Articles

Formation, Structure, and Reactivity of Dibenzo-*p*-quinodimethane Stabilized as η^6-Ligands of (Cyclopentadienyl)- and (Pentamethylcyclopentadienyl)ruthenium Cations

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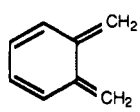
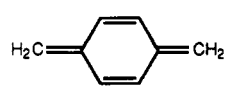
Reaction of [2.2](9,10)anthracenophane (**3**) with 2 or 4 equiv of $[CpRu(CH_3CN)_3]^+PF_6^-$ (Cp = η^5-cyclopentadienyl) results in thermally forbidden [6 + 6] cleavage of the enthano bridges to form stable complexes (*trans*-$[(CpRu)_2(\eta^6,\eta^6$-dibenzo-*p*-quinodimethane$)]^{2+}(PF_6^-)_2$ (**7**) and $[(CpRu)(\eta^6$-dibenzo-*p*-quinodimethane$)]^+PF_6^-$ (**8**), respectively) of highly reactive dibenzo-*p*-quinodimethane (**4**). X-ray structural analysis of **7** shows it to crystallize in the triclinic space group $P\bar{1}$ with a = 10.664 (4) Å, b = 8.948 (3) Å, c = 7.411 (3) Å, α = 97.14 (2)°, β = 101.46 (2)°, γ = 100.60 (2)°, and Z = 1. The dibenzo-*p*-quinodimethane moiety in **7** is nearly flat, in contrast to the shallow boat conformation determined for its Cp* (Cp* = η^5-pentamethylcyclopentadienyl) analogue **5** and the full boat conformation calculated for **4**. Localization of electrons in one benzo ring of **3** as an η^6-ligand of ($CpRu^+$) appears to cause a loss of aromaticity in the remaining anthracene moiety, driving cleavage of the ethano bridges by rearomatization to form the noncomplexed benzo ring. Forming the second aromatic ring is a necessary structural feature in the reaction as shown for *anti*-[2.2](1,4)naphthalenophane (**10**), which reacts with $[CpRu(CH_3CN)_3]^+PF_6^-$ to form the noncleaved *trans*-$[(CpRu)_2($*exo*-η^6,η^6-*anti*-[2.2](1,4)-naphthalenophane$)]^{2+}(PF_6^-)_2$ complex **13**. X-ray structural analysis of **13** shows it to crystallize in the monoclinic space group $C2/m$ with a = 23.281 (5) Å, b = 9.334 (2) Å, c = 7.512 (2) Å, β = 103.45 (3)°, and Z = 2. The ethano bridges of **13** do not show significant elongation relative to the structure of **10**. The potential synthetic utility of Ru stabilized dibenzo-*p*-quinodimethanes was shown by the hydrogenation of $[(Cp^*Ru)(\eta^6$-dibenzo-*p*-quinodimethane$)]^+CF_3SO_3^-$ (**6**), followed by photolysis to remove (Cp^*Ru^+) and give pure *cis*-9,10-dihydro-9,10-dimethylanthracene. Treatment of **6** with bromine gave 9,10-bis(bromomethyl)anthracene. Photolysis of **6** in acetonitrile removes (Cp^*Ru^+), generating **4** which polymerizes to form poly((1,9)-anthracenylene).

Introduction

o- and *p*-quinodimethane species (**1** and **2**) are highly reactive organic intermediates with a variety of synthetic uses. Molecular orbital calculations show that the reac-



o-Quinodimethane (1)



p-Quinodimethane (2)

tivity of *o*- and *p*-quinodimethanes results from a high free valence at their terminal methylene carbons,[1] leading to rapid dimerization, polymerization, or further reaction when generated under normal conditions.[2-5] *o*-Quinodimethanes have received considerable attention, especially with respect to generation and subsequent use as dienes in Diels–Alder reactions.[5] This sequence has found use in syntheses of numerous compounds,[5] including anthracyclinoid antibiotics.[6] *p*-Quinodimethanes are important intermediates in the formation of cyclophanes[2,7] and in the synthesis of poly(*p*-xylylene)'s (Parylene),[7,8] which are used as coatings. Although the generation and use of *o*-quinodimethanes in synthesis is fairly well-known, difficulties in the generation and control of reactivity of *p*-quinodimethanes have limited their availability and utility. Methods to stabilize *p*-quinodimethanes or to generate them in a controlled fashion would greatly facilitate the continued development of their chemistry and synthetic utility.

The stabilization of reactive *o*-quinodimethane species by transition metal complexation is well precedented. Several *o*-quinodimethane complexes of iron,[9,10] cobalt,[11]

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(6) Kerdesky, F. A. J.; Ardecky, R. J.; Lakshimikantham, M. V.; Cava, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 1992.
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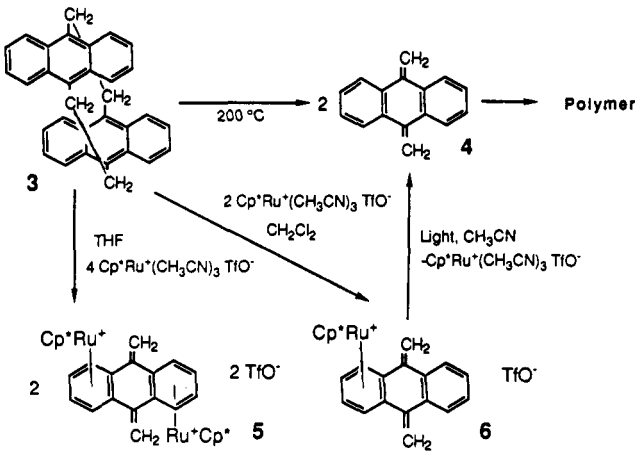
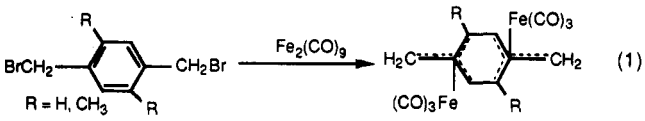
Scheme I

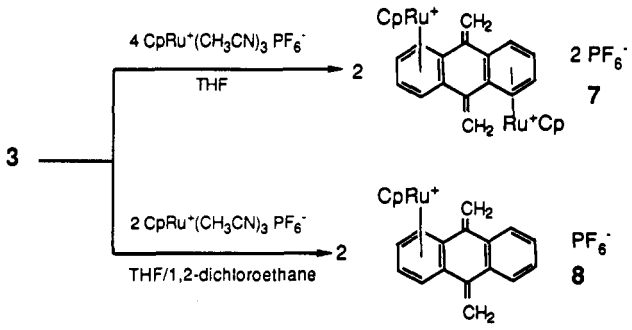


and ruthenium[12-15] have been isolated, and a few were used for further transformations. Similar stabilization of *p*-quinodimethanes by metals to allow their characterization and use still presents a challenge. Reaction of 1,4-bis(bromomethyl)benzene's with diiron nonacarbonyl is known to give bis(tricarbonyliron)–*p*-quinodimethane's (eq 1), but synthetic yields are extremely low (<4%).[16] The use of these complexes for in situ generation and reaction of *p*-quinodimethane has not yet been clearly demonstrated.



We have reported[17] that in a novel, thermally forbidden [6 + 6] cycloreversion reaction, treatment of [2.2](9,10)-anthracenophane (**3**) with $[Cp^*Ru(CH_3CN)_3]^+TfO^-$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$, $TfO^- = CF_3SO_3^-$) results in cleavage of the ethano bridges under mild conditions to generate complexes **5** and **6** (Scheme I), which are stabilized by (Cp^*Ru^+) groups through coordination of one or both of the outer benzo rings of dibenzo-*p*-quinodimethane[18] (**4**) as η^6-ligands. These compounds and reactions represent both a new class of materials and an "η^6-methodology" for the stabilization of appropriate reactive intermediates. We report here expansion of this class of compounds to include (η^5-cyclopentadienyl)ruthenium cations as a stabilizing group and X-ray structural investigations of these metal-stabilized dibenzo-*p*-quinodimethane species. Initial investigations of the generality of this methodology, as well as initial studies of the reactivity and potential synthetic utility of metal-stabilized dibenzo-*p*-quinodimethanes, are discussed.

