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THE SYNTHESIS AND ELECTROCHEMICAL BEHAVIOR OF BIS (η^6-HEXAMETHYLBENZENE)(η^6,η^6-TRIPLE-LAYERED [2.2]PARACYCLOPHANE)DIRUTHENIUM(II,II) TETRAKIS(TETRAFLUOROBORATE) AND ITS RELATED MIXED-VALENCE ION

HEE CHOL KANG, KLAUS-DIETER PLITZKO, V. BOEKELHEIDE*
Department of Chemistry, University of Oregon, Eugene, OR 97403 (U.S.A.)

HIROYUKI HIGUCHI and SOICHI MISUMI*
The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567 (Japan)

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Summary

The synthesis and characterization of (η^6-hexamethylbenzene)(η^6-triple-layered[2.2]paracyclophane)ruthenium(II) bis(tetrafluoroborate), (**4**) and bis(η^6-hexamethylbenzene)(η^6,η^6-triple-layered[2.2]paracyclophane)diruthenium(II,II) tetrakis(tetrafluoroborate) (**6**) together with their corresponding ruthenium(0) derivatives (**5** and **7**) are described. Cyclic voltammetry shows **4** to be reduced by a two-electron, reversible wave, $E_{1/2}$(SCE) -0.816 ± 0.008 V, and **6** to undergo reduction by two overlapping, reversible two-electron waves, $E^{I}_{1/2}$(SCE) -0.698 ± 0.005 V and $E^{II}_{1/2}$(SCE) -0.796 ± 0.005 V. The comproportionation constant, K_c, for the equilibrium between **6**, **7**, and the coresponding $Ru^{II}Ru^{0}$ mixed-valence ion (**11**) is 2.1×10^3. Although this large value of K_c indicates significant interaction between the two ruthenium atoms of **11**, the extent of interaction is appreciably smaller than that found for **2**, the previous example of a mixed-valence ion in this series.

Results and discussion

The outstanding characteristic of $[2_n]$cyclophanes is the interaction between the aromatic decks and the accompanying π-electron delocalization [1–3]. The possibility that oligomers and polymers formed by transition metal complexation, as illustrated by **1** [10], might show extended π-electron delocalization has been discussed previously [4–8]. If the overall structure of **1** requires the assignment of more than one formal oxidation state to the individual transition metal atoms, the

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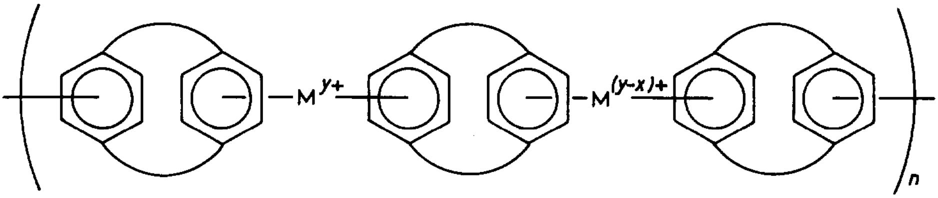
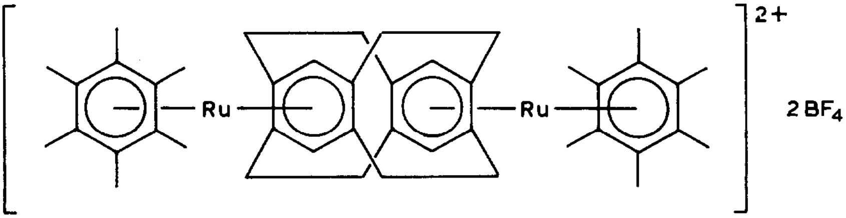
possibility of complete π-electron delocalization is greatly enhanced. An obvious test of this concept is to construct model subunits of **1**, where $n = 1$, and examine their properties to see if such model subunits exhibit mixed-valence ion behavior. At present the outstanding example of such a model subunit is the ruthenium complex **2** [9]. This molecule has been studied in some detail and has been shown to be a mixed-valence ion Class II, whose E_{th} and E_{op} energy terms, with respect to the net two-electron intervalence transfer involved, are 12.7 ± 0.8 and 56.5 ± 0.3 kcal/mol, respectively [9].



