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The Australian National University, Canberra, A.C.T., Australia 2600

Protonation of Arene Cyclooctatetraene Complexes of Zerovalent Ruthenium. Single-Crystal X-ray Study of the Isomeric Cyclooctatrienyl Complexes $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(1,3,5\text{-}C_6H_3Me_3)]PF_6$ and $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(1,3,5\text{-}C_6H_3Me_3)]PF_6$

M. A. BENNETT,* T. W. MATHESON, G. B. ROBERTSON, A. K. SMITH, and P. A. TUCKER

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Protonation (HPF_6, HBF_4, CF_3CO_2H) of Ru(arene)(COT) (arene = mesitylene, hexamethylbenzene, or *tert*-butylbenzene; COT = cyclooctatetraene) gives $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(arene)]^+$ cations which can be isolated as PF_6 or BF_4 salts. The mesitylene and hexamethylbenzene species isomerize almost completely on warming in organic solvents to $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(arene)]^+$ cations, but in the presence of CF_3CO_2H isomerization is incomplete. ^1H and ^{13}C NMR data for the isomeric C_8H_9 complexes are reported and discussed. In contrast with the behavior of $Fe(CO)_3(COT)$, there is no evidence for the formation of 2–6-η-bicyclo[5.1.0]octadienyl species on protonation either of Ru(arene)(COT) (arene = $C_6H_3Me_3$, C_6Me_6) or of $Ru(CO)_3(COT)$. The *tert*-butylbenzene-containing cation $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(C_6H_5\text{-}t\text{-}Bu)]^+$ isomerizes in solution to an inseparable mixture of starting material and an unidentified cation, whereas the benzene species $[Ru(C_8H_9)(C_6H_6)]PF_6$ obtained from $Ru(C_6H_6)(COT)$ and HPF_6 rapidly decomposes in organic solvents. In the monodeuterio complexes $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_8D)(arene)]^+$ (arene = C_6Me_6, $C_6H_5\text{-}t\text{-}Bu$) obtained from Ru(arene)(COT) and CF_3CO_2D, the entering deuteron is probably exo to the metal atom and it does not shift during the subsequent isomerization. The salt $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(C_6H_3Me_3)]PF_6$ (**1**) crystallizes in space group $C2/c$, with $a = 37.137$ (5) Å, $b = 7.3343$ (6) Å, $c = 15.634$ (2) Å, $\beta = 121.63$ (2)°, and $Z = 8$; $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(C_6H_3Me_3)]PF_6$ (**2**) crystallizes in space group $Pn2_1a$ or $Pnma$, with $a = 7.843$ (1) Å, $b = 9.014$ (1) Å, and $c = 25.367$ (3) Å. The structures were solved by heavy-atom methods and refined by least-squares methods to $R = 0.034$ for 4017 reflections (**1**) and to $R = 0.046$ for 1329 reflections (**2** in $Pn2_1a$). In **1** the η^6-mesitylene ring carbon atoms eclipse an approximately planar 1–5-η-C_8H_9 pentadienyl unit. The Ru–C(pentadienyl) bond lengths are not equal, the terminal distances [Ru–C(4) 2.175 (4) Å, Ru–C(8) 2.202 (3) Å] and the central distance [Ru–C(2) 2.172 (4) Å] being greater than the other two [Ru–C(1) 2.135 (4) Å, Ru–C(3) 2.144 (4) Å]. In **2** the C_8H_9 group is bound to ruthenium via an asymmetric η^3-allylic unit and a symmetric η^2-olefinic bond. In the allylic bond, one of the Ru–C(terminal) distances [Ru–C(14) 2.345 (14) Å] is ca. 0.1 Å longer than either the central bond [Ru–C(15) 2.244 (15) Å] or the other terminal bond [Ru–C(16) 2.233 (6) Å], whereas the Ru–C distances to the coordinated olefin do not differ significantly [mean value 2.211 (14) Å]. The mesitylene ligand in **1** is slightly nonplanar and has a twist-boat conformation, with Ru–C(arene) distances ranging from 2.224 to 2.257 Å. Relief of strain in the eight-membered ring may provide the driving force for isomerization of the 1–5-η- to the 1–3:6-7-η-C_8H_9 complexes.

Introduction

Cyclooctatetraene (COT) complexes of transition metals in low oxidation states can often be protonated by strong acids to give complexes containing the $C_8H_9^+$ ion, but the structure of the product and the mode of protonation depend on the metal, the bonding mode of COT, and the nature of the acid. Structures I–VI which have been proposed for various C_8H_9 complexes formed by protonation are shown in Figure 1. Protonation of $Fe(CO)_3(1\text{-}4\text{-}\eta\text{-}COT)$ with HSO_3F at −120 °C proceeds in exo fashion to give the 1–5-η-cyclooctatrienyl complex I [$X = Fe(CO)_3$][1] which undergoes ring closure above −60 °C to give the stable 2–6-η-bicyclo[5.1.0]octadienyl cation II [$X = Fe(CO)_3$].[2] In concentrated H_2SO_4 or in $HBF_4/(CH_3CO)_2O$, $Ru(CO)_3(1\text{-}4\text{-}\eta\text{-}COT)$ is reported to give initially the bicyclic 2–6-η-species II [$X = Ru(CO)_3$], but in contrast to the iron system this isomerizes to a stable cation formulated either as a 1–4:7-η-cyclooctatrienyl III or a 1–3:6-7-η-cyclooctatrienyl IV [$X = Ru(CO)_3$], which can also be isolated by treatment of $Ru(CO)_3(1\text{-}4\text{-}\eta\text{-}COT)$ in ether with aqueous HPF_6;[3] no evidence for the 1–5-η-cyclooctatrienyl complex I [$X = Ru(CO)_3$] has been reported. Different behavior is observed if the acid contains a strongly coordinating anion. Hydrogen chloride reacts with $M(CO)_3(1\text{-}4\text{-}\eta\text{-}COT)$ (M = Fe, Ru) to give 1–3-η-cyclooctatrienyl complexes IV [$X = MCl(CO)_3$].[4] The d^8 complexes $M(C_5R_5)(COT)$ (M = Co, Rh, Ir; R = H, CH_3) differ from the isoelectronic $M(CO)_3(COT)$ (M = Fe, Ru) compounds in that the thermodynamically stable isomer contains 1-2:5-6-η-COT, although the 1–4-η isomer can sometimes be detected or isolated.[5,6] Treatment of $M(C_5H_5)(1\text{-}2{:}5\text{-}6\text{-}\eta\text{-}COT)$ (M = Co, Rh) with an excess of CF_3CO_2H gives initially 2–6-η-bicyclo[5.1.0]octadienyl cations II [$X = CoC_5H_5$, RhC_5H_5] which isomerize completely and irreversibly to 1–3:6-7-η-cyclo-

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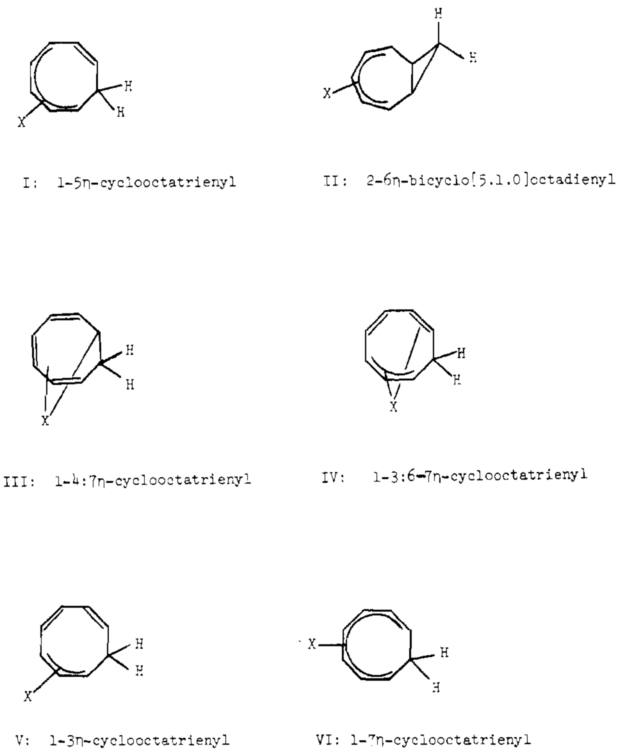

I: 1-5η-cyclooctatrienyl
II: 2-6η-bicyclo[5.1.0]octadienyl
III: 1-4:7η-cyclooctatrienyl
IV: 1-3:6-7η-cyclooctatrienyl
V: 1-3η-cyclooctatrienyl
VI: 1-7η-cyclooctatrienyl

Figure 1. Bonding modes for C_8H_9.

octatrienyl cations IV.[7] Use of CF_3CO_2D establishes that in these cases the proton enters endo with respect to the metal. Low-temperature protonation of $Ir(C_5H_5)(1\text{-}2{:}5\text{-}6\text{-}\eta\text{-COT})$ gives a detectable hydridodiene cation $[IrH(C_5H_5)(COT)]^+$, which, on warming to room temperature, isomerizes to a mixture of the 2-6-η-bicyclo[5.1.0]octadienyl II and 1-3:6-7-η-cyclooctatrienyl IV [$X = IrC_5H_5$].[7] An isomeric mixture of II and IV [$X = RhC_5Me_5$] is also obtained by treatment of $Rh(C_5Me_5)(1\text{-}4\text{-}\eta\text{-COT})$ with CF_3CO_2H at low temperature, but the ratio (3:2) differs from that obtained by similar treatment of the corresponding, more stable isomer $Rh(C_5Me_5)(1\text{-}2{:}5\text{-}6\text{-}\eta\text{-COT})$ (4:1). Moreover, the stereochemistry of protonation is exo in the case of the 1–4-η-isomer and endo in the case of the 1,2,5,6-η isomer.[5] Finally, protonation of the d^6 complex $Mo(CO)_3(1\text{-}6\text{-}\eta\text{-COT})$ occurs endo to give a complex thought to contain the 1-7-η-cyclooctatrienyl or homotropylium cation VI [$X = Mo(CO)_3$].[8]

The structural assignments in this bewildering array of results have been based solely on necessarily complex NMR spectra and have not been supported by definitive X-ray structural analysis. We have studied the protonation of Ru(arene)(COT) complexes[9] for comparison with the behavior of the isoelectronic $Ru(CO)_3$ and RhC_5H_5 complexes and have characterized the products by X-ray crystallography.

Experimental Section

^1H NMR spectra were recorded at 34 °C on Varian HA-100 or Jeolco MH-100 instruments with the use of $(CH_3)_4Si$ as internal reference. ^{13}C NMR spectra were obtained on a Jeolco FX-60 instrument operating at 15.04 MHz. IR spectra were measured as Nujol mulls on a PE 457 spectrometer. Analyses were carried out in the microanalytical laboratories of the Australian National University; those for the arene complexes are given in Table I. ^1H and ^{13}C NMR data are listed in Tables II–V. The complexes Ru(arene)(COT)

Table I. Analytical Data for $[Ru(arene)(C_8H_9)]Y$ Complexes

		calcd		found	
arene	Y	% C	% H	% C	% H
		$1\text{-}5\text{-}\eta\text{-}C_8H_9$			
C_6Me_6	PF_6	46.8	5.3	46.7	5.5
C_6Me_6	BF_4	52.8	5.9	52.7	5.8
$C_6H_3Me_3$	PF_6	43.3	4.5	43.1	4.8
C_6H_5-*t*-Bu	PF_6	44.4	4.7	44.4	4.8
C_6H_5-*t*-Bu	BF_4	50.6	5.4	50.4	5.6
C_6H_6	PF_6	39.2	3.5	39.1	3.7
		$1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9$			
C_6Me_6[a]	PF_6	46.8	5.3	46.6	5.1
$C_6H_3Me_3$[b]	PF_6	43.3	4.5	43.0	4.6
C_6H_5-*t*-Bu[c]	PF_6	44.4	4.7	44.4	4.8
C_6H_5-*t*-Bu[c]	BF_4	50.6	5.4	50.7	5.4

[a] Anal. Calcd for $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_8D)(C_6Me_6)]PF_6$: C, 46.7; H, 5.3. Found: C, 46.9; H, 5.4. [b] Anal. Calcd for $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_3Me_3)]PF_6$: C, 43.2; H, 4.5. Found: C, 42.9; H, 4.5. [c] Isomeric mixture (see text).

