Preparation, Electrochemical Oxidation, and XPS Studies of Unsymmetrical Ruthenocenes Bearing the Pentamethylcyclopentadienyl Ligand

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Abstract: The reaction of dichloro(pentamethylcyclopentadienyl)ruthenium(III) oligomer with alkali metal salts of a variety of cyclopentadienyl derivatives provided a convenient synthetic approach to unsymmetrical ruthenocenes. In addition, reaction of dichloro(pentamethylcyclopentadienyl)ruthenium(III) oligomer with diazotetrachlorocyclopentadiene gave (η^5-pentamethylcyclopentadienyl)(η^5-pentachlorocyclopentadienyl)ruthenium(II). With use of the general approaches outlined, ruthenocenes were prepared where one-half of the sandwich was the pentamethylcyclopentadienyl group and the other was (a) cyclopentadienyl, (b) indenyl, (c) fluorenyl, (d) acetylcyclopentadienyl, or (e) pentachlorocyclopentadienyl. Electrochemical studies and XPS studies were carried out on all five unsymmetrical ruthenocenes and on decamethylruthenocene and ruthenocene in order to determine the electronic effects of the various ligands. These studies showed that the order of decreasing electron-donating power was fluorenyl, pentamethylcyclopentadienyl, indenyl, cyclopentadienyl, acetylcyclopentadienyl, and pentachlorocyclopentadienyl. Single-crystal X-ray analyses were carried out on (η^5-pentamethylcyclopentadienyl)(η^5-pentachlorocyclopentadienyl)ruthenium(II), (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II), and (η^5-pentamethylcyclopentadienyl)(η^5-fluorenyl)ruthenium(II). (η^5-Pentamethylcyclopentadienyl)(η^5-pentachlorocyclopentadienyl)ruthenium(II) crystallized in the orthorhombic space group *Pnma* with $a = 8.531$ (2) Å, $b = 14.208$ (4) Å, $c = 14.541$ (2) Å. The calculated density was 1.785 g/cm^3 for four molecules in the unit cell at room temperature. The unweighted R factor for the structure was 0.041, and data were collected with use of a variable-rate ω–2θ scan technique and graphite monochromatized Mo Kα radiation. After Lorentz–polarization corrections, 1206 reflections with $2\theta = 0$–52° were observed for $[F_o^2 \geq 2\sigma(F_o^2)]$. ($\eta^5$-Pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) crystallized in the monoclinic space group $P2_1/n$ with $a = 13.029$ (16) Å, $b = 12.789$ (13) Å, $c = 9.546$ (7) Å, $\beta = 95.31$ (8)°. The calculated density was 1.473 g/cm^3 for four molecules in the unit cell at room temperature. The unweighted R factor for the structure was 0.037, and the data were collected by using a variable-rate ω–2θ scan technique and graphite monochromatized Mo Kα radiation. After Lorentz–polarization corrections, 1861 reflections with $2\theta = 0$–52° were observed for $[F_o^2 \geq 2\sigma(F_o^2)]$. ($\eta^5$-Pentamethylcyclopentadienyl)(η^5-fluorenyl)ruthenium(II) crystallized in the monoclinic space group $P2_1/a$ with $a = 22.923$ (8) Å, $b = 8.813$ (5) Å, $c = 19.149$ (8) Å, $\beta = 107.40$ (3)°. The calculated density was 1.445 g/cm^3 for eight molecules in the unit cell at room temperature. The unweighted R factor for the structure was 0.060, and the data were collected by using a variable-rate ω–2θ scan technique and graphite monochromatized Mo Kα radiation. After Lorentz–polarization corrections, 5811 reflections with $2\theta = 0$–51° were observed for $[F_o^2 \geq 2\sigma(F_o^2)]$.

As part of our continuing studies of the use of electron spectroscopy for chemical analysis (ESCA, XPS) in the evaluation of the effects of ligand substitution on the electronic character of complexed transition metals,[1] we desired access to a series of ruthenocenes in which one of the ligands remained constant while the other was varied in electronic character. Our approach was initially based on the premise that we would use the pentamethylcyclopentadienyl moiety as our constant ligand because of the availability of dichloro(pentamethylcyclopentadienyl)ruthenium(III) oligomer (**1**)[2] as a starting material.

Although the chemistry of the ferrocenes has been extensively studied[3] since ferrocene's first preparation in 1951,[4] the corresponding chemistry[5] of ruthenium, the second member of the iron triad, has been much less explored, primarily due to the lack of convenient, reasonable scale, high-yield synthetic approaches to the ruthenocenes. Recently, several reports have appeared that make the ruthenocenes more accessible.[2,6,7] These recent reports[7] prompted us to describe herein our alternate approaches to unsymmetrical ruthenocenes. In addition, we describe a detailed evaluation of the electronic effects of the various ligands on the complexed ruthenium through both electrochemical oxidation and XPS studies.

Reaction of **1** with cyclopentadienyllithium in refluxing tetrahydrofuran for 12 h afforded pentamethylruthenocene (**2**) in 87% yield after purification by column chromatography on alumina. The ease of this preparation indicated that **1** could serve as a convenient starting material for a variety of unsymmetrical ruthenocenes. As shown below, this concept proved to be correct. Addition of indenyllithium to **1** followed by 4 h of reflux in
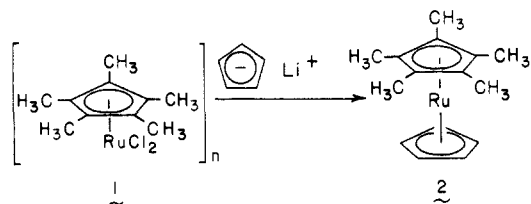
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Table I. Oxidation Potentials and XPS Binding Energies for a Series of Ruthenocene Derivatives

compd	$E_{1/2}$(V vs SCE)^a ± 0.02 V	Ru(3d$_{5/2}$) binding energies ± 0.1 eV
4	0.34	279.6
8	0.42^b	279.9
3	0.43	280.1
2	0.54	280.2
5	0.74	280.3
7^c	0.80	280.7
6	1.30	280.8

^{a} The method of Gagne[14] was used. All measurements were made with ferrocene as an internal standard ($E° = 0.31$ V vs SCE) and then referenced to SCE. ^{b} Reversible oxidation. ^{c} Note that 7, which lacks the pentamethylcyclopentadienyl group, should not be considered as a member of this series.

tetrahydrofuran gave light yellow crystals of (η^5-pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) (3) in 59% yield after purification by column chromatography on alumina. Similarly, 1 reacted with fluorenyllithium at room temperature in tetrahydrofuran over 4 h to give a 48% yield of (η^5-pentamethylcyclopentadienyl)(η^5-fluorenyl)ruthenium(II) (4), and addition of sodium acetylcyclopentadienide[8] afforded light yellow crystals of (η^5-pentamethylcyclopentadienyl)(η^5-acetylcyclopentadienyl)ruthenium(II) (5) in 79% yield.

