3324 J. Am. Chem. Soc. 1986, 108, 3324-3334

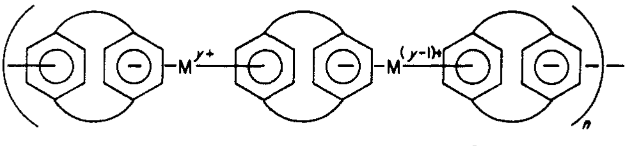
Ruthenium Complexes of $[2_n]$Cyclophanes. A General Synthesis of Bis(η^6-$[2_n]$cyclophane)ruthenium(II) Compounds and Related Chemistry

R. Thomas Swann,[1a] **A. W. Hanson,***[1b] **and V. Boekelheide***[1a,c]

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403, and Atlantic Research Laboratory, National Research Council of Canada, Halifax, Nova Scotia, Canada B3H 3Z1. *Received November 21, 1985*

Abstract: Polymers of metal complexes of cyclophanes have interest as potential electrical conductors. We now report a general method of synthesis for bis(η^6-$[2_n]$cyclophane)ruthenium(II) derivatives which provides access to model subunits of such polymers. The synthetic sequence involves capping $[2_n]$cyclophanes with arene–ruthenium(II) complexes, removing the arene cap by hydride reduction followed by treatment with acid, and then coupling the (η^6-$[2_n]$cyclophane)ruthenium(II) solvate with another molecule of $[2_n]$cyclophane. In this way bis(η^6-$[2_2]$(1,4)cyclophane)ruthenium(II) bis(tetrafluoroborate) (**5**), bis(η^6-$[2_2]$(1,3)cyclophane)ruthenium(II) bis(tetrafluoroborate) (**7**), bis(η^6-$[2_3]$(1,3,5)cyclophane)ruthenium(II) bis(tetrafluoroborate) (**8**), and (η^6-$[2_2]$(1,4)cyclophane)(η^6-$[2_2]$(1,3)cyclophane)ruthenium(II) bis(tetrafluoroborate) (**6**) were synthesized. Treatment of **5** with (η^6-$[2_2]$(1,4)cyclophane)ruthenium(II) solvate then gave the tris(η^6-$[2_2]$(1,4)cyclophane)diruthenium(II) derivative **13**, a model subunit of a transition metal–cyclophane polymer. When **5** was treated with (η^6-hexamethylbenzene)ruthenium(II) solvate, an oligomer, **12**, having three ruthenium atoms in the chain, formed. The electrochemical behavior of these new complexes has been examined and provides indirect evidence for intervalence electron transfer in the examples having more than one ruthenium atom. Hydride reduction of (η^6-hexamethylbenzene)(η^6-$[2_2]$(1,4)cyclophane)ruthenium(II) bis(tetrafluoroborate), **9**, gave (η^4-hexamethyl-1,4-cyclohexadiene)(η^6-$[2_2]$(1,4)cyclophane)ruthenium(0), **10**, whose structure is established by X-ray crystallographic analysis. An analysis of the electronic and ^{1}H NMR spectra of prototype examples of the $[2_n]$cyclophane–ruthenium(II) complexes is reported. Treatment of (η^6-hexamethylbenzene)(η^4-$[2_2]$(1,4)cyclophane)ruthenium(0) with acid converts the ruthenium-bound, cyclophane–benzene ring to a cyclohexadienyl moiety as present in **26**, whose structure is established by X-ray crystallographic analysis. This novel reaction appears to be general as shown by the conversion of (η^6-hexamethylbenzene)(η^4-$[2_4]$(1,2,4,5)cyclophane)ruthenium(0), **28**, by acid to **29** and the conversion of bis(hexamethylbenzene)ruthenium(0), **30**, to **31**. Red-Al (Aldrich) reduction of **31** gives a bis(η^5-hexamethylcyclohexadienyl)ruthenium(II) derivative, **32**, an analogue of ruthenocene. Similarly, **26** was reduced by Red-Al to **34**, a cyclophane-containing bis(cyclohexadienyl) analogue of ruthenocene.

An outstanding characteristic of $[2_n]$cyclophanes, as revealed particularly from photoelectron and ESR studies,[2,3] is the interaction of the two aromatic decks to give one overall π-electron system. One of our goals has been to examine whether this delocalization can be extended through transition-metal complexation.[4,5] If so, a polymer can be envisioned which should show interesting electrical properties and possibly conductivity. One of the advantages of transition-metal–cyclophane complexes is that the individual metal atoms can have different formal oxidation states, and so the question of π-electron delocalization in the polymer can be tested by examining the mixed valence properties of appropriate subunits. To do such experiments, though, synthetic access to such subunits is needed. We now describe a convenient synthetic route for preparing ruthenium–$[2_n]$cyclophane complexes of this type.[6]



potential metal-cyclophane polymer[6]

In designing an appropriate subunit molecule, we were influenced by questions of synthetic feasibility, probable stability of the complex, and the likelihood that the subunit might show the properties of a mixed-valence ion class III. The latter qualification is, of course, the ultimate test for a completely electron-delocalized system. Although bis(arene)chromium compounds have been much studied, Elschenbroich and Heck have shown that the cation of bis(diphenyl)dichromium is a localized mixed-valence class I compound,[7] and so chromium does not appear to us to be a suitable metal. Ferrocene derivatives are very stable compounds, and the cation of bis(fulvalene)diiron is a class III mixed-valence ion.[8] However, the mixed-valence properties of biferrocenyl derivatives change in subtle, and somewhat unpredictable, ways with changes in structure, and these derivatives range in classification from class I to class III.[8-10] Unfortunately, iron forms relatively weak bonds with $[2_n]$cyclophanes.[11-14] Therefore, we chose to study ruthe-

---

[1] (a) University of Oregon. (b) National Research Council of Canada, Halifax. (c) To whom inquiries regarding this manuscript should be addressed. For $[2_n]$cyclophane nomenclature, see: Boekelheide, V. *Top. Curr. Chem.* **1983**, *113*, 87–143.

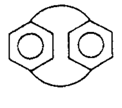
[2] Heilbronner, E.; Yang, Z.-Z. *Top. Curr. Chem.* **1984**, *115*, 1–55.

[3] Gerson, F. *Top. Curr. Chem.* **1984**, *115*, 57–105.

[4] Preliminary publication of portions of this manuscript include: (a) Swann, R. T.; Boekelheide, V. *Tetrahedron Lett.* **1984**, *25*, 899–900. (b) Swann, R. T.; Hanson, A. W.; Boekelheide, V. *J. Am. Chem. Soc.* **1984**, *106*, 818–819.

[5] Laganis, E. D.; Finke, R. G.; Boekelheide, V. *Tetrahedron Lett.* **1980**, *21*, 4405–4408.

[6] The following is a generalized structure representing any one of the possible $[2_n]$cyclophanes



[7] Elschenbroich, Ch.; Heck, J. *J. Am. Chem. Soc.* **1979**, *101*, 6773–6776.

[8] LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhof, U. T.; Eilbracht, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181–3187.

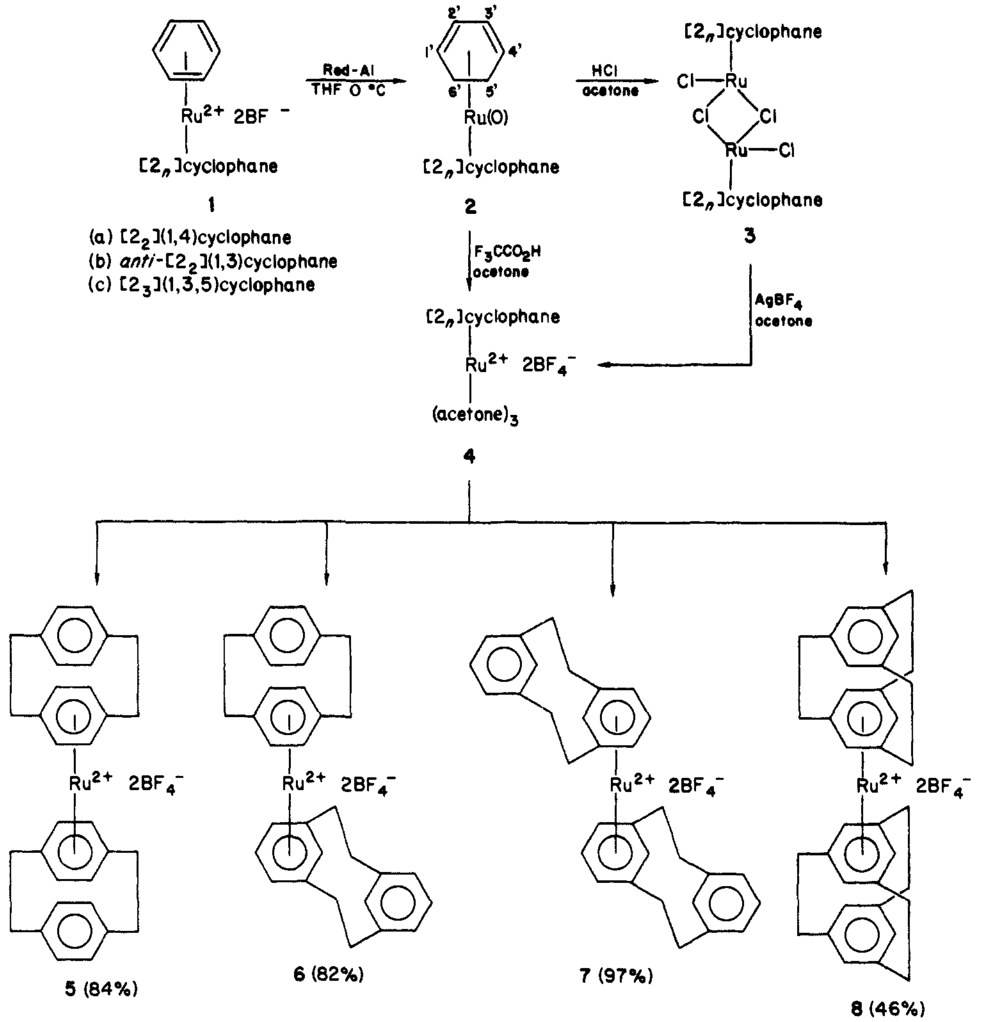
[9] (a) Desbois, M.-H.; Guillin, J.; Mariot, J.-P.; Varret, F.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1985**, 447–449. (b) Desbois, M.-H.; Astruc, D. *J. Am. Chem. Soc.* **1985**, *107*, 5280–5282.

[10] (a) Dong, T.-Y.; Cohn, M. J.; Hendrickson, D. N.; Pierpont, C. G. *J. Am. Chem. Soc.* **1985**, *107*, 4777–4778. (b) Cohn, M. J.; Dong, T. Y.; Hendrickson, D. N.; Geib, S. J.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1985**, 1095–1097.

[11] Laganis, E. D.; Finke, R. G.; Boekelheide, V. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2657–2658.

0002-7863/86/1508-3324$01.50/0

Scheme I



nium, a member of the iron family but forming much stronger bonds with arenes than does iron.

Bennett's synthesis of ruthenium–arene complexes[15] can readily be applied to synthesize arene–ruthenium capped [2_n]cyclophanes.[5] However, the Bennett procedure is only successful for preparing bis(η^6[2_n]cyclophane)ruthenium(II) derivatives in special cases.[16] The difficulty in the Bennett approach to [2_n]cyclophanes has been finding a way to prepare (η^6-[2_n]cyclophane)ruthenium(II) solvates. It occurred to us that a possible method of accomplishing our goal would be to make an arene–ruthenium capped [2_n]-cyclophane and then remove the arene cap to give an (η^6-[2_n]-cyclophane)ruthenium(II) solvate. This ruthenium solvate could then be used to cap another [2_n]cyclophane molecule, either of the same or different structure. This general approach, as outlined in Scheme I, proved to be quite successful in practice.

The (η^6-benzene)(η^6-[2_n]cyclophane)ruthenium(II) bis(tetrafluoroborates), **1a–c**, were prepared by the Bennett method following procedures described previously.[17] Based on earlier studies of hydride reductions of bis(arene)ruthenium(II) derivatives,[18-20] we found that **1a–c** were reduced by sodium bis(methoxyethoxy)aluminum hydride (Red-Al) in tetrahydrofuran at 0 °C to **2a–c**, respectively, in yields of 67–93%.[21] Reaction of η^4-diene–ruthenium(0) complexes with aqueous acid has been shown to remove the diene ligand.[19,22] Similarly, **2a–c**, on treatment with aqueous hydrochloric acid in acetone, gave the dimeric chlorides, **3a–c**, in yields of 71–98%. Treatment of the dimeric chlorides, **3a–c**, with silver tetrafluoroborate in acetone gave the corresponding solvates, **4a–c**. Finally, capping of the appropriate [2_n]cyclophanes with the appropriate (η^6-[2_n]cyclophane)ruthenium(II) solvate gave the desired bis(η^6-[2_n]cyclophane)ruthenium(II) bis(tetrafluoroborates), **5**, **6**, **7**, and **8**, in the yields indicated. Thus, the reaction sequence presented in Scheme I is clearly a useful, general method for preparing (η^6-[2_n]-cyclophane)ruthenium(II) solvates and bis(η^6-[2_n]cyclophane)-ruthenium(II) bis(tetrafluoroborates).