(arene = C_6H_6, C_6H_5-*t*-Bu, 1,3,5-$C_6H_3Me_3$, or C_6Me_6)[9] and $Ru(CO)_3(COT)$[10,11] were prepared as described previously.

Protonations. (1–5-η-Cyclooctatrienyl)(η^6-hexamethylbenzene)ruthenium(II) Hexafluorophosphate ($[Ru(1\text{–}5\text{-}\eta\text{-}C_8H_9)(C_6Me_6)]PF_6$). A solution of 60% aqueous HPF_6 in ice-cold propionic anhydride was added dropwise under nitrogen to a solution of $Ru(C_6Me_6)(COT)$ (0.10 g, 0.27 mmol) in degassed ether (10 mL). A reddish oily solid formed immediately. When further addition of acid caused no more precipitation, the mixture was stirred at room temperature for 30 min. The supernatant liquid was removed by decantation and, after being washed with ether, the residue was dissolved in acetone (10 mL). Addition of ether (5 mL) to the cold, filtered solution initially gave oily brown material which was removed by filtration. Addition of more ether gave pale yellow crystals of $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(C_6Me_6)]PF_6$ (0.105 g, 76%). The corresponding BF_4 salt was prepared similarly with use of 40% aqueous HBF_4 in propionic anhydride.

(1–3:6-7-η-Cyclooctatrienyl)(η^6-hexamethylbenzene)ruthenium(II) Hexafluorophosphate ($[Ru(1\text{–}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(C_6Me_6)]PF_6$). A solution of $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(C_6Me_6)]PF_6$ (0.17 g, 0.33 mmol) in acetone (10 mL) was heated at ca. 50 °C for 6 h. After this period conversion into the 1-3:6-7-η isomer was almost complete, as shown by ^1H NMR spectroscopy. Solvent was removed in vacuo, and the residue was recrystallized from acetone/ether or dichloromethane/ether to give yellow crystals of $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(C_6Me_6)]PF_6$ (0.09 g, 53%). After 4 days in CD_2Cl_2 containing a few drops of CF_3CO_2H, this salt had partly reverted to the 1-5-η-C_8H_9 isomer, the proportion of the latter at equilibrium being 20–30% as estimated by the relative intensities of the C_6Me_6 methyl singlets.

The salts $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(arene)]Y$ (arene = mesitylene or *tert*-butylbenzene; Y = PF_6 or BF_4) and $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(1,3,5\text{-}C_6H_3Me_3)]Y$ (Y = PF_6 or BF_4) were prepared similarly to the corresponding hexamethylbenzene salts. In their IR spectra (Nujol mulls) the 1-5-η-C_8H_9 salts showed a weak band at ca. 1675 cm^{-1}, tentatively assigned to the C=C stretching mode of the uncoordinated double bond. In the 1-3:6-7-η-C_8H_9 salts a weak band at ca. 1650 cm^{-1} was similarly assigned. Isomerization of the *tert*-butylbenzene salts $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(C_6H_5\text{-}t\text{-}Bu)]Y$ (Y = PF_6 or BF_4) did not proceed to completion under the conditions described above, and attempts to separate the isomers by fractional crystallization were unsuccessful.

Addition of 60% aqueous HPF_6 to an ether solution of $Ru(C_6H_6)(C_8H_8)$ gave an off-white precipitate which analyzed satisfactorily for $[Ru(C_8H_9)(C_6H_6)]PF_6$ (yield ca. 40%). The sale decomposed on attempted recrystallization or isomerization, and ^1H NMR spectra could not be obtained.

Deuteration Reactions. To a solution of the Ru(arene)(COT) complex in $CDCl_3$ was added dropwise deuteriotrifluoroacetic acid,

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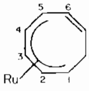
Table II. ^1H NMR Spectra of 1-5-η-Cyclooctatrienyl Complexes $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(arene)]^+$[a,b]

species	solvent	H(3)	H(6), H(7)	H(2), H(4)	H(1), H(5)	H(8)(endo)	H(8)(exo)	others
$[Ru(C_8H_9)(C_6Me_6)]PF_6$	$(CD_3)_2CO$	6.12 (t, $J_{23} = J_{34} = 7$)	5.50 (m)	4.72 (m)	3.86 (m)	2.33[c]	1.70 (½AB q, $J_{AB} = 22$)	2.29 (s, C_6Me_6)
$[Ru(C_8H_9)(C_6Me_6)]PF_6$	CD_2Cl_2	5.94 (t, $J_{23} = J_{34} = 6$)	5.52 (m)	4.52 (app q)	3.72 (app q)	2.42[c]	1.74 (½AB q, $J_{AB} = 24$)	2.24 (s, C_6Me_6)
$Ru(C_6Me_6)(COT)$	$CDCl_3/CF_3CO_2H$	5.83 (t, $J_{23} = J_{34} = 7$)	5.50 (m)	4.42 (app q)	3.68 (app q)	2.33[c]	1.71 (½AB q,[d] $J_{AB} = 22$)	2.22 (s, C_6Me_6)
$[Ru(C_8H_9)(C_6H_3Me_3)]PF_6$	$(CD_3)_2CO$	6.32 (t, $J_{23} = J_{34} = 7$)	5.57 (m)	5.13 (m)	4.28 (m)	2.48[c]	1.80 (½AB q, $J_{AB} = 24$)	2.31 (s, $C_6H_3\mathit{Me}_3$), 6.28 (s, $C_6\mathit{H}_3Me_3$)
$[Ru(C_8H_9)(C_6H_3Me_3)]PF_6$	CD_2Cl_2	6.18 (t,[e] $J_{23} = J_{34} = 7$)	5.55 (m)	5.07 (app q)	4.16 (m)	2.42[c]	1.80 (½AB q, $J_{AB} = 22$)	2.28 (s, $C_6H_3\mathit{Me}_3$) 6.05 (s, $C_6\mathit{H}_3Me_3$)
$[Ru(C_8H_9)(C_6H_5\text{-}t\text{-}Bu)]PF_6$	$(CD_3)_2CO$	6.28 (m)[e]	5.59 (m)	5.26 (m)	4.80 (m)	2.44 (½AB q, $J_{AB} = 20$)	1.82 (½AB q, $J_{AB} = 20$)	1.37 (s, *t*-Bu), 6.28,[f] 6.60 (m, C_6H_5)
$Ru(C_6H_5\text{-}t\text{-}Bu)(COT)$	$CDCl_3/CF_3CO_2H$	6.20 (m)[e]	5.54 (m)	5.09 (app q)	4.66 (m)	2.39 (½AB q, $J_{AB} = 22$)	1.73 (½AB q,[d] $J_{AB} = 22$)	1.31 (s, *t*-Bu), 6.20 (m, C_6H_5)[f]

[a] Chemical shifts δ (±0.05) (multiplicity and coupling constants J (±0.5 Hz), in parentheses, measured at 100 MHz) at 32 °C; app q = apparent quartet. [b] Protons numbered according to attached carbon atoms



[c] Peak partly obscured by arene methyl singlet; δ calculated from $\delta(H_{exo})$ and J_{AB}. [d] Absent from spectrum in $CDCl_3/CF_3CO_2D$. [e] Overlaps with arene multiplet. [f] Overlaps with multiplet due to H(3).

CF_3CO_2D, which had been freshly prepared from trifluoroacetic anhydride and D_2O. Solvents were removed in vacuo, and the oily residue was dissolved in the minimum volume of acetone. The $[Ru(C_8H_8D)(arene)]PF_6$ salt was precipitated as a yellow solid by addition of a saturated aqueous solution of NH_4PF_6 and was recrystallized from acetone/ether.

Protonation of $Ru(CO)_3(1\text{-}4\text{-}\eta\text{-}COT)$. Addition of 60% aqueous HPF_6 to an ether solution of $Ru(CO)_3(COT)$ (ca. 0.1 g) precipitated the salt $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(CO)_3]PF_6$, the ^1H NMR spectrum of which agreed with that reported in ref 3. Anal. Calcd for $C_{11}H_9F_6O_3PRu$: C, 30.3; H, 2.1. Found: C, 30.6; H, 2.5.

Addition of $HBF_4/(CH_3CO)_2O$ to solid $Ru(CO)_3(COT)$ gave a clear solution from which a solid $[Ru(C_8H_9)(CO)_3]BF_4$ salt was precipitated by dilution eith ether. Anal. Calcd for $C_{11}H_9BF_4O_3Ru$: C, 35.0; H, 2.4. Found: C, 35.3; H, 2.2. The ^1H NMR spectrum of this salt showed it to contain $1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9$ and, contrary to the statement in ref 3, there was no evidence for a bicyclo[5.1.0]octadienyl species, even when the salt was precipitated ca. 15 s after addition of $HBF_4/(CH_3CO)_2O$. The ^1H NMR spectra of $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(CO)_3]^+$ salts in CD_3CN underwent irreversible change with time indicative of reaction with the solvent, so that the spectrum reported[3] for the supposed bicyclo[5.1.0]octadienyl species in CD_3CN is suspect.

Collection and Reduction of X-ray Intensity Data. Single crystals of $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(C_6H_3Me_3)]PF_6$ (**1**) and $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(C_6H_3Me_3)]PF_6$ (**2**) were obtained from acetone/ether and from chloroform, respectively.

Crystal Data. 1: $C_{17}H_{21}F_6PRu$, fw 471.4, space group $C2/c$, $a = 37.137$ (5) Å, $b = 7.3343$ (6) Å, $c = 15.634$ (2) Å, $\beta = 121.63$ (2)°, $V_{calcd} = 3625.7$ Å^3, $Z = 8$.

2: $C_{17}H_{21}F_6PRu$, fw 471.4, space group $Pn2_1a$ or $Pnma$, $a = 7.843$ (1) Å, $b = 9.014$ (1) Å, $c = 25.367$ (3) Å, $V_{calcd} = 1793.4$ Å^3, $Z = 4$.

Unit cell dimensions of single crystals of the hexamethylbenzene salts $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(C_6Me_6)]Y$ and $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(C_6Me_6)]Y$ ($Y = PF_6$, BF_4) are listed in Table XII. The structure of $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(C_6Me_6)]BF_4$ was determined (monoclinic, Cc or $C2/c$, 1781 independent data, $R = 0.085$), but very large thermal motions (or static disorder) were apparent. Structural details have been deposited as supplementary material. Crystals of the hexamethylbenzene adducts were uniformly less satisfactory for structure analysis than those of the mesitylene adducts **1** and **2**.

Intensity data for **1** and **2** were measured on a Picker FACS-I automatic four-circle diffractometer. Details of the data collection are given in Table VI. For each isomer, monitoring of "standard" reflections indicated a small isotropic linear decrease in intensity with time. The intensities were corrected accordingly, assuming decomposition to be independent of 2θ. A redetermination of cell dimensions showed that these quantities had not changed over the period of data collection. Reflection intensities were corrected for absorption and reduced to $|F_o|$.[12] Equivalent reflections were averaged and the unique "observed" data sets sorted.

Solution and Refinement of the Structure. Atomic scattering factors and corrections for the anomalous scattering of Ru and P were taken from ref 13. The position of the ruthenium atom was located, in each case, from a three-dimensional Patterson synthesis. The remaining nonhydrogen atoms were located from subsequent difference Fourier syntheses. The structures were refined initially by block-diagonal and finally by full-matrix least-squares calculations. The function minimized in each case was $\sum w(|F_o| - |F_c|)^2$, where the weights w were given by $\sigma(F_o)^{-2}$.[12] At the end of the refinements, the quantity $w(|F_o| - |F_c|)^2$ was approximately independent of $|F_o|$ and

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(12) Quantities referred to are defined by: Lp (Lorentz–polarization factor) $= (\cos^2 2\theta + \cos^2 2\theta_m)/[(\sin 2\theta)(1 + \cos^2/2\theta_m)]$; I (peak intensity) $= [CT - (t_p/2t_b)(B_1 + B_2)]$, where CT is the total peak count in t_p s, and B_i are the background counts each in t_b s; $|F_o| = (IT/Lp)^{1/2}$, where T is the transmission factor as calculated by the method of J. de Meulenaer and H. Tompa [*Acta Crystallogr.* **1965**, *19*, 1014]; $\sigma(I) = [CT + (t_p/2t_b)^2(B_1 + B_2)]^{1/2}$ and $\sigma(F_o) = ([\sigma(I)/Lp]^2 + \rho|F_o|^4)^{1/2}/2|F_o|$, where ρ, the instrumental "uncertainty" factor = 0.002; $\sigma_s(F_o)$ (the standard deviation from counting statistics alone) $= [\sigma(I)/(2Lp|F_o|)]$; $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; the standard deviation of an observation of unit weight $= [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, where m is the number of parameters and n the number of observations.

