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A Study of the Synthesis and Properties of Ruthenium Complexes of $[2_n]$ Cyclophanes

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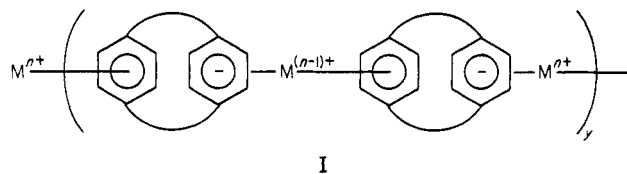
The synthesis of a series of 15 (η^6 -cyclophane)(η^6 -arene)ruthenium complexes is described where the arene component varies among benzene, *p*-cymene, mesitylene, and hexamethylbenzene, and the cyclophane component varies among [2.2]paracyclophane, *anti*-[2.2]metacyclophane, [2₃](1,3,5)cyclophane, [2₃](1,2,4)(1,2,5)cyclophane, [2₄](1,2,3,4)cyclophane, [2₄](1,2,3,5)cyclophane, [2₄](1,2,4,5)cyclophane, [2₅](1,2,3,4,5)cyclophane, and [2₆](1,2,3,4,5,6)cyclophane (superphane). Also, four triple-layered analogues, (η^6, η^6 -cyclophane)bis(η^6 -arene)diruthenium(II) complexes, have been prepared where the arene component varies among *p*-cymene, mesitylene, and hexamethylbenzene, and the cyclophane component is either [2.2]paracyclophane or [2₄](1,2,4,5)cyclophane. The cyclic voltammetry and spectral properties of these compounds are described and discussed, particularly in relation to the molecular geometry of the individual complexes.

The development of new synthetic methods has recently made possible the preparation of all of the symmetrical $[2_n]$ cyclophanes.² It is of interest, therefore, to examine how changes in geometry and changes in distance between decks affects the properties of these molecules. Of particular interest are the transition-metal complexes of the $[2_n]$ cyclophanes. In this paper we report on the preparation and properties of a series of ruthenium complexes of $[2_n]$ cyclophanes.

The π -electron interaction between decks of $[2_n]$ -cyclophanes is sufficiently strong that these molecules behave as one π -electron systems with respect to their physical and chemical properties.^{2,3} Also, Misumi and Otsubo have prepared multilayered cyclophanes with as many as six decks, and these likewise behave as one π -electron systems.⁴ Thus, a polymer molecule consisting of a huge pillar of a multilayered cyclophane should have a π -electron system delocalized over the whole of the molecule. Such molecules could be expected to have interesting properties of potential practical value.

However, to prepare such a polymer by the stepwise procedures of Misumi and Otsubo would be an exceedingly

difficult task. The synthesis of a polymer in which the monomer unit is a transition-metal complex of a cyclophane is a much more feasible undertaking. Furthermore, if the molecule were designed so that the transition-metal atoms along the polymer chain differed in their formal oxidation states, as shown for structure I, this would provide the electron holes necessary for a conduction band and the polymer should be a unidimensional, electrical conductor.



For preparing a polymer such as I, the traditional methods for forming transitional-metal complexes of cyclophanes and arenes have severe limitations. In an early study, Cram and Wilkinson⁵ showed that [2.2]paracyclophane reacts with hexacarbonylchromium to give a tricarbonylchromium complex, and, later, Misumi et al.⁶ extended this to form the bis(tricarbonylchromium) complex of [2.2]paracyclophane(II) as well as tricarbonyl-

