Compounds **9**, **10**, **11**, **16**, and **25** were prepared similarly following this procedure. See the Supplementary Material section for experimental details.

Bis(η^6-hexamethylbenzene)(η^5,η^5-[2_2](1,4)cyclophane)diruthenium(II,II) Bis(tetrafluoroborate) (7). Model Chemical Reduction Procedures with Cobaltocene. A mixture of 316.9 mg (0.293 mmol) of **4** and 110.7 mg (0.586 mmol) of cobaltocene in 12 mL of methanol was stirred at room temperature for 2.5 h under an inert atmosphere. After concentration of the greenish-yellow mixture, the residue was washed into a thimble and then placed in a Schlenk-Soxhlet apparatus, where it was extracted with 1,2-dimethoxyethane for 48 h to remove the cobaltocenium tetrafluoroborate. The remaining contents in the thimble consisted of 225.4 mg (85%) of **7** as a reddish brown solid. Recrystallization of this by solution in dichloromethane followed by a slow vapor diffusion of ether afforded small red crystals: mp > 280 °C dec; ^{1}H and ^{13}C NMR data (see Table II).

Compounds **12** and **13** were likewise prepared following this procedure. See the Supplementary Material section for experimental details.

Bis(η^6-hexamethylbenzene)(η^5,η^5-*anti*-[2_2](1,3)cyclophane)diruthenium(II,II) Bis(tetrafluoroborate) (8). Model Chemical Reduction Procedure with Bis(hexamethylbenzene)ruthenium(0). A mixture of 100 mg (0.092 mmol) of **5**[13] and 39 mg (0.092 mmol) of bis(hexamethylbenzene)ruthenium)(0)[13] in 7 mL of methanol was stirred at room temperature for 20 h under an inert atmosphere. After removal of solvent by concentration, the residue was taken up in dichloromethane, and this solution was filtered to remove insoluble residues. Concentration of the filtrate followed by crystallization of the residue from dichloromethane subjected to slow vapor diffusion with acetone gave 70 mg (83%) of a red solid. When the reduction was repeated by using the model cobaltocene procedure previously described for **7**, the product was identical and, again, was isolated in 83% yield as red crystals: mp >200 °C dec; ^{1}H and ^{13}C NMR (see Table II); λ_{max} (CH_2Cl_2) 391.5 (ϵ, 7800) and 325.5 nm (ϵ, 8700); λ_{max} (CH_3OH) 385 (ϵ, 10700) and 322 nm (ϵ, 12600). Anal. Calcd for $C_{40}H_{52}Ru_2B_2F_8{\cdot}CH_2Cl_2$: C, 49.57; H, 5.27. Found: C, 49.17; H, 5.55. The presence of a molecule of dichloromethane of crystallization was confirmed by an X-ray analysis.[46]

Compound **14** was likewise prepared following this procedure. See the Supplementary Materials section for experimental details.

Acknowledgment. We thank the National Science Foundation for their support of this investigation under Grants CHE-8709775 and CHE-8603728. K.-D.P. thanks the Studienstiftung des Deutschen Volkes for a Discussion Stipend (1985-1987).

Supplementary Material Available: Tables of atomic coordinates and interatomic distances and bond angles derived from the crystallographic analysis of **7** and a detailed experimental section (30 pages); tables of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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

(45) Boekelheide, V.; Hollins, R. A. *J. Am. Chem. Soc.* **1972**, *95*, 3201-3208.

(46) An X-ray analysis of **8**, carried out by Oneida Research Services, confirmed the presence of a molecule of dichloromethane of crystallization. We thank Dr. Michael D. Ward and E. I. du Pont de Nemours & Co. for providing this service.

Bis(η^6-hexamethylbenzene)(η^6,η^6-polycyclic aromatic)diruthenium(II,II) Complexes and Their Two-Electron Reduction to Cyclohexadienyl Anion Complexes[1]

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Received January 8, 1990

Abstract: The bis(η^6-hexamethylbenzene)(η^6,η^6-polycyclic aromatic)diruthenium(II,II) complexes **10**, **14**, **16**, **18**, **20**, and **22**, where the polycyclic aromatic ligands are phenanthrene, 9,10-dihydrophenanthrene, biphenyl, 3,3′,5,5′-tetramethylbiphenyl, 4,5,9,10-tetrahydropyrene, and triphenylene, respectively, have been synthesized and their electrochemical properties measured. A two-electron chemical reduction of each of these 4+ diruthenium complexes has led to the isolation and characterization of each of their corresponding 2+ diruthenium complexes: **11**, **15**, **17**, **19**, **21**, and **23**. On the basis of analyses of their ^{1}H and ^{13}C NMR spectra, structural assignments have been made for all of these 2+ diruthenium complexes. Although the phenanthrene derivative **11** is a class II mixed-valence ion having a Ru(0) site and a Ru(II) site, all of the other 4+ diruthenium complexes undergo two-electron reduction by changing the biphenyl moiety of their polycyclic aromatic ligand into two cyclohexadienyl anions joined by a carbon-carbon double bond. That the bis(cyclohexadienyl anion) system present in these 2+ diruthenium complexes is subject to electrophilic attack was shown by the easy protonation of **17**, leading to the formation of **37**. The 4+ diruthenium complex of biphenylene **42** was prepared, and it undergoes a similar two-electron reduction to give **43**. In contrast, though, the highly rigid 4+ diruthenium complex of pyrene **35** shows two separate one-electron reduction waves. The bis(η^6-biphenyl)ruthenium(II) bis(tetrafluoroborate) derivatives **49**, **50**, and **51** were prepared. A single-crystal X-ray analysis of **49** shows the molecule to have a syn conformation.

The possibility that polymers derived from transition-metal complexes of [2_n]cyclophanes might show interesting electrical properties associated with electron delocalization has led us to prepare various model monomers related to such polymers and examine their properties.[2-4] [2_n]Cyclophanes are attractive ligands because their π-electron systems are delocalized, yet they present two arene decks for metal complexation, as is necessary for polymer formation. Another class of compounds offering π-electron delocalization combined with two sites for metal com-

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(1) Preliminary communication: Plitzko, K.-D.; Boekelheide, V. *Angew. Chem.* **1987**, *99*, 715-717; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 700-702.

(2) Laganis, E. D.; Finke, R. G.; Boekelheide, V. *Tetrahedron Lett.* **1980**, *21*, 4405-4408.

(3) Voegeli, R. H.; Kang, H. C.; Finke, R. G.; Boekelheide, V. *J. Am. Chem. Soc.* **1986**, *108*, 7010-7016.

(4) Plitzko, K.-D.; Rapko, B.; Gollas, B.; Wehrle, G.; Weakley, T.; Pierce, D.; Geiger, W. E., Jr.; Haddon, R. C.; Boekelheide, V. *J. Am. Chem. Soc.* **1989**, *111*, XXXX.

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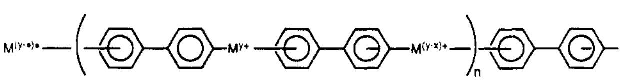
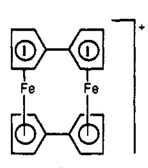
plexation is the polycyclic aromatics. As shown below, a simple example of a polymer derived from transition-metal complexes of a polycyclic aromatic would be **1**. The presence of differing formal oxidation states for the metal atoms in the polymer could create a mixed-valence state enhancing electron delocalization throughout the polymer molecule.



1

Early work on metal complexes of polycyclic aromatics has shown that bis(fulvalene)diiron undergoes oxidation to give a delocalized (class III) mixed-valence ion, **2**,[5] whereas bis(biphenyl)dichromium oxidizes to a localized (class I) mixed-valence ion, **3**.[6] Hendrickson et al. prepared a number of bis(cyclopentadienyliron) complexes of polycyclic aromatic molecules and reported that the electrochemical behavior of these complexes indicated interaction between the two iron atoms.[7] This excited our interest in polycyclic aromatics. However, our experience with metal complexes of [2_n]cyclophanes indicated clearly that ruthenium complexes are more stable and easier to handle than the corresponding iron complexes.[8] On this basis, then, we began a systematic exploration of the synthesis and properties of model ruthenium complexes of polycyclic aromatics. The first polycyclic aromatic ligand to be examined was phenanthrene, **5**, which, on treatment with (η^6-hexamethylbenzene)ruthenium(II)$^{2+}$ solvate, **4**, readily gave the corresponding monoruthenium derivate **7** in 99% yield. Cyclic voltammetry of **7** showed a reversible two-electron reduction wave ($E_{1/2}$ = −0.599 V). Furthermore, chemical reduction of **7**, by using either cobaltocene or bis(hexamethylbenzene)ruthenium(0),[4] gave the corresponding (η^6-hexamethylbenzene)(η^4-phenanthrene)ruthenium(0) derivative **9**. The η^4-hapticity of the phenanthrene ligand is quite apparent from the ^{1}H NMR spectrum of **9**. Oxidation of **9** with $NOBF_4$ smoothly converted **9** back to **7** in 99% yield.