The conversion of the benzene rings of **1a–c** to the 1,3-cyclohexadienes ring in **2a–c** might be presumed to be simply the result of a direct 1,2-hydride attack. However, when (η^6-hexamethylbenzene)(η^6-[2_2](1,4)cyclophane)ruthenium(II) bis(tetrafluoroborate), **9**, was reduced using Red-Al, as before, the product was (η^4-*exo*-3',6'-dihydrohexamethyl-1,4-cyclohexadiene)(η^6-[2_2](1,4)cyclophane)ruthenium(0), **10**. The initial assignment of the structure for **10** was based on the symmetry of its ^{1}H NMR spectrum, only two methyl signals with a doublet at δ 1.58 (6 H) and a singlet at δ 1.26 (12 H), and the literature precedent that

---

(12) Koray, A. R. *J. Organomet. Chem.* **1981**, *212*, 233–235.

(13) Swann, R. T.; Boekelheide, V. *J. Organomet. Chem.* **1982**, *231*, 143–149.

(14) Elzinga, J.; Rosenblum, M. *Tetrahedron Lett.* **1982**, *23*, 1535–1536.

(15) (a) Bennett, M. A.; Matheson, T. W. *J. Organomet. Chem.* **1979**, *175*, 87–93. (b) Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* **1980**, *19*, 1014–1021.

(16) Rohrbach, W. D.; Boekelheide, V. *J. Org. Chem.* **1983**, *48*, 3673–3678.

(17) Laganis, E. D.; Voegeli, R. H.; Swann, R. T.; Finke, R. G.; Hopf, H.; Boekelheide, V. *Organometallics* **1982**, *1*, 1415–1420.

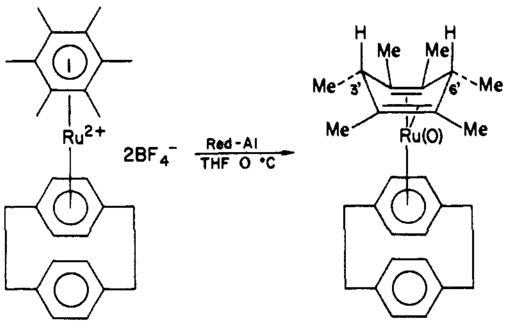
(18) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458–4463.

(19) Grundy, S. L.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1982**, 379–380.

(20) Rybinskaya, M. I.; Kaganovich, V.; Kudinov, A. *J. Organomet. Chem.* **1982**, *235*, 215–219.

(21) Although other metal hydrides can be used to effect this transformation, Red-Al has been the most satisfactory in our experience.

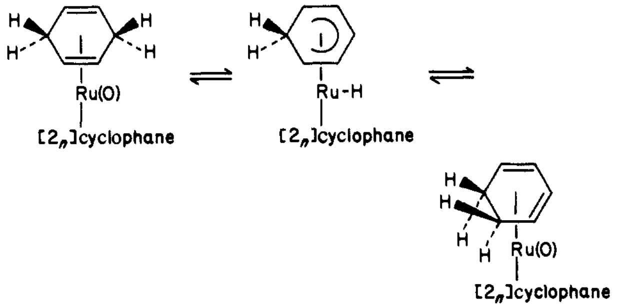
(22) Pertici, P.; Vitulli, G.; Lazzaroni, R.; Salvadori, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1019–1022.



9 **10**

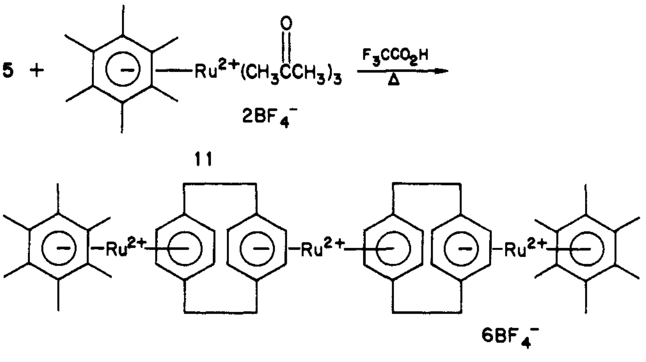
nucleophilic attack on arene–metal ions occurs exo to the least hindered arene.[23–26] Confirmation of this assignment was then made by a single-crystal X-ray analysis, and this result is shown in Figure 1.[26] The cyclohexadiene ring of **10** is clearly boat-shaped with the newly introduced hydrogens being exo at the C(3′) and C(6′) carbons.

This result raises the question of whether, in the other examples where hydride attack on benzene rings gave the 1,3-cyclohexadiene moieties present in **2a–c**, the initial products are not actually 1,4-cyclohexadienes. The availability of endo C–H bonds in **2a–c** would allow equilibration of the initial 1,4-cyclohexadiene moiety to the more stable 1,3-cyclohexadiene via a hydrido–ruthenium intermediate (see eq 1). Such metal-mediated hydrogen shifts have been proposed previously.[27,28]



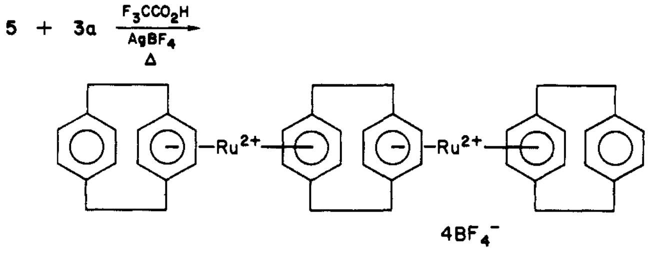
(1)

Experiments to extend the chain length of the bis(η^6-[2_n]-cyclophane)ruthenium(II) bis(tetrafluoroborates) were conducted with **5**. Several problems arise with respect to further capping. In the usual solvents, such as acetone, some solvolysis of the [2_n]cyclophane–ruthenium(II) bond may occur, leading to complicated mixtures. Through trial and error it was found that such solvolysis is minimal in pure trifluoroacetic acid as solvent. Thus, treating **5** with an excess of the trisacetone solvate of (η^6-hexamethylbenzene)ruthenium(II) bis(tetrafluoroborate), **11**, in neat trifluoroacetic acid gave the tris(ruthenium) derivative **12** in 92% yield. The structure of **12** is readily evident from its simple, symmetrical ^{1}H NMR spectrum in which the inner and outer cyclophane aromatic protons appear as two narrowly separated singlets at δ 6.36 and 6.47.



12

To prepare specific oligomers containing purely [2_n]cyclophaneruthenium(II) units poses a different problem, though. (η^6-[2_2](1,4)Cyclophane)ruthenium(II) tris(acetone) solvate, **4a**, is a reactive monomer which, on heating in acetone, self-condenses to give a complicated mixture of oligomers that cannot readily be separated into pure individual components. Although with this monomer self-condensation cannot be avoided in capping reactions using **4a**, it can be controlled to some extent by the choice of reaction conditions and purification methods. Thus, by preparing the tris(trifluoroacetate) solvate of (η^6-[2_2](1,4)cyclophane)ruthenium(II) bis(tetrafluoroborate) and using it to cap **5** in neat trifluoroacetic acid followed by a workup involving selective precipitation and fractional crystallization, the desired tris([2_2](1,4)cyclophane)diruthenium derivative, **13**, was obtained in 12% yield. The structure of **13** is evident from its elemental analysis and from its simple, symmetrical ^{1}H NMR spectrum in which the three types of aromatic protons appear as three singlets at δ 6.20, 6.32, and 6.99.



13

Both **12** and **13** are of particular interest with respect to their electrochemical reduction and the possibility of observing electron transfer between the ruthenium atoms in their corresponding mixed-valence ions. For purposes of comparison with respect to electrochemical behavior, the additional ruthenium(II) complexes **14**,[17] **15**, and **16** were prepared, following the usual Bennett procedure.[15,17] Good crystals of **16** readily formed, and, to gain knowledge regarding the detailed geometry of [2_n]cyclophane–ruthenium(II) complexes, an X-ray single-crystal structural analysis was made.[29] It was of particular interest to compare the geometry of **16** with that of the corresponding free cyclophane, *anti*-4,12-dimethyl[2_2](1,3)cyclophane, **17**.[30] The crystal structure of **16** is illustrated in Figure 2, and the unbound benzene deck of **16** is boat-shaped with the C(12) and C(15) carbons being displaced 0.18 and 0.09 Å below the plane of the ring. This is almost the precise geometry observed for the benzene decks of **17**. However, the benzene deck of the cyclophane bound to ruthenium is slightly chair-shaped with the C(4) carbon being 0.20 Å above the plane of the ring, whereas the C(7) carbon is 0.02 Å below the plane. The reason for this change in geometry of the benzene deck of **16** on ruthenium complexation is not clear, but it does mean that extrapolation of the geometry of cyclophane–ruthenium complexes from that of the free cyclophanes must be done with caution.

Electrochemistry. It is known that, in bis(arene)ruthenium(0) compounds, ruthenium prefers to be bound η^6, η^4, so that one of the arene rings distorts to a boat-shaped geometry.[31–33] For a

---

(23) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047–3077.

(24) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024–2030.

(25) (a) Bird, P. H.; Churchill, M. R. *Chem. Commun.* **1967**, 777–778. (b) Treichel, P. M.; Shubkin, R. L. *Inorg. Chem.* **1967**, *6*, 1328–1334.

(26) Compound **10** crystallized in the tetragonal system $P4_12_12$ (or $P4_32_12$), with $a = 12.298$ (3) Å, $c = 15.040$ (3) Å ($T = 24$ °C, Mo Kα, $\lambda\alpha_1 = 0.7093$ Å), $U = 2274.7$ Å^3, $Z = 4$, Dm = 1.39 (1), Dx = 1.383 g cm^{-3}. The structure was solved by the heavy-atom method and refined to $R = 0.030$ for 2577 reflections with $I > 3\sigma(I)$. Detailed information is given in the supplementary material.

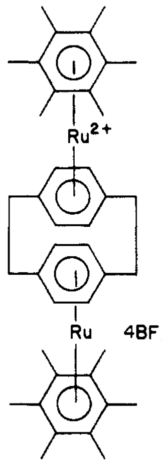
(27) Johnson, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 7395–7396.

(28) Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2875–2883.

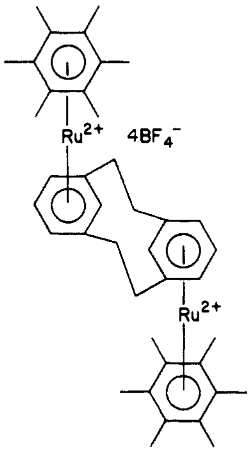
(29) Hanson, A. W. *Cryst. Struct. Commun.* **1982**, *11*, 1019–1026.

(30) Hanson, A. W. *Acta Crystallogr.* **1962**, *15*, 956–960.

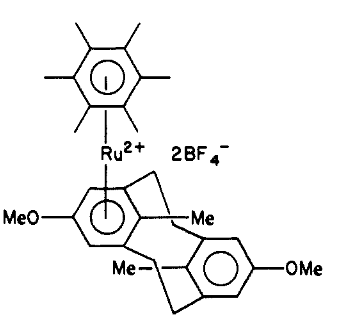
(31) Fischer, E. O.; Elschenbroich, Ch. *Chem. Ber.* **1970**, *103*, 162–172.



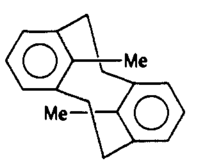
14



15



16



17

series of (η^6-hexamethylbenzene)ruthenium(II) capped $[2_n]$-cyclophanes, it was found that electrochemical reduction occurs generally via a two-electron wave, and the ease of reduction is governed primarily by the ability of the $[2_n]$cyclophane ligand to assume an appropriate geometry for η^4-bonding to the ruthenium(0) atom.[17,34] Thus (η^6-hexamethylbenzene)(η^6-$[2_6]$-(1,2,3,4,5,6)cyclophane)ruthenium(II), having $E_{1/2}$ (vs. SCE) = −0.95 V, is the most difficult member of this series to reduce because its extremely rigid framework does not allow distortion to provide a suitable η^4-geometry.[35] On the other hand, free $[2_4]$(1,2,4,5)cyclophane has boat-shaped benzene decks,[36] well-suited for η^4-bonding, and (η^6-hexamethylbenzene)(η^6-$[2_4]$-(1,2,4,5)cyclophane)ruthenium(II), $E_{1/2}$ = −0.50 V, is the easiest member to reduce. Also, (η^6-hexamethylbenzene)(η^6-$[2_2]$(1,4)-cyclophane)ruthenium(II), **18**, is reduced quite easily, having $E_{1/2}$ = −0.69 V. Although free $[2_2]$(1,4)cyclophane has boat-shaped benzene decks,[37] the prow and stern of these boat-shaped decks are directed away from the complexed ruthenium(II) ion and so would not seem to be well-suited for η^4-bonding. Since much of the present study is concerned with ruthenium complexes of $[2_2]$(1,4)cyclophane, it was important to examine the properties of a $[2_2]$(1,4)cyclophaneruthenium(0) complex in greater detail.