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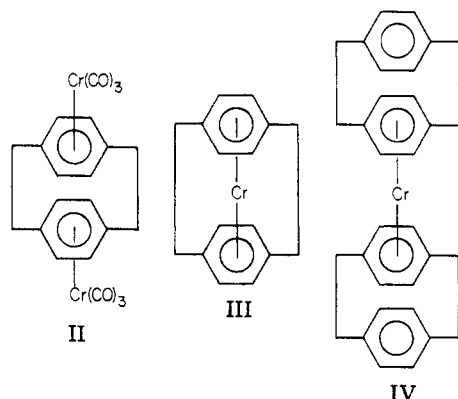
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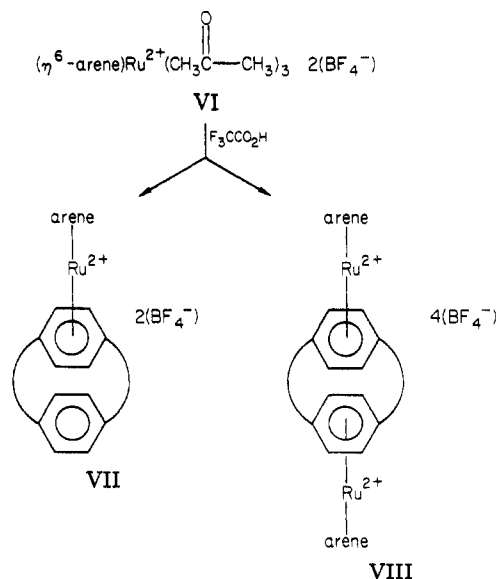
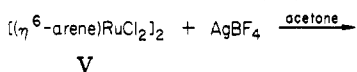
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chromium complexes of various multilayered cyclophanes. As yet, though, no useful method for removing carbonyls from such complexes to make multilayered oligomers has ever evolved. Similarly, the metal atom technique^{7,8} has been employed to prepare (η^{12} -[2.2]paracyclophane)chromium(0), structure III, as well as bis(η^6 -[2.2]paracyclophane)chromium(0), structure IV. But, again the metal atom technique is not useful for preparing oligomers or polymers of transition-metal complexes of cyclophanes.



Recently, Bennett and his colleagues reported a convenient method for preparing bis(η^6 -arene)ruthenium(II) complexes.^{9,10} This procedure offered the potential of preparing oligomer and polymer ruthenium complexes of cyclophanes, and, in a preliminary communication,¹¹ we reported using this method for preparing ruthenium(II) complexes of [2.2]paracyclophane. The procedure is outlined below. Treatment of a bis(arene)dichlorobis(μ -chloro)diruthenium(II), V, with silver tetrafluoroborate in



acetone gives the solvated (η^6 -arene)ruthenium(II) bis-(tetrafluoroborate), VI. Treatment of VI with 1 equiv of cyclophane in the presence of trifluoroacetic acid as cat-

alyst gives the double-layered (η^6 -arene)(η^6 -cyclophane)-ruthenium(II) bis(tetrafluoroborate), VII, in good to excellent yields. When VI is used in excess, the corresponding triple-layered (η^6 , η^6 -cyclophane)bis(η^6 -arene)diruthenium(II) tetrakis(tetrafluoroborate), VIII, is formed.

Table I summarizes the ¹H NMR spectral properties, elemental analyses, and yields for the preparation of 19 ruthenium complexes of [2_n]cyclophanes, including a range of arenes and a broad range of [2_n]cyclophanes. The method is indeed a general one, and the compilation of ¹H NMR spectra in Table I provides an interesting insight into the nature of the ruthenium bond and how it affects the magnetic environment of the cyclophane moiety. The ruthenium complexes of the [2_n]cyclophanes are generally isolated as microcrystalline powders that are difficult to crystallize. They are stable to air and to storage at room temperature. Although of limited solubility in most organic solvents, they are soluble in dimethyl sulfoxide and in nitromethane.

Previous studies of the ¹H NMR spectra of transition-metal complexes of [2_n]cyclophanes have been limited to tricarbonylchromium complexes^{6,12} and the iron complexes of [2.2]metacyclophanes.¹³ In trying to interpret the ¹H NMR spectra of metal complexes of cyclophanes, one has first to understand the spectra of the free cyclophanes themselves. The magnetic environment of all the [2_n]cyclophanes, where one deck is directly over the opposite deck, is somewhat complex and the chemical shifts of the aromatic protons of the cyclophanes cannot be accurately approximated by reference to the simple arene analogues. For example, the aromatic protons of [2.2]paracyclophane, IX, appear at δ 6.47, whereas the aromatic protons of *p*-xylene are at δ 7.05. This upfield shift of -0.58 ppm is due to shielding from the opposite aromatic ring and is common to all of the symmetrical [2_n]cyclophanes with the exception of *anti*-[2.2]metacyclophane, X. The absolute value of the upfield shift varies for the individual cyclophanes depending on their geometry and substitution pattern, but the overall behavior pattern is the same.

