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Preparation and X-ray Crystal Structures of $[(\eta^6\text{-chrysene})(\eta^6\text{-4-methylisopropylbenzene})\text{ruthenium}][BF_4]_2$ and $[(\eta^6\text{-perylene})(\eta^6\text{-4-methylisopropylbenzene})\text{ruthenium}][BF_4]_2$

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Introduction

As part of a program of research aimed at exploring the physical and structural properties of large fused ring systems containing one or more transition metals, we recently began a systematic exploration of novel ruthenium(II) sandwich complexes in which the ligands consisted of polycyclic aromatic hydrocarbons.[1] In this note we describe the preparation, characterization and X-ray crystal structures of two novel Ru^{II}-(arene) complexes, $(\eta^6$-chrysene$)(\eta^6$-4-methylisopropylbenzene$)$Ru$][BF_4]_2$ and $(\eta^6$-perylene$)(\eta^6$-4-methylisopropylbenzene$)$Ru$]$-$[BF_4]_2$.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk techniques under oxygen-free nitrogen or an inert atmosphere glovebox. The chloro-bridged Ru(II) dimer, [(4-methylisopropylbenzene)Ru(Cl)$_2$]$_2$ and the tris(acetone)$(\eta^6$-4-methylisopropylbenzene$)$Ru$][BF_4]_2$ complexes were prepared according to the literature procedure.[2ab] Acetone was dried over molecular sieves and all halogenated solvents were distilled over P_2O_5. α-Terpinene (1-isopropyl-4-methyl-1,3-cyclohexadiene) and chrysene were purchased from the Aldrich Chemical Co., Inc., and used as received. Perylene was obtained from the Sigma Chemical Co., and the ruthenium(III) chloride hydrate was obtained from the Engelhard Corp. NMR spectra were recorded on a Bruker AM-250 spectrometer using nitromethane-d_3 and referenced to TMS.

Preparation of $(\eta^6$-chrysene$)(\eta^6$-4-methylisopropylbenzene$)$Ru]-$[BF_4]_2$. A 0.300 g (0.49 mmol) sample of the chloro-bridged Ru(II) dimer was suspended in 10.0 mL of acetone to which was added 0.390 g (2.0 mmol) of $AgBF_4$. The reaction mixture was stirred at room temperature for 15 min after which the AgCl precipitate was separated and the solution fraction transferred to a second Schlenk flask. The solution was taken to dryness by removal of the solvent under reduced pressure. To the resulting tris(acetone) complex, present as a yellow oil, was then added an excess of chrysene (0.250 g, 1.10 mmol) and 10.0 mL of CH_2Cl_2. The reaction mixture was refluxed for 48 h. The yellow solid that resulted upon solvent removal was isolated by filtration and washed with CH_2Cl_2 (5 mL) and an equal proportion of diethyl ether. The compound was recrystallized from a nitromethane−diethyl ether solution and the yield was 0.461 g (74%) of a clean yellow powder that melted with decomposition beginning at 278 °C.

^{1}H NMR (CD_3NO_2, δ): 6.46 (d, 2H, $J = 6.62$ Hz), 6.37 (d, 2H, $J = 6.62$ Hz), 2.55 (sep, 1H, $J = 6.82$ Hz), 1.74 (s, 3H), 1.16 (d, 3H, $J = 6.90$ Hz), 1.04 (d, 3H, $J = 6.92$ Hz) (4-methylisopropylbenzene); 9.42 (d, 1H, $J = 9.47$ Hz), 8.91 (d, 1H, $J = 9.05$ Hz), 8.67 (d, 1H, $J = 9.04$ Hz), 8.47 (m, 2H), 8.23, (t, 1H, $J = 9.37$ Hz), 7.97 (m, 4H), 7.16 (m, 2H), 6.64 (t, 2H, $J = 6.72$ Hz) (chrysene).