(**1**)



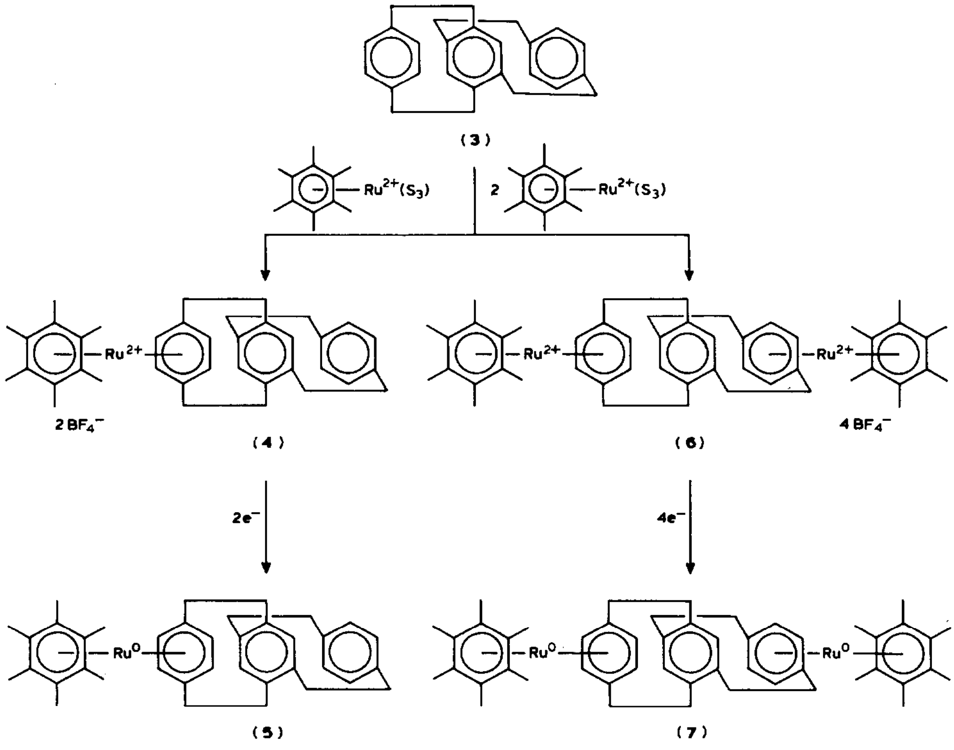
(**2**)

The mixed-valence ion **2** is unusual both because its intervalence transfer is a net two-electron process and because the lower oxidation states of ruthenium are involved. On the other hand the mixed-valence ions of the ruthenium ammines (Ru^{III}–Ru^{II} compounds) have been studied extensively [10–12], and the theory of one-electron intervalence transfer of such mixed-valence ions is relatively well understood [13–15]. Of particular interest has been the extent of the metal–metal interaction and the role of the bridging ligand. The extent of the interaction between the metal atoms is known to decrease as the distance between the metal atoms increases [16]. Also, the polarity and bulk of the bridging ligand may play a significant role [17]. As an extension of our study of the properties of the mixed-valence ion **2**, we now report on the preparation and properties of ruthenium complexes of triple-layered [2.2]paracyclophane, a bridging ligand providing an increased distance of separation between the ruthenium atoms, but a ligand which is also bulky and non-polar, being analogous to the $[2_4](1,2,4,5)$cyclophane ligand of **2**.

The choice of triple-layered [2.2]cyclophane (**3**) was based on the fact that extensive studies of the multilayered cyclophanes have shown that π-electron delocalization is present in these multilayered compounds just as in the $[2_n]$cyclophanes [18]. The evidence for π-electron delocalization in **3** is based on various electronic spectra, absorption, emission, and charge-transfer absorption of complexes [19], NMR spectra [19,20], and the ESR and ENDOR spectra of the corresponding radical anion [21] and radical cation [22]. In addition the exact geometry of **3** is known from a single crystal X-ray analysis of the corresponding 12-bromo derivative of **3** [23].

As shown in the reaction scheme (Scheme 1), treatment of **3** with the tris(acetone) solvate of (η^6-hexamethylbenzene)ruthenium(II), following established procedures [7], readily gave the mono-capped derivative **4** in 85% yield. The composition and spectral characteristics of **4** are in accord with its assigned structure. When **3** was treated with an excess of the (η^6-hexamethylbenzeneruthenium(II) tris(acetone) solvate in neat trifluoroacetic acid, the bis-capped derivative **6** was isolated in 97% yield. Again, the composition and spectral characteristics of **6** are in accord with its assigned structure.