Reduction of **18** by either chemical means or bulk electrolysis readily gave the corresponding ruthenium(0) derivative **19** isolated in high yield as orange crystals. The ^{1}H NMR spectrum of **19** shows a singlet at δ 1.96 (18 H), and so the hexamethylbenzene ligand is bound η^6 to ruthenium. If the $[2_2]$(1,4)cyclophane ligand in **19** had the same geometry as the corresponding free cyclophane molecule, it would be symmetrical, and the protons at C(7) and C(8) should be equivalent; likewise, those at C(4) and C(5) should be equivalent. Instead, the part of the ^{1}H NMR spectrum of **19**, relating to the $[2_2]$(1,4)cyclophane ligand is quite complicated with no two aromatic protons having the same chemical shift. However, if one assumes that the $[2_2]$(1,4)cyclophane is bound η^4 with the geometry shown in structure **19**, a rational interpre-

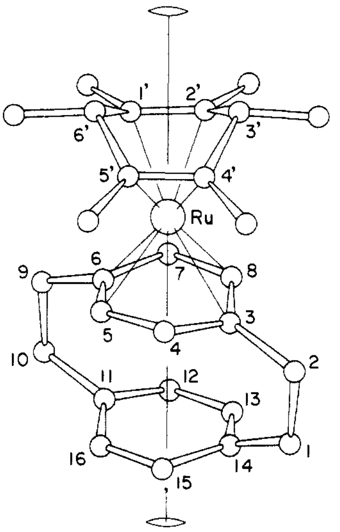


Figure 1. Structure of **10** as determined by X-ray crystallography.[26] The Ru atom lies on a crystallographic two-fold axis. The Ru–C bonds range from 2.135 (3) to 2.365 (3) Å. C(1′)–C(2′) = 1.411 (4) Å; other C–C bond lengths and bond angles are consistent with the proposed formulation.

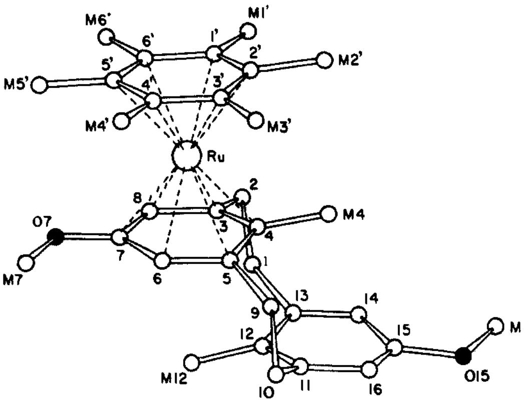


Figure 2. Structure of **16** as determined by X-ray crystallography.[29] The Ru–C(1′ through 6′) bond lengths range from 2.22 to 2.26 Å; Ru–O (3), 2.29 (2) Å; Ru–C (4), 2.22 (2); Ru–C (5), 2.36 (2); Ru–C (6), 2.26 (2); Ru–C (7), 2.24 (2); Ru–C (8), 2.23 (2). (M = methyl; O = oxygen).

Table I. Electrochemical Data for the Ruthenium(II)–$[2_n]$Cyclophane Complexes

compd[a]		$E_{1/2}$ or E_{p_c} (vs. SCE)[b] (V)	ΔE_p[c] (mV)	i_a/i_c	coulmtry[d]
5		−0.616 ± 0.003	134	0.95	1.99
6		−0.589 ± 0.003	59	0.88	1.98
7		−0.613 ± 0.003	55	0.88	1.95
8		−0.831 ± 0.003	63	0.59	~2.0
		−1.01 ± 0.01	70	0.19	
12		−0.570 ± 0.003	49	0.80	
		−0.724 ± 0.003	45	irr	
	E_{p_c}	−1.667 ± 0.003		irr	
13	E_{p_c}	−0.294 ± 0.003	76	irr	
	E_{p_c}	−1.615 ± 0.003		irr	

[a] Compounds **14** and **15** underwent decomposition during cyclic voltammetry, giving no useful data. [b] Measurements were made at 20 °C using propylene carbonate as solvent and at a scan rate of 100 mV/s. [c] ΔE_p values have been corrected by comparison with the ΔE_p for ferricinium ion measured immediately after in the same cell. [d] Separation of the individual waves for **8** was not possible, and the value given is for both waves combined.

---

(32) Darensbourg, M. Y.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 7425–7428.

(33) Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *28*, 2049–2059.

(34) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347–350.

(35) Hanson, A. W.; Cameron, T. S. *J. Chem. Res., Synop.* **1980**, 336–337.

(36) Hanson, A. W. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *33*, 2003–2007.

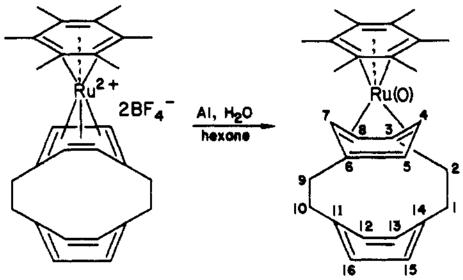
(37) Hope, H.; Bernstein, J.; Trueblood, K. N. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *28*, 1733–1743.

Table II. Electronic Spectral Data for Metal Complexes **20**, **21**, **22**, **5**, and **14** ($\lambda_{max}(\epsilon)$); Transition Assignment[a]

20	**21**	**22**	**5**	**14**
235 (4.6×10^4) π–d	210 (6.0×10^4) π–d	215.5 (3.9×10^4) π–d	216.5 (4.1×10^4) π–d	229 ($\sim 5 \times 10^4$) π–d
254 (6.8×10^3)[c] π–d	235 (2.6×10^3)[c] π–d	234 (1.9×10^4)[c] π–d	230 (3.5×10^4)[c] π–d	
325 (3.4×10^3) d–d	261 (2.5×10^3) d–d	273 (5.5×10^4)[c]		280 (8.0×10^3)[c] d–d
456 (96) d–d	305 (2.4×10^2)[c] d–d		304 (6.3×10^3)[c] π–d	333 (7.5×10^2)[c] d–d
534 (38)[c] d–d	349 (1.2×10^2)[c] d–d	343 (1.2×10^3)[c] π–d	355 (2.5×10^3)[c] π–d	380 (3.5×10^2)[c] d–d

[a] All of the ruthenium(II) complexes were measured at room temperature as BF_4^- salts dissolved in acetonitrile. [b] Spectral data for **20** is that given in ref 41. [c] A shoulder.

tation of the ^1H NMR spectrum can be made, and this interpretation is supported by double resonance decoupling experiments. We assign the two high field signals at δ 1.43 (1 H) and 1.49 (1 H) to the protons at C(7) and C(4), since they are closest to the ruthenium atom and are not equivalent. The protons at C(5) and C(8) are somewhat farther away from ruthenium and are assigned to the signals at δ 4.08 (1 H) and 4.28 (1 H). The aromatic protons of the unbound benzene deck are still further removed from the environment of the ruthenium atom and are assigned to the signals at δ 6.58 (1 H), 6.61 (1 H), 6.81 (1 H), and 7.04 (1 H). Although the geometry suggested for **19** may appear unusual, examination of molecular models suggests that this geometry is easily attained by a simple twisting motion around the axes of the C(4)–C(5) and C(7)–C(8) bonds. However, the molecular model experiments also suggest that simultaneous twisting in this fashion of both benzene decks of a $[2_2](1,4)$cyclophane molecule would be exceedingly difficult, if not impossible. This indicates that there would be a significant energy barrier for simultaneous η^4-bonding to ruthenium at each face of a $[2_2](1,4)$cyclophane molecule. This conclusion is of importance with respect to the properties of oligomers of $[2_2]$(1,4)cyclophane–ruthenium complexes where the $[2_2](1,4)$cyclophane ligand is bound to two ruthenium atoms.



18 **19**

The data from our electrochemical measurements are summarized in Table I. As shown previously,[17] the effect of substituting one hexamethylbenzene ligand of bis(η^6-hexamethylbenzene)ruthenium(II) by $[2_2](1,4)$cyclophane, as in **18**, is to make the $E_{1/2}$ value more positive by 330 mV. In large part this difference is due to the ease with which the $[2_2](1,4)$cyclophane moiety can adopt the necessary geometry for η^4-bonding as in **19**, whereas deforming the aromatic hexamethylbenzene ring to a boat-shape for η^4-bonding has a high energy barrier.[32] Comparing **18** to **5**, where both ligands are now $[2_2](1,4)$cyclophane, we find that **5** is reduced more readily than **18** by 180 mV.[38] Thus, having two ligands that can readily deform to provide η^4-bonding is better than having one, but by something less than twice the difference.

When the $[2_2](1,4)$cyclophane moiety in **5** is replaced by $[2_2](1,3)$cyclophane, as in **6** and **7**, there is very little change in the $E_{1/2}$ values. The free $[2_2](1,3)$cyclophane molecule has boat-shaped benzene decks,[39] and so it is probably comparable to $[2_2](1,4)$cyclophane with respect to ease of deforming to provide η^4-bonding. However, there are other factors besides the ability to provide suitable geometry for η^4-bonding that influence the ease of reduction. This is evident in the case of **8**. When one of the hexamethylbenzene ligands of bis(η^6-hexamethylbenzene)ruthenium(II) is replaced by $[2_3](1,3,5)$cyclophane, the $E_{1/2}$ value becomes more positive by 110 mV.[17] The free $[2_3](1,3,5)$cyclophane molecule is extremely rigid,[40] and its deformation to provide η^4-bonding would be expected to have a higher energy barrier than that for hexamethylbenzene. The greater ease of reduction with the $[2_3](1,3,5)$cyclophane ligand is attributed to the greater ability of the $[2_3](1,3,5)$cyclophane moiety to accept negative charge. We now find that when the second hexamethylbenzene ligand is also replaced by $[2_3](1,3,5)$cyclophane, as in **8**, cyclic voltammetry shows two reversible, one-electron waves at $E_{1/2} = -0.831 \pm 0.003$ and $E'_{1/2} = -1.01 \pm 0.01$ V. This suggests that there is no great change in the geometry of **8** during the introduction of the first electron and that the more negative voltage required for introduction of the second electron is primarily an electrostatic effect. The two-electron reduction product of **8** may be the first true example of a 20-electron ruthenium(0) complex.

The tris(η^6-$[2_2](1,4)$cyclophane)diruthenium(II) derivative **13** shows two irreversible reduction waves at $E_{p_c} = -0.294 \pm 0.003$ V and $E'_{p_c} = -1.615 \pm 0.003$ V. The reduction of the diruthenium compound **13** occurs more readily than its monoruthenium analogue **5** by 322 mV. This large difference strongly suggests electron interaction between the two ruthenium atoms in the reduced species.[9b] The effect is too large to be accounted for simply by the coulombic effect of two isolated ruthenium(II) ions per molecule instead of one. Unfortunately, though, both reduction waves are irreversible, and the possibility of preparing and isolating a mixed-valence ion corresponding to **13** with an overall charge of 2^+ does not seem feasible.

In the case of **12**, three reduction waves are seen in which the first two are largely reversible, whereas the third is not. Although the first $E_{1/2}$ at -0.570 ± 0.003 V is lower than those of analogous monoruthenium complexes, the difference is not so striking. Quite possibly there is some electron interaction between ruthenium atoms in the reduced species derived from **12**. However, the lability of the intermediates formed during the reduction of **12** seems again to preclude the possibility of isolating and studying a pure sample of a mixed-valence ion derived from **12**.

Electronic Spectra. Hendrickson et al. have measured the electronic spectra of certain bis(η^6-arene)iron(II) complexes and have made assignments for their electronic transitions.[41] Elzinga and Rosenblum have reported the spectra for two bis(η^6-$[2_n]$-cyclophane)iron(II) complexes.[42] We have now examined the electronic spectra of bis(η^6-hexamethylbenzene)ruthenium(II), **21**, comparing it to that of bis(η^6-hexamethylbenzene)iron(II),

---

(38) In comparing $E_{1/2}$ values measured in acetone, as in ref 17, with those in Table I, where the solvent is propylene carbonate, one must realize that $E_{1/2}$ values in acetone are approximately 119 mV more positive than those measured in acetone under the same conditions. Propylene carbonate has been used in the present study because of the greater solubility and stability it provides for these complexes.

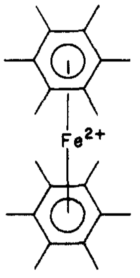
(39) Brown, C. J. *J. Chem. Soc.* **1953**, 3278–3285.

(40) Hanson, A. W. *Cryst. Struct. Commun.* **1980**, *9*, 1243–1248.

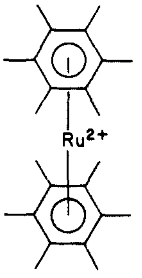
(41) Morrison, W. H.; Ho, E. Y.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 500–506.

(42) Elzinga, J.; Rosenblum, M. *Organometallics* **1983**, *2*, 1214–1219.

