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Synthesis of Unsymmetrical Ruthenocenes by Gas Phase Electrocyclic Reactions of Pentadienylruthenium Complexes

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Reduction of $RuCl_3{\cdot}3H_2O$ with zinc in the presence of 5,5-dimethylcyclohexadiene yields bis(6,6-dimethylcyclohexadienyl)ruthenium (3). Similar reactions of $[Cp^*RuCl_2]_n$ with 2,4-di-*tert*-butylpentadiene and 5,5-dimethylcyclohexadiene yield two new ruthenium pentadienyl compounds Cp*Ru(2,4-di-*tert*-butylpentadienyl) (4) and Cp*Ru(η^5-6,6-dimethylcyclohexadienyl) (5), respectively. Gas phase pyrolysis of Cp*Ru(η^5-2,4-dimethylpentadienyl) (1), Cp*Ru(η^5-cyclooctadienyl) (2), Cp*Ru(2,4-di-*tert*-butylpentadienyl) (4), and bis(η^5-2,4-dimethylpentadienyl)ruthenium (9) at 400–450 °C led to electrocyclic reaction and yielded Cp*Ru(η^5-1,3-dimethylcyclopentadienyl) (6), Cp*Ru(η^5-1,2-dihydropentalenyl) (7), Cp*Ru(η^5-1,3-di-*tert*-butylcyclopentadienyl) (8), and Ru(η^5-1,3-dimethylcyclopentadienyl) (11), respectively. Ru(η^5-6,6-dimethylcyclohexadienyl)$_2$ (3) was not volatile under these conditions while Cp*Ru(η^5-6,6-dimethylcyclohexadienyl) (5) survived the pyrolysis unchanged. Single crystal X-ray diffraction studies were completed on 9 and 11. Monoclinic 9 crystallized in the $P2_1/c$ space group with $a = 8.5945(17)$ Å, $b = 13.3257(31)$ Å, $c = 12.0851(22)$ Å, and $\beta = 110.670(14)°$. Monoclinic 11 crystallized in the $P2_1/n$ space group with $a = 10.332(3)$ Å, $b = 8.807(2)$ Å, $c = 13.884(3)$ Å, and $\beta = 106.27(2)°$.

Introduction

The synthesis and reactivity of metal complexes bearing one or two pentadienyl ligands ("open metallocenes") continue to be of interest in catalytic applications and as precursors for metal films.[1,2] One of the less explored reactions of open metallocenes is the apparent electrocyclic ring closure of a pentadienyl to a cyclopentadienyl ligand with the accompanying loss of hydrogen. Such processes have been suggested by fragmentation patterns of open metallocenes in a mass spectrometer[3] and isolated from reactions of two pentadienylruthenium compounds, (η^5-C_5H_7)Ru(PPh_3)$_2$Cl and (η^5-2,4-$Me_2C_5H_5$)$_2$Ru.[2,4] A similar reaction was observed for the related osmium compound, (η^5-2,4-$Me_2C_5H_5$)$_2$Os.[2] In the present paper we report on the synthesis, characterization, and gas phase reactivity of (η^5-1,1-$Me_2C_6H_6$)$_2$Ru and four Cp*Ru(η^5-pentadienyl) complexes.

Experimental Section

All compounds described in this work were handled using Schlenk techniques, using an M. I. Braun glovebox under a purified argon or nitrogen atmosphere, or on a vacuum line equipped with oil diffusion and mechanical pumps (10^{-3} Torr).[5] Hexane was purified by refluxing over Na/benzophenone and distilled prior to use. Absolute ethanol was degassed prior to use but was not dried. Deuterated benzene was purchased from Cambridge Isotope Laboratories and dried by refluxing over Na/benzophenone. $RuCl_3{\cdot}nH_2O$ was purchased from Strem Chemical Co. and used as received. 1,3-Cyclooctadiene and zinc dust were purchased from Aldrich Chemical Co. Other substituted pentadienes, 2,4-dimethyl-1,3-pentadiene,[6] 4-di-*tert*-butyl-1,3-pentadiene,[7] and 6,6-dimethyl-1,3-cyclohexadiene[8] were prepared by literature methods. $[Cp^*RuCl_2]_n$,[9] Cp*Ru(η^5-2,4-$Me_2C_5H_5$) (1), and Cp*Ru(η^5-cyclooctadienyl) (2)[10] were prepared by published procedures.

