Reactions of Polycyclic Arene Systems Stabilized and Activated by Cyclopentadienylruthenium Cations

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One vinylidene group of [(CpRu)(η^6-dibenzo-*p*-quinodimethane)]$^+PF_6^-$ (1) (Cp = η^5-cyclopentadienyl), in which highly reactive dibenzo-*p*-quinodimethane is stabilized by coordination to ruthenium, underwent Diels–Alder cycloaddition from the *exo* face with 2,3-dimethyl-1,3-butadiene to give a novel spiro derivative of dibenzo-*p*-quinodimethane (2). X-ray analysis of 2 ($C_{27}H_{27}F_6PRu$) confirmed its structure and showed it to crystallize in the monoclinic space group $P2_1/n$ with a = 16.079(5) Å, b = 11.682(3) Å, c = 13.508(4) Å, β = 91.03(3)°, and Z = 4. The Cp* (Cp* = η^5-pentamethylcyclopentadienyl) analogue of 1 did not react with 2,3-dimethyl-1,3-butadiene. The η^6-localization effect of cyclopentadienylruthenium cations can also be used to activate polycyclic aromatic hydrocarbons toward Diels–Alder and catalytic hydrogenation reactions. [(Cp*Ru)(η^6-anthracene)]$^+$TfO$^-$ (3) underwent quantitative Diels–Alder reaction from the *exo* face with maleic anhydride under mild conditions (83 °C) to give [*trans*-(*endo*-Cp*Ru)(η^6-9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride)]$^+$TfO$^-$ (4) selectively. Reaction of anthracene under identical conditions gave only 19% conversion. Reaction of maleic anhydride with [CpRu(η^6-naphthalene)]$^+PF_6^-$ (6) was not successful. However, hydrogenation of 6 in methanol (1 atm, 24 °C, 6 h) took place smoothly in the presence of a heterogeneous Pd/C catalyst to give [CpRu(η^6-1,2,3,4-tetrahydronaphthalene)]$^+PF_6^-$ (7) in high yield. The Cp* analogue of 6 gave similar results. Noncomplexed naphthalene remained largely unreacted under identical conditions (61% remaining), and a substantial proportion remained (32%) after 24 h. The Cp*Ru and CpRu groups in 4 and 7 can be removed by photolysis in acetonitrile to cleanly give 9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride (5) and 1,2,3,4-tetrahydronaphthalene (8), respectively, as well as generating Cp– and Cp*–ruthenium tris(acetonitrile) salts, which can be used to make more complexed arene.

Introduction

It has long been known that coordination to a transition metal will modify the π system of aromatic compounds, resulting in changes in electronic structure and chemical properties. The use of transition metal moieties to activate arenes has attracted a considerable amount of attention, particularly if the arene is activated toward reactions that are unfavorable or even unknown in the free arene. Most prominent is the use of $Cr(CO)_3$ and $CpFe^+$ fragments to activate substituted arenes toward nucleophilic aromatic displacement.[1] Activation of aromatic hydrocarbons is relatively rare. It has recently been shown that phenyl compounds can complex with $(NH_3)_5Os^{2+}$ in an η^2-coordination fashion, disrupting aromaticity and resulting in systems where the rest of the ring acts like a diene toward catalytic hydrogenation and other reactions.[2] It has also been shown that naphthalene can complex with $(NH_3)_5Os^{2+}$ in an η^2-coordination fashion, disrupting aromaticity and resulting in 6-electron aromatic localization in the noncomplexed ring. The "nonaromatic" part of the molecule then acts like an organometallic derivative of a polyene.[3] These results show that coordination of a polycyclic aromatic hydrocarbon with a metal moiety to cause aromatic localization in one ring and disrupt aromaticity in the rest of the molecule is a viable strategy toward enhancing and controlling its reactivity.

$CpRu^+$ and Cp^*Ru^+ fragments (Cp = η^5-cyclopentadienyl, Cp* = η^5-pentamethylcyclopentadienyl) fragments show a high affinity for π-arene coordination under mild conditions to form sandwich compounds of the type [Cp(*)Ru(arene)]$^+$.[4-16] We have recently reported utilization of the strong η^6-localization effect of Cp(*)Ru$^+$ fragments to stabilize the active organic species dibenzo-*p*-quinodimethane and have studied the structure and reactivity of the resulting complexes.[14-16] Dibenzo-*p*-quinodimethane can otherwise only be generated with difficulty, in small amounts at low temperature, so little is known about its reactivity other than spontaneous

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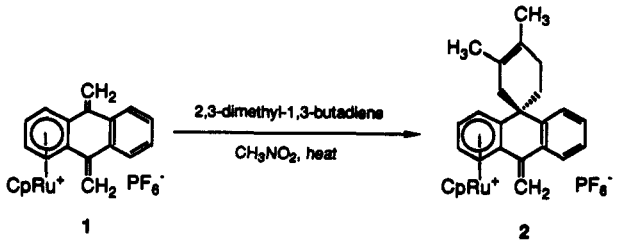
Scheme 1



1 2

dimerization or polymerization on warming.[17,18] Stabilization of dibenzo-*p*-quinodimethane by η^6-localization of one of its benzo rings allows it to take part in reactions which are otherwise difficult or impossible to perform using the parent hydrocarbon.[15] In principle, the same η^6-complexation effect used to stabilize dibenzo-*p*-quinodimethane could be used to localize one benzene moiety of a polycyclic arene, reducing the aromatic character of the rest of the ring system and enhancing its reactivity. Several monocationic and dicationic η^6-Cp(*)Ru$^+$ complexes of polycyclic arenes such as naphthalene, anthracene, phenanthrene, and pyrene have been reported.[6,12] However, in contrast to their CpFe$^+$ analogues, reactivities of these Cp(*)Ru$^+$ aromatic hydrocarbon complexes have been much less explored.[12]