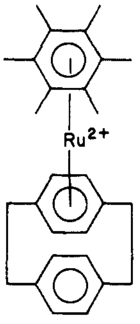
20,[41] as well as observing the changes caused by replacing first one and then both hexamethylbenzene moieties of **21** by $[2_2]$-(1,4)cyclophane, as in **22** and **5**, respectively. In addition, we have looked at the effect of the presence of two ruthenium(II) atoms attached to the same $[2_2]$(1,4)cyclophane, as in **14**. The data are summarized in Table II.



20



21



22

In the interpretation of the spectrum of **20** by Hendrickson et al.,[41] the two intense, high-energy bands at 235 and 254 nm were assigned to symmetry-allowed transitions between occupied ligand π-orbitals and vacant metal d-orbitals. The less intense, lower energy bands at 325, 456, and 534 nm were assigned to symmetry-forbidden, metal d–d-orbital transitions. The analogous ruthenium(II) complex, **21**, likewise exhibits five bands with a similar intensity pattern to that of **20**. The absorption bands of the ruthenium(II) complex all appear at shorter wavelength than those of iron, but this is in accord with the hypsochromic shift observed in going from ferrocene to ruthenocene.[43] By analogy with the iron complexes, we assign the two short wavelength bands of **21** to π–d transitions and the three longer wavelength bands to symmetry-forbidden d–d transitions.

As the hexamethylbenzene ligands are replaced by $[2_2]$(1,4)-cyclophane moieties, there is little change in the shortest wavelength band of the spectrum. This suggests that this π–d transition observed for the $[2_2]$(1,4)cyclophane complexes originates from low-energy orbitals having primarily ruthenium-bound deck π-character. This is best understood by examination of the qualitative molecular orbital interaction diagram presented in Figure 3. This diagram shows the important qualitative orbital mixing which arises when two benzene rings are brought into close proximity with bis(η^6-benzene)ruthenium(II) to form **5**.[44] For clarity, the effect of the bridging alkanes is omitted. It is also assumed that only slight mixing occurs between the $1e_{1u}$ orbitals of the ruthenium-bound benzene deck of the cyclophane and the e_{1u} orbitals of the unbound benzene deck, since there is a significant disparity in their energies. For **21**, the short wavelength absorptions are associated with $1e_{1u}$ to $2e_{1g}$ transitions.[41,43] With complexes bearing a cyclophane these absorptions correspond to transitions from the lower e_{1u} set of orbitals in the center of Figure 3 to the vacant e_{1g} d orbitals.

The absorption bands at 343 nm for **22** and at 304 and 355 nm for **5** appear to be too intense to be assigned to symmetry-forbidden d–d transitions. Instead, based on symmetry considerations, we propose a specific "cyclophane-to-metal" band involving a transition from the higher lying e_{1u} orbitals (largely of unbound deck π-character) in the center of Figure 3 to a vacant ruthenium d-orbital.

We encountered difficulties in obtaining the electronic spectrum of **14**. The absorption band at 229 nm decreased in intensity upon repeated scans, giving rise to a new absorption at 216 nm. Apparently, photochemical cleavage of a $[2_2]$(1,4)cyclophane–ruthenium(II) bond is occurring, resulting in the formation of **22** plus the acetonitrile solvate of (η^6-hexamethylbenzene)ruthenium(II). Possibly, having two ruthenium(II) ions bound to the same cyclophane is mutually weakening, so that excitation of an electron from an occupied π-orbital (ligand–metal bonding) to a vacant d-orbital leads to dissociation of the complex.

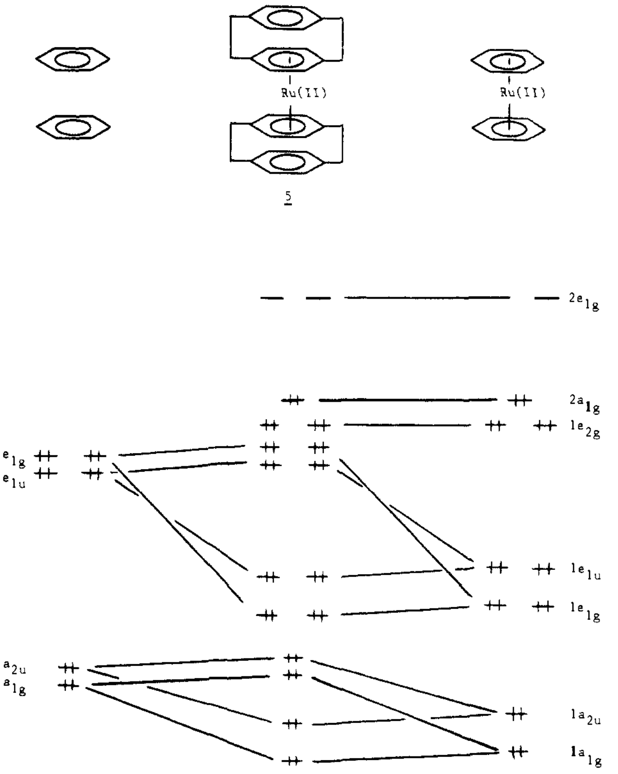


Figure 3. Molecular orbital interaction diagram for bis(η^6-$[2_2]$(1,4)-cyclophane)ruthenium(II).

^{1}H NMR Analysis. In an earlier study of $[2_n]$cyclophane–iron(II) complexes,[45] we showed that the ^{1}H NMR spectra of metal complexes of *anti*-$[2_2]$(1,3)cyclophanes are ideally suited for analyzing the effects of metal complexation with respect to changes in ring current and charge density for each benzene deck of the cyclophane. In *anti*-$[2_2]$(1,3)cyclophane the aromatic protons at the C(6), C(7), and C(8) carbons show an AB_2 pattern that is essentially the same in chemical shift and multiplicity as in *m*-xylene, i.e., these protons are isolated from the ring current in the other benzene deck. However, the C(4) proton is almost directly over the center of the opposite deck and, as a result of the ring current in the opposite deck, its signal is strongly shifted upfield. This is illustrated by structure **23**, where the numbers in parentheses are the δ values for the associated protons measured in acetonitrile-d_6 at room temperature. Thus, by analyzing the ^{1}H NMR spectra of the mono- and bis(capped) ruthenium(II) derivatives **24** and **15**, respectively, we can deduce the effect of ruthenium(II) complexation on both the ring current and charge density of each of the cyclophane decks.

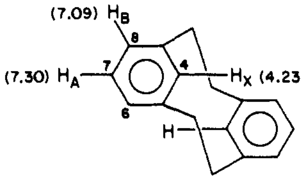
From examination of the chemical shift value for the aromatic AB_2 protons of **23**, **24**, and **15**, it is apparent that ruthenium(II) complexation leads to an upfield shift of 0.4–0.8 ppm. This involves a complex of factors including changes in bond order, ring current, and charge density plus the direct influence of the magnetic anisotropy of the ruthenium ion. In the case of **24**, the $A'B'_2$ protons of the unbound deck move downfield about 0.2 ppm and this must be largely due to a change in charge density as the result of electron transfer to the opposite, complexed benzene deck. The remarkable upfield shift of the H_X proton of **24** to δ 2.57 is a combination of the same factors affecting the AB_2 protons but with the effect of the ring current of the opposite deck remaining essentially unchanged. On the other hand, the $H_{X'}$ proton moves downfield 0.8 ppm and this must be largely the result of loss of

---

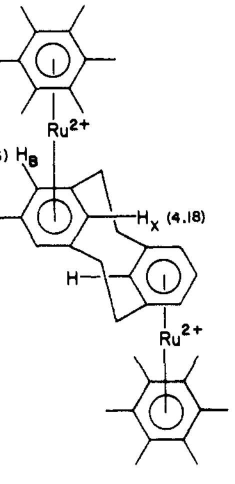
[43] Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603-3612.

[44] For a discussion of ligand–metal orbital interactions in bis(arene)-metal complexes, see: Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499-525.

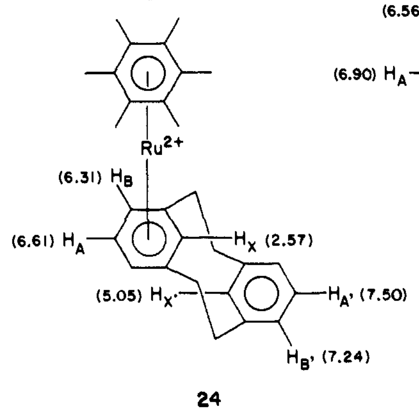
[45] Swann, R. T.; Boekelheide, V. *J. Organomet. Chem.* **1982**, *231*, 143-149.



23



15

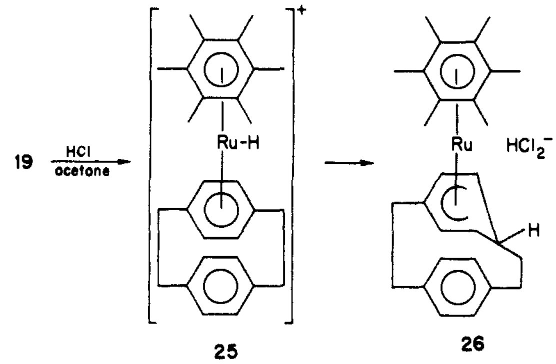


24

ring current in the ruthenium-bound benzene deck. At first glance it is surprising that the chemical shift of the H_X proton (δ 4.18) of **15** is essentially the same as that for the H_X proton of the free cyclophane **23**. This, though, is the result of compensating effects. Ruthenium complexation of this benzene deck bearing the H_X proton of **15** leads to an upfield shift just as it does for **24**. However, ruthenium complexation of the opposite deck leads to a decrease in ring current and thus provides a downfield shift for H_X proton of **15**. The two effects appear to be nearly equal in magnitude.

It is fortunate that the ^1H NMR spectra of *anti*-[2_2](1,3)-cyclophane are subject to analysis in this way because it provides an insight into the fundamental changes occurring during metal complexation that is not available from the spectra of the metal complexes of the other [2_n]cyclophanes where the decks are directly over each other.

Ruthenium(II) Complexes of Cyclohexadienyl Anions. In Scheme I the reaction of (η^4-cyclohexadiene)(η^6-[2_n]-cyclophane)ruthenium(0) derivatives with acid was employed to prepare (η^6-[2_n]cyclophane)ruthenium(II) solvates, with the cyclohexadiene ligand being converted to cyclohexene. Also, (η^6-arene)(η^4-[2_n]cyclophane)ruthenium(0) derivatives are readily prepared either by bulk electrolysis or chemical reduction, as described for the preparation of **19**. It was of interest, therefore, to see whether treatment of derivatives such as **19** with acid would lead to cleavage of the arene or cyclophane ligand in a similar manner to that observed for **2a–c**. In fact, treatment of **19** with a solution of concentrated hydrochloric acid in acetone gave the novel structure **26** in 67% yield. The skeletal structure assigned to **26** is clearly suggested by its ^1H NMR spectrum. However, elemental analysis of **26** showed the unexpected presence of the additional elements of hydrogen chloride. A single-crystal X-ray analysis of **26** confirmed the correctness of the skeletal assignment and showed the counter ion to be the unusual hydrogen dichloride anion.[4b] This anion can be readily exchanged for other counter ions such as the hexafluorophosphate anion and so is not significant to the structure of the organic moiety of **26**. The structure of **26**, as deduced from X-ray analysis, is presented in Figure 4.[4b]



25 **26**

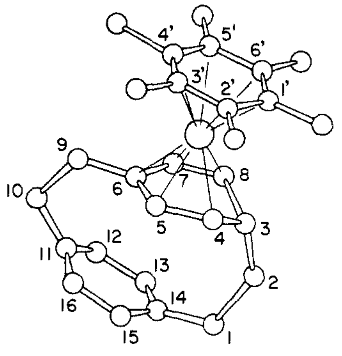


Figure 4. Structure of **26** as determined by X-ray crystallography.[4b] A view of the metal–organic ion (H atoms omitted). Ru–C bonds range from 2.17 (1) to 2.24 (1) Å. Some C–c distances (Å): 3–2, 1.56 (2); 3–4, 1.53 (2); 3–8, 1.51 (2); 4–5, 1.42 (2); 7–8, 1.40 (2); 5–6, 1.41 (2); 6–7, 1.42 (2) Å. Other C–C bond distances and bond angles are consistent with the proposed formulation. Linear HCl_2^- ion omitted.

Although Wilkinson et al. have reported that the reaction of bis(η^6-benzene)ruthenium(II) with phenyllithium gives bis(η^5-1-phenylcyclohexadienyl)ruthenium(II),[18] and Stahl and Ernst have described the formation of bis(η^5-pentadienyl)ruthenium(II) derivatives (open ruthenocenes) by the reaction of pentadienes with ruthenium trichloride and zinc,[46] this apparently is the first example of preparing (η^5-cyclohexadienyl)ruthenium(II) complexes by reaction of acid with bis(arene)ruthenium(0) derivatives. The fact that in structure **26** the hydrogen has been added endo to the benzene deck of the cyclophane ligand suggests that addition of acid first leads to a hydridoruthenium bond, as in **25**, and then hydrogen transfer to the cyclophane ligand occurs. Probably, transfer of hydrogen to the cyclophane deck is preferred over transfer to the hexamethylbenzene ligand because protonation of the benzene deck of the [2_2](1,4)cyclophane results in a large relief of ring strain.

