Synthesis of and Stereospecific Hydride Migration in Cationic (Tricyclic arene)(cyclooctadiene)ruthenium(II) Complexes

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The (tricyclic arene)ruthenium(0) complex [Ru(η^4-1,5-COD)(η^6-phenanthrene)] (**4**) (COD = cyclooctadiene) is prepared by reduction of [Ru(acac)$_2$(η^4-1,5-COD)] (**3**) (acac = acetylacetonato) with sodium phenanthrene in 15% yield. Similar treatment of **3** with sodium anthracene gives a mixture of [Ru(η^4-1,5-COD)(η^6-anthracene)] (**6**) and [Ru(η^4-1,5-COD)(η^6-9,10-dihydroanthracene)] (**7**) in 3:1 molar ratio, from which only **7** can be isolated in a pure state. Protonation of **4** by HPF_6 yields the cationic hydridoruthenium(II) complex [RuH(η^4-1,5-COD)(η^6-phenanthrene)]PF_6, [**5**]PF_6, in 53% yield, whereas similar protonation of **7** gives an equilibrium mixture of a hydrido diene complex [RuH(η^4-1,5-COD)(η^6-9,10-dihydroanthracene)]PF_6, [**8**]PF_6, and an agostic cyclooctenyl complex [Ru(η^1,η^3-C_8H_{13})(η^6-9,10-dihydroanthracene)]PF_6, [**9**]PF_6, in 4:1 molar ratio at 295 K in CD_2Cl_2, in which the *endo*-methylene protons of the COD ligand and the agostic hydride in [**9**]PF_6 exchange rapidly on the NMR time scale, even at 193 K. Thermodynamic parameters for the equilibrium between [**8**]PF_6 and [**9**]PF_6 in acetone-d_6 have been derived from variable-temperature NMR experiments; $\Delta H° = -12 \pm 1$ kJ mol^{-1}, $\Delta G° = 1 \pm 2$ kJ mol^{-1}, and $\Delta S° = -44 \pm 4$ J K^{-1} mol^{-1}. The large negative entropy is consistent with the agostic formulation. As expected, the η^3-cyclooctenyl complex can be trapped as [Ru(1−3-η^3-C_8H_{13})(η^6-9,10-dihydroanthracene)(CO)]PF_6, [**10**]PF_6, in 80% yield on exposure of the equilibrium mixture of [**8**]PF_6 and [**9**]PF_6 to an atmosphere of CO. Addition of D_2O to the equilibrium mixture leads to selective facile deuteration of the hydride and *endo*-methylene protons of the 1,5-COD and cyclooctenyl ligands. Such *endo*-selective H/D exchange reaction is also observed for [**5**]PF_6.

Introduction

The zerovalent ruthenium complex [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)] (**1**)[1] has been widely used as a labile precursor for organometallic synthesis and homogeneous catalysis.[2] The corresponding complexes [Ru(η^4-1,5-COD)(η^6-arene)] containing monocyclic arenes seem to be generally less reactive, although they have been employed as catalyst precursors for the tail-to-tail dimerization of acrolein[3] and acrylonitrile.[4] Polycyclic arenes are usually more easily displaced from a metal atom than are monocyclic arenes owing to the ease of ring slippage via intermediates of lower hapticity.[5] For example, naphthalene is readily displaced from the complex [Ru(η^4-1,5-COD)(η^6-$C_{10}H_8$)] (**2**) by other arenes in the presence of acetonitrile,[6,7] and alkynes undergo stoichiometric cyclotrimerization on reaction with **2**, thus providing alternative routes to [Ru(η^4-1,5-COD)(η^6-arene)] complexes.[8] The combination of **1** with acetonitrile also catalyzes olefin isomerizations (1,5-COD to 1,3-COD,[9] 1-hexene to 2-hexene,[9] and allyl ethers to corresponding vinyl ethers[10]), C=C and C=O hydrogenation,[7] and tail-to-tail dimerization of methyl acrylate,[11] whereas the corresponding monocyclic arene complexes under the same conditions are less active or inactive.

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(1) Abbreviations: 1,3,5-COT = 1,3,5-cyclooctatriene (C_8H_{10}); 1,5-COD = 1,5-cyclooctadiene (C_8H_{12}); 1,3-COD = 1,3-cyclooctadiene (C_8H_{12}); acac = acetylacetonato (2,4-pentanedionato, $C_5H_7O_2$).

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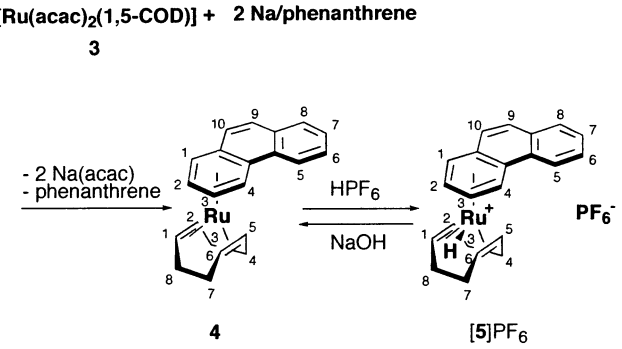
Scheme 1



Another interesting property of the [Ru(η^4-1,5-COD)(η^6-arene)] complexes is their reversible protonation by HPF_6 or HBF_4 to give hydrido complexes that were formulated as [RuH(η^4-1,5-COD)(η^6-arene)]$^+$.[7,12−14] Deuterium labeling studies showed that there was facile exchange between Ru-H and the CH_2 protons of 1,5-COD, presumably resulting from successive insertion/elimination processes, but detailed understanding was lacking.

In this article, we report an extension of these studies to the new Ru(1,5-COD) complexes of the tricyclic arenes phenanthrene, anthracene, and 9,10-dihydroanthracene.

Results and Discussion

η^6-Phenanthrene Complexes. Although complex **2** was first prepared by treatment of **1** with naphthalene under hydrogen,[6] it is more conveniently obtained from the reaction of [Ru(acac)$_2$(η^4-1,5-COD)] (**3**) with sodium naphthalene.[7] Similarly, reduction of **3** with sodium phenanthrene in THF at −78 °C gave [Ru(η^4-1,5-COD)(η^6-phenanthrene)] (**4**) (Scheme 1) as a light yellow solid that was unavoidably contaminated with free phenanthrene.

In contrast to the naphthalene reaction, the free hydrocarbon could not be removed by fractional sublimation, and separation also could not be achieved by fractional crystallization or chromatography. To isolate **4** in a pure state, the crude solid was treated with HPF_6, and the yellow hydrido salt [RuH(η^4-1,5-COD)(η^6-phenanthrene)]PF_6, [**5**]PF_6, that precipitated was washed with ether to remove free phenanthrene. The yield of [**5**]PF_6 was 53%. Deprotonation of [**5**]PF_6 in ether with aqueous NaOH gave pure **4**; although this reaction is probably quantitative, the yield of pure material after recrystallization was only 15%.

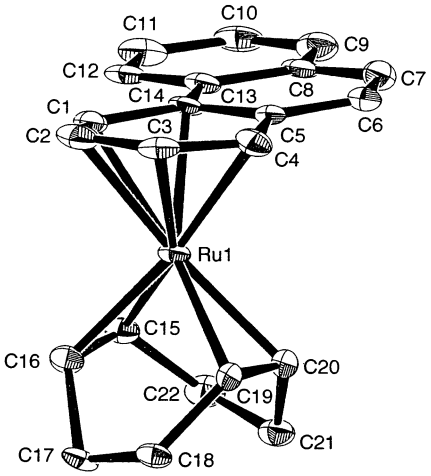


Figure 1. Molecular structure of [Ru(η^4-1,5-COD)(η^6-phenanthrene)] (**4**). All hydrogen atoms are omitted for clarity and ellipsoids represent 50% probability.