Table 1. Crystal Data for $[(\eta^6$-chrysene$)(\eta^6$-4-methylisopropylbenzene$)$Ru$][BF_4]_2$ and $[(\eta^6$-perylene$)(\eta^6$-methylisopropylbenzene$)$Ru$][BF_4]_2$

formula	$C_{28}H_{28}B_2F_8Ru$	$C_{30}H_{26}B_2F_8Ru$
fw	637.2	661.2
cryst system	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
a/Å	9.660(3)	12.805(5)
b/Å	10.823(4)	20.109(8)
c/Å	13.678(5)	20.471(5)
α/deg	86.77(3)	90
β/deg	87.00(3)	90
γ/deg	64.12(2)	90
V/Å	1284.0(8)	5271(4)
Z	2	8
ϱ/(Mg/m^3)	1.648	1.666
μ/mm^{-1}	0.671	0.657
F(000)	640	2656
R^a	0.0491	0.0586
$R_w{}^b$	0.0496	0.0536
quantity minimized	$\sum w(F_o - F_c)^2$	

[a] $R = \sum[F_o - F_c]/\sum F_o$. [b] $R_w = [[\sum([F_o - F_c)^2]/[\sum w(F_o)^2]]^{1/2}$.

^{13}C NMR (CD_3NO_2, δ): 120.9, 111.9, 94.4, 92.2, 32.3, 22.2, 22.0, 17.6 (4-methylisopropylbenzene); 135.8, 134.0, 133.5, 131.3, 130.9, 130.3, 130.1, 125.2, 125.0, 124.7, 122.0, 102.6, 101.9, 95.1, 94.4, 94.0, 93.6, 88.8 (chrysene).

Anal. Calcd for $C_{28}H_{26}B_2F_8Ru$: C, 52.74; H, 4.08. Found: C, 51.62; H, 4.58.

Preparation of $(\eta^6$-perylene$)(\eta^6$-4-methylisopropylbenzene$)$Ru]-$[BF_4]_2$. The same procedure as above was used in the preparation of the perylene complex. The tris(acetone)ruthenium(II) product prepared from 0.153 g (0.25 mmol) of the chloro-bridged dimer in acetone and 0.195 g (1.0 mmol) of $AgBF_4$ was reacted with 0.151 g (0.60 mmol) of perylene in $CHCl_3$. Then 0.252 g of a dark red powder that melted with decomposition at 280 °C was isolated in 74% yield.

^{1}H NMR (CD_3NO_2, δ): 6.34 (d, 1H, $J = 6.43$ Hz), 6.25 (d, 1H, $J = 6.22$ Hz), 6.12 (m, 2H), 2.54 (sep, 1H, $J = 6.75$ Hz), 1.79 (s, 3H), 1.16 (d, 3H, $J = 7.18$ Hz), 1.08 (d, 3H, $J = 7.11$ Hz) (4-methylisopropylbenzene); 8.86 (d, 1H, $J = 7.55$ Hz), 8.58 (m, 2H), 8.29 (m, 2H), 8.16 (d, 1H, $J = 8.25$ Hz), 7.95 (d, 1H, $J = 8.90$ Hz), 7.83 (m, 2H), 7.73 (d, 1H, $J = 6.76$ Hz), 7.70 (d, 1H, $J = 6.35$ Hz), 7.14 (t, 1H, $J = 6.35$ Hz) (perylene).

^{13}C NMR (CD_3NO_2, δ): 106.6, 111.9, 95.1, 94.5, 94.4, 32.5, 22.4, 17.7 (4-methylisopropylbenzene); 139.6, 137.6, 135.5, 135.0, 134.2, 130.5, 130.4, 129.7, 129.1, 128.3, 127.7, 127.5, 122.3, 120.8, 105.0, 96.1, 94.6, 92.4, 91.9, 85.1 (perylene).

Anal. Calcd for $C_{30}H_{26}B_2F_8Ru$: C, 54.45; H, 3.96. Found: C, 54.27; H, 3.95. Crystallographic Determination of the Structures

Crystal data and experimental parameters are summarized in Table 1. Data collection for both complexes 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 Kα (0.710 73 Å) radiation. Refined cell parameters were determined from the setting angles of 25 reflections with 15° < 2θ < 30° for the chrysene complex and 40 reflections with 15° < 2θ < 30° for perylene product. The scan rate was variable, 3−15° min^{-1}; the scan range was 1.2° in ω. The data were corrected for Lorentz and polarization effects and for absorption. Absorption corrections were applied empirically on the basis of azimuthal scans of several strong reflections spanning a range of 2θ values. In neither structure were corrections for extinction deemed necessary. Structure solution and refinement was carried out using the SHELXTL-PLUS collection of crystallographic software.[3] For both complexes 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

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standard difference-Fourier techniques and refined anisotropically using scattering factors that included terms for anomalous dispersion.[4] Hydrogen atoms were included in idealized positions with fixed isotropic $U = 0.08$ Å^2.