(13) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 99–101; (b) pp 149–150.

Table III. ^{13}C NMR Spectra of 1-5-η-Cyclooctatrienyl Complexes $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(arene)]^+$ [a]

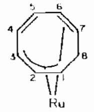
species	solvent (temp, °C)	C(6)	C(7)	C(3)	C(2) (C(4))	C(4) (C(2))	C(1), C(5)	C(5), C(1)	C(8)	arene C	others
$[Ru(C_8H_9)(C_6Me_6)]PF_6$	CD_2Cl_2 (−20)	126.5 (d, 160)	121.6 (d, 156)	102.9 (d, 160)	87.3 (d, 161)	85.7 (d, 161)	61.3 (d, ~135)	58.4 (d, ~135)	25.2 (t, 122)	105.7	16.4 (q, 133, CMe)
$Ru(C_6Me_6)(COT)$	CD_2Cl_2/CF_3CO_2H (−10)	126.6	121.8	103.1	87.8	86.1	61.8	59.0	25.3[b]	105.8	16.5
$[Ru(C_8H_9)(C_6H_3Me_3)]PF_6$	CD_2Cl_2 (−70)	126.5 (d, 155)	121.6 (d, 160)	103.4 (d, 160)	86.0 (d, ~150)	83.4 (d, ~150)	60.5 (d, ~140)	57.4 (d, ~140)	26.2 (t, ~125)	109.1 (CMe), 93.2 (d, 174, CH)	19.2 (q, 133, CMe)
$[Ru(C_8H_9)(C_6H_5\text{-}t\text{-}Bu)]BF_4$	CD_2Cl_2 or $CDCl_3$ (0)	127.4	121.7	104.1	85.2	83.0	56.6	53.8	26.5	131.4 (C-t-Bu), 92.9, 92.5, 91.9 (CH)	34.6 (CMe_3), 30.9 (CMe_3)

[a] Chemical shifts δ measured at 15.04 MHz; multiplicity and J_{CH} in parenthesis; carbon atoms numbered as in Table II. [b] Absent from spectrum in CD_2Cl_2/CF_3CO_2D.

Table IV. ^1H NMR Spectra of 1-3:6-7-η-Cyclooctatrienyl Complexes $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)L]PF_6$ ($L = C_6Me_6, C_6H_3Me_3, 3CO$)[a,b]

arene	H(4)	H(5)	H(3)	H(6)	H(1)	H(2)	H(7)	H(8)(endo)	H(8)(exo)	others
C_6Me_6	5.31 (dd, J_{34}, J_{56} = 1, 1.5)		4.42 (dd, J_{23} = 7, J_{34} = 1)	4.14 (dd, J_{67} = 7, J_{56} = 1.5)	3.77 (m)	3.33 (m)	2.93 (app q)	3.33 (m)	2.62 (m)[c]	2.33 (s, C_6Me_6)
$C_6H_3Me_3$	5.36 (dd, J_{34}, J_{56} = 1, 1.5)		4.76 (m, $J_{23} = J_{67}$ = 7, J_{34}, J_{56} = 1.0, 1.5)		4.04 (m)		3.36 (m)		2.66 (m)[c]	2.28 (s, $C_6H_3Me_3$), 6.20 (s, $C_6H_3Me_3$)
$(CO)_3$[d]	5.68 (dd, J_{45} = 8.0, J_{34} = 3.9)	5.34 (dd, J_{45} = 8.0, J_{56} = 3.9)	5.06 (m)	6.48 (dd, J_{56} = 2.3, J_{67} = 8.0)	5.06 (m)		4.41 (q, J_{67} = 8.0, J_{78} = 8.0)	3.70 (m)		

[a] Chemical shifts (δ) measured in acetone-d_6 at 32 °C (100 MHz). [b] Protons numbered according to attached carbon atoms.



[c] Absent from spectrum of monodeuterio complex $[Ru(C_8H_8D)(arene)]PF_6$. [d] Data from ref 3.

Table V. ^{13}C NMR Spectra of 1-3:6-7-η-Cyclooctatrienyl Complexes $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)L]PF_6$ ($L = C_6Me_6, C_6H_3Me_3, 3CO$)[a]

ligand	solvent (temp, °C)	C(4)	C(5)	C(3) (C(6))	C(2)	C(6) (C(3))	C(1)	C(7)	C(8)	arene C	others
C_6Me_6	CD_2Cl_2, (−80)	132.2 (d, 160)	130.6 (d, 158)	86.7 (d, 160)	86.2 (d, 160)	76.1 (d, 170)	37.1 (d, 164)	35.1 (d, 164)	19.7[b] (t, 129)	104.9	16.1 (q, 129, CMe)
$C_6H_3Me_3$	CD_2Cl_2 (20)	131.9 (d, 156)	131.4 (d, 156)	84.7 (d, 160)	82.3 (d, 160)	76.4 (d, 150)	37.9 (d, 168)	33.8 (d, 168)	19.5[b] (t, 133)	109.3 (CMe), 92.2 (d, 172, CH)	18.4 (q, 129, CMe)
$(CO)_3$	$(CD_3)_2CO$ (20)	130.9 (d, 168)	127.8 (d, 168)	111.4 (d, 164)	99.5 (d, 168)	71.2 (d, 168)	70.4 (d, 168)	47.5 (d, 176)	19.5 (t, 140)		

[a] Carbon atoms numbered as in Table IV. [b] Absent from spectrum in CD_2Cl_2/CF_3CO_2D.

Table VI. Details of X-ray Data Collection for the Isomers $[Ru(C_8H_9)(C_6H_3Me_3)]PF_6$

	1-5-η-C_8H_9 (1)	1-3:6-7-η-C_8H_9 (2)
radiation (λ, Å)	Mo Kα (0.7107)	
monochromator ($2\theta_m$, deg)	graphite (12.16)	
tube takeoff angle, deg	3.0	
scan speed, deg/min	2	
scan technique	θ-2θ	
scan half-width,[a] deg	0.75	0.85
limits of collectn, deg	$3 < 2\theta < 60$	$3 < 2\theta < 55$
bkgd counting time[b] (t_b), s	10	10
"std reflctns" [c]	32,0,0 281 0, 0, −12	0,24,0 015 600
data collected	$hk\bar{l}$, $\bar{h}k\bar{l}$	hkl, $hk\bar{l}$
total no. of intens measured	5684	4874
no. of independent "obsd" reflctns (n)[d]	4017	1329
R_s[e]	0.019	0.027
temp during collectn, °C	23 ± 1	23 ± 1
crystal faces with their perpendicular distances (cm) to an arbitrary point in the crystal (in parentheses)	100 (0.0038), 100 (0.0038), 10$\bar{1}$ (0.0400), $\bar{1}$01 (0.0238), 05$\bar{1}$ (0.0100), 05$\bar{1}$ (0.0100), $\bar{2}$12 (0.0200)	001 (0.0025), 00$\bar{1}$ (0.0025), 100 (0.0198), $\bar{1}$00 (0.0198), 010 (0.0038), 0$\bar{1}$0 (0.0038)
μ(Mo Kα), cm^{-1}	9.9	9.9
crystal stability	4% isotropic decay	8% isotropic decay

[a] The scan, in 2θ, is from the half-scan-width below the Mo Kα_1 maximum to the half-scan-width above the Mo Kα_2 maximum for each reflection. [b] Two stationary background counts were made on each side of the peak scan. [c] "Standard reflections" were monitored every 97 reflections of the period of data collection. [d] Reflections were regarded as observed if $I > 3\sigma(I)$ and the individual background counts (B_i) differed by less than $10\sigma(B_i)$. [e] R_s (the statistical R factor) = $\Sigma\sigma_s(F_o)/\Sigma|F_o|$.

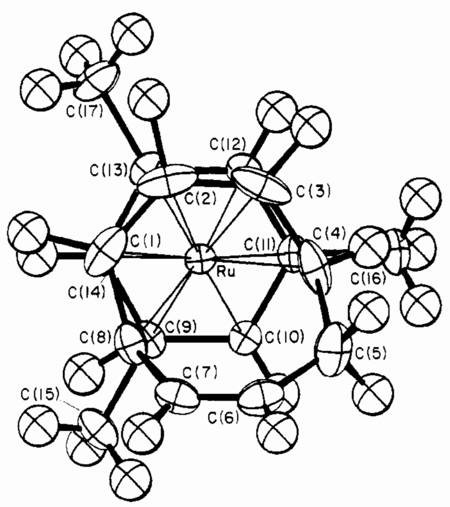


Figure 2. Molecular structure of $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(C_6H_3Me_3)]^+$ (**1**). Hydrogen atom numbering follows that of the attached carbon atoms.

(sin θ)/λ. No extinction effects were evident so no extinction corrections were applied.

Isomer 1. The geometry of and atom numbering for the cation, which lies in a general position, are shown in Figure 2. One of the two independent anions is on an inversion center at $^1/_4$, $^1/_4$, 0, the other is on a twofold axis at 0, y, $^1/_4$. The packing of cations and anions in the unit cell is illustrated in Figure 3. An initial difference Fourier synthesis indicated the second PF_6 ion to be disordered in a plane containing the diad axis (Figure 3). On the basis of the existence of eight distinct electron density maxima around the phosphorus atom in this plane, we consider the disorder to be best described by the half occupancy of two PF_6 octahedra, the second being rotated approximately 45° about the P(2)–F(21) axis relative to the first (Figure 3). After initial least-squares refinement, a difference Fourier synthesis allowed the hydrogen atoms to be located. The mesitylene hydrogen atoms were fixed at positions optimized[14] with respect to the molecular geometry every two cycles. Coordinates of all hydrogen atoms except H(3) and H(4) of the C_8H_9 ring were refined in the least-squares calculations. Possibly because of the large thermal motions of the attached carbon atoms C(3) and C(4), hydrogen atoms H(3) and H(4) did not refine to reasonable positions and were therefore included in the structure factor calculations at fixed positions determined from a difference map. All hydrogen atoms were given temperature factors of $B = 7$ Å^2. Full-matrix least-squares analysis, including the refinement of anisotropic temperature factors for the nonhydrogen atoms, converged with $R = 0.034$ ($R_w = 0.046$) for the 4017 reflections. The maximum shift in the final cycle was $<0.1\sigma$. A difference synthesis computed at the end of the refinement showed no features with absolute height greater than 0.4 e Å^{-3}. The standard deviation of an observation of unit weight[12] was 1.46. Final atomic coordinates with estimated standard deviations are listed in Table VII. Listings of anisotropic thermal parameters, interionic contacts, and observed and calculated structure factors are available (see paragraph concerning supplementary material).

Isomer 2. Systematic absences ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) indicate space group $Pn2_1a$ (nonstandard setting of $Pna2_1$) or *Pnma*. The position of the ruthenium atom, located from the Patterson synthesis, at $y = {}^1/_4$ imposes a mirror plane on the initial difference Fourier synthesis. Subsequent difference Fourier syntheses showed that, with the possible exception of atoms C(12) through C(15) (Figure 2), the cation and anion do seem to obey the crystallographic mirror symmetry imposed upon them in space group *Pnma*. In the region of C(13) and C(14), however, two pairs of mirror-related peaks were evident, one pair being within bonding distance of ruthenium. The conclusion is that the complex contains 1-3:6-7-η-C_8H_9 which, of course, cannot have m symmetry. It remained to decide which of the two space groups, $Pn2_1a$ or *Pnma*, to adopt. If the former were correct, only atoms C(13) and C(14) break the (now noncrystallographic) mirror symmetry to any extent, whereas for space group *Pnma* a statistically disordered structure is implied.

We proceeded with full-matrix least-squares refinement based on the first hypothesis. Parameters related by the pseudo-mirror plane were treated as parameters related by crystallographic symmetry in space group *Pnma*. Anisotropic thermal parameters were specified for all nonhydrogen atoms except for C(12) through C(15) which, because of high correlations between, in particular, β_{22} parameters, were refined with an isotropic temperature factor.

