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Synthesis of Unsymmetrical Ruthenium(II) Sandwich Complexes Containing Large Polycyclic Benzenoid Aromatic Ligands and the X-ray Crystal Structure of [(η^6-pyrene)(η^6-4-(methylisopropyl)benzene)ruthenium][BF$_4$]$_2$

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Summary: A new series of Ru(II) sandwich complexes has been prepared by reacting (4-(methylisopropyl)-benzene)Ru^{2+} with pyrene, triphenylene, 4H-cyclopentaphenanthrene, 4,5-benzopyrene, and 1,2:5,6-dibenzanthracene. An X-ray crystal structure of the pyrene complex was determined, and it was found that the Ru atom coordinates in an η^6 manner to the six arene carbon atoms of the 4-(methylisopropyl)benzene ligand and one of the rings of the pyrene molecule to form an unsymmetrical sandwich complex. The crystals are triclinic, space group $P\bar{1}$, with lattice constants a = 12.909(6) Å, b = 13.359(7) Å, c = 17.150(5) Å, α = 105.20(3)°, β = 105.20(4)°, γ = 105.91(4)°, and V = 2626(2) Å^3.

The use of large polycyclic benzenoid aromatics as ligands in the preparation of new ruthenium sandwich complexes has been explored to only a limited extent.[1] Molecular orbital considerations suggest a special stability for specific electron configurations,[2a] and band structure calculations predict a wealth of interesting conductive and low-dimensional solid state properties for a number of such systems.[2b] The presence of two or more fused arene rings permits the preparation of complexes containing two or more transition metals, as well as polymeric systems. There is currently a great deal of interest in the material properties of organometallic polymers, since band structure calculations suggest that many should behave an intrinsic semiconductors or metals following the introduction of nonintegral valence.[2b] Transition metal arene complexes have also recently been used as building blocks in the construction of low-dimensional molecular solids exhibiting conductivity and ferromagnetism, and this is currently a very promising area of research.[3,4]

Much of our recent work has been directed toward the development of new synthetic procedures for the preparation of complexes containing a transition metal coordinated to a variety of large polycyclic benzenoid aromatics. In our earliar work we focused on the use of nonfused ring systems but found that the preparative procedures used did not work as well when extended to include large fused systems.[6a,b] In this paper we present a route useful in the preparation of larger Ru(II) arene sandwich complexes and describe the X-ray crystal structure of [(η^6-pyrene)-(η^6-4-(methylisopropyl)benzene)Ru][BF$_4$]$_2$.

Results and Discussion

Cleavage of the chloro-bridged Ru(II) dimer by halide abstraction using a silver salt in acetone results in the formation of a monomeric dication containing three molecules of acetone and a coordinated molecule of 4-(methylisopropyl)benzene.[5] Since the acetone ligands are only weakly coordinating, they are easily displaced by a variety of arenes to produce unsymmetrical η^6,η^6-sandwich complexes. In earlier investigations it was found that satisfactory yields could be obtained by using trifluoroacetic acid as the solvent and allowing the reaction mixture to reflux for a short period of time, typically 15 min or less.[6a] However, in reactions involving large polycyclic benzenoid aromatics we found that improved product yields (*ca.* 40–80%) could be obtained using milder conditions and a noncoordinating solvent such as CH$_2$Cl$_2$.[6b,c] Longer reaction times were required; however problems associated with the formation of a Ru(II) trifluoroacetate complex were avoided. All products were isolated as air-stable solids exhibiting good solubility in nitromethane, DMSO, and acetonitrile. In reactions involving 1,2-benzoanthracene, however, no product could be isolated. One possible reason may be the extreme insolubility of this particular arene in the solvents used in these investigations, this particularly arene being only slightly soluble at best in solvents such as benzene.

The ^{1}H and ^{13}C NMR spectra of these complexes display trends similar to those observed in other ruthenium complexes containing large polycyclic benzenoid aromatics.[6–8] In all instances the proton resonances for hydrogens attached to the carbons of the coordinated arene ring are shifted upfield relative to those of the free arene,

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typically 1–2 ppm. Accompanying this is a slight downfield shift for the remaining protons, although typically considerably less pronounced in nature. In instances where the complex possesses a plane of symmetry, six of the isopropyl methyl protons in the 4-(methylisopropyl)benzene ligands appear as a doublet in the ^{1}H NMR spectrum. Conversely, when the complex lacks any discernible elements of symmetry, as for example with 1,2:5,6-dibenzanthracene, 4*H*-cyclopentaphenanthrene, or 4,5-benzopyrene, a pair of doublets for these hydrogen atoms is seen. In these latter complexes the protons are diasteriotopic, thus accounting for the observed splitting present in the form of a closely spaced set doublets. A similar spectral feature was also observed in the ^{1}H NMR spectrum of [(η^6-chrysene)(η^6-4-(methylisopropyl)benzene)Ru][BF_4]$_2$, whose structure has recently been determined and shown to be a sandwich complex where the ruthenium center coordinates to one of the terminal rings of the chrysene ligand.[6c]

The ^{13}C NMR chemical shift data for the complexes prepared in this investigation reveal a consistent pattern. Chemical shifts toward higher fields are seen in the ^{13}C spectrum for carbon atoms involved in coordination to the transition metal center, a trend that is now well-established for a number of transition metal arene complexes. The ^{13}C chemical shifts are most dramatic for those carbons bound directly to the transition metal, and this frequently provides a useful means of identifying to which ring the transition metal is bound. In many instances this has proven to be useful in making preliminary structural assignments, many of which have later been verified crystallographically. For the complexes prepared in this investigation the ^{13}C and ^{1}H NMR data are consistent with the structures given below in Figure 1.

