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Crystal and Molecular Structure of Bis(η^6-benzene)ruthenium(II) *p*-Toluenesulfonate

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$[Ru(C_6H_6)_2](tos)_2$ (tos = *p*-toluenesulfonate) crystallizes in the triclinic space group $P\bar{1}$ with a = 7.065 (2) Å, b = 8.280 (2) Å, c = 11.060 (3) Å, α = 84.44 (2)°, β = 76.35 (2)°, γ = 68.42 (2)° (T = 125 K), and Z = 1. The structure was refined to 2.5% for 4438 reflections with $F_o > 10\sigma(F_o)$. The two benzene rings of the sandwich cation are ecliptic, symmetry-related by a center of inversion at the Ru site. After correction for thermal motion average distances are Ru–C = 2.225 (1), C–C = 1.418 (1), and C–H (uncorrected) = 0.919 (14) Å. The Ru–center of the benzene plane distance is 1.717 Å.

Introduction

Bis(arene) sandwich compounds with two η^6-ligands are well-established species for the chromium triad.[2] They occur as 18-electron systems belonging to the d^6 configuration of the zerovalent metals. Another bonding mode, again in agreement with the 18-electron rule, is realized in the neutral bis(arene) compounds of iron, ruthenium, and osmium. One ligand is η^6-coordinated and the other one η^4-coordinated.[3] In the corresponding $M(arene)_2^{2+}$ complex ions, both ligands are equivalent and η^6-coordinated as demonstrated by spectroscopic data.[4] In contrast to a variety of mono(arene)ruthenium compounds[4] no complete structural study appears to have been carried out for bis(arene) sandwich complexes. As part of our study of coordination and metalloorganic ruthenium compounds[5] we report in this paper the molecular structure of the bis(η^6-benzene)ruthenium(II) ion.

Experimental Section

$[Ru(C_6H_6)_2](tos)_2$ (tos = *p*-toluenesulfonate): $[Ru(C_6H_6)(H_2O)_3](tos)_2$ (0.5 g) was refluxed in a mixture of 20 mL benzene and 20 mL of trifluoroacetic acid for 0.5 h.[6] Evaporation to dryness afforded a colorless powder. Crystals were grown by slow cooling of a methanol solution from 50 to 0 ° C, and their stoichiometry was confirmed by elemental analyses. The density was determined by flotation in a $CCl_4/CHBr_3$ mixture.

Collection and Reduction of Intensities. An irregularly prismatic crystal (0.10 × 0.16 × 0.19 mm) was measured on a CAD4 Enraf-Nonius diffractometer equipped with a standard liquid-nitrogen cryostat (graphite-monochromated Mo Kα radiation, λ = 0.71069 Å). Lattice parameters (Table I) were determined from 17 accurately centered reflections with $12° < 2\theta < 15°$. Three check reflections measured every hour did not show any systematic intensity fluctuations. Intensities were corrected for Lorentz and polarization effects but not for absorption.

Solution and Refinement of the Structure. The positions of Ru and S atoms were obtained from a Patterson map. The remaining atoms, including the hydrogen atoms of the benzene and tosylate rings were located by subsequent Fourier, difference Fourier, and least-squares calculations. Rotational disorder of the CH_3 group of the anion was resolved by assuming two different orientations (60°) of the CH_3 group with occupancies of 0.5 for the six H positions. Isotropic thermal parameters for H, one for the benzene hydrogens, one for the tosylate ring hydrogens, and one for the CH_3 hydrogens, were included in the refinement. After convergence the final difference Fourier map revealed maximal and minimal residual electron densities of 1.06 and −1.2 e Å^{-3} in the immediate neighborhood of Ru. All the calculations were performed with the SHELX-76 system,[7] and neutral atom scattering factors including real and imaginary anomalous dispersion corrections were used.[8] Final positional parameters are listed in Table II.

