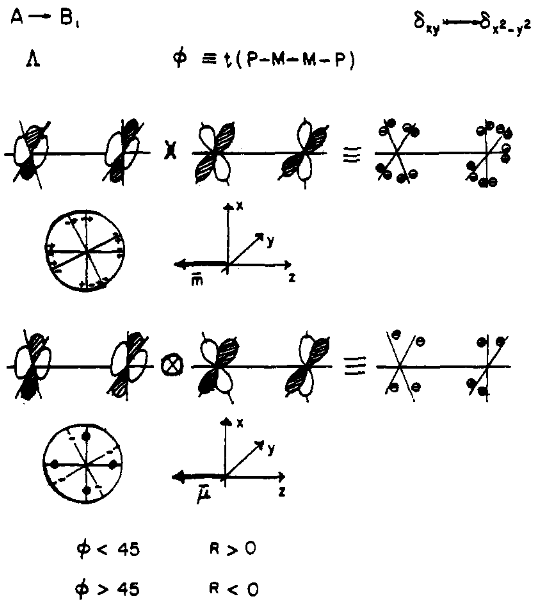

Figure 11. Transition density analysis of the $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ transition.

the next two CD bands are believed to be due to the magnetic dipole $\pi_{yz} \rightarrow \delta^*_{xy}$ and $\pi_{xz} \rightarrow \delta^*_{xy}$ transitions. The highest energy CD is assigned as the electron-dipole-allowed $\pi_{yz} \rightarrow \delta_{x^2-y^2}$ transition. A weak but real CD is observed in the gap between the $\delta_{xy} \rightarrow \delta^*_{xy}$ and $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ transitions, and on careful examination, weak absorption can be detected also. There is no obvious one-electron transition that could give rise to such a very weak absorption (much weaker than the $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ magnetic-dipole transition) in this energy region. We therefore assign the transition as the magnetic- and electric-dipole-forbidden two-electron promotion $\delta_{xy}{}^2 \rightarrow \delta^*_{xy}{}^2$. The energy of this transition is much less than twice its one-electron counterpart, but this is not unexpected since it is known that the electron correlation energy is a major contributor to the $\delta_{xy} \rightarrow \delta^*_{xy}$ energy.

Acknowledgment. We thank the National Science Foundation for support of the work at Texas A&M University, and the SERC for a studentship (to I.F.F.).

Registry No. β-Mo_2Cl_4(*S,S*-dppb)$_2$·C_4H_8O, 88968-77-8; β-Mo_2Cl_4(*S,S*-dppb)$_2$·4CH_3CN, 89015-84-9; β-Mo_2Br_4(*S,S*-dppb)$_2$·$^1/_2C_4H_8O$, 102341-14-0; $Mo_2(O_2CCF_3)_4$, 36608-07-8; $K_4Mo_2Cl_8$, 25448-39-9; Mo, 7439-98-7.

Supplementary Material Available: A table of anisotropic thermal displacement parameters and a view of the entire molecule of β-Mo_2Cl_4(*S,S*-dppb)$_2$ showing the atom-labeling scheme used in the crystal structure of the THF solvate (Figure 2), a complete table of positional parameters for β-Mo_2Br_4(*S,S*-dppb)$_2$, listings of general temperature factors for all three structures, and complete tables of bond lengths and angles for all three structures (27 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Synthesis and Reactivity of $[(\eta^5\text{-}C_5R_5)Ru(\eta^6\text{-arene})]PF_6$ (R = H, CH_3) Complexes of Naphthalene, Anthracene, Pyrene, Chrysene, and Azulene. Kinetic Studies of Arene Displacement Reactions in Acetonitrile Solutions

Amy M. McNair and Kent R. Mann*

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The synthesis and characterization of new $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]PF_6$ and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-arene})]PF_6$ complexes are reported (arene = naphthalene, anthracene, pyrene, chrysene, azulene). Kinetic studies of arene displacement by acetonitrile for five of these complexes are reported. The values obtained for k_{obsd} range from 1.3×10^{-2} s^{-1} to 4.6×10^{-6} s^{-1} in 2.73 M CH_3CN. The differences between the rates observed for the $C_5H_5^-$ complexes and the $C_5(CH_3)_5^-$ compound are explained in terms of an associative mechanism. Rate constants for the ruthenium compounds containing pyrene and chrysene were found to be approximately 4 orders of magnitude larger, respectively, than those for the corresponding Fe complexes. This is believed to be an effect of the difference in the sizes of the two metals and their subsequent susceptibility toward nucleophilic attack. The temperature and concentration dependence of the rate constant k was studied for the reaction of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$ with CH_3CN. The $\Delta S^\ddagger$ of -13.3 (9) eu and $\Delta H^\ddagger = +14.9$ (3) kcal/mol confirm the associative nature of the displacement reaction. The straight-line plot obtained for k_{obsd} vs. $[CH_3CN]$ is consistent with a rate equation of the general form rate = $k[M][CH_3CN]$ where [M] is the concentration of the metal complex. Two mechanisms consistent with the data are proposed and discussed; one includes a preequilibrium between a η^6-arene metal complex and a η^4-arene species, while the other involves direct nucleophilic attack on the metal center of the η^6 complex.

Introduction

Work in our group has concentrated on the photochemical replacement of arenes in $[(\eta^5\text{-}C_5H_5)M(\eta^6\text{-arene})]^+$ and $[(C^5\text{-}C_5(CH_3)_5)M(\eta^6\text{-arene})]^+$ complexes (M = Fe, Ru; $C_6H_5^-$ = cyclopentadienyl anion, $C_5(CH_3)_5^-$ = pentamethylcyclopentadienyl anion; arene = substituted benzene) with ligands such as acetonitrile.[1-4] The photochemical ring-release mechanism is dependent on the nucleophilicity of the incoming ligand and the electronic and steric characteristics of the arene ring. Acetonitrile attack at the metal-centered excited state is believed to be the primary step in these reactions. For arene = substituted benzene, the thermal replacement of the arene by three acetonitrile ligands has not been observed. We now wish to report the synthesis and reactivity of polycyclic aromatic $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+$ and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-arene})]^+$ complexes with the arenes naphthalene, anthracene, pyrene, and chrysene and the pseudo-arene azulene. Many of these new compounds exhibit facile *thermal*

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(1) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.
(2) Schrenk, J. L.; Palazzotto, M. C.; Mann, K. R. *Inorg. Chem.* **1983**, *22*, 4047.
(3) McNair, A. M.; Schrenk, J. L.; Mann, K. R. *Inorg. Chem.* **1984**, *23*, 2633.
(4) Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1980**, *19*, 3007.

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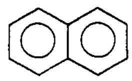
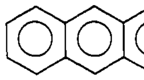


naphthalene



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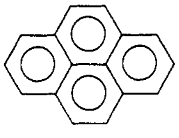
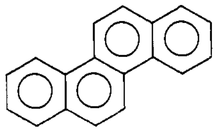
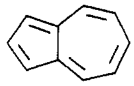


pyrene



chrysene



azulene

arene displacement reactions in acetonitrile to form tris(acetonitrile) adducts (reactions 1 and 2). These reactions occur at

$$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+ + 3CH_3CN \rightarrow [(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]^+ + \text{arene} \quad (1)$$

$$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-arene})]^+ + 3CH_3CN \rightarrow [(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]^+ + \text{arene} \quad (2)$$

room temperature in the absence of light.

Previously, the lability of metal complexes of polycyclic aromatic ligands relative to their substituted-benzene counterparts has been observed.[5-9] Various explanations have been put forth to explain this reactivity. X-ray crystallography of polyaromatic complexes of Cr ($Cr(CO)_3(\eta^6$-arene)) where arene = naphthalene, anthracene, phenanthrene) has revealed significantly longer bond lengths between the metal and the carbon atoms at the ring-fusion positions. This difference in bonding has been proposed to result in facile "ring slippage" and enhanced reactivity.[5,10] Other studies[7] have stressed that complexes of polycyclic aromatic ligands such as naphthalene and phenanthrene with larger localization energies require more energy to localize the six π electrons. This results in complex instability and higher reactivity. Finally, the rearomatization of the unbound portion of the polyaromatic ligand upon either full or partial displacement from the metal may improve the energetics of any rearrangements necessary for activation and subsequent reaction of the metal complexes.[9,11,12]

Kinetic investigations of reactions 1 and 2 were undertaken to discern the mechanism of arene replacement in the new ruthenium complexes. The concentration and temperature dependencies of the reactions were investigated for $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]PF_6$.

Experimental Section

General Considerations. All synthetic procedures were carried out under an inert N_2 atmosphere unless otherwise noted. Solvents used were of spectroscopic grade and were used without further purification. Azulene was purchased from Aldrich Chemical Co. and used without further purification. $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$[1] and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$[13] were prepared by literature procedures. ^1H NMR spectra were recorded on a Varian Associates CFT 20 NMR spectrometer equipped with a 79.5-MHz proton accessory. Chemical shifts, δ, are relative to $(CH_3)_4Si$. The high-field ^1H NMR spectra were recorded on a Nicolet NT-300 MHz instrument. IR spectra were recorded on a Perkin-Elmer 297. UV-Vis spectra were recorded on a Cary 17D spectrometer equipped with computer control. Elemental analyses were performed by MHW Laboratories. $(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-pyrene})PF_6$ and $(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-chrysene})PF_6$ have been previously reported[14] and were obtained as gifts from Dr. M. C. Palazzotto of the 3M Co.