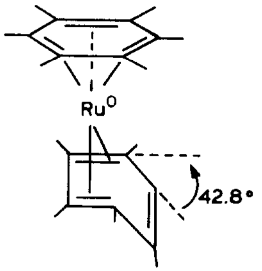
The well-known reduction of the planar bis(η^6-hexamethylbenzene)ruthenium(II) ion gives the corresponding η^6,η^4-ruthenium(0) derivative as a fluxional molecule [24,25], whose crystal structure X-ray analysis reveals the η^4-bound arene to be boat-shaped, as shown by **8** [26]. In related studies on the reduction of (η^6-hexamethylbenzene)(η^6-$[2_2](1,4)$cyclophane)ruthenium(II) bis(tetrafluoroborate) (**9**) we



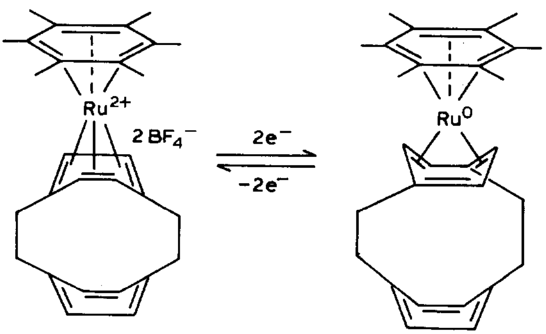
SCHEME 1

found that the ruthenium(0) atom was bound η^6 to the hexamethylbenzene ring and η^4 to the cyclophane [7]. Based on ^{1}H and ^{13}C NMR analyses it was deduced that the ruthenium-bound deck of the cyclophane had twisted from the boat-shaped conformation with prow and stern of the boat directed away from the ruthenium(II) ion as in **9**, to a boat-shaped conformation with the prow and stern of the boat directed toward the ruthenium(0) atom, as shown by **10**. In view of this earlier unexpected behavior, it was important to prepare the ruthenium(0) derivative **5** and compare the nature of its bonding and geometry with that of **10**.

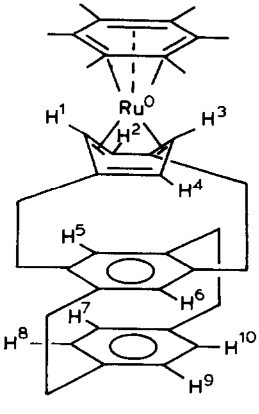
Chemical reduction of **4**, using bis(hexamethylbenzene)ruthenium(0) (**8**) as an "electron reservoir" reducing agent following an earlier published procedure [7], cleanly led to the formation of **5** in 95% yield. The ^{1}H NMR spectrum of **5** clearly demonstrates that the ruthenium(0) atom in **5** is bound η^6 to the hexamethylbenzene ring and η^4 to the cyclophane, with the geometry of the ruthenium-bound deck of the cyclophane being quite analogous to that present in **10**. Thus, the methyl protons of the hexamethylbenzene ring in **5** appear as a singlet at δ 1.98; the H^7, H^8, H^9, and H^{10} protons of the unbound deck of the cyclophane give a singlet at 6.58; the H^5 and H^6 protons of the central deck provide two singlets at 6.15 and 5.86; and finally the H^2, H^4 and H^1, H^3 groups of protons of the ruthenium(0) bound deck appear as two sets of double doublets in the region of 4.21 and 4.07 and in the region of 1.78 and 1.58, respectively. This is exactly what would be expected for structure **5**.



(8)



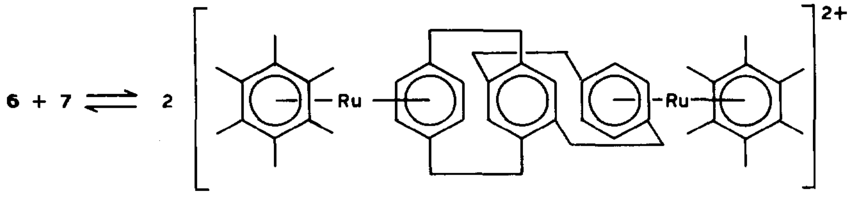
(9) (10)



(5)

Similarly, chemical reduction of **6**, using two equivalents of bis(hexamethylbenzene)ruthenium(0) (**8**) readily gave the bis-capped ruthenium(0) derivative **7**. The ^1H NMR spectrum of **7** likewise shows that the two hexamethylbenzene rings are bound η^6 to the ruthenium(0) atom, a singlet appearing at δ 1.95 corresponds to the 36 methyl protons. The remaining proton signals (Ar*H* and CH_2) are a complex group of multiplets between δ 4.10 and 1.20. There are two obvious conformations possible for the overall η^4,η^4-bonding of the cyclophane to the two ruthenium(0) atoms and, probably **7** is a mixture with both of these conformations being present.