When the individual cyclophanes are converted to (η^6 -arene)(η^6 -cyclophane)ruthenium(II) complexes, compounds 3–6 and 8–19 in Table I, the aromatic protons of the complexed cyclophane deck are shifted upfield in the range usually of -0.51 to -0.73 ppm. This is very similar to the upfield shifts of aromatic protons on ruthenium complexation of simple arenes, as observed by Bennett and Matheson.¹⁰ The upfield shift of these aromatic protons during complexation is undoubtedly a combination of effects—rehybridization of the bound aromatic ring carbons, loss of ring current, and the direct effect of the magnetic anisotropy of the metal atom.

However, the aromatic protons of the unbound deck of these same ruthenium complexes, compounds 3–6 and 8–19 in Table I, all show a downfield shift in the range of $+0.46$ to $+0.65$ ppm. The distance of these protons from the metal is sufficiently great that direct magnetic anisotropy effects from the metal are probably negligible. The two obvious effects causing this downfield shift are (1) a loss of ring current in the bound aromatic ring causing a decrease in shielding from the opposite deck and (2) loss of electron density in the free aromatic ring due to electron withdrawal by the positively charged metal atom bound to the opposite deck. Unfortunately, there is no simple way of dissecting the relative importance of these two

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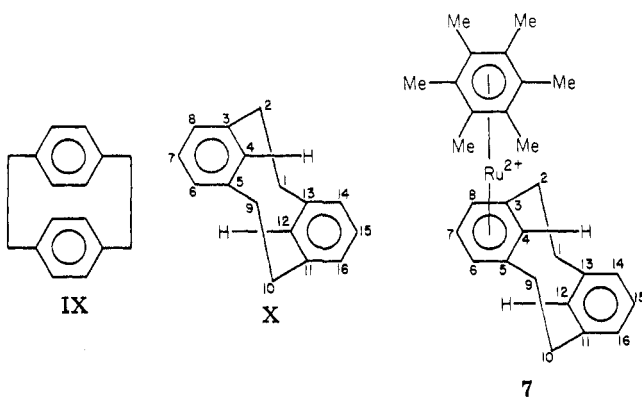
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effects for [2_n]cyclophanes where the decks are directly over each other.

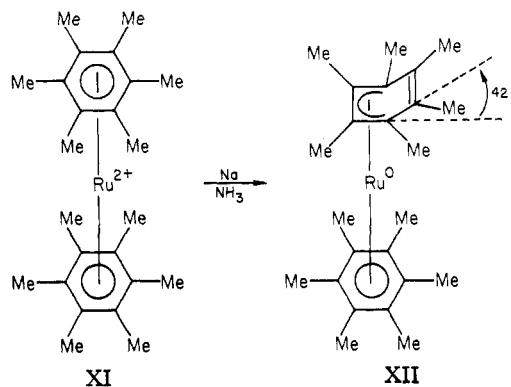
However, in the case of *anti*-[2.2]metacyclophane, X, such a dissection is possible. The X-ray crystallographic analysis of X shows the benzene rings to be asymmetrically boat-shaped with the internal carbons (C(4) and C(12)) being 0.143 Å out of the basal plane and the end carbons (C(7) and C(15)) being out of the plane by 0.042 Å.^{14,15} There is only partial overlap of the two benzene rings, but the distance between decks at C(4) and C(12) is only 2.633 Å. The ¹H NMR spectrum of X shows the aromatic protons at C(6), C(7), and C(8), as well as those at C(14), C(15), and C(16), as an AB₂X pattern in the range of δ 7.08–7.28. This is shifted only slightly from the AB₂X pattern of *m*-xylene (δ 6.92–7.22) and shows that the ring current effect from the opposite deck is negligibly small. On the other hand, the internal aromatic protons at C(4) and C(12) are directly centered over the face of the opposite benzene ring and experience a very strong shielding effect, their signal appearing at δ 4.24. Thus, for *anti*-[2.2]metacyclophane, the chemical shifts of the internal protons at C(4) and C(12) are strongly influenced by the ring current in the opposite deck and to a lesser extent by other factors such as electron density, whereas the end aromatic protons at C(6), C(7), C(8), C(14), C(15), and C(16) are primarily influenced by electron density and little affected by changes in the ring current of the opposite deck.