Complexes **4** and [**5**]PF_6 were characterized by ^{1}H, ^{1}H−^{1}H COSY, NOESY, and ^{31}P{^{1}H} NMR spectroscopy, IR spectroscopy, and elemental analyses. The ^{1}H NMR spectrum of [**5**]PF_6 shows a singlet at δ −5.82 due to the hydride ligand (cf. δ −6.73 for the corresponding naphthalene complex[7]). A pattern arising from an AMNX spin system formed by the coordinated aromatic protons is found at δ 6.33, 6.45, 6.47, and 6.95, while the uncoordinated aromatic protons appear as multiplets at lower field (δ 7.67−8.45). The four broad multiplets at δ 3.7, 3.8, 4.0, and 4.2 are assigned to the four inequivalent olefinic protons of the 1,5-COD ligand. ^{1}H−^{1}H COSY and NOESY spectra revealed that three multiplets at δ 1.5 (1H), 1.6 (1H), and 1.8 (2H) are due to the *exo*-H(4), *exo*-H(3), and *exo*-H(7 and 8) aliphatic protons of 1,5-COD, respectively. The *endo*-H(4), *endo*-H(3), and *endo*-H(7 and 8) aliphatic protons of 1,5-COD appear as three multiplets at δ 0.8 (1H), 1.4 (1H), and 2.3 (2H). The ^{31}P{^{1}H} NMR spectrum shows a septet at δ −143.8, indicating the presence of the PF_6^- anion. The IR spectrum of [**5**]PF_6 displays a characteristic medium band at 2047 cm^{-1} and a very strong band at 837 cm^{-1} assignable to ν(Ru−H) and ν(P−F) vibrations, respectively. All these observations are consistent with the proposed structure of [**5**]PF_6 containing η^6-phenanthrene.

In complex **4**, as expected, the coordinated aromatic protons are more shielded than those in [**5**]PF_6, appearing at δ 4.91 (H), 5.48 (1H), 6.07 (1H), and 6.11 (1H). In contrast to the naphthalene complex **2**, in which the olefinic protons of 1,5-COD are equivalent, those in **4** are inequivalent in pairs, appearing as a pair of 2H multiplets at δ 3.0 and 3.3; this is evidently due to the loss of the plane of symmetry through the coordinated aromatic ring. The CH_2 protons of 1,5-COD appear as two multiplets at δ 1.6 (2H) and 1.7 (6H).

The structure of **4** determined by single-crystal X-ray diffraction, which is shown in Figure 1 together with atom-labeling scheme, is very similar to that of the naphthalene analogue **2**.[15] Selected bond distances and angles are listed in Table 1. The C−C bond lengths in the coordinated aromatic ring show slight alternation

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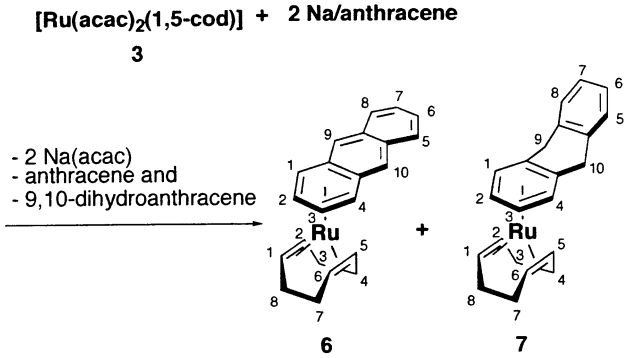
Table 1. Selected Bond Distances (Å) and Angles (deg) for 4

Ru(1)−C(1)	2.196(7)	Ru(1)−C(2)	2.275(8)
Ru(1)−C(3)	2.273(7)	Ru(1)−C(4)	2.217(7)
Ru(1)−C(5)	2.329(7)	Ru(1)−C(14)	2.311(6)
Ru(1)−C(15)	2.134(7)	Ru(1)−C(16)	2.147(7)
Ru(1)−C(19)	2.144(7)	Ru(1)−C(20)	2.141(7)
C(1)−C(2)	1.43(1)	C(1)−C(14)	1.444(10)
C(2)−C(3)	1.38(1)	C(3)−C(4)	1.40(1)
C(4)−C(5)	1.46(1)	C(5)−C(6)	1.41(1)
C(5)−C(14)	1.43(1)	C(6)−C(7)	1.36(1)
C(7)−C(8)	1.43(1)	C(8)−C(9)	1.41(1)
C(8)−C(13)	1.43(1)	C(9)−C(10)	1.39(1)
C(10)−C(11)	1.39(1)	C(11)−C(12)	1.39(1)
C(12)−C(13)	1.38(1)	C(13)−C(14)	1.462(10)
C(2)−C(1)−C(14)	121.4(7)	C(1)−C(2)−C(3)	119.9(7)
C(2)−C(3)−C(4)	120.0(7)	C(3)−C(4)−C(5)	121.7(7)
C(4)−C(5)−C(6	121.3(7)	C(4)−C(5)−C(14)	118.1(6)
C(6)−C(5)−C(14)	120.6(6)	C(5)−C(6)−C(7)	121.1(7)
C(6)−C(7)−C(8)	121.1(7)	C(7)−C(8)−C(9)	120.8(7)
C(7)−C(8)−C(13)	120.5(7)	C(9)−C(8)−C(13)	118.8(7)
C(8)−C(9)−C(10)	120.5(7)	C(9)−C(10)−C(11	120.1(7)
C(10)−C(11)−C(12)	119.9(8)	C(11)−C(12)−C(13)	121.2(7)
C(8)−C(13)−C(12	119.6(7)	C(8)−C(13)−C(14)	118.1(7)
C(12)−C(13)−C(14)	122.3(7)	C(1)−C(14)−C(5)	118.0(6)
C(1)−C(14)−C(13)	123.4(7)	C(5)−C(14)−C(13)	118.6(6)

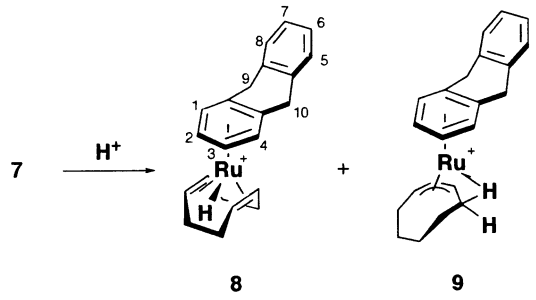
Scheme 2



[1.38(1)−1.46(1) Å] and carbon atoms C(1)−C(4) are significantly closer to the metal atom [Ru−C = 2.196(7)−2.275(8) Å] than are the carbon atoms at the ring junction [Ru−C(5) = 2.329(7) Å, Ru−C(14) = 2.311(6) Å]. A similar asymmetry in metal−carbon distances is evident in complex **2**, in [Cr(CO)$_3$(η^6-phenanthrene)],[16] and in the charge transfer adduct of the latter with 1,3,5-trinitrobenzene.[17] The coordinated aromatic ring of η^6-phenanthrene in **4** is slightly bent, as indicated by the dihedral angle of 7.7(5)° between the mean least-squares planes C(1)−C(2)−C(3)−C(4) and C(1)−C(14)−C(5)−C(4), cf. 8.4° in complex **2**.

***η*^{6}-Anthracene and *η*^{6}-9,10-Dihydroanthracene Complexes.** Treatment of complex **3** with sodium anthracene gave, unexpectedly, a 3:1 mixture of [Ru(η^4-1,5-COD)(η^6-anthracene)] (**6**) and [Ru(η^4-1,5-COD)-(η^6-9,10-dihydroanthracene)] (**7**), together with free anthracene and 9,10-dihydroanthracene (Scheme 2). After attempted separation by column chromatography on an alumina pad at −20 °C, the ratio of **6**:**7** had changed to 1:4. The 9,10-dihydroanthracene probably arises from hydrolysis of sodium anthracene by traces

Scheme 3



of water during workup.[18] Although **6** could be prepared in situ by a modification of the method of Vitulli et al.,[6] viz., the reaction of **1** with anthracene under hydrogen, all attempts to isolate it failed; it did not survive passage of the solution through alumina, although this process did not give **7** and 9,10-dihydroanthracene. The apparent enrichment of **7** at the expense of **6** therefore must be caused by partial decomposition of **6** during chromatography. Since attempts to remove free anthracene and 9,10-dihydroanthracene from the mixture of **6** and **7** were unsuccessful, the mixture was subjected to a similar protonation/deprotonation sequence as employed for the purification of **4**. As discussed below, this procedure gave pure **7**, **6** evidently being decomposed under the reaction conditions.

