4 ml, 2.5 mmol) of *p*-isopropyltoluene, 3.0 ml (19.2 mmol) of trifluoroacetic acid, and the reaction mixture heated at 90°C for 5 min. The solvent was then removed under reduced pressure and the residue, in the form of a viscous oil, was washed with 5 ml of anhydrous diethyl ether resulting in the isolation of a colorless solid that

was obtained in 67% yield (120 mg, 0.216 mmol) based on the amount of dimeric Ru^{II} starting material used. The resulting air-stable product was then isolated by filtration and washed with 5 ml of ether, followed by 5 ml of freshly distilled methanol. Recrystallization from a DMSO/methanol solution yielded numerous well-formed colorless crystals (m.p. 251°C) suitable for an X-ray crystal structure determination.

Anal. Found: Ru, 18.65; C, 44.16; H, 5.23. C₂₀H₂₈B₂F₈Ru calc.: Ru, 18.62; C, 44.18; H, 5.16%. ¹H NMR (DMSO-*d*₆ δ 6.98 (q, 4 H); 2.94 (sp, 1 H); 2.46 (s, 3 H); 1.28 (d, 6H). ¹³C NMR (DMSO-*d*₆) δ 120.6, 111.6 94.3, 92.0, 31.1, 22.2, 18.8 (*p*-isopropyltoluene); 39.5 (sp) (DMSO). IR: 3076w, 2921s, 2724w, 1546w, 1461s, 1377m, 1287w, 1067s, 905w, 722m, 684w.

3.3. Electrochemistry

The reduction potential was determined using cyclic voltammetry. To 6.0 ml of a 0.1 M solution of [NBu₄][PF₆] in nitromethane was added 2.0 ml of a 0.05 M solution of [bis(η^6 -*p*-isopropyltoluene)Ru][BF₄]₂ in spectroscopic grade 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 and scanned at several rates ranging from 50 mV/s to 10 V/s. The cathodic current increased up to ca. 2 V/s, beyond which it began to decrease.

3.4. X-Ray crystal structure determination

3.4.1. Crystal data

C₂₀H₂₈B₂F₈Ru, *M* = 543.1, monoclinic, space group *P*2₁/*n*, *a* = 10.094(2) Å, *b* = 12.996(3) Å, *c* = 17.371(3) Å, β = 94.90(1)°, *V* = 2270.4(8) Å³. *D*_(calc.) = 1.589 mg m⁻³, *Z* = 4, μ = 0.744 mm⁻¹, λ (Mo K α) = 0.71073 Å, *F*(000) = 1096, *T* = 298 K.

3.4.2. Data collection

A regularly shaped colorless crystal having approximate dimensions 0.28 × 0.16 × 0.40 mm³ was selected and mounted on the end of a glass fiber in a random orientation. Monoclinic symmetry was suggested on the basis of the interaxial angles and axial rotation photographs. Refined cell parameters were determined from the setting angles of 22 reflections with 15° < 2 θ < 30°. Data collection was carried out at ambient temperature using the ω -scanning technique in bisecting geometry on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo K α radiation. Scan rate variable, 3–15° min⁻¹; scan range, 1.2° in ω . Three standards measured every 97 data showed only minor variations in intensity (< 3.0%) over the

period of data collection. A total of 3176 reflections ($+h$, $+k$, $\pm l$; $h_{\max} = 10$, $k_{\max} = 14$, $l_{\max} = 18$) with $3.5^\circ < 2\theta < 45^\circ$ were obtained and corrected for Lorentz and polarization effects. Absorption corrections were applied empirically on the basis of azimuthal scans of seven strong reflections spanning a range of 2θ values. Equivalent reflections were merged leading to 2977 unique reflections with $R_{\text{int}} = 1.55\%$.

3.4.3. Crystal structure solution and refinement

Structure solution and refinement was carried out using the SHELXTL-PLUS (PC version) collection of crystallographic software [25]. Assignment to the $P2_1/n$ space group was made following examination of the systematically absent reflections ($0, k, 0$, $k = 2n + 1$; $h, 0, 1$, $h + l = 2n + 1$). 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 [26]. Hydrogen atoms were included in idealized positions with fixed isotropic $U = 0.08 \text{ \AA}^2$. Refinement was based on F using weights of the form $w^{-1} = [\sigma^2(F) + 0.0029(F^2)]$. The maximum shift/ σ for the final cycle was 0.001 with minimum and maximum residual electron densities of -0.61 e \AA^{-3} and $+0.74 \text{ e \AA}^{-3}$. One intense low-angle reflection ($0\ 0\ 2$) appeared to suffer from some form of extinction and was therefore omitted during the final stages of refinement. Convergence to conventional R value of $R = 0.0711$ and $R_w = 0.0854$ with a goodness-of-fit of 1.15 was obtained for 284 variable parameters and 2976 reflections with $I > 0\sigma(I)$. A list of observed and calculated structure factor amplitudes is available from one of the authors (LCP) upon request.

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