Because alkali metal salts of pentachlorocyclopentadienide cannot be readily prepared,[9] an alternate synthetic approach to 6 was needed. It had previously been demonstrated that diazotetrachlorocyclpentadiene[10] reacts with selected halide derivatives of rhodium,[11] manganese,[11] and iron[12] to produce (η^5-pentachlorocyclopentadienyl)metal complexes. When 1 was allowed
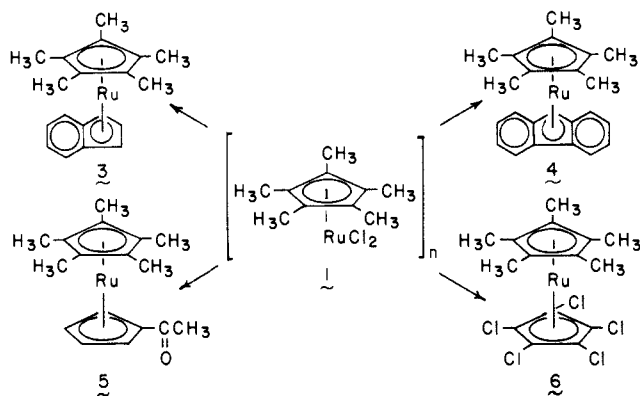
to react with diazotetrachlorocyclopentadiene in methylene chloride, vigorous gas evolution ensued and, after 15 min, 6 was obtained in 71% yield. The compounds described above constitute a series with a broad range of electronic properties. These properties were assessed through electrochemical oxidation and XPS studies.

Ruthenocene (7) has been the subject of a variety of electrochemical studies.[13] Unlike the ferrocenes, which generally exhibit reversible electrochemical oxidation–reduction cycles,[14] the oxi-

dation of 7 is not reversible. Recent electrochemical studies of decamethylruthenocene (8) showed an irreversible oxidation in acetonitrile but a reversible oxidation–reduction cycle in methylene chloride.[6] Because of the reversible nature of the oxidation of 8 in methylene chloride, we chose to use this solvent for our electrochemical oxidative studies of 2–8. Table I lists the electrochemical oxidation potentials of 2–8 as measured by cyclic voltammetry at a platinum bead electrode in methylene chloride containing 0.1 M tetra-n-butylammonium perchlorate as supporting electrolyte. The $E_{1/2}$ value observed for 7 (0.80 V) was for an irreversible process and was very similar to that previously reported (0.78 V) under similar conditions.[13c] Comparison of ruthenocene (7) with 2 and 8 gives an insight into the electron-donating properties of the pentamethylcyclopentadienyl ligand. It should be noted that for 2 and 8 the effect of methyl substitution does not appear to be additive (0.26 V for the first five methyls, but only 0.12 V for the second five methyls). In part, this may be due to the reversible oxidation of 8 and the irreversible oxidation of 2. This illustrates one of the problems encountered in the use of electrochemical oxidation to evaluate substituent effects. Comparison of 4 and 8 implies that the fluorenyl group is more electron donating than the pentamethylcyclopentadienyl group since the $E_{1/2}$ values show that 4 has a higher energy HOMO than 8. In addition, the indenyl group is close to the pentamethylcyclopentadienyl moiety from an electrochemical point of view. Lastly, we need to consider the effect of replacing one hydrogen by an acetyl and five hydrogens by five chlorines as in 5 and 6, respectively. Whereas the acetyl increases the $E_{1/2}$ by only 0.20 V relative to 2, the five chlorines increase the $E_{1/2}$ by 0.76 V relative to 2. This illustrates the strong electron-withdrawing influence of the pentachlorocyclopentadienyl group. It should be noted that comparison of the $E_{1/2}$ of 4 vs the $E_{1/2}$ of 6 indicates a 0.96 V difference in the case of oxidation through manipulation of the substituents on only one ligand of the substituted ruthenocene. This is equivalent to an effective difference of 1 in oxidation state even though both 4 and 6 are formally ruthenium(II) derivatives.[15]

The impetus for the studies outlined above was to have this series of ruthenocenes available for an extension of our use of XPS (ESCA) in evaluating the effect of substituents on the binding energy of the inner-shell electrons of the complexed metal.[1] Evaluation of the effective oxidation state of complexed transition metals is often very difficult. In those instances where electrochemical methods can be used, the results are often clouded by the lack of reversibility of the oxidation (as indicated above in the comparison of 2 and 8). The use of electrochemical methods is further complicated by the fact that in many transition-metal complexes the HOMO is not associated with the metal itself (e.g., titanocenes, zirconocenes, hafnocenes).[1a] Since XPS provides information about the inner-shell electrons, the electrochemical problems outlined above are circumvented.[16] Our previous efforts[1] and the efforts of others[15,17] have demonstrated that XPS can be an exceptionally useful tool for probing the electronic influence of ligands.

Table I lists the Ru(3d$_{5/2}$) binding energies for ruthenocenes 2–8.[18] Comparison of 7 with 8 shows a 0.8-eV change. This is consistent with the 0.8-eV change noted for the addition of ten methyl groups to titanocene dichloride and zirconocene dichloride, and the 0.9-eV change noted for the decamethylation of ferroc-

[Chemical structures of compounds 3, 5, 1, 4, and 6, with labels CH$_3$, H$_3$C, Ru, RuCl$_2$, CCH$_3$/O, Cl]

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(18) All ESCA spectra were calibrated against the C(1s) binding energy of polyethylene, which was used as the mounting support for the sample. The Ru(3d$_{3/2}$) binding energy was obscured by the C(1s) ionization.
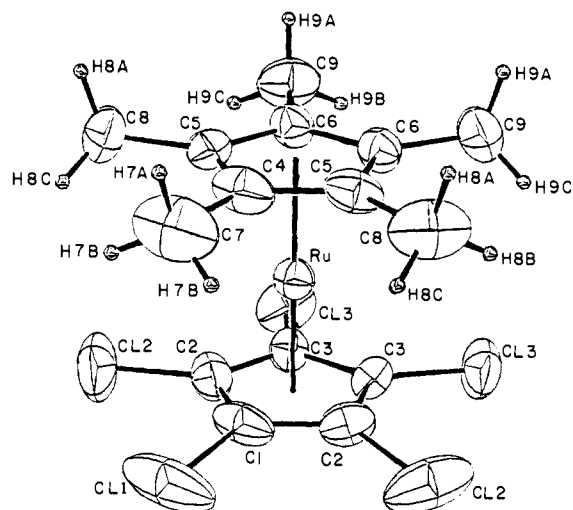
Figure 1. ORTEP drawing of (η⁵-pentachloropentadienyl)(η⁵-penta-methylcyclopentadienyl)ruthenium(II) (6).

ene.[1a] These values further substantiate the strong electron-donating effect of permethylation of the cyclopentadienyl ligand. The binding energy observed for **4** was 0.3 eV less than that observed for **8**. *This provides unequivocal evidence (in addition to the electrochemical evidence) that the fluorenyl group is a more electron donating ligand than is the pentamethylcyclopentadienyl moiety for the ruthenocenes.* This behavior of the fluorenyl ligand is in line with what might be anticipated from the binding energy of **3**, which bears the indenyl ligand. The binding energy for **3** lies between those observed for **2** and **8**, which indicates that indenyl lies between cyclopentadienyl and pentamethylcyclopentadienyl in its electron-donating properties.