To further support our assignment of the structures of the complexes prepared in this investigation, the X-ray crystal structure of a representative member of this group was determined. In the structure of [(η^6-pyrene)(4-(methylisopropyl)benzene)Ru][BF_4]$_2$ we find that the Ru(II) center coordinates in an η^6 manner to the six ring carbons of the 4-(methylisopropyl)benzene ligand and to one of the four available rings of the pyrene molecule. Limitations associated with the crystallographic intensity data, unfortunately, do not permit a critical description of the various forms of distortion to the arene ring that typically take place following coordination to a transition metal. However, perhaps more importantly, the refined structure establishes unambiguously the binding mode of the Ru atom to the pyrene ligand and permits a discussion of several of the more salient features of this complex to take place.

The asymmetric unit of this complex contains two crystallographically independent molecules, each of which possesses a Ru(II) center coordinated to one ring of the pyrene molecule and a 4-(methylisopropyl)benzene ligand. In this respect the complex bears many features in common with the structure of [(η^6-chrysene)(η^6-4-(methylisopropyl)benzene)Ru][BF_4]$_2$ whose structure we have recently determined.[6c] There are no major differences between the two crystallographically independent complexes that merit a detailed discussion; in both molecules the two sets of arene rings are separated by distances that range from 3.464 to 3.450 Å, and both the pyrene and 4-(methylisopropyl)benzene rings are nearly coplanar with dihedral angles that measure 174.4 and 179.2°. Distances from the Ru atoms to the centroids defined by the six carbon atoms of the arene rings do, however, display some variation, ranging from a minimum of 1.704 Å to a maximum of 1.760 Å. The carbon atoms comprising the coordinated arene rings adopt a staggered conformation with the methyl and isopropyl groups oriented in a manner that most likely minimizes steric interactions. While the crystallographic data are of limited precision, we find no substantial out-of-plane displacements by any of the ligand groups. Furthermore, we find no evidence of statistically alternations in any of the observed arene C–C lengths, which is typically taken as evidence for some degree of arene bond localization. Interestingly, in the lattice of this structure the molecules are arranged in pairs, with the pyrene ligands oriented back-to-back, forming a columnar network that runs along the body diagonal of the unit cell.

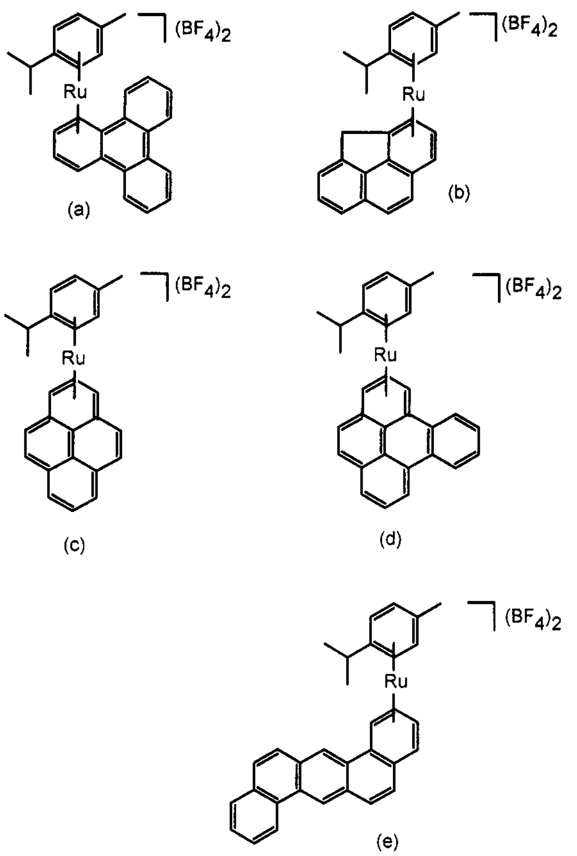

Figure 1. Schematic illustration of complexes (a–e)

It is interesting to note that when using the dicationic [(4-(methylisopropyl)benzene)Ru^{II}]$^{2+}$ fragment we find that coordination of the ruthenium atom to one of the arene rings in these aromatic fused ring systems deactivates the arene with respect to coordination of a second Ru(II) center. As a result we have not, to date, been able to insert two or more (4-(methylisopropyl)benzene)Ru^{II} dications on any large aromatic fused ring system. This is in stark contrast to work reported by others involving [(cyclopentadienyl)Fe^{II}]$^+$ or [(cyclopentadienyl)Ru^{II}]$^+$ cations where in many instances it has been possible to obtain complexes containing two, or even several, coordinated transition metals. Examples of such systems that have been subject to detailed crystallographic investigations include [(η^6-C_5Me_5Ru)$_2$(η^6,η^6-chrysene)]($O_3SCF_3^-$)$_2$,[7] as well as a rubrene derivative,[8] with two or more coordinated transition metals. The reasons behind this discrepancy remain uncertain at this time. The effect

Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	y	z	U(eq)[a]
Ru(1)	2740(1)	1853(1)	9170(1)	66(1)
Ru(2)	2155(1)	5439(1)	3848(1)	73(1)
F(1)	9563(44)	1874(67)	4560(23)	553(59)
F(2)	7934(23)	1639(21)	4001(21)	283(21)
F(3)	9289(28)	3147(20)	4444(22)	301(23)
F(4)	9179(28)	1778(21)	3394(14)	270(22)
F(5)	2544(22)	5755(22)	7066(14)	238(18)
F(6)	2177(12)	5664(16)	8191(9)	158(10)
F(7)	3637(11)	5215(15)	8042(9)	148(9)
F(8)	1966(19)	4202(17)	7165(14)	241(14)
F(9)	825(17)	1091(16)	2520(13)	240(14)
F(10)	566(16)	618(17)	1186(12)	194(12)
F(11)	2174(18)	1943(15)	2077(12)	262(14)
F(12)	1825(20)	145(21)	2000(19)	249(20)
F(13)	2593(12)	5746(13)	892(9)	134(8)
F(14)	4105(11)	5286(8)	681(7)	112(6)
F(15)	3150(11)	4562(8)	1456(7)	113(6)
F(16)	4276(11)	6309(10)	1995(8)	131(7)
B(1)	8878(29)	2115(26)	3988(19)	106(14)
B(2)	2665(28)	5204(27)	7625(13)	130(16)
B(3)	1364(21)	1089(22)	1952(14)	100(12)
B(4)	3497(24)	5545(21)	1229(15)	95(12)
C(1)	3943(18)	2670(14)	10511(10)	79(9)
C(2)	2920(18)	2098(15)	10521(10)	78(9)
C(3)	2356(17)	1009(17)	10049(10)	89(11)
C(4)	2872(14)	403(13)	9568(9)	73(8)
C(5)	2394(18)	−853(16)	9038(14)	105(11)
C(6)	2851(27)	−1287(20)	8609(13)	134(15)
C(7)	3965(18)	−717(16)	8637(10)	78(9)
C(8)	4497(24)	−1322(21)	8206(14)	125(14)
C(9)	5583(26)	−821(26)	8203(13)	123(17)
C(10)	6159(20)	349(22)	8672(13)	103(12)
C(11)	5571(19)	963(21)	9099(11)	98(12)
C(12)	6173(19)	2063(18)	9553(12)	88(11)
C(13)	5660(17)	2688(20)	9990(13)	119(11)
C(14)	4503(13)	2136(13)	10051(9)	65(7)
C(15)	3973(16)	975(12)	9576(9)	78(8)
C(16)	4512(15)	386(14)	9083(9)	68(8)
C(21)	2671(15)	1667(16)	7810(10)	85(9)
C(22)	1593(14)	1032(17)	7809(9)	89(9)
C(23)	999(13)	1509(13)	8281(9)	67(7)
C(24)	1447(15)	2625(13)	8797(9)	75(8)
C(25)	2552(13)	3303(15)	8806(11)	78(8)
C(26)	3138(14)	2846(17)	8337(9)	81(9)
C(27)	3308(16)	1163(16)	7343(10)	94(10)
C(29)	27(25)	2449(19)	9576(17)	151(19)
C(28)	829(19)	3157(21)	9295(13)	120(12)
C(30)	167(23)	3748(24)	8786(17)	143(18)
C(31)	2419(19)	5367(19)	5151(12)	100(12)
C(32)	1969(19)	4307(21)	4600(14)	123(14)
C(33)	2469(16)	3963(15)	3975(11)	79(9)
C(34)	3512(13)	4654(14)	4025(9)	77(8)
C(35)	4053(15)	4360(14)	3406(10)	75(8)
C(36)	5033(16)	5007(15)	3462(10)	84(10)
C(37)	5618(17)	6107(15)	4088(11)	96(10)
C(38)	6709(20)	6751(27)	4110(18)	137(18)
C(39)	7208(30)	7815(29)	4732(28)	187(26)
C(40)	6766(29)	8175(25)	5379(21)	163(18)
C(41)	5703(22)	7486(19)	5333(12)	127(12)
C(42)	5077(36)	7785(21)	5932(16)	163(20)
C(43)	4045(29)	7113(22)	5902(13)	142(17)
C(44)	3499(16)	6082(16)	5217(10)	91(9)
C(45)	4044(12)	5709(12)	4623(8)	65(7)
C(46)	5112(16)	6409(14)	4669(9)	81(9)
C(51)	638(14)	4687(16)	2639(11)	83(9)
C(52)	509(43)	5303(26)	3263(27)	236(34)
C(53)	746(33)	6084(40)	3538(19)	160(30)
C(54)	2042(41)	6898(17)	3540(16)	200(25)
C(55)	2278(18)	6270(21)	2904(14)	122(12)
C(56)	1627(15)	5156(15)	2472(10)	72(9)
C(57)	−150(22)	3545(20)	2245(15)	163(16)
C(58)	2308(29)	7752(31)	3822(27)	1452(98)
C(59)	3571(30)	8427(30)	3993(26)	288(38)
C(60)	2154(56)	8851(30)	3810(32)	576(142)