Having in hand both **6** and **7**, we anticipated that combining equimolar quantities of the Ru^{2+}–Ru^{2+} ion with the Ru^0–Ru^0 species would give us the desired mixed-valence ion **11** (Ru^{2+}–Ru^0), as shown by eq. 1. However, experimental difficulties were encountered in carrying out this reaction that have not yet been resolved. We have not been able to find a common solvent in which both **6** and **7** can be dissolved, and attempts to carry out the reaction as a heterogeneous mixture have not provided anything from which **11** could be isolated in a pure state. Although chemical reduction using bis(hexamethylbenzene)ruthenium(0) (**8**) proved to be an efficient and convenient method for preparing the mixed-valence ion **2** [10], similar attempts to convert **6** to **11** were unrewarding.

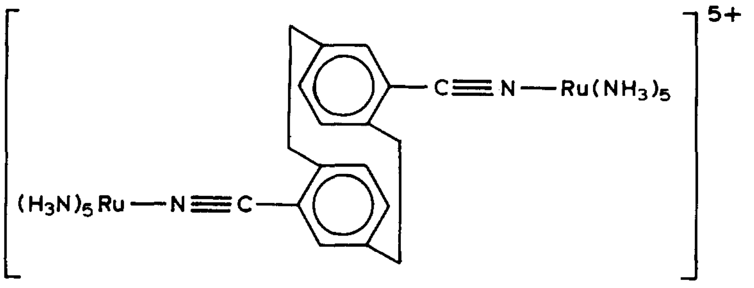


(1)

(11)

$$K_c = [11]/[6]\,[7] \qquad (2)$$

Richardson and Taube have presented persuasive arguments that measurement of the comproportionation constant, K_c (eq. 2), for mixed-valence ions is one of the better physical methods for evaluating the extent of interaction between metal atoms [28–30]. Although electrochemistry has long been used for measuring comproportionation constants, Richardson and Taube have refined these procedures to allow the determination of K_c when the separation of redox potentials is small and also for cases when it is not possible to isolate the mixed-valence ion or to measure the absorption spectrum of its intervalence transfer band [28,29]. It should be noted, though, that even if there is no interaction between metal atoms, the value of K_c wil be 4, due to the statistical factor. Relevant to the present study, the one example Richardson and Taube included in their work on ruthenium ammines, where a cyclophane moiety was present in the bridging ligand, is that given by **12**. The comproportionation constant for the formation of **12** was found to be approximately 4, indicating essentially no interaction between the ruthenium atoms in this case.



(**12**)

Electrochemical behavior

The cyclic voltammogram of **4** was measured at 100 mV/s scan rate using a 0.1 *M* solution of $(n\text{-Bu})_4N^+\ PF_6^-$ in propylene carbonate with ferrocene as an internal reference standard and is presented in Fig. 1. As shown, reduction occurs by a net two-electron, reversible wave having the characteristics: $E_{p,c}$ -0.844 ± 0.008 V; $E_{p,a}$ -0.787 ± 0.009 V; ΔE_p 57 ± 3 mV; i_a/i_c 0.844 ± 0.014; and $E_{1/2}$(SCE) -0.816 ± 0.008 V. Coulometry showed the uptake of 2.03 electrons, and a plot of $i_c/\sqrt{\text{scan rate}}$ is a straight line, indicating a diffusion controlled process. Thus, the electrochemical reduction of **4** is well behaved, and **4** is only slightly more difficult to reduce than