Comparison of the binding energies of **2** and **5** demonstrates that the acetyl group exercises only a small electron-withdrawing influence. This may indicate that although the acetyl group is inductively electron withdrawing, it can back-donate electrons in a conjugative manner.[19] Overall, an acetyl group is approximately as electron withdrawing as a methyl group is electron donating in this system.

(η⁵-Pentachlorocyclopentadienyl)(η⁵-pentamethylcyclopentadienyl)ruthenium(II) (**6**) is quite interesting in that it has a binding energy very similar to that of ruthenocene (**7**). This shows that, inductively, the pentachlorocyclopentadienyl ligand is a balance for the pentamethylcyclopentadienyl ligand as assessed by XPS. Comparison of the binding energy of **6** with that of **4** shows a 1.2-eV change as a function of changing the substitution pattern of a single Cp ligand! This implies that the *effective* oxidation state of ruthenium varies by more than one with no change in the formal oxidation state in the series of ruthenocenes studied.[15]

Because of the balance between the pentamethylcyclopentadienyl ligand and the pentachlorocyclopentadienyl ligand in **6**, we determined the single-crystal X-ray structure of **6**, in order to ascertain whether the ruthenium nucleus was displaced from a central position between the two ligands. Colorless hexagons of **6** were grown by slow recrystallization from trichloroethylene. Table II lists the bond lengths and angles for **6**. Figure 1 provides the ORTEP drawing of **6**, As can be noted from the ORTEP drawing, the heteroannular substituents are eclipsed, which is consistent with other ruthenocene structures.[7b,d,20-22] Examination of the

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Table II. Bond Lengths (Å) and Bond Angles (deg) for (η⁵-Pentachlorocyclopentadienyl)(η⁵-pentamethylcyclopentadienyl)-ruthenium(II) (**6**)

Bond Lengths			
Ru-C1	2.152 (9)	Ru-C4	2.191 (8)
Ru-C2	2.150 (5)	Ru-C5	2.183 (5)
Ru-C3	2.147 (5)	Ru-C6	2.185 (5)
C1-Cl1	1.715 (9)	C4-C7	1.481 (13)
C2-Cl2	1.720 (6)	C5-C8	1.503 (9)
C3-Cl3	1.724 (5)	C6-C9	1.501 (8)
C1-C2	1.420 (8)	C4-C5	1.436 (7)
C2-C3	1.397 (8)	C5-C6	1.424 (8)
C3-C3'	1.417 (10)	C6-C6'	1.426 (11)
Ru-C1CENT	1.783 (1)	Ru-C2CENT	1.816 (1)

Bond Angles			
C2-C1-Cl1	126.2 (4)	C5-C4-C7	126.1 (3)
C1-C2-Cl2	125.9 (5)	C4-C5-C8	126.1 (6)
C2-C3-Cl3	126.1 (4)	C5-C6-C9	125.7 (5)
C3-C2-Cl2	125.8 (5)	C6-C5-C8	126.1 (6)
Cl3-C3-C3'	125.3 (2)	C9-C6-C6'	126.0 (4)

Table III. Bond Lengths (Å) and Bond Angles (deg) for (η⁵-Pentamethylcyclopentadienyl)(η⁵-indenyl)ruthenium(II) (**3**)

Bond Lengths			
Ru-C1	2.169 (6)	C4A-C7A	1.446 (8)
Ru-C2	2.198 (6)	C4-C5	1.332 (11)
Ru-C3	2.196 (6)	C5-C6	1.425 (12)
Ru-C4A	2.227 (6)	C6-C7	1.351 (11)
Ru-C7A	2.220 (5)	C7-C7A	1.415 (8)
Ru-C8	2.157 (5)	C8-C9	1.428 (8)
Ru-C9	2.154 (5)	C8-C12	1.424 (7)
Ru-C10	2.170 (5)	C8-C13	1.506 (8)
Ru-C11	2.175 (5)	C9-C10	1.444 (8)
Ru-C12	2.167 (6)	C9-C14	1.493 (8)
C1-C2	1.407 (8)	C10-C11	1.406 (7)
C1-C7A	1.431 (8)	C10-C15	1.503 (9)
C2-C3	1.405 (8)	C11-C12	1.432 (8)
C3-C4A	1.419 (8)	C11-C16	1.507 (8)
C4A-C4	1.412 (9)	C12-C17	1.495 (8)

Bond Angles			
C1-C2-C3	108.4 (5)	C12-C8-C13	125.6 (6)
C2-C3-C4A	108.8 (5)	C8-C9-C10	108.2 (5)
C3-C4A-C4	133.7 (6)	C8-C9-C14	127.5 (6)
C3-C4A-C7A	107.4 (5)	C10-C9-C14	125.2 (6)
C4-C4A-C7A	118.9 (6)	C9-C10-C11	108.1 (5)
C4A-C4-C5	120.6 (7)	C9-C10-C15	125.3 (6)
C4-C5-C6	120.6 (7)	C11-C10-C15	126.6 (6)
C6-C7-C7A	119.4 (7)	C10-C11-C12	108.7 (5)
C1-C7A-C4A	106.7 (5)	C10-C11-C16	126.5 (6)
C1-C7A-C7	134.4 (6)	C12-C11-C16	124.4 (5)
C4A-C7A-C7	118.8 (6)	C8-C12-C11	107.5 (5)
C9-C8-C12	108.5 (5)	C8-C12-C17	126.8 (6)
C9-C8-C13	125.9 (5)	C11-C12-C17	125.6 (5)

ruthenium-carbon distances for the ruthenium-pentachlorocyclopentadienyl portion of **6** showed a range of 2.147-2.152 Å. The corresponding values for the ruthenium-pentamethylcyclopentadienyl portion of **6** were 2.183-2.191 Å. This established that the ruthenium nucleus was not spaced evenly between the electron-withdrawing and electron-donating cyclopentadienyl ligands. This can be represented in an alternate manner by noting the cyclopentadienyl centroid to ruthenium distance, which is 1.783 Å to the pentachlorocyclopentadienyl ring and 1.816 Å to the pentamethylcyclopentadienyl ring. Decamethylruthenocene has a related value of 1.808 Å,[7b,d] while decachlororuthenocene has a distance of 1.799 Å.[21] Ruthenocene shows a ruthenium to cyclopentadienyl centroid distance of 1.816 Å.[22] In **6**, the ruthenium-pentachlorocyclopentadienyl centroid distance is less than the related distance in decachlororuthenocene, while the ruthenium-pentamethylcyclopentadienyl centroid distance is greater than that observed for decamethylruthenocene. This indicates that the ruthenium is held closer to the electron-deficient chloro-substituted ring as a result of the electron donation of the electron-rich methyl-substituted ring.