The characterization of the anthracene complex **6** rests solely on the ^{1}H NMR spectrum, which shows typical shielded resonances at δ 4.98 (2H) and 6.12 (2H), assignable to the coordinated aromatic protons, together with a pair of multiplets at δ 7.39 (2H) and 7.86 (2H) due to the protons in the outer, uncoordinated ring and a singlet at δ 7.91 (2H) due to the protons in the central ring. The olefinic and methylene protons of 1,5-COD appear at δ 3.7 and 1.66−1.84, respectively.

The ^{1}H NMR spectrum of the dihydroanthracene complex **7** shows an AA′XX′ pattern at δ 4.45 (2H) and 5.67 (2H) assignable to the protons in the coordinated aromatic ring and an AB quartet at δ 3.48 (2H) and 3.92 (2H) due to the diastereotopic *exo*- and *endo*-methylene protons at the 9,10-positions of dihydroanthracene. The remaining four aromatic protons appear as a multiplet at δ 7.2. The olefinic protons of 1,5-COD occur as just one 4H singlet at δ 2.93, and the *endo*- and *exo*-methylene protons of 1,5-COD occur as a pair of 4H multiplets at δ 1.5 and 1.7, as shown by NOESY and COSY.

Protonation of the *η*^{6}-9,10-Dihydroanthracene Complex 7. Treatment of **7** with HPF_6 in ether gave a yellow solid containing two cationic species, which we formulate on the basis of their NMR spectra as a hydrido complex [RuH(η^4-1,5-COD)(η^6-9,10-dihydroanthracene)] PF_6, [**8**]PF_6, and an agostic cyclooctenyl complex [Ru(η^1,η^3-C_8H_{13})(η^6-9,10-dihydroanthracene)]-PF_6, [**9**]PF_6 (Scheme 3). The total yield of isolated solid was 53%, and the ratio of [**8**]PF_6 to [**9**]PF_6 in CD_2Cl_2 at 295 K estimated from the ^{1}H NMR spectra was 4:1. A similar reaction occurred with HBF_4, the ratio of [**8**]BF_4 to [**9**]BF_4 in CD_2Cl_2 at 293 K being 5:1.

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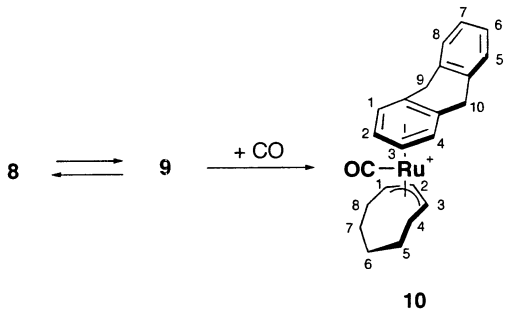
Table 2. Equilibrium Constants (K = 9/8) in Acetone-d_6

T (K)	K
300	0.69
306	0.60
313	0.55
318	0.54
323	0.47

The ^{1}H NMR spectrum of the predominant species [**8**]-PF_6 resembles in its essential features those of the naphthalene and phenanthrene analogues. It contains a singlet hydride resonance at δ −6.68 (1H) (cf. −5.82 for [**5**]PF_6, −6.73 for [RuH(η^4-1,5-COD)(η^6-naphthalene)]-PF_6[7]), two broad singlets at δ 3.15 (2H) and 4.13 (2H) due to the olefinic protons of 1,5-COD, and four 2H multiplets at δ 1.6, 1.7, 1.9, and 2.1 assigned to the *exo*-7 and -8, *exo*-3 and -4, and *endo*-7 and -8 methylene protons of 1,5-COD, respectively. An AB quartet pattern at δ 3.72 (2H) and 4.06 (2H) is assigned to the diastereotopic *endo*- and *exo*-methylene protons of coordinated 9,10-dihydroanthracene, and an AA′BB′ pattern at δ 6.12 (2H) and 6.31 (2H) is due to the coordinated aromatic protons; the uncoordinated aromatic protons coincidentally appear as a 4H singlet at δ 7.34.

The presence of 9,10-dihydroanthracene in the minor species is evident from a characteristic AB quartet at δ 3.59 and 3.87 due to the *endo*- and *exo*-9,10-methylene protons. However, the resonances arising from the Ru−H(COD) fragment are very different from those of [**8**]-PF_6, consisting of two broad resonances at δ −1.16 (5H) and 2.67 (8H). The former is assigned to the exchange average of an agostic Ru-*H*-C group and the four *endo*-CH_2 protons of the coordinated cyclooctenyl group; the second resonance arises from the exchange-averaged *exo*-CH_2 protons and olefinic protons. In agreement, all the carbons of the eight-membered ring are equivalent at room temperature, appearing as a broad signal at δ 44.2 ($^1J_{CH}$ = 137 Hz). It seems likely, therefore, that **9** has an allylic structure, [Ru(η^1,η^3-C_8H_{13})(η^6-9,10-dihydroanthracene)]$^+$, in which the electronic unsaturation at the metal center is relieved by an agostic interaction with the C−H bond adjacent to the allylic group (Scheme 3). Similar agostic structures have been established crystallographically for the η^3-cyclooctenyl complexes [M(1−3-η^3-C_8H_{13})L_3]$^+$ [M = Fe, L = P(OMe)$_3$;[19] M = Ru, L = P(OMe)Ph_2[20]] and for the protonation product [RuH(η^4-$C_{18}H_{15}$)(η^6-$C_6H_3Me_3$)]PF_6 ($C_{18}H_{15}$ = 2,3-dimethylene-5,6,7,8-dibenzobicyclo[2.2.2]octane).[21] When the equilibrium mixture of [**8**]PF_6 and [**9**]PF_6 in CD_2Cl_2 was cooled below room temperature, the signals at δ −1.16 and 2.67 gradually broadened and collapsed into the baseline at 213 K, while the other signals due to [**8**]PF_6 and [**9**]PF_6 remained sharp, but further cooling to 193 K caused no change and no approach to a limiting spectrum was possible. Thus the process of hydride migration between the metal atom and the carbon atom adjacent to the allylic group (or, viewed alternatively, the reversible rapid *cis*-insertion of 1,3-COD into Ru−H and subsequent *cis*-β-H elimination) cannot be slowed on the NMR time scale.

Scheme 4



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Measurements of the NMR spectrum of the mixture of [**8**]PF_6 and [**9**]PF_6 over a range of temperatures also showed that the two species are in equilibrium in solution. The equilibrium constant K (K = [**9**]/[**8**]) decreased reversibly from 0.69 to 0.47 in the range 300−323 K in acetone-d_6, as shown in Table 2. The derived

$$\mathbf{8} \underset{}{\overset{K}{\rightleftharpoons}} \mathbf{9} \qquad (1)$$

ΔH° = -12 ± 1 [kJ mol^{-1}]
ΔG° = 1 ± 2 [kJ mol^{-1}]
ΔS° = -44 ± 4 [J K^{-1} mol^{-1}]

thermodynamic parameters are estimated to be ΔH° = −12 ± 1 kJ mol^{-1}, ΔS° = −44 ± 4 J mol^{-1} K^{-1}, and ΔG° = 1 ± 2 kJ mol^{-1}.

Exposure of the equilibrium mixture of [**8**]PF_6 and [**9**]-PF_6 to CO (0.1 MPa) at room temperature gave immediately the η^3-cyclooctenyl complex [Ru(CO)(1−3-η^3-C_8H_{13})(η^6-9,10-dihydroanthracene)]PF_6, [**10**]PF_6, in 80% yield (Scheme 4).