We have been continuing our investigations of the reactivity and synthetic utility of Cp(*)Ru$^+$-stabilized dibenzo-*p*-quinodimethane and in the process have extended our studies to include investigation of the activation effects of Cp(*)Ru$^+$ fragments on polycyclic arene systems. We report here the use of [(CpRu)(η^6-dibenzo-*p*-quinodimethane)]$^+$PF$_6^-$ (1) as a dienophile in Diels–Alder reaction with 2,3-dimethyl-1,3-butadiene to selectively yield a mono-*exo*-cycloaddition product 2, in which one vinylidene group remains nonreacted. Conversely, [(Cp*Ru)(η^6-anthracene)]$^+$TfO$^-$ (3) (TfO$^-$ = $CF_3SO_3^-$), can act as an activated enophile in Diels–Alder addition with maleic anhydride. Catalytic hydrogenation of naphthalene is also facilitated by complexation with Cp(*)Ru$^+$. Initial investigations of the scope and potential of this η^6-coordination strategy and these types of reactions are discussed.

Results and Discussion

Diels–Alder Reaction of [(CpRu)(η^6-dibenzo-*p*-quinodimethane)]$^+$PF$_6^-$ (1) with 2,3-Dimethyl-1,3-butadiene. One vinylidene group of [(CpRu)(η^6-dibenzo-*p*-quinodimethane)]$^+$PF$_6^-$ (1)[15] undergoes Diels–Alder reaction when heated with an excess of 2,3-dimethyl-1,3-butadiene in nitromethane, forming the *exo*-dimethylcyclohexenyl isomer (2) (Scheme 1) in good isolated yield (73%). The remaining exocyclic double bond did not undergo Diels–Alder reaction, even after heating to reflux for 3 days. ^{1}H-NMR spectroscopy (CD_3NO_2) showed the remaining vinylidene hydrogens of complex 2 appear as two singlets at δ 6.05 and 6.00, respectively, which are comparable in shift to the corresponding protons of 1 ($(CD_3)_2CO$, δ 6.23, 6.19),[15] and the parent hydrocarbon dibenzo-*p*-quinodimethane (THF-d^8, δ 5.80).[17] The four sets of equivalent aromatic hydrogens in 1 become eight nonequivalent protons in 2, four of which are shielded by coordination to the CpRu$^+$ moiety,[15] and the two allylic methyl groups appear in their normal range as singlets at δ 1.67 and 1.48. ^{1}H-NMR spectroscopy showed that only one of the two possible isomers resultings from cycloaddition of the diene from the *exo* or *endo* face of 1 was produced, which was assigned to be the *exo*-dimethylcyclohexenyl isomer (2) (Scheme 1). Although the structure of 2 was confirmed by an X-ray analysis (vide infra), assignment of the *exo* structure was reasonable because the CpRu$^+$ group in 1 has been shown to act as a directing group[15] and could block *endo*-cycloaddition. Structure 2 is also consistent with NMR data which show that the non-allylic methylene protons of the spiro-cyclohexenyl ring appear between δ 2.60 and 2.20, deshielded considerably from normal values (δ 1.65)[19] by their proximity to the Ru cation. Such deshielding effects have been observed for the methyl groups in η^6-(Cp*Ru$^+$)-*cis*-(*exo*-9,10-dihydro)-9,10-dimethylanthracene.[15] To the best of our knowledge, the hydrocarbon ligand in 2 represents a previously unknown carbon skeletal architecture, attesting to the potential of highly reactive arene systems stabilized by η^6-coordination to allow reactions which are otherwise difficult or impossible to perform on the parent hydrocarbon. If desired, the unique parent hydrocarbon could be isolated by photolysis of 2 in acetonitrile.[13,15]

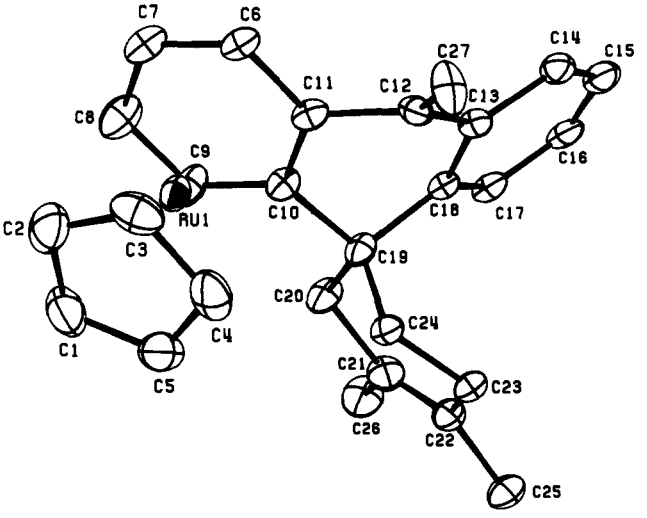


Figure 1. ORTEP drawing (20% probability ellipsoids) of 2. Hexafluorophosphate counterions have been omitted for clarity.