Scheme II



Results and Discussion

Synthesis and Characterization of (Cp^*Ru^+)- and ($CpRu^+$)-Stabilized Dibenzo-*p*-quinodimethane. Full details of the synthesis and spectral characterization of mono- and bis(Cp^*Ru^+) stabilized dibenzo-*p*-quinodimethanes **6** and **5** by reaction of **3** with $[Cp^*Ru(CH_3CN)_3]^+TfO^-$ in the proper stoichiometry and solvent have been reported (Scheme I).[17] As a first step toward demonstrating the generality of this methodology and increasing the availability of benzo-*p*-quinodimethanes stabilized by (cyclopentadienyl–Ru^+) groups, replacement of the pentamethylcyclopentadienyl ligands in **5** and **6** by inexpensive cyclopentadienyl ligands was desirable. The cyclopentadienyl ligands change both the steric accessibility of the quinodimethane *exo*-methylenes and the electronic structure of the complexes through a lack of electron-donating methyl groups, allowing us to begin to investigate electronic versus structural effects in these complexes. Reaction of **3** with ca. 4 equiv of $[CpRu(CH_3CN)_3]^+PF_6^-$ ($Cp = \eta^5$-cyclopentadienyl)[19,20] in tetrahydrofuran (THF) at room temperature generates the bis($CpRu^+$)–dibenzo-*p*-quinodimethane complex **7** in good (74%) yield (Scheme II), while reaction with ca. 2 equiv of $[CpRu(CH_3CN)_3]^+PF_6^-$ gives the mono($CpRu^+$) complex of dibenzo-*p*-quinodimethane **8** in good (78%) yield. As with the reactions described in Scheme I, poorly soluble **3** dissolves as reaction occurs. The structures of both complexes **7** and **8** were determined by spectroscopic analysis and in the case of **7** by X-ray diffraction of a single crystal (vide infra). Both crystals and solutions of bis(ruthenium) compounds **5** and **7** are very stable to air and moisture. Mono(ruthenium) compounds **6** and **8** are fairly stable in the solid state, but their solutions are somewhat reactive, most likely to atmospheric oxygen.

The ^{1}H-NMR spectra of bis- and mono($CpRu^+$) complexes **7** and **8** exhibit characteristic chemical shifts[21] compared to those of their (Cp^*Ru^+) analogues and noncomplexed **4**. The shielding effects of the ($CpRu^+$) groups (ignoring solvent effects) on the complexed benzo rings in **7** ($(CD_3)_2CO$, δ 7.09, 6.61) and **8** ($(CD_3)_2CO$, δ 7.06, 6.55) are not as strong as those seen for bis- and mono-(Cp^*Ru^+) complexes **5** (CD_2Cl_2, δ 6.61, 6.12) and **6** ($CDCl_3$, δ 6.38, 6.18),[17] reflecting the expectation that the Cp ring is less electron releasing than Cp*. Indeed, chemical shifts of the noncomplexed benzo rings in **6** (δ 7.75, 7.46) and **8** (δ 7.90, 7.58) are indicative that ($CpRu^+$) has a stronger electron-withdrawing effect than the (Cp^*Ru^+) moiety. These electron-withdrawing effects are also shown by the

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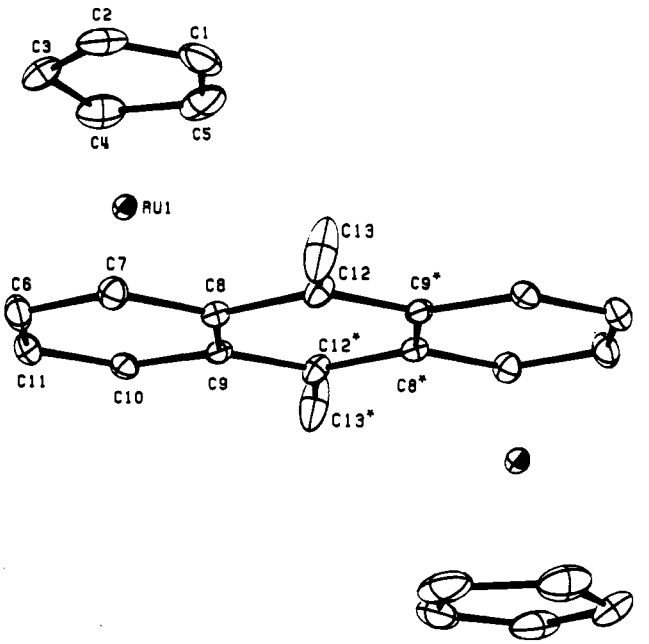

Figure 1. ORTEP drawing of 7. Hydrogen atoms and hexafluorophosphate counterions have been omitted for clarity.

Table I. Crystallographic Data for 7 and 13

	7	13
formula	$C_{26}H_{22}Ru_2P_2F_{12}$	$C_{34}H_{30}Ru_2P_2F_{12}$
M_r	826.53	930.68
cryst sys	triclinic	monoclinic
space group	$P\bar{1}$	$C2/m$
a, Å	10.664 (4)	23.281 (5)
b, Å	8.948 (3)	9.334 (2)
c, Å	7.411 (3)	7.512 (2)
α, deg	97.14 (2)	
β, deg	101.46 (2)	103.45 (3)
γ, deg	100.60 (2)	
V, Å^3	671.7	1587.6
Z	1	2
D_{calc}, g/cm^{-3}	2.04	1.94
$F(000)$	404	920
radn (graph monochromator) (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
μ(Mo Kα), cm^{-1}	13.2	11.3
2θ range, deg	1.5–50	1.5–50
no. of reflcns measd	2919	1933
no. of unique reflcns ($I > 2\sigma(I)$)	2598	1756
R	0.023	0.031
R_w	0.029	0.036

downfield shift for the methylene protons of complexes **5** (δ 6.43), **6** (δ 5.98, 6.05), **7** (δ 6.65), and **8** (δ 6.19, 6.23) relative to that of noncomplexed **4** (THF-d_8, δ 5.80).[22] The additivity of these effects can be seen by comparing these methylene chemical shifts for **5** and **6** or **7** and **8**.

A single-crystal X-ray structure determination was carried out on bis(CpRu$^+$) complex **7**, and an ORTEP drawing of it is shown in Figure 1. Collection data and cell parameters are given in Table I, and atomic coordinates, in Table II. Selected bond lengths and angles are given in Tables III and IV. As found for the (Cp*Ru$^+$) groups in the previously reported bis(Cp*Ru$^+$) complex **5**,[17] the (CpRu$^+$) groups in **7** are clearly constrained by crystallographic symmetry to be trans to one another, and the bond angles and lengths of the dibenzo-*p*-quinodimethane moiety are consistent with the proposed structure. The structural features of the Cp–Ru$^+$–arene moiety in **7** are generally consistent with those of known Cp–Ru$^+$–arene complexes, although surprisingly few have been reported.[23] The Cp centroid–Ru and arene centroid–

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Table II. Atomic Coordinates for the Non-Hydrogen Atoms of 7

atom	x	y	z
Ru(1)	0.24630 (2)	1.18921 (2)	0.43298 (2)
P(1)	0.28384 (7)	0.70505 (8)	–0.07403 (10)
F(1)	0.3231 (2)	0.7574 (3)	0.1475 (3)
F(2)	0.1650 (2)	0.5787 (2)	–0.0526 (3)
F(3)	0.3763 (2)	0.5848 (2)	–0.0546 (3)
F(4)	0.1920 (2)	0.8250 (2)	–0.0957 (3)
F(5)	0.2467 (3)	0.6499 (3)	–0.2921 (3)
F(6)	0.4043 (2)	0.8323 (2)	–0.0892 (3)
C(1)	0.1733 (4)	1.1709 (4)	0.1365 (4)
C(2)	0.3018 (4)	1.1805 (4)	0.1649 (4)
C(3)	0.3648 (3)	1.3201 (4)	0.2733 (4)
C(4)	0.2745 (4)	1.4015 (3)	0.3184 (4)
C(5)	0.1481 (4)	1.3041 (5)	0.2279 (5)
C(6)	0.3722 (2)	1.0907 (3)	0.6412 (4)
C(7)	0.2681 (2)	0.9728 (3)	0.5335 (3)
C(8)	0.1355 (2)	0.9843 (2)	0.5190 (3)
C(9)	0.1079 (2)	1.1196 (2)	0.6128 (3)
C(10)	0.2162 (2)	1.2386 (3)	0.7165 (3)
C(11)	0.3458 (3)	1.2235 (3)	0.7321 (3)
C(12)	0.0278 (2)	0.8595 (3)	0.4024 (3)
C(13)	0.0520 (3)	0.7365 (4)	0.3119 (5)