The ^{1}H NMR spectrum of [**10**]PF_6 shows no hydride signal, and the η^3-allylic protons appear at δ 4.38 (dt, 2H) and 4.44 (t, 1H). The IR spectrum shows a single, intense ν(CO) band at 1996 cm^{-1}, as expected for a monocarbonyl species. The exclusive formation of **10** from the mixture of **8** and **9** confirms that these two species are in rapid equilibrium. Complex [**5**]PF_6 also reacted with CO to give a η^3-cyclooctenyl complex [Ru(CO)(1−3-η^3-C_8H_{13})(η^6-phenanthrene)]PF_6, [**11**]PF_6, isolated in 91% yield. This observation demonstrates that **5** also exists in equilibrium with an agostic η^3-cyclooctenyl isomer, even though the latter is undetectable by NMR spectroscopy. A similar conclusion holds for the analogous complexes of monocyclic arenes examined previously.[12]

Deuteration Studies. Addition of D_2O to the equilibrium mixture of [**8**]PF_6 and [**9**]PF_6 caused immediate disappearance of all the *endo*-methylene proton resonances of the C_8H_{13} fragment of **9**, the corresponding *exo*-protons and the 9,10-dihydroanthracene protons being unaffected. The signals due to Ru−H and the *endo*-methylene protons of 1,5-COD in **8** also disappeared, but more slowly. Addition of a base such as Na_2CO_3, NaOH, or Et_3N to the equilibrium mixture of **8** and **9** regenerated the ruthenium(0)-1,5-COD complex **7**, and when the same experiment was carried out with the equilibrium mixture of [**8**-d_5]PF_6 and [**9**-d_5]PF_6, complex **7**-d_4 selectively deuterated in the *endo*-positions was formed.

These results, taken together with the spectroscopic data, can be accounted for by a series of protonation/

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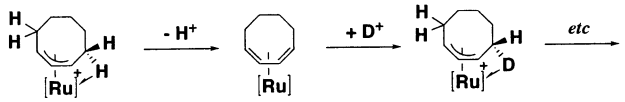
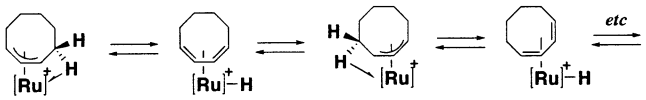
Scheme 5



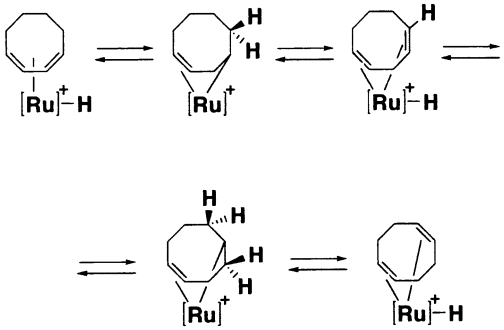
[Ru] = Ru(η^6-arene)

Scheme 6



[Ru] = Ru(η^6-arene)

Scheme 7



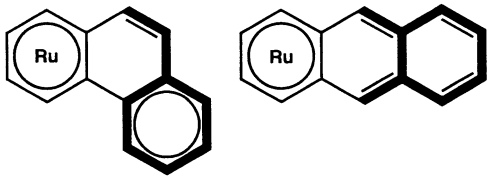
[Ru] = Ru(η^6-arene)

deprotonation and reversible *cis*-insertions of a Ru−H bond into the C=C double bonds. Rapid incorporation of deuterium from D_2O into **9** requires reversible loss of the proton in the agostic C−H bond, which is weakened as a result of the interaction with the metal center[22] (Scheme 5). As shown in Scheme 6, repeated C−H bond cleavages of this type, possibly involving a discrete RuH(1,3-COD) intermediate, bring about migration of the η^3-allylic fragment around the ring and incorporate deuterium atoms exclusively and rapidly into the *endo*-positions of the cyclooctenyl unit. The hydride may also migrate to one of the inner diene carbon atoms, thus deconjugating the double bonds in the ring and leading finally to the stable hydrido 1,5-COD isomer **8**, as shown in Scheme 7. Evidently this process has a higher activation barrier than that shown in Scheme 6, and the reverse process in which Ru−H adds to one of the double bonds of the more rigid 1,5-COD fragment in **8** is also likely to be slow.

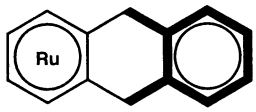
Addition of D_2O to a dichloromethane solution of **5** also led to regioselective and stereoselective deuteration of the hydride and *endo*-methylene protons of coordinated 1,5-COD, even though no isomer analogous to **9** could be detected in this case. It should also be noted that hydride migration in **5**, **8**, and **9** occurs only within the COD moiety and does not involve the coordinated arene.[23]

(22) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1−124.

Chart 1



4 **6**



7

Discussion

The reduction of [Ru(acac)$_2$(η^4-1,5-COD)] (**3**) by the radical anion of phenanthrene gives the complex [Ru(η^4-1,5-COD)(η^6-phenanthrene)] (**4**), which appears to be comparable in stability to the similarly prepared naphthalene analogue **2**. Although the corresponding η^6-anthracene complex **6** is formed from **3** and sodium anthracene, it is too unstable to survive the workup conditions, the main product being the more stable 9,10-dihydroanthracene complex [Ru(η^4-1,5-COD)(η^6-9,10-dihydroanthracene)] (**7**). Thus, as in the Cr(CO)$_3$ series,[24,25] angular fusion of an additional ring to naphthalene does not greatly affect the stability of the Ru(1,5-COD) complex, whereas linear fusion causes a decrease in stability. Following an argument first advanced by Nicholson,[26] we can correlate these observations with a loss of aromaticity, or increased bond localizations, in the uncoordinated part of the aromatic molecule.[27,28] Chart 1 shows phenanthrene, anthracene, and 9,10-dihydroanthracene coordinated to Ru(1,5-COD), the coordinated aromatic rings being represented as completely localized. The molecules remaining after removal of these rings still have aromatic character in the cases of **4** and **7** (similar to styrene and *o*-xylene, respectively), whereas in the case of **6** the residual molecule is similar to *o*-xylylene, which is less favored.

Like their monocyclic arene counterparts,[12] the tricyclic arene complexes **4** and **7** are protonated reversibly to form monohydrido complexes, a reaction that provides a convenient means of separating the parent complexes from unchanged arene. Although the spectroscopic evidence obtained in the earlier work[12] favored the formulation of [RuH(η^4-1,5-COD)(η^6-arene)]$^+$ for the protonation products, the possibility that isomerization to η^4-1,3-COD had occurred could not be completely excluded, especially as it had been claimed that protonation of [Ir(η^4-1,5-COD)(η^5-C_5H_5)] gave [IrH(η^4-1,3-COD)-

(23) Protonation of η^2-anthracene in its [Os(NH$_3$)$_5$]$^{2+}$ complex and of η^4-anthracene in its [Mn(CO)$_3$]$^-$ complex has been reported: (a) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953−1978. (b) Veauthier, J. M.; Chow, A.; Fraenkel, G.; Geib, S. J.; Cooper, N. J. *Organometallics* **2000**, *19*, 661−671.

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(η^5-C_5H_5)]$^+$.[29] We believe that the problem is resolved by the observation that protonation of **7** yields *two* products in equilibrium: the main product is the hydrido complex [RuH(η^4-1,5-COD)(η^6-9,10-dihydroanthracene)]$^+$ (**8**), and the minor product the fluxional, agostic, η^3-cyclooctenyl cation complex [Ru(η^6-9,10-dihydroanthracene)(η^1,η^3-C_8H_{13})]$^+$ (**9**). Although the formation of **9** is favored enthalpically, it is disfavored by the large negative entropy term, which may reflect the more congested environment associated with the agostic interaction. In contrast, the hydrido diene complexes [RuH(η^4-1,5-COD)L_3]$^+$ (L = various tertiary phosphines) isomerize irreversibly to the corresponding agostic cyclooctenyl complexes [Ru(η^1,η^3-C_8H_{13})L_3]$^+$.[14a] The exchange of deuterium from D_2O with Ru−H and the endo-methylene protons of COD in **8**/**9**, and the irreversible reaction with CO to give the η^3-cyclooctenyl complex **10**, are very similar to those reported for the monocyclic arene complexes [RuH(η^4-1,5-COD)(η^6-arene)]$^+$ [12] and suggest that these complexes also exist in equilibrium with agostic η^3-cyclooctenyl isomers. Presumably the amounts were too small or the resonances were too broad to be detected by NMR spectroscopy.