Table I. Crystal Data and Refinement Parameters for $[Ru(C_6H_6)_2](tos)_2$

formula	$RuC_{26}H_{26}S_2O_6$
fw	599.7
space group	$P\bar{1}$
T, K	125
a, Å	7.065 (2)
b, Å	8.280 (2)
c, Å	11.060 (3)
α, deg	84.44 (2)
β, deg	76.35 (2)
γ, deg	68.42 (2)
V, Å^3	584.6
Z	1
D_{exptl}, g cm^{-3}	1.66
D_{calcd}, g cm^{-3}	1.67
μ, cm^{-1}	8.5
$F(000)$	306
max θ, deg	35
h	0–11
k	−12 to +13
l	−17 to +17
no. of unique refl measd	5154
no. of unique refl with $I < 5\sigma(I)$	4438
weight function	$w = (\sigma^2(F) + 0.001391F^2)^{-1}$
R	0.025
R_w	0.027
final shift per error	0.04

Description and Discussion of the Structure

The Ru atom sits on an inversion center: the two symmetry-related benzene rings of the sandwich are exactly parallel and eclipsed (Figure 1). The approximate symmetry of the cation is D_{6h}. The projection of the metal position onto the benzene ligand coincides with the ring center within error limits. The largest deviation of the carbon atoms from their least-squares plane is 0.003 Å. Carbon–carbon distances do not show significant fluctuations. Correspondingly, the angles of the benzene ring reflect the approximate symmetry, their average being 120.00 (8)°. The hydrogen atoms are slightly bent away from the benzene plane, toward the metal center. Al-

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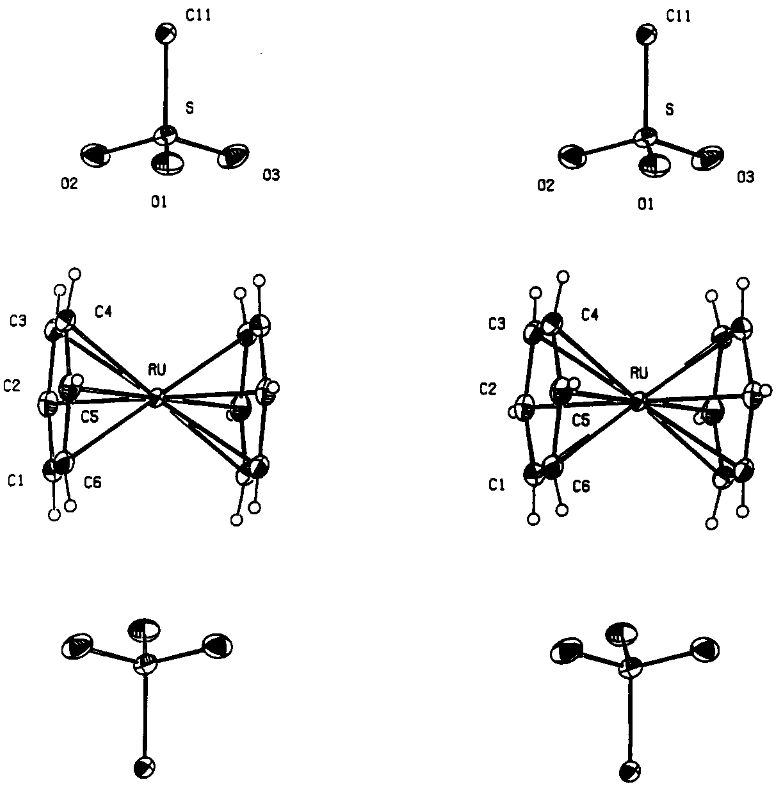

Figure 1. Stereoview of the $Ru(C_6H_6)_2^{2+}$ cation together with the two closest SO_3 groups of the counterion *p*-toluenesulfonate.