In order to confirm the structure of 2 and to understand the steric environment and nonreactivity of the remaining exocyclic double bond, a single-crystal X-ray structure determination was performed and an ORTEP drawing is shown in Figure 1. Data collection and cell parameters are given in Table 1. Atomic coordinates for 2 are listed in Table 2, and selected bond lengths and angles are given in Table 3. The Cp and arene rings are essentially coplanar (dihedral angle = 3.8(18)°) and the structural features of the CpRu$^+$–arene moiety in 2 are generally consistent with those of known complexes of this type.[15] The bond lengths between carbons C(21)–C(22) (1.332(18)Å), resulting from Diels–Alder reaction, and C(12)–C(27) (1.327(13) Å), the remaining vinylidene group, are typical for isolated C–C double bonds. As expected, the C(10)–C(19) and C(18)–

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Table 1. Crystallographic Data for 2

formula	$C_{27}H_{27}RuPF_6$
M_r	597.55
cryst sys	monoclinic
space group	$P2_1/n$
a, Å	16.079(5)
b, Å	11.682(3)
c, Å	13.508(4)
β, deg	91.03(3)
V, Å^3	2536.9
Z	4
D_{calc}, g/cm^{-3}	1.565
$F(000)$	1208
radn (graphite monochromator) (λ, Å)	Mo Kα (0.710 69)
μ(Mo Kα), cm^{-1}	8.3
2θ range, deg	1.5–50
no. of reflcns measd	4457
no. of unique reflcns ($I > 2\sigma(I)$)	2411
R	0.057
R_w	0.068
GOF	2.3

Table 2. Atomic Coordinates for Non-Hydrogen Atoms of 2

atom	x	y	z
Ru(1)	0.17155(5)	0.22155(7)	0.08832(5)
P(1)	0.3688(2)	0.2139(2)	0.3888(2)
F(1)	0.3047(4)	0.2970(5)	0.3371(5)
F(2)	0.3947(6)	0.3135(7)	0.4587(6)
F(3)	0.4346(5)	0.1318(6)	0.4378(4)
F(4)	0.3428(5)	0.1149(6)	0.3148(5)
F(5)	0.4325(5)	0.2490(8)	0.3114(7)
F(6)	0.3020(6)	0.1735(9)	0.4595(7)
C(1)	0.0440(8)	0.2345(15)	0.1373(12)
C(2)	0.0974(12)	0.2487(14)	0.2176(12)
C(3)	0.1434(7)	0.1481(19)	0.2297(9)
C(4)	0.1153(10)	0.0727(11)	0.1530(15)
C(5)	0.0537(8)	0.1294(15)	0.0970(9)
C(6)	0.3080(6)	0.2456(8)	0.0875(6)
C(7)	0.2695(8)	0.3528(9)	0.0961(7)
C(8)	0.2089(8)	0.3893(9)	0.0265(7)
C(9)	0.1850(8)	0.3118(8)	−0.0540(7)
C(10)	0.2243(5)	0.2051(7)	−0.0653(5)
C(11)	0.2846(5)	0.1719(8)	0.0066(5)
C(12)	0.3289(5)	0.0618(8)	−0.0090(6)
C(13)	0.3506(6)	0.0454(8)	−0.1151(6)
C(14)	0.4270(6)	−0.0002(9)	−0.1405(7)
C(15)	0.4505(7)	−0.0047(9)	−0.2405(8)
C(16)	0.3948(8)	0.0395(9)	−0.3130(7)
C(17)	0.3157(7)	0.0843(8)	−0.2877(6)
C(18)	0.2941(5)	0.0863(7)	−0.1872(6)
C(19)	0.2082(6)	0.1239(7)	−0.1548(6)
C(20)	0.1558(6)	0.1853(8)	−0.2351(6)
C(21)	0.1191(6)	0.0991(11)	−0.3125(7)
C(22)	0.1149(6)	−0.0134(10)	−0.2975(7)
C(23)	0.1478(6)	−0.0705(8)	−0.2036(6)
C(24)	0.1571(5)	0.0182(7)	−0.1178(6)
C(25)	0.0777(7)	−0.0973(11)	−0.3747(8)
C(26)	0.0870(9)	0.1662(12)	−0.4046(7)
C(27)	0.3550(8)	−0.0057(11)	0.0643(6)

C(19) bonds (1.554(11) and 1.522(12) Å, respectively) between the Diels–Alder vinylidene reaction site and the benzo rings are elongated compared to the C(11)–C(12) and C(12)–C(13) bonds (1.487(13) and 1.495(12) Å, respectively) between the remaining vinylidene group and the benzo rings. The newly formed C(19)–C(20) and C(23)–C(24) bonds (1.540(12) and 1.560(12) Å, respectively) are of characteristic C-C single-bond length, as is the bond between carbons C(19)–C(24) (1.570(12) Å) in 2, corresponding to the original vinylidene group from 1. The two methyl groups of the cyclohexenyl moiety are essentially eclipsed, with a C(26)–C(21)–C(22)–C(25) torsional angle of 1.6(17)°.

Of particular interest, the ORTEP drawing in Figure 1 shows that the central ring of coordinated dibenzo-*p*-quinodimethane in 2 adopts a clear boat form with a

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2

Ru(1)–C(1)	2.171(14)	C(10)–C(11)	1.414(11)
Ru(1)–C(2)	2.155(17)	C(10)–C(19)	1.554(11)
Ru(1)–C(3)	2.149(15)	C(11)–C(12)	1.487(13)
Ru(1)–C(4)	2.153(15)	C(12)–C(13)	1.495(12)
Ru(1)–C(5)	2.183(14)	C(12)–C(27)	1.327(13)
Ru(1)–C(6)	2.212(10)	C(13)–C(14)	1.387(13)
Ru(1)–C(7)	2.199(11)	C(13)–C(18)	1.403(12)
Ru(1)–C(8)	2.218(11)	C(14)–C(15)	1.410(14)
Ru(1)–C(9)	2.206(9)	C(15)–C(16)	1.414(16)
Ru(1)–C(10)	2.264(8)	C(16)–C(17)	1.422(16)
Ru(1)–C(11)	2.221(8)	C(17)–C(18)	1.408(12)
C(1)–C(2)	1.380(23)	C(18)–C(19)	1.522(12)
C(1)–C(5)	1.354(24)	C(19)–C(20)	1.540(12)
C(2)–C(3)	1.396(26)	C(19)–C(24)	1.570(12)
C(3)–C(4)	1.427(24)	C(20)–C(21)	1.560(14)
C(4)–C(5)	1.402(22)	C(21)–C(22)	1.332(18)
C(6)–C(7)	1.402(15)	C(21)–C(26)	1.550(16)
C(6)–C(11)	1.436(12)	C(22)–C(23)	1.519(14)
C(7)–C(8)	1.408(16)	C(22)–C(25)	1.543(16)
C(8)–C(9)	1.460(14)	C(23)–C(24)	1.560(12)
C(9)–C(10)	1.408(13)		