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

Table 2. Selected Bond Lengths (Å) and Angles (deg)

Ru(1)–C(1)	2.205(14)	Ru(1)–C(2)	2.198(17)
Ru(1)–C(3)	2.168(22)	Ru(1)–C(4)	2.239(19)
Ru(1)–C(14)	2.247(15)	Ru(1)–C(15)	2.289(20)
Ru(1)–C(21)	2.260(17)	Ru(1)–C(22)	2.212(13)
Ru(1)–C(23)	2.209(15)	Ru(1)–C(24)	2.228(20)
Ru(1)–C(25)	2.229(21)	Ru(1)–C(26)	2.237(21)
Ru(2)–C(31)	2.200(23)	Ru(2)–C(32)	2.219(30)
Ru(2)–C(33)	2.168(22)	Ru(2)–C(34)	2.268(19)
Ru(2)–C(44)	2.307(15)	Ru(2)–C(45)	2.329(15)
Ru(2)–C(51)	2.218(15)	Ru(2)–C(52)	2.033(52)
Ru(2)–C(53)	2.215(51)	Ru(2)–C(54)	2.172(29)
Ru(2)–C(55)	2.191(28)	Ru(2)–C(56)	2.182(16)
C(1)–C(2)	1.339(30)	C(1)–C(14)	1.399(29)
C(2)–C(3)	1.355(24)	C(3)–C(4)	1.426(30)
C(4)–C(5)	1.555(24)	C(4)–C(15)	1.413(26)
C(5)–C(6)	1.196(41)	C(6)–C(7)	1.414(38)
C(7)–C(8)	1.395(39)	C(7)–C(16)	1.361(23)
C(8)–C(9)	1.380(43)	C(9)–C(10)	1.441(37)
C(10)–C(11)	1.457(39)	C(11)–C(12)	1.366(30)
C(11)–C(16)	1.363(29)	C(12)–C(13)	1.398(37)
C(13)–C(14)	1.517(28)	C(14)–C(15)	1.431(20)
C(15)–C(16)	1.448(28)	C(21)–C(22)	1.416(26)
C(21)–C(26)	1.470(26)	C(21)–C(27)	1.469(31)
C(22)–C(23)	1.410(27)	C(23)–C(24)	1.398(21)
C(24)–C(25)	1.458(25)	C(24)–C(28)	1.499(34)
C(25)–C(26)	1.387(29)	C(29)–C(28)	1.464(41)
C(28)–C(30)	1.559(44)	C(31)–C(32)	1.357(31)
C(31)–C(44)	1.416(30)	C(32)–C(33)	1.436(35)
C(33)–C(34)	1.375(25)	C(34)–C(35)	1.450(27)
C(34)–C(45)	1.379(19)	C(35)–C(36)	1.286(26)
C(36)–C(37)	1.441(22)	C(37)–C(38)	1.420(34)
C(37)–C(46)	1.368(30)	C(38)–C(39)	1.403(44)
C(39)–C(40)	1.417(62)	C(40)–C(41)	1.397(43)
C(41)–C(42)	1.510(50)	C(41)–C(46)	1.446(23)
C(42)–C(43)	1.367(51)	C(43)–C(44)	1.420(26)
C(44)–C(45)	1.449(27)	C(45)–C(46)	1.408(24)
C(51)–C(52)	1.261(52)	C(51)–C(56)	1.395(27)
C(51)–C(57)	1.450(28)	C(52)–C(53)	0.956(57)
C(53)–C(54)	1.727(60)	C(54)–C(55)	1.362(47)
C(54)–C(58)	1.039(43)	C(55)–C(56)	1.385(27)
C(58)–C(59)	1.540(50)	C(58)–C(60)	1.540(67)
C(59)–C(60)	2.030(83)		
C(2)–C(1)–C(14)	120.5(15)	C(1)–C(2)–C(3)	121.9(21)
C(2)–C(3)–C(4)	121.0(19)	C(3)–C(4)–C(5)	128.3(17)
C(3)–C(4)–C(15)	118.3(14)	C(5)–C(4)–C(15)	113.4(17)
C(4)–C(5)–C(6)	124.1(21)	C(5)–C(6)–C(7)	121.9(20)
C(6)–C(7)–C(8)	118.1(19)	C(6)–C(7)–C(16)	120.9(22)
C(8)–C(7)–C(16)	121.0(20)	C(7)–C(8)–C(9)	121.4(22)
C(8)–C(9)–C(10)	117.6(29)	C(9)–C(10)–C(11)	119.7(23)
C(10)–C(11)–C(12)	117.0(21)	C(10)–C(11)–C(16)	118.0(20)
C(12)–C(11)–C(16)	124.7(24)	C(11)–C(12)–C(13)	119.4(22)
C(12)–C(13)–C(14)	120.8(19)	C(1)–C(14)–C(13)	125.6(15)
C(1)–C(14)–C(15)	120.0(16)	C(13)–C(14)–C(15)	114.4(17)
C(4)–C(15)–C(14)	118.2(17)	C(4)–C(15)–C(16)	119.6(13)
C(14)–C(15)–C(16)	122.1(16)	C(7)–C(16)–C(11)	122.1(21)
C(7)–C(16)–C(15)	119.7(17)	C(11)–C(16)–C(15)	118.2(16)
C(22)–C(21)–C(26)	116.2(18)	C(22)–C(21)–C(27)	121.8(16)
C(26)–C(21)–C(27)	122.0(16)	C(21)–C(22)–C(23)	121.8(16)
C(22)–C(23)–C(24)	122.4(16)	C(23)–C(24)–C(25)	117.1(17)
C(23)–C(24)–C(28)	123.5(17)	C(25)–C(24)–C(28)	119.3(15)
C(24)–C(25)–C(26)	121.0(15)	C(21)–C(26)–C(25)	121.5(16)
C(24)–C(28)–C(29)	117.3(23)	C(24)–C(28)–C(30)	110.8(20)
C(29)–C(28)–C(30)	108.0(22)	C(32)–C(31)–C(44)	119.8(24)
C(31)–C(32)–C(33)	120.4(22)	C(32)–C(33)–C(34)	119.6(15)
C(33)–C(34)–C(35)	122.2(13)	C(33)–C(34)–C(45)	121.1(17)
C(35)–C(34)–C(45)	116.5(14)	C(34)–C(35)–C(36)	121.7(14)
C(35)–C(36)–C(37)	122.8(20)	C(36)–C(37)–C(38)	118.6(22)
C(36)–C(37)–C(46)	116.2(17)	C(38)–C(37)–C(46)	124.9(18)
C(37)–C(38)–C(39)	114.7(30)	C(38)–C(39)–C(40)	123.5(33)
C(39)–C(40)–C(41)	118.2(23)	C(40)–C(41)–C(42)	124.6(22)
C(40)–C(41)–C(46)	120.2(25)	C(42)–C(41)–C(46)	115.1(21)
C(41)–C(42)–C(43)	125.2(21)	C(42)–C(43)–C(44)	116.4(28)
C(31)–C(44)–C(43)	118.4(23)	C(31)–C(44)–C(45)	119.1(15)
C(43)–C(44)–C(45)	122.3(20)	C(34)–C(45)–C(44)	119.1(14)
C(34)–C(45)–C(46)	120.6(16)	C(44)–C(45)–C(46)	120.2(13)
C(37)–C(46)–C(41)	117.8(19)	C(37)–C(46)–C(45)	121.7(13)
C(41)–C(46)–C(45)	120.4(19)	C(52)–C(51)–C(56)	114.9(24)
C(52)–C(51)–C(57)	117.9(27)	C(56)–C(51)–C(57)	126.6(20)
C(51)–C(52)–C(53)	135.3(58)	C(52)–C(53)–C(54)	116.9(53)
C(53)–C(54)–C(55)	106.2(21)	C(53)–C(54)–C(58)	118.3(49)
C(55)–C(54)–C(58)	131.3(46)	C(54)–C(55)–C(56)	122.1(25)
C(51)–C(56)–C(55)	118.9(19)	C(54)–C(58)–C(59)	116.5(48)
C(54)–C(58)–C(60)	149.5(41)	C(59)–C(58)–C(60)	82.5(35)
C(58)–C(59)–C(60)	48.8(24)	C(58)–C(60)–C(59)	48.8(26)