Table III. Selected Bond Lengths (Å) for 7 with Comparative Bond Lengths for 4 and 5

	bis(CpRu$^+$) compd 7	bis(Cp*Ru$^+$) compd 5[a]	dibenzoquinodimethane (4)[b]
Ru(1)–Cp	1.795 (3)	1.809 (5)	
Ru(1)–Bz	1.703 (3)	1.707 (5)	
C(6)–C(7)	1.411 (4)	1.404 (11)	1.405
C(6)–C(11)	1.394 (4)	1.396 (8)	1.400
C(7)–C(8)	1.421 (3)	1.426 (10)	1.413
C(8)–C(9)	1.428 (3)	1.425 (7)	1.432
C(8)–C(12)	1.485 (3)	1.484 (10)	1.487
C(9)–C(10)	1.432 (3)	1.426 (10)	1.413
C(9)–C(12)*	1.477 (3)	1.484 (10)	1.487
C(10)–C(11)	1.396 (3)	1.404 (11)	1.405
C(12)–C(13)	1.311 (4)	1.324 (8)	1.355

[a] Average length and standard deviation of all representative bonds in **5**.[17] [b] Average values for all representative bonds in **4** from MNDO calculations;[24] average errors in MNDO individual bond length and angle calculations are 0.014 Å and 2.319°, respectively.[39]

Table IV. Other Selected Bond Lengths (Å) and Angles (deg) for 7

Ru(1)–C(1)	2.155 (3)	C(2)–C(1)–C(5)	109.9 (3)
Ru(1)–C(2)	2.179 (3)	C(1)–C(2)–C(3)	108.7 (3)
Ru(1)–C(3)	2.182 (3)	C(2)–C(3)–C(4)	110.0 (3)
Ru(1)–C(4)	2.170 (3)	C(3)–C(4)–C(5)	105.3 (3)
Ru(1)–C(5)	2.148 (4)	C(1)–C(5)–C(4)	106.2 (3)
Ru(1)–C(6)	2.216 (3)	C(7)–C(6)–C(11)	119.9 (2)
Ru(1)–C(7)	2.194 (2)	C(6)–C(7)–C(8)	121.3 (2)
Ru(1)–C(8)	2.227 (2)	C(7)–C(8)–C(9)	119.0 (2)
Ru(1)–C(9)	2.234 (2)	C(7)–C(8)–C(12)	120.2 (2)
Ru(1)–C(10)	2.191 (2)	C(9)–C(8)–C(12)	120.8 (2)
Ru(1)–C(11)	2.216 (2)	C(8)–C(9)–C(10)	118.1 (2)
C(1)–C(2)	1.329 (6)	C(8)–C(9)–C(12)*	121.4 (2)
C(1)–C(5)	1.393 (5)	C(10)–C(9)–C(12)*	120.5 (2)
C(2)–C(3)	1.373 (5)	C(9)–C(10)–C(11)	122.0 (2)
C(3)–C(4)	1.376 (5)	C(6)–C(11)–C(10)	119.7 (2)
C(4)–C(5)	1.445 (5)	C(8)–C(12)–C(13)	121.3 (2)
		C(8)–C(12)–C(9)*	117.8 (2)
		C(13)–C(12)–C(9)*	120.9 (2)

(23) (a) Kruger, G. J.; du Preez, A. L.; Haines, R. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1302. (b) Huckett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686. (c) Moriarty, R. M.; Ku, Y.; Gill, U. S.; Gilardi, R.; Perrier, R. E.; McGlinchey, M. J. *Organometallics* **1989**, *8*, 960.

Ru distances are 1.795 (3) and 1.703 (3) Å, respectively. The Cp and arene rings are essentially coplanar (dihedral angle = 1.2 (2)°), with a Cp centroid–Ru–arene centroid angle of 179.1 (2)°. The Cp ring carbons, however, are not symmetrically bonded to the Ru atom, the C–Ru bonds ranging from 2.148 (4) to 2.182 (3) Å, with corresponding differences in the Cp C–C bond lengths (1.329 (6)–1.445 (5) Å). This is in contrast to **5**, where the Cp* rings are essentially symmetrical. Although distortion of the Cp ring is a common feature of other $CpRu^+$–arene compounds,[23] the Cp ring in **7** appears to be an extreme case and its distortion may be due to secondary interactions with the *exo*-methylene groups.

We have reported the X-ray structure determination of bis(Cp^*Ru^+) complex **5**,[17] and structural parameters for dibenzo-*p*-quinodimethane (**4**) have been derived from MNDO calculations by Dewar.[24] Selected bond length data for **5** and calculating bonding parameters for **4** are included in Table III for comparison with those of bis($CpRu^+$) complex **7**. Perhaps the most striking observation from this data is that, despite differences in reactivity, the structural features of the dibenzo-*p*-quinodimethane moieties in **4**, **5**, and **7** are remarkably similar. The only obvious significant differences concern the bond lengths of the *exo*-methylenes and the torsional angles about those *exo*-methylenes that lead to boat conformations in **4** and **5**. Of particular interest, the bond lengths of the *exo*-methylene groups (C_{12}–C_{13}) were found to be 1.311 (4) Å for **7**, 1.325 (6) and 1.323 (6) Å for **5** and calculated to be 1.356 (14) and 1.355 (14) Å for **4**. The small elongation of the methylene bonds for **4** is consistent with some diradical character. The values for **5** and **7** are typical, if not somewhat short, for isolated C–C double bonds, showing the π-electron localization effected by the Ru moieties and suggesting that the effect is somewhat stronger for the more electron-withdrawing ($CpRu^+$) group. This localization effect is shown more dramatically by the observation that there is a trend toward planarity of the dibenzo-*p*-quinodimethane moiety in going from non-complexed **4** to bis(Cp^*Ru^+) complex **5** to bis($CpRu^+$) complex **7**. The dibenzo-*p*-quinodimethane moiety is nearly planar in **7** with torsional angles between the benzo rings and *exo*-methylenes, C_7–C_8–C_{12}–C_{13} and C_9–C_8–C_{12}–C_{13}, of only 0.5 (4) and 1.7 (3)°, respectively. The corresponding torsional angles increase in **5** to average values of 14.3 (10) and 14.7 (8)°, where the dibenzo-*p*-quinodimethane moiety assumes a clear boat form. The corresponding average torsional angles for the boat form calculated for **4** are 32.2 (33) and 32.9 (33)°, respectively. The flattening out of the dibenzo-*p*-quinodimethane moiety with Ru complexation suggests that electronic effects play a prominent role in determining its structure. This is in contrast to calculations that suggest the boat conformation of **4** to be 11 kcal/mol more stable than planar **4**, the difference arising from steric interactions between hydrogens on the *exo*-methylenes and at the 1-positions of the benzo rings.[24] A nonplanar geometry was also observed for a stable dibenzo-*p*-quinodimethane substituted by phenyl groups at the 1-positions.[25] However, if only steric effects were involved for **3** and **5**, it might have been expected that flattening of the dibenzo-*p*-quinodimethane moiety would occur to a greater degree in **5** because of interaction of the methylenes with the bulky Cp* rings.