Experimental Section

All manipulations and reactions were performed under dry nitrogen with use of standard Schlenk and vacuum line techniques. Diethyl ether, THF, and hexane were distilled over benzophenone ketyl, and CH_2Cl_2 was distilled from Drierite; these solvents were stored under nitrogen. The complexes [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)] (**1**),[30,31] [Ru(η^4-1,5-COD)(η^6-naphthalene)] (**2**),[7] and [Ru(acac)$_2$(η^4-1,5-COD)] (**3**)[32] were prepared according to literature procedures; in the case of **1**, magnetic stirring was used instead of sonication. All other reagents were obtained from commercial suppliers (Wako Pure Chemical Industries, Kanto, and TCI) and used as received. Low-temperature chromatographic separation was carried out on Al_2O_3 (Merck, Activity I, 250 mesh) contained in a jacketed column with a G3 glass frit maintained at −20 to −30 °C. ^{1}H NMR spectra were recorded on JEOL LA 300 (300.4 MHz for ^{1}H) and Varian Gemini 300 (300.1 MHz for ^{1}H) spectrometers. Benzene-d_6 was distilled over sodium wire and stored under vacuum. Methylene dichloride-d_2 and acetone-d_6 were distilled over P_4O_{10} and stored under nitrogen. Deuterated water was employed as received. Chemical shifts (δ) are given in ppm, relative to internal TMS for ^{1}H and ^{13}C and external 85% H_3PO_4 in deuterated water for ^{31}P. All coupling constants are given in Hz. All signals in the ^{1}H NMR spectra were assigned by using ^{1}H−^{1}H COSY and phase sensitive-NOESY techniques. Signals in the ^{13}C{^{1}H} NMR spectrum were assigned by using ^{13}C−^{1}H shift correlation and DEPT-135° techniques. GC−MS spectra were measured on a Shimadzu QP-2000 by the electron impact method (70 eV) using a HR-1 (0.25 mm ϕ × 30 m) column. FAB MS analyses were performed by use of a VG ZAB-2SEQ or a JEOL GCmate II analyzer. Elemental analyses were carried out on a Perkin-Elmer 2400 series II CHN analyzer. Temperature-controlled reactions were performed by use of a EYELA LA-50 cryostatted stirrer.

[RuH(η^4-1,5-COD)(η^6-phenanthrene)]PF_6, [5]PF_6. A THF solution (ca. 8 mL) of sodium phenanthrene (285 mg, 1.60 mmol) was added to a THF solution (5 mL) of **3** (305 mg, 0.750 mmol) at −78 °C. The reaction mixture was stirred for 2 days and allowed to warm to room temperature. The resulting solution was purified by column chromatography through an Al_2O_3 pad. The filtrate was evaporated to dryness to give a yellow powder. Several drops of HPF_6 were added to a solution of the yellow powder in Et_2O to give a light yellow precipitate, which was collected, washed with Et_2O, and dried in vacuo. Recrystallization from CH_2Cl_2/Et_2O gave yellow crystals of [**5**]PF_6 (215 mg, 0.403 mmol) in 53% yield. ^{1}H NMR (300.4 MHz, CD_2Cl_2, 295 K): δ −5.82 (s, 1H, Ru-*H*), 0.8 (m, 1H, *endo*-4-CH_2 in COD), 1.4 (m, 1H, *endo*-3-CH_2 in COD), 1.5 (m, 1H, *exo*-4-CH_2 in COD), 1.6 (m, 1H, *exo*-3-CH_2 in COD), 1.8 (m, 2H, *exo*-7- and 8-CH_2 in COD), 2.3 (m, 2H, *endo*-7- and 8-CH_2 in COD), 3.7 (br m, 1H, 5-C*H* in COD), 3.8 [br m, 1H, 1-(or 6)C*H* in COD], 4.0 [br m, 1H, 6-(or 1)C*H* in COD], 4.2 (br m, 1H, 2-C*H* in COD), 6.33, 6.45, 6.47, 6.95 [AMNX, 4H, 1-, 2-(or 3), 3-(or 2), 4-C*H* in coord aromatic ring], 7.67 (d, ^3J = 9 Hz, 1H, 10-C*H* in central aromatic ring), 7.940, 7.942, 8.15, 8.45 [AMXY, 4H, 6-(or 7), 7-(or 6), 8-, 5-C*H* in uncoord aromatic ring], 8.26 (d, ^3J = 9 Hz, 1H, 9-C*H* in central aromatic ring). ^{31}P{^{1}H} NMR (121.6 MHz, CD_2Cl_2, 296 K): δ −143.8 (sep, $^1J_{PF}$ = 710 Hz, PF_6^-). IR (KBr, cm^{-1}): 3106 (m), 3019 (m), 2947 (m), 2921 (m), 2889 (m), 2843 (m), 2047 (m), 1604 (m), 1542 (m), 1503 (m), 1477 (m), 1436 (m), 1426 (m), 1340 (m), 1307 (m), 1266 (m), 1231 (m), 1165 (m), 1021 (m), 1000 (m), 837 (vs), 728 (sh), 556 (s). Anal. Calcd for $C_{22}H_{23}F_6PRu\cdot CH_2Cl_2$: C, 44.67; H, 4.07. Found: C, 44.64; H, 3.79.

[Ru(η^4-1,5-COD)(η^6-phenanthrene)] (4). Aqueous NaOH (0.1 g, 3 mmol) solution (ca. 5 mL) was added to an Et_2O solution (5 mL) of **3** (41.9 mg, 0.078 mmol) at room temperature, and the mixture was stirred overnight. The Et_2O layer was separated through a Teflon cannula, and the resulting water layer was extracted three times with Et_2O. The combined Et_2O solutions were dried over anhydrous Na_2SO_4 and evaporated to dryness. The resulting yellow solid was recrystallized from Et_2O/hexane to give yellow crystals of **4** in 15% yield (4.9 mg, 0.012 mmol). ^{1}H NMR (300.4 MHz, CD_2Cl_2, 294 K): δ 1.6 [m, 2H, *endo* protons for 3-(or 4) and 7-(or 8)CH_2 in COD], 1.7 [m, 6H, *exo* protons for 3-, 4-, 7-, and 8-*C*H_2 and *endo* protons for 4-(or 3), 8-(or 7)CH_2 in COD], 3.0 [m, 2H, 1-(or 2) and 5-(or 6)C*H* in COD], 3.3 [m, 2H, 2-(or 1) and 6-(or 5)-C*H* in COD], 4.91 (d, ^3J = 5.4 Hz, 1H, 1-C*H* in coord aromatic ring), 5.48 (d, ^3J = 5.4 Hz, 1H, 4-C*H* in coord aromatic ring), 6.07 [t, ^3J = 5.4 Hz, 1H, 2-(or 3)C*H* in coord aromatic ring], 6.11 [t, ^3J = 5.4 Hz, 1H, 3-(or 2)C*H* in coord aromatic ring], 7.33 (d, ^3J = 9.0 Hz, 1H, 10-C*H* in central aromatic ring), 7.59, 7.86, 8.13 (AMXX′, 4H, 6- and 7-, 8-, 5-C*H* in uncoord aromatic ring), 7.64 (d, ^3J = 9.0 Hz, 1H, 9-C*H* in central aromatic ring). Anal. Calcd for $C_{22}H_{22}Ru$: C, 68.19; H, 5.72. Found: C, 68.20; H, 6.08.

[Ru(η^4-1,5-COD)(η^6-anthracene)] (6). Complex **3** (200 mg, 0.491 mmol) was reduced by a mixture of anthracene (218 mg, 1.22 mmol) with an excess of sodium in dry THF at 0 °C for 1 day, the solution being allowed to come to room temperature. Removal of all volatile materials without column chromatography gave a mixture of **6** and **7** in 3:1 ratio (monitored by NMR). Since complex **6** could not be isolated, it was characterized spectroscopically. ^{1}H NMR (300.4 MHz, CD_2Cl_2, 295 K): δ 1.66−1.84 (m, CH_2 in COD, obscured by overlap with a THF signal and estimated by COSY), 3.7 (C*H* in COD, obscured by overlap with a THF signal and estimated by COSY), 4.98 (m, 2H, coord aromatic ring), 6.12 (m, 2H, coord aromatic ring), 7.39 (m, 2H, uncoord aromatic ring), 7.86 (m, 2H, uncoord aromatic ring), 7.91 (s, 2H, 9- and 10-C*H* in central aromatic ring).