^1H and $^{13}C\{^1H\}$ spectra were recorded on a Varian 300XL spectrometer in 5-mm tubes equipped with a Teflon valve (J. Youngs). Proton chemical shifts are relative to residual protons in the solvent (C_6D_5H at δ 7.15 ppm or $CDCl_3$ at δ 7.24 ppm). ^{13}C chemical shifts are relative to solvent (C_6D_6 at 128 ppm or $CDCl_3$ at 77.0 ppm). Melting points were determined in open capillaries and are uncorrected.

Synthesis of Bis(6,6-dimethylcyclohexadienyl)ruthenium (3). By analogy to the procedure developed for the synthesis of bis(pentadienyl)ruthenium compounds,[11] 1.00 g of $RuCl_3{\cdot}nH_2O$ (4.44 mmols based on $n = 1$) was dissolved in 40 mL of absolute ethanol containing 7 mL of 5,5-dimethylcyclohexadiene. Then 3.5 g of Zn dust (300 mesh) was added and the mixture refluxed for 8 h. After cooling to room temperature, the solvent was evaporated under vacuum. The residue was extracted with 50 mL of hexane at reflux for 1 h, cooled, and filtered through a glass frit covered with a 1-cm layer of alumina (Brockman activity I). The residue was extracted further with 10 × 15 mL of hexane and filtered through alumina as above. The combined filtrates were evaporated under vacuum, yielding a light brown oil which was crystallized from hexane at −78 °C, giving 0.36 g of (η^5-6,6-$(CH_3)_2C_6H_5$)$_2$Ru (28% based on $RuCl_3{\cdot}H_2O$) as a pale yellow solid. Mp: 44–46 °C. Anal. Calcd for (η^5-6,6-$(CH_3)_2C_6H_5$)$_2$Ru, $C_{16}H_{22}Ru$: C, 60.93; H, 7.03. Found: C, 61.68; H, 7.02. ^1H

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(C_6D_6): δ 0.64 (s, 6 H), 1.45 (s, 6 H), 2.94 (d, *J* = 5.7 Hz, 2 H), 4.25 (pseudo t, *J* = 5.7 Hz, 2 H), 5.01 (pseudo t, *J* = 5.7 Hz, 1 H). ^{13}C (C_6D_6): δ 32.19, 35.45, 49.02, 81.64, 83.87.

Consistent with literature reports, similar experiments with 2,4-hexadiene and 2,4-di-*tert*-butyl-1,3-pentadiene yielded red oils which could not be further purified.[11]

Synthesis of (Pentamethylcyclopentadienyl)(2,4-di-*tert*-butylpentadienyl)ruthenium (4). By extension of literature procedures reported for the synthesis of (pentamethylcyclopentadienyl)(pentadienyl)ruthenium compounds,[1a,10] 0.235 g (0.76 mmol) of Cp^*RuCl_2 was stirred in 20 mL of absolute ethanol containing 1.5 mL of 2,4-di-*tert*-butyl-1,3-pentadiene for 3 h at room temperature. Then 0.3 g of zinc dust was added and the mixture stirred for an additional 1 h. After filtration through a pad of glass wool, the solvent was evaporated under vacuum. The yellow-orange residue was extracted with 4 × 20-mL aliquots of hexane. The combined extracts were passed through a 2-cm column of alumina and evaporated to dryness under vacuum, yielding 0.115 g (36% yield) of (pentamethylcyclopentadienyl)-(2,4-di-*tert*-butylpentadienyl)ruthenium (4). Mp: 74–76 °C. Anal. Calcd for $C_{23}H_{29}Ru$: C, 67.95; H, 7.19. Found: C, 68.67; H, 7.62. ^1H (C_6D_6): δ 0.086 (d, *J* = 2.7 Hz, 2 H), 1.22 (s, 18 H, ^tBu), 1.77 (s, 15 H, Cp*), 2.48 (d, *J* = 2.7 Hz, 2 H), 5.55 (s, 1 H). ^{13}C ($CDCl_3$): δ 11.90, 30.45, 31.20, 35.12, 38.18, 85.28, 90.29.