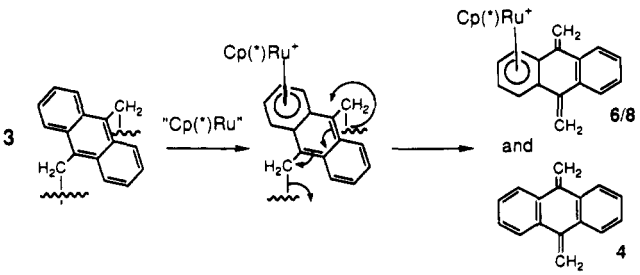
Alternative routes to the bis(Cp^*Ru^+) and bis($CpRu^+$) complexes **5** and **7** were discovered while trying to make model compounds for these systems. Reaction of 9,10-bis(chloromethyl)anthracene[3] (**9**) with $[Cp^*Ru(CH_3CN)_3]^+TfO^-$ or $[CpRu(CH_3CN)_3]^+PF_6^-$ in THF resulted in a mixture of **5** or **7**, nonreacted **9**, and what is likely $[Cp(^*)RuCl_2]_x$. Using a 3/1 Ru-reagent/**9** ratio resulted in better yields of **5** or **7** but difficulties in separation of the resulting mixtures, and use of excess Ru reagent make this route less desirable. This type of reaction may have eventual importance in the synthesis of other quinodimethane species stabilized using this methodology.

Formation of (Cp^*Ru^+)- and ($CpRu^+$)-Stabilized Dibenzo-*p*-quinodimethanes from [2.2]Paracyclophanes. Under normal conditions, [2.2]paracyclophanes undergo thermal cleavage ($T > 100$ °C) of a single ethano bridge to form bis(benzyl) diradicals which go on to polymerize, reclose, or otherwise react.[26] The dibenzo-*p*-quinodimethane moiety which is produced in the reactions presented here can be considered the result of a [6 + 6] cycloreversion reaction, which is thermally forbidden by Woodward–Hoffmann rules.[27] We have carried out the synthesis of bis(Cp^*Ru^+) complex **5** in the dark with no apparent change in reaction time or yield, so the reaction does not appear to be photolytic. To the best of our knowledge, the reactions shown in Schemes I and II are the first examples of a cyclophane ring opening under such mild conditions. A better understanding of the driving force behind formation of **5**–**8** and the mechanism by which ring opening of **3** occurs under these conditions would give insight into the general practicability of this type of reaction on other cyclophanes and may suggest ways to use metals to promote cycloreversion reactions. However, mechanistic investigation of these reactions is compliciated by the insolubility of **3** and the heterogeneous nature of the reactions.

In spite of insolubility problems, experimental observations allow for some speculation on the mechanism of ring opening of **3** by ($Cp(^*)Ru^+$). The mechanism of ligand displacement from the ($CpRu^+$) reagent by arenes has been investigated,[28] and it is possible that initial η^4-complexation occurs on the central ring of the anthracene moieties in **3**, followed by cleavage of the ethano bridges as the ($Cp(^*)Ru^+$) fragment "slips" to complex the outer rings in an η^6-fashion. We have no evidence for this, and the focus here will be on the ring opening of **3**, presumably after the first η^6-complexation has occurred. First, attempts to observe or isolate a noncleaved mono(Cp^*Ru^+) complex of **3** on reaction in THF by varying the (Cp^*Ru^+) reagent stoichiometry failed, suggesting that ring cleavage occurs after only one (Cp^*Ru^+) moiety attaches. Second, reaction of **3** with 1 equiv of $[Cp^*Ru(CH_3CN)_3]^+TfO^-$ in CH_2Cl_2 gave only mono(Cp^*Ru^+) complex **6** and nonreacted **3** by ^{1}H-NMR. This suggests that once cleavage occurs (see Scheme III), nonreacted **3** and **4** go on to produce more mono(Cp^*Ru^+) complex **6** but addition of a second (Cp^*Ru^+) moiety to form **5** is relatively slow, consistent with electron-withdrawing effects. Finally, reaction of **3**

(24) Dewar, M. J. S. *J. Am. Chem. Soc.* **1982**, *104*, 1477.
(25) Dickerman, S. C.; Berg, J. H.; Haase, J. R.; Varma, R. *J. Am. Chem. Soc.* **1967**, *89*, 5457.
(26) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1967**, *89*, 3078.
(27) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley Interscience: New York, 1976.
(28) Koefod, R. S.; Mann, K. R. *J. Am. Chem. Soc.* **1990**, *112*, 7287.

Scheme III



with 1 equiv of bis(CpRu$^+$) complex **7** in THF did not result in ligand exchange to form mono(CpRu$^+$) complex **8**, showing that **8** is not produced by equilibration. Similarly, disproportionation of monocomplexes **6** or **8** in THF to form biscomplexes **5** or **7** was not observed. It is clear that synthesis of these complexes is strongly affected by reaction conditions, especially stoichiometry and those that affect solubilization.

Anthracenophane **3** is certainly strained through π–π repulsion between the tightly held anthracene rings. Complexation by the (Cp(*)Ru$^+$) group might be expected to withdraw some electron density, reducing the π–π interactions and actually stabilizing the complex somewhat. However, the observations above suggest that the cleavage of **3** that does occur results from localization of the electrons in one benzo ring as an η^6-ligand, causing a loss of aromaticity in the remaining portion of the anthracene ring and forming an *o*-quinodimethane moiety (Scheme III). It has been suggested that such *o*-quinodimethane moiety formation leads to the difficulty encountered in attaching a second (Cp*Ru$^+$) group in an η^6-fashion to anthracene.[29] Cleavage of the ethano bridges would then be driven by rearomatization to form the noncomplexed benzo ring. This suggests that having the possibility of forming the second aromatic ring is a necessary structural feature in the reaction.

In order to test the hypothesis above and investigate the general applicability of this methodology to ring open [2.2]paracyclophanes, we attempted synthesis of **12**, the (CpRu$^+$) complex of benzo-*p*-quinodimethane (**11**) from the corresponding *anti*-[2.2](1,4)naphthalenophane (**10**),[30] as shown in Scheme IV. If the second benzo ring is required to provide a driving force for cleavage by rearomatizing, it would be expected that **10** not cleave but rather give an ansa-complex with the bridges intact. Reaction of **10** with excess [CpRu(CH$_3$CN)$_3$]$^+$PF$_6^-$ did not show any evidence of ring cleavage to form **12** but gave *trans*-[(CpRu)$_2$-(*exo*-η^6,η^6-*anti*-[2.2](1,4)naphthalenophane)]$^{2+}$(PF$_6^-$)$_2$ (**13**) in good (68%) yield. The ^{1}H-NMR spectrum of **13** (CD$_3$NO$_2$) reveals two doublet of doublets at δ 6.85 and 6.40, characteristically shielded by the (CpRu$^+$) group relative to those of **10** (ignoring solvent effects) at δ 7.75 and 7.43 (CDCl$_3$). The singlet from the two inner ring protons in **13** (δ 6.21) is deshielded relative to that of **10** (δ 5.80) by the electron-withdrawing effect of the (CpRu$^+$) groups. These observations are consistent with the (CpRu$^+$) groups being attached to the outer benzo rings of **10**.

A single-crystal X-ray structure determination was carried out on **13**, and an ORTEP drawing of it is shown in Figure 2. Collection data and cell parameters are given in Table I, and atomic coordinates, in Table V. Selected

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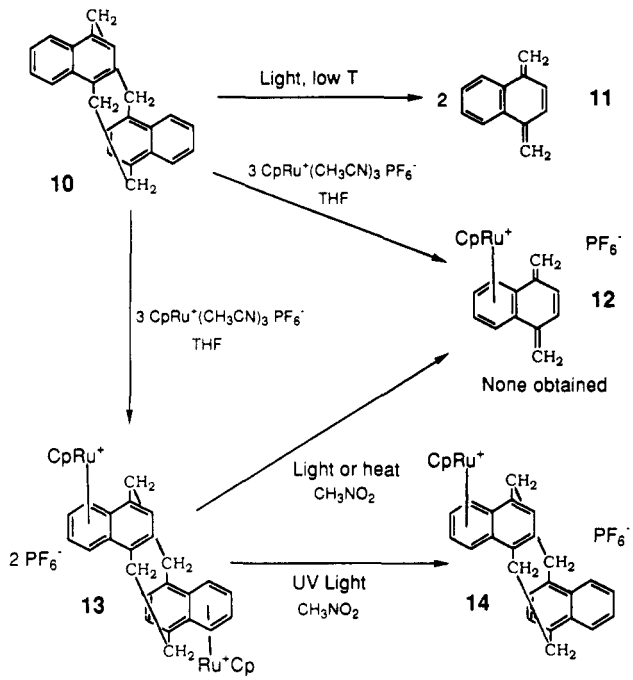
(30) Brown, G. W.; Sondheimer, F. *J. Am. Chem. Soc.* **1967**, *89*, 7116.