C(2)–C(1)–C(5)	110.5(14)	C(10)–C(19)–C(18)	105.1(7)
C(1)–C(2)–C(3)	108.1(14)	C(10)–C(19)–C(20)	110.2(7)
C(2)–C(3)–C(4)	106.0(12)	C(10)–C(19)–C(24)	108.3(6)
C(3)–C(4)–C(5)	108.1(13)	C(18)–C(19)–C(20)	114.8(7)
C(1)–C(5)–C(4)	107.3(13)	C(18)–C(19)–C(24)	110.4(7)
C(9)–C(10)–C(19)	123.8(8)	C(20)–C(19)–C(24)	107.9(7)
C(11)–C(10)–C(19)	118.0(7)	C(19)–C(20)–C(21)	111.6(8)
C(6)–C(11)–C(12)	120.4(7)	C(20)–C(21)–C(22)	123.7(9)
C(10)–C(11)–C(12)	117.7(7)	C(20)–C(21)–C(26)	109.1(10)
C(11)–C(12)–C(13)	111.5(7)	C(22)–C(21)–C(26)	127.2(10)
C(11)–C(12)–C(27)	123.6(8)	C(21)–C(22)–C(23)	122.9(9)
C(13)–C(12)–C(27)	124.3(9)	C(21)–C(22)–C(25)	122.9(9)
C(12)–C(13)–C(14)	120.6(8)	C(23)–C(22)–C(25)	114.2(9)
C(12)–C(13)–C(18)	117.6(8)	C(22)–C(23)–C(24)	110.9(8)
C(13)–C(18)–C(19)	118.6(7)	C(19)–C(24)–C(23)	109.2(7)
C(17)–C(18)–C(19)	121.5(8)		

C(6)–C(11)–C(10)–C(9)	2.2(12)
C(6)–C(11)–C(12)–C(27)	37.9(14)
C(9)–C(10)–C(19)–C(20)	9.4(12)
C(9)–C(10)–C(19)–C(24)	108.3(10)
C(14)–C(13)–C(12)–C(27)	32.4(15)
C(14)–C(13)–C(18)–C(17)	1.8(14)
C(17)–C(18)–C(19)–C(20)	13.9(12)
C(17)–C(18)–C(19)–C(24)	108.3(9)
C(19)–C(20)–C(21)–C(22)	16.3(13)
C(19)–C(24)–C(23)–C(22)	51.3(10)
C(20)–C(21)–C(22)–C(23)	1.6(16)
C(25)–C(22)–C(21)–C(26)	1.6(17)

dihedral angle between the planes of the two benzo rings of 128.0(4)° and torsional angles between the benzo rings and the vinylidene group, C(6)–C(11)–C(12)–C(27) and C(14)–C(13)–C(12)–C(27), of 37.9(14) and 32.4(15)°, respectively. These latter angles are comparable to the corresponding average torsional angles for the boat form calculated for dibenzo-*p*-quinodimethane (32.2(33) and 32.9(33)°).[15,20] The boat form in 2 relieves ring strain resulting from sp^3 hybridization at C(19) without causing torsional strain in the rigid benzo rings as a chair conformation would. Surprisingly, the C(20) and C(27) methylene groups in 2 bend toward the CpRu$^+$ moiety instead of bending away, as might be expected to reduce interaction, if any, between the CpRu$^+$ moiety and the "axial" C(24) methylene group ((C(9)-C(10)-C(19)-C(24) and C(17)-C(18)-C(19)-C(24); 108.3(10) and 108.3(9)°, respectively). This may be due to stronger steric interactions between the CpRu$^+$ moiety and the noncomplexed benzo ring if the boat were to invert, but there is no evidence to support this. Given the propensity of these types of compounds to go into boat conformations, if the vinylidene

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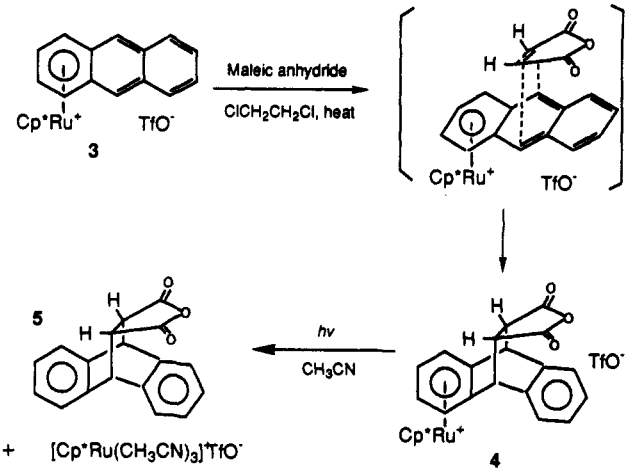
group in 2 underwent Diels–Alder reaction, molecular models clearly show unfavorable 1,4-diaxial interactions of the methylene groups corresponding to C(24) and C(27) in 2, as well as a second possible interaction with the $CpRu^+$ moiety. If the boat were to invert, bridgehead diaxial interactions between C(20) and its corresponding methylene group on the second cyclohexenyl ring would still occur, along with possible steric interactions between the $CpRu^+$ moiety and the noncomplexed benzo ring. Together these steric factors likely inhibit the Diels–Alder reaction of the remaining vinylidene double bond under the reaction conditions, although undefined electronic factors may also contribute. Unlike complex 1, its Cp* analogue[14] did not undergo Diels–Alder reaction with 2,4-dimethyl-1,3-butadiene under the same reaction conditions. This is likely due to stronger unfavorable steric interactions arising from the greater bulk of the Cp* ring.