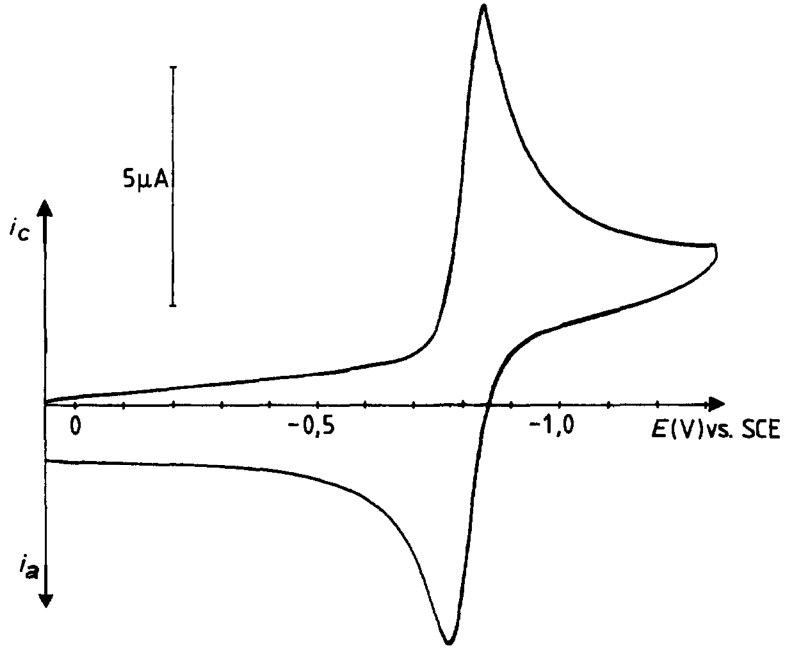


Fig. 1. Cyclic voltammogram of **4** measured in a 0.1 *M* solution of $(n\text{-}C_4H_9)N^+\ PF_6^-$ in propylene carbonate at 25°C and at a scan rate of 100 mV/s.

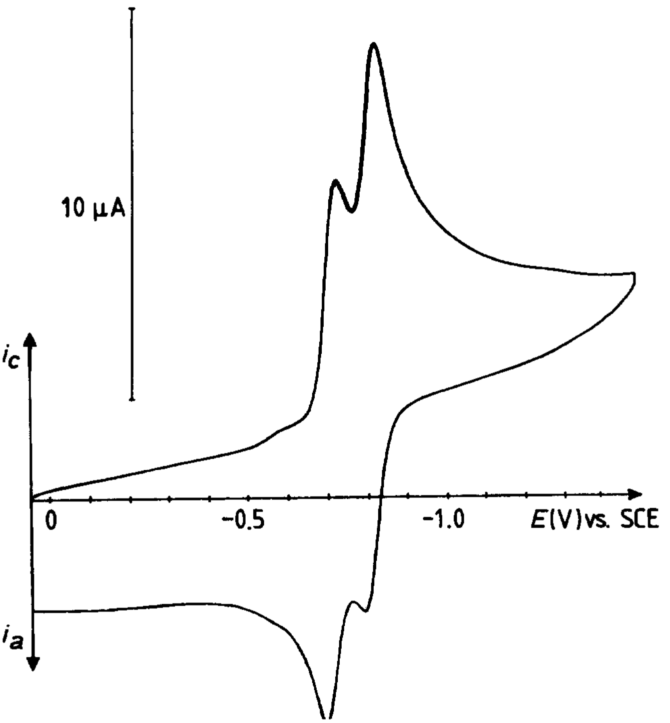


Fig. 2. Cyclic voltammogram of **6** measured in a 0.1 *M* solution of $(n\text{-}C_4H_9)_4N^+$ PF_6^- in propylene carbonate at 25°C and at a scan rate of 100 mV/s.

(η^6-hexamethylbenzene)(η^6-[2.2]paracyclophane)ruthenium(II), which has $E_{1/2}$(SCE) -0.69 ± 0.007 [5].

The cyclic voltammogram of **6** was measured similarly and is given in Fig. 2. In this case there are two reversible reduction waves that are not completely separated. The characteristics of the first wave are $E^{\mathrm{I}}_{\mathrm{p,c}}$ -0.730 ± 0.005 V; $E^{\mathrm{I}}_{\mathrm{p,a}}$ -0.665 ± 0.005 V; $\Delta E^{\mathrm{I}}_{\mathrm{p}}$ 39 ± 10 mV; and $E^{\mathrm{I}}_{1/2}$(SCE) -0.698 ± 0.005 V; the characteristics of the second wave are $E^{\mathrm{II}}_{\mathrm{p,c}}$ -0.831 ± 0.005 V, $E^{\mathrm{II}}_{\mathrm{p,a}}$ -0.761 ± 0.007 V, $\Delta E^{\mathrm{II}}_{\mathrm{p}}$ 44 ± 10 mV, and $E^{\mathrm{II}}_{1/2}$(SCE) -0.796 ± 0.005 V. For coulometric measurement the two waves shown in Fig. 2 can not be separated, but the overall value found is 4.01 electrons, as expected. Again, a plot of $i_c/\sqrt{\text{scan rate}}$ is a straight line, indicating a diffusion controlled process.