Initially, no hydrogen atoms were included in the scattering model, but a difference synthesis exhibited peaks of ca. 0.3–0.5 e Å^{-3} at or close to expected hydrogen atom positions. Contributions from hydrogen atoms, at positions computed from the carbon coordinates, were therefore included in all subsequent scattering models. The hydrogen thermal parameters were set equal to the equivalent isotropic

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(14) The hydrogen atom positions were computed assuming either sp^2 or sp^3 hybridization of the appropriate carbon atom. The C–H bond length was assumed to be 0.95 Å. The methyl hydrogen atomic positions were calculated by finding, from the observed residual electron density, the optimal value of α such that the three C–C–C–H torsion angles were α, $\alpha + 120$, and $\alpha + 240°$. For **1**, α was in each case 90 (±5)° and for **2** α was 90 (±5)° for C(1) and 30 (±5)° for C(5) and C(8).

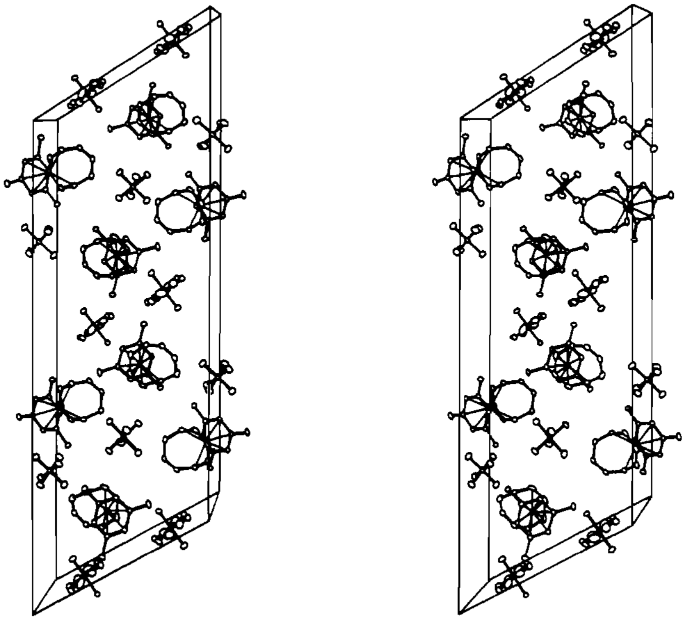

Figure 3. Packing diagram for $[Ru(1-5-\eta-C_8H_9)(C_6H_3Me_3)]PF_6$ (**1**).

values for the attached carbons and were recomputed along with the atom coordinates every two cycles. At convergence (parameter shift-to-esd ratio < 0.2) $R = 0.0469$ and $R_w = 0.0532$ for 1329 independent reflections ($I \geq 3\sigma(I)$) and 122 parameters. For the alternate absolute configuration of $Pn2_1a$ ($y = -y$), convergence values were $R = 0.0472$, $R_w = 0.0539$: the R_w ratio is significant at the 0.5% level.[15] Next, we tested the centrosymmetric arrangement, space group *Pnma*, with statistical disordering (equal occupancy) of mirror related molecules. Structure factor agreement for this model, with $R = 0.0469$ and $R_w = 0.0527$, was slightly but significantly better (0.5% level)[15] than for either hand of the ordered noncentrosymmetric model. These data suggest that the packing is close to (but not exactly) centrosymmetric and contains, predominantly, molecules having the first described ($R_w = 0.0532$) $Pn2_1a$ absolute configuration. Accordingly, the scattering model was further modified to comprise an admixture of the two mirror related $Pn2_1a$ configurations in unequal proportion (equal proportion results in the *Pnma* model described above). As expected the structure factor agreement was significantly better (0.5% level)[15] than for any previous model [$R = 0.0467$, $R_w = 0.0524$; composition, 0.7 (1) of configuration 1, 0.3 (1) of configuration 2]. Structural parameters from all the refinements are very similar. Tabulated values are those for the last discussed (disordered $Pn2_1a$) model. Residual electron densities in a final difference Fourier map did not exceed ±0.7 e Å^{-3}. The standard deviation of an observation of unit weight[12] was 1.99.

The final atomic coordinates are listed Table VII, and the geometry and atom numbering of the cation are illustrated in Figure 4. The packing of cations and anions in the unit cell is shown in Figure 5, and the structures of the cations in **1** and **2** are compared in Figure 6. Listings of anisotropic thermal parameters, interionic contacts, and calculated structure factors have been deposited as supplementary material.

Computer Programs. Those programs used were part of a package collected and assembled by Dr. D. Taylor and Dr. P. O. Whimp and individually described elsewhere.[9] All calculations were performed on the Univac 1100/42 of the Australian National University Computer Services Centre.

Results and Discussion

Pale yellow crystalline salts of formula $[Ru(1-5-\eta-C_8H_9)(arene)]Y$ (arene = C_6Me_6, 1,3,5-$C_6H_3Me_3$, C_6H_5-*t*-Bu; Y = PF_6, BF_4) are obtained in good yield from reaction of aqueous HPF_6 or HBF_4 in propionic anhydride with ether solutions of the ruthenium(0) complexes Ru(arene)(COT). The 1–5-η-bonding mode has been established by single-crystal X-ray study of the mesitylene complex $[Ru(1-5-\eta-C_8H_9)(C_6H_3Me_3)]PF_6$ (**1**) (see below). The ^1H NMR spectra of these salts in the region δ 4–7 (Table II and Figure 7) are essentially the same as those of solutions obtained by treatment of Ru(arene)(COT) in $CDCl_3$ with a slight excess of trifluoroacetic acid, either at room temperature or at −70 °C. In acetone, chloroform, or dichloromethane over ca. 6 h at 40–60 °C, the hexamethylbenzene and mesitylene complexes isomerize almost completely to the corresponding 1–3:6-7-η-C_8H_9 salts, which can be isolated in 50–60% yield. The analogous monodeuterio complexes containing 1–5-η-C_8H_8D and 1–3:6-7-η-C_8H_8D are obtained by using CF_3CO_2D in place of CF_3CO_2H. The presence of 1–3:6-7-η-C_8H_9 has also been confirmed by X-ray study of the mesitylene complex $[Ru(1-3:6-7-\eta-C_8H_9)(C_6H_3Me_3)]PF_6$ (**2**) (see below). The *tert*-butylbenzene salts $[Ru(1-5-\eta-C_8H_9)(C_6H_5-t-Bu)]Y$ (Y = PF_6, BF_4) isomerize to an equilibrium mixture of isomers containing ca. 30% of the 1–5-η species which could not be separated by repeated fractional crystallization. Addition of CF_3CO_2H to a solution of $[Ru(1-3:6-7-\eta-C_8H_9)(C_6Me_6)]PF_6$ caused slow

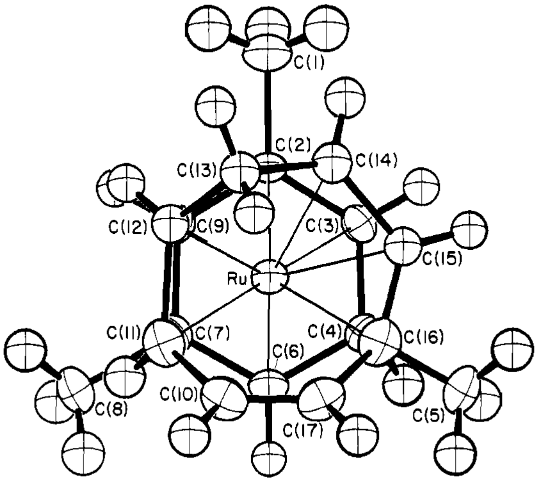

Figure 4. Molecular structure of $[Ru(1-3:6-7-\eta-C_8H_9)(C_6H_3Me_3)]^+$ (**2**). Hydrogen atom numbering follows that of the attached carbon atoms.

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(15) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502–510.

(16) Greco, A.; Carbonaro, A.; Cambisi, F.; Dall'Asta, G. *Chim. Ind.* (*Milan*) **1970**, *52*, 877–880.

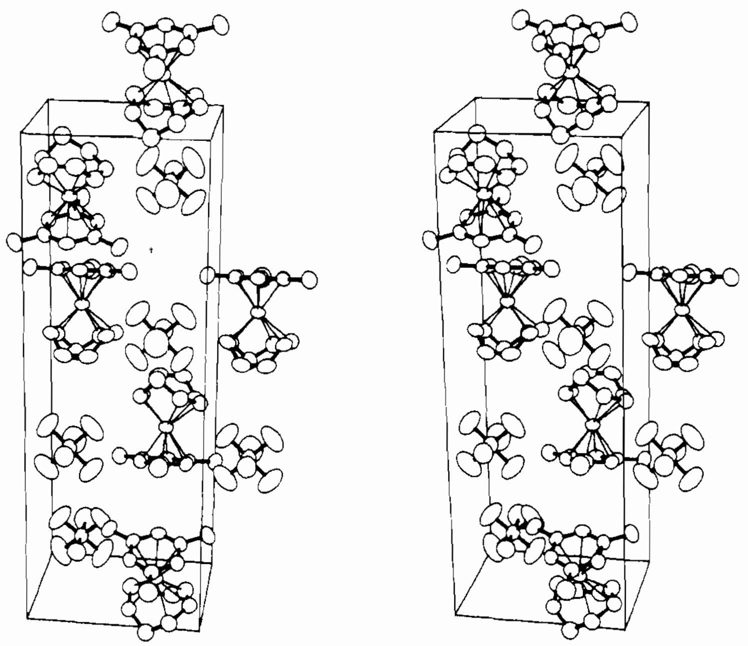

Figure 5. Packing diagram for $[Ru(1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)(C_6H_3Me_3)]PF_6$ (**2**).

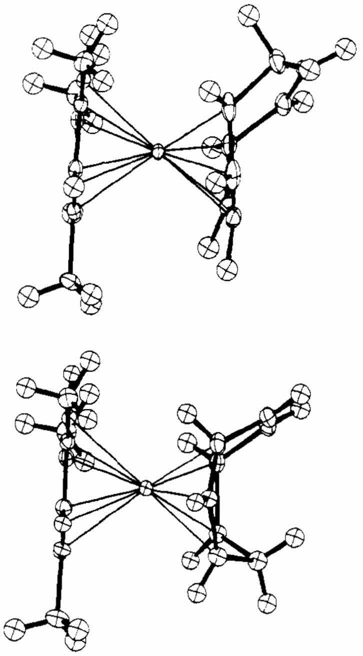

Figure 6. Comparison of $1\text{-}5\text{-}\eta\text{-}C_8H_9$ (**1**) and $1\text{-}3{:}6\text{-}7\text{-}\eta\text{-}C_8H_9$ (**2**) structures.

reversal of the initial isomerization to give an equilibrium mixture containing ca. 20–30% of the $1\text{-}5\text{-}\eta\text{-}C_8H_9$ isomer.

Although the benzene complex $Ru(C_6H_6)(COT)$ is rapidly decomposed by trifluoroacetic acid, the salt $[Ru(C_8H_9)(C_6H_6)]PF_6$ is precipitated when 60% aqueous HPF_6 is added dropwise to $Ru(C_6H_6)(COT)$ in ether. Its ^1H NMR spectrum could not be recorded owing to rapid decomposition in solution, so the mode of binding of C_8H_9 in this case is unknown.

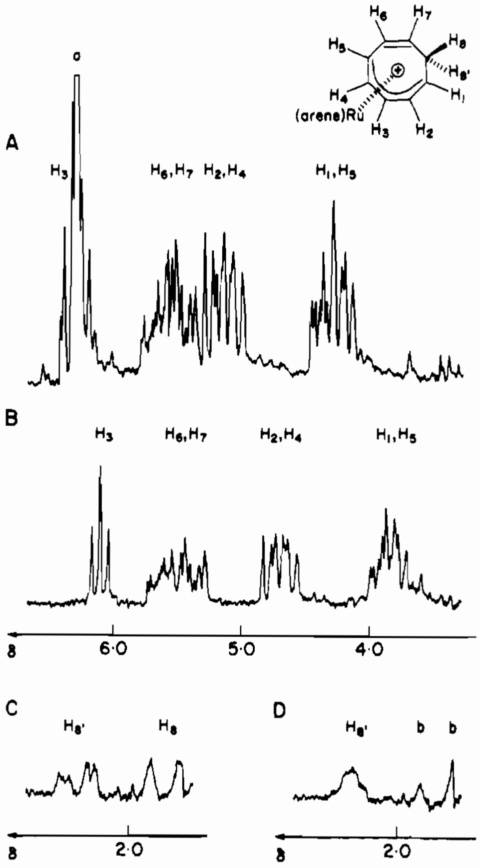

Figure 7. ^1H NMR spectra of $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(arene)]^+$. A: arene = $C_6H_3Me_3$, in acetone-d_6; methyl and methylene regions are not shown. Signal labeled "a" is due to aromatic protons of mesitylene. B: arene = C_6Me_6, in acetone-d_6; methyl and methylene regions are not shown. C: arene, $C_6H_5\text{-}t\text{-}Bu$, in $CDCl_3/CF_3CO_2H$, showing methylene resonance of $1\text{-}5\text{-}\eta\text{-}C_8H_9$. D: arene = $C_6H_5\text{-}t\text{-}Bu$, in $CDCl_3/CF_3CO_2D$, in methylene region; signals labeled "b" result from incomplete deuteration and correspond to much less than one proton.