Table IV. Bond Lengths (Å) and Bond Angles (deg) for (η⁵-Pentamethylcyclopentadienyl)(η⁵-fluorenyl)ruthenium(II) (4 and 4*)ᵃ

4: Bond Lengths

Ru-C$_{1A}$	2.227 (5)	Ru-C$_{14}$	2.143 (6)	C$_{5A}$-C$_5$	1.421 (8)	C$_{10}$-C$_{15}$	1.499 (9)
Ru-C$_{4A}$	2.226 (5)	C$_{1A}$-C$_1$	1.429 (8)	C$_{5A}$-C$_{8A}$	1.436 (8)	C$_{11}$-C$_{12}$	1.460 (9)
Ru-C$_{5A}$	2.243 (5)	C$_{1A}$-C$_{4A}$	1.448 (8)	C$_5$-C$_6$	1.365 (10)	C$_{11}$-C$_{16}$	1.489 (8)
Ru-C$_{8A}$	2.240 (5)	C$_{1A}$-C$_9$	1.436 (7)	C$_6$-C$_7$	1.425 (11)	C$_{12}$-C$_{13}$	1.432 (9)
Ru-C$_9$	2.183 (6)	C$_1$-C$_2$	1.351 (9)	C$_7$-C$_8$	1.329 (10)	C$_{12}$-C$_{17}$	1.473 (10)
Ru-C$_{10}$	2.155 (6)	C$_2$-C$_3$	1.419 (10)	C$_8$-C$_{8A}$	1.434 (8)	C$_{13}$-C$_{14}$	1.431 (9)
Ru-C$_{11}$	2.158 (6)	C$_3$-C$_4$	1.345 (9)	C$_{8A}$-C$_9$	1.428 (8)	C$_{13}$-C$_{18}$	1.513 (9)
Ru-C$_{12}$	2.156 (6)	C$_4$-C$_{4A}$	1.424 (8)	C$_{10}$-C$_{11}$	1.414 (9)	C$_{14}$-C$_{19}$	1.492 (10)
Ru-C$_{13}$	2.169 (5)	C$_{4A}$-C$_{5A}$	1.447 (8)	C$_{10}$-C$_{14}$	1.442 (8)		

4: Bond Angles

C$_1$-C$_{1A}$-C$_{4A}$	119.0 (5)	C$_4$-C$_{4A}$-C$_{5A}$	133.9 (6)	C$_{5A}$-C$_{8A}$-C$_9$	109.0 (5)	C$_{11}$-C$_{12}$-C$_{13}$	107.3 (6)
C$_1$-C$_{1A}$-C$_9$	132.6 (6)	C$_{4A}$-C$_{5A}$-C$_5$	131.8 (6)	C$_8$-C$_{8A}$-C$_9$	133.1 (6)	C$_{11}$-C$_{12}$-C$_{17}$	125.8 (6)
C$_{4A}$-C$_{1A}$-C$_9$	108.4 (5)	C$_{4A}$-C$_{5A}$-C$_{8A}$	107.6 (5)	C$_{1A}$-C$_9$-C$_{8A}$	107.6 (5)	C$_{13}$-C$_{12}$-C$_{17}$	126.7 (6)
C$_{1A}$-C$_1$-C$_2$	119.5 (6)	C$_5$-C$_{5A}$-C$_{8A}$	120.5 (5)	C$_{11}$-C$_{10}$-C$_{14}$	108.2 (6)	C$_{12}$-C$_{13}$-C$_{14}$	108.1 (5)
C$_1$-C$_2$-C$_3$	121.2 (6)	C$_{5A}$-C$_5$-C$_6$	117.8 (7)	C$_{11}$-C$_{10}$-C$_{15}$	126.6 (6)	C$_{12}$-C$_{13}$-C$_{18}$	126.1 (6)
C$_2$-C$_3$-C$_4$	121.8 (6)	C$_5$-C$_6$-C$_7$	122.4 (6)	C$_{14}$-C$_{10}$-C$_{15}$	125.3 (6)	C$_{14}$-C$_{13}$-C$_{18}$	125.6 (6)
C$_3$-C$_4$-C$_{4A}$	119.7 (6)	C$_6$-C$_7$-C$_8$	120.5 (6)	C$_{10}$-C$_{11}$-C$_{12}$	108.2 (5)	C$_{10}$-C$_{14}$-C$_{13}$	108.2 (6)
C$_{1A}$-C$_{4A}$-C$_4$	118.8 (5)	C$_7$-C$_8$-C$_{8A}$	120.9 (7)	C$_{10}$-C$_{11}$-C$_{16}$	127.0 (7)	C$_{10}$-C$_{14}$-C$_{19}$	125.9 (6)
C$_{1A}$-C$_{4A}$-C$_{5A}$	107.2 (5)	C$_{5A}$-C$_{8A}$-C$_8$	117.9 (6)	C$_{12}$-C$_{11}$-C$_{16}$	124.8 (7)	C$_{13}$-C$_{14}$-C$_{19}$	125.9 (6)

4*: Bond Lengths

Ru*-C$_{1A}$*	2.245 (6)	C$_{1A}$*-C$_1$*	1.420 (10)	C$_{5A}$*-C$_5$*	1.403 (9)	C$_{11}$*-C$_{12}$*	1.423 (9)
Ru*-C$_{4A}$*	2.236 (6)	C$_{1A}$*-C$_{4A}$*	1.425 (9)	C$_{5A}$*-C$_{8A}$*	1.450 (9)	C$_{11}$*-C$_{16}$*	1.514 (9)
Ru*-C$_{5A}$*	2.230 (5)	C$_{1A}$*-C$_9$*	1.449 (10)	C$_5$*-C$_6$*	1.362 (12)	C$_{12}$*-C$_{13}$*	1.430 (8)
Ru*-C$_{8A}$*	2.244 (6)	C$_{1A}$*-C$_9$*	1.449 (10)	C$_6$*-C$_7$*	1.392 (14)	C$_{12}$*-C$_{13}$*	1.430 (8)
Ru*-C$_9$*	2.191 (7)	C$_1$*-C$_2$*	1.349 (15)	C$_7$*-C$_8$*	1.358 (13)	C$_{12}$*-C$_{17}$*	1.499 (9)
Ru*-C$_{10}$*	2.152 (6)	C$_2$*-C$_3$*	1.412 (15)	C$_8$*-C$_{8A}$*	1.432 (10)	C$_{13}$*-C$_{14}$*	1.408 (9)
Ru*-C$_{11}$*	2.139 (6)	C$_3$*-C$_4$*	1.358 (12)	C$_{8A}$*-C$_9$*	1.405 (9)	C$_{13}$*-C$_{18}$*	1.490 (9)
Ru*-C$_{12}$*	2.147 (5)	C$_4$*-C$_{4A}$*	1.420 (10)	C$_{10}$*-C$_{11}$*	1.422 (9)	C$_{14}$*-C$_{19}$*	1.503 (9)
Ru*-C$_{13}$*	2.616 (6)	C$_{4A}$*-C$_{5A}$*	1.449 (9)	C$_{10}$*-C$_{14}$*	1.426 (8)		
Ru*-C$_{14}$*	2.166 (6)			C$_{10}$*-C$_{15}$*	1.515 (10)		