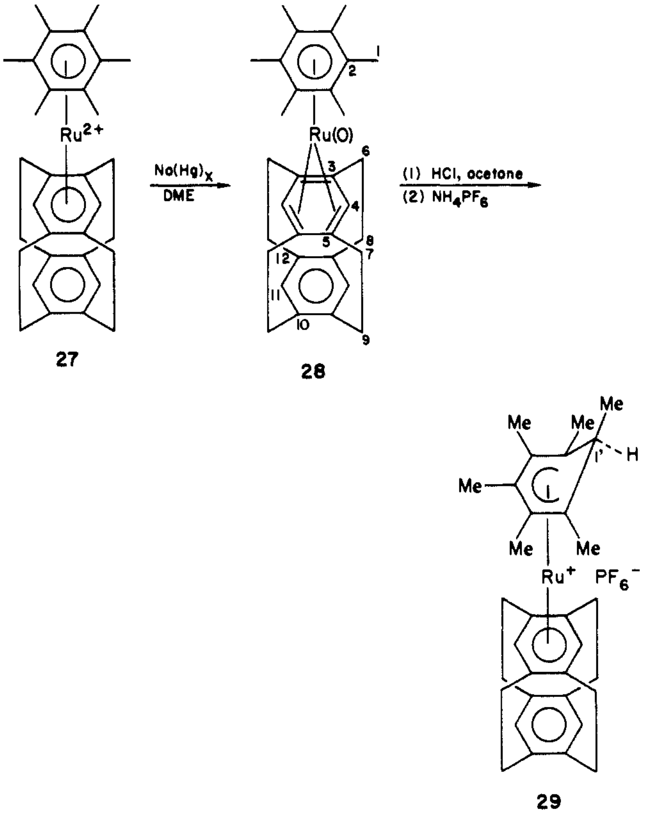
Support for these conclusions arose from a similar experiment employing [2_4](1,2,4,5)cyclophane. Reduction of (η^6-hexamethylbenzene)(η^6-[2_4](1,2,4,5)cyclophane)ruthenium(II) bis(tetrafluoroborate), **27**, either chemically or by bulk electrolysis, gave the corresponding ruthenium(0) derivative **28** in good yield. When **28** was treated with hydrochloric acid in acetone, the solution turned a deep red, suggestive of a hydridoruthenium intermediate, and then slowly turned yellow. Treatment of the yellow solution with ammonium hexafluorophosphate followed by workup gave **29** as yellow crystals in 76% yield. In this case, protonation of the benzene deck of [2_4](1,2,4,5)cyclophane does not lead to relief of cyclophane ring strain, so that hydrogen transfer occurs preferentially to the hexamethylbenzene ligand. The structure of **29** is readily evident from its ^1H NMR spectrum. The methyl group at C(1′) appears as a doublet at δ 0.28 (3 H), and the remaining methyl signals are singlets at 1.62 (6 H), 1.89 (6 H), and 2.27 (3 H). As expected for structure **29**, the aromatic protons of the cyclophane moiety appear as two singlets at δ 4.48 (2 H, C(5) and C(8)), and 6.51 (2 H, C(12) and C(15)).

The assignment of infrared stretching frequencies to endo and exo carbon–hydrogen bonds of cyclic diene–metal complexes has been a subject of controversy.[18,24–26,47] More recently, there appears to be general agreement that endo C–H bonds absorb in the region of 2950 cm^{-1}, whereas exo C–H bonds absorb around 2750 cm^{-1}. One consequence of our present study is that **26**, whose structure has been established by X-ray analysis to have an endo C–H bond, absorbs strongly at 2924 cm^{-1} but shows no absorption around 2750 cm^{-1}. Thus, the correctness of the current inter-

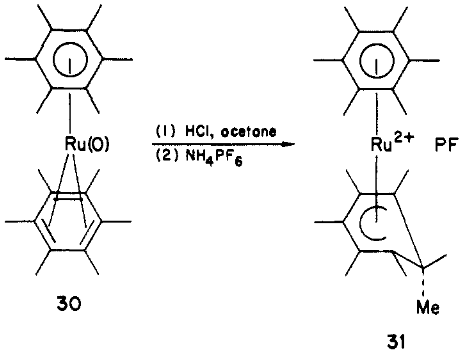
---

(46) Stahl, L.; Ernst, R. D. *Organometallics* **1983**, *2*, 1229–1234.

(47) Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3753–3767.

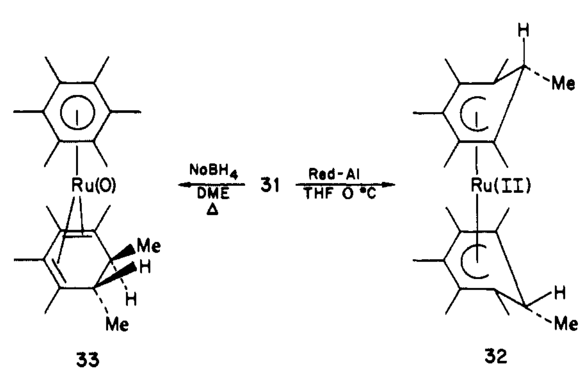


pretation of infrared structural assignments for endo and exo C–H bonds is established. Furthermore, **29** shows an absorption band at 2950 cm^{-1} and this provides additional support for the presence of the endo C–H bond in our structural assignment for **29**. To explore whether the acid-induced conversion of bis(η^6-arene)ruthenium(0) derivatives to (η^5-cyclohexadienyl)ruthenium(II) derivatives is a general reaction, we have examined the case of bis(η^6-hexamethylbenzene)ruthenium(0) **30**.[31] Treatment of **30**



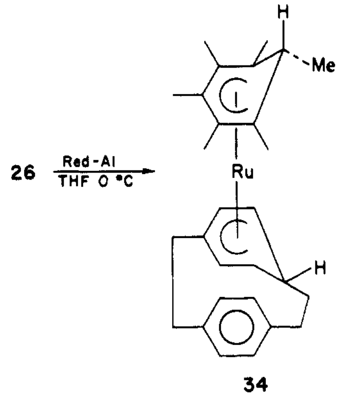
with a solution of hydrochloric acid in acetone, followed by treatment with aqueous ammonium hexafluorophosphate, readily gave the cyclohexadienyl derivative **31**. Our assignment of structure to **31** is clearly supported by its ^{1}H NMR and infrared spectra, and so the generality of this reaction sequence is demonstrated.

The availability of **31** made it of interest to see whether we could make bis(η^5-cyclohexadienyl)ruthenium(II) derivatives, which would be ruthenocene analogues. When a solution of **31** in tetrahydrofuran was treated with Red-Al at 0 °C, a smooth conversion occurred to give **32** in 89% yield. Since hydride attack on the hexamethylbenzene ring is expected to occur exo, **32** should have both exo and endo C–H bonds. In accord with this assignment the infrared spectrum of **32** shows strong absorption bands at both 2962 and 2760 cm^{-1}. Also, the ^{1}H NMR spectrum of **32** shows two distinct hexamethylcyclohexadienyl patterns corresponding to the two slightly different endo and exo rings. The fact that hydride attack occurred exclusively on the hexamethylbenzene ring rather than on the hexamethylcyclohexadienyl



ring could not be predicted. Somewhat surprisingly, though, treatment of **31** with sodium borohydride in boiling 1,2-dimethoxyethane (DME) gave the alternate product **33**, where hydride attack occurred on the hexamethylcyclopentadienyl ring. The assignment of structure for **33** is again evident from its spectra. The reason for the difference in behavior with the two, relatively similar, hydride reagents is not clear. It might be thought that **32** is a product of kinetic control, whereas **33** is the more stable thermodynamic product. However, heating **32** with sodium borohydride in DME did not convert it to **33**.

To provide a second example of a cyclohexadienyl analogue of ruthenocene the reduction of **26** using Red-Al in THF at 0 °C was carried out. This gave the neutral bis(η^5-cyclohexadienyl)ruthenium(II) derivative **34** as yellow crystals in 92% yield. Again, the infrared and ^{1}H NMR spectra of **34** are in good accord with its assigned structure.



Experimental Section[48]

(η^6-Benzene)(η^6-*anti*-[2$_2$](1,3)cyclophane)ruthenium(II) Bis(tetrafluoroborate) (1b). Model Procedure for Arene–Ruthenium(II) Capping. A solution of 1.380 g (5.52 mmol) of bis(η^6-benzene)dichlorobis(μ-chloro)diruthenium[15] and 2.268 g (11.65 mmol) of silver tetrafluoroborate in 35 mL of acetone was stirred at room temperature for 30 min. The precipitate of silver chloride was removed by filtration (in cases where the silver chloride was finely divided a bed of Celite was used for the filtration), and two 5-mL aliquots of acetone were used to wash the precipitate. To the combined filtrate and washings was added 230 mg (1.10 mmol) of *anti*-[2$_2$](1,3)cyclophane and 35 mL of trifluoroacetic acid. The resulting mixture was boiled under reflux for 1 h, cooled to 0 °C, and diluted with 100 mL of ether. The tan precipitate, which formed, was collected by filtration and washed with ether. It was then taken up in 10 mL of nitromethane and reprecipitated by addition of 100 mL of ether. Crystallization of the product was then accomplished by dissolving the precipitate in nitromethane and placing this solution in an environment where slow diffusion of ether into the solution could occur.

---

[48] ^{1}H NMR spectra were measured by using a Nicolet NT 360 spectrometer. Mass spectra were obtained with a CEC-21B-110 instrument set at 70 eV. UV–vis spectra were recorded by using a Hitachi 110A spectrometer. Infrared spectra were obtained on a Beckman IR 4240 spectrometer. Electrochemical experiments were performed by using a Princeton Applied Research electrochemical station (Model 175 Universal Programmer, Model 173 Potentiostat-Galvanostat, and a Model 174A Polarographic Analyzer). Melting points were determined in sealed, evacuated capillary tubes with a Mel-Temp apparatus and are uncorrected. Elemental analyses were determined by Dr. R. Wielesek of the University of Oregon Microanalytical Laboratories and by Schwarzkopf Microanalytical Laboratory, Inc.

This gave 534 mg (86%) of transparent, colorless crystals: mp >270 °C dec; ^{1}H NMR (CD_3NO_2) δ 7.60 (1 H, t, J = 7.6 Hz, C(15)*H*), 7.35 (2 H, dd, J = 7.6 Hz, J' = 1.7 Hz, C(14) and C(16)H), 7.02 (1 H, t, J = 6.1 Hz), 6.85 (2 H, dd, J = 6.1 Hz, J' = 0.8 Hz), 6.80 (s, 6 H, Ar*H*), 5.34 (1 H, t, J = 1.7 Hz, C(12)*H*), 3.59–3.53 (2 H, m, CH_2), 3.36–3.31 (2 H, m, CH_2), 3.32 (1 H, s, C(4)H), 2.59–2.51 (2 H, m, CH_2), 2.34–2.26 (2 H, m, CH_2). Double resonance experiments showed coupling between the signals at 7.35 and 5.34 and between those at 6.85 and 3.32. Anal. Calcd for $C_{22}H_{22}RuB_2F_8$: C, 47.09; H, 3.95. Found: C, 46.93; H, 3.95.

(η^6-Benzene)(η^6-[2_3](1,3,5)cyclophane)ruthenium(II) Bis(tetrafluoroborate) (1c). This was prepared following the procedure described for **1b**. Using 158 mg of bis(η^6-benzene)dichlorobis(μ-chloro)diruthenium,[15] 254 mg of silver tetrafluoroborate, and 100 mg of [2_3](1,3,5)cyclophane, we isolated 260 mg (100%) of **1c** as light yellow plates: mp >265 °C dec; ^{1}H NMR ($CD_3NO)_2$) δ 6.79 (6 H, s, ArH), 6.47 (3 H, s, ArH), 5.55 (3 H, s, ArH), 3.45–2.99 (12 H, m, CH_2). Anal. Calcd for $C_{24}H_{24}RuB_2F_8$: C, 47.64; H, 4.33. Found: C, 47.98; H, 4.21.

(η^6-Hexamethylbenzene)(η^6-*anti*-[2_2](1,3)cyclophane)ruthenium(II) Bis(tetrafluoroborate) (24). This was prepared following the procedure described for **1b**. Using 75 mg of bis(η^6-hexamethylbenzene)dichlorobis(μ-chloro)diruthenium,[15,17] 90 mg of silver tetrafluoroborate, and 47 mg of *anti*-[2_2](1,3)cyclophane, we isolated 93 mg (64%) of (η^6-hexamethylbenzene)(η^6-*anti*-[2_2](1,3)cyclophane)ruthenium(II) bis(tetrafluoroborate) as pale yellow plates: mp >300 °C dec; ^{1}H NMR (CD_3CN) δ 7.50 (1 H, $\mathit{A}B_2X$, J_{AB} = 8.0 Hz, C(15H), 7.24 (2 H, $A\mathit{B}_2X$, J_{AB} = 8.0 Hz, J_{BX} = 1.5 Hz, C(14- and 16H), 6.61 (1 H, t, J = 6.0 Hz, C(7)H), 6.34 (2 H, d, J = 6.0 Hz, C(6 and 8)H), 5.05 (1 H, $AB_2\mathit{X}$, J_{BX} = 1.5 Hz, C(12)H), 3.54–2.84 (4 H, m, CH_2), 2.57 (1 H, s, C(4)H), 2.33 (18 H, s, CH_3), 1.63–2.52 (4 H, m, CH_2). Despite prolonged drying the crystals retained water of crystallization. Anal. Calcd for $C_{28}H_{34}RuB_2F_8 \cdot H_2O$: C, 50.70; H, 5.47. Found: C, 50.78; H, 4.97.