Synthesis of Compounds. $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{10}H_8)]PF_6$. A solution of 50.4 mg (0.393 mmol) of naphthalene in 20 mL of 1,2-dichloroethane was degassed approximately 5 min with nitrogen. Under positive nitrogen pressure, 103.3 mg (0.2318 mmol) of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ was added to this solution and the mixture was degassed an additional 20 min. After the mixture was heated for 18.5 h at just below the reflux temperature, the solvent was removed by rotary evaporation and the mustard-colored solid was washed with ether to remove unreacted naphthalene. The solid was next sent through a short diatomaceous-earth column in dichloromethane and dripped into an ether solution. The pale yellow microcrystalline product was collected to give 92.1 mg of pure $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{10}H_8)]PF_6$ (88% yield), mp 224–226 °C dec. Anal. Calcd for $C_{15}H_{13}RuPF_6$: C, 41.01; H, 2.98. Found: C, 41.17; H, 3.08. ^1H NMR (300 MHz, 1,2-dichloroethane-d_4): δ 4.927 (s, $C_5H_5^-$, 5 H), 6.896 (d of d, $H_{1,4}$, 2 H, J_{vic} = 4.38 Hz, J_{all} = 2.43 hz), 6.203 (d of d, $H_{2,3}$, 2 H, J_{vic} = 4.38 Hz, J_{all} = 2.43 Hz), 7.678 (m, $H_{5,8}$, 2 H), 7.607 (m, $H_{7,6}$, 2 H). Throughout: vic = vicinal; all = allylic.

$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{14}H_{10})]PF_6$. An excess, 74.3 mg (0.171 mmol), of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CH)_3]PF_6$ was added under positive nitrogen pressure to a degassed 1,2-dichloroethane solution of 27.6 mg (0.155 mmol) of anthracene. The solution was degassed an additional 10 min and then heated for 18 h. The resulting orange-yellow solution was rotovapped to dryness and sent through a short diatomaceous-earth column with methylene chloride. The product was precipitated with diethyl ether to give 68.3 mg of light orange $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{14}H_{10})]PF_6\cdot 0.5ClCH_2CH_2Cl$ (82% yield based on anthracene), mp 208–213 °C dec. Anal. Calcd for $C_{20}H_{17}ClRuPF_6$ $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{14}H_{10})]PF_6\cdot 0.5ClCH_2CH_2Cl$: C, 44.58; H, 3.18. Found: C, 44.46; H, 3.57. ^1H NMR (300 MHz, methylene-d_2 chloride): δ 4.868 (s, $C_5H_5^-$, 5 H), 6.332 (d of d, $H_{2,3}$, 2 H, J_{vic} = 4.50 hZ, J_{all} = 2.41 Hz), 7.267 (d of d, $H_{1,4}$, 2 H, J_{vic} = 4.50 Hz, J_{all} = 2.41 Hz), 7.462 (d of d, $H_{6,7}$, 2 H, J_{vic} = 6.84 Hz, J_{all} = 3.21 Hz), 7.863 (d of d, $H_{5,8}$, 2 H, J_{vic} = 6.84 Hz, J_{all} = 3.21 Hz), 8.347 (s, $H_{9,10}$, 2 H).

$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{16}H_{10})]PF_6$. A 78.5-mg (0.181-mmol) sample of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CH)_3]PF_6$ was added to 15 mL of 1,2-dichloroethane containing 52.1 mg (0.258 mmol) of pyrene. The mixture was refluxed for 14 h and the solution removed to yield a yellow solid. The solid was washed until no free pyrene was detected under a UV lamp. The solid was collected, giving 87.2 mg (94% yield) of pure $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{16}H_{10})]PF_6$. Anal. Calcd for $C_{21}H_{15}RuPF_6$: C, 49.13; H, 2.94. Found: C, 48.96; H, 3.13. ^1H NMR (300 MHz, methylene-d_2 chloride): δ 4.680 (s, Cp, 2 H), 6.407 (t, H_2, 1 H, J = 5.95 Hz), 6.896 (d, $H_{1,3}$, 2 H, J = 5.95 Hz), 7.786 (d, $H_{4,10}$, 2 H, J = 9.28 Hz), 8.141 (m, H_{5-9}, 5 H).

$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{18}H_{12})]PF_6$. A solution of 31.9 mg (0.140 mmol) of chrysene in 20 mL of 1,2-dichloroethane was degassed approximately 15 min with nitrogen. Under positive nitrogen pressure, 48.7 mg (0.112 mmol) of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ was added to this solution and the mixture was degassed an additional 20 min. The solution was allowed to stir overnight, and then the solvent was removed by rotary evaporation. The yellow solid was washed numerous times with ether to remove unreacted chrysene. The pale yellow product was collected to give 56.3 mg of pure $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{18}H_{12})]PF_6$ (93% yield), mp 200–202 °C dec. Anal. Calcd for $C_{25}H_{21}Cl,2RuPF_6$ ($[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{18}H_{12})]PF_6\cdot ClCH_2CH_2Cl$): C, 47.04; H, 3.32. Found: C, 47.12; H, 3.96. ^1H NMR (300 MHz, 1,2-dichloroethane-d_4): δ 4.921 (s, $C_5H_5^-$, 5 H), 6.379 (d of d, $H_{2/3}$, 1 H, J = 5.75 Hz), 6.434 (d of d, $H_{2/3}$, 1 H, J = 5.75 Hz), 6.976 (d, H_1, 1 H, J = 5.75 Hz), 7.671 (d, H_4, 1 H, J = 5.75 Hz), 7.747 (d, $H_{11/12}$ or $H_{5/6}$, 1 H, J = 9.50 Hz), 7.705 (d of d of d, $H_{8/9}$, 1 H, J_{vic} = 8.40, J_{all} = 1.35), 7.827 (d of d of d, $H_{8/9}$, 1 H, J_{vic} = 8.40, J_{all} = 1.47), 8.299 (d, $H_{7/10}$, 1 H, J_{vic} = 8.40 Hz, J_{all} = 1.70 Hz), 8.225 (d, $H_{11/12}$ or $H_{5/6}$, 1 H, J = 8.97 Hz), 8.469 (d, $H_{11/12}$ or $H_{5/6}$, 1 H, J = 8.99 Hz), 8.694 (d, $H_{7/10}$, 1 H, J = 8.22), 8.805 (d, $H_{11/12}$ or $H_{5/6}$, 1 H, J = 9.49 Hz).

$[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-}C_{10}H_8)]PF_6$. A solution consisting of 20.7 mg (0.162 mmol) of azulene and approximately 20 mL of 1,2-dichloroethane was degassed with nitrogen for 15 min. Under positive nitrogen pressure, 68.3 mg (0.157 mmol) of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ was added to the blue solution. The solution immediately changed to a deep plum color. The reaction was stirred for 1.5 h to ensure completeness, and the solvent was then removed by rotary evaporation. The resulting dark solid was washed numerous times with hexane to remove unreacted azulene. The product was sent through a short diatomaceous-earth column in methylene chloride two times for further purification. After evaporation of the solvent, 55.1 mg of dark crystalline $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-}C_{10}H_8)]PF_6$ was

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(5) Cais, M.; Fraenkel, D.; Weidenbaum, K. *Coord. Chem. Rev.* **1975**, *16*, 27.

(6) Sievert, A. C.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 489.

(7) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654 and references therein.

(8) Bennett, M. A.; Matheson, T. W. *J. Organomet. Chem.* **1979**, *175*, 87.

(9) Kundig, E. P.; Perret, C.; Spichiger, S. *J. Organomet. Chem.* **1985**, *286*, 183.

(10) Kunz, v. V.; Nowwacki, W. *Helv. Chim. Act* **1967**, *50*, 1052.

(11) Crabtree, R. H.; Parnell, C. P. *Organometallics* **1984**, *3*, 1727.

(12) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396.

(13) A brief account of the synthesis of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$ is given in: McNair, A. M.; Boyd, D. C.; Mann, K. R. *Organometallics* **1986**, *5*, 303. A more detailed description of the synthesis of this compound will appear.[40]

(14) Morrison, W. H.; Ho, E. Y.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3603.

recovered (80% yield). Anal. Calcd for $C_{16}H_{14.5}N_{0.5}RuPF_6$ ($[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-}C_{10}H_8)]PF_6\cdot 0.5CH_3CN$): C, 41.79; H, 3.17. Found: C, 41.64; H, 3.33. ^{1}NMR (300 MHz, acetone-d_6): δ 5.188 (s, $C_5H_5^-$, 5 H), 6.254 (d, $H_{2,9}$, 2 H, J = 2.98 Hz), 6.505 (t, H_1, 1 H, J = 2.98 Hz), 7.385 (d of d, $H_{5,7}$, 2 H, J = 9.39 Hz, J = 9.36 Hz), 7.610 (t of t, H_6, 1 H, J_{vic} = 9.40 Hz, J_{all} = 1.42 Hz), 8.236 (d of d, $H_{4,8}$, 2 H, J_{vic} = 9.36 Hz, J_{all} = 1.42 Hz).