4*: Bond Angles

|							
C$_1$*-C$_{1A}$*-C$_{4A}$*	119.3 (8)	C$_4$*-C$_{4A}$*-C$_{5A}$*	132.6 (7)	C$_{5A}$*-C$_{8A}$*-C$_9$*	108.2 (6)	C$_{11}$*-C$_{12}$*-C$_{13}$*	107.4 (5)
C$_1$*-C$_{1A}$*-C$_9$*	139.9 (8)	C$_{4A}$*-C$_{5A}$*-C$_5$*	132.1 (7)	C$_8$*-C$_{8A}$*-C$_9$*	133.7 (7)	C$_{11}$*-C$_{12}$*-C$_{17}$*	126.4 (6)
C$_{4A}$*-C$_{1A}$*-C$_9$*	107.8 (6)	C$_{4A}$*-C$_{5A}$*-C$_{8A}$*	107.3 (6)	C$_{1A}$*-C$_9$*-C$_{8A}$*	108.6 (6)	C$_{13}$*-C$_{12}$*-C$_{17}$*	126.2 (6)
C$_{1A}$*-C$_1$*-C$_2$*	119.4 (9)	C$_5$*-C$_{5A}$*-C$_{8A}$*	120.6 (7)	C$_{11}$*-C$_{10}$*-C$_{14}$*	108.3 (6)	C$_{12}$*-C$_{13}$*-C$_{14}$*	108.7 (6)
C$_1$*-C$_2$*-C$_3$*	121.3 (8)	C$_{5A}$*-C$_5$*-C$_6$*	118.3 (8)	C$_{11}$*-C$_{10}$*-C$_{15}$*	125.7 (6)	C$_{12}$*-C$_{13}$*-C$_{18}$*	126.8 (6)
C$_2$*-C$_3$*-C$_4$*	121.5 (9)	C$_5$*-C$_6$*-C$_7$*	122.3 (8)	C$_{14}$*-C$_{10}$*-C$_{15}$*	125.9 (6)	C$_{14}$*-C$_{13}$*-C$_{18}$*	124.3 (6)
C$_3$*-C$_4$*-C$_{4A}$*	118.8 (8)	C$_6$*-C$_7$*-C$_8$*	121.9 (9)	C$_{10}$*-C$_{11}$*-C$_{12}$*	107.9 (5)	C$_{10}$*-C$_{14}$*-C$_{13}$*	107.7 (5)
C$_{1A}$*-C$_{4A}$*-C$_4$*	119.6 (6)	C$_7$*-C$_8$*-C$_{8A}$*	118.8 (8)	C$_{10}$*-C$_{11}$*-C$_{16}$*	126.3 (7)	C$_{10}$*-C$_{14}$*-C$_{19}$*	124.5 (6)
C$_{1A}$*-C$_{4A}$*-C$_{5A}$*	107.8 (6)	C$_{5A}$*-C$_{8A}$*-C$_8$	118.1 (7)	C$_{12}$*-C$_{11}$*-C$_{16}$*	125.6 (6)	C$_{13}$*-C$_{14}$*-C$_{19}$*	127.8 (6)

ᵃTwo distinct molecules exist in the unit cell.
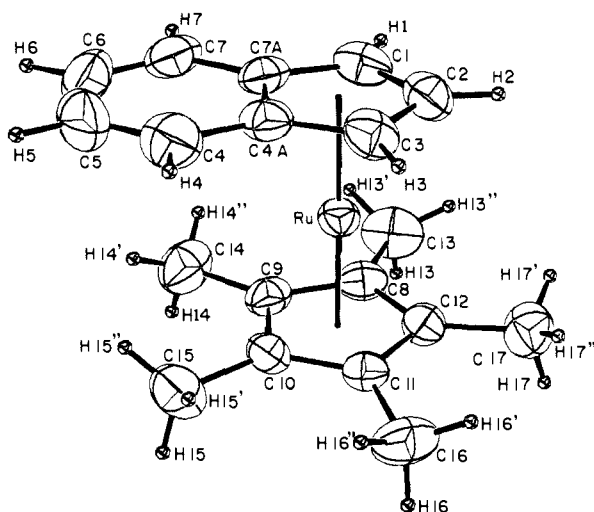
Figure 2. ORTEP drawing of (η⁵-pentamethylcyclopentadienyl)(η⁵-indenyl)ruthenium(II) (3).

The chlorine atoms of **6** were bent out of the plane of the cyclopentadienyl ring by an average of 4.5°, while the methyl groups of **6** were bent out of the plane of the cyclopentadienyl ring by only 0.7°.

The large electron-donating effect observed for the fluorenyl ligand and the smaller electron-donating effect of the indenyl ligand made the structural assignments of **3** and **4** particularly crucial. It is well-established that both the indenyl and fluorenyl
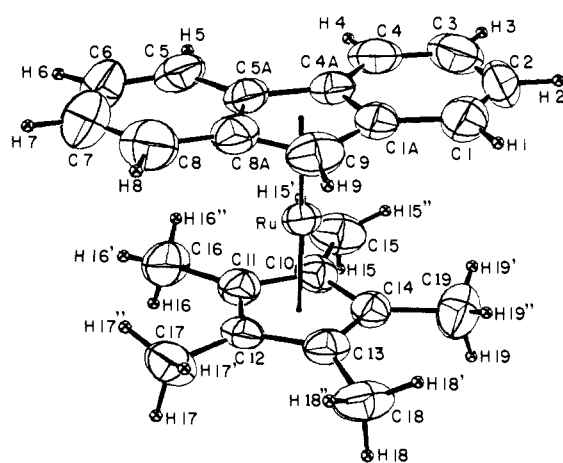
Figure 3. ORTEP drawing of (η⁵-pentamethylcyclopentadienyl)(η⁵-fluorenyl)ruthenium(II) (4).

ligands can exist in a η⁶, η⁵, η³, or η¹ bonding mode.[23] "Slippage" from one form to another frequently occurs during oxidation/reduction reactions and η⁵ to η³ slippage has often been invoked as preceding certain substitution reactions. Thus, we were concerned about the structures of **3** and **4**. Because of this concern,

(23) For a recent review of this phenomenon, see: O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307. See also: Marder, T. B.; Calabrese, J. C.; Roe, D. C.; Tulip, T. H. *Organometallics* **1987**, *6*, 2012. Faller, J. W.; Crabtree, R. H.; Habib, A. *Ibid.* **1985**, *4*, 929 and references contained therein.