(η^6-Hexamethylbenzene)(η^6-*anti*-4,12-dimethyl-7,15-dimethoxy[2_2](1,3)cyclophane)ruthenium(II) Bis(tetrafluoroborate) (16). This was prepared following the procedure described for **1b**. Using 62 mg of (η^6-hexamethylbenzene)dichlorobis(η-chloro)diruthenium,[15,17] 74 mg of silver tetrafluoroborate, and 50 mg of *anti*-4,12-dimethyl-7,15-dimethoxy[2_2](1,3)cyclophane,[49] we isolated 120 mg of **16** as yellow prisms: mp >200 °C dec; ^{1}H NMR (CD_3NO_2) δ 6.92 (2 H, s, C(14 and 16)H), 6.54 (2 H, s, C(6 and 8)H), 4.14 (3 H, s, OCH_3), 3.69 (3 H, s, OCH_3), 3.32–2.60 (8 H, m, CH_2), 2.40 (18 H, s, CH_3), 1.14 (3 H, s, C(12)–CH_3), 0.67 (3 H, s, C(4)CH_3). Anal. Calcd. for $C_{33}H_{42}O_2RuB_2F_8$: C, 52.41; H, 5.77. Found: C, 52.21; H, 5.68.

Bis(η^6-hexamethylbenzene)(η^6,η^6-*anti*-[2_2](1,3)cyclophane)diruthenium(II) Tetrakis(tetrafluoroborate) (15). This was prepared following the procedure described for **1b**. Using 489 mg of (η^6-hexamethylbenzene)dichlorobis(μ-chloro)diruthenium,[15] 585 mg of silver tetrafluoroborate, and 28 mg of *anti*-[2_2](1,3)cyclophane, we isolated 65 mg (46%) of **15** as fine yellow needles: mp >250 °C dec; ^{1}H NMR (CD_3CN) δ 6.90 (2 H, t, J = 6.5 Hz, C(7 and 15)H), 6.56 (4 H, d, J = 6.5 Hz, C(6, 8, 14, 16)H), 4.18 (2 H, s, C(4 and 12)H), 3.41 (4 H, d, J = 8.0 Hz, CH_2), 2.48 (4 H, d, J = 8.0 Hz, CH_2), 2.41 (18 H, s, CH_3). Anal. Calcd for $C_{40}H_{52}Ru_2B_4F_{16}$: C, 44.39; H, 4.84. Found: C, 43.78; H, 5.00.

Bis(η^6-hexamethylbenzene)(η^6,η^6-*anti*-4,12-dimethyl-7,15-dimethoxy-[2_2](1,3)cyclophane)diruthenium(II) Tetrakis(tetrafluoroborate). This was prepared following the procedure described for **1b**. Using 779 mg of silver tetrafluoroborate, 564 mg of (η^6-hexamethylbenzene)dichlorobis(μ-chloro)diruthenium,[15,17] and 49 mg of *anti*-4,12-dimethyl-7,15-dimethoxy[2_2](1,3)cyclophane,[49] wwe isolated 50 mg (26%) of small yellow needles: mp >290 °C dec; ^{1}H NMR (CD_3NO_2) δ 6.78 (4 H, s, ArH), 4.23 (6 H, s, OCH_3), 3.54–3.12 (8 H, m, CH_2), 2.44 (36 H, s, CH_3), 1.27 (6 H, s, CH_3). Anal. Calcd for $C_{44}H_{56}O_2Ru_2B_4F_{16} \cdot 3H_2O$: C, 43.52; H, 5.11. Found: C, 43.43; H, 4.85.

(η^4-1,3-Cyclohexadiene)(η^6-[2_2](1,4)cyclophane)ruthenium(0) (2a). To a slurry of 1.001 g (1.784 mmol) of (η^6-benzene)(η^6-[2_2](1,4)-cyclophane)ruthenium(II) bis(tetrafluoroborate), **1a**,[17] in 50 mL of dry, degassed tetrahydrofuran at 0 °C was added with stirring 2.0 mL (6.80 mmol) of a 3.4 M solution of sodium bis(methoxyethoxy)aluminum hydride (Red-Al) in toluene. The solution soon became a clear, dark amber. After 3 h, degassed water (0.5 mL) was added. The resulting black mixture was concentrated in a glove box, and the residue was extracted with five 50-mL aliquots of degassed hexane. Filtration of the hexane extracts followed by concentration gave 522 mg of a yellow solid whose ^{1}H NMR spectrum indicated it to be an 82:18 mixture of **2a** and [2_2](1,4)cyclophane (67% conversion of **1a** to **2a**). Sublimation of the solid provided a pure sample of **2a** as a yellow, air-sensitive solid. Recrystallization of this from hexane gave transparent yellow needles: mp 152–154 °C; ^{1}H NMR (C_6D_6) δ 6.47 (4 H, s, ArH), 4.75 (2 H, dd, J = 4.3 Hz, J' = 2.0 Hz, C(2′ and 3′)H), 4.18 (4 H, s, ArH), 3.20–3.08 (2 H, m, C(1′ and 4′)H), 2.85–2.41 (8 H, m, CH_2), 1.81–1.53 (4 H, m, C(5′ and 6′)H); MS, *m/e* 390, 310, 286, 208, 206, 182, 180, 104, 80, 78. Anal. calcd for $C_{22}H_{24}\,{}^{102}Ru$ 390.092, found (high resolution mass spectrum) 390.092. Cyclic voltammetry (0.1 M (n-$C_4H_9)_4NPF_6$ in acetone): E_{pa} = −0.385 V (vs. SCE), irreversible oxidation.

(η^4-1,3-Cyclohexadiene)(η^6-*anti*-[2_2](1,3)cyclophane)ruthenium(0) (2b). This was prepared following the same procedure described for **2a**. Using 199 mg (0.355 mmol) of **1b** in 10 mL of tetrahydrofuran and 0.4 mL of Red-Al solution, there was isolated 113 mg (77% conversion) of a yellow solid which, by ^{1}H NMR was an 89:9 mixture of **2b** and free *anti*-[2_2](1,3)cyclophane. After removal of the free cyclophane by sublimation, recrystallization of **2b** from hexane gave yellow crystals: mp 138–139 °C; ^{1}H NMR (C_6D_6) δ 7.16 (1 H, t, J = 7.5 Hz, ArH), 6.86 (2 H, dd, J = 7.5 Hz, J' = 1.4 Hz, ArH), 5.38 (1 H, brs, ArH), 5.08 (2 H, dd, J = 5.4 Hz, J' = 0.7 Hz, ArH), 4.09 (1 H, t, J = 5.4 Hz, ArH), 4.76 (2 H, dd, J = 4.5 Hz, J' = 2.4 Hz, C(2′ and 3′)H), 3.11–3.08 (2 H, m, C(1′ and 4′)H), 2.81–2.76 (2 H, m, CH_2), 2.45–2.40 (2 H, m, CH_2), 2.33 (1 H, s, ArH), 2.12–2.04 (2 H, m, CH_2), 1.77–1.61 (6 H, m, CH_2). Double resonance experiments showed the signals at 6.86 and 5.38 to be coupled, as were also those at 5.08 and 2.33. Anal. calcd for $C_{22}H_{24}\,{}^{102}Ru$ 390.092, found (high resolution mass spectrum) 390.093.

(η^4-1,3-Cyclohexadiene)(η^6-[2_3](1,3,5)cyclophane)ruthenium(0) (2c). This was prepared following the same procedure described for **2a**. Using 118 mg (0.202 mmol) of **1c** in 5 mL of tetrahydrofuran and 0.23 mL of Red-Al solution, there was isolated directly from the hexane extraction 78 mg (93%) of pure **2c** as yellow crystals: mp 171–172 °C dec; ^{1}H NMR (C_6D_6) δ 5.01 (3 H, s, ArH), 4.95 (2 H, dd, J = 4.5 Hz, J = 2.2 Hz, -C(2′ and 3′)H), 3.75 (3 H, s, ArH), 3.26–3.16 (2 H, m, C(1′ and 4′)H), 2.70–2.22 (12 H, m, CH_2), 1.86–1.54 (4 H, m, -C(5′ and 6′)H). Anal. calcd for $C_{24}H_{26}\,{}^{102}Ru$ 416.107, found (high resolution mass spectrum) 416.107.

(η^4-*exo*-3′,6′-Dihydrohexamethyl-1,3-cyclohexadiene)(η^6-[2_2](1,4)-cyclophane)ruthenium(0) (10). This was prepared following the same procedure described for **2a**. Using 152 mg (0.235 mmol) of **9**[17] in 7 mL of tetrahydrofuran and 0.28 mL (0.95 mmol) of Red-Al solution, there was isolated directly from concentration of the hexane extracts 105 mg (94%) of pure **10** as yellow crystals. The sample for X-ray analysis was obtained by recrystallization of **10** from ether to give yellow needles: mp >190 °C dec; ^{1}H NMR (C_6D_6) δ 6.48 (4 H, s, ArH), 3.86 (2 H, q, J = 7.0 Hz, C(3′ and 6′)H), 3.64 (4 H, s, ArH), 2.84–2.23 (8 H, m, CH_2), 1.58 (6 H, d, J = 7.0 Hz, CH_3), 1.26 (12 H, s, CH_3); MS, *m/e* 474, 370, 208, 162, 147, 104. Anal. calcd for $C_{28}H_{36}\,{}^{102}Ru$ 474.185, found (high resolution mass spectrum) 474.186.

Bis(η^6-[2_2](1,4)cyclophane)dichlorobis(η-chloro)diruthenium (3a). To a solution of 815 mg (2.09 mmol) of **2a** in 100 mL of dry, degassed acetone stirred under purified nitrogen was added 1.60 mL of degassed concentrated hydrochloric acid. After the mixture had been stirred at room temperature for 1 h, the precipitate was collected by filtration, washed with acetone, and then dried to give 759 mg (96%) of a brick-red powder: mp >250 °C dec; ^{1}H NMR ($D_3C)_2SO$) δ 6.86 (8 H, s, ArH), 5.21 (8 H, s, ArH), 3.23–2.71 (16 H, m, CH_2). Anal. Calcd for $C_{32}H_{32}Ru_2Cl_4$: C, 50.54; H, 4.24. Found: C, 49.97; H, 4.04.

Bis(η^6-*anti*-[2_2](1,3)cyclophane)dichlorobis(μ-chloro)diruthenium (3b). This was prepared following the same procedure described for **3a**. Using 106.5 mg (0.273 mmol) of **2b** in 12 mL of acetone and 0.26 mL of concentrated hydrochloric acid, we isolated 73.3 mg of a red powder: mp >250 °sC dec; ^{1}H NMR (($CD_3)_2SO$) δ 5.29 (2 H, t, J = 4.2 Hz, ArH), 5.17 (4 H, d, J = 4.2 Hz, ArH), 4.41 (4 H, d, J = 3.2 Hz, ArH), 4.37 (2 H, t, J = 3.2 Hz, ArH), 4.16 (2 H, s, ArH), 2.96–2.94 (4 H, m, CH_2), 2.76–2.74 (4 H, m, CH_2), 2.43–2.39 (4 H, m, CH_2), 2.25 (2 H, s, ArH), 2.09–2.05 (4 H, m, CH_2). Anal. Calcd for $C_{32}H_{32}Ru_2Cl_4$: C, 50.54; H, 4.24. Found: C, 50.68; H, 4.28.

Bis(η^6-[2_3](1,3,5)cyclophane)dichlorobis(μ-chloro)diruthenium (3c). This was prepared following the procedure described for **3a**. Using 165 mg (0.397 mmol) of **2c** in 20 mL of acetone and 0.35 mL of concentrated hydrochloric acid, we isolated 158 mg (98%) of a lavender powder: mp >265 °C dec; ^{1}H NMR (($CD_3)_2SO$) δ 6.30 (6 H, s, ArH), 4.68 (6 H, s, ArH), 3.09–2.63 (24 H, m, CH_2). Anal. Calcd for $C_{36}H_{36}Ru_2Cl_4$: C, 53.21; H, 4.47; Cl, 17.45. Found: C, 52.87; H, 4.56; Cl, 16.88.