Synthesis of (Pentamethylcyclopentadienyl)(6,6-dimethylcyclohexadienyl)ruthenium (5). Using the same procedure as for 4, 0.500 g (1.63 mmol) of Cp^*RuCl_2, 1.5 mL of 5,5-dimethylcyclohexadiene, and 0.800 g of zinc yielded 0.0496 g (9% yield) of (pentamethylcyclopentadienyl)(6,6-dimethylcyclohexadienyl)ruthenium (5). Mp: 38–40 °C. Anal. Calcd for $C_{18}H_{26}Ru$: C, 62.94; H, 7.63. Found: C, 63.41; H, 6.88. ^1H (C_6D_6): δ 0.54 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.82 (s, 15 H, Cp*), 2.00 (d, *J* = 5.7 Hz, 2 H), 3.92 (d of d, *J* = 5.7, 5.6 Hz, 2 H), 5.11 (t, *J* = 5.6 Hz, 1 H). ^{13}C (C_6D_6): δ 11.54, 30.20, 34.12, 36.92, 43.25, 79.89, 80.36, 88.94.

Gas Phase Electrocyclic Ring Closure Studies. Compounds 1, 2, 4, and 5 were sublimed under dynamic vacuum (80 °C/0.1 Torr) through a 1 × 14 in. (o.d.) Pyrex tube seated in a Lindbergh tube furnace at 400–450 °C. Bis(5,5-dimethylcyclohexadienyl)ruthenium (3) was not volatile under these conditions. Pale yellow, air stable solids 6–8 were collected from the walls of the reaction tube at the exit from the oven from pyrolysis of 1, 2, and 4, respectively, and were identified as mixed pentamethylcyclopentadienyl(substituted cyclopentadienyl)ruthenium compounds by ^1H and ^{13}C NMR and elemental analysis. Compound 5 was recovered unchanged under these conditions.

(Pentamethylcyclopentadienyl)(1,3-dimethylcyclopentadienyl)ruthenium (6). A 0.0417-g sample of 1 yielded 0.0220 g (53% yield) of (pentamethylcyclopentadienyl)(1,3-dimethylcyclopentadienyl)ruthenium (6) at 400 °C. Mp: 62–64 °C. Anal. Calcd for $C_{17}H_{24}Ru$: C, 61.98; H, 7.34. Found: C, 61.78; H, 6.98. ^1H (C_6D_6): δ 1.68 (s, 6 H, Me), 1.84 (s, 15 H, Cp*), 4.00 (s, 2 H), 4.78 (s, 1 H).

(Pentamethylcyclopentadienyl)(1,2-dihydropentalenyl)ruthenium (7). A 0.0307-g sample of 2 yielded 0.0157 g (50% yield) of (pentamethylcyclopentadienyl)(1,2-dihydropentalenyl)ruthenium (7) at 450 °C. Mp: 92–95 °C. Anal. Calcd for $C_{18}H_{24}Ru$: C, 63.32; H, 7.08. Found: C, 63.24; H, 6.72. ^1H (C_6D_6): δ 1.76 (s, 15 H, Cp*), 1.9–2.3 (m, 6 H), 4.05 (s, 2 H), 4.10 (s, 1 H).

(Pentamethylcyclopentadienyl)(1,3-di-*tert*-butylcyclopentadienyl)ruthenium (8). A 0.045-g sample of 4 yielded 0.0075 g (17% yield) of (pentamethylcyclopentadienyl)(1,3-di-*tert*-butylcyclopentadienyl)ruthenium (8) at 450 °C. Mp: 62–65 °C. Anal. Calcd for $C_{23}H_{27}Ru$: C, 68.29; H, 6.73. Found: C, 68.36; H, 7.78. ^1H: (C_6D_6) δ 1.21 (s, 18 H, ^tBu), 1.90 (s, 15 H, Cp*), 3.95 (s, 2 H), 4.19 (s, 1 H); ($CDCl_3$) δ 1.09 (s, 18 H, ^tBu), 1.87 (s, 15 H, Cp*), 3.86 (s, 2 H), 4.02 (s, 1 H). ^{13}C ($CDCl_3$): δ 12.53, 30.50, 31.01, 66.48, 68.75, 73.50, 84.29.