Table V. Distance between the Centroids of the Planes of the Five-Membered Ring Ligands for a Series of Ruthenocenes

compd	ligand A	ligand B	distance (Å)
9	pentachlorocyclopentadienyl	pentachlorocyclopentadienyl	3.598
6	pentachlorocyclopentadienyl	pentamethylcyclopentadienyl	3.599
8	pentamethylcyclopentadienyl	pentamethylcyclopentadienyl	3.616
7	cyclopentadienyl	cyclopentadienyl	3.632
3	pentamethylcyclopentadienyl	indenyl	3.632
4	pentamethylcyclopentadienyl	fluorenyl[a]	3.634
4*	pentamethylcyclopentadienyl	fluorenyl[a]	3.646

[a]Two different molecules exist in the unit cell.

unequivocal evidence for the structures of **3** and **4** was obtained by single-crystal X-ray analysis. Table III lists the bond lengths and bond angles for **3**, while Table IV lists the same data for **4**. Figures 2 and 3 provide ORTEP drawings of **3** and **4**, respectively.

As can be seen from Tables III and IV and from the ORTEP drawings of **3** and **4**, both the indenyl and fluorenyl ligands are η^5 in their association with the ruthenium. For **3**, it is of interest to note that both the pentamethylcyclopentadienyl ring and the indenyl moiety are essentially planar. The ruthenium resides 1.792 Å from the centroid of the pentamethylcyclopentadienyl ring and 1.840 Å from the plane of the five-membered ring of the indenyl moiety. The dihedral angle between the planes of the two five-membered rings was 4.3°. For **4**, both five-membered rings are essentially planar, with dihedral angles between the planes of 1.8° and 2.6°, respectively, for the two different molecules in the unit cell. The ruthenium to pentamethylcyclopentadienyl centroid distances were 1.777 and 1.781 Å for the two different molecules, while the fluorenyl five-membered ring plane distances to the rutheniums were 1.857 and 1.865 Å, respectively.

Table V lists the distance between the centroids of the planes of the five-membered rings of a series of ruthenocenes. As can be seen, the overall distances remain fairly constant at 3.622 ± 0.024 Å. In general, the ruthenium resides closer to the more electron-withdrawing cyclopentadienyl moiety than to the more electron-donating cyclopentadienyl derivative. The possible exception to this generality is found for **3**, where the ruthenium is 0.048 Å closer to the pentamethylcyclopentadienyl ring than to the indenyl five-membered ring. In this case, both electrochemical data and XPS data indicate that the electronic effect of the indenyl system is very similar to that of the pentamethylcyclopentadienyl system. Again, with the possible exception of **3**, in the unsymmetrical systems **4, 4***, and **6**, the ruthenium is not symmetrically located between the two five-membered ligands, but instead it is displaced toward the less electron-donating ligand. For **4, 4***, and **6**, the ruthenium is closer to the less electron-donating ligand by 0.080, 0.084, and 0.033 Å, respectively.

In summary, we have developed a straightforward approach to the synthesis of a variety of unsymmetrical ruthenocenes. Evaluation of the electronic effects of the various substituents by XPS and electrochemical studies showed the following order of decreasing electron donation: fluorenyl > pentamethylcyclopentadienyl > indenyl > cyclopentadienyl > acetylcyclopentadienyl > pentachlorocyclopentadienyl. Lastly, single-crystal X-ray studies of **3, 4**, and **6** showed an unsymmetrical placement of ruthenium between the two rings.

Experimental Section

Proton magnetic resonance spectra were obtained on a Varian HF-T-80, Nicolet NT-300, or Perkin-Elmer R-24B NMR spectrometer. Carbon magnetic resonance spectra were obtained on a Nicolet NT-300 NMR spectrometer. Infrared spectra were recorded on a Beckman Model 4240 infrared spectrophotometer. Mass spectra were obtained on an AEI-MS30 instrument in the electron impact mode at electron energies of either 20 or 70 eV. Melting points were determined on a Thomas-Hoover Uni-Melt appraratus and are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory.

Photoelectron spectra were obtained on a Physical Electronics Industries, Inc., ESCA-Auger-SIMS system equipped with a Model 15-720 specimen introduction/reaction chamber, using Mg Kα radiation. The samples were run on a polyethylene-coated aluminum chip, and each sample was calibrated against the C(1s) binding energy (284.6 eV) of polyethylene. Electrochemical measurements were performed on a Princeton Applied Research Polarographic Analyzer equipped with a

Houston Instrument Omnigraphic 2000 recorder. A saturated NaCl-SCE was used as the reference electrode, with a platinum bead working electrode. The oxidation potentials were evaluated by cyclic voltammetry at 25 °C, using solutions that were ca. 10^{-3} M in substrate, and with a scan rate of 100 mV/s. Potentials were measured against the ferrocene/ferricenium couple ($E° = 0.31$ V vs SCE by definition[14])[24] and referenced to SCE.

All reactions were run under purified nitrogen or argon, using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under argon just prior to use.

Indene, fluorene, and ruthenocene were purchased from the Aldrich Chemical Company. Ruthenium(III) chloride was purchased from Alfa Products. Tetra-*n*-butylammonium perchlorate was purchased from the G. Frederick Smith Chemical Company.

Sodium acetylcyclopentadienide,[8] pentamethylcyclopentadiene,[25] and diazotetrachlorocyclopentadiene[10] were prepared according to the literature procedures.

Bis(η^5-pentamethylcyclopentadienyl)ruthenium(II) (8) and (η^5-Pentamethylcyclopentadienyl)ruthenium(III) Dichloride Oligomer (1). In a 250-mL Schlenk flask was placed ruthenium trichloride (5.0 g, 24 mmol), pentamethylcyclopentadiene (7.27 g, 53.4 mmol), and 100 mL of ethanol. The solution was refluxed for 3 h and then allowed to cool to room temperature. The brown precipitate was collected on a fine frit and was washed with two 10-mL portions of ethanol, two 10-mL portions of ether, and 100 mL of pentane. Vacuum drying afforded 4.12 g (56% yield) of **1** as a brown powder: ^{1}H NMR (CDCl$_3$) δ 4.95 (br s, $w_{1/2}$ ∼ 20 Hz) [lit.[2] ^{1}H NMR (CDCl$_3$) δ 4.95].