Ruthenium complexation of *anti*-[2.2]metacyclophane, as shown by 7 (compound 7 of Table I), leads to an upfield shift of the AB₂X pattern of the C(6), C(7), and C(8) protons of the metal-complexed ring of about -0.70 ppm, a normal upfield shift for ruthenium complexation of an arene. As expected, the AB₂X pattern of the C(14), C(15), and C(16) protons of the free benzene deck move downfield about +0.19 ppm. However, the internal proton at C(12) of the free benzene deck appears at δ 5.05, a downfield shift of +0.81 ppm. The additional downfield shift of +0.62 ppm of the internal proton at C(12), as compared to the protons at C(14), C(15), and C(16), must be due to a decreased ring current in the ruthenium-complexed benzene deck. Thus, it is evident that for [2_n]cyclophanes the magnetic effects on the unbound ring due to ruthenium complexation at the opposite deck are largely from electron withdrawal and loss of ring current in the metal-bound deck with other effects such as the direct magnetic anisotropy of the metal atom or changes in geometry being relatively small.

One of the interesting features of the previous work on (η⁶-arene)(η⁶-arene')ruthenium(II) complexes has been their reduction to the corresponding ruthenium(0) com-

plexes. Fischer and Elschenbroich prepared bis(η⁶-hexamethylbenzene)ruthenium(0), XII, by the sodium-ammonia reduction of bis(η⁶-hexamethylbenzene)ruthenium(II) bis(hexafluorophosphate), XI, and showed by variable-temperature ¹H NMR studies that it was a fluxional molecule.¹⁶ Later, Muetterties¹⁷ measured the kinetics of this valence tautomerization (activation energy = 16.1 kcal/mol) and explored the catalytic activity of the ruthenium(0) complex for hydrogenation of aromatic hydrocarbons.¹⁸ An X-ray crystallographic analysis of XII shows that in the crystalline state one of the hexamethylbenzene rings is bent away from planarity by 45°. ¹⁹ Thus, the reduced complex has been assigned the (η⁶-hexamethylbenzene)(η⁴-hexamethylbenzene)ruthenium(0) structure shown by XII. The corresponding (η⁶-benzene)(η⁴-benzene)ruthenium(0) complex apparently decomposes to benzene and ruthenium metal too quickly for comparable studies to be made.¹⁶



It occurred to us that an electrochemical study of the two-electron reduction of (arene)ruthenium(II) complexes would both be useful in its own right and would help provide an insight into the nature of the metal-arene bonding of ruthenium(II) cyclophane complexes. In another paper,²⁰ the theory and mechanism of the electrochemical, two-electron reduction of the double-layered ruthenium(II) complexes of the principal [2_n]cyclophanes are discussed in detail together with the influential role played by the rigid cyclophane geometry. In Table II, the cyclic voltammetric and coulometric results are summarized for a number of the ruthenium(II) complexes, whose preparation is presently being described.

The electrochemical reduction of bis(hexamethylbenzene)ruthenium(II) has apparently not been reported previously and it is listed first in Table II for comparison. The *i*_a/*i*_c ratio is a measure of the chemical reversibility of the electrochemical oxidation-reduction process (bis(arene)Ru²⁺ + 2e ⇌ bis(arene)Ru⁰), and the value for bis(hexamethylbenzene)Ru²⁺ is only 36%, appreciably less than for most of the [2_n]cyclophane complexes. The stabilizing effect of arene-methyl groups, as previously noted by Fischer and Elschenbroich,¹⁶ is also evident from the electrochemical data. The electrochemical reduction of (η⁶-hexamethylbenzene)(η⁶-durene)ruthenium(II) is only 22% reversible (*i*_a/*i*_c = 0.22 at 100 mV/s), and for (η⁶-hexamethylbenzene)(η⁶-*p*-xylene)ruthenium(II) the reduction is completely irreversible. There is also a consistent pattern that the presence of arene-methyl groups