Bis(1,3-dimethylcyclopentadienyl)ruthenium (11). A 0.0796-g (0.27-mmol) sample of bis(η^5-2,4-dimethylpentadienyl)ruthenium (9)[2,11] yielded 0.0653 g (84% yield) of a >95:5 mixture of compounds 10:11 at 450 °C which could be separated by sublimation. (1,3-Dimethylcyclopentadienyl)(2,4-dimethylpentadienyl)ruthenium, 10: ^1H NMR (C_6D_6) δ 0.39 (d, *J* = 3 Hz, 2 H, endo CH_2), 1.67 (s, 6 H, CH_3), 1.83 (s, 6 H, CH_3), 2.60 (d, 2 H, exo CH_2), 4.34 (s, 2 H, CH of Cp ring), 4.45 (s, CH of pentadienyl ring), 5.17 (s, CH of Cp ring). Anal. Calcd for $C_{14}H_{22}Ru$: C, 58.11; H, 6.69. Found: C, 58.29; H, 7.12.

Table I. Structure Determination Summary

	9	11
Crystal Data		
empirical formula	$C_{14}H_{22}Ru$	$C_{14}H_{18}Ru$
cryst size (mm)	0.30 × 0.30 × 0.30	0.30 × 0.25 × 0.15
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
unit cell dimens		
a (Å)	8.5945(17)	10.332(3)
b (Å)	13.3257(31)	8.807(2)
c (Å)	12.0851(22)	13.884(3)
β (deg)	110.670(46)	106.27(2)
vol (Å^3)	1294.99(46)	1212.8(5)
Z	4	4
fw	291.4	287.4
dens (calc) (Mg/m^3)	1.495	1.574
abs coeff (mm^{-1})	1.156	1.234
F(000)	600	584
Data Collection		
diffractometer used	Siemens R3m/V	Siemens R3m/V
radiation; λ (Å)	Mo Kα; 0.710 73	Mo Kα; 0.710 73
temp (K)	298	298
monochromator	highly oriented graphite crystal	
2θ range (deg)	5.0–45.0	5.0–45.0
scan type	2θ–θ	2θ–θ
scan speed (deg/min)	constant; 2.00 in ω	
scan range (ω) (deg)	0.65 plus Kα separation	
bckgd measmt	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time	
std reflns	3 measured every 97 reflns	
index ranges	$-9 \le h \le 9, -14 \le k \le 14, -13 \le l \le 13$	$-11 \le h \le 11, -9 \le k \le 9, -14 \le l \le 14$
no. of reflns collcd	6764	6373
no. of ind reflns	1693 (R_{int} = 4.36%)	1592 (R_{int} = 3.45%)
no. of obs reflns	1490 ($F > 6.0\sigma(F)$)	1357 ($F > 4.0\sigma(F)$)
abs corr	semiempirical	semiempirical
min/max transm	0.2700/0.4924	0.5324/0.7458
Solution and Refinement		
system used	Siemens SHELXTL PLUS (VMS)	
solution	direct methods	
refinement method	full-matrix least squares	
quantity minimized	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
extinction coeff	$\chi = 0.0004(4)$ where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$	$\chi = 0.00043(11)$ where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
H atoms	riding model, fixed isotropic *U*	
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0006F^2$	$w^{-1} = \sigma^2(F) + 0.0004F^2$
no. of param refined	225	147
final *R* indices (obs data) (%)	$R = 3.47, R_w = 4.77$	$R = 4.09, R_w = 4.11$
R indices (6.0σ data) (%)	$R = 3.09, R_w = 3.52$	$R = 3.31, R_w = 3.13$
goodness of fit	1.39	1.28
largest and mean Δ/σ	0.001, 0.000	0.004, 0.001
data-to-param ratio	7.5:1	10.8:1
largest diff peak (e Å^{-3})	0.82	1.10
largest diff hole (e Å^{-3})	–0.58	–0.87

Pyrolysis of 0.0394 g (0.14 mmol) of the mixture described above yielded 0.0142 g (36% yield) of bis(1,3-dimethylcyclopentadienyl)ruthenium (11). ^1H NMR (C_6D_6): δ 1.78 (s, 6 H, CH_3), 4.34 (s, 2 H), 4.37 (s, 1 H). Anal. Calcd for $C_{14}H_{18}Ru$: C, 58.52; H, 6.31. Found: C, 58.45; H, 6.22.