The washings were reduced in volume and applied to a 1 cm × 10 cm column of basic alumina to remove unwanted insoluble impurities. Elution with ether, followed by removal of the solvent under reduced pressure, afforded 1.01 g (12% yield) of pure white decamethylruthenocene (**8**): ^{1}H NMR (CDCl$_3$) δ 1.64 (s) [lit.[2] ^{1}H NMR (CDCl$_3$) δ 1.64].

(η^5-Pentamethylcyclopentadienyl)(η^5-cyclopentadienyl)ruthenium(II) (2). In a 200-mL Schlenk flask was placed freshly distilled cyclopentadiene (0.5 g, 7.6 mmol) and 50 mL of tetrahydrofuran. To the stirred solution under nitrogen was added 4.0 mL (7.2 mmol) of a 1.8 M solution of methyllithium in diethyl ether. The solution was stirred for 1 h, and then dichloro(pentamethylcyclopentadienyl)ruthenium(III) oligomer (1.00 g, 3.25 mmol) was added and the solution was refluxed for 12 h. The solvent was removed under reduced pressure to give a red-black solid, which was extracted with 400 mL of hot hexane. Passage of this solution through a 10-cm basic alumina column to remove unwanted insoluble impurities, followed by removal of the solvent under reduced pressure, afforded 0.85 g (87% yield) of an off-white solid: mp (sealed tube) 138–139 °C; IR (KBr) 3105, 2960, 2943, 2882, 2845, 1473, 1450, 1413, 1379, 1100, 1067, 1031, 994, 796, 693 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.18 (s, 5 H), 1.97 (s, 15 H); ^{13}C NMR (CDCl$_3$) δ 84.92, 72.14, 12.37; mass spectrum, *m/e* calcd for C$_{15}$H$_{20}$Ru 302.0608, found 302.0602.

Anal. Calcd for C$_{15}$H$_{20}$Ru: C, 59.78; H, 6.69. Found: C, 59.88; H, 6.70.

(η^5-Pentamethylcyclopentadienyl)(η^5-indenyl)ruthenium(II) (3). In a 50-mL Schlenk flask was placed indene (0.196 g, 1.68 mmol) and 20 mL of tetrahydrofuran. To the stirred solution under nitrogen was added 0.94 mL (1.69 mmol) of a 1.8 M solution of methyllithium in diethyl ether. The solution was stirred for 1 h, and then dichloro(pentamethylcyclopentadienyl)ruthenium(III) oligomer (0.515 g, 1.68 mmol) was added. The solution was refluxed for 4 h, and then the volatiles were removed under reduced pressure to give a deep red, gummy solid. This solid was

(24) Due to the irreversible nature of the ruthenocene oxidations, the observed oxidation potentials ($E_{1/2}$) do not necessarily reflect the thermodynamic oxidation potentials ($E°$). Thus, the values listed can only be used as approximate indications of the ligand electronic effects. For a discussion of this effect, see: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, NY, 1980; p 19.

(25) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1.

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triturated with 200 mL of hot hexane, and the hexane solution was passed through a 10-cm basic alumina column to remove unwanted insoluble impurities. A bright yellow fraction was collected; removal of the solvent under reduced pressure afforded 0.350 g (59% yield) of a yellow-orange solid: mp (sealed tube) 62–63 °C; IR (KBr) 3080, 2970, 2945, 2890, 1473, 1456, 1380, 1337, 1031, 796, 736, 720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.10 (q of d, 4 H), 4.94 (d, 2 H), 4.61 (t, 1 H), 1.83 (s, 15 H); ^{13}C NMR (CDCl$_3$) δ 125.01, 120.88, 92.04, 82.29, 76.76, 68.25, 10.88; mass spectrum, m/e calcd for C$_{19}$H$_{22}$Ru 352.0765, found 352.0773.

Anal. Calcd for C$_{19}$H$_{22}$Ru: C, 64.93; H, 6.31. Found: C, 65.08; H, 6.42.

(η^5-Pentamethylcyclopentadienyl)(η^5-fluorenyl)ruthenium(II) (4). In a 50-mL Schlenk flask was placed fluorene (0.68 g, 4.1 mmol) and 20 mL of tetrahydrofuran. To the stirred solution under nitrogen was added 2.4 mL (4.3 mmol) of a 1.8 M solution of methyllithium in diethyl ether. The solution was stirred for 1 h, and then dichloro(pentamethylcyclopentadienyl)ruthenium(III) oligomer (0.50 g, 1.6 mmol) was added. The solution was stirred for 4 h, and then the solvent was removed under reduced pressure. The residue was dissolved in 50 mL of hot hexane and filtered through a 5-cm basic alumina column, and then the hexane was removed under reduced pressure. The excess fluorene was removed by sublimation at 50 °C (0.1 mmHg), and the residue was sublimed at 100 °C (0.1 mmHg) to afford 0.32 g (48% yield) of a bright orange solid: mp (sealed tube) 139–140 °C; IR (KBr) 3045, 2960, 2900, 1457, 1376, 1351, 1332, 1190, 1028, 975, 881, 793, 729, 718, 705, 615 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.77 (d, 2 H), 7.38 (d, 2 H), 7.13 (d of t, 4 H), 5.35 (s, 1 H), 1.47 (s, 15 H); ^{13}C NMR (CDCl$_3$) δ 124.72, 123.66, 122.13, 119.73, 96.20, 88.44, 79.62, 62.38, 9.39; mass spectrum, m/e calcd for C$_{23}$H$_{24}$Ru 402.0921, found 402.0902.

Anal. Calcd for C$_{23}$H$_{24}$Ru: C, 68.80; H, 6.02. Found: C, 68.68; H, 6.08.

(η^5-Pentamethylcyclopentadienyl)(η^5-acetylcyclopentadienyl)ruthenium(II) (5). In a 50-mL Schlenk flask was placed sodium acetylcyclopentadienide (0.60 g, 4.6 mmol), dichloro(pentamethylcyclopentadienyl)ruthenium(III) oligomer (0.70 g, 2.3 mmol), and 20 mL of tetrahydrofuran. The solution was refluxed for 4 h, and the solvent was then removed under reduced pressure to give a black solid. The solid was triturated with 100 mL of hot hexane, and this was passed through a 10-cm column of basic alumina to remove unwanted insoluble impurities. A light yellow band was eluted with diethyl ether, and removal of the solvent under reduced pressure afforded 0.62 g (79% yield) of a light yellow solid: mp (sealed tube) 116–117 °C; IR(KBr) 3305, 3105, 3090, 2970, 2955, 2890, 1665, 1474, 1452, 1427, 1396, 1381, 1372, 1363, 1350, 1338, 1274, 1108, 1067, 1054, 1031, 1010, 951, 884, 832, 811, 655 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.54 (d of m, 4 H), 2.14 (s, 3 H), 1.84 (s, 15 H); ^{13}C NMR (CDCl$_3$) δ 198.07, 86.24, 85.19, 76.57, 72.78, 26.46, 11.30; mass spectrum, m/e calcd for C$_{17}$H$_{22}$ORu 344.0708, found 344.0707.