[(η^6-chrysene)(η^6-4-methylisopropylbenzene)Ru][BF$_4$]$_2$. Crystals suitable for and X-ray crystal structure determination were obtained following crystallization from a nitromethane–diethyl ether solution. A single well-formed regularly shaped yellow crystal of the chrysene complex 0.24 mm × 0.40 mm × 0.40 mm in size 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. Three standards measured every 97 data showed only minor variations in intensity (< 3.0%) over the period of data collection. A total of 3624 reflections ($+h$, $+k$, $+l$; $h_{\max} = 10$, $k_{\max} = 11$, $l_{\max} = 14$) with $3.5° < 2\theta < 45°$ were obtained and equivalent reflections were merged resulting in 3384 unique reflections with $I > 0\sigma(I)$ and $R_{\text{int}} = 1.02\%$. Absorption corrections were applied empirically on the basis of several strong reflections spanning a range of 2θ values (minimum and maximum transmission, 0.728 and 0.775, respectively). Intensity statistics favored the centrosymmetric $P\bar{1}$ space group. 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 alternate positions with 50% occupancy factors for three of the four F atoms. Refinement was based on F using weights of the form $w^{-1} = [\sigma^2(F) + 0.0012(F^2)]$. The maximum shift/$\sigma$ for the final cycle was 0.102 with minimum and maximum residual electron densities of −0.49 and +1.18 e Å^{-3}. Convergence to conventional R values of $R = 0.0504$ and $R_w = 0.0617$ with a goodness-of-fit of 1.32 was obtained for 406 variable parameters and 3384 reflections with $I > 0\sigma(I)$.

[(η^6-perylene)(η^6-4-methylisopropylbenzene)Ru][BF$_4$]$_2$. Slow crystallization from a nitromethane–diethyl ether solution led the formation of numerous well-formed crystals. A regularly shaped red crystal displaying a prismatic habit with dimensions 0.12 mm × 0.16 mm × 0.40 mm was selected and mounted on the end of a glass fiber in a random orientation. Orthorhombic symmetry was suggested on the basis of the interaxial angles and confirmed by a axial rotation photographs. Three standards measured every 97 data showed only minor variations in intensity (< 3.0%) over the period of data collection. A total of 3384 unique reflections ($+h$, $+k$, $+l$; $h_{\max} = 13$, $k_{\max} = 21$, $l_{\max} = 22$) with $3.5° < 2\theta < 45°$ were collected. Absorption corrections were applied empirically on the basis of azimuthal scans of several strong reflections (minimum and maximum transmission, 0.591 and 0.682, respectively). Refinement was based on F using weights of the form $w^{-1} = [\sigma^2(F) + 0.0005(F^2)]$. For the final cycle the maximum shift/σ was 0.000 with minimum and maximum residual electron densities of +0.74 and −0.75 e Å^{-3}. Convergence to conventional R values of $R = 0.0753$ and $R_w = 0.0618$ with a goodness-of-fit of 1.32 was obtained for 370 variable parameters and 2101 reflections with $I > 1\sigma(I)$.

Results and Discussion

A key step in the syntheses of these complexes involves cleavage of the chloro-bridged [(4-methylisopropylbenzene)-ruthenium(Cl)$_2$]$_2$ dimer by halide abstraction using a silver salt in acetone. This results initially in the formation of a monomeric dication containing three coordinated molecules of acetone, two of which then undergo an interesting type of aldol condensation to produce a product whose structure has been previously described.[2b] Since these ligand groups are only weakly coordinating, the addition of an arene leads to their displacement and the formation of an η^6,η^6-sandwich complex. Good product yields can ordinarily be obtained using trifluoroacetic acid as a solvent and allowing the reaction mixture to reflux for a short period of time, typically 15 min or less.[1a] However, in these investigations we found that better product yields were obtained using milder conditions and non-coordinating solvents such as dichloromethane or chloroform.[1b,c] Longer reactions times are required, however, problems associated with the formation of a Ru(II) trifluoroacetate complex are avoided. The products obtained from these reactions are all air-stable solids that exhibit good solubility in nitromethane, DMSO, and acetonitrile.