Bis(η^6-[2_2](1,4)cyclophane)ruthenium(II) Bis(tetrafluoroborate) (5). (A) A mixture of 122 mg (0.320 mmol) of **3a** and 126 mg (0.647 mmol) of silver tetrafluoroborate in 6 mL of acetone was stirred at room temperature for 30 min. After removal of the silver chloride by filtration followed by washing of the precipitate with 2 mL of acetone, 66 mg (0.32 mmol) of [2_2](1,4)cyclophane and 6 mL of trifluoroacetic acid were added to the filtrate, and the resulting mixture was boiled under reflux for 3 h. After the solution had cooled to room temperature, it was diluted

---

(49) Boekelheide, V.; Phillips, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 1695–1704.

with 80 mL of ether. The resulting yellow precipitate was collected by filtration and washed with ether. The yellow solid was then taken up in 3 mL of nitromethane and again precipitated by addition of 80 mL of ether to give 187 mg (84%) of **5** as a yellow solid. This, on recrystallization from a mixture of nitromethane and ether, yielded transparent yellow plates: mp >260 °C dec; ^{1}H NMR (CD_3NO_2) δ 6.95 (8 H, s, ArH), 5.91 (8 H, s, ArH), 3.44–2.97 (16 H, m, CH_2). Anal. Calcd for $C_{32}H_{32}RuB_2F_8$: C, 55.60; H, 4.67. Found: C, 55.29; H, 4.64.

(**B**) A mixture of 60 mg (0.154 mmol) of **2a** and 326 mg (1.57 mmol) of [2_2](1,4)cyclophane in 15 mL of dry, degassed acetone was boiled under reflux while adding 11 mL of degassed trifluoroacetic acid. The reaction mixture was then boiled under reflux for an additional 35 min. After the solution had cooled, it was concentrated to a volume of 5 mL, and a solution of 209 mg of tetra-*n*-butylammonium tetrafluoroborate was added with stirring. The solution was then filtered, and 50 mL of ether was added to the filtrate. This caused the separation of 106 mg (100%) of yellow powder, identical in all respects with the sample of **5** prepared via procedure A.

(η^6-[2_2](1,4)Cyclophane)(η^6-*anti*-[2_2](1,3)cyclophane)ruthenium(II) Bis(tetrafluoroborate) (6). This was prepared following the A procedure given above for **5**. Using 122 mg (0.320 mmol) of **3a**, 126 mg of silver tetrafluoroborate, and 73 mg of *anti*-[2_2](1,3)cyclophane in eventually 8 mL of acetone and 6 mL of trifluoroacetic acid, there was isolated 191 mg of yellow powder. Its ^{1}H NMR spectrum indicated it to be a 95:5 mixture of **6** and **5**, representing an 82% conversion of **3a** to **6**. Presumably, the **4a** solvate disproportionates to give the small amount of **5** observed. Recrystallization of this mixture from a combination of nitromethane and ether yielded 73 mg (33%) of **6** as yellow needles: mp 264–265 °C dec; ^{1}H NMR (CD_3NO_2) δ 7.52 (1 H, t, J = 7.6 Hz, ArH), 7.26 (2 H, dd, J = 7.6 Hz, J' = 1.7 Hz, ArH), 6.95 (4 H, s, ArH), 6.66 (1 H, t, J = 6.0 Hz, ArH), 6.50 (2 H, d, J = 6.0 Hz, ArH), 5.99 (4 H, s, ArH), 5.24 (1 H, t, J = 1.7 Hz, ArH), 3.48–3.42 (2 H, m, CH_2), 3.38–3.34 (4 H, m, CH_2), 3.18–3.13 (2 H, m, CH_2), 3.10 (1 H, s, ArH), 3.07–3.03 (4 H, m, CH_2), 2.50–2.42 (2 H, m, CH_2), 2.14–2.05 (2 H, m, CH_2). Anal. Calcd for $C_{32}H_{32}RuB_2F_8$: C, 55.60; H, 4.67. Found: C, 55.65; H, 4.64.

Bis(η^6-*anti*-[2_2](1,3)cyclophane)ruthenium(II) Bis(tetrafluoroborate) (7). This was prepared following the same procedure A described for **5**. Using 39 mg (0.103 mmol) of **3b**, 42 mg (0.215 mmol) of silver tetrafluoroborate, and 22 mg (0.107 mmol) of *anti*-[2_2](1,3)cyclophane in eventually 4.5 mL of acetone and 3 mL of trifluoroacetic acid, there was isolated, after precipitation from nitromethane with ether, 69 mg (97%) of **7** as a white powder: mp 265–266 °C dec; ^{1}H NMR (CD_3NO_2) δ 7.53 (2 H, t, J = 7.6 Hz, ArH), 7.27 (4 H, dd, J = 7.6 Hz, J' = 1.6 Hz, ArH), 6.73 (2 H, t, J = 6.0 Hz, ArH), 6.57 (4 H, d, J = 6.0 Hz, ArH), 5.26 (2 H, t, J = 1.6 Hz, ArH), 3.51–3.45 (4 H, m, CH_2), 3.19–3.14 (4 H, m, CH_2), 3.06 (2 H, s, ArH), 2.51–2.43 (4 H, m, CH_2), 2.13–2.05 (4 H, m, CH_2). Anal. Calcd for $C_{32}H_{32}RuB_2F_8$: C, 55.60; H, 4.67. Found: C, 55.55; H, 4.58.

Bis(η^6-[2_3](1,3,5)cyclophane)ruthenium(II) Bis(tetrafluoroborate) (8). This was prepared following the procedure A described for **5**. Using 50 mg (0.061 mmol) of **3c**, 51 mg (0.26 mmol) of silver tetrafluoroborate, and 30 mg (0.126 mmol) of [2_3](1,3,5)cyclophane in eventually 6 mL of acetone and 4 mL of trifluoroacetic acid, there was isolated, after precipitation from nitromethane with ether, 42 mg (46%) of **8** as a yellow powder: mp >305 °C dec; ^{1}H NMR (CD_3NO_2) δ 6.34 (6 H, s, ArH), 5.21 (6 H, s, ArH), 3.27–2.86 (24 H, m, CH_2). For analysis, a sample was recrystallized from nitromethane and, as the analysis showed, occluded nitromethane in the crystals. Anal. Calcd for $C_{36}H_{36}RuB_2F_8\cdot 0.5(CH_3NO_2)$: C, 56.65; H, 4.85; N, 0.90. Found: C, 56.70; H, 4.90; N, 0.90.

Bis(η^6-hexamethylbenzene)bis(η^6,η^6-[2_2](1,4)cyclophane)tris(ruthenium)(II) Hexakis(tetrafluoroborate) (12). The (η^6-hexamethylbenzene)ruthenium(II) tris(acetone) solvate, **11**, was prepared by stirring a mixture of 142 mg (0.425 mmol) of bis(η^6-hexamethylbenzene)dichlorobis(μ-chloro)diruthenium and 173 mg (0.888 mmol) of silver tetrafluoroborate in 5 mL of acetone for 5 min. After removal of the precipitate by filtration, the filtrate was concentrated leaving **11** as a reddish-orange solid. To this was added 30 mg (0.043 mmol) of **5** and 5 mL of trifluoroacetic acid. The mixture was boiled under reflux for 10 min and then cooled. The orange precipitate, which formed, was collected by filtration and washed with ether, giving 62 mg (92%) of **12** as a yellow powder: mp >250 °C dec; ^{1}H NMR (CD_3NO_2) δ 6.47 (8 H, s, ArH), 6.36 (8 H, s, ArH), 3.49 (16 H, s, CH_2), 2.51 (36 H, s, CH_3). Anal. Calcd for $C_{56}H_{68}Ru_3B_6F_{24}$: C, 42.97; H, 4.38; F, 29.13. Found: C, 42.40; H, 4.36; F, 29.87.

Bis(η^6-[2_2](1,4)cyclophane)(η^6,η^6-[2_2](1,4)cyclophane)diruthenium(II) Tetrakis(tetrafluoroborate) (13). A mixture of 42 mg (0.055 mmol) of **3a**, 45 mg (0.230 mmol) of silver tetrafluoroborate, and 76 mg (0.109 mmol) of **5** in 2 mL of trifluoroacetic acid was boiled under reflux for 5 h. After the mixture had cooled to room temperature, it was filtered through a bed of Celite to remove the silver chloride precipitate, and the Celite bed was washed with four 1-mL aliquots of trifluoroacetic acid. The combined filtrate and washings were diluted with 40 mL of ether. The yellow precipitate, that formed, was collected by filtration, washed with ether, and dried. The resulting solid was taken up in 1.6 mL of nitromethane and filtered through Celite, by using two 0.4 mL aliquots of nitromethane to wash the Celite bed. The combined filtrate and washings were diluted with 50 mL of ether, and the precipitate, which separated, was collected, washed with ether, and dried. An analysis of this yellow solid (80 mg) by ^{1}H NMR indicated it to be a 0.9:1.0 mixture of **13** and **5**. This was dissolved in 2.6 mL of nitromethane, and then 1.9 mL of tetrahydrofuran was added slowly with stirring. The resulting precipitate was collected, washed with ether, and dried to give 21 mg of a yellow solid which, by ^{1}H NMR analysis, consisted of a mixture of **13** and **5** in a ratio of 6:1. Recrystallization of this from nitromethane using the technique of slow vapor diffusion of tetrahydrofuran yielded 15 mg (12%) of pure **13** as yellow needles: mp >240 °C dec; ^{1}H NMR (CD_3NO_2) δ 6.99 (8 H, s, ArH), 6.32 (8 H, s, ArH), 6.20 (8 H, s, ArH), 3.39 (16 H, s, CH_2), 3.48–3.02 (8 H, m, CH_2). Anal. Calcd for $C_{48}H_{48}Ru_2B_4F_{16}$: C, 49.10; H, 4.12. Found: C, 49.03; H, 4.11.

Bis(hexamethylbenzene)ruthenium(0) (30). Although the preparation of **30** has been described previously,[31] the following procedure is a much more convenient one.[50] In a three-necked flask purged with pure argon was placed 304 mg (0.508 mmol) of bis(η^6-hexamethylbenzene)ruthenium(II) bis(tetrafluoroborate), **21**,[15] and 2.70 g of aluminum powder. Then, 50 mL of degassed hexane and 50 mL of degassed water were added via a stainless steel cannula. The mixture was stirred vigorously while 9.1 mL of an aqueous, 0.75 M sodium hydroxide solution was introduced via a syringe. Stirring was continued for 2 h. The yellow hexane solution was transferred, via a cannula, to an argon-purged Schlenk filtration tube containing a bed of Celite. The filtrate was collected in a Schlenk flask. The aqueous phase in the reaction flask was washed twice with 50-mL portions of hexane, and these hexane extracts were transferred as before. The combined hexane extracts were concentrated in a glove box. The resulting yellow solid was again taken up in hexane and filtered through Celite to remove traces of moisture. Concentration of this hexane filtrate gave 212 mg (98%) of air-sensitive, orange crystals whose ^{1}H NMR spectrum matched those reported previously for **30**.[31,32]

(η^6-Hexamethylbenzene)(η^4-[2_2](1,4)cyclophane)ruthenium(0) (19). The preparation of **19** was carried out following the same procedure just described for **30**. Using 506 mg (0.785 mmol) of **18**,[17] 4.20 g of aluminum powder, 100 mL of hexane, and 100 mL of water, there was isolated 61 mg (98%) of **19** as air-sensitive, orange crystals: mp 200–202 °C; ^{1}H NMR (C_6D_6) δ 7.04 (1 H, dd, J = 6.8 Hz, ArH), 6.81 (1 H, br d, J = 6.8 Hz, ArH), 6.61 (1 H, br d, J = 8.2 Hz, ArH), 6.57 (1 H, dd, J = 8.2 Hz, J' = 1.3 Hz, ArH), 4.28 (1 H, dd, J = 4.3 Hz, J' = 1.8 Hz, ArH), 4.08 (1 H, d, J = 4.9 Hz, ArH), 3.12–2.43 (8 H, set of multiplets, CH_2), 1.96 (18 H, s, CH_3), 1.49 (1 H, dd, J = 4.9 Hz, J' = 1.8 Hz, ArH), 1.43 (1 H, br d, J = 4.3 Hz). Double resonance experiments showed the following pairs to be coupled: δ 7.04 and 6.81; 6.61 and 6.57; 4.28 and 1.43; 4.08 and 1.49; 4.08 and 1.43; and 4.28 and 1.49. The properties of this sample matched completely with those of a sample of **19** prepared by bulk electrolysis of **18**.[51] The mass spectrum of **19** showed a *m/e* pattern at 466, 468, 470, 472, 474, and 476 that was in full accord with the predicted ruthenium isotope distribution pattern for **19**.[51] Anal. Calcd for $C_{28}H_{34}Ru$: C, 71.30; H, 7.27. Found: C, 71.37; H, 7.48.[51]

(η^6-Hexamethylbenzene)(η^5-3*H*-[2_2](1,4)cyclophane)ruthenium(II) Hydrogen Dichloride (26). To a solution of 92 mg (0.195 mmol) of **19** in 25 mL of degassed acetone there was added 0.16 mL of degassed concentrated hydrochloric acid. The initial solution, which was a pale yellow, quickly turned blood red and then became yellow again. After the solution had been stirred for 2 h at room temperature, it was concentrated, leaving a light yellow solid. This was taken up in 6 mL of acetonitrile and filtered, and the filtrate was diluted with 45 mL of ether. The resulting precipitate was collected, washed with ether, and dried to give 72 mg (67%) of **26** as a light yellow powder: mp >200 °C dec; ^{1}H NMR (CD_3NO_2) δ 7.21 (2 H, d, J = 8.0 Hz, ArH), 7.13 (2 H, d, J = 8.0 Hz, ArH), 4.08 (2 H, d, J = 6.9 Hz, C(5 and 7)H), 3.15–3.11 (2 H, m, CH_2), 3.08–3.02 (1 H, pseudo quintet, J = J' = 5.9 Hz, C(3)H), 2.90–2.87 (2 H, pseudo t, C(4 and 8)H), 2.51–2.48 (2 H, pseudo t, J = 6.7 Hz, C(1)H), 2.42–2.38 (2 H, m, CH_2), 2.18 (18 H, s, CH_3),

---

(50) Muetterties, E. L.; Cwirla, W. W., personal communication. We thank Professor Muetterties for providing us with a description of this method prior to publication.