$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{10}H_8)]PF_6$. To a degassed solution of 25 mL of 1,2-dichloroethane and 45.0 mg (0.3511 mmol) of naphthalene was added 69.2 mg (0.1372 mmol) of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$ under positive nitrogen pressure. The solution was degassed further and then heated gently for 3 h. The yellow solution was taken to dryness, and the resultant solid was washed with diethyl ether to remove unreacted naphthalene. Collection of the yellow powder yielded 63.3 g of slightly impure $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{10}H_8)]PF_6$ (91% yield). The powder was purified further by sending a methylene chloride solution of the compound through a short alumina column to remove any remaining naphthalene and then eluting with acetone to recover the pale yellow compound, mp 252–253 °C dec. Anal. Calcd for $C_{20}H_{23}RuPF_6$: C, 47.15; H, 4.55. Found: C, 46.99; H, 4.69. ^{1}H NMR (300 MHz, methylene-d_2 chloride): δ 1.648 (s, $C_5(CH_3)_5^-$, 15 H), 5.929 (d of d, $H_{2,3}$, 2 H, J_{vic} = 4.43 Hz, J_{all} = 2.44 Hz), 6.389 (d of d, $H_{1,4}$, 2 H, J_{vic} = 4.43 Hz, J_{all} = 2.44 Hz), 7.487 (d of d, $H_{7,6}$, 2 H, J_{vic} = 6.73 Hz, J_{all} = 3.20 Hz), 7.690 (d of d, $H_{5,8}$, 2 H, J_{vic} = 6.73 Hz, J_{all} = 3.20 Hz).

$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{14}H_{10})]PF_6$. A 93.1-mg (0.185-mmol) sample of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$ was added to a degassed solution of 15 mL of 1,2-dichloroethane and 42.5 mg (0.238 mmol) of anthracene and degassed for an additional 5 min. During this time a transient green color was observed, which quickly faded to give a bright golden orange solution. The solution was heated gently for 4 h, and the solvent was removed by rotary evaporation. The product was dissolved in a minimal amount of methylene chloride and placed on an alumina column. The column was first eluted with methylene chloride to remove unreacted anthracene and then acetone to yield the product. After addition of diethyl ether, 62.0 mg of deep yellow $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{14}H_{10})]PF_6$ was recovered (60% yield), mp 231–234 °C dec. Anal. Calcd for $C_{24}H_{25}RuPF_6$: C, 51.52; H, 4.50. Found: C, 51.34; H, 4.77. ^{1}H NMR (300 MHz, methylene-d_2 chloride): δ 1.539 (s, $C_5(CH_3)_5^-$, 15 H), 6.025 (d of d, $H_{2,3}$, 2 H, J_{vic} = 4.50 Hz, J_{all} = 2.42 Hz), 6.725 (d of d, $H_{1,4}$, 2 H, J_{vic} = 4.50 Hz, J_{all} = 2.42 Hz), 7.482 (d of d, $H_{6,7}$, 2 H, J_{vic} = 6.77 Hz, J_{all} = 3.19 Hz), 7.887 (d of d, $H_{5,8}$, 2 H, J_{vic} = 6.77 Hz, J_{all} = 3.19 Hz), 8.173 (s, $H_{9,10}$, 2 H).

$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{16}H_{10})]PF_6$. A 32.2-mg (0.159-mmol) sample of pyrene was dissolved in approximately 15 mL of 1,2-dichloroethane and degassed with nitrogen for 20 min. Under positive pressure of nitrogen, 60.8 mg (0.121 mmol) of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$ was added and the mixture was gently heated for 20 h. After removal of the solvent the product was chromatographed on a short alumina column and eluted into diethyl ether. Recovery gave 52.0 mg of bright yellow $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{16}H_{10})]PF_6$ (74% yield), mp 252–256 °C dec. Anal. Calcd for $C_{26}H_{25}RuPF_6$: C, 53.52; H, 4.32. Found: C, 53.34; H, 4.40. ^{1}H NMR (300 MHz, methylene-d_2 chloride): δ 1.311 (s, $C_5(CH_3)_5^-$, 15 H), 6.119 (t, H_2, 1 H, J = 5.89 Hz), 6.403 (d, $H_{1,3}$, 2 H, J = 5.89 Hz), 7.528 (d, $H_{4,10}$, 2 H, J = 9.29), 8.149 (m, H_{5-9}, 5 H).

$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{18}H_{12})]PF_6$. A solution of 37.6 mg (0.165 mmol) of chrysene in 15 mL of 1,2-dichloroethane was degassed approximately 15 min with nitrogen. Under positive nitrogen pressure, 60.0 mg (0.119 mmol) of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$ was added to this solution and the mixture was degassed an additional 20 min. After the mixture was refluxed for approximately 18 h, the solvent was removed by rotary evaporation. The yellow solid was eluted down a short alumina column into a flask of ether to purify and remove the unreacted ligand. The pale yellow product was collected to give 63.3 mg of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{18}H_{12})]PF_6$ (87% yield), mp 257–259 °C dec. Anal. Calcd for $C_{28}H_{27}RuPF_6$: C, 55.17; H, 4.46. Found: C, 55.02; H, 4.42. ^{1}H NMR (300 MHz, 1,2-dichloroethane-d_4): δ 1.496 (s, $C_5(CH_3)_5^-$, 15 H), 6.032 (d of d, $H_{2/3}$, 1 H, J = 5.70Hz), 6.072 (d of d, $H_{2/3}$, 1 H, J = 6.29 Hz), 6.415 (d, H_1, 1 H, J = 5.44 Hz), 7.102 (d, H_4, 1 H, J = 5.82 Hz), 7.498 (d, $H_{11/12}$ or $H_{5/6}$, 1 H, J = 9.44 Hz), 7.758 (d of d of d, $H_{8/9}$, 1 H, J_{vic} = 7.93 Hz, J_{all} = 1.44 Hz), 7.823 (d of d of d, $H_{8/9}$, 1 H, J_{vic} = 7.45 Hz, J_{all} = 1.17 Hz), 8.077 (d, $H_{7/10}$, 1 H, J_{vic} = 8.29 Hz, J_{all} = 1.38 Hz), 8.189 (d, $H_{11/12}$ or $H_{5/6}$, 1 H, J = 9.00 Hz), 8.295 (d, $H_{11/12}$ or $H_{5/6}$, 1 H, J = 8.90 Hz), 8.707 (d, $H_{7/10}$, 1 H, J = 8.47 Hz), 8.846 (d, $H_{11/12}$ or $H_{5/6}$, 1 H, J = 9.46 Hz).

$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-}C_{10}H_8)]PF_6$. A solution of 105 mg (0.230 mmol) of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_6H_6)PF_6$, dissolved in 20 mL of acetonitrile, was placed in a quartz test tube and thoroughly degassed. The tube was then photolyzed for 48 h in front of a standard high-pressure mercury lamp. The solvent was removed under vacuum to yield yellow $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$. A degassed solution of 31.2 mg (0.243 mmol) of azulene in 1,2-dichloroethane was added to the $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$ via cannula. Upon addition of the azulene solution, the solution turned a deep plum color but was allowed to stir for an additional 1 h to ensure completeness of reaction. The solvent was removed under vacuum, and the resultant solid was dissolved in a minimal amount of CH_2Cl_2 and sent through a short diatomaceous-earth column to remove impurities. After precipitation with pentane, 101.2 mg of plum $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-}C_{10}H_8)]PF_6$ was recovered by filtration (86% yield), mp 203–205 °C dec. Anal. Calcd for $C_{20}H_{23}RuPF_6$: C, 47.15; H, 4.55. Found: C, 46.91; H, 4.67. ^{1}H NMR (300 MHz, methylene-d_2 chloride): δ 1.797 (s, $C_5(CH_3)_5^-$, 15 H), 5.592 (d, $H_{2,9}$, 2 H, J = 2.99 Hz), 5.912 (t, H_1, 1 H, J = 2.99 Hz), 7.129 (d of d, $H_{5,7}$, 2 H, J = 9.53 Hz, J = 9.85 Hz), 7.573(d, $H_{4,8}$, 2 H, J = 9.53 Hz, 7.607 (t, H_6, 1 H, J = 9.85).

Reaction of $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-azulene})]PF_6$ with CO. A solution of 20.0 mg (0.0455 mmol) of $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-azulene})]PF_6$ in 5–10 mL of methylene chloride was purged with CO for 45 min. The solution color changed from plum to brown-yellow within 10 min. After the mixture was stirred overnight, the solution color had become dark. The volume was reduced, and pentane was added to precipitate the product. A light gray solid was isolated and was assigned as $[(\eta^5\text{-}C_5H_5)Ru(CO)_3]PF_6$ by comparison to literature values[15,16] (3.2 mg, 21% yield).

Reaction of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-azulene})]PF_6$ with CO. A solution of 40.9 mg (0.0803 mmol) of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-azulene})]PF_6$ in 5–10 mL of methylene chloride was purged with CO for 45 min. After the mixture was stirred overnight under a slow flow of CO, the solution was the bright blue color characteristic of the free ligand, azulene. The volume was reduced, and pentane was added to precipitate the product. A white solid was isolated and was identified as $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CO)_3]PF_6$ by comparison to literature values[17] (26.7 mg, 83% yield).

Thermal Reaction of $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-azulene})]PF_6$ with CD_3CN. A sample of $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-azulene})]^+$ was placed in an NMR tube, protected from light, and 0.5 mL of CD_3CN was added. A proton NMR spectrum of the solution after 15 min indicated that all of the starting material had reacted to give quantitative amounts of free azulene and $[(\eta^5\text{-}C_5H_5)Ru(CD_3CN)_3]PF_6$.

Thermal Reaction of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-azulene})]PF_6$ with CD_3CN. A sample of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-azulene})]^+$ was placed in an NMR tube, protected from light, and 0.5 mL of CD_3CN was added. A proton NMR spectrum of the solution after 10 min indicated that 40% of the starting material had reacted to give free azulene and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CD_3CN)_3]PF_6$.