[RuH(η^4-1,5-COD)(η^6-9,10-dihydroanthracene)]PF_6, [8]PF_6, and [Ru(η^1,η^3-C_8H_{13})(η^6-9,10-dihydroanthracene)]PF_6, [9]PF_6. A THF solution (ca. 8 mL) of sodium anthracene (628 mg, 3.52 mmol) was added to a THF solution (5 mL) of **3** (652 mg, 1.60 mmol) at −78 °C. The reaction mixture was stirred for 2 days while being allowed to come to room

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temperature. The resulting solution was filtered through an alumina pad, and the solution was evaporated to dryness. The resulting yellow powder was dissolved in Et_2O, and a few drops of HPF_6 was added to give a light yellow precipitate, which was separated and dried under vacuum to give a reddish brown precipitate of a mixture of [**8**]PF_6 and [**9**]PF_6 (4:1 in CD_2Cl_2 at 295 K) in 53% yield (324 mg, 0.606 mmol). NMR data for [**8**]PF_6: ^{1}H NMR (300.4 MHz, CD_2Cl_2, 295 K): δ −6.68 (s, 1H, Ru-*H*), 1.6 (dm, 2H, *exo*-7- and 8-CH_2 in COD), 1.7 (dm, 2H, *exo*-3- and 4-CH_2 in COD), 1.9 (m, 2H, *endo*-3- and 4-CH_2 in COD), 2.1 (m, 2H, *endo*-7- and 8-CH_2 in COD), 3.15 (m, 2H, 1- and 6-C*H* in COD), 3.72 (d, ^2J = 16.5 Hz, 2H, *endo*-9- and 10-CH_2 in central ring), 4.06 (d, ^2J = 16.5 Hz, 2H, *exo*-9- and 10-CH_2 in central ring), 4.13 (m, 2H, 2- and 5-C*H* in COD), 6.12, 6.31 (AA′BB′, 4H, 1- and 4-, 2- and 3-C*H* in coord aromatic ring), 7.34 (s, 4H, 5-, 6-, 7-, and 8-C*H* in arene). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 296 K): δ 31.1 (s, $^1J_{CH}$ = 108 Hz, 7- and 8-*C*H_2 in cod), 32.5 (s, $^1J_{CH}$ = 130 Hz, 3- and 4-*C*H_2 in cod), 34.3 (s, $^1J_{CH}$ = 131 Hz, 9- and 10-*C*H_2 in central ring), 65.2 (s, $^1J_{CH}$ = 160 Hz, 1- and 6-*C*H in cod), 74.9 (s, $^1J_{CH}$ = 154 Hz, 2- and 5-*C*H in cod), 94.4 (s, $^1J_{CH}$ = 178 Hz, 1- and 4-*C*H in coord aromatic ring), 95.6 (s, $^1J_{CH}$ = 180 Hz, 2- and 3-*C*H in coord aromatic ring), 112.8 [s, 4a-(or 8a) and 9a-(or 10a)*C* in ring junction], 127.9 (s, 5-, 6-, 7-, and 8-*C*H in uncoord aromatic ring), 133.5 [s, 8a-(or 4a) and 10a-(or 9a)*C* in ring junction]. ^{31}P{^{1}H} NMR (121.6 MHz, CD_2Cl_2, 296 K): δ −143.6 (sept, $^1J_{PF}$ = 711 Hz, PF_6^-). NMR data for [**9**]PF_6: ^{1}H NMR (300.4 MHz, CD_2Cl_2, 226 K): δ −1.16 (s, 5H, *endo* protons for 5-, 6-, 7-, and 8-CH_2 in C_8H_{13} and Ru-*H*-C), 2.67 (s, 8H, 1-, 2-, 3-, and 4-C*H*, and *exo* protons for 5-, 6-, 7-, and 8-CH_2 in C_8H_{13}), 3.59 (d, ^2J = 17 Hz, 2H, *endo*-9- and 10-CH_2 in central ring), 3.87 (d, ^2J = 17 Hz, 2H, *exo*-9- and 10-CH_2 in central ring), 5.96 (m, 2H, 1- and 4-C*H* in coord aromatic ring), 6.1 (2- and 3-C*H* in coord aromatic ring: obscured by the signal due to **8** and estimated by COSY), 7.3 (uncoord aromatic ring: obscured by the signals due to **8** and estimated by COSY). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 295 K): δ 31.9 (s, $^1J_{CH}$ = 131 Hz, 9- and 10-*C*H_2 in central ring), 44.2 (br, $^1J_{CH}$ = 137 Hz, 1-, 2-, 3-, and 4-*C*H in C_8H_{13}), 84.8 [s, $^1J_{CH}$ = 178 Hz, 2-(or 3)*C* in coord aromatic ring], 86.1 [s, $^1J_{CH}$ = 174 Hz, 3-(or 2)*C* in coord aromatic ring]. IR data for the mixture of [**8**]PF_6 and [**9**]PF_6: IR (KBr, cm^{-1}): 3100−2850 (w), 2136 (br), 1900−1300 (br), 1210 (vs), 836 (vs), 735 (vs). FAB MS data for the mixture of [**8**]PF_6 and [**9**]PF_6: FAB-MS *m*/*z* 391.0974 (M^+). Calcd for $C_{22}H_{25}Ru$ = 391.1000. Error = −2.6. Anal. Calcd for $C_{22}H_{25}F_6PRu\cdot 0.5CH_2Cl_2$: C, 46.76; H, 4.53. Found: C, 47.19; H, 4.16.

[RuH(η^4-1,5-COD)(η^6-9,10-dihydroanthracene)]BF_4, [8]BF_4, and [Ru(η^1,η^3-C_8H_{13})(η^6-9,10-dihydroanthracene)]BF_4, [9]BF_4. The procedure was similar to that described above for the PF_6^- salt. A THF solution of **3** (479.8 mg, 1.177 mmol) was added to a mixture of anthracene (499.2 mg, 2.804 mmol) and sodium (260.1 mg, 11.31 mmol) in THF (15 mL) at −68 °C, and the reaction mixture was stirred overnight at −30 °C for 8 h. The resulting solution was filtered through an Al_2O_3 pad at 0 °C. Removal of all volatile matter from the filtrate gave a rusty-red powder (696.7 mg). The crude powder was dissolved in dry Et_2O (40 mL) at −30 °C. Ten drops of aqueous HBF_4 (42% aqueous) was added to the solution, and the mixture was stirred for 5 min at −30 °C, during which time a yellow precipitate formed. The supernatant liquid was removed by decantation, and the resulting yellow solid was washed with Et_2O (10 mL and then 5 mL). The resulting solid was dried in vacuo and then recrystallized from cold CH_2Cl_2 (2 mL)/Et_2O (100 μL). Removal of the brown supernatant gave light brown microcrystals of a mixture of [**8**]BF_4 and [**9**]BF_4 (5:1 in CD_2Cl_2 at 293 K). Yield: 22% (123.5 mg, 0.260 mmol). NMR data for [**8**]BF_4: ^{1}H NMR (300.1 MHz, CD_2Cl_2, 293 K): δ −6.62 (s, 1H, Ru-*H*), 1.6 (dm, 2H, *exo*-7- and 8-CH_2 in COD), 1.7 (dm, 2H, *exo*-3- and 4-CH_2 in COD), 1.9 (m, 2H, *endo*-3- and 4-CH_2 in COD), 2.1 (m, 2H, *endo*-7- and 8-CH_2 in COD), 3.16 (m, 2H, 1- and 6-C*H* in COD), 3.74 (d, ^2J = 16.5 Hz, 2H, *endo*-9- and 10-CH_2 in central ring), 4.05 (d, ^2J = 16.5 Hz, 2H, *exo*-9- and 10-CH_2 in central ring), 4.16 (m, 2H, 2- and 5-C*H* in COD), 6.17, 6.37 (AA′BB′, 4H, 1- and 4-, and 2- and 3-C*H* in coord aromatic ring), 7.34 (s, 4H, 5-, 6-, 7-, and 8-C*H* in uncoord aromatic ring). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 296 K): δ 31.2 (s, 7- and 8-*C*H_2 in COD), 32.4 (s, 3- and 4-*C*H_2 in COD), 34.3 (s, 9- and 10-*C*H_2 in arene), 65.3 (s, 1- and 6-*C*H in COD), 74.9 (s, 2- and 5-*C*H in COD), 94.46 (s, 1- and 4-*C*H in coord aromatic ring), 95.9 (s, 2- and 3-*C*H in coord aromatic ring), 128.0 (s, 5-, 6-, 7-, and 8-*C*H in uncoord aromatic ring), 133.6 [s, 8a-(or 4a) and 10a-(or 9a)*C* in ring junction]. NMR data for [**9**]BF_4: ^{1}H NMR (300.1 MHz, CD_2Cl_2, 226 K): δ −1.14 (s, 5H, *endo*-5-, 6-, 7-, and 8-CH_2 in C_8H_{13} and Ru-*H*-C), 2.68 (s, 8H, 1-, 2-, 3-, and 4-C*H*, and *exo*-5-, 6-, 7-, and 8-CH_2 in C_8H_{13}), 3.65 (d, ^2J = 16 Hz, 2H, *endo*-9- and 10-CH_2 in central ring), 3.87 (d, ^2J = 16 Hz, 2H, *exo*-9- and 10-CH_2 in central ring), 5.96 (m, 2H, 1- and 4-C*H* in coord aromatic ring), 6.1 (2- and 3-C*H* in coord aromatic ring: obscured by the signals due to [**8**]BF_4 and estimated by COSY), 7.3 (obscured by the signals due to [**8**]BF_4 and estimated by COSY). IR spectrum of the mixture of [**8**]BF_4 and [**9**]BF_4. IR (KBr, cm^{-1}): 3072 (w), 3009 (w), 2964 (w), 2944 (w), 2932 (w), 2896 (w), 2882 (w), 2839 (w), 1458 (m), 1425 (m), 1092 (m), 1052 (s), 1038 (s), 987 (w), 969 (w), 956 (w), 756 (m).