NMR Spectra. The ^1H NMR spectra of $[Ru(arene)(1\text{-}5\text{-}\eta\text{-}C_8H_9)]^+$ (arene = C_6Me_6, $C_6H_3Me_3$, $C_6H_5\text{-}t\text{-}Bu$) are summarized in Table II, and some representative spectra are shown in Figure 7, together with the atom labeling. Resonances have been assigned by proton-decoupling experiments and by comparison with the spectra of related cyclic 1-5-η-pentadienyl complexes, e.g., $[Fe(1\text{-}5\text{-}\eta\text{-}C_8H_9)(CO)_3]^+$,[1] $Fe(C_5H_5)(1\text{-}5\text{-}\eta\text{-}C_8H_9)$,[16] $[Fe(1\text{-}5\text{-}\eta\text{-}C_8H_8CPh_3)(CO)_3]^+$,[17] $[Fe(1\text{-}5\text{-}\eta\text{-}C_8H_{11})(CO)_3]^+$,[18] $M(1\text{-}5\text{-}\eta\text{-}C_7H_7)(1\text{-}5\text{-}\eta\text{-}C_7H_9)$ (M = Fe, Ru),[19,20] $Mn(1\text{-}5\text{-}\eta\text{-}C_7H_9)(CO)_3$,[21] and $[Fe(1\text{-}5\text{-}\eta\text{-}C_7H_9)$-

Table VII

(a) Atom Coordinates and Isotropic Thermal Parameters for the 1-5-η-C_8H_9 Isomer (1)

ATOM	X/A	Y/B	Z/C	B(A**2)
RU	0.12483(1)	0.09961(3)	0.08010(2)	•
C(1)	0.0907(2)	0.3496(5)	0.0486(3)	•
C(2)	0.1271(3)	0.3872(5)	0.0499(4)	•
C(3)	0.1675(2)	0.3247(7)	0.1187(6)	•
C(4)	0.1802(1)	0.2213(6)	0.2087(4)	•
C(5)	0.1825(2)	0.2808(8)	0.7048(3)	•
C(6)	0.1473(2)	0.3624(6)	0.3020(3)	•
C(7)	0.1088(2)	0.3529(5)	0.2291(4)	•
C(8)	0.0902(1)	0.2702(5)	0.1293(3)	•
C(9)	0.0847(1)	-0.1531(4)	0.0497(3)	•
C(10)	0.1276(1)	-0.1930(4)	0.1200(2)	•
C(11)	0.1591(1)	-0.1632(4)	0.0967(2)	•
C(12)	0.1476(1)	-0.0860(4)	0.0037(3)	•
C(13)	0.1053(1)	-0.0341(4)	-0.0659(2)	•
C(14)	0.0745(1)	-0.0711(4)	-0.0410(2)	•
C(15)	0.0510(1)	-0.1978(6)	0.0720(3)	•
C(16)	0.2041(1)	-0.2139(5)	0.1696(3)	•
C(17)	0.0938(2)	0.0559(6)	-0.1637(3)	•
P(1)	0.25	0.25	0.0	•
P(2)	0.0	0.46811(25)	0.25	•
F(11)	0.2973(1)	0.2740(5)	0.0852(2)	•
F(12)	0.2427(1)	0.1269(4)	0.0721(3)	•
F(13)	0.2364(1)	0.4229(4)	0.0354(3)	•
F(21)	0.0494(1)	0.4693(5)	0.3237(2)	•
F(22)	0.0056(3)	0.3148(17)	0.1879(8)	•
F(23)	0.0060(4)	0.6177(18)	0.1902(9)	•
F(24)	0.0036(3)	0.4758(26)	0.1547(7)	•
F(25)	0.0	0.2668(17)	0.25	•
F(26)	0.0	0.6768(23)	0.25	•
H(1)	0.057(1)	0.360(5)	-0.030(3)	7.0
H(2)	0.129(1)	0.442(5)	-0.022(3)	7.0
H(51)	0.206(1)	0.377(5)	0.325(3)	7.0
H(52)	0.192(1)	0.143(6)	0.346(3)	7.0
H(6)	0.154(1)	0.436(5)	0.362(3)	7.0
H(7)	0.091(1)	0.399(5)	0.241(3)	7.0
H(8)	0.064(1)	0.229(5)	0.106(3)	7.0
H(151)	0.04	-0.320	0.050	7.0
H(152)	0.061	-0.192	0.143	7.0
H(153)	0.027	-0.115	0.038	7.0
H(10)	0.136	-0.238	0.186	7.0
H(161)	0.21	-0.338	0.159	7.0
H(162)	0.224	-0.137	0.164	7.0
H(163)	0.211	-0.207	0.238	7.0
H(12)	0.169	-0.064	-0.013	7.0
H(171)	0.086	-0.030	-0.216	7.0
H(172)	0.07	0.138	-0.185	7.0
H(173)	0.117	0.128	-0.157	7.0
H(14)	0.046	-0.038	-0.088	7.0
H(4)	0.2 5	0.15	0.723	7.0
H(3)	0.195	0.295	0.1 5	7.0

(b) Atom Coordinates and Isotropic Thermal Parameters for the 1-3:6-7-η-C_8H_9 Isomer (2)

ATOM	X/A	Y/B	Z/C	B(A**2)
RU	0.0547(1)	0.25	0.1199(1)	•
C(1)	0.4717(13)	0.25	0.1539(4)	•
C(2)	0.2899(10)	0.25	0.1693(3)	•
C(3)	0.2002(7)	0.1171(7)	0.1781(2)	•
C(4)	0.0275(7)	0.1141(7)	0.1936(2)	•
C(5)	-0.0615(9)	-0.0316(8)	0.2031(2)	•
C(6)	-0.0563(11)	0.25	0.2010(3)	•
C(7)	0.0275(7)	0.3859(7)	0.1936(2)	•
C(8)	-0.0615(9)	0.5316(8)	0.2031(2)	•
C(9)	0.2002(7)	0.3829(7)	0.1781(2)	•
C(10)	-0.2301(8)	0.1790(8)	0.0412(2)	•
C(11)	-0.1040(9)	0.0931(8)	0.0726(2)	•
C(16)	-0.1040(9)	0.4069(8)	0.0726(2)	•
C(17)	-0.2301(8)	0.3210(8)	0.0412(2)	•
P(1)	-0.0017(3)	0.75	0.3811(1)	•
F(1)	0.0219(6)	0.6240(7)	0.3396(2)	•
F(2)	0.0219(6)	0.8760(7)	0.3396(2)	•
F(3)	-0.0249(8)	0.6252(6)	0.4217(2)	•
F(4)	-0.0249(8)	0.8748(6)	0.4217(2)	•
F(5)	0.1987(8)	0.75	0.3884(2)	•
F(6)	-0.2002(9)	0.75	0.3728(3)	•
C(12)	0.083(2)	0.103(2)	0.052(1)	4.8(3)
C(12')	0.083(2)	0.397(2)	0.052(1)	4.8(3)
C(13)	0.132(2)	0.204(1)	0.010(1)	6.0(3)
C(13')	0.132(2)	0.296(1)	0.010(1)	6.0(3)
C(14)	0.178(2)	0.339(2)	0.042(1)	5.7(3)
C(14')	0.178(2)	0.161(2)	0.042(1)	5.7(3)
C(15)	0.052(2)	0.444(2)	0.064(1)	5.0(3)
C(15')	0.052(2)	0.056(2)	0.064(1)	5.0(3)
H(3)	0.258	0.025	0.173	4.4
H(6)	-0.173	0.25	0.211	4.2
H(9)	0.258	0.475	0.173	4.4
H(10)	-0.312	0.127	0.021	6.2
H(11)	-0.134	0.037	0.103	5.9
H(11')	-0.134	0.463	0.103	5.9
H(12)	0.168	0.040	0.067	4.8
H(12')	0.168	0.460	0.067	4.8
H(131)	0.227	0.169	-0.009	5.9
H(131')	0.227	0.331	-0.009	5.9
H(132)	0.040	0.223	-0.013	5.9
H(132')	0.040	0.277	-0.013	5.9
H(14)	0.294	0.359	0.047	5.6
H(14')	0.294	0.141	0.047	5.6
H(15)	0.088	0.541	0.073	4.8
H(15')	0.088	-0.041	0.073	4.8
H(16)	-0.147	0.442	0.105	5.9
H(16')	-0.147	0.058	0.105	5.9
H(17)	-0.312	0.373	0.021	6.2
H(101)	0.541	0.25	0.185	7.0
H(102)	0.496	0.163	0.134	7.0
H(103)	0.496	0.337	0.134	7.0
H(501)	-0.179	-0.021	0.195	6.1
H(502)	-0.013	-0.106	0.181	6.1
H(503)	-0.048	-0.060	0.239	6.1
H(801)	-0.179	0.521	0.195	6.1
H(802)	-0.048	0.560	0.239	6.1
H(803)	-0.013	0.606	0.181	6.1

$(CO)_3]^+$.[22,23] Thus the triplet at lowest field is assigned to the central allylic proton H(3), which is coupled to the two-proton multiplet at δ ca. 4.7 (H(2), H(4)). The multiplet at δ ca. 5.5 is therefore assigned to the protons (H(6), H(7)) on the uncoordinated double bond and the resonance at δ ca. 4.0 to the outer dienyl protons H(1), H(5). The methylene proton signals are partially obscured by the arene methyl resonances in the mesitylene and hexamethylbenzene complexes, but in the *tert*-butylbenzene complex they appear as an AB quartet (with small superimposed couplings), so the chemical shifts of the obscured resonances in $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(arene)]^+$ (arene = C_6Me_6, $C_6H_3Me_3$) can be calculated. A similar AB pattern is observed for the methylene protons in $Fe(C_5H_5)$-$(1\text{-}5\eta\text{-}C_8H_9)$,[16] whereas in $[Fe(1\text{-}5\text{-}\eta\text{-}C_8H_9)(CO)_3]^{+}$[1] and its

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derivatives,[17] the chemical shifts of the exo- and endo-CH_2 protons are almost the same. In the ^1H NMR spectra of the monodeuterio complexes, the highest field CH_2 resonance (δ ca. 1.70) disappears and, in the case of the *tert*-butylbenzene complex, the remaining half of the AB quartet at lower field becomes a single broad peak (Figure 7). In the case of exo- and endo-substituted cycloheptatriene chromium tricarbonyls, it has been shown[24] that the exo-methylene proton resonance occurs at higher field than that of the endo proton. Assuming the same to be true in the present instances, the experiment with CF_3CO_2D establishes that protonation must occur exo with respect to the metal, as is also the case for $Rh(C_5Me_5)(1-4-\eta\text{-COT})$,[5] $Fe(CO)_3(1-4-\eta\text{-COT})$,[1,7,25] $Ru(CO)_3(1-4-\eta\text{-COT})$,[3] and $Fe(CO)_3(1-4-\eta\text{-}C_7H_8)$ (C_7H_8 = cycloheptatriene).[22,23] It should be noted that in bicyclo[5.1.0]octadienyl complexes (II)[5,7] and in the 1–7-η-cyclooctatrienyl complexes (VI),[8] the exo-methylene protons resonate at lower field than the endo, and in 1–3-η-C_8H_9 complexes, conflicting assignments have been given.[4,26,27]

^{13}C NMR data for the $[Ru(1-5-\eta\text{-}C_8H_9)(\text{arene})]^+$ complexes are given in Table III. Assignments have been made by analogy with those given for $[Fe(1-5-\eta\text{-}C_8H_9)(CO)_3]^+$[28] and its triphenylmethyl derivatives.[17] The two signals at lowest field are due to carbon atoms C(6), C(7) of the uncoordinated double bond, and the signal at δ ca. 25, which is a triplet in the ^1H-coupled spectrum, is readily assigned to the methylene carbon atom C(8). The remaining five signals are upfield from the normal olefinic region and arise from the dienyl carbon atoms. The two most shielded signals are assigned to the terminal carbon atoms C(1), C(5), the next pair to the inner carbon atoms C(2), C(4), and the resonance at lowest field to the central carbon atom C(3). This ordering is not general for 1-5η-dienyl complexes, and examples are known where the central carbon atom of a coordinated dienyl fragment appears at higher field than some of the other carbon atoms e.g. $[Fe(1-5-\eta\text{-}C_6H_7)(CO)_3]^+$.[29–31] This difference may be related to the differing pattern of metal–carbon bond lengths observed in our 1–5-η-C_8H_9 complexes compared with those in typical 1–5-η-cyclohexadienyl compelxes (see below). The methylene carbon resonance is not observed in the spectra of the monodeuterated cations $[Ru(1-5-\eta\text{-}C_8H_8D)(\text{arene})]^+$, confirming that a >CHD group has been generated.