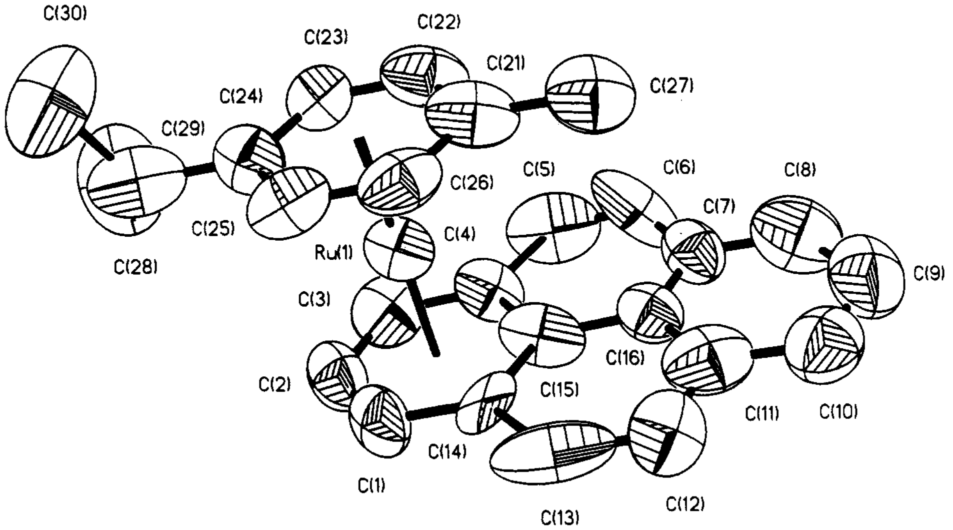

Figure 2. View of one of the two independent molecules, illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. The two BF_4 counterions are not shown and H atoms have been omitted for clarity.