The overall electrochemical reduction of **6** is summarized by eq. 3 with the associated pertinent data listed below.

$$\mathbf{6} \xrightleftharpoons{n_1\,e^-} \mathbf{11} \xrightleftharpoons{n_2\,e^-} \mathbf{7} \qquad (3)$$

$$n_1 = n_2 = 2$$

$E^{\mathrm{I}}_{1/2}$(SCE) -698 ± 5 mV $\qquad$ $E^{\mathrm{II}}_{1/2}$(SCE) -796 ± 5 mV

$\Delta E_{1/2}$ 98 ± 5 mV

ΔE_{p} 165 ± 5 mV

$E^{\mathrm{II}}_{\mathrm{p}} - E^{\mathrm{I}}_{\mathrm{p}/2}$ 125 ± 6 mV [31]

The electrochemical determination of the comproportionation constant, K_c, is given by eq. 4.

$$K_c = \exp\left[\frac{(n_1E_1^0 - n_2E_2^0)F}{\mathrm{RT}}\right] = \exp\left[\frac{2(E_1^0 - E_2^0)F}{\mathrm{RT}}\right] \quad (4)$$

In the present instance, where $n_1 = n_2 = 2$, the exponential term becomes that shown on the right. Commonly, $E_1^0 - E_2^0$ is approximated by $\Delta E_{1/2}$; from eq. 3 this is found to be 98 ± 5 mV, which gives $K_c = 2.1 \times 10^3$. Other ways to approximate $E_1^0 - E_2^0$ include using ΔE_p (165 ± 5 mV from eq. 3), which yields a value of $K_c = 4.1 \times 10^5$, or $E_p - E_{p/2}$ (125 ± 6 mV) [32], which corresponds to $K_c = 1.7 \times 10^4$. Clearly, which ever of these numbers is used the value of K_c for the equilibrium given by eq. 2 is a fairly large number, indicating a definite interaction between the two ruthenium atoms present in **11**.

The observed value of K_c for the equilibrium forming the mixed-valence ion **2** is 1.1×10^{18}, where $\Delta E_{1/2}$, measured by cyclic voltammetry, is 533 mV [9]. Obviously, the interaction between the two ruthenium atoms in **2** is much stronger than that in **11**. In part this can be attributed to the greater distance between the ruthenium atoms in **11** as compared to **2**. In the case of **2**, based on an X-ray analysis of $[2_4](1,2,4,5)$cyclophane [32], and the average $\mathrm{Ru^{II}}$– and $\mathrm{Ru^0}$–arene distances found for bis(hexamethylbenzene)ruthenium(0) (**8**) [26], the distance between ruthenium atoms is estimated to be 6.22 Å. In contrast to the measured distance between decks for $[2_4](1,2,4,5)$cyclophane of 2.69 Å, the distance between the outer decks for triple-layered [2.2]paracyclophane is 6.28 Å, based on an X-ray analysis of its 12-bromo derivative [23,33]. This leads to an overall estimate for the distance between ruthenium atoms in **11** of 9.88 Å. Although the greater distance between ruthenium atoms in **11** compared to **2** undoubtedly contributes to lowering the extent of interaction between the two ruthenium atoms in **11**, as compared to **2**, it is probably not the major effect. For both **2** and **11** a change in nuclear positions must occur as the bonding of ruthenium to the cyclophane changes from η^6 to η^4 or vice versa. Based on an examination of molecular models this required movement appears to be much smaller for **2** than for **11**, and so the energy barrier for intervalence electron transfer is inherently much smaller for **2** than for **11**.