Structural Determination. A single crystal of bis(η^5-2,4-dimethylpentadienyl)ruthenium (9) and bis(1,3-dimethylcyclopentadienyl)ruthenium (11) suitable for study by X-ray diffraction was selected from sublimed samples and mounted in sealed capillaries.[2] Data for both crystals were collected on a Siemens R3m/V diffractometer. Solution and refinement were performed using Siemens SHELXTL PLUS (VMS) software. Parameters for data collection and structural quality are summarized in Table I. Both structures were solved using direct methods and refined

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for 9

	x	y	z	U(eq)[a]
Ru(1)	2216(1)	1283(1)	1983(1)	36(1)
C(1)	3851(6)	2515(4)	1874(5)	48(2)
C(2)	3601(6)	2565(3)	2961(4)	45(2)
C(3)	1966(6)	2613(3)	3002(4)	45(2)
C(4)	477(6)	2463(3)	2053(4)	49(2)
C(5)	391(6)	2321(4)	866(4)	54(2)
C(6)	5068(6)	2502(5)	4122(5)	62(2)
C(7)	−1099(7)	2303(5)	2329(7)	64(3)
C(11)	2818(7)	242(4)	796(4)	56(2)
C(12)	3987(5)	107(3)	1956(4)	45(2)
C(13)	3539(6)	−53(3)	2957(4)	48(2)
C(14)	1880(5)	−6(3)	2986(4)	46(2)
C(15)	496(6)	48(4)	1943(5)	49(2)
C(16)	5811(6)	267(4)	2173(6)	61(2)
C(17)	1689(8)	42(4)	4184(5)	63(2)
H(1A)	5072(52)	2303(28)	1900(33)	39(10)
H(1B)	3348(68)	2924(41)	1297(48)	78(17)
H(3)	1916(41)	2633(26)	3717(33)	26(9)
H(2A)	6012(79)	2087(45)	4046(52)	98(18)
H(5A)	−628(53)	2107(28)	335(35)	38(10)
H(5B)	900(56)	2824(33)	536(39)	57(12)
H(6A)	5396(81)	3194(54)	4315(58)	113(21)
H(6B)	4834(64)	2173(37)	4716(47)	74(16)
H(7A)	−1635(75)	2941(44)	2240(49)	91(18)
H(7B)	−915(59)	2154(37)	2949(44)	49(17)
H(7C)	−2060(72)	1838(45)	1470(51)	98(17)
H(11A)	1999(57)	−250(34)	507(39)	55(12)
H(11B)	3259(44)	497(26)	282(33)	33(10)
H(13)	4423(47)	−5(28)	3733(32)	26(9)
H(15A)	−596(61)	216(32)	1968(37)	53(12)
H(15B)	494(54)	−408(35)	1443(40)	55(13)
H(16A)	6288(62)	−328(40)	2223(43)	70(15)
H(16B)	6416(64)	609(39)	2868(49)	73(16)
H(16C)	6105(52)	616(34)	1523(40)	59(12)
H(17A)	750(75)	411(41)	4134(46)	82(17)
H(17B)	2567(55)	413(31)	4737(38)	47(11)
H(17C)	1438(70)	−651(47)	4396(49)	98(18)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for 11

	x	y	z	U(eq)[a]
Ru(1)	1293(1)	868(1)	3448(1)	29(1)
C(11)	−699(5)	692(6)	3687(4)	36(2)
C(12)	−490(5)	−596(6)	3134(4)	39(2)
C(13)	−311(5)	−60(6)	2215(4)	42(2)
C(14)	−412(5)	1556(6)	2206(4)	42(2)
C(15)	−652(5)	2023(6)	3116(4)	42(2)
C(16)	−896(6)	3631(7)	3404(5)	60(2)
C(17)	−552(5)	−2237(6)	3435(5)	54(2)
C(21)	2910(5)	1089(6)	4842(4)	36(2)
C(25)	2925(4)	2381(6)	4231(4)	37(2)
C(24)	3182(5)	1821(6)	3339(4)	39(2)
C(23)	3308(5)	216(6)	3412(4)	40(2)
C(22)	3135(4)	−256(6)	4345(4)	36(2)
C(27)	3288(5)	−1831(6)	4759(5)	54(2)
C(26)	2860(6)	4004(6)	4498(5)	54(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

by full-matrix least squares for which the function minimized was $\Sigma w(F_o - F_c)^2$ for which $w^{-1} = \sigma^2(F) + 0.006F^2$. Hydrogen atoms were located by the riding model with fixed isotropic U. Positional parameters for the non-hydrogen atoms in 9 and 11 are listed in Tables II and III.