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Table I
 $(\eta^6\text{-Arene}^1)(\eta^6\text{-arene}^2)\text{ruthenium(II) Bis(tetrafluoroborate)}$

compd	arene ¹	arene ²	yield, %	anal. found (calcd)		¹ H NMR ^a
				C	H	
1	hexamethylbenzene	<i>p</i> -xylene	93	44.20 (44.23)	5.28 (5.20)	2.26 (6 H, s, Me), 2.42 (18 H, s, Me), 6.73 (4 H, s, ArH) ^b
2	hexamethylbenzene	durene	94	46.00 (46.26)	5.84 (5.65)	2.50 (12 H, s, Me), 2.31 (18 H, s, Me), 6.67 (2 H, s, ArH) ^b

compd	arene	cyclophane	yield, %	anal. found (calcd)		¹ H NMR ^a
				C	H	
Double-Layered ($\eta^6\text{-Arene}$)($\eta^6\text{-cyclophane}$)ruthenium(II) Bis(tetrafluoroborate)						
3	benzene	[2.2]para-cyclophane	97	47.03 (47.09)	3.58 (3.95)	2.99-3.49 (8 H, m, CH ₂), 6.08 (4 H, s, ArH), 6.56 (6 H, s, ArH), 7.00 (4 H, s, ArH) ^c
4	mesitylene	[2.2]para-cyclophane	99	49.56 (49.78)	4.91 (4.68)	2.25 (9 H, s, Me), 2.96-3.48 (8 H, m, CH ₂), 5.99 (4 H, s, ArH), 6.49 (3 H, s, ArH), 6.94 (4 H, s, ArH) ^c
5	<i>p</i> -cymene	[2.2]para-cyclophane	86	50.18 (50.60)	4.79 (4.90)	1.18 (6 H, d, <i>J</i> = 4.2 Hz, CHMe ₂), 2.27 (3 H, s, Me), 2.73 (sp, <i>J</i> = 4.2 Hz, CHMe ₂), 2.95-3.53 (8 H, m, CH ₂), 6.10 (4 H, s, ArH), 6.54 (4 H, s, ArH), 6.98 (4 H, s, ArH) ^c
6	hexamethylbenzene	[2.2]para-cyclophane	92	50.49 (50.70)	5.20 (5.47) ^{d,e}	2.34 (18 H, s, Me), 2.93-3.44 (8 H, m, CH ₂), 5.82 (4 H, s, ArH), 6.88 (4 H, s, ArH) ^c
7	hexamethylbenzene	[2.2]meta-cyclophane	71	50.78 (50.71)	4.97 (5.43) ^f	1.63-2.52 (4 H, m, CH ₂), 2.33 (18 H, s, Me), 2.57 (1 H, AB ₂ X), 2.84-3.54 (4 H, m, CH ₂), 5.05 (1 H, AB ₂ X), 6.34 (2 H, AB ₂ X), 6.61 (1 H, AB ₂ X), 7.24 (2 H, AB ₂ X), 7.50 (1 H, AB ₂ X) ^c
8	hexamethylbenzene	[2 ₃](1,3,5)-cyclophane	85	53.58 (53.68)	5.37 (5.41) ^f	2.40 (18 H, s, Me), 2.69-3.33 (12 H, m, CH ₂), 5.09 (3 H, s, ArH), 6.24 (3 H, s, ArH) ^c
9	hexamethylbenzene	[2 ₃](1,2,4)(1,2,5)-cyclophane	70	49.68 (50.30)	4.61 (5.00) ^g	2.52 (18 H, s, Me), 3.0-3.6 (12 H, m, CH ₂), 5.06 (1 H, s, ArH), 5.89 (1 H, s, ArH), 6.35 (2 H, s, ArH), 7.34 (2 H, s, ArH)
10	hexamethylbenzene	[2 ₄](1,2,3,4)-cyclophane	91	54.20 (53.73)	5.59 (5.59) ^h	2.29 (18 H, s), 2.44-3.65 (16 H, m, CH ₂), 5.74 (2 H, s, ArH), 6.70 (2 H, s, ArH)
11	hexamethylbenzene	[2 ₄](1,2,3,5)-cyclophane	93	52.44 (52.41)	5.72 (5.58)	2.34 (18 H, s, Me), 2.45-3.65 (16 H, m, CH ₂), 5.23 (2 H, s, ArH), 6.42 (2 H, s, ArH) ^c
12	benzene	[2 ₄](1,2,4,5)-cyclophane	92	50.56 (50.93)	4.21 (4.27) ⁱ	2.55-3.73 (16 H, s, CH ₂), 5.69 (2 H, s, ArH), 6.46 (6 H, s, ArH), 6.71 (2 H, s, ArH) ^c
13	hexamethylbenzene	[2 ₄](1,2,4,5)-cyclophane	95	52.11 (52.41)	5.78 (5.58) ^j	2.32 (18 H, s, Me), 2.50-3.68 (16 H, m, CH ₂), 5.45 (2 H, s, ArH), 6.61 (2 H, s, ArH) ^c
14	hexamethylbenzene	[2 ₅](1,2,3,4,5)-cyclophane	94	55.00 (54.98)	5.43 (5.66) ^h	2.23 (18 H, s, Me), 2.49-3.61 (20 H, m, CH ₂), 5.40 (1 H, s, ArH), 6.59 (1 H, s, ArH) ^c
15	hexamethylbenzene	[2 ₆](1,2,3,4,5,6)-cyclophane (superphane)	91	55.36 (55.05)	5.72 (5.90) ⁱ	2.25 (18 H, s, Me), 2.72-3.39 (24 H, m, CH ₂) ^c