Diels–Alder Reaction of [(Cp*Ru)(η^6-anthracene)]$^+$TfO$^-$ (3) with Maleic Anhydride. There are many reports on Diels–Alder reactions involving polycyclic aromatic hydrocarbons. Many of these cycloaddition reactions require severe reaction conditions, such as high pressure, high temperature, and a large excess of dienophile, since disruption of aromaticity is involved.[21] Development of an effective system using organometallic groups to activate polyarene systems toward cycloaddition reactions would have considerable significance. The η^6-complexation effect of Cp(*)Ru^+ fragments used to stabilize dibenzo-*p*-quinodimethane could also localize one benzene moiety of a polycyclic arene and disrupt aromaticity in the rest of the ring system. As a consequence, the noncomplexed portion of the arene might be regarded as a conjugated polyene which is fused to the η^6-arene-Cp(*)Ru^+ system; e.g., complexation of naphthalene or anthracene to Cp(*)Ru^+ fragments would leave noncomplexed diene and *o*-quinodimethane moieties, respectively, which could react with dienophiles in Diels–Alder reactions.

Anthracene is known to undergo Diels–Alder reaction at the central 9 and 10 carbons with maleic anhydride.[21,22] [(Cp*Ru)(η^6-anthracene)]$^+$TfO$^-$ (3)[12] undergoes rapid, quantitative (by ^{1}H-NMR) Diels–Alder reaction with a modest excess of maleic anhydride at relatively low temperature (refluxing 1,2-dichloroethane, 83 °C, 2 h), giving selectively [*trans*-(*endo*-Cp*Ru)(η^6-9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride)]$^+$TfO$^-$ (4) in 65% isolated yield (Scheme 2). Reaction of anthracene with maleic anhydride under conditions identical to those used for reaction of 3 gave only 19% 9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride (5)[22] (by ^{1}H-NMR). Prolonging the reaction time to 2 days still did not give complete reaction (83% conversion). ^{1}H-NMR spectroscopy on 4 showed only one isomer was produced in the reaction for which the methine protons α to the anhydride are shifted somewhat downfield (acetone-d_6, δ 3.88) from those of noncomplexed 9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride (5) (acetone-d_6, δ 3.77). It has been shown for similar Diels–Alder adducts that the α-methine protons are sensitive to shielding effects from the benzo ring they are positioned over.[23] If reaction was assumed to occur from the *exo* face of 3 because of

Scheme 2



steric hindrance as in the Diels–Alder reaction of 1, the *trans-endo* structure was assigned to 4 as the methine protons are somewhat deshielded relative to those of 5, due to their positioning over the more electron-deficient, complexed benzene ring. This assignment is also consistent with chemical shifts of the aromatic protons in 4 and 5 which show that the benzo rings positioned beneath the anhydride group[23] remain basically unchanged (δ 7.54, 7.48 and δ 7.55, 7.40, respectively), while those of the benzo rings away from the anhydride change dramatically (δ 6.51, 6.02 and δ 7.25, respectively).

^{1}H-NMR spectroscopy on 4 also showed that it retained variable amounts of recrystallization solvent (CH_3NO_2, δ 4.45) tenaciously, leading to erratic elemental analyses. However, fast atom bombardment (FAB) mass spectrometry clearly showed an intense base peak at *m/e* 513 corresponding to 4 with loss of its counterion ($CF_3SO_3^-$), followed by a strong peak at *m/e* 415 corresponding to loss of maleic anhydride. Isotopic distributions were nearly identical to calculated values. In order to further confirm the structure of 4, photolysis of an acetonitrile solution of 4 in a quartz tube for 2 days generated, after workup, [Cp*Ru(CH_3CN)$_3$]$^+$TfO$^-$ (which can be reused to make 3)[8,13] and 9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride[22] (5) in 63% and 64% isolated yield, respectively.

The preference for formation of the *endo-trans* product 4 can be explained as being due to normal secondary orbital overlap effects involving the orbitals of the carbonyl carbons on the dienophile with those on the carbons of the developing double bond in the noncomplexed benzo ring.[21] As shown in Scheme 2, the complexed benzene ring has its orbitals involved in bonding to the $CpRu^+$ group, so the secondary overlap occurs with the noncomplexed ring. The high selectivity of this cycloaddition reaction, which is attributed to the complexation influence of the Cp*Ru^+ moiety, may have potential application in organic synthesis.

The exact nature of the activation of the Cp*Ru^+ moiety is not yet clear. One possibility is that 3 is not more reactive than anthracene but since Diels–Alder reactions are equilibrium reactions,[21] the Cp*Ru^+ moiety could be acting as a "trap" by stabilizing the product once it is formed,[16] driving the reaction to completion even at modest temperatures. The more likely possibly is that 3 is activated toward Diels–Alder reaction by the Cp*Ru^+ moiety simply acting as an η^6-localizing group, isolating the rest of the

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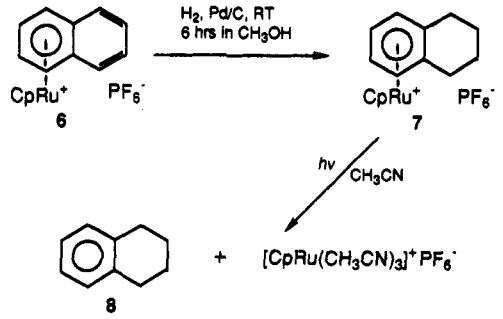
(22) Mayo, D. W.; Pike, R. M.; Butcher, S. S. *Microscale Organic Laboratory*, 2nd ed.; Wiley: New York, 1989; pp 190–192.
(23) Oku, A.; Ohnishi, Y.; Mashio, F. *J. Org. Chem.* **1972**, *37*, 4264.