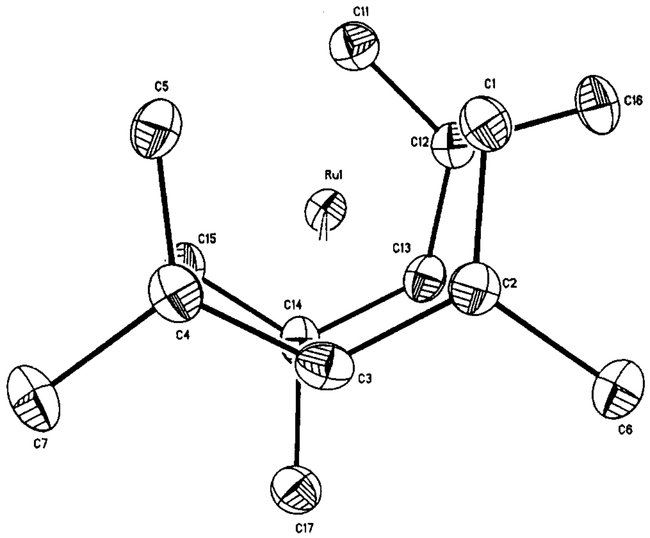

Figure 1. Crystal structure of Ru(η^5-2,4-$Me_2C_5H_5$)$_2$ (9) showing the gauche-eclipsed conformation.

Table IV. Bond Lengths (Å) for 9

Ru(1)–C(1)	2.195(5)	Ru(1)–C(2)	2.177(4)
Ru(1)–C(3)	2.212(5)	Ru(1)–C(4)	2.191(5)
Ru(1)–C(5)	2.168(5)	Ru(1)–C(11)	2.185(6)
Ru(1)–C(12)	2.193(5)	Ru(1)–C(13)	2.214(4)
Ru(1)–C(14)	2.180(5)	Ru(1)–C(15)	2.202(5)
C(1)–C(2)	1.406(8)	C(2)–C(3)	1.425(7)
C(2)–C(6)	1.522(6)	C(3)–C(4)	1.399(6)
C(4)–C(5)	1.423(8)	C(4)–C(7)	1.520(9)
C(11)–C(12)	1.419(6)	C(12)–C(13)	1.408(8)
C(12)–C(16)	1.510(7)	C(13)–C(14)	1.440(7)
C(14)–C(15)	1.397(6)	C(14)–C(17)	1.514(9)
C(1)–H(1A)	1.077(47)	C(1)–H(1B)	0.870(52)
C(5)–H(5A)	0.929(38)	C(5)–H(5B)	0.960(50)
C(11)–H(11A)	0.935(45)	C(11)–H(11B)	0.901(44)
C(15)–H(15A)	0.976(54)	C(15)–H(15B)	0.857(49)

Table V. Bond Angles (deg) for 9

C(1)–C(2)–C(3)	120.8(4)	C(1)–C(2)–C(6)	120.6(5)
C(3)–C(2)–C(6)	118.5(5)	C(2)–C(3)–C(4)	126.4(5)
C(3)–C(4)–C(5)	123.6(5)	C(3)–C(4)–C(7)	117.9(5)
C(5)–C(4)–C(7)	118.0(4)	C(11)–C(12)–C(13)	123.7(5)
C(11)–C(12)–C(16)	118.9(5)	C(13)–C(12)–C(16)	117.0(4)
C(12)–C(13)–C(14)	126.0(4)	C(13)–C(14)–C(15)	121.0(5)
C(13)–C(14)–C(17)	117.9(4)	C(15)–C(14)–C(17)	121.0(5)