Measurement of Kinetic Parameters. General Methods for Ruthenium Complexes. The procedure for determining the rate constants involved monitoring the absorption changes that occurred during the course of reaction 1 or 2 as a function of time. Sampling was controlled through computer software designed for this purpose. All samples were delivered into quartz cells equipped with serum stoppers via pipette or syringe from a prepared methylene chloride stock solution of known concentration. Acetonitrile was introduced by syringe while the cell was in the cell holder. Timing of the reaction was begun at the addition of the acetonitrile followed by thorough shaking of the solutions to ensure adequate mixing. Initial concentrations of a given metal compound were kept constant for all runs performed except where noted. All manipulations were carried out in the absence of light.

The value of k_{obsd} for each experiment was determined by least-squares evaluation of a plot of ln $[(A_t - A_f)/l]$ vs. time according to eq 3, where

$$\ln [(A_t - A_f)/l] = \ln [(\epsilon_i - \epsilon_f)C_0] - k_{obsd}t \qquad (3)$$

A_t = absorption at time t, A_f = absorption at infinity, l = path length of cell, ϵ_i = extinction coefficient of reactants at monitoring wavelength, and ϵ_f = extinction coefficient of products at monitoring wavelength. All plots based on eq 3 were linear through at least 6 half-lives. The precision of the rate constants reported here is ±10%.

The procedural modifications for determining the temperature dependence of the arene displacement reaction are as follows. Cells, stock solutions, and acetonitrile were equilibrated in a circulating bath of ethylene glycol/water at the desired temperature for at least $^1/_2$ h before introduction to the cell holder. The temperature of the cells was controlled (±0.5 °C) by circulating the thermostated solvent mixture through a cell holder filled with the ethylene glycol/water mixture. Temperatures were monitored with a copper–constantan thermocouple immersed in the solutions.

Measurement of k_{obsd} for $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-pyrene})]PF_6$ and $[(\eta^5\text{-}C_5(CH_3)_5)Fe(\eta^6\text{-chrysene})]PF_6$. Stock solutions were prepared for both

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(15) Jungbauer, A.; Behrens, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1083.

(16) Kruse, A. E.; Angelici, R. J. *J. Organomet. Chem.* **1970**, *24*, 231.

(17) Nelson, G. O. *Organometallics* **1983**, *2*, 1475.

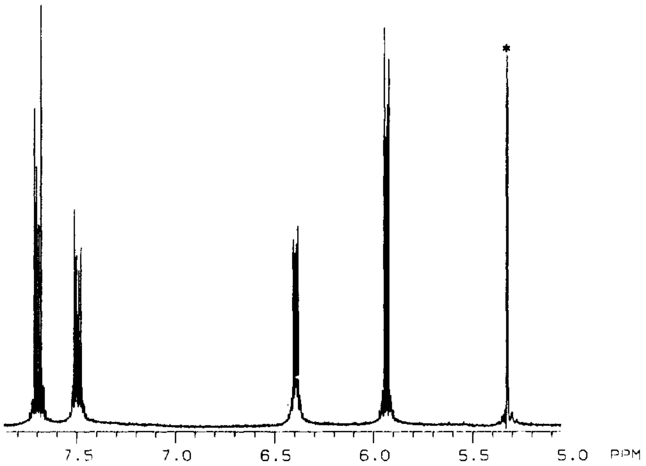


Figure 1. ^{1}H NMR spectrum of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-naphthalene})]^+$ in dichloromethane-d_2 showing an enlargement of the aromatic region. The starred peak is due to solvent.

metal complexes in pure acetonitrile ($[[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-pyrene})]PF_6] = 2.1 \times 10^{-2}$ M; $[[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-chrysene})]PF_6] = 2.0 \times 10^{-2}$ M). Stock solutions were protected from light at all times. Aliquots were removed at time intervals of 2 h–2 days, and changes in absorption after addition of 1,10 phenanthroline were monitored as described previously to determined whether loss of the arene had occurred.[4] Plots of absorbance vs. time yielded straight lines.[18] The slopes were divided by the pseudo-first-order concentrations of metal complex to give values for the pseudo-first-order rate constant k_{obsd} ($[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-pyrene})]^+$, $k_{obsd} = 1.7 \times 10^{-8}$ s^{-1}; $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-chrysene})]^+$, $k_{obsd} = 2.7 \times 10^{-9}$ s^{-1}). To ensure that no secondary processes occurred during the long time period of the experiments (approximately 2 weeks), parallel experiments were performed in the unreactive solvent, methylene chloride. Only slight variations in absorbance due to variations introduced by the sampling techniques were observed.

Results and Discussion

Synthesis, Purification, and Characterization of Compounds. The $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]PF_6$ and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-arene})]PF_6$ complexes arene = naphthalene, anthracene, pyrene, chrysene) are prepared by treatment of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ or $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$ with the appropriate ligand. This general synthetic method has been employed previously in the synthesis of other $C_5H_5^-$ and $C_5(CH_3)_5^-$ ruthenium compounds.[3,13] The replacement of the acetonitrile ligands by the polyaromatic compound is particularly facile, often requiring very little or no heat and short reaction times. Purification of the $C_5(CH_3)_5^-$ compounds was accomplished by column chromatography on alumina with acetone or methylene chloride as the eluant. This procedure works particularly well for the removal of unreacted arene and decomposed starting material. The C_5H_5–Ru–arene compounds are more reactive and decompose in acetone on alumina or silica gel columns. This is presumably due to the more facile removal of the coordinated ring system (vide infra). Successful purification of these complexes was accomplished by elution with methylene chloride on a column of diatomaceous earth. The elutant was run into a flask of diethyl ether to precipitate the product. In this manner both decomposition products and unreacted starting materials were removed. Some decomposition of these compounds occurred in the solid state over long periods of time. Cold storage, in a nitrogen atmosphere, alleviated this problem.

The formulation of these $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]PF_6$ and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-arene})]PF_6$ salts was confirmed through ^{1}H NMR and elemental analyses. The ^{1}H NMR spectrum of the representative complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-naphthalene})]^+$ is shown in Figure 1. All of the new compounds exhibit a characteristic upfield shift of the protons in the ring bound to the ruthenium that allows the identification of the binding mode of the multiring systems. Binding is identical in both the $C_5H_5^-$ and $C_5(CH_3)_5^-$ complexes. The naphthalene ligand is bound through one of the two rings, and the proton NMR spectrum displays two sets of four-line patterns assignable to the protons on this ring (see Figure 1). The anthracene ligand binds through an end ring, leaving the middle ring and one end ring uncomplexed. This is in contrast to the hydrogenation products obtained during previous attempts to synthesize the Fe analogues. These result only in isolation of the 9,10-dihydroanthracene products.[19] The ^{1}H NMR spectrum of the bound anthracene ligand is similar to that of the naphthalene complexes but includes a resonance assigned to the 9,10-position hydrogens. The proposed structures of the pyrene and chrysene compounds are shown.

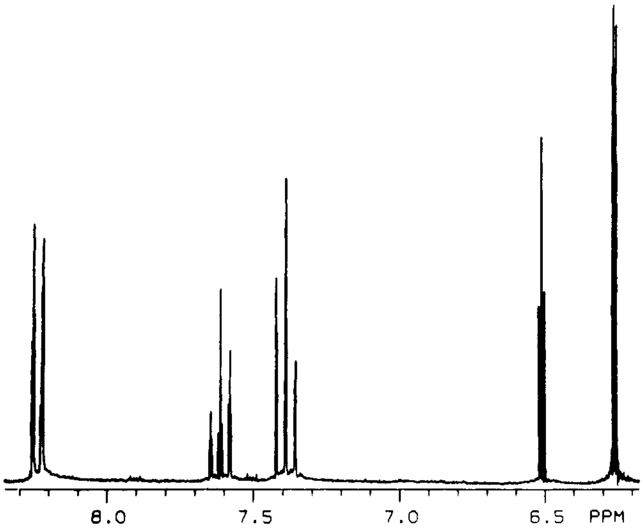
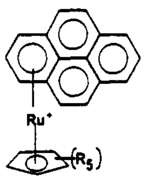
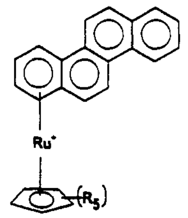


Figure 2. ^{1}H NMR spectrum of $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-azulene})]PF_6$ in acetone-d_6 showing an enlargement of the coordinated azulene resonances.



$[(\eta^5\text{-}C_5R_5)Ru(\eta^6\text{-pyrene})]^+$



$[(\eta^5\text{-}C_5R_5)Ru(\eta^6\text{-chrysene})]^+$

^{1}H NMR spectra of the pyrene adducts reveal a doublet and a triplet shifted upfield from the free ligand resonances that are consistent with the binding mode of the ring assigned. the chrysene complexes display more complicated proton spectra due to the low symmetry of the ring system after ligation to the metal. However, four doublets are shifted upfield, consistent with binding to an end ring rather than a middle ring, which would result in significant shift for only two resonances.

An azulene complex was formed upon addition of the yellow compound $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ to a blue solution of azulene in dichloroethane. An immediate color change occurred to a deep plum color. Purification of the dark solid by column chromatography gave a dark microcrystalline product with an analysis consistent with the formulation $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-}C_{10}H_8)]PF_6\cdot 0.5CH_3CN$. The presence of 0.5 mol of *free* CH_3CN is confirmed by proton NMR and presumably originates from the acetonitrile ligands formerly bound in $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$. The binding mode of the azulene was determined by ^{1}H NMR spectroscopy (Figure 2). The proton NMR spectrum reveals two sets of peaks with the characteristic upfield shift from the uncoordinated ligand, a doublet at 6.254 ppm and a triplet at 6.505 ppm. The splitting patterns of these two sets of

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[18] The extent of decomposition monitored is very small so that pseudo-zero-order kinetics apply.