[Ru(η^4-1,5-COD)(η^6-9,10-dihydroanthracene)] (7). Similar to the method for the preparation of **4**, reaction of a mixture of [**8**]PF_6 and [**9**]PF_6 with aqueous NaOH gave **7**. Yield: 55%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, 297 K): δ 1.5 (m, 4H, *endo*-CH_2 in COD), 1.7 (m, 4H, *exo*-CH_2 in COD), 2.93 (s, 4H, C*H* in COD), 3.48 (d, ^2J = 15.3 Hz, 2H, *endo*-9- and 10-CH_2 in central ring), 3.92 (d, ^2J = 15.3 Hz, 2H, *exo*-9- and 10-CH_2 in central ring), 4.45, 5.67 (AA′XX′, 4H, 1- and 4-, and 2- and 3-C*H* in coord aromatic ring), 7.2 (m, 4H, 5-, 6-, 7-, and 8-C*H* in arene). FAB-MS *m*/*z* 389.0 (M^+ − H). Calcd for $C_{22}H_{23}Ru$ = 389.085.

Thermodynamic Study of Equilibrium between [9]PF_6 and [8]PF_6. For the thermodynamic study of equilibrium between [**8**]PF_6 and [**9**]PF_5, a solution containing [**8**]PF_6 and [**9**]PF_6 in acetone-d_6 was employed. The sample was placed in a thermostated NMR probe set at 27, 33, 40, 45, and 50 °C with the temperature calibrated by a methanol standard. The NMR probe was stable to within 1 °C of the set temperature. The equilibrium constant (K = [**9**]/[**8**]) was estimated from relative amounts of [**9**]PF_6 and [**8**]PF_6 by integration of well-separated resonances: two coordinated aromatic ring protons at δ 6.03 (at 27 °C), four *endo*-methylene protons of C_8H_{13} and Ru−H−C proton at δ 0.37 (seven protons) for **9**, four coordinated aromatic ring protons at δ 6.0 and 6.6, and a hydride at δ −6.24 (five protons) for **8**.

Reaction of a Mixture of [8]PF_6 and [9]PF_6 with CO. An equilibrium mixture of [**8**]PF_6 and [**9**]PF_6 (4.4 mg, 0.0082 mmol) was placed in a NMR tube. Dry dichloromethane-d_2 (600 μL) was transferred into the NMR tube under vacuum. Carbon monoxide (0.1 MPa) was introduced to give [Ru(CO)(1−3-η^3-C_8H_{13})(η^6-9,10-dihydroanthracene)]PF_6, [**10**]PF_6, in 80% yield (estimated by NMR). The IR spectrum was measured after removal of all volatile material. ^{1}H NMR (300.4 MHz, CD_2Cl_2, 299 K): δ 1.19−1.41 [m, 7H, *endo*- and *exo*-5-CH_2, *endo*-(or *exo*)4- and 8-CH_2, and *endo*-(or *exo*)6-CH_2 in C_8H_{13}], 1.67 [m, 1H, *exo*-(or *endo*)6-CH_2 in C_8H_{13}], 2.02−2.11 [m, 2H, *exo*-(or *endo*)4- and *exo*-(or *endo*)8-CH_2 in C_8H_{13}], 3.80 (d, ^2J = 17 Hz, 2H, *endo*-9- and 10-CH_2 in central ring), 4.10 (d, ^2J = 17 Hz, 2H, *exo*-9- and 10-CH_2 in central ring), 4.38 (dt, ^3J = 8.3, 7.2 Hz, 2H, 1- and 3-C*H* in C_8H_{13}), 4.44 (t, ^3J = 8.3 Hz, 1H, 2-C*H* in C_8H_{13}), 6.43, 6.44 (AA′BB′, 4H, 1- and 4-, 2-, and 3-C*H* in coord aromatic ring), 7.34 (s, 4H, 5-, 6-, 7-, and 8-C*H* in uncoord aromatic ring). ^{31}P{^{1}H} NMR (121.6 MHz, CD_2Cl_2, 298 K): δ −143.5 (sept, $^1J_{PF}$ = 710 Hz, PF_6^-). IR (KBr, cm^{-1}): 3095 (w), 3013 (w), 2925 (m), 2849 (w), 1996 (vs), 1459 (m), 1425 (m), 835 (vs), 557 (s).

Reaction of [5]PF_6 with CO. Following a similar procedure, treatment of complex [**5**]PF_6 (6.5 mg, 0.012 mmol) with

CO (0.1 MPa) gave [Ru(CO)(1−3-η^3-C_8H_{13})(η^6-phenanthrene)]-PF_6, [**11**]PF_6, in 91% yield (estimated by NMR). ^{1}H NMR (300.4 MHz, CD_2Cl_2, 299 K): δ 1.28−1.57 (m, 8H, 4-, 5-, 6-, 7-, and 8-CH_2 in C_8H_{13}), 1.96 (t, ^3J = 8.3 Hz, 1H, 2-CH in C_8H_{13}), 2.27 (m, 2H, 4- and 8-CH_2 in C_8H_{13}), 4.05 [q, ^3J = 8.3 Hz, 1H, 1-(or 3)CH in C_8H_{13}], 4.21 [q, ^3J = 8.3 Hz, 1H, 3-(or 1)CH in C_8H_{13}], 6.75 [t, ^3J = 5.4 Hz, 1H, 2-(or 3)CH in coord aromatic ring], 6.76 [t, ^3J = 5.4 Hz, 1H, 3-(or 2)CH in coord aromatic ring], 7.34 [d, ^3J = 5.4 Hz, 1H, 1-(or 4)CH in coord aromatic ring], 7.38 [d, ^3J = 9.3 Hz, 1H, 9-(or 10)CH in central aromatic ring], 7.91−8.03 [m, 3H, 6- and 7-CH and 5-(or 8)CH in uncoord aromatic ring], 8.06 [d, ^3J = 9.3 Hz, 1H, 10-(or 9)CH in central aromatic ring], 8.48 [m, 1H, 8-(or 5)CH in uncoord aromatic ring]. ^{31}P{^{1}H} NMR (121.6 MHz, CD_2Cl_2, 295 K): δ −143.5 (sept, $^1J_{PF}$ = 710 Hz, PF_6^-).