(51) Voegeli, R. H., Ph.D. Dissertation, University of Oregon, Eugene, OR, March 1984.

1.47–1.41 (2 H, m, CH_2). Anal. Calcd for $C_{28}H_{36}RuCl_2$: C, 61.76; H, 6.66; Cl, 13.02. Found: C, 61.90; H, 6.70; Cl, 14.12.

(η^6-Hexamethylbenzene)(η^4-[2_4](1,2,4,5)cyclophane)ruthenium(0) (28). A mixture of 120 mg (0.172 mmol) of **27** and 5.87 g of a 2% sodium-mercury amalgam in 10 mL of degassed 1,2-dimethoxyethane was stirred vigorously at room temperature for 8 h. After decantation from the excess amalgam, the solution was concentrated. The resulting grey residue was extracted with three 10-mL portions of hexane and filtered, and the filtrate was concentrated to give 60 mg (67%) of **28** as yellow crystals [mg 215–217 °C; ^{1}H NMR (C_6D_6) δ 6.60 (2 H, s, ArH), 3.30–2.30 (16 H, m, CH_2), 1.34 (2 H, s, ArH), 1.84 (18 H, s, CH_3)]. The properties of this sample matched completely with those of a sample of **28** prepared by the bulk electrolysis of **27**.[51] The mass spectrum of **28** showed an *m*/*e* pattern at 518, 522, 524, 526, and 528 that was in full accord with the predicted isotope distribution pattern for **28**.[51]

The ^{13}C NMR (C_6D_6), both decoupled and partially coupled to define proton spin multiplicity, δ 16.9 (q, C-1), 31–33 (t, C's-6–9), 67.9 (d, C-4), 90.6 (s, C-3), 91.6 (s, C-2), 135.0 (s, C-5), 135.8 (d, C-11), 141.1 (s, C-10), and 141.2 (s, C-12) confirms that the complex is unsymmetrical and supports the assignment as drawn for structure **28**.[51] Anal. Calcd for $C_{32}H_{38}Ru$: C, 73.39; H, 7.31. Found: 73.56; H, 7.39.[51]

(η^6-[2_4](1,2,4,5)Cyclophane)(η^5-*endo*-6*H*-hexamethylcyclohexadienyl)ruthenium(II) Hexafluorophosphate (29). This was prepared following the procedure described earlier for **26**. Using 67 mg (0.127 mmol) of **28** and 0.12 mL of concentrated hydrochloric acid in 10 mL of degassed acetone, there was isolated a yellow crystalline solid. This was taken up in a mixture of 2 mL of water and 5 mL of acetone, and 5 mL of an aqueous solution containing 220 mg of ammonium hexafluorophosphate was added. The resulting yellow precipitate was collected by filtration and dried. Recrystallization of this from nitromethane with a slow diffusion of ether gave 66 mg (76%) of **29** as pale yellow crystals: mp 273 °C dec; ^{1}H NMR (CD_3NO_2) δ 6.51 (2 H, s, ArH), 4.48 (2 H, s, ArH), 3.48–3.38 (4 H, m, CH_2), 3.24–3.14 (4 H, m, CH_2), 3.01–2.91 (4 H, m, CH_2), 2.59–2.49 (4 H, m, CH_2), 2.26 (3 H, s, CH_3), 2.21 (1 H, q, $J = 6.5$ Hz, $\equiv$CH), 1.89 (6 H, s, CH_3), 1.62 (6 H, s, CH_3), 0.27 (3 H, d, $J = 6.5$ Hz). Anal. Calcd for $C_{32}H_{39}RuPF_6$: C, 57.39; H, 5.87. Found: C, 57.23; H, 5.97.

(η^6-Hexamethylbenzene)(η^5-6*H*-hexamethylcyclohexadienyl)ruthenium(II) Hexafluorophosphate (31). To a solution of 109 mg (0.256 mmol) of bis(hexamethylbenzene)ruthenium(0), **30**, in 40 mL of degassed acetone there was added 0.22 mL of concentrated hydrochloric acid. The resulting cloudy solution was stirred for 30 min and then concentrated. The crude residue was taken up in 2 mL of acetonitrile and filtered, and the filtrate was diluted with 150 mL of ether. The yellow precipitate, which separated, was collected and then redissolved in 3 mL of water. To this was added a solution of 140 mg of ammonium hexafluorophosphate in 3 mL of water. The yellow precipitate, that formed, was collected, washed with water, and dried. This gave 79 mg (54%) of **31** as a yellow powder: mp 350–352 °C dec; ^{1}H NMR (CD_3NO_2) δ 2.26 (1 H, q, C(6)H), 2.22 (3 H, s, CH_3), 2.19 (18 H, s, CH_3), 1.81 (6 H, s, CH_3), 1.53 (6 H, s, CH_3), 0.34 (3 H, d, $J = 6.5$ Hz, CH_3); IR (KBr) ν_{max} 3011, 2956 (s), 2916 (s), 2864 (m), 1628 (m), 1437 (m), 1387 (s), 1068 (m), 1052 (m), 1016 (s), 1001 (s), 868 (s), 853–832 (vs), 554 (vs) cm^{-1}. Anal. Calcd for $C_{24}H_{37}RuPF_6$: C, 50.43; H, 6.52; F, 19.94. Found: C, 50.27; H, 6.47; F, 19.66.

(η^5-*exo*-6′*H*-Hexamethylcyclohexadienyl)(η^5-*endo*-6*H*-hexamethylcyclohexadienyl)ruthenium(II) (32). To a slurry of 148 mg (0.259 mmol) of **31** in 10 mL of dry, degassed tetrahydrofuran stirred at 0 °C under a nitrogen atmosphere there was added 0.28 mL (0.952 mmol) of a 3.4 M solution of Red-Al in toluene. The mixture slowly became clear yellow, and, after it had been stirred for 3.5 h, 0.10 mL of degassed water was introduced. The mixture was concentrated in a glove box, and the residue was extracted with two 7-mL portions of hexane. After filtration, slow concentration of the filtrate gave 99 mg (89%) of **32** as yellow crystals: mp >170 °C dec; ^{1}H NMR (C_6D_6) δ 2.82 (1 H, q, $J = 7.3$ Hz, *exo*-C(6′)H), 2.36 (1 H, q, $J = 6.5$ Hz, *endo*-C(6)H), 1.73 (3 H, s, CH_3), 1.70 (3 H, s, CH_3), 1.62 (6 H, s, CH_3), 1.53 (6 H, s, CH_3), 1.47 (6 H, s, CH_3), 1.39 (6 H, s, CH_3), 1.30 (3 H, d, $J = 7.3$ Hz, CH_3), 0.51 (3 H, d, $J = 6.5$ Hz, CH_3); IR (KBr) ν_{max} 2968 (s), 2952 (s), 2942 (s), 2898 (s), 2866 (s), 2760 (s), 1453 (s), 1440 (s), 1390 (m), 1378 (s), 1048 (m), 1015 (s), 993 (s) cm^{-1}. Anal. calcd for $C_{24}H_{38}$ ^{102}Ru 428.208, found (high resolution mass spectrum) 428.208.

(η^6-Hexamethylbenzene)(η^4-*endo*-5*H*-*exo*-6*H*-hexamethyl-1,3-cyclohexadiene)ruthenium(0) (33). A slurry of 58 mg (0.102 mmol) of **31** and 27 mg (0.71 mmol) of sodium borohydride in 2 mL of dry 1,2-dimethoxyethane was boiled under reflux in a nitrogen atmosphere for 17 h. After removal of the solvent, the residue was extracted with two 3-mL portions of hexane. The combined extracts were slowly concentrated to give 40 mg (91%) of **33** as yellow crystals: mp >290 °C dec; ^{1}H NMR (C_6D_6) δ 1.86 (18 H, s, CH_3), 1.77 (3 H, s, CH_3), 1.75 (3 H, s, CH_3), 1.27 (3 H, s, CH_3), 1.24 (1 H, m, $\equiv$CH), 1.20 (3 H, s, CH_3), 1.10 (1 H, m, $\equiv$CH), 1.04 (3 H, d, $J = 6.1$ Hz, CH_3), 1.01 (3 H, d, $J = 6.6$ Hz, CH_3). Double resonance experiments showed the signals at 1.24 and 1.10, and those at 1.10 and 1.04 to be coupled. Anal. Calcd for $C_{24}H_{38}Ru$: C, 67.41; H, 8.96. Found: C, 67.50; H, 8.68.

(η^5-*exo*-6′*H*-Hexamethylcyclohexadienyl)(η^5-3*H*-[2_2](1,4)-cyclophane)ruthenium(II) (34). This was prepared following the procedure described for **32**. Using 149 mg (0.241 mmol) of **29** and 0.27 mL (0.92 mmol) of a 3.4 M solution of Red-Al in toluene in 10 mL of dry, degassed tetrahydrofuran, there was isolated, after recrystallization from hexane, 107 mg (94%) of **34** as yellow crystals: mp 150 °C dec; ^{1}H NMR (C_6D_6) δ 7.15 (2 H, d, $J = 8.0$ Hz, ArH), 7.02 (2 H, d, $J = 8.0$ Hz, ArH), 3.18 (1 H, pseudo quintet, $J = J' = 5.7$ Hz, C(3)H), 3.11 (2 H, d, $J = 6.1$ Hz, C(5 and 7)H), 2.82–2.77 (2 H, m, CH_2), 2.76 (1 H, q, C(6′)H), 2.59–2.55 (2 H, pseudo t, C(4 and 8)H), 2.41–2.37 (2 H, pseudo t, $J = 6.1$ Hz, C(1)H), 1.90 (3 H, s, CH_3), 1.72–1.68 (2 H, m, CH_2), 1.55 (6 H, s, CH_3), 1.49–1.43 (2 H, m, CH_2), 1.29 (6 H, s, CH_3), 1.28 (3 H, d, $J = 7.0$ Hz, CH_3). Double resonance experiments showed the signals at 2.76 and 1.28 to be coupled. IR (KBr) ν_{max} 3012 (m), 2993 (m), 2983 (m), 2925 (s), 2905 (s), 2852 (m), 2743 (m), 1503 (m), 1448 (m), 1434 (s), 1381 (m), 1373 (m), 805 (m), 714 (m), 526 (s) cm^{-1}; MS, *m*/*e* 474, 436, 356, 210, 208, 162, 147. Anal. calcd for $C_{28}H_{36}$ ^{102}Ru 474.186, found (high resolution mass spectrum) 474.181.

Acknowledgment. We thank the National Science Foundation for their support of this investigation under Grant CHE-8400421. We thank Dr. Winfried Lenk for contributions related to the experiments with [2_4](1,2,4,5)cyclophane.

Registry No. 1a, 77089-76-0; **1b**, 90614-00-9; **1c**, 101810-15-5; **2a**, 90590-75-3; **2b**, 90590-67-3; **2c**, 101810-16-6; **3a**, 90590-76-4; **3b**, 90590-68-4; **3c**, 101858-48-4; **5**, 90614-02-1; **6**, 90699-84-6; **7**, 90590-72-0; **8**, 101810-18-8; **9**, 77089-82-8; **10**, 101834-57-5; **11**, 101810-21-3; **12**, 101810-20-2; **13**, 101810-23-5; **14**, 77089-86-2; **15**, 101834-54-2; **16**, 83835-56-7; **18**, 77089-82-8; **19**, 88453-36-5; **21**, 71861-30-8; **24**, 82871-55-4; **26**, 88453-43-4; **27**, 82871-65-6; **28**, 83927-90-6; **29**, 101834-59-7; **30**, 32732-05-1; **31**, 88453-41-2; **32**, 88453-42-3; **33**, 101810-24-6; **34**, 88453-39-8; bis(η^6-benzene)dichlorobis(μ-chloro)diruthenium, 37366-09-9; bis(η^6-hexamethylbenzene)dichlorobis(μ-chloro)diruthenium, 67421-02-7; bis(η^6-hexamethylbenzene)(η^6,η^6-*anti*-4,12-dimethyl-7,15-dimethoxy[2_2](1,3)cyclophane)diruthenium(II) tetrakis(tetrafluoroborate), 101834-56-4.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters; interatomic distances and bond angles; observed and calculated structure factors derived from the crystallographic analysis of **10** (34 pages). Ordering information is given on any current masthead page.