anthracene ring as an *o*-quinodimethane, which has a relatively high HOMO, keeping in mind that the metal affects the molecular orbitals. It has been suggested that the Cp(*)Ru$^+$ moiety acts as an electron-withdrawing group,[15] which would lower the HOMO (and LUMO), perhaps facilitating "inverse demand" Diels–Alder reaction.[21] However, thermal reactions of **3** with either an excess of tetracyanoethylene, an electron-deficient dienophile, or ethyl vinyl ether, an electron-rich dienophile, for 2 days were not successful. Ongoing kinetic studies using both **3** and its CpRu$^+$ analogue and a wide variety of dienophiles with different electronic and steric demands are needed to reach a definitive conclusion as to what factors are responsible for the reactivity enhancement. These studies should also provide additional insight into the general utility of this type of reaction and help elucidate the details of the regio- and stereochemical aspects of this metal-promoted cycloaddition process.

Diels–Alder reaction of naphthalene with maleic anhydride (30-fold excess of the dienophile at 100 °C for 24 h) is known to result in less than 1% of the adduct since the reaction is thermodynamically unfavorable.[24] This reaction can be driven to 78% conversion at 100 °C and high pressure (10 000 atm).[25] Naphthalenes with alkyl substituents show enhanced reactivity toward cycloaddition reactions.[23] However, use of organometallic groups to activate naphthalene toward cycloaddition reactions has not been reported to our knowledge. We have attempted to use the coordination effect of the CpRu$^+$ fragment to facilitate the cycloaddition reaction of naphthalene. [CpRu(η^6-naphthalene)]$^+$PF$_6^-$ (**6**) was synthesized by following the literature procedure.[6] For comparative purposes, heating **6** with an excess of maleic anhydride (CH_3NO_2, reflux, 2 days) did not result in reaction. More severe reaction conditions may be needed to assess whether the CpRu$^+$ has any effect on naphthalene in this reaction.

Hydrogenation of [CpRu(η^6-naphthalene)]$^+$PF$_6^-$ (6). The results of Diels–Alder reactions on [(Cp*Ru)(η^6-anthracene)]$^+$TfO$^-$ (**3**) and [(CpRu)(η^6-naphthalene)]$^+$PF$_6^-$ (**6**) suggest that whether or not a Cp(*)Ru$^+$ fragment has a strong enough η^6-localization effect on the naphthalene system to isolate the other 4 π-electrons as a diene-like moiety, facilitating a reaction, is rather sensitive to energy considerations. Palladium-catalyzed hydrogenation of naphthalene to selectively form tetralin (1,2,3,4-tetrahydronaphthalene) requires less vigorous conditions for facile reaction (1000 psig and 115–120 °C)[26] than Diels–Alder reactions on naphthalene and, indeed, occurs slowly even at room temperature and 1 atm of hydrogen. Hydrogenation of **6** (5% Pd/C, 1 atm of H_2, methanol, room temperature, 6 h) took place smoothly to give [CpRu(η^6-1,2,3,4-tetrahydronaphthalene)]$^+$PF$_6^-$ (**7**) in high isolated yield (92%, Scheme 3). Hydrogenation of naphthalene under identical conditions showed 61% had not reacted (by ^{1}H-NMR), and even after 24 h, 32% naphthalene remained. ^{1}H-NMR spectroscopy on **7** showed the aromatic hydrogens (acetone-d_6, δ 6.27, 2H; δ 6.18, 2H) to be shielded[15] relative to tetralin ($CDCl_3$, δ 7.06, 4H). The hydrogens on the noncomplexed aromatic ring in **6** (acetone-d_6, δ 7.87 and 7.65) disappeared for **7**, and

Scheme 3



new peaks appeared at ca. δ 2.85 (4H), 2.06 (2H), and 1.86 (2H), corresponding to the aliphatic hydrogens in tetralin (δ 2.75, 4H, and 1.79, 4H). When **7** was dissolved in acetonitrile and irradiated in a quartz tube for 2 days, the tetralin ligand was released from the complex. After workup, [CpRu(CH$_3$CN)$_3$]$^+$PF$_6^-$ (which can be reused to make **6**) and tetralin (**8**) were recovered in 85% and 93% yield, respectively. Hydrogenation of [Cp*Ru(η^6-naphthalene)]$^+$TfO$^-$ under the same conditions gave comparable results.

The reactions presented in Scheme 3 are significant in a number of respects. The facile hydrogenation of **6** compared with free naphthalene demonstrated that η^6-coordination to the CpRu$^+$ fragment localizes the aromatic π-system to a degree sufficient to enhance the reactivity of noncoordinated benzo diene. Hydrogenations of naphthalene catalyzed by more active platinum, iridium, and rhodium produce mixtures of tetralin and decalin in which the latter is the predominant product.[26] The η^6-coordination of CpRu$^+$ to naphthalene afforded selective reduction of only the benzo ring under mild conditions and may be able to act as a protecting group, allowing the use of more active catalysts without overreduction. The reactions in Scheme 3 offer a reasonable model for the hydrogenation of other polycyclic aromatic systems and present some promise of being able to be modified into a catalytic cycle. The results presented here also contrast with the failure to hydrogenate [CpFe(η^6-naphthalene)]$^+$PF$_6^-$ with a Pt/C catalyst.[27] These observations suggest that the localization effect of the CpRu$^+$ fragment on arenes is much stronger than that of CpFe$^+$ and is consistent with the conclusion of Koelle that the metal–arene bond in Ru complexes is more covalent in character than those of Fe complexes.[12]

In order to further explore the activating effect of the Cp(*)Ru$^+$ group on polycyclic aromatic systems, we have extended this study to the pyrene system. Generally, pyrene undergoes hydrogenation under severe conditions to give mixtures of perhydropyrenes. For example, catalytic hydrogenation of pyrene with Raney nickel catalyst under high pressure at 250 °C yields a mixture of three perhydropyrenes.[28] To our knowledge, no effective catalyst has been developed to selectively reduce pyrene. In principle, the CpRu$^+$ group should localize 6 π-electrons in one benzene ring of the pyrene system, which should then undergo hydrogenation to form a 4,5,9,10-tetrahydropyrene complex. The pyrene complex [(CpRu)(η^6-pyrene)]$^+$PF$_6^-$ was synthesized according to the literature,[6] and hydrogenation was attempted with a Pd/C catalyst at

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room temperature. However, ^{1}H-NMR spectroscopy showed that under these reaction conditions hydrogenated product was not formed. More severe conditions may be needed for the hydrogenation to occur.