Table II. Final Atomic Positional Parameters and B_{eq} Values with Standard Deviations in Parentheses at 125 K

atom	x/a	y/b	z/c	B_{eq}, Å^2
Ru	0.00000	0.00000	0.00000	0.953 (3)
C1	0.0314 (2)	-0.0023 (2)	0.7959 (1)	1.53 (2)
H1	0.061 (4)	-0.097 (3)	0.755 (2)	2.3 (2)*
C2	0.2029 (2)	0.0301 (2)	0.8189 (1)	1.54 (2)
H2	0.344 (4)	-0.044 (3)	0.785 (2)	2.3 (2)*
C3	0.1673 (2)	0.1691 (2)	0.8969 (1)	1.57 (2)
H3	0.280 (4)	0.172 (3)	0.920 (2)	2.3 (2)*
C4	-0.0382 (2)	0.2752 (2)	0.9510 (1)	1.52 (2)
H4	-0.068 (4)	0.358 (3)	1.007 (2)	2.3 (2)*
C5	-0.2092 (2)	0.2435 (2)	0.9273 (1)	1.45 (2)
H5	-0.347 (4)	0.317 (3)	0.965 (2)	2.3 (2)*
C6	-0.1740 (2)	0.1043 (2)	0.8499 (1)	1.54 (2)
H6	-0.284 (4)	0.080 (3)	0.840 (2)	2.3 (2)*
S	0.2247 (1)	0.3266 (1)	0.2047 (1)	1.259 (3)
O1	0.0004 (2)	0.3886 (1)	0.2153 (1)	1.81 (1)
O2	0.3391 (2)	0.3287 (2)	0.0768 (1)	2.12 (2)
O3	0.3042 (2)	0.1594 (1)	0.2662 (1)	2.33 (2)
C11	0.2739 (2)	0.4770 (2)	0.2851 (1)	1.21 (1)
C12	0.4745 (2)	0.4819 (2)	0.2620 (1)	1.40 (2)
H12	0.570 (4)	0.408 (3)	0.205 (2)	2.3 (2)*
C13	0.5146 (2)	0.5974 (2)	0.3262 (1)	1.57 (2)
H13	0.654 (4)	0.603 (3)	0.304 (2)	2.3 (2)*
C14	0.3577 (2)	0.7090 (2)	0.4142 (1)	1.55 (2)
C15	0.1579 (2)	0.7013 (2)	0.4376 (1)	1.59 (2)
H15	0.046 (4)	0.780 (3)	0.496 (2)	2.3 (2)*
C16	0.1159 (2)	0.5859 (2)	0.3731 (1)	1.40 (2)
H16	-0.025 (4)	0.584 (3)	0.391 (2)	2.3 (2)*
C17	0.4042 (3)	0.8345 (2)	0.4818 (1)	2.25 (2)
H171	0.503 (8)	0.883 (7)	0.420 (5)	3.2 (5)*
H172	0.574 (6)	0.780 (8)	0.480 (6)	3.2 (5)*
H173	0.500 (8)	0.774 (7)	0.549 (5)	3.2 (5)*
H174	0.319 (8)	0.844 (8)	0.573 (4)	3.2 (5)*
H175	0.275 (7)	0.937 (6)	0.522 (5)	3.2 (5)*
H176	0.366 (9)	0.943 (6)	0.430 (5)	3.2 (5)*

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = (8\pi^2/3)\sum_i(\sum_j(U_{ij}a_i^*a_j^*\mathbf{\bar{a}}_i \times \mathbf{\bar{a}}_j))$.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $[Ru(C_6H_6)_2]^{2+}$