[19] Sutherland, R. G.; Chen, S. C.; Pannekoek, J.; Lee, C. C. *J. Organomet. Chem.* **1975**, *101*, 221.

Table I. Electronic Absorption Spectra of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]PF_6$ and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-arene})]PF_6$ Complexes[a]

complex	λ_{max} $(\epsilon_{max})^b$
$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-naphthalene})]^+$	364 $(780)^c$
$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-anthracene})]^+$	480 (1320)
$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-pyrene})]^+$	355 $(7470)^c$
$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-chrysene})]^+$	380 $(2066)^c$
$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-naphthalene})]^+$	365 $(760)^c$
$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$	480 (2400)
$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-pyrene})]^+$	360 $(3150)^c$
$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-chrysene})]^+$	370 $(2450)^c$
$[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-azulene})]^+$	515 (1296)
$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-azulene})]^+$	505 (1349)

[a] Determined at 25 °C. [b] Wavelength (λ) in nm; extinction coefficient (ε) in M^{-1} cm^{-1} (±10%). [c] Shoulder.

resonances are consistent with their assignment to the 5-membered ring of the azulene ligand bound in a η^5 manner to the ruthenium atom. The remaining azulene peaks appear between 7.0 and 7.3 ppm and are assigned to the uncoordinated 7-membered ring. The splitting patterns observed for the azulene resonances indicate no structural changes in the ligand other than coordination to the metal center.

$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-azulene})]PF_6$ is synthesized in an analogous manner starting with $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$. The dark plum solid has an elemental analysis consistent with that of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-}C_{10}H_8)]PF_6$ and does not contain solvent molecules of crystallization. The ^1H NMR spectrum is again consistent with binding of the azulene to the ruthenium through the 5-membered ring. The majority of previously reported metal complexes of azulene have demonstrated unusual structural changes in the azulene ligand upon coordination, such as coupling of two azulene rings to form dimers.[20] $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-azulene})]^+$ and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-azulene})]^+$ are notable examples of the few metal complexes of azulene that exhibit normal coordination of an intact azulene to the metal center.

UV-vis absorption spectra were recorded for the compounds in the ligand field (LF) spectral region. These results are summarized in Table I. The wavelength of maximum absorption for all the compounds exhibits a red-shift relative to those of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]PF_6$ complexes in which the arene is a simple benzenoid ring. Spectra consist of a single absorption peak or a shoulder on the low-energy side of an intense UV absorption feature. The low-energy feature is tentatively assigned either to the $a^1E_1 \leftarrow {}^1A_1$ d-d transition by comparison to previous assignments or to a weak MLCT transition.[3] The molar extinction coefficients for the absorption bands in these compounds are large for d-d transitions and may reflect a moderate degree of metal-ligand orbital mixing.

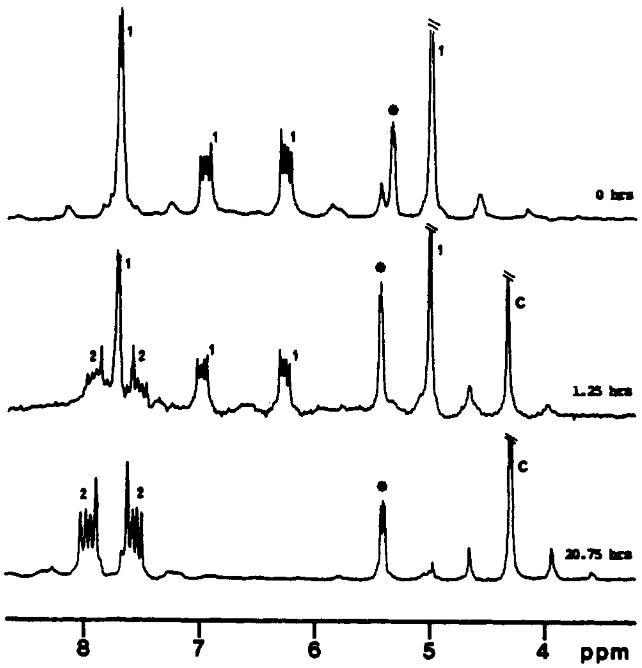

Figure 3. ^1H NMR spectra of the reaction mixture resulting from the reaction of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-naphthalene})]PF_6$ with CD_3CN in CD_2Cl_2 at room temperature. Peaks labeled 1 are due to the starting material; peaks labeled 2 denote free naphthalene, and C is the Cp^- resonance of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$. The starred peak is due to the residual protons in CD_2Cl_2.

Chemical Reactivity Studies. The nature of ligand replacement reactions is of fundamental interest in inorganic chemistry. This type of reaction is an important step in many catalytic and stoichiometric transformations that involve transition-metal complexes.[21,22] For arene complexes, the coordinated arene may be replaced by carbon monoxide, phosphines, phosphites, or solvent molecules or it can be replaced by a different arene. There have been a number of kinetic studies of arene displacement reactions in metal complexes of Cr, Mo, Mn, and W[9,23-30] and arene exchange phenomena in Ir, Cr, Ru, and Mo compounds[6,31-34] in recent years. Although no kinetic data were accumulated, the displacement of the benzene ring from $[Ir(\eta^6\text{-}C_6H_6)(\eta^4\text{-}1,3\text{-cyclohexadiene})]^+$ by phosphines, pyridine, and acetonitrile has also been reported.[35] An associative mechanism with direct attack of the incoming ligand at the metal center is proposed for many of the arene displacement reactions.[23-30] However, a preequilibrium between a η^6-bound arene and a η^4 arene has been proposed for the arene displacement of $[Cr(\eta^6\text{-naphthalene})_2]$ and $[Cr(CO)_3(\eta^6\text{-naphthalene})]$[9] and most arene-exchange[36] reactions.[6,31-34] The existence of a rapid preequilibrium step in these reactions remains consistent with the kinetic data and is supported by theoretical studies that reveal that the direct attack of a nucleophile at the metal is highly unfavorable.[31,37] Rate expressions for both mechanisms are often indistinguishable under the conditions employed (vide infra), and to date no clear answer has been found to explain the data accumulated on these arene-exchange and displacement reactions. Very little hard evidence has been reported to support the presence of a η^6 to η^4 equilibria, but one example of a η^4 intermediate containing the incoming ligand has been provided. Gandolfi and Cais in 1977 reported evidence supporting a $[Cr(CO)_3(\eta^4\text{-naphthalene})THF]$ complex as an intermediate in the solvolysis of $[Cr(CO)_3(\eta^6\text{-naphthalene})]$ in THF.[38] To better understand the mechanism of the acetonitrile

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(20) Dauben, H. J., Jr.; Gadek, F. A.; Harmon, K. M.; Pearson, D. L. *J. Am. Chem. Soc.* **1957**, *79*, 4557.

(21) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967.

(22) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

(23) Al-Kathumi, K. M.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1973**, 1683.

(24) John, G. R.; Kane-Maguire, L. A. P.; Swiegart, D. A. *J. Organomet. Chem.* **1976**, *120*, C47.

(25) Kane-Maguire, L. A. P.; Swiegart, D. A. *Inorg. Chem.* **1979**, *18*, 700.

(26) Al-Kathumi, K. M.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1974**, 428.

(27) Gower, M.; Kane-Maguire, L. A. P. *Inorg. Chim. Acta* **1979**, *37*, 79.

(28) Pidcock, A.; Taylor, B. W. *J. Chem. Soc. A* **1967**, 877.

(29) Zingales, F.; Chiesa, A.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 2707.

(30) Pidcock, A.; Smith, A. D.; Taylor, B. W. *J. Chem. Soc. A* **1967**, 872.

(31) Muetterties, E. L.; Bleeke, J. R.; Sievert, A. C. *J. Organomet. Chem.* **1979**, *178*, 197.

(32) Zimmerman, C. L.; Shaner, S. L.; Roth, S. A.; Willeford, B. R. *J. Chem. Res., Synop.* **1980**, 108.

(33) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(34) Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 4445.

(35) Draggett, P. T.; Green, M.; Lowrie, S. F. W. *J. Organomet. Chem.* **1977**, *135*, C60.

(36) The discrimination between "arene displacement" and "arene exchange" has been challenged in view of growing opinion that the initial steps of arene-exchange phenomena actually involve the stepwise displacement of the arene by solvent molecules.

(37) Albright, T. A.; Carpenter, B. K. *Inorg. Chem.* **1980**, *19*, 3092.

Table II. Kinetic Data[a] for Reactions of $[(\eta^5\text{-}C_5R_5)Ru(\eta^6\text{-arene})]PF_6$ (R = H, CH_3) and $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-arene})]PF_6$ with CH_3CN

complex	k_{obsd},[b] s^{-1}
$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-naphthalene})]^+$	4.1×10^{-5} (3)
$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-anthracene})]^+$	1.3×10^{-2} (3)
$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-pyrene})]^+$	3.7×10^{-5} (3)
$[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-chyrsene})]^+$	4.6×10^{-6} (1)
$[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$	2.7×10^{-3} (3)
$[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-chrysene})]^+$	2.7×10^{-9} (2)
$[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-pyrene})]^+$	1.7×10^{-8} (2)

[a] Data recorded at 22 ± 3 °C. $[CH_3CN] = 2.73$ M in CH_2Cl_2 for the Ru complexes; $[CH_3CN] = 19.14$ M for the Fe complexes. [b] Number in parentheses represents the number of determinations averaged. k_{obsd} is the pseudo-first-order rate constant.

displacement of the polyaromatic ring in the C_5H_5–Ru and $C_5(CH_3)_5$–Ru polyaromatic complexes, chemical reactivity and kinetic studies were initiated under a variety of conditions.