Conclusion

We have demonstrated the potential synthetic utility of Cp(*)Ru$^+$-stabilized arenes by facile Diels–Alder reaction of [(CpRu)(η^6-dibenzo-*p*-quinodimethane)]$^+$PF$_6^-$ with 2,3-dimethyl-1,3-butadiene to form a unique spiro derivative of dibenzo-*p*-quinodimethane. In this reaction, the CpRu$^+$ group acted as a steric directing group to give one regioisomer. The difficulty of generating and controlling the reaction of highly reactive dibenzo-*p*-quinodimethane makes this type of spiro architecture difficult to construct otherwise. The same η^6-localization effect of cyclopentadienylruthenium cations can be used to significantly activate anthracene toward Diels–Alder reaction with maleic anhydride and naphthalene toward catalytic hydrogenation under mild conditions. Further studies to investigate the origin of these activation effects and to assess the scope and synthetic potential of this η^6-localization strategy for the activation of polycyclic arenes are ongoing, using a variety of polycyclic aromatic compounds coordinated to Cp(*)Ru$^+$.

Experimental Section

General Comments. All reactions and manipulations were conducted under a prepurified nitrogen atmosphere using standard Schlenk line or glovebox techniques. Solvents were obtained commercially and used as received or dried and distilled from appropriate drying agents under nitrogen before use. Maleic anhydride was recrystallized from dry chloroform. The [(Cp*Ru)(η^6-anthracene)]$^+$TfO$^-$ complex (**3**)[12] was synthesized according to the procedure for making its hexafluorophosphate salt[6] but using the analogous triflate reagent.[8] All other compounds were either used as received or were prepared using procedures from the literature as noted in the text. Activity grade I neutral alumina (Sigma Chemical) was used for all short column filtration and chromatography. NMR spectral data are referenced to tetramethylsilane as an internal standard. Mass spectral data were collected on a Kratos MS 25-RF mass spectrometer. Photolyses were carried out using a preparative Rayonet photochemical reactor (254-nm source).

Diels–Alder Reaction of [(CpRu)(η^6-dibenzo-*p*-quinodimethane)]$^+$PF$_6^-$ (1) with 2,3-Dimethyl-1,3-butadiene. A flask was charged with 100 mg (0.19 mmol) of **1**,[15] 1.5 mL of 2,3-dimethyl-1,3-butadiene (1.1 g, 13 mmol), and 25 mL of dry CH_3NO_2 as solvent. The flask was fitted with a condenser, and the solution was heated with stirring (magnetic) to reflux solvent for 12 h. Most of the solvent was removed under reduced pressure, and 30 mL of diethyl ether was added. A white precipitate formed, which was filtered out, washed twice with 4 mL of ether, and dried under reduced pressure to yield 85 mg (73%) of addition complex **2**. An analytical sample and crystals of **2** suitable for X-ray structure determination were obtained by slow diffusion of diethyl ether vapor into a concentrated solution of **2** in nitromethane. Mp (CH_3NO_2/Et_2O): 192 °C. ^{1}H-NMR (300 MHz, CD_3NO_2): δ 7.67 (1H, m, noncoordinated arene ring), 7.58 (1H, m, noncoordinated arene ring), 7.40 (2H, 2 m, noncoordinated arene ring), 6.67 (1H, d, J = 6 Hz, coordinated arene ring), 6.60 (1H, d, J = 6 Hz, coordinated arene ring), 6.25 (1H, m, coordinated arene ring), 6.15 (1H, m, coordinated arene ring), 6.05 (1H, s, C=CH$_2$), 6.00 (1H, s, C=CH$_2$), 4.92 (5H, s, Cp), 2.20–2.60 (6H, m, 3CH$_2$), 1.67 (3H, s, CH$_3$), 1.48 (3H, s, CH$_3$). Anal. Calcd for $C_{27}H_{27}F_6PRu$: C, 54.26; H, 4.55. Found: C, 53.79; H, 4.64.

Diels–Alder Reaction of [(Cp*Ru)(η^6-anthracene)]$^+$TfO$^-$ (3) with Maleic Anhydride. A flask was charged with 100 mg (0.18 mmol) of **3**, 26 mg (0.27 mmol) of maleic anhydride, and 15 mL of dry 1,2-dichloroethane as solvent. The flask was fitted with a condenser, and the solution was heated with stirring (magnetic) to reflux the solvent for 2 h. Most of the solvent was removed under reduced pressure, the residue was chromatographed on a short alumina column (CH_3NO_2 eluent), and the yellow band containing the product was collected. The desired fraction was concentrated under reduced pressure, and 35 mL of ether was added. The product was collected by filtration and dried under reduced pressure to give 76 mg (65%) of *trans*-[(*endo*-Cp*Ru)(η^6-9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride)]$^+$TfO$^-$ (**4**) as a stable, white crystalline solid. An analytical sample was obtained by slow vapor diffusion of diethyl ether into a concentrated nitromethane solution of **4**. Mp (CH_3NO_2/Et_2O): >220 °C dec. ^{1}H-NMR (300 MHz, acetone-d_6): δ 7.54 (2H, m, noncoordinated arene), 7.48 (2H, m, noncoordinated arene), 6.51 (2H, m, coordinated arene), 6.02 (2H, m, coordinated arene), 5.04 (2H, m, 2CH), 3.88 (2H, m, 2CH), 1.64 (15H, s, Cp*). Anal. Calcd for $C_{29}H_{27}F_3O_6SRu$: C, 52.65; H, 4.08. Typical found: C, 48.34; H, 3.62. MS (FAB): *m/e* 513 ($M^+ - SO_3CF_3$, 100), 415 (loss of maleic anhydride, 33), 371 (27).