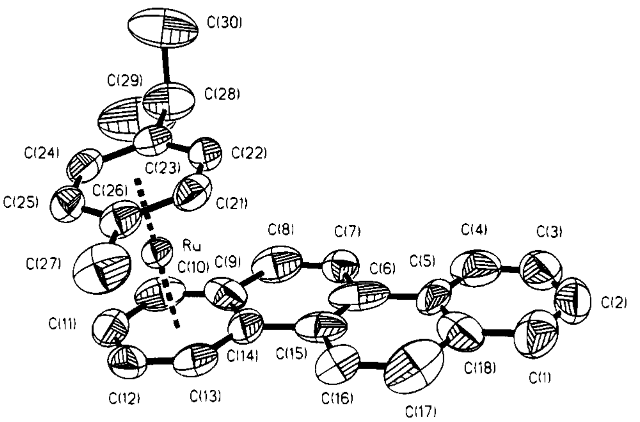

Figure 1. View of the [(η^6-chrysene)(η^6-4-methyl-isopropylbenzene)-Ru][BF$_4$]$_2$ structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. The two BF$_4^-$ counterions are not shown and H atoms have been omitted for clarity.

The ^{1}H and ^{13}C NMR spectra of the chrysene and perylene complexes display trends similar to those observed in other transition metal complexes containing arene ligands. In all instances the proton resonances for hydrogens attached to the coordinated arene are shifted upfield relative to the free arene, typically 1–2 ppm. This upfield shift is accompanied by a slight downfield shift for the remaining protons. ^{13}C NMR chemical shift data for the complexes prepared in this investigation also reveal a consistent pattern of upfield chemical shifts *circa* 20–30 ppm for carbon atoms coordinated to the Ru^{2+} center relative to the free arenes. The observed ^{13}C and ^{1}H and chemical shifts for the 4-methylisopropylbenzene ligands are in agreement with those of other Ru(II) sandwich complexes, although in both of these complexes the methyls of the isopropyl group are diastereotopic and appear as a pair of doublets.

Subtle changes in the C–C bond lengths are occasionally observed in arenes following coordination to a transition metal. To explore this and verify the proposed mode of bonding of the transition metal, the crystal structures of both the chrysene and perylene complexes were determined.

In the structure of the chrysene complex we find no significant changes in the chrysene ligand as a consequence of coordination (Figure 1). In fact, bond lengths and angles associated with the metal bound chrysene ligand are similar to those observed in the X-ray crystal structure of free chrysene,[5] and various π-molecular complexes where chrysene acts as an electron acceptor in donor:acceptor systems.[6] In many respects it bears considerable similarity to the structure of [(C$_5$Me$_5$)Ru(η^6-chrysene)][PF$_6$], which possesses an (C$_5$Me$_5$)Ru$^+$ fragment, also coordinated to one of the end rings.[7] The dihedral angle defined by the coordinated C atoms of the two arene groups measures 4.2°, and there are no major out-of-plane displacements by any of the carbons. The ruthenium atom is located nearly equidistant

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for [(chrysene)(4-methylisopropylbenzene)Ru][BF_4]^2