Structural Results and Discussion

Structural studies of bis(η^5-2,4-dimethylpentadienyl)ruthenium (9) and bis(1,3-dimethylcyclopentadienyl)ruthenium (11) were undertaken to determine any unusual structural features which might contribute to the electrocyclic ring closure reaction, as well as to confirm the assignment of products from our earlier report on the stepwise ring closure reactions of 9. Ru(η^5-2,4-$Me_2C_5H_5$)$_2$ adopts a gauche-eclipsed structure similar to that for Ru(η^5-2,3,4-$Me_3C_5H_4$)$_2$ and M(η^5-2,4-$Me_2C_5H_5$)$_2$ (M = V, Cr, Fe) (Figure 1, Tables IV and V).[11b,12] The angle between two planes defined by (a) C(3), Fe, and the midpoint between C(1) and C(5) and (b) C(13), Fe, and the midpoint between C(11) and C(15) was found to be 50.5° compared to the idealized value of 60° and a value of 52.5° for Ru(η^5-2,3,4-$Me_3C_5H_4$)$_2$.[11b] The two pentadienyl ligand planes are bent relative to one another, with a tilt angle of 15.6°, slightly smaller than the tilt angle in Ru(η^5-2,3,4-$Me_3C_5H_4$)$_2$ (Figure 2). The average ruthenium-carbon distance of 2.188(6) Å is identical to that observed for Ru(η^5-2,3,4-$Me_3C_5H_4$)$_2$ (2.188(3) Å) and slightly shorter than that for Ru(C_5H_5)$_2$ (2.196(3) Å).[11b] The methyl substituents are bent toward the ruthenium atom by an average of 9.3 Å, similar to the tilt observed for the methyl groups in the 2 and 4 positions of Ru(η^5-2,3,4-$Me_3C_5H_4$)$_2$ and other bis-

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(12) Ernst, R. D. *Struct. Bonding* **1984**, *57*, 1.

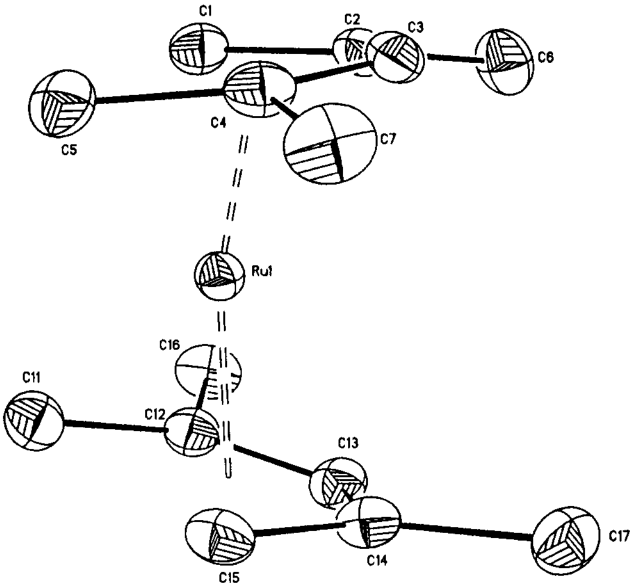


Figure 2. Perspective view and numbering scheme of Ru(η^5-2,4-$Me_2C_5H_5$)$_2$ (**9**) showing the tilt angle between the two dimethylpentadienyl ligand planes.

Table VI. Angle (deg) of Intercept of the C–H and C–C Vectors with the Corresponding Pentadienyl Plane for 9[a]

C(1)–H(1a)	−16.5	C(11)–H(11a)	47.1
C(1)–H(1b)	46.6	C(11)–H(11b)	−16.0
C(3)–H(3)	4.9	C(13)–H(13)	−10.4
C(5)–H(5a)	−11.6	C(15)–H(15a)	−14.2
C(5)–H(5b)	46.9	C(15)–H(15b)	54.8
C(1)–C(6)	−10.5	C(11)–C(16)	−8.4
C(5)–C(7)	−8.4	C(15)–C(17)	−9.8

[a] Negative values represent bonds that lie on the same side of the pentadienyl plane as the metal ion.

(2,4-dimethylpentadienyl) metal compounds.[12] Of greatest interest to the observed electrocyclic ring closure reaction are the relative positions of the hydrogens on the terminal carbons of the pentadienyl ligands. The H_{endo} atoms were observed to be bent away from the ruthenium by an average of 48.9°, while the H_{exo} atoms were bent down toward the ruthenium by an average of 14.6° (Table VI). Similar trends were observed for the corresponding hydrogens in Ru(η^5-2,3,4-$Me_3C_5H_4$)$_2$ (42 and 17°, respectively).