Table I (Continued)

compd	arene	cyclophane	yield, %	anal. found (calcd)		¹ H NMR ^a
				C	H	
Triple-Layered (η ⁶ ,η ⁶ -Cyclophane)bis(η ⁶ -arene)diruthenium(II) Tetrakis(tetrafluoroborate)						
16	mesitylene	[2.2]para-cyclophane	18	40.82 (40.92)	3.86 (4.03)	2.23 (18 H, s, Me), 3.46 (8 H, s, CH ₂), 6.47 (8 H, s, ArH), 6.70 (6 H, s, ArH) ^c
17	<i>p</i> -cymene	[2.2]para-cyclophane	53	41.89 (42.14)	4.17 (4.32)	1.21 (12 H, d, <i>J</i> = 4.2 Hz, CHMe ₂), 2.33 (6 H, s, Me), 2.81 (2 H, sp, CHMe ₂), 3.44 (8 H, s, CH ₂), 6.54 (8 H, s, ArH), 6.69 (8 H, s, ArH) ^c
18	hexamethylbenzene	[2.2]para-cyclophane	87	42.40 (42.96)	4.64 (5.05)	2.38 (36 H, s, Me), 3.36 (8 H, s, CH ₂), 6.20 (8 H, s, ArH) ^c
19	hexamethylbenzene	[2 ₄](1,2,4,5)-cyclophane	72	44.24 (44.47)	4.77 (5.26) ^m	2.57 (36 H, s, Me), 3.07-3.70 (16 H, m, CH ₂), 6.25 (4 H, s, ArH)

^a Values in δ with Me₄Si as internal reference. ^b In Me₂SO-*d*₆. ^c In D₃CCN. ^d Calcd for C₂₈H₃₄B₂F₈Ru·H₂O. ^e C₂₈H₃₄Ru⁺ ion observed at *m/e* 472 (field desorption mass spectrum (FDMS)) with the appropriate isotope distribution. ^f C₃₀H₃₆Ru⁺ ion at 498 (FDMS). ^g Calcd for C₃₀H₃₆B₂F₈Ru·2H₂O. ^h Calcd for C₃₂H₃₈B₂F₈Ru·H₂O. ⁱ C₂₈H₃₄Ru⁺ ion at 440 (FDMS). ^j Calcd for C₃₂H₃₈B₂F₈Ru·2H₂O. ^k C₃₂H₃₈Ru⁺ ion at 524 (FDMS). ^l Calcd for C₃₄H₄₀B₂F₈Ru·H₂O. ^m Calcd for C₃₆H₄₂B₂F₈Ru·2H₂O. ⁿ C₃₆H₄₂Ru⁺ ion at 576 (FDMS). ^o Calcd for C₄₄H₅₆B₄F₁₆Ru₂·3H₂O.