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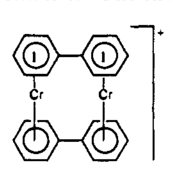

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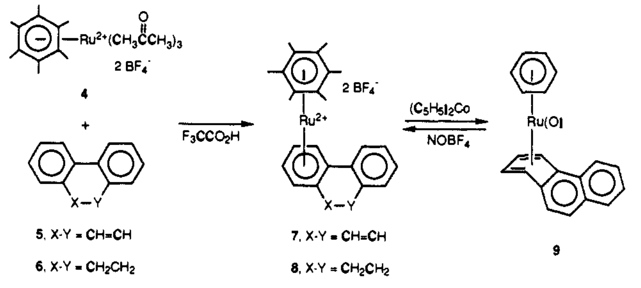
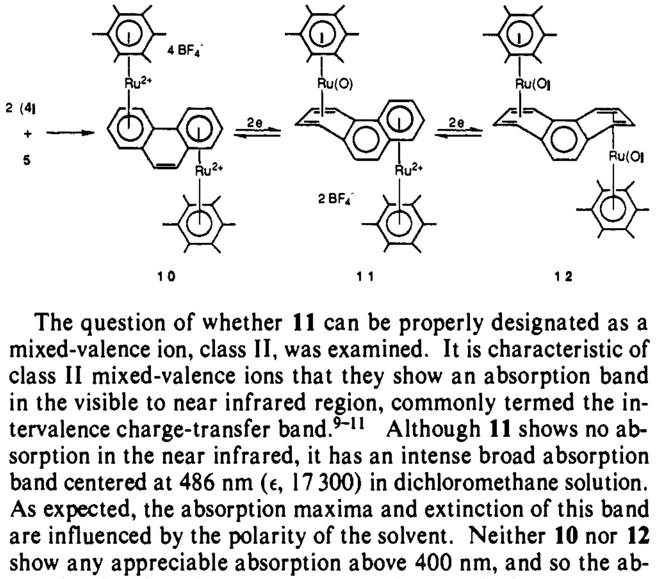


When phenanthrene, **5**, was treated with an excess of the capping reagent, **4**, the corresponding biscapped complex **10** was isolated in 77% yield. Cyclic voltammetry and coulometry experiments with **10** showed two reversible two-electron reduction waves ($E_{1/2}$ = −0.185 V; $E'_{1/2}$ = −0.677 V). When **10** is subjected to chemical reduction, by using either two or four electron equivalents, both **11** and **12** can be prepared separately in high yields. Also, combining equimolar quantities of **10** and **12** in a methanol solution results in a complete conversion to **11**. No detectable amounts of **10** and **12** are present under equilibration conditions. As evidence that structural integrity is maintained in **11** and **12**, it was shown by separate oxidations of **11** and **12**, by using either $NOBF_4$ or ferrocinium hexafluorophosphate, that **10** is regenerated in essentially quantitative yield.

The structures of **9** and **10** can be deduced fairly readily from their ^{1}H and ^{13}C NMR spectra. The ruthenium(II)-bound aromatic protons, η^6-hapticity in the monocapped derivative **7** and the biscapped complex **10**, show resonances in the range of δ 7.35–8.35, whereas the ruthenium(0)-bound diene protons in the monocapped derivative **9** and the biscapped complex **12** exhibit resonances in the region of δ 2.62–5.42. However, **11** shows one set of aromatic protons in the range of δ 7.15–7.63, corresponding to a ruthenium(II)-bound site, and a second set of diene protons in the region of δ 3.22–6.36, corresponding to a ruthenium(0) site. Likewise, the ^{13}C resonances observed for **11** can be dissected as corresponding to a ruthenium(0) diene site and a ruthenium(II) aromatic site.

The ^{1}H and ^{13}C spectra of **10** show only one type of hexamethylbenzene, and the ^{1}H and ^{13}C NMR spectra for **12**, although having different chemical shift values than those found for **10**, show only one type of hexamethylbenzene. In contrast, **11** shows two types of hexamethylbenzene protons [δ 1.90 (18 H, s, Ru(0) site) and 2.04 (18 H, s, Ru(II) site)] and two types of hexamethylbenzene ^{13}C carbons [δ 73.1 (Ru(II) site) and 68.7 (Ru(0) site)]. Finally, COSY (correlated spectroscopy) and NOESY (nuclear Overhauser effect spectroscopy) NMR experiments were carried out with **11**, making possible the complete and certain position assignments for all proton chemical shift values of **11**.



The question of whether **11** can be properly designated as a mixed-valence ion, class II, was examined. It is characteristic of class II mixed-valence ions that they show an absorption band in the visible to near infrared region, commonly termed the intervalence charge-transfer band.[9-11] Although **11** shows no absorption in the near infrared, it has an intense broad absorption band centered at 486 nm (ϵ, 17 300) in dichloromethane solution. As expected, the absorption maxima and extinction of this band are influenced by the polarity of the solvent. Neither **10** nor **12** show any appreciable absorption above 400 nm, and so the absorption band at 486 nm appears to be a typical intervalence transfer band.

Actually, the absorption band for **11** is closely similar to that observed earlier for bis(η^6-hexamethylbenzene)(η^6,η^4-[2_4](1,2,4,5)cyclophane)diruthenium(II,0) bis(tetrafluoroborate), **13**,[3] which was shown to be a class II mixed-valence ion, with an energy barrier ($\Delta H^{\ddagger}$) of 12.7 ± 0.8 kcal/mol for its net two-electron intervalence transfer. In the case of **13**, NMR spectral studies showed a symmetrical time-averaged spectrum at room temperature, and cooling to −45 °C was required to observe the separate Ru(II) and Ru(0) sites corresponding to the equilibrium of **13a** $\rightleftharpoons$ **13b**.[3] Since the NMR spectra of **11** already show separate Ru(II) and Ru(0) sites at room temperature, the ^{1}H NMR spectrum of **11** in a solution of ethylene glycol-d_6 was measured at higher temperatures to see whether coalescence might occur. But even at 170 °C, the highest temperature experimentally feasible, no change in the spectrum occurred. The energy barrier

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(5) Le Vanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, U. T.; Eilbracht, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181–3187.

(6) Elschenbroich, C.; Heck, J. *J. Am. Chem. Soc.* **1979**, *101*, 6773–6776.

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

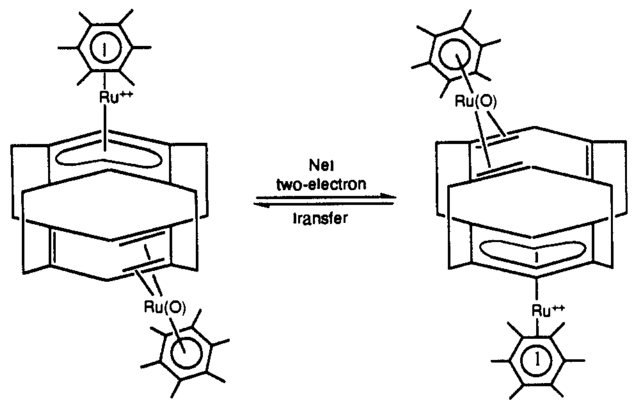
(8) Laganis, E. D.; Voegeli, R. H.; Swann, R. T.; Finke, R. G.; Hopf, H.; Boekelheide, V. *Organometallics* **1982**, *1*, 1415–1420.

(9) Felix, F.; Ludi, A. *Inorg. Chem.* **1978**, *17*, 1782–1785.

(10) Powers, M. J.; Meyers, T. J. *Inorg. Chem.* **1978**, *17*, 1785–1790.

(11) Taube, H. *Ann. New York Acad. Sci.* **1978**, *313*, 481–495.

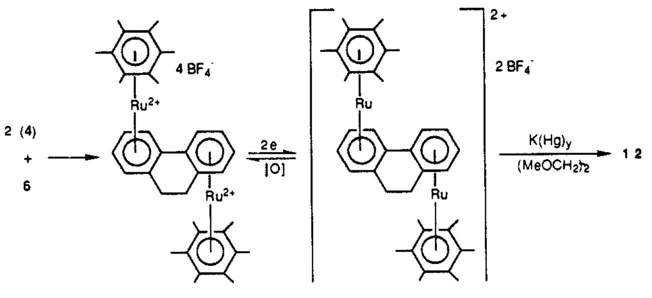
for a net two-electron intervalence transfer in **11** must be exceptionally high.



13a **13b**

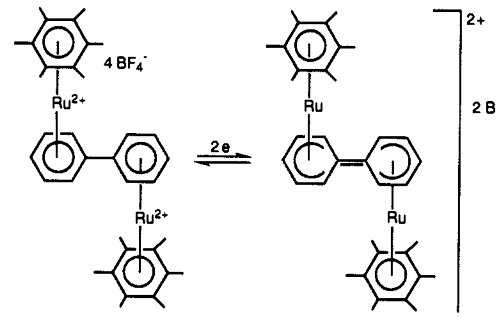
The capping of 9,10-dihydrophenanthrene, **6**, with (η^6-hexamethylbenzene)ruthenium(II) solvate, **4**, occurred smoothly to give **8**. Cyclic voltammetry and coulometry of **8** showed an apparent irreversible two-electron reduction wave (E_{pc} = −0.854 V). Because the electrochemical reduction of **8** appeared to be irreversible, no attempt was made to prepare and isolate the corresponding Ru(0) derivative from **8**.