	125 K	corr		125 K	corr
Ru-C1	2.217 (1)	2.221	C1-C2	1.415 (2)	1.419
Ru-C2	2.223 (1)	2.227	C2-C3	1.417 (2)	1.421
Ru-C3	2.220 (1)	2.224	C3-C4	1.411 (2)	1.415
Ru-C4	2.222 (1)	2.226	C4-C5	1.412 (2)	1.415
Ru-C5	2.225 (1)	2.229	C5-C6	1.415 (2)	1.419
Ru-C6	2.217 (1)	2.221	C6-C1	1.411 (2)	1.416
Ru-C_{av}	2.221 (1)	2.225 (1)	C-C_{av}	1.414 (1)	1.418 (1)
C-plane-Ru	1.713	1.717	C1-H1	0.877 (25)	
C1-C2-C3	119.7 (1)		C2-H2	0.965 (25)	
C2-C3-C4	120.2 (1)		C3-H3	0.903 (24)	
C3-C4-C5	120.0 (1)		C4-H4	0.907 (24)	
C4-C5-C6	119.9 (1)		C5-H5	0.958 (24)	
C5-C6-C1	120.2 (1)		C6-H6	0.903 (23)	
C6-C1-C2	120.0 (1)		C-H_{av}	0.919 (14)	

though these shifts are small, i.e., comparable to their standard deviations, all of them are in the same direction and of the same order of magnitude, 0.07 Å. Important interatomic distances and angles for the cation are collected in Table III. The overall geometry is described by the Ru-ring center distance, 1.713 Å, and the average Ru-C, 2.221 (1)Å, C-C, 1.414 (1) Å, and C-H, 0.919 (14) Å, distances. Available values for eclipsed ruthenocene, measured at 101 K, are 1.816, 2.186, and 1.430 Å.[9] The smaller radius of the cyclopentadienyl ring (1.216 vs. 1.414 Å) is compensated by an increase of the Ru-ring distance (~0.1 Å). The net effect on the Ru-C distances is a shortening of only 0.035 Å.

The crystal structure consists of neutral assemblies of $[Ru(C_6H_6)_2](tos)_2$ (Figure 1). The negatively charged SO_3 groups of two tosylate anions point toward two open faces of the hexagonal-prismatic cation with an average Ru-O distance of 4.41 (12) Å. Corresponding nonbonded O-H distances are in the range 2.24-2.58 Å. We notice an approximately parallel arrangement of the benzene rings of the counterion and the coordinated arenes (Figure 2). The

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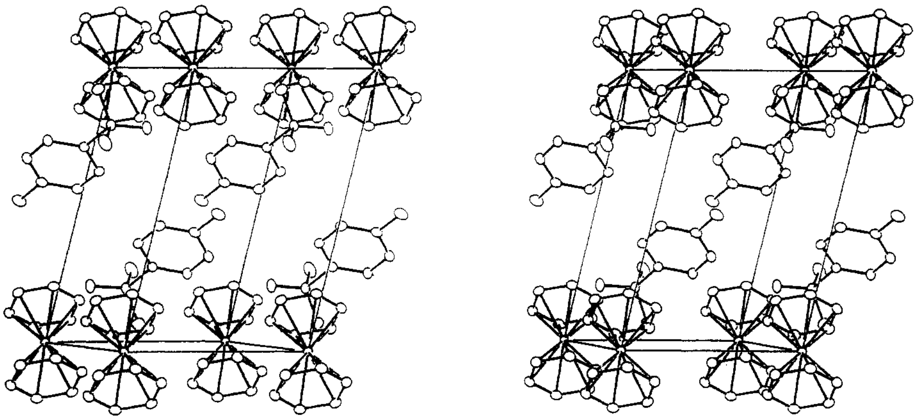

Figure 2. The unit cell of $Ru(C_6H_6)_2$(*p*-toluenesulfonate)$_2$

Table IV. Structural Properties of 18-Electron M(arene)$_2$ Sandwich Compounds

compd	M–C, Å	M–plane, Å	*R*
$Ru(C_6H_6)_2^{2+}$ [a]	2.225 (1)	1.717	0.025
$Ru(C_6Me_6)$(cyclophane)$^{2+}$ [b]	2.22 (2)–2.36 (2)	1.72, 1.80	0.058
$Cr(C_6H_6)_2$ [c]	2.144–2.147	1.609	0.031
Mo(toluene)$_2$ [d]	2.255–2.282	1.78	0.062
W(toluene)$_2$ [e]	2.25–2.32	1.79	0.035

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geometry of the tosylate anion shows the expected geometry and does not require special comment.