The ^1H NMR spectra of $[Ru(1-3:6-7-\eta\text{-}C_8H_9)(\text{arene})]^+$ (arene = C_6Me_6, $C_6H_3Me_3$) are listed in Table IV and shown in Figure 8. Assignments have been made with the aid of proton-decoupling experiments. In the hexamethylbenzene complex, the lowest field signal at δ 5.31, which corresponds to two protons, is assigned to protons H(4), H(5) on the uncoordinated double bond. This resonance is coupled (J = 1.0, 1.5 Hz, respectively) to the doublets at δ 4.42 and 4.14 which correspond to H(3) and H(6). We suggest that the lower field doublet be assigned to H(3) since H(3) is likely to be more affected by the positive charge than H(6). H(3) is coupled to H(2) (J = 7 Hz), which appears as a triplet at δ 3.34 overlapping with another multiplet (see below), and H(6) is coupled (J = 7 Hz) with H(7) at δ 2.93. The highest field multiplet at δ 2.62 is absent from the spectrum of the monodeuterio complex and is assigned to the exo-methylene protons H(8), as in most earlier work[5,7] (see, however, ref 32). The overlapping multiplet at δ 3.34 loses some of its couplings and becomes broadened in the spectrum of the monodeuterio complex and is assigned to the endo-methylene proton H(8′), while the remaining multiplet at δ 3.78 is assigned to H(1). The resonances due to H(1) and H(7) also show changes in pattern in the spectrum of $[Ru(1-3:6-7-\eta\text{-}C_8H_8D)(C_6Me_6)]^+$, which confirms their assignment to protons adjacent to the methylene protons. The ^1H NMR spectrum of the mesitylene complex $[Ru(1-3:6-7-\eta\text{-}C_8H_9)(C_6H_3Me_3)]^+$ is apparently simpler than that of the analogous hexamethylbenzene complex, largely as a consequence of downfield shifts of the resonances due to H(1), H(2), H(6), and H(7), leading to fortuitous overlap of the following pairs of signals: H(3)/H(6), H(1)/H(2), and H(7)/H(8′). Not surprisingly, these bear little resemblance to those reported for other complexes containing 1–3:6-7-η-C_8H_9, e.g., $[Ru(C_8H_9)(CO)_3]^+$,[3] $[M(C_5H_5)(C_8H_9)]^+$,[7] $[M(C_5Me_5)(C_8H_9)]^+$ (M = Rh, Ir),[5] and $Co(C_8H_9)(1-4-\eta\text{-COT})$,[32] and the structure certainly could not have been deduced solely on the basis of NMR spectroscopy. The ^1H NMR spectrum of the isomer formed incompletely from $[Ru(C_6H_5\text{-}t\text{-}Bu)(1-5-\eta\text{-}C_8H_9)]^+$ differs from those of the C_6Me_6 and 1,3,5-$C_6H_3Me_3$ complexes and has not yet been analyzed successfully; X-ray structural analysis of the product is in progress.

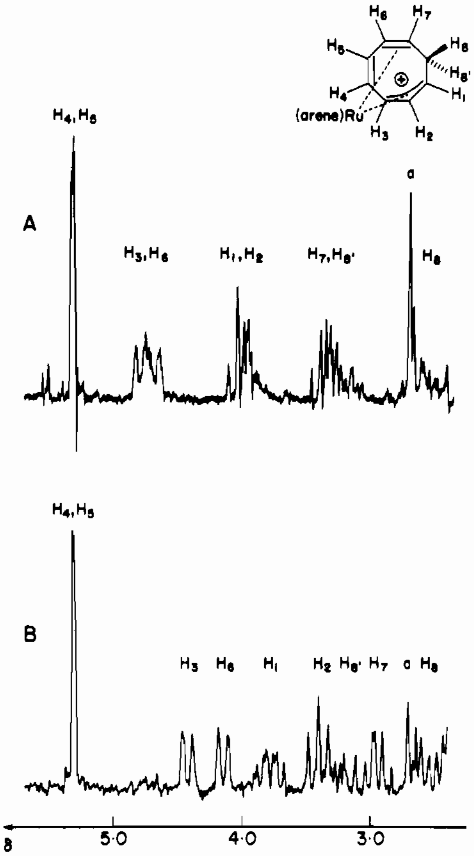

Figure 8. ^1H NMR spectra of $[Ru(1-3:6-7-\eta\text{-}C_8H_9)(\text{arene})]^+$ (arene = $C_6H_3Me_3$ (A), C_6Me_6 (B)] in acetone-d_6. Arene resonances are not shown. Signal labeled "a" is due to impurity.

^{13}C NMR data for the $[Ru(1-3:6-7-\eta\text{-}C_8H_9)(\text{arene})]^+$ complexes are given in Table V, together with those of the

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analogous tricarbonyl, which have not been reported previously. The spectra of the areneruthenium species closely resemble that given for $[Rh(C_5H_5)(1\text{-}3\text{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)]^{+7}$ and have been assigned by analogy. The two signals at lowest field are due to carbon atoms C(4), C(5) of the uncomplexed double bond and the signal at δ ca. 20, which is coupled to two protons, arises from the methylene carbon atom C(8). The last signal is absent from the spectrum of the monodeuterio complex, which is consistent with the assignment. The remaining C_8H_9 resonances are assigned, in order of increasing field, to C(3), C(2), C(6), C(1), and C(7), the central allylic carbon atom being at higher field than one of the outer allylic carbon atoms. Although, as noted earlier, this is not unprecedented, the assignment of C(3) and C(6) must be regarded as tentative. It is worth noting that there is disagreement on the assignment of the ^{13}C NMR spectrum of butadieneiron tricarbonyl in FSO_3H/SO_2, which is considerably simpler than the spectra reported here.[33,34]

Structure of $[Ru(1\text{-}5\text{-}\eta\text{-}C_8H_9)(C_6H_3Me_3)]PF_6$ (1). The geometry of the cation is shown in Figure 2 and compared with that of the 1-3:6-7-η-isomer in Figure 6. The atom labeling used to describe these structures is not the same as that used for the NMR spectra. Bond lengths and angles with standard deviations estimated from the full variance/covariance matrix are listed in Table VIII. The results of some best plane calculations and selected torsion angles are collected in Table IX. The carbon atoms of the C_8H_9 group have markedly anisotropic thermal parameters. The major vibration axes are roughly tangential to the ring (Figure 2), suggesting that the C_8H_9 group librates about an axis perpendicular to the η^5-pentadienyl plane. A simple analysis based on this model, with the axis passing through the metal atom, gives an upper limit of 11.7 (23)° for the root-mean-square amplitude of libration. The resulting increases in Ru–C and C–C bond lengths[35] are at most 0.03 Å, and the bond lengths in Table VIII have not been corrected.

The cation contains η^6-mesitylene and 1-5-η-C_8H_9 attached to a ruthenium atom, the ring carbon atoms being eclipsed. The pentadienyl carbon atoms are only approximately planar (Table IX), the mean plane being inclined at 6.1° to the arene mean plane. Atoms C(8), C(1), C(3), and C(4) form a slightly better plane, C(2) being displaced 0.09 Å from it away from the ruthenium atom, which lies 1.54 Å from the pentadienyl mean plane. The Ru–C(pentadienyl) bond lengths are not equal, the terminal distances [Ru–C(4) 2.175 (4), Ru–C(8) 2.202 (3) Å] and the central distance [Ru–C(2) 2.172 (4) Å] being greater than the other two [Ru–C(1) 2.135 (4), Ru–C(3) 2.144 (4) Å]. Although the longer bonds are to the carbon atoms which eclipse methyl-bearing carbon atoms of the mesitylene ring, this is unlikely to be responsible for the variation in bond lengths because there are no short intramolecular nonbonded contacts between the η^5-pentadienyl carbon (or hydrogen) atoms and the mesitylene methyl groups. A similar trend in M–C distances is evident for the η^5-cycloheptatrienyl ring in the complexes $M(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$ (M = Fe, Ru),[36,37] whereas in η^5-cyclohexadienyl complexes such as $Mn(\eta^5\text{-}C_6H_7)(CO)_3$[38] and *trans*-$Mn_2(CO)_6$(azulene)[39] there is a general tendency for the M–C distances to decrease from the terminal carbon atoms toward the central carbon atom. This difference may be related to greater ring strain in the η^5-C_7H_7 and η^5-C_8H_9 systems. The difference in Ru–C(4) and Ru–C(8) bond lengths may be due to the asymmetry of the 1-5-η-C_8H_9 ligand since there is a small difference between the C(1)–C(8) and C(3)–C(4) torsion angles (Table IX), suggestive of differing interactions of C(4) and C(8) with the metal. However, significantly different Ru–C(terminal) distances [2.219 (5), 2.186 (5) Å] are also observed to the η^5-cycloheptadienyl ligand in $Ru(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$,[37] in which similar asymmetry is absent.

Table VIII. Bond Lengths (Å) and Angles (Deg) with Estimated Standard Deviations (in Parentheses) for the 1-5-η-C_8H_9 Isomer (1)