Scheme IV



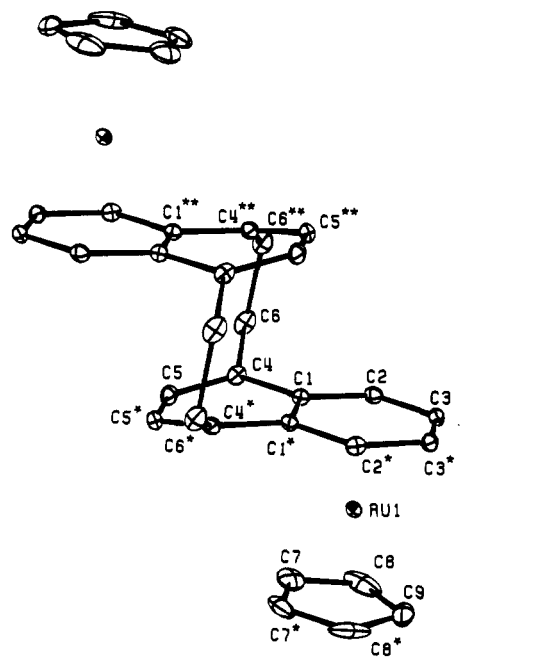


Figure 2. ORTEP drawing of **13**. Hydrogen atoms and hexafluorophosphate counterions have been omitted for clarity.

bond lengths and angles are given in Table VI. The structure consists of two (CpRu$^+$) units bonded to the exo faces of the outer benzo rings of **10** as η^6-ligands. The general bonding features of the Cp–Ru$^+$–arene ring in **13** are comparable to the structures of **7** and other Cp–Ru$^+$–arene derivatives.[23] The distances of the Cp and benzo ring ligand centroids to ruthenium are 1.818 (2) and 1.716 (3) Å, respectively. It is easily seen in Figure 2 that the noncoordinated aromatic rings in **13** are bent from planarity (ca. 15°) into a boat conformation. The naphthalene moieties are slightly translated along their long axes toward each other, resulting in increased overlap and a C4–C6–C6**–C4** dihedral angle of 13.5 (3)°. This has been attributed in **10** to relieving eclipsing hydrogen interactions between the naphthalene moieties and on the

Table V. Atomic Coordinates for the Non-Hydrogen Atoms of 13

atom	*x*	*y*	*z*
Ru(1)	0.16753 (1)	0.00000 (0)	−0.04339 (3)
P(1)	0.14175 (6)	0.50000 (0)	0.48889 (17)
F(1)	0.1209 (2)	0.5000 (0)	0.2696 (4)
F(2)	0.1638 (2)	0.5000 (0)	0.7023 (4)
F(3)	0.0958 (1)	0.3777 (3)	0.4964 (4)
F(4)	0.1895 (1)	0.3809 (3)	0.4745 (3)
C(1)	0.0802 (1)	0.0769 (3)	−0.0022 (3)
C(2)	0.1272 (1)	0.1509 (3)	0.1203 (3)
C(3)	0.1725 (1)	0.0751 (3)	0.2401 (3)
C(4)	0.0330 (1)	0.1534 (3)	−0.1283 (3)
C(5)	−0.0010 (1)	0.0760 (3)	−0.2665 (3)
C(6)	0.0155 (1)	0.3007 (3)	−0.0828 (5)
C(7)	0.1707 (2)	0.0716 (4)	−0.3152 (4)
C(8)	0.2205 (3)	0.1181 (6)	−0.1935 (6)
C(9)	0.2526 (2)	0.0000 (0)	−0.1113 (7)

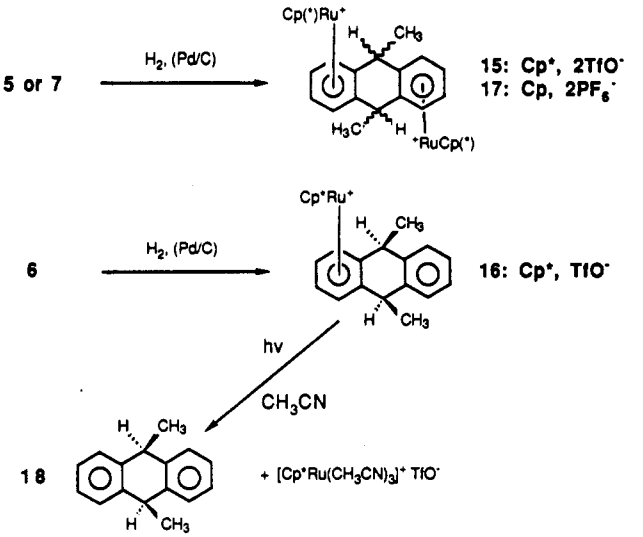
Table VI. Selected Bond Lengths (Å) and Angles (deg) for 13

Ru(1)–Cp	1.818 (2)	Cp–Ru(1)–Bz	176.8 (1)
Ru(1)–Bz	1.716 (3)	C(2)–C(1)–C(4)	121.8 (2)
Ru(1)–C(1)	2.243 (2)	C(2)–C(1)–C(1)*	118.8 (2)
Ru(1)–C(2)	2.216 (3)	C(4)–C(1)–C(1)*	119.3 (2)
Ru(1)–C(3)	2.219 (2)	C(1)–C(2)–C(3)	121.0 (2)
Ru(1)–C(7)	2.165 (4)	C(2)–C(3)–C(3)*	120.2 (2)
Ru(1)–C(8)	2.157 (5)	C(1)–C(4)–C(5)	116.9 (3)
C(1)–C(2)	1.433 (4)	C(1)–C(4)–C(6)	120.4 (2)
C(1)–C(4)	1.460 (4)	C(5)–C(4)–C(6)	121.4 (2)
C(1)–C(1)*	1.435 (4)	C(4)–C(5)–C(5)*	122.2 (2)
C(2)–C(3)	1.407 (4)	C(4)–C(6)–C(6)**	112.3 (3)
C(3)–C(3)*	1.402 (4)	C(8)–C(7)–C(7)*	108.5 (4)
C(4)–C(5)	1.359 (4)	C(7)–C(8)–C(9)	109.2 (4)
C(4)–C(6)	1.496 (4)	C(8)–C(9)–C(8)*	104.6 (5)
C(5)–C(5)*	1.418 (4)	C(1)–C(1)*–C(2)*	118.8 (2)
C(6)–C(6)**	1.577 (5)	C(1)–C(1)*–C(4)*	119.3 (2)
C(7)–C(8)	1.369 (7)	C(3)–C(3)*–C(2)*	120.2 (2)
C(7)–C(7)*	1.336 (6)	C(5)–C(5)*–C(4)*	122.2 (2)
C(8)–C(9)	1.393 (6)	C(7)–C(7)*–C(8)*	108.5 (4)
		C(9)–C(8)*–C(7)*	109.2 (4)
		C(6)–C(6)**–C(4)**	112.3 (3)

methylene bridges.[31] Comparison with known X-ray structural data for **10**, though limited and of poor refinement (R = 0.155),[31] shows that the attachment of the ($CpRu^+$) moiety alters the naphthalenophane ligand structure very little. Most importantly for this study, the C6–C6** and C4–C6 bonds (1.577 (5) and 1.496 (4) Å, respectively), which would be strongly involved in any splitting apart of the naphthalenophane moiety to form **12**, are essentially unchanged from the corresponding bonds in **10** (1.577 and 1.508 Å, respectively). These results show that attaching the ($CpRu^+$) moieties to the naphthalenophane does not alter its electronic structure enough to result in cleavage of the ethano bridges without some other driving force, e.g. rearomatization of a second ring.