Table 3. ^{1}H NMR Absorptions (ppm) of Complexes in CD_3NO_2

complex	
a	6.61 (d, 2H, *J* = 8.25 Hz), 6.35 (d, 2H, *J* = 8.20 Hz), 2.47 (sep, 1H, *J* = 6.82 Hz), 1.61 (s, 3H), 1.09 (d, 6H, *J* = 6.66 Hz) (4-(methylisopropyl)benzene); 8.84 (d, 2H, *J* = 8.25 Hz), 8.69 (d, 2H, *J* = 8.20 Hz), 8.37 (m, 2H), 8.14 (t, 2H, *J* = 7.20 Hz), 8.00 (t, 2H, *J* = 7.06 Hz), 7.21 (m, 2H) (triphenylene)
b	6.62 (d, 2H, *J* = 6.18 Hz), 6.57 (d, 2H, *J* = 6.12 Hz), 2.58 (sep, 1H, *J* = 6.86 Hz), 1.15 (dd, 6H, J_1 = 6.90, J_2 = 6.92 Hz) (4-(methylisopropyl)benzene); 8.61 (d, 1H, *J* = 9.34 Hz), 8.21 (m, 2H), 7.89 (d, 1H, *J* = 9.22 Hz), 7.70 (d, 1H, *J* = 6.13 Hz), 7.53 (d, 1H, *J* = 5.96 Hz), 6.87 (t, 1H, *J* = 6.05 Hz), 6.22 (t, 1H, *J* = 6.49 Hz), 4.84 (dd, 2H, J_1 = 33.80, J_2 = 33.88 Hz) (4*H*-cyclopentaphenanthrene)
c	6.35 (d, 2H, *J* = 6.69 Hz), 6.05 (d, 2H, *J* = 6.61 Hz), 2.54 (sep, 1H, *J* = 6.87 Hz), 1.68 (s, 3H), 1.10 (d, 6H, *J* = 6.91 Hz) (4-(methylisopropyl)benzene); 8.80 (d, 2H, *J* = 9.62 Hz), 8.71 (d, 2H, *J* = 8.20 Hz), 8.54 (1H, *J* = 6.98 Hz), 8.17 (d, 2H, *J* = 8.26 Hz), 7.76 (d, 2H, *J* = 6.30 Hz), 7.13 (t, 1H, *J* = 6.23 Hz) (pyrene)
d	6.01 (d, 2H, *J* = 6.59 Hz), 5.91 (d, 2H, *J* = 6.52 Hz), 2.45 (sep, 1H, *J* = 6.84 Hz), 1.58 (s, 3H), 1.04 (dd, 6H, *J* = 6.90 Hz) (4-(methylisopropyl)benzene); 9.24 (d, 1H, *J* = 7.76 Hz), 9.04 (d, 1H, *J* = 8.09 Hz), 8.86 (d, 1H, *J* = 8.06 Hz), 8.71 (d, 1H, *J* = 9.22 Hz), 8.51 (m, 2H), 8.30 (m, 2H), 8.11 (t, 1H, *J* = 6.42 Hz), 7.76 (d, 1H, *J* = 6.08 Hz), 7.27 (t, 1H, *J* = 6.09 Hz), 6.25 (t, 1H, *J* = 6.39 Hz) (4,5-benzopyrene)
e	6.60 (d, 2H, *J* = 6.68 Hz), 6.33 (d, 2H, *J* = 6.56 Hz), 2.51 (sep, 1H, *J* = 6.86 Hz), 1.63 (dd, 6H, J_1 = 6.67 Hz, J_2 = 6.73 Hz) (4-(methylisopropyl)benzene); 9.26 (d, 1H, *J* = 7.31 Hz), 9.03 (d, 1H, *J* = 6.54 Hz), 8.53 (d, 1H, *J* = 7.31 Hz), 8.51 (d, 1H, *J* = 6.54 Hz), 8.27 (d, 1H, *J* = 7.26 Hz), 8.00 (m, 3H, *J* = 6.87 Hz), 7.82 (m, 2H), 7.51 (t, 2H, *J* = 6.81 Hz), 7.01 (t, 1H, *J* = 6.53 Hz), 6.93 (t, 1H, *J* = 6.72 Hz), (1,2:5,6-dibenzanthracene)