The arene complexes are stable in CH_2Cl_2 solutions, but thermal displacement is facile in CH_3CN. This behavior contrasts with that observed for $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-benzene})]^+$, which may be refluxed in CH_3CN for days in the dark with no apparent reaction. The extent of displacement of the polycyclic aromatic arene ligands in acetonitrile solutions was monitored through the use of ^1H NMR spectroscopy. In all cases thermal reaction at room temperature results in the complete conversion to the tris(acetonitrile) complex and free ligand. Proton NMR spectra that follow the reaction of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-naphthalene})]PF_6$ with acetonitrile-d_3 in dichloromethane-d_2 are depicted in Figure 3. The related azulene complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-azulene})]PF_6$ or $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-azulene})]PF_6$ that are bound through the C_5 ring and might be expected to show the inert behavior exhibited by ruthenocene rapidly undergo azulene displacement by acetonitrile upon dissolution. For both complexes the ring replacement occurred rapidly (100% conversion in 15 min for $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-azulene})]PF_6$ and 40% conversion of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-azulene})]PF_6$ in 10 min) and cleanly as determined by the appearance of new resonances at 4.29 and 1.60 ppm assignable to $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$, respectively.

The higher reactivity of the azulene complexes is also illustrated via the reactions of the complexes with the weaker nucleophile CO, which displaces the azulene in both of these complexes. Bubbling a solution of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-anthracene})]^+$ with CO for 20 h led to no observable reaction. In contrast, bubbling a solution of $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-azulene})]PF_6$ with CO results in a change in color to yellow-brown after a few minutes. A new $C_5H_5^-$ resonance at 5.50 ppm as well as new bound-azulene resonances are observed when a proton NMR spectrum of this brown solution is recorded. After CO has been passed through the solution for additional time, the solution turns dark blue-green, indicative of uncoordinated azulene. Workup of the reaction mixture yielded a gray precipitate. This gray precipitate is identified as $[(\eta^5\text{-}C_5H_5)Ru(CO_3]PF_6$ by comparison of its IR and NMR spectra with literature values.[15,16] Similar reactivity is observed when a solution of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-azulene})]PF_6$ is treated with a stream of CO. At intermediate times, a new $C_5(CH_3)_5^-$ resonance is observed in the proton NMR spectrum, and at completion, a blue solution of azulene and a white powder are obtained. NMR and IR characterization of this powder agrees well with literature values reported for $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CO)_3]PF_6$.[17] In both reactions the final complex reflects complete displacement of the azulene with coordination of three CO ligands. The intermediates in these reactions were not successfully isolated because they are contaminated by the presence of both the starting material and the final product.

Kinetic Measurements of Arene Displacement by CH_3CN. The k_{obsd} values for the acetonitrile displacement reaction (reactions 1 and 2) were measured in CH_2Cl_2/CH_3CN, with UV–vis spectroscopy, for the following compounds: $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]PF_6$ (arene = naphthalene, anthracene, pyrene, chrysene), $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-arene})]PF_6$ (arene = anthracene). These data are summarized in Table II. The changes that occur in the UV–vis spectrum, from 600 to 300 nm, were recorded for one trial of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-pyrene})]^+$ (see Figure 4), but otherwise reactions were monitored at one wavelength by using software specifically designed for this purpose. The rate constants for the reactions of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-naphthalene})]^+$, $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-pyrene})]^+$, and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-chrysene})]^+$ were not measured spectrophotometrically due to the slow rate of reaction for these complexes. As estimated by ^1H NMR, these reactions were from 20 to 100 times slower than the analogous reaction of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene}]^+$, in the order chrysene < pyrene < naphthalene.[39]

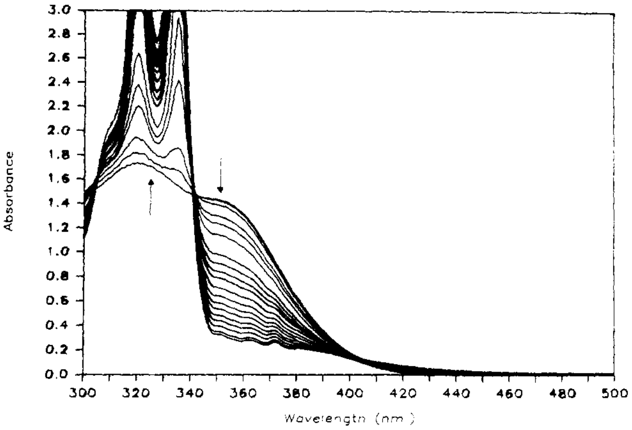

Figure 4. UV–vis spectra recorded during the reaction of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-pyrene})]^+$ with CH_3CN in CH_2Cl_2. The high-energy absorption band increases while the low-energy band decreases as the reaction proceeds. Spectra were obtained over approximately a 20-h time period.

The pseudo-first-order rate constants (Table II) measured for the $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-polyaromatic})]^+$ complexes with $[CH_3CN] = 2.73$ M are between 1.3×10^{-2} and 4.6×10^{-6} s^{-1} in the order anthracene > naphthalene > pyrene > chrysene. The k_{obsd} measured for $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$ (2.7×10^{-3} s^{-1}) is approximately a factor of 5 smaller than that measured for the corresponding $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-anthracene})]^+$ complex (1.3×10^{-2} s^{-1}). An increase in the Ru–arene bond strength in the $C_5(CH_3)_5^-$ complex or greater steric restriction due to the five methyl groups may cause the observed decrease in rates. A trend of similar magnitude is seen in the photochemical arene release from ruthenium complexes of $C_5H_5^-$ and $C_5(CH_3)_5^-$.[40] In the photochemical reaction the effect stems from electronic rather than steric considerations.

The values of k_{obsd} for the displacement of arene from $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-pyrene})]PF_6$ and $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-chrysene})]PF_6$ in pure (19.14 M) CH_3CN were measured for comparison with the ruthenium complexes (measured in 2.73 M CH_3CN). Surprisingly, the compounds exhibit rate constants about 4 orders of magnitude *slower* than their ruthenium analogues, respectively (with the assumption that complexes of each metal react via a second-order mechanism: arene = pyrene, M = Ru, $k_{obsd} = 3.7 \times 10^{-3}$ s^{-1}; arene = pyrene, M = Fe, $k_{obsd} = 1.7 \times 10^{-8}$ s^{-1}; arene = chrysene, M = Ru, $k_{obsd} = 4.6 \times 10^{-6}$ s^{-1}, arene = chrysene, M = Fe, $k_{obsd} = 2.7 \times 10^{-9}$ s^{-1}). In studies of $[(\eta^6\text{-arene})M(CO)_3]^+$ complexes (M = Mn, Re) attack at the metal by acetonitrile is much more rapid at Re.[22] The difference in the size of the two metals is believed to control the magnitude of the rate constant. An associative mechanism for arene displacement for the Re and Mn systems has been suggested. In a similar manner the C_5H_5–Ru–polyaromatic complexes are more susceptible to

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(38) Gandolfi, O.; Cais, M. *J. Organomet. Chem.* **1977**, *125*, 141.

(39) Despite the low thermal reactivity of these three compounds, they all display very facile displacement of the polycyclic aromatic rings under *photochemical* conditions.[40]

(40) Schrenk, J. L.; McNair, A. M.; McCormick, F. B.; Mann, K. R., submitted for publication in *Inorg. Chem.*

(41) ΔH^* and ΔS^* were obtained from an Eyring plot.

Table III. Concentration Study of the Kinetics of Reaction of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]PF_6$ with CH_3CN^a in CH_2Cl_2

$[CH_3CN]$, M	k_{obsd},^{b} s^{-1}	$[CH_3CN]$, M	k_{obsd},^{b} s^{-1}
1.125	6.4×10^{-3} (3)	10.44	1.3×10^{-2} (5)
2.73	2.7×10^{-4} (3)	14.35	1.5×10^{-2} (6)
6.38	8.0×10^{-3} (4)	16.24	2.0×10^{-2} (5)
9.07	8.2×10^{-3} (5)	18.01	2.2×10^{-2} (5)

^{a}The initial [complex] was maintained at approximately 4×10^{-4} M for all runs. ^{b}Number in parentheses represents the number of determinations averaged. k_{obsd} is the pseudo-first-order rate constant.

Table IV. k_{obsd} Values for Reaction of 9.07 M Acetonitrile in CH_2Cl_2 with $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]PF_6$ at Different Temperatures^a

T, °C	k_{obsd},^{b} s^{-1}	T, °C	k_{obsd},^{b} s^{-1}
2	1.3×10^{-3} (1)	11	3.0×10^{-3} (4)
5	1.6×10^{-3} (1)	21	8.1×10^{-3} (5)
6	1.8×10^{-3} (1)	30	1.6×10^{-2} (4)

^{a}The initial [complex] was maintained at approximately 4×10^{-4} M for all runs. ^{b}Number in parentheses represents the number of determinations averaged. k_{obsd} is the pseudo-first-order rate constant.

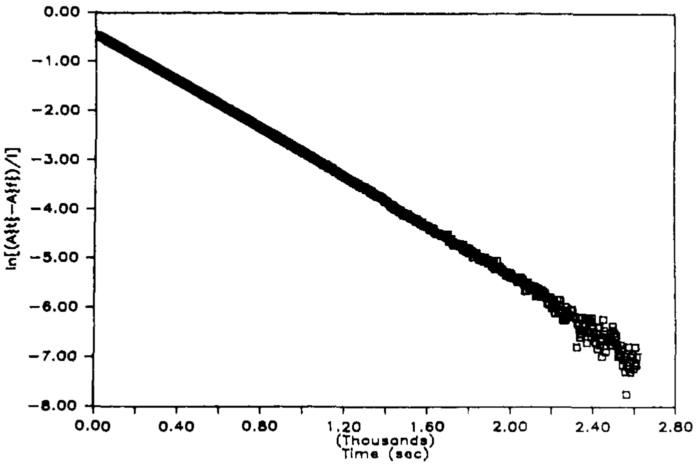


Figure 5. Plot of ln $[(A_t - A_f)/I]$ vs. time for $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$ in 2.73 M acetonitrile/dichloromethane at 22 °C. The absorbance was monitored at 480 nm.

nucleophilic attack than the Fe compounds and might be expected to have larger k_{obsd} values if the reaction is associative.