Although the electrochemical reduction of **6** to **11** and of **11** to **7** occurs as two-electron waves in each case, there is good evidence from our electrochemical studies on the reduction of (η^6-arene)(η^6-$[2_n]$cyclophane)ruthenium(II) ions that these net two-electron reductions are actually two one-electron steps [34]. A similar mechanism would be expected to hold for the reductions of **6** and **11**. Furthermore, **2** and **11** are both mixed-valence ions Class II, exhibiting a net two-electron intervalence transfer. However, our studies on the properties of **2** suggest that the intervalence transfer for **2** involves two one-electron steps [9]. It would be expected that **11** would follow a similar mechanism.

Experimental

*(η^6-Hexamethylbenzene)(η^6-triple-layered[2.2]paracyclophane)ruthenium(II) bis(tetrafluoroborate) (**4**)*

A mixture of 75 mg (0.112 mmol) of bis(η^6-hexamethylbenzene)dichlorobis(μ-chloro)diruthenium(II) [5] and 90 mg (0.462 mmol) of silver tetrafluoroborate in 2 ml of acetone was stirred at room temperature for 30 min. The resulting precipitate of silver chloride was collected by filtration and washed with two 3 ml aliquots of acetone. The combined filtrate and washings were added dropwise over a period of 40 min, using a pressure-equalizing funnel, to a boiling solution of triple-layered [2.2]cyclophane (3) in 2 ml of acetone and 2 ml of trifluoroacetic acid. After the solution had boiled under reflux for 10 min, it was cooled, the volume was reduced to 3 ml using a stream of nitrogen, and 70 ml of ether was added. The yellow precipitate, which separated was collected by filtration and washed with ether. The resulting yellow solid was dissolved in 1 ml of nitromethane and this solution was placed in an atmosphere where a slow diffusion of ether into the solution could occur. This gave 147 mg (85%) of yellow crystals: m.p. > 260°C (dec.); ^{1}H NMR (CD_3NO_2) δ 6.33 (4H, s, Ar*H*), 5.99 (2H, s, Ar*H*) 5,66 (2H, d, *J* 6.8 Hz, Ar*H*), 5.55 (2H, d, *J* 6.8 Hz, Ar*H*), 3.55–2.70 (16H, m, CH_2), 2.39 (18H, s, CH_3); UV (propylene carbonate) λ_{max} 277 nm (ε 4513) and 317.5 (3556). Anal. Found: C, 58.55; H, 5.86. $C_{38}H_{44}RuB_2F_8$ calc: C, 58.86; H, 5.72%.

(η^6-Hexamethylbenzene)(η^4-triple-layered[2.2]paracyclophaneruthenium(0) (5)

Method A. A mixture of 70 mg (0.090 mmol) of (η^6-hexamethylbenzene)(η^6-triple-layered[2.2]paracyclophane)ruthenium(II) bis(tetrafluoroborate) (4), and 2.10 g of a 2% sodium-mercury amalgam in 10 ml of degassed 1,2-dimethoxyethane was stirred vigorously for 5 h in an inert atmosphere. After decantation from the excess amalgam, the solution was concentrated. The residual grey solid was extracted with three 10 ml portions of degassed hexane, filtered, and the filtrate was concentrated to give 45 mg (83%) of **5** as yellow-orange crystals: m.p. 219–222°C; ^{1}H NMR (C_6D_6) δ 6.58 (4H, s, Ar*H*), 6.15 (1H, s, Ar*H*), 5.86 (1H, s, Ar*H*), 4.21 (1H, dd, *J* 4.7, *J'* 1.8 Hz, =C*H*), 4.07 (1H, br d, *J* 4.9 Hz, =C*H*), 3.60–2.05 (16H, m, CH_2), 1.99 (18H, s, CH_3), 1.78 (1H, dd, *J* 4.9, *J'* 1.8 Hz, =C*H*), 1.58 (1H, br d, *J* 4.7 Hz); the mass spectrum of **5** showed an *m/e* pattern with signals at 596, 598, 600, 602, 604, and 606 fully in accord with the predicted ruthenium isotope pattern for **5**. Anal. Found: C, 75.75; H, 7.45. $C_{38}H_{44}Ru$ calc: C, 75.84; H, 7.37%.