	x	*y*	*z*	*U*(eq)[a]
Ru	1386(1)	2207(1)	2540(1)	41(1)
F(1)	3351(4)	3339(3)	8456(3)	125(1)
F(2)	1668(4)	3503(4)	9583(4)	125(1)
F(2A)	2662(5)	1730(5)	8995(4)	193(1)
F(3)	3618(5)	1425(4)	9324(4)	133(1)
F(3A)	4301(5)	2270(5)	9774(5)	236(1)
F(4)	3876(5)	2927(5)	10039(4)	182(1)
F(4A)	1827(5)	3551(4)	9792(4)	152(1)
F(5)	−2030(3)	1128(3)	4649(2)	96(1)
F(6)	−3811(4)	873(4)	3831(4)	152(1)
F(6A)	−3492(4)	1588(5)	3375(4)	184(1)
F(7)	−3566(4)	2732(4)	3638(4)	107(1)
F(7A)	−4422(4)	2800(4)	4751(4)	141(1)
F(8)	−4577(5)	2334(5)	4980(5)	210(1)
F(8A)	−4103(4)	766(4)	4654(4)	114(1)
B(1)	3099(4)	2762(4)	9300(4)	83(1)
B(2)	−3497(4)	1679(4)	4317(4)	74(1)
C(1)	−1174(4)	2559(4)	7814(4)	84(1)
C(2)	−2714(4)	3164(4)	8003(3)	89(1)
C(3)	−3734(4)	3959(4)	7314(4)	91(1)
C(4)	−3262(4)	4159(4)	6413(4)	94(1)
C(5)	−1731(4)	3571(4)	6147(3)	73(1)
C(6)	−1155(4)	3788(4)	5118(4)	83(1)
C(7)	−2243(4)	4616(4)	4469(3)	57(1)
C(8)	−1779(4)	4848(4)	3524(4)	85(1)
C(9)	−167(4)	4268(3)	3210(3)	67(1)
C(10)	396(4)	4459(4)	2262(3)	74(1)
C(11)	2004(4)	3886(4)	2048(3)	74(1)
C(12)	2986(4)	3111(4)	2779(3)	66(1)
C(13)	2426(4)	2873(4)	3689(3)	63(1)
C(14)	870(4)	3454(4)	3930(3)	61(1)
C(15)	351(4)	3155(4)	4974(3)	70(1)
C(16)	1489(4)	2359(4)	5605(3)	61(1)
C(17)	912(4)	2202(4)	6581(4)	101(1)
C(18)	−651(4)	2763(4)	6840(4)	77(1)
C(21)	1600(4)	181(3)	3099(3)	53(1)
C(22)	126(4)	920(3)	2722(3)	51(1)
C(23)	−88(4)	1470(3)	1755(3)	54(1)
C(24)	1271(4)	1259(3)	1187(3)	53(1)
C(25)	2732(4)	525(3)	1553(3)	56(1)
C(26)	2928(4)	−36(3)	2530(3)	54(1)
C(27)	4522(4)	−800(4)	2935(4)	83(1)
C(28)	−1696(4)	2218(4)	1385(4)	82(1)
C(29)	−1983(4)	3342(4)	690(4)	162(1)
C(30)	−2148(4)	1162(4)	1001(4)	123(1)

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

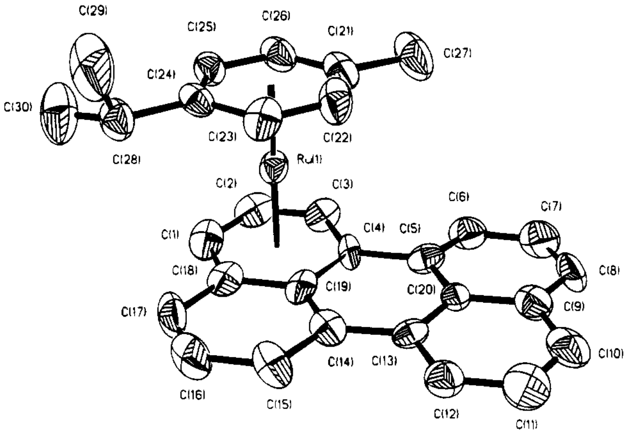

Figure 2. The structure of [(η^6-perylene)(η^6-4-methylisopropylbenzene)Ru][BF_4]$_2$. Thermal ellipsoids have been drawn at the 50% probability level. Not shown are the two BF_4^- counterions, and for clarity the H atoms have been omitted.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for [(perylene)(4-methylisopropylbenzene)Ru][BF_4]$_2$