A study of the effect of varying the concentration of acetonitrile on the rate of arene displacement was completed to determine the order of the reaction in acetonitrile concentration. The reaction of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]PF_6$ was chosen for detailed study because of the relative ease of obtaining the large amount of metal complex required and the convenient time scale for its reaction with CH_3CN. k_{obsd} under pseudo-first-order conditions was measured at eight different acetonitrile concentrations between 1 and 18 M. The data are summarized in Table III, and a plot of ln $[(A_t - A_f)/I]$ vs. time for a typical kinetic run is shown in Figure 5. Plots of k_{obsd} vs. $[CH_3CN]$ (Figure 6) yield a straight line that passes through the origin, indicating a first-order dependence of the reaction on acetonitrile concentration. The variation of k_{obsd} with $[CH_3CN]$ for $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$ is consistent with an overall second-order rate law for arene displacement with a second-order rate constant $k = 1.2 \times 10^{-3}$ M^{-1} s^{-1}. Activation parameters for the reaction of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$ with acetonitrile were obtained from an Arrhenius plot (Figure 7) of rate data (Table IV) collected over a 28 °C temperature range with $[CH_3CN] = 9.07$ M. A least-squares fit of the six points gave $E_a = +15.4$ (3) kcal/mol and ln $A = 19.3$ (4) with derived values of $\Delta H^{*} = +14.9$ (3) kcal/mol and $\Delta S^{*} = -13.3$ (9) eu.

Discussions of Proposed Reaction Mechanisms. The data collected are consistent with a second-order rate expression: rate $= k[M][CH_3CN]$ (M = the metal complex). We have considered

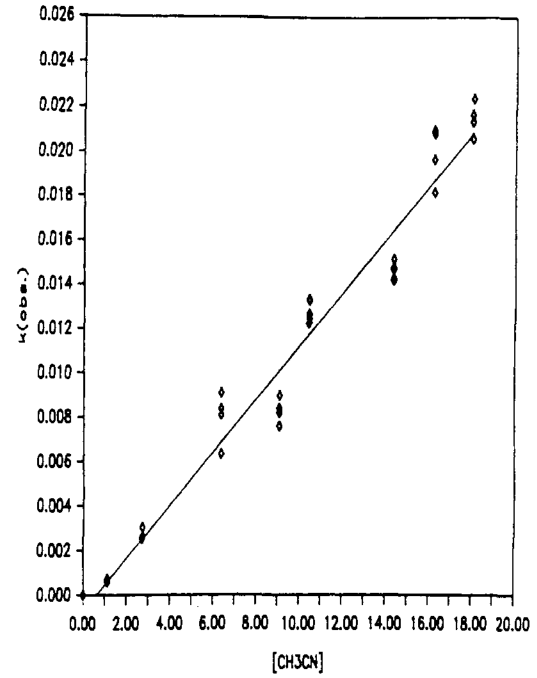


Figure 6. Plot of k_{obsd} vs. $[CH_3CN]$ for the reaction of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$ with acetonitrile in dichloromethane. The values of k_{obsd} are those from Table III. The least-squares straight line has slope = 1.20×10^{-3} M^{-1} s^{-1}; intercept = -7.5×10^{-4} s^{-1}.

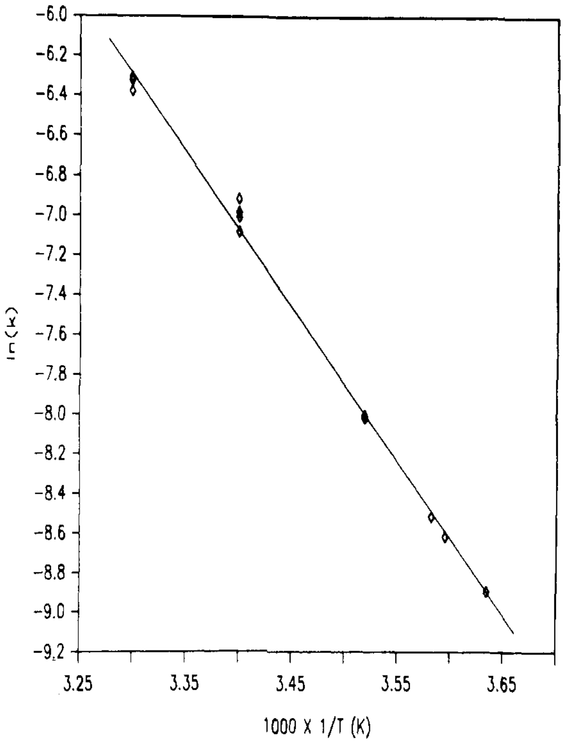
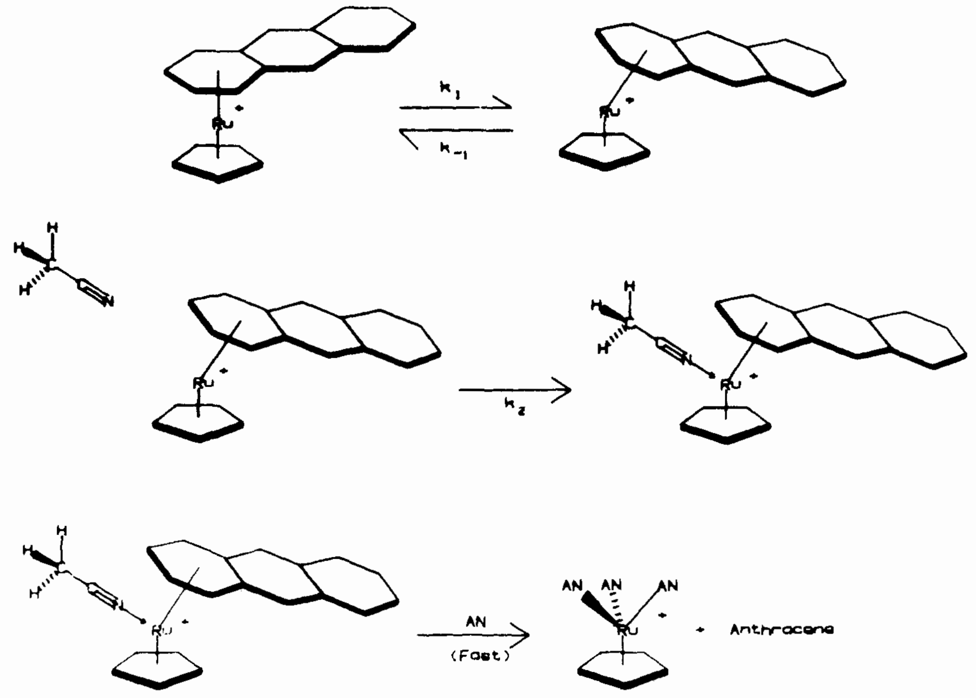


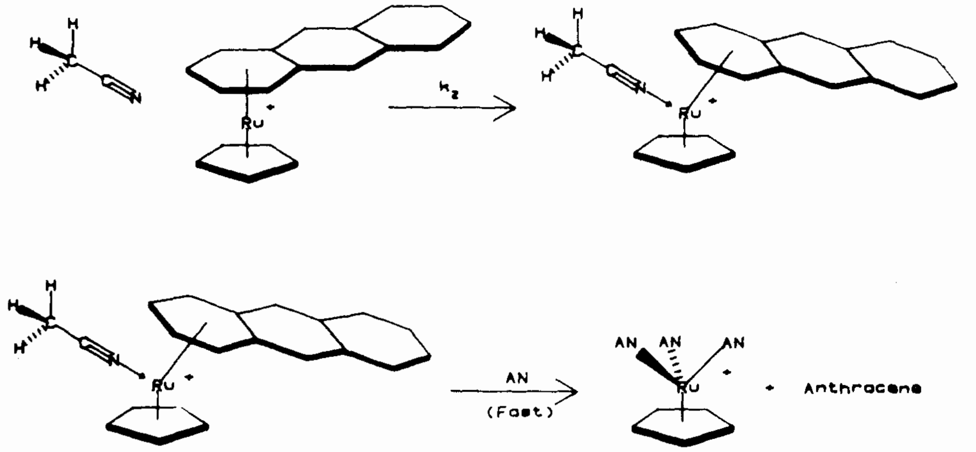
Figure 7. Plot of ln k vs. $1/T$ for the reaction of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$ in acetonitrile. The second-order rate constant values are derived from those in Table III by dividing the table values of $[CH_3CN] = 9.07$ M. The least-squares straight line has slope = -7.77×10^3 mol K; intercept = 19.34.

two mechanisms for the arene displacement from $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+$ and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-arene})]^+$ polyaromatic complexes by acetonitrile. In the first mechanism a preequilibrium between the parent η^6-bound arene complex and a coordinatively unsaturated, η^4-bound complex precedes acetonitrile attack at the metal center (Scheme I). In the second mechanism (Scheme II), direct attack of the acetonitrile at the η^6 metal complex produces $[(\eta^5\text{-}C_5H_5)Ru(\eta^4\text{-arene})(CH_3CN)]^+$ via either a purely associative mechanism or an interchange mechanism of associative character.