Table 4. ^{13}C NMR Absorptions (ppm) of Complexes in CD_3NO_2

complex	
a	119.7, 111.1, 93.5, 90.8, 30.3, 20.2, 15.4 (4-(methylisopropyl)benzene); 133.3, 132.0, 129.3, 125.6, 124.2, 121.3, 100.6, 92.5, 86.1 (triphenylene)
b	118.1, 109.9, 93.0, 90.6, 30.2, 20.3, 20.0, 14.9 (4-(methylisopropyl)benzene); 142.3, 138.7, 133.8, 130.0, 126.3, 125.8, 120.3, 114.5, 99.6, 93.1, 89.9, 89.7, 89.0, 87.5, 37.9 (4*H*-cyclopentaphenanthrene)
c	120.4, 108.5, 94.4, 89.3, 30.1, 20.1, 15.3 (4-(methylisopropyl)benzene); 139.0, 132.3, 131.7, 131.5, 122.3, 117.3, 101.5, 94.4, 92.1, 88.2 (pyrene)
d	118.1, 109.4, 92.7, 90.9, 30.2, 20.0, 15.2 (4-(methylisopropyl)benzene); 139.4, 133.4, 132.7, 132.5, 130.8, 129.8, 127.5, 127.4, 125.9, 125.6, 124.7, 121.7, 102.2, 101.3, 93.6, 91.4, 89.9, 89.5, 86.2, 83.6 (4,5-benzopyrene)
e	120.7, 110.2, 93.5, 91.5, 30.3, 20.2, 20.0, 15.4 (4-(methylisopropyl)benzene); 140.2, 132.1, 131.8, 139.7, 129.5, 128.5, 128.3, 127.3, 126.2, 126.0, 125.1, 122.8, 119.5, 119.2, 101.1, 100.4, 92.8, 92.1, 90.8, 90.4, 85.6 (1,2:5,6-dibenzanthracene)

may be largely electrostatic in origin since we are working with dicationic Ru(II) complexes. However, at this time it remains to be established if this is indeed the case, or if perhaps more subtle factors are at work.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques under oxygen-free nitrogen or in an inert atmosphere glovebox. Acetone was dried over molecular sieves and all halogenated solvents were distilled over P_2O_5. α-Terpinene (1-isopropyl-4-methyl-1,4-cyclohexadiene), pyrene, triphenylene, 4*H*-cyclopentaphenanthrene, 4,5-benzopyrene, 1,2:5,6-dibenzanthracene, and 1,2-benzoanthracene 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 nitromethane-d_3 and referenced to TMS. Crystallographic data were collected on a Siemens R3m/V diffractometer, and elemental analyses were performed by Texas Analytical Laboratories, Inc., and Atlantic Microlab, Inc.

Preparation of [(acetone)$_3$(η^6-4-(methylisopropyl)benzene)Ru][BF$_4$]$_2$. The chloro-bridged Ru(II) dimer, [(4-methylisopropyl)benzene)Ru(Cl)$_2$]$_2$, was prepared using the literature procedure.[5b] $AgBF_4$ was used to abstract the halide ions in acetone solvent, producing the tris(acetone)(4-(methylisopropyl)benzene)ruthenium(II) dication, as previously described.[6]

Preparation of [(η^6-triphenylene)(η^6-4-(methylisopropyl)benzene)Ru][BF$_4$]$_2$ (a). To 0.300 g (0.49 mmol) of the chloro-bridged Ru(II) dimer in 10.0 mL of acetone was added 0.390 g (2.0 mmol) of $AgBF_4$. The reaction mixture was stirred for 15 min at room temperature and then transferred to a clean Schlenk flask through a cannula, one end of which was covered with filter paper. The solution was taken to dryness under reduced pressure. CH_2Cl_2 (10 mL) was introduced in the flask along with triphenylene (0.300 g, 1.34 mmol) and the reaction mixture refluxed for 48 h. The resulting yellow solid was isolated by filtration and rinsed with 5.0 mL of CH_2Cl_2 followed by 10.0 mL of diethyl ether. The yield was 0.450 g (72% yield) of a pale yellow solid that did not melt, but began to decompose at 258 °C. Anal. Calc for $C_{28}H_{26}B_2F_8Ru$: C, 52.74; H, 4.08. Found: C, 52.21; H, 4.09.

Preparation of [(η^6-4*H*-cyclopentaphenanthrene)(η^6-4-(methylisopropyl)benzene)Ru][BF$_4$]$_2$ (c). The chloro-bridged dimer (0.200 g, 0.34 mmol) was cleaved in 10.0 mL of acetone using $AgBF_4$ (0.260 g, 1.34 mmol). After 15 min of stirring at room temperature, the solutions was filtered and transferred to a clean Schlenk flask. The solvent was removed under reduced pressure, and to the resulting yellow oil was added 0.200 g (1.05 mmol) of 4*H*-cyclopentaphenanthrene dissolved in 10.0 mL of CH_2Cl_2. The reaction mixture was refluxed for 48 h, and the resulting greenish yellow precipitate was washed with CH_2Cl_2 (5.0 mL) and 10.0 mL of diethyl ether. The yield after drying was 0.220 g (54%) of a clean yellow-green powder that decomposed at 212 °C. Anal. Calc for $C_{25}H_{24}B_2F_8Ru$: C, 50.07; H, 4.04. Found: C, 50.13; H, 4.07.

Preparation of [(η^6-pyrene)(η^6-4-(methylisopropyl)benzene)Ru][BF$_4$]$_2$ (d). To a Schlenk flask containing 0.300 g (0.49 mmol) of the chloro-bridged dimer in 15.0 mL of acetone was added 390 mg (2.0 mmol) of $AgBF_4$. The reaction mixture was stirred for 15 min at room temperature, after which the solution was filtered to remove the AgCl precipitate and transferred to a new Schlenk flask through a cannula. The resulting yellow solution was taken to dryness under reduced pressure. CH_2Cl_2 (10.0 mL) was added to the flask along with 0.200 g (0.99 mmol) of pyrene and the reaction mixture refluxed for 48 h. This resulted in the formation of a dark yellow solid that was isolated by filtration and washed with CH_2Cl_2 (5.0 mL) followed by 10.0 mL of diethyl ether. The yield was 0.453 g (76%) of a dark yellow powder that began to decompose at 214 °C. Anal. Calc for $C_{26}H_{24}B_2F_8Ru$: C, 51.06; H, 3.92. Found: C, 51.09; H, 3.92.