When **6** was treated with an excess of the capping reagent, **4**, the biscapped complex **14** was isolated in 80% yield. Cyclic voltammetry and coulometry of **14** showed a reversible two-electron reduction wave ($E_{1/2}$ = −0.185 V), followed by a second, apparently irreversible, wave with a very broad anodic return. In their studies of certain Ir(III) and Ir(I) complexes, Bowyer and Geiger encountered a similar phenomenon.[12] They found that this behavior was due to a slow charge transfer, and, by either changing the nature of the electrode or raising the temperature, they were able to obtain voltammograms exhibiting a nice reversible wave. In the case of **14**, it was also found that raising the temperature[1] or changing the electrode from platinum to mercury had a large effect on the shape of the second reduction wave.[13] A two-electron chemical reduction of **14**, with either bis(hexamethylbenzene)ruthenium(0) or cobaltocene, readily gave the corresponding 2+ ion **15**, as dark red crystals in essentially quantitative yield. Since the redox potential for the second two-electron reduction wave is extremely negative ($E_{1/2}$ = −1.177 V), further reduction of **15** to a neutral diruthenium(0,0) species requires a strong reducing agent. Attempted reduction of **15** with potassium amalgam in 1,2-dimethoxyethane, though, gave not the expected product but instead the diruthenium(0,0) derivative of phenanthrene, **12**. Apparently, potassium amalgam promotes dehydrogenation as well as reduction. To examine the exact nature of **15** it was first shown that oxidation of **15**, either by $NOBF_4$ or ferrocenium hexafluorophosphate, reconverted it to **14** in essentially quantitative yield. Thus, it appeared that no skeletal change had occurred during the formation of **15** from **14**. The electronic spectrum of **15** showed a single broad absorption band, λ_{max} (CH_2Cl_2) 475 nm (ϵ, 18690). Although the absorption band for **15** occurs in the same general region of the ultraviolet as that of **11** and is subject to similar shifts due to solvent polarity, the absorption band for **15** is much sharper than that of **11**, as would be appropriate if **15** were a class III delocalized ion. Furthermore, the ^1H and ^{13}C NMR spectra of **15** are completely symmetrical and are unchanged when a solution of **15** in a mixture of CD_2Cl_2 and $CHClF_2$ is cooled to −135 °C. Thus, any energy barrier to intervalence electron transfer for **15** must necessarily be very small. Finally, an X-ray photoemission spectrum of **15** shows only one type of ruthenium atom, which has a $Ru_{3d5/2}$ binding energy of 281.9 eV.

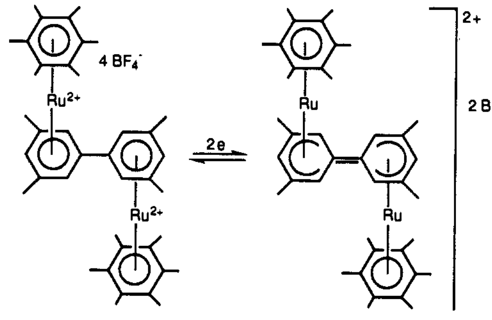


14 **15**

In view of these data we decided to explore the question of whether the behavior of 9,10-dihydrophenanthrene as a ligand for diruthenium complexation was a general phenomenon. The analogous polycyclic aromatic ligands examined included biphenyl, 3,3′,5,5′-tetramethylbiphenyl, 4,5,9,10-tetrahydropyrene, and triphenylene. In each case treatment of the ligand with an excess of the capping reagent, **4**, readily gave the corresponding diruthenium complex in high yield, and so allowed the preparation of **16**, **18**, **20**, and **22**, respectively.



16 **17**



18 **19**

The 2+ monoruthenium(II) complexes **25**, **26**, **27**, and **28** were also prepared so that their spectral properties and electrochemical behavior could be compared with those of the 4+ and 2+ diruthenium complexes of the corresponding hydrocarbon ligands.

The electrochemical data for the 4+ diruthenium complexes **10**, **14**, **16**, **18**, and **22** plus the 2+ monoruthenium complexes **7**, **8**, **25**, **26**, **27**, and **28** are summarized in Table I. Of the 2+ monoruthenium complexes only those having either phenanthrene or triphenylene as ligands show a nice two-electron reduction wave, $E_{1/2}$ being −0.599 and −0.633 V, respectively, for **7** and **28**. The reason for lack of reversibility in the other 2+ monoruthenium complexes is not clear. It may be simply a matter of solvolysis, since metal complexes of benzene and simple benzene derivatives are well-known for their ease of solvolysis.

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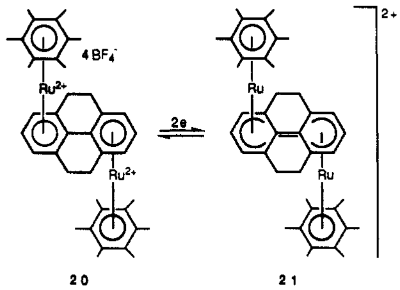
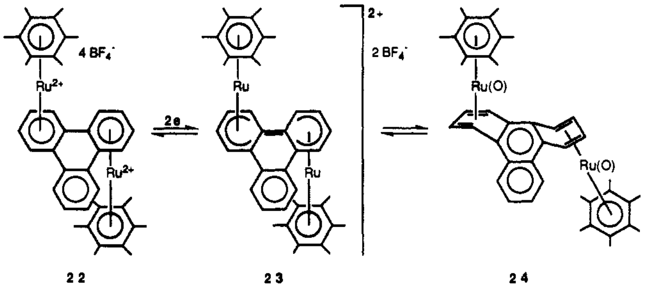
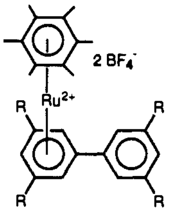
(12) Bowyer, W. J.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5657–5663.

(13) Private communication from Professor W. E. Geiger and D. T. Pierce of the University of Vermont, who examined the double potential step chronoamperometry of compounds **14**, **16** and **20** by modeling the complicated wave shape of their second couples following a modified EE mechanism by using finite difference simulations, as described for the reduction of bis(η^6-hexamethylbenzene)ruthenium^{2+} (Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7636–7638). The theoretical fits, so obtained, are consistent for **14**, **16**, and **20** each having a Nernstian 2+/+ couple and a quasi-reversible +/0 couple, $k_{s,2}$ ca. 10^{-4} cm s^{-1}, with an E^0 separation ($E^0_{2+/+} - E^0_{+/0}$ of ca. +90 mV.

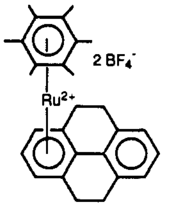






25, R = -H

26, R = -Me



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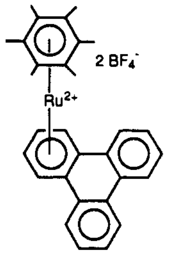


28

On the other hand, the first reduction waves for all of the 4+ diruthenium complexes listed in Table I are reversible two-electron waves with their $E_{1/2}$ values lying in the range of -0.161 to -0.245 V. The fact that the 4+ diruthenium complexes undergo reduction at a potential about 400 mV more positive than the potentials required for the corresponding 2+ monoruthenium complexes suggests that there is a special stabilization occurring in the formation of the 2+ diruthenium complexes. It should also be noted that the difference between the first and second redox potentials of the 4+ diruthenium complexes is very large, the separation being about 1 V for **14**, **16**, **18**, and **20** but only about 0.5 V for **10** and **22**.

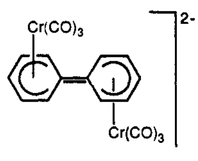
The differences in electrochemical behavior evident in Table I are also present in the behavior of these complexes on attempted chemical reductions. Reduction of the phenanthrene complex **10** can be accomplished in high yield with either bis(hexamethylbenzene)ruthenium(0) or cobaltocene to give the 2+ ion **11**, when two-electron equivalents are employed, or the neutral ruthenium complex **12**, when four-electron equivalents are employed. Similarly the 4+ diruthenium complex of triphenylene **22** can be converted in high yield to either the 2+ ion **23** or the neutral complex **24**.

Likewise, the 4+ diruthenium complexes **14**, **16**, **18**, and **20** are readily converted by chemical reduction to the corresponding 2+ ions **15**, **17**, **19**, and **21**, which are stable complexes that can easily be isolated and fully characterized. However, attempted chemical reductions to convert the 4+ ions **14**, **16**, **18**, and **20** or the 2+ ions **15**, **17**, **19**, and **21** to their corresponding neutral diruthenium(0,0) derivatives led only to decomposition.