Method B. A mixture of 20 mg (0.025 mmol) of **4** and 10 mg of bis(hexamethylbenzene)ruthenium(0) (**8**), in 10 ml of dry, degassed methanol was stirred at room temperature for 5 h in an inert atmosphere. After the reaction mixture was concentrated, the residue was extracted with three 10 ml portions of degassed hexane, and the insoluble bis(η^6-hexamethylbenzene)ruthenium(II) bis(tetrafluoroborate) was removed by filtration. The filtrate was then concentrated to give 14 mg (95%) of **5** as yellow-orange crystals, identical in all respects with the sample of **5** prepared as described in Method A.

Bis(η^6-hexamethylbenzene)(η^6,η^6-triple-layered[2.2]paracyclophane)diruthenium(II,II) tetrakis(tetrafluoroborate) (6)

A mixture of 915 mg (1.37 mmol) of bis(η^6-hexamethylbenzene)dichlorobis(μ-chloro)diruthenium(II) and 1.068 g (5.49 mmol) of silver tetrafluoroborate in 5 ml of acetone was stirred at room temperature for 30 min. After removal of the silver chloride by filtration, the filtrate was concentrated to dryness. To the residue was added 95 mg (0.28 mmol) of triple-layered [2.2]paracyclophane, (3), followed by 5 ml of trifluoroacetic acid, and the mixture was boiled under reflux for 2 h. After the solution had cooled to room temperature, 5 ml of acetone was added. The yellow precipitate, which formed, was collected by filtration and washed with acetone. The yellow solid was then taken up in 5 ml of propylene carbonate and precipitated by addition of 80 ml of ether to give 300 mg (97%) of **6** as a pale yellow solid: m.p. > 335°C; ^{1}H NMR (CD_3NO_2) δ 6.47 (2H, s, ArH), 5.78 (4H, d, J 6.8 Hz, ArH), 5.70 (4H, d, J 6.8 Hz, ArH), 3.65–2.90 (16H, m, CH_2), 2.40 (36H, s, CH_3): UV (propylene carbonate), λ_{max} 279.5 cm (ε 11638), Anal. Found: C, 49.05; H, 5.15. $C_{50}H_{62}Ru_2B_4F_{16}$ calc: C, 49.53; H, 5.15%.

Bis(η^6-hexamethylbenzene)(η^4,η^4,-triple-layered[2.2]paracyclophane)diruthenium(0,0) (7)

A mixture of 50 mg (0.041 mmol) of bis(η^6-hexamethylbenzene)(η^6,η^6-triple-layered[2.2]paracyclophane)diruthenium(II,II) tetrakis(tetrafluoroborate) (**6**) and 35 mg (0.082 mmol) of bis(hexamethylbenzene)ruthenium(0) (**8**) in 20 ml of dry, degassed methanol was stirred at room temperature for 20 h in a nitrogen-filled glove box. The reaction mixture was concentrated, and the residual solid was extracted with five 10 ml aliquots of dry, degassed dichloromethane. After filtration, the dichloromethane filtrate was concentrated, and the resulting yellow solid was washed with three 5 ml portions of hexane to give 20 mg (57%) of a yellow powder: m.p. > 295°C (dec.); ^{1}H NMR (CD_2Cl_2) δ 1.95 (36H, s, CH_3), the rest of the protons (ArH and CH_2) were spread between δ 4.10 and 1.20 as a complex series of multiplets. The sample, 7, was not sufficiently volatile to allow the measurement of its mass spectrum without decomposition. However, the signal for the parent ion, centered at 864, showed the isotope pattern distribution expected for **7**. Also, among the decomposition products were a set of isotope signals matching those of the parent peak for the mono-capped complex, **5**. Anal. Found: C, 68.96; H, 7.01. $C_{50}H_{62}Ru_2$ calc: C, 69.41; H, 7.22%.

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35 ^{1}H NMR spectra were measured using a General Electric QE spectrometer. Mass spectra were obtained with a CEC-21b-110 instrument set at 70 eV. Electrochemical experiments were performed using a Princeton Applied Research electrochemical station (Model 175 Universal Programmer, Model 173 Potentiostat-Galvanostat, and a Model 174A Polarographic Analyzer). Cyclic voltammetry was carried out in a cell containing a 0.1 *M* solution of tetra(n-butyl)ammonium hexafluorophosphate in propylene carbonate with a platinum bead electrode as the working electrode, a platinum wire (placed coaxial to the working electrode as a counter-electrode), and a silver wire, isolated from the bulk solution by a single-fritted compartment, as a quasi-reference-electrode. Coulometry was carried out using a PAR Model 377 cell with a platinum mesh basket electrode.