Anal. Calcd for C$_{17}$H$_{22}$ORu: C, 59.45; H, 6.46. Found: C, 59.69; H, 6.58.

(η^5-Pentamethylcyclopentadienyl)(η^5-pentachlorocyclopentadienyl)ruthenium(II) (6). In a 100-mL Schlenk flask was placed dichloro(pentamethylcyclopentadienyl)ruthenium(III) oligomer (1.03 g, 3.35 mmol), diazotetrachlorocyclopentadiene (0.80 g, 3.48 mmol), and 25 mL of methylene chloride. Upon addition of the methylene chloride, vigorous gas evolution occurred. After cessation of the gas evolution (∼15 min), the volatiles were removed under reduced pressure to give a black solid. This solid was titurated with 200 mL of hot hexane, followed by passage through a 10-cm column of basic alumina to remove unwanted insoluble impurities; removal of the hexane eluent at reduced pressure afforded 1.13 g (71% yield) of a white solid: mp (sealed tube) >300 °C; IR (KBr) 2960, 2915, 2950, 1475, 1450, 1388, 1380, 1353, 1344, 1032, 682 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.69 (s); ^{13}C NMR (CDCl$_3$) δ 91.06, 87.14, 8.86; mass spectrum, m/e calcd for C$_{15}$H$_{15}$Cl$_5$Ru 471.8660, found 471.8669.

Anal. Calcd for C$_{15}$H$_{15}$Cl$_5$Ru: C, 38.04; H, 3.19. Found: C, 38.07; H, 3.32.

Structure Determination for (η^5-Pentachlorocyclopentadienyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (6). The colorless crystals of C$_{15}$H$_{15}$Cl$_5$Ru belong to the orthorhombic space group *Pnma*. The measured cell constants a = 8.531 (2) Å, b = 14.208 (4) Å, c = 14.541 (2) Å give a calculated density of 1.785 g/cm^3 for four molecules in the unit cell at room temperature.[26] Data were collected on a fully auto-

mated Enraf-Nonius CAD-4 diffractometer with a variable-rate ω–2θ scan technique and graphite monochromatized Mo Kα radiation (λ = 0.71069 Å). After Lorentz–polarization corrections, 1206 of 1806 unique reflections (67%) with 2θ ≤ 52° were observed for [$F_o^2 ≥ 2\sigma(F_o^2)$]. A combination of Patterson and Fourier synthesis was used to locate all of the non-hydrogen atoms.[27] The hydrogen atoms were included at idealized positions. All of the non-hydrogen atoms were refined by full-matrix least-squares analysis with anisotropic thermal parameters. The final discrepancy factors are R = 0.041 and R_w = 0.044.

Structure Determination for (η^5-Pentamethylcyclopentadienyl)(η^5-Indenyl)ruthenium(II) (3). The yellow-orange crystals of C$_{19}$H$_{22}$Ru belong to the monoclinic space group $P2_1/n$. The measured cell constants a = 13.029 (16) Å, b = 12.798 (13) Å, c = 9.546 (7) Å, β = 95.41 (8)° gave a calculated density of 1.473 g/cm^3 for four molecules in the unit cell at room temperature. Data were collected on a fully automated Enraf-Nonius CAD4 diffractometer with a variable-rate ω–2θ scan technique and graphite monochromatized Mo Kα radiation (λ = 0.71069 Å). After Lorentz–polarization corrections, 1861 of 3034 unique reflections (61%) with 2θ ≤ 52° were observed for [$F_o^2 ≥ 2\sigma(F_o^2)$]. A combination of Patterson and Fourier synthesis was used to locate all of the non-hydrogen atoms.[27] The hydrogen atoms were included at idealized positions. All of the non-hydrogen atoms were refined by full-matrix least-squares analysis with anisotropic thermal parameters. The final discrepancy factors were R = 0.037 and R_w = 0.039.

Structure Determination for (η^5-Pentamethylcyclopentadienyl)(η^5-fluorenyl)ruthenium(II) (4). The orange crystal of C$_{23}$H$_{24}$Ru belongs to the monoclinic space group $P2_1/a$. The measured cell constants a = 22.923 (8) Å, b = 8.813 (5) Å, c = 19.149 (8) Å, β = 107.40 (3)° gave a calculated density of 1.445 g/cm^3 for eight molecules in the unit cell at room temperature. The unit cell contained two distinct molecules of C$_{23}$H$_{24}$Ru. Data were collected on a fully automated Enraf-Nonius CAD4 diffractometer with a variable-rate ω–2θ scan technique and graphite monochromatized Mo Kα radiation (λ = 0.71069 Å). After Lorentz–polarization corrections, 5811 of 7231 unique reflections (80%) with 2θ ≤ 52° were observed for [$F_o^2 ≥ 2\sigma(F_o^2)$]. A combination of Patterson and Fourier synthesis was used to locate all of the non-hydrogen atoms.[27] The hydrogen atoms were included at idealized positions. All of the non-hydrogen atoms were refined by full-matrix least-squares analysis with anisotropic thermal parameters. The final discrepancy factors were R = 0.060 and R_w = 0.059.

Registry No. 1, 96503-27-4; **2,** 100462-22-4; **3,** 115560-11-7; **4,** 115560-12-8; **5,** 115560-13-9; **6,** 115560-14-0; **7,** 1287-13-4; **8,** 84821-53-4; ruthenium trichloride, 10049-08-8; pentamethylcyclopentadiene, 4045-44-7; cyclopentadiene, 542-92-7; indene, 95-13-6; fluorene, 86-73-7; sodium acetylcyclopentadienide, 115533-64-7; diazatetrachlorocyclopentadiene, 21572-61-2.

Supplementary Material Available: ORTEP drawings for **3, 4,** and **6** and tables of positional parameters, general temperature factor expressions, bond distances, bond angles, least-squares planes, and interatomic distances for **3, 4, 4*,** and **6** (47 pages); listing of observed and calculated structure factors for **3, 4, 4*,** and **6** (36 pages). Ordering information is given on any current masthead page.

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(26) A projection of the unit cell is included in the supplementary material. The molecules stack with an intermolecular alignment of the η^5-pentamethylcyclopentadienyl moiety and the η^5-pentachlorocyclopentadienyl moiety with an intermolecular stacking distance of approximately 4 Å.

(27) All calculations were carried out on a PDP 11/34 computer with the Enraf-Nonius SDP programs. This crystallographic computing package is described by: Frentz, B. A. In *Computing in Crystallography*; Schenk, H., Oltof-Hazelkamp, R., Von Konigweld, H., Bassie, G. S., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.