Table II. Electrochemical Measurements of the Double-Layered Ruthenium(II) Complexes

(η⁶-Arene¹)(η⁶-arene²)ruthenium(II) Bis(tetrafluoroborate)

compd	arene ¹	arene ²	<i>E</i> _{1/2} vs. SCE	<i>i</i> _a / <i>i</i> _c , 100 mV/s	coulometry
1	hexamethylbenzene	hexamethylbenzene	-1.02	0.36	2.04
2	hexamethylbenzene	<i>p</i> -xylene	-0.85	irrev	
2	hexamethylbenzene	durane	-0.93	0.22	1.97

Double-Layered (η⁶Arene)(η⁶-cyclophane)ruthenium(II) Bis(tetrafluoroborate)

compd	arene	cyclophane	<i>E</i> _{1/2} vs. SCE	<i>i</i> _a / <i>i</i> _c , 100 mV/s	coulometry
3	benzene	[2.2]paracyclophane	-0.50	0.81	1.84
6	hexamethylbenzene	[2.2]paracyclophane	-0.69	0.94	1.96
7	hexamethylbenzene	[2.2]metacyclophane	-0.71	0.81	2.03
8	hexamethylbenzene	[2 ₃](1,3,5)cyclophane	-0.91	0.27	1.49 ^a
9	hexamethylbenzene	[2 ₃](1,2,4)(1,2,5)cyclophane	-0.67	0.83	1.98
10	hexamethylbenzene	[2 ₄](1,2,3,4)cyclophane	-0.82 and -0.93	0.79	1.96
11	hexamethylbenzene	[2 ₄](1,2,3,5)cyclophane	-0.83 and -0.95	0.38	2.04
12	benzene	[2 ₄](1,2,4,5)cyclophane	-0.31	0.85	1.96
13	hexamethylbenzene	[2 ₄](1,2,4,5)cyclophane	-0.50	0.96	2.02
14	hexamethylbenzene	[2 ₅](1,2,3,4,5)cyclophane	-0.74 and -0.83	0.80	2.01
15	hexamethylbenzene	[2 ₆](1,2,3,4,5,6)cyclophane	-0.95	0.27	1.49 ^a

^a The explanation for these abnormal values is given in ref 20.

increases the half-wave potential by about -0.04 V/methyl group.

All of the (η⁶-hexamethylbenzene)(η⁶-cyclophane)ruthenium(II) complexes are reduced at lower potential than bis(hexamethylbenzene)ruthenium(II) itself. The predominant factor influencing the reduction potential appears to be the geometry of the cyclophane decks. The cyclophanes having boat-shaped decks (presumably well suited for η⁴ complexation), particularly [2.2]paracyclophane and [2₄](1,2,4,5)cyclophane, are most readily reduced. (η⁶-Benzene)(η⁶-[2₄](1,2,4,5)cyclophane)ruthenium(II), compound 12 in Table II, has a half-wave potential of only -0.31 V, and, even though benzene is the attached arene, the reduction is 85% reversible. Compound 15 in Table II, containing the superphane moiety, is not readily reduced (*E*_{1/2} = -0.95 V), presumably because the extremely rigid cyclophane cannot distort to a suitable η⁴ geometry. For compounds 11 and 14, containing the [2₄](1,2,3,5)cyclophane and [2₅](1,2,3,4,5)cyclophane moieties, the cyclic voltammogram shows the reduction as

two distinct one-electron steps.