Addition of D_2O to [5]PF_6 and Reduction with NEt_3. Complex [**5**]PF_6 (9.6 mg, 0.018 mmol) was placed in an NMR tube into which CD_2Cl_2 (600 μL) was transferred under vacuum. Dry nitrogen gas was introduced into the NMR tube, which was capped by an Aldrich rubber septum. D_2O (3.2 μL, 0.16 mmol) was added from a hypodermic syringe. After 1 h at room temperature, the ratio between **5** and **5**-d_5 was found to be 1.0:2.3. NMR spectrum for [**5**-d_5]PF_6: ^{1}H NMR (300.4 MHz, CD_2Cl_2, 294 K): δ 1.5 (br, 1H, *exo*-4-CH_2 in COD), 1.6 (m, 1H, *exo*-3-CH_2 in COD), 1.7 (br, 2H, *exo*-7- and 8-CH_2 in COD), 3.7 (br m, 1H, 5-CH in COD), 3.8 [br m, 1H, 1-(or 6)CH in COD], 3.9 [br m, 1H, 6-(or 1)CH in COD], 4.1 (br dd, ^3J = 9.3, 3.6 Hz, 1H, 2-CH in COD), 6.3, 6.43, 6.46, 6.91 [AXYZ, 4H, 1-CH, 2-(or 3)CH, 3-(or 2)CH, and 4-CH in coord aromatic ring], 7.66 (d, ^3J = 9.0 Hz, 1H, 10-CH in central aromatic ring), 7.92, 7.94, 8.14, 8.43 [AMXY, 4H, 6-(or 7), 7-(or 6), 8-, 5-CH in uncoord aromatic ring], 8.24 (d, ^3J = 9.0 Hz, 1H, 9-CH in central aromatic ring). After 1 h at room temperature, NEt_3 (5.0 μL, 0.036 mmol) was added to the NMR tube from a hypodermic syringe. NMR data for **4**-d_4: ^{1}H NMR (300.4 MHz, CD_2Cl_2, 294 K): δ 1.68 (br s, 4H, *exo* protons for 3-, 4-, 7-, and 8-CH_2), 3.01 [br d, ^3J = 8 Hz, 2H, 1-(or 2) and 5-(or 6)CH in COD], 3.34 [br d, ^3J = 8 Hz, 2H, 2-(or 1) and 6-(or 5)CH in COD], 4.91 (d, ^3J = 5.4 Hz, 1H, 1-CH in coord aromatic ring), 5.48 (d, ^3J = 5.4 Hz, 4-CH in coord aromatic ring), 6.07 [t, ^3J = 5.4 Hz, 1H, 2-(or 3)CH in coord aromatic ring], 6.11 [t, ^3J = 5.4 Hz, 1H, 3-(or 2)CH in coord aromatic ring], 7.34 (d, ^3J = 9.0 Hz, 1H, 10-CH in central aromatic ring), 7.6, 7.86, 8.14 (AMXX′, 4H, 6- and 7-, 8-, 5-CH in uncoord aromatic ring), 7.64 (d, ^3J = 9.0 Hz, 1H, 9-CH in central aromatic ring).

Addition of D_2O to an Equilibrium Mixture of [8]PF_6 and [9]PF_6 and Reduction with NEt_3. An equilibrium mixture of [**8**]PF_6 and [**9**]PF_6 (7.9 mg, 0.015 mmol) in CD_2Cl_2 was treated with 10 equiv of D_2O (2.9 μL, 0.15 mmol). NMR data for [**8**-d_5]PF_6: ^{1}H NMR (300.4 MHz, CD_2Cl_2, 298 K): δ 1.6 (br s, 2H, *exo*-7- and 8-CH_2 in COD), 1.7 (br s, 2H, *exo*-3- and 4-CH_2 in COD), 3.1 (m, 2H, 1- and 6-CH in COD), 3.70 (d, ^2J = 17.4 Hz, 2H, *endo*-9- and 10-CH_2 in central ring), 4.04 (d, ^2J = 17.4 Hz, 2H, *exo*-9- and 10-CH_2 in central ring), 4.17 (m, 2H, 2- and 6-CH in COD), 6.06, 6.30 (AA′BB′, 4H, 1- and 4-, 2- and 3-CH in coord aromatic ring), 7.33 (s, 4H, 5-, 6-, 7-, 8-CH in uncoord aromatic ring). NMR data for [**9**-d_5]PF_6: ^{1}H NMR (300.4 MHz, CD_2Cl_2, 298 K): δ 2.63 (s, 8H, 1-, 2-, and 3- and 4-CH, and *exo* protons for 5-, 6-, 7-, and 8-CH_2 in C_8H_{13}), 3.59 (d, ^2J = 16.5 Hz, 2H, *endo*-9- and 10-CH_2 in central ring), 3.85 (d, ^2J = 16.5 Hz, 2H, *exo*-9- and 10-CH_2 in central ring), 5.94 (m, 2H, 1- and 4-CH in coord aromatic ring), 6.1 (2H, 2- and 3-CH in coord aromatic ring: obscured by the signals due to **8**-d_5 and estimated by COSY), 7.3 (4H, aromatic protons in uncoord aromatic ring: obscured by the signals due to **8**-d_5). Addition of NEt_3 (5.0 μL, 0.036 mmol) to a mixture of [**8**-d_5]-PF_6 and [**9**-d_5]PF_6 quantitatively gave **7**-d_4. NMR data for **7**-d_4: ^{1}H NMR (300.4 MHz, CD_2Cl_2, 297 K): δ 1.62 (s, 4H, *exo*-CH_2 in COD), 2.92 (s, 4H, CH in COD), 3.47 (d, ^2J = 16.5 Hz, 2H, *endo*-9- and 10-CH_2 in central ring), 3.92 (d, ^2J = 16.5 Hz, 2H, *exo*-9- and 10-CH_2 in central ring), 4.45, 5.66 (AA′XX′, 4H, 1- and 4-, 2- and 3-CH in coord aromatic ring), 7.23 (m, 4H, 5-, 6-, 7-, and 8-CH in uncoord aromatic ring).

Table 3. Physical and Crystallographic Parameters for 4

formula	$C_{22}H_{22}Ru$
fw	387.49
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a (Å)	11.158(2)
b (Å)	12.752(4)
c (Å)	11.969(2)
β (deg)	113.31(1)
V (Å^3)	1564.0(6)
Z	4
measd temp (K)	93.2
cryst dimens (mm × mm × mm)	0.2 × 0.2 × 0.2
cald density (g cm^{-3})	1.645
μ (cm^{-1})	1.000
radiation	Mo Kα (0.7107 Å)
no. of reflns	3954
reflns av R equivalents	0.044
reflns θ max	27.52
no. of total reflns	3606
no. of reflns used	2465
reflns threshold expression	$F^2 > 3.0\sigma(F^2)$
R (R_w)	0.0563 (0.0731)
goodness of fit	1.802

Reaction of [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)] (1) with Anthracene under H_2. Anthracene (60.7 mg, 0.341 mmol) and **1** (100 mg, 0.317 mmol) were placed in a Schlenk tube into which THF (ca. 5 mL) was introduced by bulb-to-bulb distillation. The solution was stirred under hydrogen atmosphere (0.1 MPa) for 6 h at room temperature. After removal of all volatile material, the resulting solid was extracted with THF and filtered through a Celite pad. The resulting solution was evaporated to dryness to give crude **6** as a light brown solid. It could not be purified because it decomposed readily.

X-ray Structure Analysis of 4. Single crystals of **4** suitable for X-ray analysis were obtained from a mixture of CH_2Cl_2 and hexane. A single crystal was selected by using a monochromated microscope and mounted in a capillary tube (Glass, 0.7 mm ϕ), which was sealed by small flame torch. Diffraction experiments were performed on a Rigaku RASA-7R diffractometer with graphite-monochromated Mo Kα radiation. The crystallographic data and details associated with data collection for **4** are given in Table 3. The data were processed using the teXsan crystal solution package[33] operating on a SGI O2 workstation. The structure was solved by direct methods. An absorption correction was applied with the program Psi Scan. All non-hydrogen atoms were found on difference maps and were refined anisotropically. All hydrogen atoms were located in the calculated positions. Crystallographic thermal parameters and bond distances and angles have been deposited as Supporting Information.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters and bond lengths and angles for **4**. Variable-temperature NMR spectra for the mixture of [**8**]PF_6 and [**9**]PF_6. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0205997

(33) *teXsan*: Crystal Structure Analysis Package; Molecular Structure Corporation: The Woodlands, TX, 1985 and 1999.