Photolysis of [*trans*-(*endo*-Cp*Ru)(η^6-9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride)]$^+$TfO$^-$ (4). A 250-mL quartz tube was charged with 300 mg (0.45 mmol) of **4** and 100 mL of dry acetonitrile. The tube was sealed under nitrogen and irradiated and stirred (magnetic) without cooling for 3 days in a Rayonet reactor. Solvent was removed from the dark brown solution under reduced pressure, and the solid was extracted three times with 10 mL of diethyl ether. The residue was dried under reduced pressure, and ^{1}H-NMR spectroscopy showed it to be recovered [Cp*Ru(CH_3CN)$_3$]$^+$TfO$^-$ (145 mg, 63%).[8,13] The diethyl ether solution was concentrated to 3 mL and eluted with CH_2Cl_2 through a short alumina column. After removal of solvent, 95 mg (0.34 mmol) of solid 9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride was obtained in 65% yield, the structure of which was confirmed using ^{1}H-NMR and MS spectroscopy by comparison with an authentic sample.[22] MP 261–263 °C. (lit. mp[22] 261–262 °C). ^{1}H-NMR: (300 MHz, acetone-d_6): δ 7.55 (2H, m, arene), 7.40 (2H, m, arene), 7.25 (4H, m, arene), 4.93 (2H, m, 2CH), 3.77 (2H, m, 2CH). MS (70 eV): m/e 276 (M^+, 10), 178 (100).

Hydrogenation of [(CpRu((η^6-naphthalene)]$^+$PF$_6^-$ (6). A flask was charged with 150 mg (0.29 mmol) of **6**,[8] 25 mL of CH_3OH, and 100 mg of 5% Pd–C. The solution was stirred (magnetic) for 6 h at room temperature under 1 atm of hydrogen. The catalyst was removed by filtration, the solvent was removed under reduced pressure, and the residue was chromatographed on a short alumina column (MeOH eluent). Most of the MeOH was removed under reduced pressure, 10 mL of diethyl ether was added, and the solid product was collected by filtration and dried under reduced pressure to give 138 mg (92%) of [(CpRu)(η^6-1,2,3,4-tetrahydronaphthalene)]$^+$PF$_6^-$ (**7**) as a white crystalline solid. Mp (CH_3NO_2/Et_2O): >185 °C dec. ^{1}H-NMR (300 MHz, acetone-d_6): δ 6.27 (2H, m, coordinated arene), 6.18 (2H, m, coordinated arene), 5.49 (5H, s, Cp), 2.95–2.75 (4H, br m, benzylic CH$_2$), 2.06 (2H, m, CH$_2$), 1.86 (2H, m, CH$_2$). Anal. Calcd for $C_{29}H_{27}F_3O_6SRu$: C, 40.64; H, 3.86. Found: C, 40.96; H, 3.63.

Photolysis of [(CpRu)(η^6-1,2,3,4-tetrahydronaphthalene)]$^+$PF$_6^-$ (7). A 250-mL quartz tube was charged with 250 mg (0.56 mmol) of **7** and 100 mL of dry acetonitrile. The tube was sealed under nitrogen and irradiated and stirred (magnetic) for 2 days without cooling in a Rayonet reactor. Solvent was removed from the dark brown solution under reduced pressure, and the solid was extracted three times with 10 mL of diethyl ether. The residue was dried under reduced pressure and ^{1}H-NMR spectroscopy showed it was [CpRu(CH_3CN)$_3$]$^+$PF$_6^-$ (206 mg, 85%).[6,13] The extract was concentrated to 2 mL and eluted with petroleum ether through a short alumina column. After removal of solvent, 69 mg (93%) of 1,2,3,4-tetrahy-

dronaphthalene, pure by ^{1}H-NMR,[29] was obtained. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.06 (4H, m, arene), 2.75 (4H, m, $2CH_2$), 1.79 (4H, m, $2CH_2$). MS (70 eV): *m/e* 132 (M^+, 44), 104 (87), 91 (38), 77 (11), 36 (100).

X-ray Structural Analysis of 2, the Diels–Alder Adduct of [(CpRu)(η^6-dibenzo-*p*-quinodimethane)]$^+PF_6^-$ with 2,3-Dimethyl-1,3-butadiene. Light yellow crystals of the cycloaddition product **2** suitable for X-ray analysis were grown by slow vapor diffusion of diethyl ether into nitromethane solution. A crystal of **2** with dimensions of ca. 0.45 × 0.30 × 0.25 mm was used for data collection. Cell dimensions and intensities were collected at room temperature on an Enraf-Nonius CAD4 diffractometer by methods standard in this laboratory.[30] The data were corrected for Lorentz and polarization effects; absorption corrections were not applied as they were judged to be insignificant. The structure was solved by the heavy-atom method and refined anisotropically by least-squares analysis (SHELX76).[31] The data quality did not allow location of hydrogen atoms, and they are not included in the refinement. In general all the atoms displayed large thermal motion which resulted in a high percentage of "unobserved" reflections. Final crystallographic parameters are presented in Table 1.

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Supplementary Material Available: Listings of anisotropic thermal parameters, bond lengths and angles, and torsional angles for **2** (8 pages). Ordering information is given on any current masthead page.

OM930551G

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