Scheme I. $\eta^6 \rightleftharpoons \eta^4$ Preequilibrium Mechanism for Displacement of Anthracene by Acetonitrile in $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$ (Methyl Groups Omitted for Clarity)



Scheme II. Direct Nucleophilic Attack Mechanism for Displacement of Anthracene by Acetonitrile in $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$ (Methyl Groups Omitted for Clarity)



In both mechanisms, further attacks by additional CH_3CN molecules are assumed to be rapid. The steady-state rate equation for Scheme I is shown in eq 4. At high concentrations of CH_3CN,

$$\text{rate} = \frac{k_2k_1[M][CH_3CN]}{k_{-1} + k_2[CH_3CN]} \qquad (4)$$

a saturation effect is predicted. Experimentally, a linear dependence of the rate on acetonitrile concentration is observed with no saturation up to 18.01 M $[CH_3CN]$. This result is consistent with the rate law in eq 4 if $k_{-1} \gg k_2[CH_3CN]$. For this situation, the approximate rate law is

$$\text{rate} \approx k_2K[M][CH_3CN] \qquad (5)$$

where $K = k_1/k_{-1}$ is mathematically indistinguishable from the rate expression derived for Scheme II (eq 6). The concentration

$$\text{rate} = k_2[M][CH_3CN] \qquad (6)$$

dependence of the arene displacement rate is then consistent with either mechanism. The negative $\Delta S^{\ddagger}$ derived from the temperature dependence data indicates that the reaction shows considerable associative character, also consistent with either mechanism.

To obtain direct evidence for the intermediacy of coordinatively unsaturated η^4 species in the absence of nucleophiles, variable-temperature ^1H NMR spectra were recorded for $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-naphthalene})]^+$, $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-anthracene})]^+$, and $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$. When dichloroethane solutions of either $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-naphthalene})]^+$ or $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$ are heated to 110 °C in the NMR spectrometer probe, neither line broadening nor coalescence of the NMR signals is observed. Cooling a methylene chloride solution of $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-anthracene})]^+$ to −100 °C in the NMR probe also has no affect on the coordinated anthracene ^1H NMR signals. This indicates that, under these conditions, migration of the Ru atom from one ring to another and Ru–arene bond cleavage are slow on the NMR time scale. The behavior of these complexes parallels that of $[Cr(CO)_3(\eta^6\text{-naphthalene})]$, $[Cr(\eta^6\text{-naphthalene})_2]$, $[(\eta^5\text{-}C_5H_5)Ir(\eta^6\text{-naphthalene})](PF_6)_2$, and $[(C^5\text{-}C_5H_5)Ir(\eta^6\text{-phenanthrene})](PF_6)_2$, which have been investigated previously.[7,9,42] The absence of rapid movement[43] of the

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(42) Nicholas, K. M.; Kerber, R. C.; Stiefel, E. I. *Inorg. Chem.* **1971**, *10*, 1519.

(43) "Rapid movement" includes dissociation of the arene, a $\eta^6 \rightarrow \eta^4$ "ring slip", and the $\eta^6 \rightarrow \eta^{6'}$ movement (i.e., η^6 end ring to η^6 center ring). All of these processes have been treated theoretically[12] and are relatively high-energy processes.

metal with respect to the ring system is consistent with theoretical studies.

Although these NMR studies offered no direct evidence for intermediate species of reduced hapticity in the arene systems, the observation of intermediates in the reactions of the azulene complexes in CH_2Cl_2 solutions with the very weak nucleophile CO and the rapidity of the reactions indicate that the mechanism for arene replacement in this case quite likely occurs through an $\eta^5 \rightleftharpoons \eta^3$ preequilibrium. The trapping efficiency of the weak nucleophile CO at low concentrations suggests that kinetic measurements conducted on the reaction of the Ru–azulene systems with better nuclephiles at high concentration may show the expected saturation effect and further support the operation of a $\eta^6 \rightleftharpoons \eta^4$ preequilibrium in the arene systems.

Acknowledgment. A.M.M. acknowledges a Louise T. Dosdall Fellowship in Science. This research was supported by Department of Energy Grant DOE/DEAC02-83ER13103. The Cary Model 17-D spectrometer was made available by funding received in part from the National Science Foundation (Grant CHE-23857).

Registry No. $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{10}H_8)]PF_6$, 102538-40-9; $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{14}H_{10})]PF_6$, 102575-39-3; $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{16}H_{10})]PF_6$, 102575-41-7; $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_{18}H_{12})]PF_6$, 102538-42-1; $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-}C_{10}H_8)]PF_6$, 102538-44-3; $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{10}H_8)]PF_6$, 102575-43-9; $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{14}H_{10})]PF_6$, 102575-45-1; $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{16}H_{10})]PF_6$, 102575-47-3; $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_{18}H_{12})]PF_6$, 102538-46-5; $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^5\text{-}C_{10}H_8)]PF_6$, 102575-49-5; $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_{18}H_{12})]^+$, 92140-26-6; $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_{16}H_{10})]^+$, 70755-98-5; $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$, 80049-61-2; $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CH_3CN)_3]PF_6$, 99604-67-8; $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-}C_6H_6)]PF_6$, 99631-48-8; $[(\eta^5\text{-}C_5H_5)Ru(CO)_3]PF_6$, 31741-71-6; $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CO)_3]PF_6$, 102538-47-6; $[(\eta^5\text{-}C_5H_5)Ru(CD_3CN)_3]PF_6$, 102538-49-8; $[(\eta^5\text{-}C_5(CH_3)_5)Ru(CD_3CN)_3]PF_6$, 102538-51-2.

Supplementary Material Available: ^1H NMR spectra of $[(\eta^5\text{-}C_5(CH_3)_5)Ru(\eta^6\text{-anthracene})]^+$, $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-pyrene})]^+$, and $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-chrysene})]^+$ (3 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Polyaza Cavity-Shaped Molecules. 9. Ruthenium(II) Complexes of Annelated Derivatives of 2,2′:6,2″-Terpyridine and Related Systems: Synthesis, Properties, and Structure

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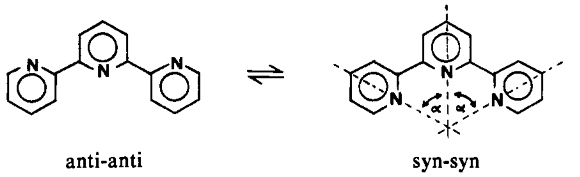
Annelated derivatives of 2,2′:6,2″-terpyridine and their dibenzo- and dipyrido-fused analogues coordinate with ruthenium(II) in an octahedral fashion even when the conformation of the free ligand is highly distorted from planarity. NMR chemical shift data have been used as a sensitive probe of shielding and deshielding effects dependent upon the relative orientation of the terpyridine ligands about the metal atom. An X-ray structure has been determined for the complex $Ru(\mathbf{1d})_2[PF_6]_2$ with the molecular formula $C_{48}H_{52}F_{12}N_6OP_2Ru$, which crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell and a = 10.237 (1) Å, b = 13.250 (1) Å, c = 19.761 (3) Å, α = 73.59 (1)°, β = 89.59 (1)°, and γ = 72.22 (1)°. Coordination of ruthenium(II) with the bis(tetramethylene)-bridged terpyridine **1d** does not greatly alter the geometry of complexation at the metal center. Instead the ligand distorts to accommodate coordination and a substantial degree of this distortion is manifested by nonplanarity in the individual pyridine rings. Despite these changes, which might be expected to affect the electronic properties of the complex, no dramatic differences are observed in the electronic absorptions as a function of bridge length.

Introduction

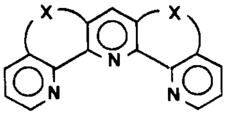
When pyridine rings are bonded to one another through their 2- and/or 6-positions, a situation is created where trigonal nitrogen atoms are joined in a 1,4-fashion that is particularly favorable to metal chelate ring formation. The prototypical example is 2,2′-bipyridine, which is known to form a wide variety of bidentate metal complexes. The next higher homologue, 2,2′:6,2″-terpyridine,[1] is also an excellent ligand, which can act in a tridentate fashion, forming two five-membered chelate rings that share a common bond between the metal and central nitrogen.

Two important observations can be made regarding terpyridine as a ligand. In its uncomplexed form this molecule is postulated to exist in an anti-anti conformation in which the H–H and nitrogen lone-pair repulsions are minimized.[2] To coordinate effectively terpyridine must adopt the syn-syn conformation. Relatively free rotation about the 2,2′- and 6,2″-bonds make this conformation readily accessible. If one assumes an unperturbed hexagonal geometry for the pyridine rings, the locus of the axes passing through the center of each ring would be significantly outside the cavity of the molecule. If a metal atom were to be located at this locus, coplanar with and equidistant from all three pyridines, the N–M–N bond angles (α) would be about 60°, which is substantially distorted from the orthogonality preferred by octahedral metal complexes.



anti-anti syn-syn

We have recently synthesized a series of bisannelated terpyridines (**1b–d**) in which the relative orientation of the three connected pyridine rings is controlled by polymethylene bridges between the 3,3′- and 5,3″-positions. Both the dihedral angles



1a, X = H, H
b, X = $(CH_2)_2$
c, X = $(CH_2)_3$
d, X = $(CH_2)_4$

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(1) The central ring of terpyridine is assigned unprimed numbers to preserve consistency among structures **1**, **2**, and **3**.

(2) Nakamoto, K. *J. Phys. Chem.* **1960**, *64*, 1420.

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