NMR Spectral Properties of the 2+ Diruthenium Complexes. Our initial studies had shown that the 2+ diruthenium complex of phenanthrene **11** is a class II mixed-valence ion.[1] In contrast, the 2+ diruthenium complex of 9,10-dihydrophenanthrene **15** shows completely symmetrical ^{1}H and ^{13}C NMR spectra that remains unchanged even when **15** is cooled to -135 °C in a mixture of CD_2Cl_2 and $CDClF_2$. This raised the question of whether **15** was in fact a class III mixed-valence ion. Examination of the ^{1}H and ^{13}C NMR spectra of the additional 2+ diruthenium complexes **17**, **21**, and **23** showed that all of these are completely symmetrical and remain unchanged at temperatures below -100 °C. Thus, the 2+ phenanthrene ion **11** is the apparent exception, whereas the behavior of the 2+ 9,10-dihydrophenanthrene ion **15** is the more general phenomenon. The ^{1}H and ^{13}C NMR spectral data for the 2+ diruthenium complexes are summarized in Table II.

A striking feature of the NMR data for the 2+ diruthenium complexes **15**, **17**, **19**, **21**, and **23** is the large chemical shift differences between adjacent aromatic carbons, both for the ^{1}H and ^{13}C spectra. This chemical shift pattern is rather similar to the ^{1}H and ^{13}C NMR spectra of the "open" metallocenes described in detail by Ernst.[14] Another class of compounds, showing this type of pattern of ^{1}H and ^{13}C NMR spectra, is the dianion of (η^6,η^6-biphenyl)$[Cr(CO)_3]_2$, **29**,[15] and its spectra are included in Table II for comparison. In addition, Astruc et al. have recently shown that the 2+ diiron complex of biphenyl **30** undergoes a two-electron reduction changing the biphenyl ligand to the corresponding bis(cyclohexadienyl anion), **31**, whose structure was established by a single crystal X-ray analysis.[16]

In an accompanying paper,[4] we describe the general phenomenon that 4+ diruthenium complexes of $[2_n]$cyclophanes, such as the $[2_2](1,4)$cyclophane derivative **32**, undergo a two-electron reduction to give 2+ ions corresponding to **33**. A single-crystal X-ray analysis confirms that the cyclophane ligand of **33** has two cyclohexadienyl anion decks connected by an extremely long carbon-carbon bond. In view of these analogies now available from two-electron reductions of dimetallic complexes of polycyclic aromatics and $[2_n]$cyclophanes, the 2+ diruthenium complexes **15**, **17**, **19**, **21**, and **23** have all been assigned structures containing two bis(cyclohexadienyl anion) moieties joined by a carbon-carbon double bond. It would, of course, be desirable to have at least



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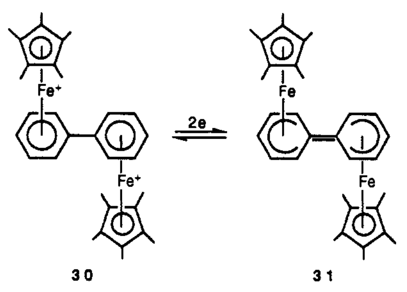

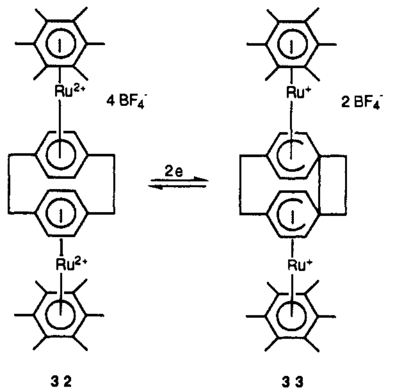

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[14] Stahl, L.; Ernst, R. D. *Organometallics* **1983**, *2*, 1224-1229.

[15] Schulte, L. D.; Rieke, R. D. *J. Org. Chem.* **1987**, *52*, 4827-4829.

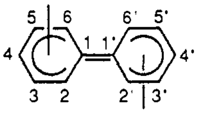
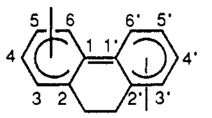
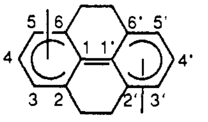
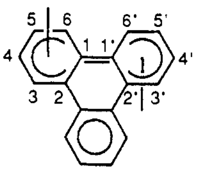
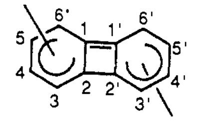
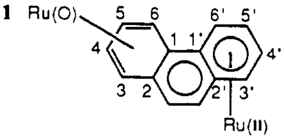
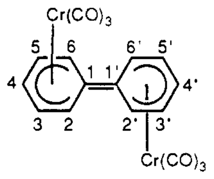
[16] Lacoste, M.; Varret, F.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1987**, *109*, 6504-6506. See, also: (a) Lacoste, M.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1987**, 667-669. (b) Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F.; Trautwein, G.; Villeneuve, G. *J. Am. Chem. Soc.* **1989**, *111*, 5800-5809. (c) Lacoste, M.; Rabaa, H.; Astruc, D.; Le Beuze, A.; Saillard, J.-Y.; Precigoux, G.; Courseille, C.; Ardoin, N.; Bowyer, W. *Organometallics* **1989**, *8*, 2233-2242. (d) Koelle, U.; Wang, M. H. *Organometallics* **1990**, *9*, 195-198.

Table I. Electrochemical Data[a]

	$4^+/2^+$						$2^+/0$					
compd	E_{pa}	E_{pc}	ΔE_p	$E_{1/2}$	i_a/i_c	n	E_{pa}	E_{pc}	ΔE_p	$E'_{1/2}$	i_a/i_c	n
Diruthenium Complexes of Polycyclic Aromatics												
10	−0.150	−0.219	69	−0.185	0.91	2.0	−0.652	−0.700	48	−0.677	0.99	2.0
14	−0.176	−0.215	39	−0.195	1.00	1.9	−1.009	−1.344	335	−1.177	irr	2
16	−0.143	−0.178	33	−0.161	0.97	1.8	−1.043	−1.381	336	−1.212	rev	1.7
18	−0.208	−0.247	39	−0.228	0.91	2.0		−1.500			irr	
20	−0.220	−0.268	34	−0.245	1.00	1.9	−1.132	−1.300	154	−1.216	irr	
22	−0.165	−0.220	55	−0.193	0.88	2.0	−0.754	−0.792	38	−0.774	1.00	2.0
Monoruthenium Complexes of Polycyclic Aromatics												
7							−0.572	−0.626	54	−0.599	0.74	2.0
8								−0.854			irr	
25								−0.796			irr	
26								−0.881			irr	
27								−0.856			irr	
28							−0.605	−0.661	56	−0.633	0.45	2.0

[a] Cyclic voltammograms were measured in propylene carbonate at room temperature at a scan rate of 100 mV/s; n was measured by coulometry. E_{pa}, E_{pc}, $E_{1/2}$, and $E'_{1/2}$ are measured in V and have a probable error of ±0.005 V and are referred to SCE based on a simultaneous measurement of the ferrocene redox potential (+0.383 V). ΔE_p is in mV.

Table II. NMR Spectra of the 2+ Diruthenium Polycyclic Aromatic Complexes

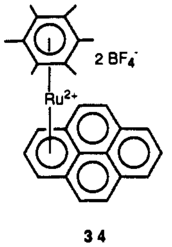
		^{1}H NMR chemical shift values & J values							^{13}C NMR chemical shift values, type, and assignments							
compd	aromatic ligand	C2 and C2′	C3 and C3′	C4 and C4′	C5 and C5′	C6 and C6′	CH_2	$ArCH_3$	C1 and C1′	C2 and C2′	C3 and C3′	C4 and C4′	C5 and C5′	C6 and C6′	HMB	HMB-Me
17		4.01 (6.9)	4.93 (5.4)	5.92 (5.1)	4.93 (5.4)	4.01 (6.9)		2.22	108.0 s	61.9 d	88.1 d	83.3 d	88.1 d	61.9 d	103.4 s	16.9 q
15			4.71 (5.0) (1.1)	5.84 (5.0)	4.85 (6.8) (1.1)	4.12 (6.8) (1.1)	2.03 (9.6) 1.52 (9.6)	2.13	108.1 s	79.4 s	81.3 d	87.7 d	87.4 d	62.3 d	102.5 s	16.5 q
21			4.79 (4.8)	5.80 (4.8)	4.79 (4.8)		2.16 (9.6)	2.00	110.0 s	79.8 s	87.6 d	66.9 d	87.6 d	79.8 s	102.3 s	15.9 q
23			5.38 (m)	6.41 (5.2)	5.38 (m)	4.02 (6.5)		1.98	111.6 s	89.9 s	81.8 d	86.6 d	81.8 d	68.4 d	102.4 s	16.3 q
43			5.38 (6.5)	5.97 (6.1) (1.0)	5.84 (7.2) (1.0)	6.22 (6.5)		2.13 q (HMB-CH_3)	111.7 s	105.8 s	87.8 d	80.2 d	86.5 d	79.3 d	105.3 s	15.8 q
			4.09 (7.2)	5.90 (6.1) (1.0)	4.94 (7.2) (1.0)	6.20 (6.5)		1.91 q (Cp-Me)	109.5 s	98.6 s	86.8 d	80.1 d	85.6 d	55.1 d	97.4 s (Cp)	9.2 q (Cp-Me)
11			3.67 (m)	6.36 (5.8)	5.98 (5.8)	3.22 (5.8)		1.90 (Ru(0))	79.0 s	86.1 s	60.0 d	76.1 d	73.1 d	59.1 d	91.5 s(Ru-O)	23.6 q(Ru-O)
			7.61 (m)	7.63 (m)	7.41 (m)	7.13 (m)		2.04 (Ru(II))	101.1 s	105.0 s	117.9 d	116.6 d	114.2 d	110.8 d	91.4 s(Ru-II)	22.9 q(Ru-II)
29		2.88 (7.0)	4.29 (7.0) (5.5)	4.67 (5.2)	4.29 (7.0) (5.5)	2.88 (7.0)			102.2 s	67.2 d	98.0 d	69.6 d	98.0 d	67.2 d		

one example of a 2+ diruthenium complex of a polycyclic aromatic whose structure had been determined by a single-crystal X-ray analysis. Unfortunately, despite considerable effort expended over a lengthy period of time, we have been unable to obtain crystals from any one of these complexes which are suitable for X-ray analysis.