The high reactivity of benzo-*p*-quinodimethane (**11**) generally precludes its isolation and characterization under normal conditions. However, **11** can be formed by pyrolysis or photocleavage of **10** and trapping at low temperature.[18,32] Corresponding attempts to form the ($CpRu^+$)-stabilized benzoquinodimethane **12** by thermolysis or photolysis of **13** have been unsuccessful. Heating solutions of **13** in CH_3NO_2 to a gentle reflux for 24 h did not result in any detectable reaction by ^{1}H-NMR spectroscopic analysis. When this solution was irradiated in a quartz tube (450 W, Hg lamp, 4 h, no cooling), one of $CpRu^+$–arene bonds was broken, forming monocoordinated complex **14** (Scheme IV), which was identified by ^{1}H-NMR spectroscopic analysis but not characterized further. Attempts to synthesize **12** by photocleavage of **10** to form **11** at low temperature,[32] followed by trapping with ($CpRu^+$) or (Cp^*Ru^+) groups, are ongoing.

Scheme V



Reactivity of (Cp^*Ru^+)- and ($CpRu^+$)-Stabilized Dibenzo-*p*-quinodimethanes. The potential synthetic utility and chemical reactivities of complexes **5**–**8** were initially investigated by hydrogenation, bromination, and thermal- and photo-ligand displacement reactions in acetonitrile.

Hydrogenation. Hydrogenation of bis(Cp^*Ru^+) complex **5** (MeOH, Pd–C, 1 atm of H_2, room temperature) takes place slowly (2 days) to give bis(Cp^*Ru^+) complexes **15** (92%) as a ca. 1:1 (by ^{1}H-NMR) mixture of *cis*- and *trans*-9,10-dihydro-9,10-dimethylanthracene isomers (Scheme V). Separation of the isomers by column chromatography was unsuccessful. Hydrogenation of mono(Cp^*Ru^+) complex **6** under the same conditions for 24 h gives the mono(Cp^*Ru^+)–*cis*-(*exo*-9,10-dihydro)-9,10-dimethylanthracene complex **16** as the only product in 84% yield. Although we assign the methyl groups in **16** as being endo from obvious reaction geometry considerations, the NMR spectrum of **16** is also consistent with this geometry as suggested from NMR work on the ($CpFe^+$) analogue of **16**.[33] In the ^{1}H-NMR spectrum of **16**, the methyl groups are shifted downfield ($CDCl_3$, δ 1.81) relative to *cis*-9,10-dihydro-9,10-dimethylanthracene[33] (**19**) (CD_3CN, δ 1.51). This is similar to the shift found for the *endo*-methyl groups of the ($CpFe^+$) analogue of **16** (CD_2Cl_2, δ 2.00), in contrast to the *exo*-methyl ($CpFe^+$) isomer (CD_2Cl_2, δ 1.59), which changes relatively little from **19**.

Hydrogenation of complex **7** gave analogous results to yield bis($CpRu^+$) complexes **17** (Scheme V). Complexes **15**–**17** are stable, colorless solids. These hydrogenation reactions demonstrate that use of cyclopentadienylruthenium moieties to block one face of a molecule from attack by a reagent is a potentially useful strategy to achieve regio- or stereoselectivity with potential applications in organic synthesis, especially since the ruthenium moiety can be easily removed afterward.[34] Reactions to afford 9,10-dihydro-9,10-dimethylanthracenes generally

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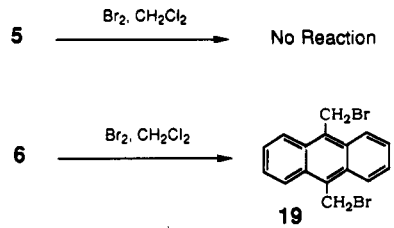
(32) Kaupp, G. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 442.
(33) Sutherland, R. G.; Pannekoek, W. J.; Choi, C. L. *Can. J. Chem.* **1978**, *56*, 1782.
(34) Pearson, A. J.; Park, J. G. *J. Org. Chem.* **1992**, *57*, 1744.

Scheme VI



result in a mixture of the cis and trans isomers,[35] and synthesis of the pure cis isomer **18** originally required a lengthy sequence of stereospecific reactions.[36] Perhaps the best sequence reported to obtain pure **18** consists of a ligand-exchange reaction between ferrocene and 9,10-dimethylanthracene to give the ($CpFe^+$) analogue of **16** in 25% yield, followed by pyrolytic sublimation (80% yield).[33] The overall yield of **18** from relatively expensive 9,10-dimethylanthracene is 20%. However, we have found that easily synthesized [2.2]anthracenophane[3] (**3**) can be reacted with $[Cp^*Ru(CH_3CN)_3]^+TfO^-$ to give mono-(Cp^*Ru^+) complex **6** in high yield (91%).[17] Hydrogenation of **6** proceeds well (84%) to give **16**, which can be photolyzed in acetonitrile to yield **18** (48%) (Scheme V). The overall yield of **18** from **3** is 37%, and the scheme has the advantage that the original ruthenium reagent is regenerated and can be reused.[34] Use of the ($CpRu^+$) group in the above sequence would be more cost effective.

Bromination. Bis(Cp^*Ru^+) complex **5** did not undergo bromination in CH_2Cl_2 solution (Scheme VI), even on heating the solvent to reflux for 2 h. However, complex **6** readily undergoes 1,6-dibromination in CH_2Cl_2 at 0 °C to form 9,10-bis(bromomethyl)anthracene[3] (**19**) (by ^1H-NMR and MS). These results suggest that the nonreactivity of **5** is due to steric hindrance by the two bulky (Cp^*Ru^+) groups on each side of the quinodimethane moiety, although additive electronic effects of having two (Cp^*Ru^+) groups cannot be ruled out. It is also possible that **6** allows tetrabromination, followed by 1,4-dibromide elimination to give **19**.

Thermal and Photodecomposition in Acetonitrile. When acetonitrile solutions of complex **6** were heated to reflux for 24 h under nitrogen, no reaction occurred. However, when the same solutions are irradiated (450-W Hg lamp) in a quartz tube, displacement of dibenzo-*p*-quinodimethane (**4**) by acetonitrile occurred (Scheme I). **4** rapidly polymerized, and insoluble solids were formed. Infrared spectrocopy confirmed that this solid is poly-((1,9)-anthracenylene) by comparison with an authentic sample,[3] showing that **6** can be used to generate free quinodimethane **4** under mild and controlled conditions. It was also clear from the IR spectrum of the resulting polymer that some of the arene rings still have (Cp^*Ru^+) groups attached to them (1285 cm^{-1}, $-SO_3^-$ from triflate). Experiments to probe the synthetic utility of controlled generation of **4** from ($Cp(^*)Ru^+$) compounds **5–8** are ongoing. This result has further significance since the photoreaction should generate the original ruthenium reagent $[Cp^*Ru(CH_3CN)_3]^+TfO^-$, which can be recovered and reused as discussed above for the synthesis of **18**.

Conclusion

The reactions and complexes discussed here are noteworthy for several elements of importance and novelty. First, they represent only the second synthesis of a *p*-quinodimethane species stabilized by an organometallic moiety. This use of η^6-coordination by the ML_x groups represents a new strategy toward the stabilization of these reactive intermediates. Second, to the best of our knowledge, metal-promoted ring opening of a [2.2]paracyclophane species is unknown (normally the cyclophane moiety stays intact). This is especially intriguing because the [6 + 6] cycloreversion reaction to form a *p*-quinodimethane from a [2.2]paracyclophane is a thermally forbidden reaction by orbital symmetry. However, this does not appear to be a general method for ring opening [2.2]-paracyclophanes and other structural requirements for the reaction exist. Third, characterization of the resulting complexes adds to structural knowledge concerning reactive *p*-quinodimethane species, for which little structural information exists. Finally, development of metal-stabilized *p*-quinodimethane complexes and their chemistry may lead to expanded use of *p*-quinodimethanes in organic synthetic strategies. We have shown their potential synthetic utility in a stereospecific synthesis of *cis*-9,10-dihydro-9,10-dimethylanthracene. Further investigations of their synthetic potential are ongoing.