	x	*y*	*z*	*U*(eq)
Ru(1)	1849(1)	1408(1)	660(1)	37(1)
F(1)	3494(7)	3983(4)	1566(4)	91(4)
F(2)	5203(8)	4107(5)	1491(5)	138(5)
F(3)	4559(8)	3137(4)	1661(5)	131(5)
F(4)	4346(8)	3633(7)	715(4)	163(6)
F(5)	8373(8)	754(8)	699(5)	177(7)
F(6)	8461(9)	1644(5)	1243(11)	272(12)
F(7)	9135(8)	773(7)	1609(4)	148(6)
F(8)	7408(8)	889(5)	1537(4)	111(5)
B(1)	4400(16)	3715(9)	1347(10)	63(8)
B(2)	8336(18)	1014(11)	1279(10)	78(9)
C(1)	1398(13)	435(6)	1108(7)	52(6)
C(2)	914(11)	491(6)	505(7)	51(6)
C(3)	1506(10)	605(6)	−59(7)	44(6)
C(4)	2614(12)	659(5)	−22(5)	38(5)
C(5)	3262(11)	787(5)	−604(6)	41(4)
C(6)	2820(11)	788(6)	−1212(6)	54(6)
C(7)	3434(14)	898(7)	−1778(7)	68(7)
C(8)	4476(14)	1002(6)	−1706(6)	61(6)
C(9)	4979(12)	1006(6)	−1098(7)	46(6)
C(10)	6064(14)	1066(6)	−1021(8)	61(7)
C(11)	6551(13)	1030(6)	−430(8)	65(6)
C(12)	5958(12)	911(6)	124(7)	46(5)
C(13)	4886(11)	844(5)	88(6)	34(5)
C(14)	4257(10)	707(5)	672(7)	40(5)
C(15)	4672(12)	635(5)	1294(6)	51(6)
C(16)	4028(14)	514(6)	1857(6)	60(6)
C(17)	2995(13)	440(6)	1796(6)	57(6)
C(18)	2481(12)	490(5)	1177(7)	39(5)
C(19)	3145(11)	613(4)	611(6)	39(4)
C(20)	4357(10)	873(5)	−532(5)	33(5)
C(21)	1670(15)	2325(6)	74(6)	55(6)
C(22)	2592(14)	2373(6)	397(7)	58(7)
C(23)	2653(12)	2286(6)	1084(7)	47(6)
C(24)	1724(12)	2176(5)	1454(5)	38(5)
C(25)	779(11)	2125(5)	1112(6)	43(5)
C(26)	703(13)	2194(6)	426(6)	50(6)
C(27)	1621(13)	2397(6)	−677(5)	88(7)
C(28)	1806(12)	2089(5)	2190(5)	50(5)
C(29)	2127(14)	2742(6)	2501(6)	102(9)
C(30)	853(12)	1820(7)	2507(7)	84(7)

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

from the arene ring centroids at distances of 1.712 and 1.748 Å and is shifted slightly toward C(23) of the 4-methylisopropylbenzene ligand and the bond that connects C(9) and C(14) in the molecule of chrysene.

The perylene molecule differs from chrysene in that it is one of the simplest types of polynuclear aromatics that formally contains a pair of single bonds. It is, in essence, a molecule consisting of a pair of fused naphthalene groups. In the structure of the complex (Figure 2) we find the transition metal to be coordinated in an η^6 manner to each of two rings with distances to the ring centroids that range from 1.713 to 1.752 Å. The coordinated arene rings are essentially parallel with a dihedral angle that measures 2.9°. We find no statistically significant differences between the ring that contains the coordinated transition metal ion and the three rings not involved in coordination. In fact, the bond lengths and angles for the perylene molecule are virtually identical to those observed in the structure of free perylene, with two long (1.474(18) Å) bonds connecting the two naphthalene moieties.[8] The molecule remains essentially planar, with no substantial out-of-plane deviations by any of the C atoms.

Structural features of the 4-methylisopropylbenzene ligand in both of these complexes compare favorably with those observed in the structure of the symmetrical sandwich complex,

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[bis(4-methylisopropylbenzene)Ru][BF_4]$_2$.[1a] C—C bonds within the arene rings vary from 1.387(5) to 1.456(23) Å and display an average length of 1.410 Å. There are no substantial out-of-plane displacement by any of the atoms, and the lack of any observable alternation in the derived C—C lengths suggests strongly that the aromatic character of the arene has been largely maintained.

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Supplementary Material Available: Complete listings of crystallographic data, bond angles and distances, atomic positional parameters for hydrogen atom coordinates, and anisotropic thermal parameters (10 pages). Ordering information is given on any current masthead page.