The displacement parameters (thermal ellipsoids) of the sandwich cation, treated as a rigid body, were analyzed.[10] The translational tensor is approximately isotropic with a root-mean-square displacement of about 0.1 Å. The largest principal value of the libration tensor is 14 deg^2. The associated axis of rotational oscillation practically coincides with the pseudohexagonal axis of the molecule. It is not possible, however, to decide to what extent the two benzene molecules oscillate in phase and out of phase. The intermediate principal value with an amplitude of 5.2 deg^2 corresponds to a rocking-type motion within the plane defined by Ru, C2, and C5. An amplitude of 2.8 deg^2 is obtained for the third eigenvalue corresponding to an analogous rocking motion in the plane defined by Ru and the centers of the C1–C6 and C3–C4 bonds. Thus the librational oscillation is smallest in the direction of the outer-sphere tosylate ligands. The combined effects of the librations lead to a correction of the bond lengths of 0.004 Å, approximately half the correction found for $Ru(C_6H_6)(H_2O)_3(SO_4)$.[11,12]

From the few reported molecular structures of dibenzene sandwich compounds we select those with a d^6 configuration of the metal center for the purpose of comparison (Table IV). $Ru(C_6Me_6)$(cyclophane)$^{2+}$ shows a distorted geometry with one significantly elongated Ru–C bond. The Ru–cyclophane ring distance is elongated to 1.8 Å; this is probably due to the fact that the coordinated cyclophane ring formally assumes a chair conformation.[13] There is a close similarity in distances among the bis(benzene) compounds of the heavy transition metals, but significantly shorter distances are found in $Cr(C_6H_6)_2$. The effect of a different electronic structure is reflected in the M to plane distances of 1.736 and 1.671 Å, found for Ti(0)[14] and V(0)[15] sandwich compounds, respectively.

Examples of Ru complexes with one η^6-arene molecule and three identical ligands completing a piano-stool arrangement appear to be restricted to $Ru(\eta^6\text{-}C_6H_6)(Bpz_4)^+$ (Bpz_4 = tetrakis(1-pyrazolyl)borate)[16] and $Ru(\eta^6\text{-}C_6H_6)(H_2O)_3^{2+}$.[11] As one C_6H_6 in $Ru(\eta^6\text{-}C_6H_6)_2^{2+}$ is replaced by the poorer electron-donating ligands Bpz^- and $(H_2O)_3$, the average Ru–C and Ru–ring distances decrease from 2.225 (1), 1.717 Å to 2.20 (3), 1.67 Å and 2.164 (5), 1.63 Å, respectively. This indicates an electronic trans influence. However, the Ru–N and Ru–O distances of 2.11 (2) and 2.117 (11) Å do not differ significantly from those observed for similar octahedral RuL_6^{2+} compounds, e.g., $Ru(py)_6^{2+}$ (2.12 (2) Å)[17] and $Ru(H_2O)_6^{2+}$ (2.122 (16) Å).[18]

Registry No. $[Ru(C_6H_6)_2](tos)_2$, 105205-38-7; $[Ru(C_6H_6)(H_2O)_3](tos)_2$, 96826-82-3; C_6H_6, 71-43-2.

Supplementary Material Available: Tables of anisotropic thermal parameters for $Ru(C_6H_6)_2(tos)_2$ and interatomic distances and angles (2 pages); a listing of structure factors for $Ru(C_6H_6)_2(tos)_2$ (27 pages). Ordering information is given on any current masthead page.

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(12) The cation is not strictly rigid. Apart from the possibility of out-of-phase ring oscillation, there is also metal-to-ring stretching motion. This follows from the fact the average value of U(C)–U(Ru) along the C–Ru direction is 16 (3) × 10^{-4} Å^2 rather than 0 Å^2 as expected for an ideal rigid body. For comparison $U(C_i)-U(C_{i+1})$, averaged over the six C–C bonds, is 5 (3) × 10^{-4} Å^2.

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