Ru–C(8)	2.202 (3)	C(7)–C(8)–C(1)	124.5 (4)
Ru–C(1)	2.135 (4)	C(8)–C(1)–C(2)	123.3 (4)
Ru–C(2)	2.172 (4)	C(1)–C(2)–C(3)	127.1 (4)
Ru–C(3)	2.144 (4)	C(2)–C(3)–C(4)	126.6 (4)
Ru–C(4)	2.175 (4)	C(3)–C(4)–C(5)	129.2 (4)
		C(4)–C(5)–C(6)	121.1 (4)
Ru–C(13)	2.227 (3)	C(5)–C(6)–C(7)	125.8 (4)
Ru–C(12)	2.248 (3)	C(6)–C(7)–C(8)	130.8 (4)
Ru–C(11)	2.250 (3)		
Ru–C(10)	2.222 (3)	C(9)–C(10)–C(11)	121.0 (3)
Ru–C(9)	2.266 (3)	C(10)–C(11)–C(12)	119.2 (3)
Ru–C(14)	2.222 (3)	C(11)–C(12)–C(13)	121.2 (3)
		C(12)–C(13)–C(14)	118.0 (3)
C(8)–C(1)	1.399 (6)	C(13)–C(14)–C(9)	122.1 (3)
C(1)–C(2)	1.369 (8)	C(14)–C(9)–C(10)	118.4 (3)
C(2)–C(3)	1.389 (8)		
C(3)–C(4)	1.442 (9)	C(14)–C(9)–C(15)	120.9 (3)
C(4)–C(5)	1.524 (7)	C(10)–C(9)–C(15)	120.7 (3)
C(5)–C(6)	1.417 (6)	C(10)–C(11)–C(16)	120.7 (3)
C(6)–C(7)	1.280 (6)	C(12)–C(11)–C(16)	120.1 (3)
C(7)–C(8)	1.466 (5)	C(12)–C(13)–C(17)	120.6 (4)
		C(14)–C(13)–C(17)	121.4 (3)
C(13)–C(12)	1.415 (5)		
C(12)–C(11)	1.402 (5)	H(1)–C(1)–C(2)	119 (2)
C(11)–C(10)	1.414 (4)	H(1)–C(1)–C(8)	117 (2)
C(10)–C(9)	1.412 (4)	H(2)–C(2)–C(1)	125 (2)
C(9)–C(14)	1.397 (5)	H(2)–C(2)–C(3)	106 (2)
C(14)–C(13)	1.416 (5)	H(3)–C(3)–C(2)	127
		H(3)–C(3)–C(4)	102
C(13)–C(17)	1.507 (5)	H(4)–C(4)–C(3)	107
C(11)–C(16)	1.495 (4)	H(4)–C(4)–C(5)	112
C(9)–C(15)	1.503 (5)	H(51)–C(5)–C(4)	96 (3)
C(6)–H(6)	0.99 (4)	H(51)–C(5)–C(6)	110 (2)
C(7)–H(7)	0.86 (4)	H(52)–C(5)–C(4)	98 (2)
C(8)–H(8)	0.89 (4)	H(52)–C(5)–C(6)	113 (2)
C(1)–H(1)	1.20 (4)	H(6)–C(6)–C(5)	116 (2)
C(2)–H(2)	1.22 (4)	H(6)–C(6)–C(7)	118 (2)
C(3)–H(3)	1.17	H(7)–C(7)–C(6)	115 (2)
C(4)–H(4)	0.98	H(7)–C(7)–C(8)	114 (3)
C(5)–H(51)	1.04 (4)	H(8)–C(8)–C(7)	107 (3)
C(5)–H(52)	1.15 (4)	H(8)–C(8)–C(1)	113 (3)
P(1)–F(11)	1.561 (3)	F(11)–P(1)–F(13)	91.9 (2)
P(1)–F(12)	1.568 (3)	F(11)–P(1)–F(12)	89.6 (2)
P(1)–F(13)	1.575 (3)	F(13)–P(1)–F(12)	90.1 (2)
P(2)–F(21)	1.573 (2)	F(21)–P(2)–F(22)	88.6 (4)
P(2)–F(22)	1.569 (8)	F(21)–P(2)–F(23)	87.5 (5)
P(2)–F(23)	1.532 (9)	F(21)–P(2)–F(24)	92.6 (3)
P(2)–F(24)	1.569 (8)	F(21)–P(2)–F(25)	90.3 (2)
P(2)–F(25)	1.477 (13)	F(21)–P(2)–F(26)	89.7 (2)
P(2)–F(26)	1.530 (17)	F(24)–P(2)–F(25)	92.1 (7)
		F(24)–P(2)–F(26)	87.9 (7)
		F(24)–P(2)–F(22)	91.5 (5)

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Table IX

Mean Planes and Distances (Å) of Atoms from Those Planes for Isomer 1

plane	atoms defining plane	distances (in square brackets)
a	C(9), C(10), C(11), C(12), C(13), C(14)	C(9) [0.02], C(10) [−0.02], C(11) [0.00], C(12) [0.02], C(13) [−0.02], C(14) [0.00], C(15) [0.10], C(16) [0.02], C(17) [−0.06], Ru [−1.74], H(8) [−2.92], H(1) [−2.99], H(2) [−3.39], H(3) [−3.01], H(4) [−2.73], C(8) [−3.27], C(1) [−3.31], C(2) [−3.47], C(3) [−3.36], C(4) [−3.18]
b	C(8), C(1), C(2), C(3), C(4)	C(8) [−0.04], C(1) [0.07], C(2) [−0.04], C(3) [0.00], C(4) [0.02], H(8) [0.30], H(1) [0.46], H(2) [0.16], H(3) [0.39], H(4) [0.46], C(5) [−1.07], C(7) [−1.24]
c	C(8), C(7), C(6), C(5)	C(8) [0.01], C(7) [−0.01], C(6) [0.01], C(5) [−0.01], H(7) [−0.08], H(6) [0.09]
d	C(8), C(1), C(7), H(8)	C(8) [−0.21], C(1) [0.06], C(7) [0.06], H(8) [0.09]
e	C(1), C(8), C(2), H(1)	C(1) [−0.05], C(8) [0.02], C(2) [0.02], H(1) [0.02]
f	C(2), C(1), C(3), H(2)	C(2) [−0.09], C(1) [0.03], C(3) [0.03], H(2) [0.03]
g	C(3), C(2), C(4), H(3)	C(3) [−0.10], C(2) [0.04], C(4) [0.03], H(3) [0.04]
h	C(4), C(3), C(5), H(4)	C(4) [−0.19], C(3) [0.06], C(5) [0.06], H(4) [0.07]

Dihedral Angles between Planes (Deg)

a and b	6.1	b and c	126.3

Torsion Angles (Deg) of the C_8H_9 Ring Bonds

C(8)–C(1)	62.2	C(1)–C(2)	13.4	C(2)–C(3)	−6.4	C(3)–C(4)	−68.4
C(4)–C(5)	52.6	C(5)–C(6)	19.2	C(6)–C(7)	−4.1	C(7)–C(8)	−78.4

Although poorly determined (see above), the pentadienyl hydrogen atoms are all bent toward the ruthenium atom, the distortion being largest for the terminal carbon atoms. Nonhydrogen substituents in η^5-pentadienyl complexes show similar behavior.[40] The distances from the pentadienyl carbon atoms to the arene plane (3.18–3.46 Å) may be short enough to allow some ligand–ligand overlap. Such overlap has been postulated[40] to account for the observed eclipsed configuration of the rings in bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II), in which the iron atom is 1.57 Å from the mean η^5-pentadienyl plane. However, in the [Ru(arene)(1–5-η-C_8H_9)]$^+$ complexes, the relative orientations of the two rings are probably determined largely by crystal packing forces because in [Ru(1–5-η-C_8H_9)(C_6Me_6)]PF_6 (supplementary material) the ring carbon atoms are staggered whereas in the present mesitylene complex they are eclipsed.

The C–C bond lengths in the η^5-pentadienyl unit [1.369 (8)–1.442 (9) Å] and the C(4)–C(5) bond length [1.524 (7) Å] are unexceptional. However, C(6)–C(5) [1.417 (6) Å] is much shorter than the last value, and the discrepancy seems too large to be accounted for solely on the basis of libration effects (see above). The C(6)–C(7) bond length [1.280 (6) Å] is also shorter than expected for a free double bond (cf. 1.335 Å for ethylene),[41] and although the difference here may arise in part from libration error, the shortening is in keeping with the remarkably high C=C stretching frequency (1675 cm^{-1}) observed in the IR spectra of the 1–5-η-C_8H_9 complexes (see Experimental Section). The C(7)–C(8) bond length [1.466 (5) Å] is very close to the C–C single-bond length in cyclooctatetraene (1.478 Å).[42] It is clear from the C(8)–C(7) torsion angle (−78.4°) that there can be no significant interaction of the localized C(6)–C(7) double bond with the η^5-pentadienyl system.

The mesitylene ligand has a twist-boat conformation similar to that observed for coordinated benzene in Ru(C_6H_6)(1,5-COD).[43] Deviations from the mean ring plane are small and follow the twistboat pattern of the six-membered ring. Variations in the Ru–C(arene) distances can be related to the distortion from planarity, as is also the case for Ru(C_6H_6)(1,5-COD).[43] The mean distance from ruthenium to C(10) and C(13), those carbon atoms furthest from the mean ring plane and on the same side as the metal atom, is 2.224 Å, whereas the corresponding mean distance to C(9) and C(12), the carbon atoms furthest from the mean plane on the opposite side to it from the metal atom, is 2.257 Å. The remaining two distances might have been expected to lie between these two values. In fact, one is long [Ru–C(11) 2.250 (3) Å] and the other is short [Ru–C(14) 2.222 (3) Å], reflecting a small displacement of the projection of the ruthenium atom on the mean ring plane from the centroid of the projected C(11)–C(14) vector toward C(14). The perpendicular distance of the metal from the arene mean plane is 1.74 Å, cf. Ru(C_6Me_6)(COT) (1.70 Å),[9] Ru(C_6H_6)(1,5-COD) (1.76 Å),[43] and Ru(η^6-C_6Me_6)(η^4-C_6Me_6) (1.75 Å).[44]

The ring angles at the methyl-substituted carbon atoms are significantly smaller (mean 118.5°) than those at the other three (mean 121.4°). This distortion is unrelated to the nonplanarity of the ring and is also observed in the arene ring of [Ru($C_6H_3Me_3$)(1–3:6-7-η-C_8H_9)]PF_6 (see below). It is probably characteristic of methyl-substituted benzenes since in free 1,2,4,5-tetramethylbenzene the angles at the methyl-substituted carbon atoms are smaller than the other two ring angles.[45]

The crystal packing (Figure 3) shows close contacts between cations related by translation along *y*, the *c* glide, the inversion center at 0, 0, 0, and the 2_1 axis at $^1/_4x$, $^1/_4z$. There are no close contacts between anions. The shorter interatomic distances associated with cation–cation and cation–anion contacts are listed in Supplementary Table III.

Structure of [Ru(1–3:6-7-η-C_8H_9)($C_6H_3Me_3$)]PF_6 (2). The geometry and atom numbering for the cation are shown in Figure 4. Bond lengths and angles with standard deviations estimated from the full variance/covariance matrix are listed in Table X. The results of some best plane calculations and selected torsion angles are collected in Table XI. As noted in the Experimental Section, the anion and cation (except for atoms C(12) through C(15)) are assumed to have exact *m* symmetry, and equivalent quantities are marked as such in Table X.

Within experimental error, bond lengths and angles in the mesitylene ligand in **2** are equal to those in **1**. The difference in Ru–C(3) and Ru–C(4) bond lengths [2.218 (6), 2.246 (5)

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Table X. Bond Lengths (Å) and Angles (Deg) with Estimated Standard Deviations (in Parentheses) for the 1–3:6-7-η-C_8H_9 Isomer **2**

Ru–C(2)	2.231 (8)	C(1)–C(2)–C(3)	121.6 (4)
Ru–C(3)	2.218 (6)	C(1)–C(2)–C(9)	
Ru–C(9)		C(3)–C(2)–C(9)	116.8 (6)
Ru–C(4)	2.246 (5)	C(2)–C(3)–C(4)	122.7 (6)
Ru–C(7)		C(2)–C(9)–C(7)	
Ru–C(6)	2.235 (7)	C(3)–C(4)–C(6)	118.1 (6)
Ru–C(11)	2.233 (6)	C(9)–C(7)–C(6)	
Ru–C(16)		C(3)–C(4)–C(5)	120.4 (6)
Ru–C(12)	2.192 (15)	C(9)–C(7)–C(8)	
Ru–C(14)	2.345 (14)	C(6)–C(4)–C(5)	121.5 (6)
Ru–C(15)	2.244 (15)	C(6)–C(7)–C(8)	
C(1)–C(2)	1.48 (1)	C(4)–C(6)–C(7)	121.7 (7)
C(4)–C(5)	1.51 (1)	C(10)–C(11)–C(12)	114.4 (7)
C(7)–C(8)		C(11)–C(12)–C(13)	122.1 (12)
C(2)–C(3)	1.41 (1)	C(12)–C(13)–C(14)	101.1 (11)
C(2)–C(9)		C(13)–C(14)–C(15)	124.3 (13)
C(3)–C(4)	1.41 (1)	C(14)–C(15)–C(16)	122.0 (13)
C(9)–C(7)		C(15)–C(16)–C(17)	133.0 (8)
C(4)–C(6)	1.40 (1)	C(16)–C(17)–C(10)	121.4 (6)
C(7)–C(6)		C(17)–C(10)–C(11)	
C(10)–C(17)	1.28 (1)	F(1)–P(1)–F(2)	93.4 (3)
C(10)–C(11)	1.49 (1)	F(3)–P(1)–F(4)	94.2 (3)
C(16)–C(17)		F(1)–P(1)–F(3)	86.2 (3)
C(11)–C(12)	1.56 (2)	F(2)–P(1)–F(4)	
C(12)–C(13)	1.44 (2)	F(1)–P(1)–F(6)	91.5 (3)
C(13)–C(14)	1.50 (2)	F(2)–P(1)–F(6)	
C(14)–C(15)	1.48 (2)	F(3)–P(1)–F(6)	88.5 (3)
C(15)–C(16)	1.29 (2)	F(4)–P(1)–F(6)	
P(1)–F(1)	1.560 (6)	F(1)–P(1)–F(5)	87.8 (3)
P(1)–F(2)		F(2)–P(1)–F(5)	
P(1)–F(3)	1.535 (6)	F(3)–P(1)–F(5)	92.3 (3)
P(1)–F(4)		F(4)–P(1)–F(5)	
P(1)–F(5)	1.582 (6)		
P(1)–F(6)	1.571 (7)		