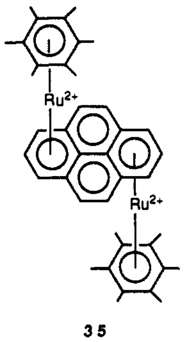
This leaves unanswered questions of geometry that are of particular interest. For example, the X-ray analysis of **31** shows the biphenyl system to be staggered with a cyclohexadienyl folding angle of 25°.[16] It is not clear how important this cyclohexadienyl folding is in promoting the formation of the cyclohexadienyl anion rings of the biphenyl system of **31**. Such a distortion for a more rigid polycyclic aromatic, such as the triphenylene derivative **23**, would appear to require introduction of a large amount of steric strain and so should make its formation extremely difficult. Yet **23** is formed with extreme ease, is well-behaved, and is exceptionally stable.

One of the puzzling questions relating to the 4+ diruthenium complexes of polycyclic aromatic ligands is why phenanthrene and 9,10-dihydrophenanthrene, which differ only by the presence of a carbon-carbon double bond, behave so differently on two-electron reduction. It is obvious that formation of the mixed-valence ion **11**, in the case of phenanthrene, creates a central benzene ring. This should lower the ground-state energy of **11** relative to the ground-state energy of a mixed-valence ion derived from 9,10-dihydrophenanthrene, which would only have the stabilization of a styrene-type resonance. However, another factor that could be important is that the phenanthrene ligand would not have the flexibility of the 9,10-dihydrophenanthrene ligand and so would offer severe steric strain to the distortion necessary for a cyclohexadienyl anion folding process.

To gain further insight regarding the question of cyclohexadienyl anion formation and its possible dependency on skeletal structure distortion we decided to examine the case of pyrene. The rigid planar pyrene ligand would undergo distortion only with extreme difficulty, and this would be true for forming a mixed-valence ion such as **11** or a distorted cyclohexadienyl anion derivative such as **31**. The 2+ monoruthenium(II) complex of pyrene **34** and the 4+ diruthenium(II,II) complex of pyrene **35** were prepared. Cyclic voltammetry of **34** showed a reversible two-electron reduction wave, $E_{1/2}$ = −0.642 V. However, cyclic voltammetry of **35** revealed a reversible one-electron reduction wave at $E_{1/2}$ = −0.028 V and a second reversible one-electron reduction wave at $E'_{1/2}$ = −0.188 V. These reduction products of **35** appear to be quite unstable, possibly due to extremely easy solvolysis, and it has not been possible to isolate and characterize either one. However, the electrochemical behavior of **35** does suggest that electrochemical reduction of the planar pyrene ligand in **35** probably follows a different pathway than that taken by the other 4+ diruthenium polycyclic aromatic ligands.



34



35

Because of the lack of structural evidence from X-ray analysis, we decided to explore the possibility of gaining insight regarding the structures of these 2+ diruthenium polycyclic aromatic complexes from their chemical behavior. Schulte and Rieke found that the dianion of (η^6,η^6-biphenyl)$[Cr(CO)_3]_2$, **29**, undergoes reaction with electrophilic reagents, such as water, to produce substitution products of the type shown by structure **36**.[15] On the basis of this presumed analogy between the 2+ diruthenium polycyclic aromatic complexes and **29**, we added dropwise a solution of *p*-toluenesulfonic acid in dichloromethane to a solution of $\mathbf{17}^{2+}$ bis(tosylate) in dichloromethane. As each drop containing the *p*-toluenesulfonic acid was added, the deep red solution of **17** became lighter until 1 equiv of acid had been added. The solution then became yellow and remained unchanged in appearance on further addition of acid. Workup of the pale yellow solution gave **37** as yellow crystals in 99% yield.

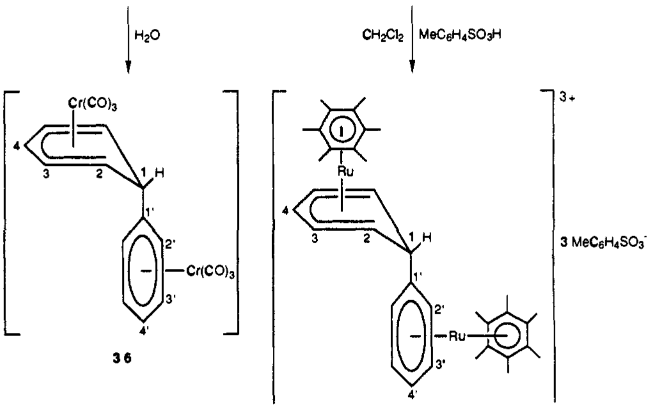
Table III. Comparison of ^{1}H and ^{13}C NMR Chemical Shift Values (δ) and Position Assignments for **36** and **37**[a]

position	C1	C2	C3	C4	C1′	C2′	C3′	C4′
				^{1}H NMR				
36	3.30	2.70	4.50	4.98		5.27	5.57	5.40
37	6.87	3.61	5.16	3.89		6.87	6.61	6.21
				^{13}C NMR				
36	41.7	51.5	95.9	75.9	122.8	95.8	93.3	92.9
37	37.2	42.3	89.6	89.4	114.2	92.1	93.6	95.7

[a] Chemical shift values for **36** are taken from ref 15 and are for solutions in DMF-d_7. Chemical shift values for **37** are from measurements in acetone-d_6.

A comparison of the ^{1}H and ^{13}C NMR spectra of **36** and **37** is presented in Table III. Although **36** has a negative charge, whereas **37** carries a 3+ charge, there are obvious similarities between the two sets of NMR spectra. In each case the ^{1}H and ^{13}C chemical shift values for the arene ring are very close to each other, whereas in the cyclohexadienyl anion ring adjacent positions show sharp differences in chemical shift values. This latter behavior is typical of "open" metallocenes[14] and cyclohexadienyl anions.[4,15] This similarity in the chemical behavior of **17** and **29** provides additional evidence that **17** and **29** have similar structures.

All of the diruthenium complexes of polycyclic aromatics we have described can be considered to be biphenyl derivatives. In an extension of this study, one question to be answered is how intimately can two aromatic rings be interrelated and still allow dimetallic complexes to be formed. Lagowski et al. have found that bis(η^6-naphthalene)chromium undergoes exchange with benzene to form the remarkable biscapped dichromium naphthalene derivative **38**, whose structure has been determined by single-crystal X-ray analysis.[17] However, attempted biscapping of naphthalene with the usual iron and ruthenium capping reagents has been unsuccessful.



36 **37**

Although, in a formal sense, biphenylene is simply a modified biphenyl, its π-electron system is different, and it undergoes a rather drastic structural change during formation of its corresponding dianion.[18,19] It was of interest, therefore, to see whether 4+ diruthenium complexes of biphenylene could be made and, if so, what the behavior of such complexes would be on two-electron reduction. Treatment of biphenylene with the capping reagent **4** as the triflate, readily gave the monocapped product **39** in 98% yield. However, all attempts to effect biscapping by use of excess reagent, higher temperatures, or prolonged reaction times failed. Fagan et al. have shown that tris(acetonitrile)(η^5-pentamethylcyclopentadienyl)ruthenium(II) triflate **41** is a powerful reagent for biscapping of [2_n]cyclophanes and ar-

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(17) Bush, B. F.; Lynch, V. M.; Lagowski, J. J. *Organometallics* **1987**, *6*, 1267–1275.

(18) Cohen, Y.; Klein, J.; Rabinovitz, M. *J. Am. Chem. Soc.* **1988**, *110*, 4634–4640.

(19) Benken, R.; Finneiser, K.; von Puttkamer, H.; Günther, H.; Eliasson, B.; Edlund, U. *Helv. Chim. Acta* **1986**, *69*, 955–961.