Experimental Section

All procedures were carried out in a glovebox under a nitrogen (N_2) atmosphere or in Schlenk-type glassware on a vacuum line. Solvents were dried and distilled from appropriate drying agents under N_2 before use. Compounds **3**, **5**, **6**, **9**, **10**, $[Cp^*Ru(CH_3CN)_3]^+SO_3CF_3^-$, and $[CpRu(CH_3CN)_3]^+PF_6^-$ 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 filtrations and chromatographies. All ^1H-NMR spectra were recorded on a Varian 300XL (300 MHz) instrument using TMS as a standard. Mass spectral data were collected on a Kratos MS 25-RF mass spectrometer. IR spectra were recorded on a Perkin-Elmer 1310 IR or Biorad FTS-7 FTIR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. Photolyses were carried out using either a Hanovia system (450-W Hg lamp) or a Rayonet reactor (254-nm source). Melting points were determined using a Mel-temp apparatus and are uncorrected. All reactions were carried out at room temperature with magnetic stirring unless otherwise noted.

$[(CpRu)_2(\eta^6,\eta^6$-dibenzo-*p*-quinodimethane)$]^{2+}(PF_6)^-_2$ (7). A flask was charged with 100 mg (0.23 mmol) of **3**, 420 mg (0.97 mmol) of $[CpRu(CH_3CN)_3]^+PF_6^-$, and 30 mL of THF. The solution was stirred for 3 days, at which time the initial dark red-orange color of the solution and solid had faded and a white solid appeared. The solution was filtered, and the white residue was washed twice with 2 mL of THF and 4 mL of ether and dried under reduced pressure to yield 385 mg (74%) of complex **7** as a white, crystalline solid. Purification was effected by slow dimethyl ether diffusion into a nitromethane solution of **7**, mp > 205 °C dec. IR (KBr): 3010, 1620, 905 cm^{-1}. Anal. Calcd for $C_{26}H_{22}F_{12}P_2Ru_2$: C, 37.77; H, 2.68. Found: C, 37.86; H, 2.85. ^1H-NMR ($(CD_3)_2CO$): δ 5.42 (10H, s, 2Cp), 7.09 (4H, dd, J = 2.4 and 4.5 Hz, coordinated arene), 6.61 (4H, dd, J = 2.4 and 4.5 Hz, coordinated arene), 6.65 (4H, s, $2C{=}CH_2$).

$[(CpRu)(\eta^6$-dibenzo-*p*-quinodimethane)$]^+(PF_6)^-$ (8). A flask was charged with 120 mg (0.29 mmol) of **3**, 268 mg (0.62 mmol) of $[CpRu(CH_3CN)_3]^+PF_6^-$, and 30 mL of THF/$ClCH_2CH_2Cl$ (50/50) as solvent. The solution was stirred for 3 days, at which time the initial dark red-orange color had faded and all the solid dissolved. Most of the solvent was removed under reduced pressure, 30 mL of diethyl ether was added, and the light yellow precipitate that formed was collected by filtration, washed twice with 4 mL of ether, and dried under reduced pressure to yield 237 mg (78%) of complex **8**. Purification was effected by slow diethyl ether diffusion into a nitromethane

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solution of **8**, mp > 235 °C dec. IR (KBr): 3010, 1625, 910 cm^{-1}. Anal. Calcd for $C_{21}H_{17}F_6PRu$: C, 48.93; H, 3.32. Found: C, 47.90; H, 3.48. ^{1}H-NMR ($(CD_3)_2CO$): δ 5.17 (5H, s, Cp), 7.90 (2H, dd, *J* = 3.3 and 5.6 Hz, noncoordinated arene), 7.58 (2H, dd, *J* = 3.3 and 5.6 Hz), 7.06 (2H, dd, *J* = 2.4 and 4.5 Hz, coordinated arene), 6.55 (2H, dd, *J* = 2.4 and 4.5 Hz), 6.23 (2H, s, C=CH_2), 6.19 (2H, s, C=CH_2). The high reactivity of **8** manifested itself in that we were unable to obtain a satisfactory elemental analysis for it, despite repeated purifications (in contrast to the mono(Cp*Ru^+) analogue **6**).[17]

Synthesis of [(Cp*Ru)$_2$(η^6,η^6-dibenzo-*p*-quinodimethane)]$^{2+}$(CF$_3$SO$_3^-$)$_2$ (5) and [(CpRu)$_2$-(η^6,η^6-dibenzo-*p*-quinodimethane)]$^{2+}$(PF$_6^-$)$_2$ (7) from 9,10-Bis(chloromethyl)anthracene (9). A flask was charged with 100 mg (0.36 mmol) of 9,10-bis(chloromethyl)anthracene (**9**), 573 mg (1.13 mmol) of [Cp*Ru(CH_3CN)$_3$]$^+SO_3CF_3^-$, and 30 mL of THF. The solution was stirred for 3 days. The solvent was removed under reduced pressure, the yellow residue was run through a short alumina column (CH_3OH eluent), and the red-orange band was collected. Most of the CH_3OH was removed under reduced pressure, and 30 mL of diethyl ether was added. The white precipitate was collected by filtration to give 109 mg (31%) of **5** (by ^{1}H-NMR).[17] The same general procedure using [CpRu(CH_3CN)$_3$]$^+PF_6^-$ as the reagent gave **7** (by ^{1}H-NMR) in 12% yield.

***trans*-[(CpRu)$_2$(*exo*-η^6,η^6-*anti*-[2.2](1,4)naphthalenophane)]$^{2+}$(PF$_6^-$)$_2$ (13).** A flask was charged with 258 mg (0.60 mmol) of [CpRu(CH_3CN)$_3$]$^+PF_6^-$, 50 mg (0.20 mmol) of **10**, and 30 mL of THF. The solution was stirred 3 days, and 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. Most of the solvent was removed under reduced pressure, 30 mL of diethyl ether was added, and the white precipitate that formed was collected by filtration and dried under reduced pressure to yield 154 mg (68%) of **13** as white crystals. Purification was effected by slow diethyl ether diffusion into a nitromethane solution of **13**, mp > 370 °C dec. Anal. Calcd for $C_{34}H_{30}F_{12}P_2Ru_2$: C, 43.88; H, 3.25. Found: C, 43.82; H, 3.40. ^{1}H-NMR (CD_3NO_2): δ 4.84 (10H, s, 2Cp), 6.85 (4H, dd, *J* = 2.4 and 4.5 Hz, coordinated arene), 6.40 (4H, dd, *J* = 2.4 and 4.5 Hz, coordinated arene), 6.21 (4H, s, noncoordinated arene), 3.72 (4H, m, $2CH_2$), 3.32 (4H, m, $2CH_2$).

Photolysis of *trans*-[(CpRu)$_2$(*exo*-η^6,η^6-*anti*-[2.2](1,4)-naphthalenophane)]$^{2+}$(PF$_6^-$)$_2$ (13). Under a positive N_2 pressure, a solution of 200 mg (0.21 mmol) **13** in 50 mL of CH_3NO_2 in a quartz tube was irradiated in a Hanovia photolysis system for 48 h at −20 °C. Solvent was removed under reduced pressure. The ^{1}H-NMR spectrum showed the residue to be mixture of **13** (60%) and mono(CpRu$^+$) complex **14** (40%). The isomers were separated by column chromatography (CH_3NO_2 eluent). Fractions containing the second orange band were concentrated under reduced pressure, 20 mL of diethyl ether was added, and the white solid which formed was collected by filtration and dried under reduced pressure to give **14**. ^{1}H-NMR (CD_3NO_2): δ 4.74 (5H, s, Cp), 6.30 (2H, dd, *J* = 2.4 and 4.5 Hz, coordinated arene), 6.30 (2H, dd, *J* = 2.4 and 4.5 Hz, coordinated arene), 7.54 (2H, dd, *J* = 3.3 and 6.6 Hz, uncoordinated, arene), 7.88 (2H, dd, *J* = 3.3 and 6.6 Hz, noncoordinated arene), 6.05 (2H, s, noncoordinated arene), 6.01 (2H, s, coordinated arene), 3.65 (4H, m, $2CH_2$), 3.15 (4H, m, $2CH_2$).