Table XI

Mean Planes and Distances (Å) of Atoms from Those Planes for Isomer **2**

plane	atoms defining plane	distances (in square brackets)
a	C(1) through C(9)	C(1) [−0.02], C(2) [+0.01], C(3) [0.00], C(4) [0.01], C(5) [−0.02], C(6) [0.02], C(7) [0.01], C(8) [−0.02], C(9) [0.00], Ru [1.74], C(11) [3.25], C(12) [3.34], C(14) [3.36], C(15) [3.09], C(16) [3.25]
b	C(10), C(11), C(17), C(16)	C(10) [0.00], C(11) [0.00], C(17) [0.00], C(16) [0.00]
c	C(10), C(11), C(12), C(13)	C(10) [0.01], C(11) [−0.01], C(12) [0.07], C(13) [−0.03], Ru [−2.01]
d	C(14), C(15), C(16)	C(14) [0.00], C(15) [0.00], C(16) [0.00], Ru [−1.84], C(13) [0.44], C(17) [0.73]
e	C(11), C(12), C(14), C(15), C(16)	C(11) [−0.01], C(12) [0.03], C(14) [0.00], C(15) [−0.16], C(16) [0.03], Ru [−1.52], C(10) [1.07], C(13) [0.91], C(17) [1.08]

Dihedral Angles between Planes (Deg)

a and e	2.0	b and c	65.9
c and d	68.6	b and d	55.5

Table XII. Cell Constants for $[Ru(C_8H_9)(C_6Me_6)]Y$ (Y = PF_6, BF_4)

empirical formula	$C_{20}H_{27}F_6PRu$		$C_{20}H_{27}F_4BRu$	
anion	PF_6		BF_4	
isomer	1–5-η[a]	1–3:6-7-η[b]	1–5-η[b,c]	1–3:6-7-η[a,b]
recrystallizn solvent	CH_2Cl_2/C_6H_6	*sec*-butyl alcohol/pentane	CH_2Cl_2/ether	$CHCl_3$/ethanol
a, Å	19.70 (3)[d]	15.89 (1)[d]	16.668 (9)[e]	20.34 (3)[d]
b, Å	16.77 (3)	8.67 (1)	16.626 (7)	7.83 (2)
c, Å	7.88 (2)	15.53 (1)	14.716 (9)	11.97 (2)
α, deg	90	90	90	90
β, deg	99.3 (5)	90	104.31 (3)	90
γ, deg	90	90	90	90
V, $Å^3$	2571	2140	3951.6	1906
Z	*f*	4	8	4
space group	$P2_1/n$	$Pna\left\{\begin{matrix}2_1\\m\end{matrix}\right.$	$C2/c$ or Cc	$Pna\left\{\begin{matrix}2_1\\m\end{matrix}\right.$

[a] Only poor quality single crystals could be obtained. [b] Rapid fadeoff of intensity for reflections with 2θ > ca. 35° (Mo Kα). [c] Intensity data were measured, and the structure was solved. Refinement was unsatisfactory (final *R* = 0.085). Very large thermal motion is apparent. Details of the structural analysis are included in the supplementary material but are not discussed further. [d] From uncalibrated precession and Weissenberg photographs recorded with use of Mo $Kα_1$ and Cu Kα radiation, respectively. [e] From a least-squares fit to the four angles optimized for each of the 12 high-angle reflections (2θ > 29°) on a Picker FACS-I diffractometer using Mo $Kα_1$ radiation. [f] The cell volume in relation to the 1–3:6-7-η isomer suggests four molecules per unit cell, probably with solvent molecules (benzene) in the crystal lattice.

Å, respectively] is probably not significant, and the mean Ru–C(arene) distances in **1** and **2** (2.239, 2.232 Å, respectively) and the perpendicular metal–arene distances (1.74, 1.74 Å, respectively) do not differ significantly. The conformation of the eight-membered ring and the metal–carbon distances to the ring are consistent only with 1–3:6-7-η bonding, not with the alternative 1–4:7-η mode, i.e., IV rather than III in Figure 1. Detailed comparison with the structures of the related 1–3:6-7-η-cyclooctadienyl complexes $Ru(\eta^6\text{-}C_6H_5BR_3)(C_8H_{11})$ (R = Ph, F)[46] and $[IrCl(C_8H_{11})(C(CF_3){=}CH(CF_3))]_2$[47] is not possible owing to the fairly high standard deviations, but equivalent quantities for comparable parts of the eight-membered rings are generally fairly similar. The Ru–C(11) and Ru–C(12) distances do not differ significantly, the mean value [2.212 (16) Å] being comparable with the mean Ru–C(olefin) distance of 2.181 Å observed in octahedral ruthenium(II) complexes of the general type $RuCl_2$ (diene)(amine)$_2$ (diene = NBD, amine = aniline[48] or piperidine;[49] diene = 1,5-COD, amine = hexylamine[49]) and with the corresponding distance of 2.17 Å in $Ru(\eta^6\text{-}C_6H_5BPh_3)(C_8H_{11})$.[46] The esd of the bond length of the coordinated olefin [C(11)–C(12) 1.55 Å] is almost certainly underestimated owing to the assumption that C(11) and C(16) are related by a mirror plane. In the η^3-allyl moiety, one of the Ru–C(terminal) distances [Ru–C(14) 2.345 (14) Å] is longer by about 0.1 Å than both the Ru–C(15) (central) distance [2.244 (15) Å] and Ru–C(16)(terminal) distance [2.233 (6) Å], which do not differ significantly from each other. Differences of a similar order of magnitude have been observed in the structures of $Ru(\eta^3\text{-2-methylallyl})_2[P(OMe)_3]_2$[50] and $Ru_2(CO)_5$(6,6-diphenylpentafulvene),[51] but in the presence case there is no obvious reason for the asymmetry (e.g., different substituents or trans ligands). Marked asymmetry is also apparent in the Ru–C distances of the η^3-allyl moieties of $Ru(\eta^6\text{-}C_6H_5BR_3)(C_8H_{11})$ (R = Ph, F).[46] Because the esd of the C(16)–C(15) bond length [1.29 (2) Å] is probably underestimated, we cannot say whether it is significantly less than the C(15)–C(14) bond length [1.48 (2)

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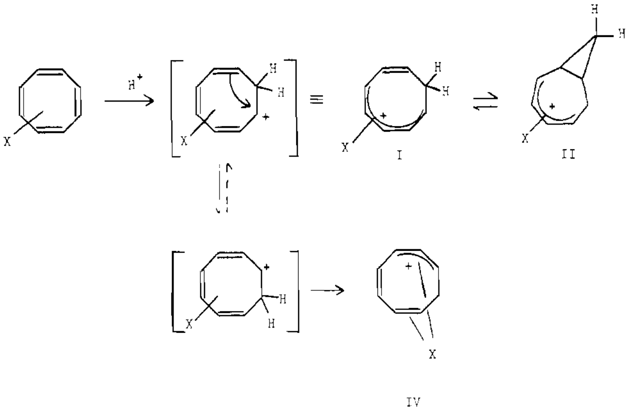

Figure 9. Protonation of 1-4-η-COT metal complexes [X = Fe(CO)$_3$, Ru(CO)$_3$, Rh(C$_5$Me$_5$), Ru(arene)].

Å]. Similarly the esd's of the interbond angles involving C(11) and C(16) are likely to be underestimated. Other bond lengths and angles in the eight-membered ring are unexceptional. In general, ring angles in **2** show much smaller deviations from ideal values than those in **1**, indicative of greater strain in 1–5-η-C$_8$H$_9$ relative to 1–3:6-7-η-C$_8$H$_9$. This is clearly because the latter can be bent easily in two places [about the C(14)–C(12) and C(11)–C(16) vectors], whereas the former can only be bent easily about the C(8)–C(4) vector.

Conclusions

The behavior of Ru(arene)(1–4-η-COT) on protonation provides an interesting comparison with that of other d^8 1–4-η-COT complexes, in particular, M(CO)$_3$(1–4-η-COT) (M = Fe,[1,2], Ru[3]) and Rh(C$_5$Me$_5$)(1–4-η-COT).[5] A general scheme is shown in Figure 9. In all cases studied, the proton appears to add at one of the uncoordinated double bonds from the site opposite the metal, this exo approach being the least sterically hindered. The resulting 1–5-η-C$_8$H$_9$ cation I appears to be thermodynamically the least stable of the various possibilities and can undergo two potentially competing transformations: ring closure to give the 2–6-η-bicyclo[5.1.0]octadienyl cation II or 1,2-hydride shift accompanied by partial decomplexation of the metal leading to the 1–3:6-7-η-cation IV. In the case of Fe(CO)$_3$(1–4-η-COT) the first alternative prevails,[1] whereas in the case of Ru(arene)(1–4-η-COT) only the second pathway is observed. The two alternatives must compete in the protonation of Rh(C$_5$Me$_5$)(1–4-η-COT) since both II and IV are observed at low temperature.[5] Although isomer I has not been detected in this case, its presence in equilibrium with IV is required to account for the isomerization of II to IV as the temperature is increased. The arene–ruthenium system thus seems to be unique in that ring closure does not effectively compete with isomerization from I to IV, though the tricarbonyl ruthenium system may be similar. A low-temperature study of the protonation of Ru(CO)$_3$(1–4-η-COT) analogous to that carried out on Fe(CO)$_3$(1-4-η-COT)[1] might be informative.

The fact that [Ru(1–3:6-7-η-C$_8$H$_9$)(C$_6$Me$_6$)]$^+$ partly reverts to the 1–5-η-C$_8$H$_9$ isomer in the presence of acid indicates that the energy difference between the isomers must be small, although it is not clear why protons should affect the position of equilibrium. The crystal structures suggest that relief of strain in the eight-membered ring may be an important factor favoring 1–3:6-7-η-coordination, although it is clearly insufficient to disfavor η^5-pentadienyl bonding in the iron tricarbonyl system. This can probably be correlated with two other general observations: (1) the Fe(CO)$_3$ group shows a remarkable preference for binding to conjugated rather than unconjugated dienes;[52,53] (2) σ-alkyl and η^2-olefin complexes of 4d- and 5d transition elements are generally more stable than their counterparts in the 3d series.

Registry No. **1**, 77357-70-1; **2**, 77357-72-3; [Ru(1-5-η-C$_8$H$_9$)(C$_6$Me$_6$)]PF$_6$, 77400-18-1; [Ru(1-5-η-C$_8$H$_9$)(C$_6$Me$_6$)]BF$_4$, 77400-19-2; [Ru(1-3:6-7-η-C$_8$H$_9$)(C$_6$Me$_6$)]PF$_6$, 77357-74-5; [Ru(1-5-η-C$_8$H$_9$)(C$_6$H$_5$-*t*-Bu)]PF$_6$, 77357-76-7; [Ru(1-5-η-C$_8$H$_9$)(C$_6$H$_5$-*t*-Bu)]BF$_4$, 77357-77-8; [Ru(1-5-η-C$_8$H$_9$)(C$_6$H$_6$)]PF$_6$, 77357-79-0; [Ru(1-3:6-7-η-C$_8$H$_9$)(C$_6$H$_5$-*t*-Bu)]PF$_6$, 77357-81-4; [Ru(1-3:6-7-η-C$_8$H$_9$)(C$_6$H$_5$-*t*-Bu)]BF$_4$, 77357-82-5; [Ru(1-3:6-7-η-C$_8$H$_9$)(CO)$_3$]PF$_6$, 33306-40-0; [Ru(1-3:6-7-η-C$_8$H$_9$)(CO)$_3$]BF$_4$, 33306-42-2; Ru(C$_6$Me$_6$)(COT), 62422-36-0; Ru(1,3,5-C$_6$H$_3$Me$_3$)(COT), 62422-35-9; Ru(C$_6$H$_6$)(COT), 62422-38-4; Ru(C$_6$H$_5$-*t*-Bu)(COT), 72765-32-3; Ru(COT)(CO)$_3$, 142282-26-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, interionic contacts, observed and calculated structure amplitudes, atom coordinates, thermal parameters, refinement details, and bond lengths and angles and a figure showing the structure of [Ru(1-5-η-C$_8$H$_9$)(C$_6$Me$_6$)]BF$_4$ (28 pages). Ordering information is given on any current masthead page.

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