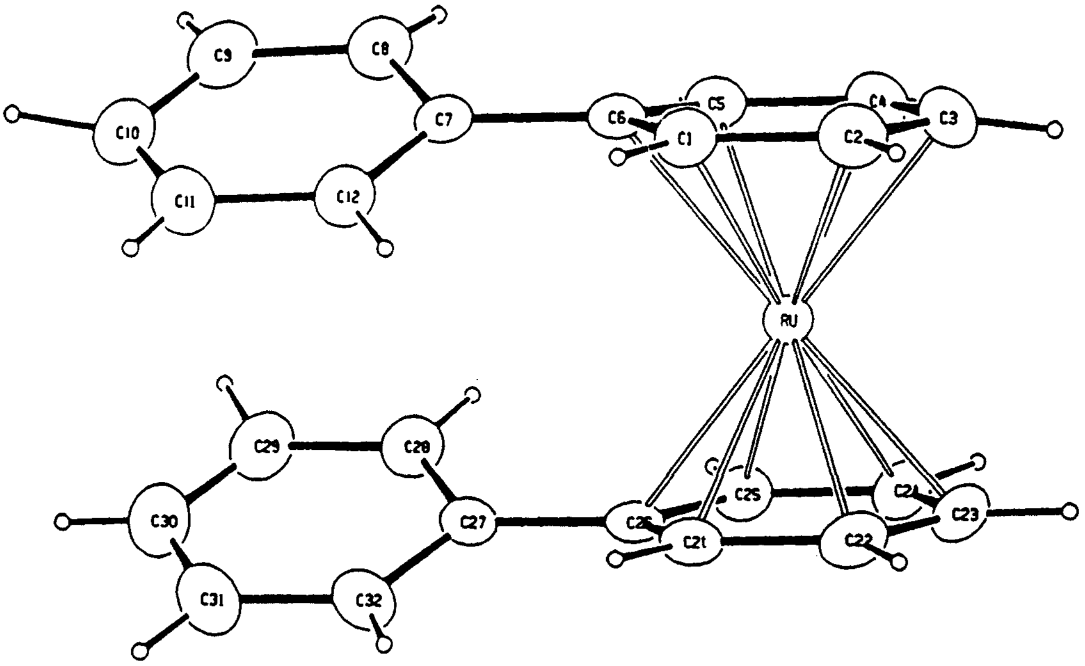
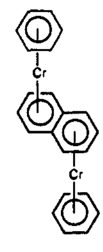
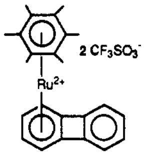


Figure 1. A computer projection of the structure of **49** obtained from an X-ray crystal structure analysis.

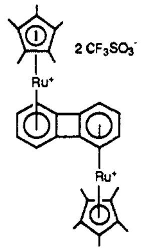
enes.[20] Treatment of biphenylene with **41** gave the biscapped derivative **40** in 66% yield. However, the redox potential for **40** is extremely negative ($E_{1/2} = -1.65$ V).



38

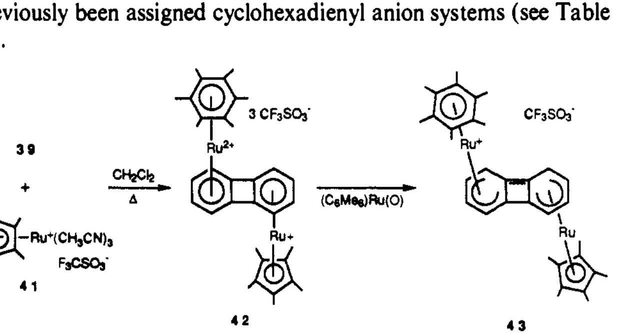


39

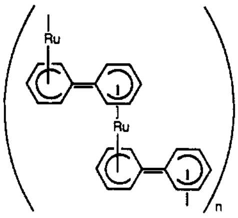


40

To obtain a diruthenium complex of biphenylene, whose redox potential would be more positive, the monocapped biphenylene **39** was treated with **41**. This gave the desired diruthenium complex **42** in 85% yield. The reduction of **42**, by using two-electron equivalents of bis(hexamethylbenzene)ruthenium(0), led to a pale yellow solid, which has been assigned structure **43**. This structural assignment for **43** is based entirely on the correspondence of its ^{1}H and ^{13}C NMR spectra to those of the other 2+ diruthenium complexes of polycyclic aromatics which have previously been assigned cyclohexadienyl anion systems (see Table II).

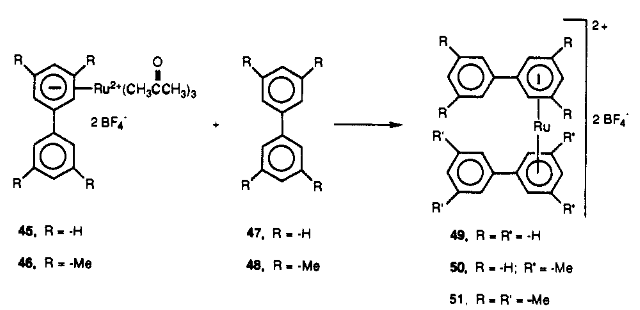


An obvious extension of the structures deduced for the 2+ diruthenium complexes of the polycyclic aromatics would be the preparation of a stacked polymer having an "open" metallocene for its monomer subunit, as shown by structure **44**. Whether or not such a polymer would show a high degree of electron delocalization would depend on how effective the cyclohexadienyl folding angle would be in isolating the carbon–carbon double bonds joining the cyclohexadienyl moieties. To explore this question suitable model compounds are needed. Several preliminary experiments have been carried out which suggest the feasibility of this approach.



44

Application of the procedures developed by Bennett et al.[21,22] made possible the preparation of the biphenyl capping reagents **45** and **46**. Treatment of biphenyl **47** with **45** gave bis(η^6-biphenyl)ruthenium(II) bis(tetrafluoroborate), **49**, in 64% yield. Similarly, the reaction between **45** and 3,3′,5,5′-tetramethylbiphenyl, **48**, gave **50**, and the reaction of **46** with **48** gave the symmetrical complex **51**.



A single-crystal X-ray analysis of **49** was made, and a computer projection of its structure is presented in Figure 1.[23,24] The two

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[20] Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698–1719.

[21] Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233–241.

[22] Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* **1980**, *19*, 1014–1021.

[23] Crystal data: $C_{24}H_{20}RuB_2F_8$, $M = 583.11$, monoclinic $P2_1/n$, a = 12.238 (3) Å, b = 14.844 (4) Å, c = 13.516 (5) Å, β = 111.65 (2)°, V = 2282.3 Å^3, $z = 4$, d_{calc} = 1.70 g/cm^3, Mo Kα radiation, λ = 0.71073 Å, μ = 7.5 cm^{-1}. See the Supplementary Material for further details.

outstanding features of the structure of **49** are the following: (1) the two biphenyl ligands are directly over each other in syn conformation and (2) the nonbonded benzene rings are tilted away from coplanarity by an angle of 24.6°. Whether this conformation is a consequence of crystal lattice forces or whether this conformation would also prevail in solution remains uncertain.

In summary, there is strong similarity between the 4+ diruthenium complexes of polycyclic aromatic ligands and the corresponding complexes of $[2_n]$cyclophanes, as described in the accompanying publication.[4] In both series the general behavior is that two-electron reduction causes the attached ligand to change from a bis(arene) structure to a bis(cyclohexadienyl anion) system. However, each series has its exception. Two-electron reduction of the 4+ diruthenium complex of $[2_4]$(1,2,4,5)cyclophane does not produce a bis(cyclohexadienyl anion) system but, instead, gives the class II mixed-valence ion **13**. Similarly, the 4+ diruthenium complex of phenanthrene **10** leads to the class II mixed-valence ion **11**.

Also, in each series it appears that for ligands offering severe steric strain to the formation of bis(cyclohexadienyl anion) systems, electron reduction of these 4+ diruthenium complexes takes a different course. In the $[2_n]$cyclophane series, cyclic voltammetry of the 4+ diruthenium complex of superphane shows two separate reversible one-electron reduction waves. Likewise, cyclic voltammetry of the 4+ diruthenium complex of pyrene shows two separate reversible one-electron reduction waves.

Experimental[25] Section

(η^6-Hexamethylbenzene)(η^6-phenanthrene)ruthenium(II) Bis(tetrafluoroborate) (7). Model Procedure (CF_3CO_2H). A mixture of 156 mg (0.225 mmol) of bis(hexamethylbenzene)dichlorobis(μ-chloro)diruthenium[22] and 182 mg (0.934 mmol) of silver tetrafluoroborate in 5 mL of acetone was stirred at room temperature for 30 min. The resulting precipitate of silver chloride was collected by filtration and washed with three 5-mL aliquots of acetone. After the combined filtrate and washings were concentrated, 100 mg (0.561 mmol) of phenanthrene and 3 mL of trifluoroacetic acid were added to the residue. This mixture was boiled under reflux for 2 h, cooled, and poured into 50 mL of ether. The white precipitate was collected by filtration and washed with ether to give 288 mg (100%) of an off-white powder. Recrystallization of this by soution in nitromethane followed by a slow ether diffusion afforded pale, yellow needles: mp >290 °C dec; ^{1}H NMR (CD_3NO_2) δ 8.72 (1 H, d, J = 8.1 Hz, ArH), 8.62 (1 H, d, J = 9.3 Hz, ArH), 8.32 (1 H, J = 7.2 Hz, ArH), 8.20–8.10 (2 H, m, ArH), 7.97–7.95 (1 H, m, ArH), 7.61 (1 H, d, J = 9.3 Hz, RuArH), 7.28–7.26 (1 H, m, RuArH), 6.96–6.90 (2 H, m, RuArH), 2.16 (18 H, s, $ArCH_3$); UV (acetone), λ_{max} 328 nm (ϵ, 2980), 364 nm (ϵ, 1890).