Preparation of [(η^6-4,5-benzopyrene)(η^6-4-(methylisopropyl)benzene)Ru][BF$_4$]$_2$ (e). To the Ru(II) dimer (0.100 g, 0.163 mmol) in 10.0 mL of acetone was added 0.130 g (0.67 mmol) of $AgBF_4$. The mixture was stirred for 15 min at room temperature and then filtered to remove the AgCl precipitate. The solvent was removed under reduced pressure and the residue treated with 4,5-benzopyrene (0.100 g, 0.40 mmol) in 10.0 mL of CH_2Cl_2. The reaction mixture was refluxed for 48 h and the yellow precipitate isolated by filtration, washed with CH_2Cl_2 (5.0 mL) followed by an additional 10.0-mL aliquot of diethyl ether. A yellow powder (0.120 g) was isolated in 56% yield. Decomposition was observed at 247 °C. Anal. Calc for $C_{30}H_{26}B_2F_8Ru$: C, 54.45; H, 3.96. Found: C, 54.48; H, 4.23.

Preparation of [(η^6-1,2:5,6-dibenzanthracene)(η^6-4-(methylisopropyl)benzene)Ru][BF$_4$]$_2$ (f). The monomeric Ru(II) cation was prepared in the usual way using 0.100 g (0.163 mmol) of the chloro-bridged Ru dimer and 0.130 g (0.67 mmol) of $AgBF_4$ in 10.0 mL of acetone. The solution fraction was transferred to a clean Schlenk flask; the solvent removed and replaced with 10.0 mL of CH_2Cl_2. 1,2:5,6-Dibenzanthracene (0.100 g, 0.36 mmol) was added, and the reaction mixture was refluxed for 68 h. The yellow precipitate that formed was isolated by decanting the solution and washed with 10.0 mL of CH_2Cl_2 followed by a second wash with 10.0 mL of diethyl ether. The yield was 0.053 g (24%) of a yellow powder that decomposed at 305 °C. Anal. Calc for $C_{32}H_{28}B_2F_8Ru$: C, 55.89; H, 4.07. Found: C, 54.48; H, 4.23.

X-ray Crystal Structure Determination of [(η^6-pyrene)(η^6-4-(methylisopropyl)benzene)Ru][BF$_4$]$_2$. Crystals suitable for a crystal structure determination were obtained following crystallization from a nitromethane–diethyl ether solution. A single well-formed regularly shaped light-yellow colored crystal approximately 0.24 × 0.28 × 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. 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 ω-scanning technique in bisecting geometry on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo Kα radiation. The scan rate was variable, 3–15° min^{-1}, and the scan range was 1.2° in ω. A total of 6654 reflections ($0 < h < 13, -14 < k < 13, -18 < l < 17$) were collected between $3.5° < 2\theta < 45°$ and merged, resulting in 6302 unique independent reflections. ($R_{\text{int}} = 1.61\%$). The data were corrected for absorption, Lorentz, and polarization effects. Absorption corrections were applied empirically on the basis of azimuthal scans of several strong reflections, spanning a range of 2θ values (min and max transmission: 0.267, 0.681, respectively). No reflections had intensities beyond the range for valid coincidence correction. During the course of collection the crystal decayed in the beam, and an attempt was made to correct for the intensity data for standard decay. Structure solution and refinement was carried out using the *SHELXTL-PC* collection of crystallographic software.[11] Intensity statistics favored the centrosymmetric $P\bar{1}$ space group. The positions of the two Ru atoms for each of the two crystallographically independent molecules were 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 and refined anisotropically using scattering factors that included terms for anomalous dispersion.[11] Hydrogen atoms were included in idealized positions with a fixed isotropic U = 0.08 Å^2. Refinement was based on F using weights of the form $w^{-1} = [\sigma^2(F) + 0.0226(F^2)]$. For the final cycle the maximum shift/σ was 0.333 (mean 0.04) with minimum and maximum residual electron densities of −1.41 and +1.36 e Å^{-3} in the vicinity of the metal atoms. During the final stages of refinement several intense low-angle reflections appeared to suffer from some form of extinction and were therefore omitted. Convergence to conventional R values of $R = 0.0949$ and $R_W = 0.1216$ with a goodness-of-fit of 0.85 was obtained for 668 variable parameters and 3167 reflections with $I > 3\sigma(I)$.

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Supplementary Material Available: Lists of atomic positional parameters for hydrogen atom coordinates, anisotropic thermal parameters, and bond distances and angles for BF_4^- groups (4 pages). Ordering information is given on any current masthead page.

OM940078M

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[11] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV (present distributor: D. Reidel, Dordrecht).