Hydrogenation of [(Cp*Ru)$_2$(η^6,η^6-dibenzo-*p*-quinodimethane)]$^{2+}$(CF$_3$SO$_3^-$)$_2$ (5). A flask was charged with 200 mg (0.21 mmol) of **5**,[17] 15 mL of CH_3OH, and 100 mg of 5% Pd–C. The solution was stirred for 3 days at 1 atm of H_2. 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 product was collected by filtration and dried under reduced pressure to give 184 mg (92%) of **15** as white crystalline solid. The mixture was not purified further and attempts to separate the isomers by column chromatography were unsuccessful. ^{1}H-NMR showed the product to be a ca. 1:1 mixture of trans and cis isomers **15**. ^{1}H-NMR (CD_3OD): *trans*-dihydro isomer, δ 1.72 (30H, s, 2Cp*), 5.80–6.55 (8H, m, arene), 3.60 (2H, q, *J* = 7.2 Hz, 2CH), 1.68 (6H, d, *J* = 7.5 Hz, $2CH_3$); *cis*-dihydro isomer, δ 1.78 (15H, s, Cp*), 1.85 (15 H, s, Cp*), 5.80–6.55 (8H, m, coordinated arene), 3.85 (2H, q, *J* = 7.2 Hz, 2CH), 1.60 (6H, d, *J* = 7.5 Hz, $2CH_3$). Assignments were made by comparison with chemical shifts for the (CpFe$^+$) *cis*-dihydro analogue of **15**[33] and correlating sets of protons by decoupling experiments.

Hydrogenation of [(Cp*Ru)(η^6-dibenzo-*p*-quinodimethane)]$^+$CF$_3$SO$_3^-$ (6). A flask was charged with 286 mg (0.49 mmol) of **6**, 20 mL of CH_3OH, and 100 mg of 5% Pd–C catalyst. The solution was stirred for 24 h at 1 atm of H_2. 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, 30 mL of diethyl ether was added, and the white crystalline solid was collected by filtration and dried under reduced pressure to give 241 mg (84%) of **16** as a single cis isomer. Purification was effected by slow diethyl ether diffusion into a nitromethane solution of **16**, mp >235 °C dec. Anal. Calcd for $C_{27}H_{31}F_3O_3RuS$: C, 54.63; H, 5.26. Found: C, 54.32; H, 5.31. ^{1}H-NMR ($CDCl_3$): δ 1.55 (15H, s, Cp*), 5.90 (2H, dd, *J* = 2.7 and 6.0 Hz, coordinated arene), 6.10 (2H, dd, *J* = 2.7 and 6.0 Hz, coordinated arene), 7.45 (2H, dd, *J* = 3.0 and 6.0 Hz, noncoordinated arene), 7.40 (2H, dd, *J* = 3.0 and 6.0 Hz, noncoordinated arene), 3.60 (2H, q, *J* = 5.7 Hz, 2CH), 1.81 (6H, d, *J* = 6.6 Hz, $2CH_3$).

***cis*-9,10-Dihydro-9,10-dimethylanthracene (18)[33] from Photolysis of 16.** A quartz tube was charged with 250 mg (0.42 mmol) of **16** and 150 mL of acetonitrile. The tube was sealed and irradiated 5 days (without cooling) in a Rayonet reactor. Solvent was removed from the dark brown solution under reduced pressure, and the solid was extracted 3 times with 10 mL of petroleum ether. The residue was dried under reduced pressure, and ^{1}H-NMR spectroscopy showed it to be recovered [Cp*Ru(CH_3CN)$_3$]$^+$TfO$^-$ (193 mg, 90%). The extract was concentrated to 3 mL and eluted with petroleum ether through a short alumina column. After removal of solvent, ^{1}H-NMR spectroscopy showed the residue to contain 89% *cis*-9,10-dihydro-9,10-dimethylanthracene) (**18**) and 11% 9,10-dimethylanthracene, which were separated by preparative TLC (Al_2O_3, petroleum ether) to give 46 mg (48%) (**18**) as a light yellow solid,[33] mp 129–131 °C (lit.[33] mp 130–131 °C). ^{1}H-NMR ($CDCl_3$): δ 7.24 (8H, m, benzo rings), 4.06 (2H, q, *J* = 7.5 Hz, 2CH), 1.55 (6H, d, *J* = 7.5 Hz, $2CH_3$). EI MS (70 eV): *m/e* 89 (55%), 178 (92), 193 (100), 208 (M^+, 48).

Bromination of [(Cp*Ru)(η^6-dibenzo-*p*-quinodimethane)]$^+$CF$_3$SO$_3^-$ (6). A flask was charged with 300 mg (0.51 mmol) of **6** and 20 mL of CH_2Cl_2 and fitted with a septum. The solution was cooled to −78 °C in a dry ice/acetone bath, and under N_2, a solution of 162 mg (1.01 mmol) of Br_2 in 20 mL of CH_2Cl_2 was added by syringe. After 20 min of stirring, the reaction was continued 20 min without cooling. The solvent was removed under reduced pressure, and the residue was washed twice with 5 mL of diethyl ether to give a black solid, which was extracted 3 times with 5 mL of $CHCl_3$. The combined extracts were filtered through a short alumina column which was washed with an additional 5 mL of $CHCl_3$. Removal of solvent under reduced pressure gave 155 mg (83%) of 9,10-bis(bromomethyl)anthracene[3] (**19**) as a yellow solid. The product was characterized without further purification. ^{1}H-NMR ($CDCl_3$): δ 7.68 (4H, dd, *J* = 3.6 and 6.9 Hz, arene), 8.35 (4H, dd, *J* = 3.6 and 6.9 Hz, arene), 5.52 (4H, s, $2CH_2Br$). EI MS (70 ev): *m/e* 80 (94%), 82 (100), 204 (73), 283 (19), 285 (19), 362 (M^+, 1), 364 (M^+, 2), 365.8 (M^+, 1).

Photolysis of [(Cp*Ru)(η^6-dibenzo-*p*-quinodimethane)]$^+$CF$_3$SO$_3^-$ (6) in CH$_3$CN Solution. In a quartz tube under positive N_2 pressure, a solution of 200 mg (0.34 mmol) of **6** in 30 mL of CH_3CN was irradiated in a Hanovia reactor for 12 h at −20 °C. The insoluble precipitate that formed was isolated by filtration, extracted several times with $CHCl_3$, and dried under

reduced pressure to give 46 mg of (66%) off-white polymer. IR (KBr) (3079 (w), 2956 (w), 1666 (m), 750 (m) cm^{-1}) showed it to be poly((1,9)-anthracenylene) by comparison with an authentic sample.[3]

X-ray Structural Analyses of Complexes 7 and 13. Light yellow crystals of **7** and **13** suitable for X-ray analysis were grown by slow diffusion of diethyl ether vapor into nitromethane solutions. Cell dimensions and data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer by methods standard in this laboratory.[37] The data were corrected for Lorentz and polarization effects; no absorption corrections were applied as they were judged to be insignificant. The structures were solved by the heavy-atom method and refined anisotropically by least-squares analysis (SHELX76).[38] In both **7** and **13**, all the hydrogen atoms (except on C9 in **13**) were located and refined isotropically. Final crystallographic parameters are presented in Table I.

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Supplementary Material Available: Listings of all atomic and hydrogen atom coordinates, anisotropic thermal parameters, bond lengths and angles, and torsional angles for **7** and **13** (12 pages). Ordering information is given on any current masthead page.

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