The preparations of compounds **8**, **20**, **22**, **25**, **26**, **27**, **28**, and **34** were all carried out following this general procedure. See the Supplementary Material section for the experimental details of these preparations.

Bis(η^6-hexamethylbenzene)(η^6,η^6-phenanthrene)diruthenium(II,II) Tetrakis(tetrafluoroborate) (10). Model Procedure (Propylene Carbonate). A mixture of 1.031 g (1.492 mmol) of bis(hexamethylbenzene)-dichlorobis(μ-chloro)diruthenium, 1.202 g (6.174 mmol) of silver tetrafluoroborate, and 69 mg (0.387 mmol) of phenanthrene in 3 mL of propylene carbonate was stirred at 100 °C under a nitrogen atmosphere for 20 h. The cooled reaction mixture was added to 250 mL of ether, to which a small amount of acetone washings of the flask was added. The resulting dark precipitate was collected by filtration and washed first with ether and then briefly with acetone. The remaining solid was extracted with 200 mL of nitromethane, followed by concentration of the nitromethane extract. A slurry of the residue in acetone was then filtered, allowing the collection of 315 mg (77%) of a pale yellow solid: mp 295 °C dec; ^{1}H NMR (CD_3NO_2) δ 8.35 (2 H, s, (C9,C10)ArH), 7.97 (2 H, d, J = 6 Hz, (C1,C8)ArH), 7.60 (2 H, d, J = 6 Hz, (C4,C5)ArH), 7.35–7.28 (4 H, m, C2,C3,C6,C7)ArH), 2.35 (36 H, s, $ArCH_3$); UV (acetone) λ_{max} 327.5 nm (ϵ, 3450).

The preparations of compounds **14**, **16**, **18**, and **35** were carried out following this general procedure. See the Supplementary Material section for experimental details.

(η^6-Hexamethylbenzene)(η^4-phenanthrene)ruthenium(0) (9). Model Chemical Reduction Procedures. Cobaltocene. A mixture of 100 mg (0.163 mmol) of **7** and 62 mg (0.326 mmol) of cobaltocene in 8 mL of methanol was stirred at room temperature for 2 h. After concentration, the residue was extracted with three 10-mL aliquots of *n*-hexane. The combined *n*-hexane extracts were concentrated to give 57 mg (79%) of **9** as orange crystals: mp > 149 °C dec; ^{1}H NMR (cyclohexane-d_{12}) δ 7.60 (1 H, d, J = 7.8 Hz, ArH), 7.33 (1 H, J = 7.8 Hz, (C5)ArH), 7.01 (1 H, t, J = 7.8 Hz, (C7)ArH), 6.89 (1 H, t, J = 7.8 Hz, (C6)ArH), 6.83 (1 H, J = 7.8 Hz, (C9)ArH), 6.52 (1 H, J = 7.8 Hz, (C10)ArH), 5.42–5.37 (2 H, m, Ru(C2,C3)ArH), 3.12 (1 H, d, J = 4.2 Hz, Ru-(C1)ArH), 2.62 (1 H, d, J = 4.2 Hz, Ru(C4)ArH), 2.03 (18 H, s, $ArCH_3$).

The preparations of compounds **19**, **21**, **23**, and **24** were all carried out following this general procedure. See the Supplementary Material section for experimental details.

Bis(η^6-hexamethylbenzene)(η^4,η^6-phenanthrene)diruthenium(0,II) Bis(tetrafluoroborate) (11). A mixture of 80 mg (0.076 mmol) of **10** and 32 mg (0.076 mmol) of bis(hexamethylbenzene)ruthenium(0) in 8 mL of methanol was stirred at room temperature for 2 h. After concentration, the residue was extracted with dichloromethane. Filtration of the dichloromethane extract followed by concentration of the filtrate gave 65 mg (97%) of **11** as dark red crystals: mp >185 °C dec; ^{1}H and ^{13}C NMR spectra (see Table II) plus ^{1}H NMR (CD_2Cl_2) δ 6.29 (1 H, dd, J_1 = 5.8 Hz, J_2 = 1.1 Hz, (C9)ArH), 4.15 (1 H, dd, J_1 = 5.8 Hz, J_2 = 1.1 Hz, (C10)ArH); ^{13}C δ 75.8 (d, C9) and 68.7 (d, C10). The ^{1}H and ^{13}C NMR spectra were unchanged when solutions of **11** in ethylene glycol-d_6 were heated up to 170 °C. UV (CH_2Cl_2) λ_{max} 486 nm (ϵ, 17 300); (acetone) λ_{max} 485 nm (ϵ, 14 500); (propylene carbonate) λ_{max} 485 nm (ϵ, 20 600); (methanol) λ_{max} 485.5 nm (ϵ, 16 000); (water) λ_{max} 483 nm (ϵ, 12 670); and (CH_3CN) λ_{max} 473 nm (ϵ, 8940).

The preparations of compounds **15** and **17** were carried out following this procedure. See the Supplementary Material section for experimental details.

Bis(η^6-hexamethylbenzene)(η^4,η^4-phenanthrene)diruthenium(0,0) (12). A mixture of 50 mg (0.048 mmol) of **10** and 41 mg (0.096 mmol) of bis(hexamethylbenzene)ruthenium(0) in 5 mL of methanol was stirred at room temperature for 2 h. The mixture was then concentrated, and the residue was taken up in *n*-hexane. After filtration, the *n*-hexane filtrate was concentrated. The residue was taken up in benzene and filtered, and the benzene filtrate was concentrated to give 31 mg (93%) of **12** as an orange solid: mp > 160 °C dec; ^{1}H NMR (C_6D_6) δ 5.93 (2 H, s, (C9,C10)ArH), 5.28–5.25 (2 H, m, ArH), 5.11–5.09 (2 H, m, ArH), 3.03 (2 H, d, J = 5.1 Hz, ArH), 2.63 (2 H, d, 5.1 Hz, (C4,C5)ArH), 1.86 (36 H, s,$ArCH_3$); UV (*n*-hexane) only small tailing absorption above 360 nm.

Bis(η^6-hexamethylbenzene)(η^5,η^6-1*H*-biphenyl)diruthenium(II,II) Tris(tosylate) (37). A sample of **17** was subjected to ion exchange to convert it to the corresponding bis(η^6-hexamethylbenzene)(η^5,η^5-biphenyl)diruthenium(II,II) bis(tosylate). To a solution of 20 mg (0.0197 mmol) of $\mathbf{17}^{2+}$ bis(tosylate) in 20 mL of dichloromethane there was added dropwise a stock solution of 5 mg of toluenesulfonic acid in 5 mL of dichloromethane. The deep red solution of **17** lightened as each drop containing toluenesulfonic acid was added. When exactly 1 equiv of acid had been added, the last traces of red color disappeared leaving a yellow solution. After concentration, the residue was dissolved in dichloromethane and exposed to a slow vapor diffusion of ether. The resulting crystals were collected by filtration giving 23 mg (99%) of yellow crystals: ^{1}H and ^{13}C NMR (see Table III for the chemical shift values of the $\mathbf{37}^{2+}$ ion).

(η^6-Hexamethylbenzene)(η^6-biphenylene)ruthenium(II) Bis(trifluoromethanesulfonate) (39). A mixture of 210 mg (0.304 mmol) of bis(η^6-hexamethylbenzene)dichlorobis(μ-chloro)diruthenium and 312 mg (1.216 mmol) of silver trifluoromethanesulfonate in 5 mL of acetone was stirred at room temperature for 30 min. The precipitate of silver chloride was removed by filtration and washed with acetone. The combined filtrate and acetone washings were concentrated. After solution of the

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[24] The X-ray analysis of **49** was made by Oneida Research Services. We thank Dr. Michael D. Ward and E. I. du Pont de Nemours & Co. for providing this service.

[25] All reactions with air-sensitive compounds were conducted either in a Vacuum Atmospheres Co. double-length drybox (Model HE-553-2-Dri-Lab) or in Schlenk-Ware. All NMR spectra were measured on a General Electric QE-300 (300 MHz) system or a Nicolet NT-360 spectrometer. Ultraviolet spectra were recorded on a Beckman DU-7 and infrared spectra with a Beckman IR 4240 spectrometer. Melting points were determined in sealed evacuated capillary tubes on a Mel-Temp apparatus and are uncorrected. Most of the ionic complexes described are powdery solids which slowly decompose over a wide temperature range. Only for those compounds, which melted without decomposition or whose decomposition was characteristic and reproducible, are measurements of melting points included. Elemental analyses were performed by Desert Analytics or Schwarzkopf Microanalytical Laboratory. Electrochemical experiments were performed by using a Princeton Applied Research Electrochemical Station including a Model 175 universal programmer, a Model 173 potentiostat-galvanostat, which included a Model 179 digital coulometer, and a Model 174A polarographic analyzer. Further experimental details, including all elemental analyses, are given in the Supplementary Material section.

residue in 3 mL of trifloromethanesulfonic acid followed by addition of 46 mg (0.304 mmol) of biphenylene, the resulting mixture was stirred at room temperature for 1 h. It was then poured into ether, the resulting precipitate was collected by filtration, and the precipitate was washed with ether. This gave 210 mg (98%) of a pale yellow solid: mp > 305 °C dec; ^{1}H and ^{13}C NMR (see Table II); MS (FAB) 416 ($\mathbf{39}^{2+}$ ion, having the expected ruthenium isotopic pattern).