It is of interest that the (η⁶-hexamethylbenzene)(η⁶-[2₃](1,2,4)(1,2,5)cyclophane)Ru²⁺, compound 9 of Table II, shows about the same reduction potential and reversibility as the corresponding [2.2]paracyclophane analogue, compound 6. Although the geometry of [2₃](1,2,4)(1,2,5)-cyclophane²¹ has not yet been determined by X-ray analysis, this result suggests that the aromatic decks of [2₃](1,2,4)(1,2,5)cyclophane have a boat-shaped distortion similar to that of [2.2]paracyclophane and are equally well suited to form η⁴-metal complexes.

Experimental Section

General Comments. Microanalyses are by Dr. Richard Wielesek of the University of Oregon Microanalytical Laboratory. ¹H NMR spectra were recorded on a Varian XL-100 spectrometer. Field desorption mass spectra are by courtesy of the University

of Illinois mass spectrometry laboratory. The solid ruthenium complexes melt with decomposition giving a melting behavior that is not useful for characterization and so is not reported.

Preparation of the Double-Layered Ruthenium(II) Complexes. The following procedure describes the preparation of (η^6 -hexamethylbenzene)(η^6 -[2₄](1,2,4,5)cyclophane)ruthenium(II) bis(tetrafluoroborate), but the same general procedure was employed for all of the other double-layered complexes, compounds 1–15 described in Table I. A solution of 65 mg (0.097 mmol) of bis(η^6 -hexamethylbenzene)dichlorobis(μ -chloro)diruthenium(II)¹⁰ and 76 mg (0.39 mmol) of silver tetrafluoroborate in 2 mL of acetone was stirred at room temperature for 20 min. The precipitate of silver chloride was removed by filtration before adding 50 mg (0.19 mmol) of [2₄](1,2,4,5)cyclophane²² and 2 mL of trifluoroacetic acid to the yellow-orange solution. The mixture was then boiled vigorously under reflux for 30 min. The cold reaction mixture was poured into 50 mL of anhydrous ether. The crude solid, which separated, was collected and redissolved in nitromethane. After filtration, the nitromethane solution was carefully diluted with anhydrous ether. This gave 127 mg (95%) of a powdery solid. Recrystallization of this from acetonitrile by slow diffusion of anhydrous ether vapor gave pale yellow crystals.

Preparation of the Triple-Layered Ruthenium(II) Complexes. The following procedure describes the preparation of (η^6, η^6 -[2₄](1,2,4,5)cyclophane)bis(η^6 -hexamethylbenzene)diruthenium(II) tetrakis(tetrafluoroborate), but the same general procedure was employed for all four of the triple-layered complexes, compounds 16–19 described in Table I. A solution of 321 mg (0.480 mmol) of bis(η^6 -hexamethylbenzene)dichlorobis(μ -chloro)diruthenium(II) and 375 mg (1.93 mmol) of silver tetrafluoroborate in 8 mL of acetone was stirred at room temperature for 20 min. After removal of the precipitate of silver chloride, 25 mg (0.096 mmol) of [2₄](1,2,4,5)cyclophane and 8 mL of trifluoroacetic acid were added and the mixture was boiled vigorously under reflux for 1.25 h. The precipitate, which had formed, was collected by filtration and washed with anhydrous ether. This gave 78 mg (72%) of a white, pure microcrystalline powder.

Electrochemical Measurements. The cyclic voltammograms were measured as a function of scan rate and are reported at 100-mV/s scan rates in acetonitrile containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate in a three-electrode cell containing a spherical platinum working microelectrode, a platinum wire counterelectrode placed coaxial to the working electrode, and a silver chloride coated silver wire quasi-reference electrode isolated from the bulk solution by a single-fritted compartment. Ferrocene was added to the solution after the initial experiment as an internal standard.²³ Acetonitrile was predried over molecular sieves and then twice distilled from calcium hydride. PAR (Princeton Applied Research) equipment consisted of a PAR Model 173 potentiostat/galvanostat driven by a PAR Model 175 universal programmer and a PAR Model 179 digital coulometer. Coulometry was carried out by using a PAR Model 377 cell with a platinum mesh (22.8 cm²) electrode.

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