Bis(η^5-pentamethylcyclopentadienyl)(η^6,η^6-biphenylene)diruthenium(II,II) Bis(trifluoromethanesulfonate) (40). A mixture of 38 mg (0.25 mmol) of biphenylene and 254 mg (0.500 mmol of tris(acetonitrile)(η^5-pentamethyldienyl)ruthenium(II) trifluoromethanesulfonate (**41**)[20] in 20 mL of dichloromethane was heated at 60 °C for 1 h. The cooled solution was filtered, and the filtrate was poured into ether. The white precipitate was collected by filtration, washed with ether, and dried. This gave 152 mg (66%) of **40** as a white solid: mp 335 °C dec; ^{1}H NMR (CD_3NO_2) δ 6.23 and 6.09 (8 H, m, ArH), 1.87 (30 H, s, CH_3); ^{13}C NMR (CD_3NO_2) δ 102.3 (s), 99.5 (s), 86.5 (d), 83.9 (d), 9.0 (q).

(η^5-Pentamethylcyclopentadienyl)(η^6-hexamethylbenzene)(η^6,η^6-biphenylene)diruthenium(II,II) Tris(trifluoromethanesulfonate) (42). A mixture of 710 mg (1.00 mmol) of **39** and 1.7 g (3.00 mmol) of **41**[20] in 20 mL of dichloromethane was heated at 60 °C for 24 h. The precipitate, which separated, was collected by filtration, washed with dichloromethane, and dried to give 930 mg (85%) of a pale yellow solid: mp 280 °C dec; ^{1}H NMR (CD_3NO_2) δ 6.95 (2 H, m, ArH), 6.87 (2 H, m, ArH), 6.68 (2 H, m, ArH), 6.39 (2 H, m, ArH), 2.45 (18 H, s, CH_3), 1.87 (15 H, s, CH_3); ^{13}C NMR (CD_3NO_2) δ 120.6 (s), 112.1 (s), 111.8 (s), 106.1 (s), 103.0 (s), 99.1 (s), 93.7 (d), 90.1 (d), 88.6 (d), 86.7 (d), 16.38 (q), 9.1 (q).

(η^6-Hexamethylbenzene)(η^5-pentamethylcyclopentadienyl)(η^5,η^5-biphenylene)diruthenium(II,II) Trifluoromethanesulfonate (43). To a solution of 70 mg (0.062 mmol) of **42** in 15 mL of methanol was added 27 mg (0.062 mmol) of bis(hexamethylbenzene)ruthenium(0), and the mixture was stirred at room temperature for 2 h. After filtration to remove the precipitate of bis(hexamethylbenzene)ruthenium(II) bis(trifluoromethanesulfonate), the filtrate was concentrated. A solution of the residue in dichloromethane was exposed to a slow diffusion of ether. Collection of the resulting crystals by filtration gave 25 mg (49%) of pale yellow needles: ^{1}H and ^{13}C NMR (see Table II); MS (FAB) *m/e* 802 (parent molecular ion showing the expected isotope distribution pattern due to ruthenium).

Bis(η^6-biphenyl)ruthenium(II) Bis(tetrafluoroborate) (49). A mixture of 2.43 g (15.5 mmol) of 3-phenyl-1,4-cyclohexadiene[27] and 2.26 g (8.0 mmol) of $RuCl_3\cdot 2H_2O$ in 25 mL of absolute ethanol was boiled under reflux for 4 h. The resulting black precipitate was removed by filtration and washed with ethanol. The combined filtrate and washings were then concentrated to give 2.47 g (95%) of bis(η^6-biphenyl)dichlorobis(μ-chloro)diruthenium as a brown powder: ^{1}H NMR (DMSO-d_6) δ 7.85–7.75 (4 H, m, ArH), 7.50–7.40 (6 H, m, ArH), 6.45–6.35 (4 H, m, ArH), 6.10–6.00 (6 H, m, ArH). A 320-mg (0.491 mmol) sample of this ruthenium chloro dimer and 382 mg (1.936 mmol) of silver tetrafluoroborate in 10 mL of acetone was stirred at room temperature for 2 h. The precipitate of silver chloride was removed by filtration, and the filtrate was concentrated to give an orange solid. This was taken up in 4 mL of trifluoroacetic acid, 1.0 g of biphenyl was added, and the mixture was boiled under reflux for 2 h. After a small amount of a white solid, which had separated, was removed by filtration, the filtrate was concentrated to give a yellow solid. This was dissolved in several milliliters of nitromethane, and ether vapor was allowed to diffuse slowly into the solution. The resulting crystals were collected by filtration, washed with ether, and dried to give 367 mg (64%) of yellow needles: mp 255 °C dec; ^{1}H NMR (CD_3NO_2) δ 7.65 (2 H, t, J = 7.2 Hz, ArH), 7.50 (4 H, d, J = 7.8 Hz, ArH), 7.44 (4 H, d, J = 6.6 Hz, ArH), 7.38 (4 H, t, J = 7.8 Hz, ArH), 7.19 (4 H, t, J = 6.3 Hz), 7.10 (2 H, t, J = 6.0 Hz, ArH). Cyclic voltammetry of **49** showed a single, irreversible wave (E_{pc} = −0.590 ± 0.005 V). For details of the crystal structure of **49** see the Supplementary Material.

(η^6-Biphenyl)(η^6-3,3′,5,5′-tetramethylbiphenyl)ruthenium(II) Bis(tetrafluoroborate) (50). A mixture of 80 mg (0.123 mmol) of (η^6-biphenyl)dichlorobis(μ-chloro)diruthenium, 96 mg (0.492 mmol) of silver tetrafluoroborate, and 193 mg (0.920 mmol) of 3,3′,5,5′-tetramethylbiphenyl in a solution of 2 mL of acetone and 4 mL of trifluoroacetic acid was boiled under reflux for 25 min. Ether was then added, causing the precipitation of a yellow-white powder. This was collected by filtration and washed with acetone. The remaining solid was extracted with nitromethane, and slow diffusion of ether into the nitromethane extract caused the separation of a yellow solid. This was collected by filtration, giving 115 mg (73%) of **50** as a yellow solid: mp 355 °C dec; ^{1}H NMR (CD_3NO_2) δ 7.64 (1 H, t, J = 7.5 Hz, ArH), 7.50 (2 H, d, J = 7.8 Hz, ArH), 7.43 (2 H, d, J = 7.8 Hz, ArH), 7.40 (2 H, m, ArH), 7.33 (2 H, s, ArH), 7.24 (1 H, s, ArH), 7.20 (1 H, t, J = 6.3 Hz, ArH), 7.16 (2 H, s, ArH), 7.06 (1 H, s, ArH), 6.92 (2 H, t, J = 6.3 Hz, ArH), 2.64 (6 H, s, CH_3), 2.27 (6 H, s, CH_3). Cyclic voltammetry of **50** showed a single, irreversible wave (E_{pc} = −0.661 ± 0.005 V).

Bis(η^6-3,3′,5,5′-tetramethylbiphenyl)ruthenium(II) Bis(tetrafluoroborate) (51). A solid mixture of 2.06 g (4.12 mmol) of bis(η^6-benzene)dichlorobis(μ-chloro)diruthenium and 9.03 g (26.0 mmol) of 3,3′,5,5′-tetramethylbiphenyl was heated at 210 °C for 15 h. The cold powdered solid was washed extensively with ether to remove the excess of 3,3′,5,5′-tetramethylbiphenyl which left 2.70 g (86%) of the ruthenium chloro dimer as a brown powder. A mixture of 551 mg (0.721 mmol) of this ruthenium chloro dimer, 561 mg (2.88 mmol) of silver tetrafluoroborate, and 303 mg (1.44 mmol) of 3,3′,5,5′-tetramethylbiphenyl in 4 mL of trifluoroacetic acid was boiled under reflux for 3 h. When ether was added to the cold solution, a solid separated which was collected by filtration and washed with ether. The resulting solid was washed briefly with acetone and dissolved in nitromethane, and the nitromethane solution was exposed to a slow diffusion of ether vapor. The crystals, which separated, were collected by filtration to give 656 mg (75%) of **51** as yellow crystals: mp 310 °C dec; ^{1}H NMR (CD_3NO_2) δ 7.21 (2 H, s, ArH), 7.12 (4 H, s, ArH), 7.03 (4 H, s, ArH), 6.84 (2 H, s, ArH), 2.45 (12 H, s, CH_3), 2.24 (12 H, s, CH_3). Cyclic voltammetry of **51** showed a single, irreversible wave (E_{pc} = −0.789 ± 0.005 V).

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Supplementary Material Available: Tables of atomic coordinates and thermal parameters and interatomic distances and bond angles derived from the crystallographic analysis of **49** and a detailed experimental section (31 pages); tables of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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