In contrast to Ru(η^5-2,4-$Me_2C_5H_5$)$_2$, Ru(η^5-1,3-$Me_2C_5H_3$)$_2$ adopts a cis-eclipsed structure (Figure 3, Tables VII and VIII). The angle between two planes defined by (a) C(11), Ru, and the midpoint between C(13) and C(14) and (b) C(21), Ru, and the midpoint between C(23) and C(24) was found to be 3.1° compared to the idealized value of 0° for a cis-eclipsed conformation.[12] The two pentadienyl ligand planes are essentially parallel, bent relative to one another by an angle of only 1.6°, less than the tilt of 3.7° observed for ferrocene (Figure 4).[11] The average ruthenium-carbon distance of 2.182(5) Å is shorter than that for ruthenocene and for **9**. The methyl substituents in **11** are bent away the ruthenium atom by an average of 1.4°.

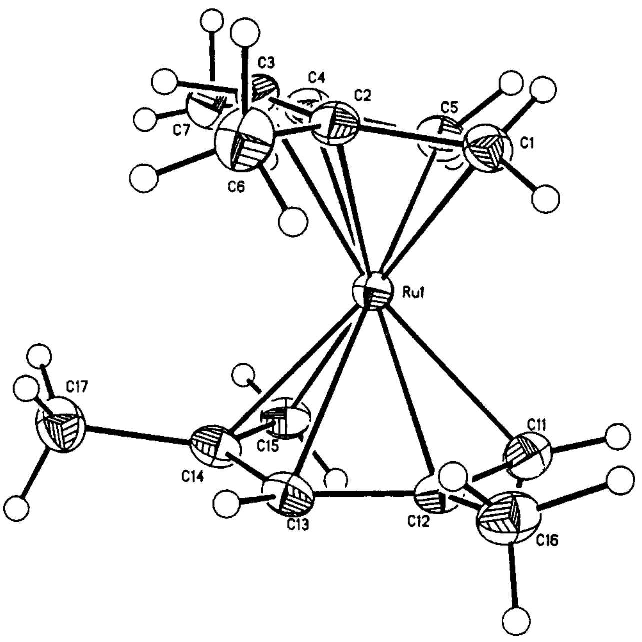


Figure 3. Perspective view of Ru(η^5-2,4-$Me_2C_5H_5$)$_2$ (**9**) showing the out-of-plane tilt of the hydrogen atoms on the dimethylpentadienyl ligands.

Table VII. Bond Lengths (Å) for 11

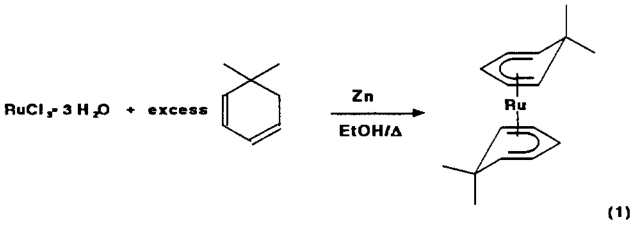
Ru(1)–C(11)	2.180(5)	Ru(1)–C(12)	2.190(5)
Ru(1)–C(3)	2.181(5)	Ru(1)–C(14)	2.177(5)
Ru(1)–C(15)	2.183(5)	Ru(1)–C(21)	2.183(4)
Ru(1)–C(22)	2.197(4)	Ru(1)–C(23)	2.174(5)
Ru(1)–C(24)	2.169(5)	Ru(1)–C(25)	2.184(4)
Ru(1)–Cp(10)	1.815	Ru(1)–Cp(20)	1.817
C(11)–C(12)	1.420(7)	C(11)–C(15)	1.424(7)
C(12)–C(13)	1.421(8)	C(12)–C(17)	1.511(8)
C(13)–C(14)	1.427(8)	C(14)–C(15)	1.414(8)
C(15)–C(16)	1.512(8)	C(21)–C(25)	1.423(7)
C(21)–C(22)	1.423(7)	C(25)–C(24)	1.426(8)
C(25)–C(26)	1.488(7)	C(24)–C(23)	1.420(7)
C(23)–C(22)	1.418(8)	C(22)–C(27)	1.492(7)

Table VIII. Bond Angles (deg) for 11

C(11)–C(12)–C(13)	107.3(4)	C(12)–C(11)–C(15)	108.8(5)
C(11)–C(12)–C(17)	126.2(5)	C(13)–C(12)–C(17)	126.3(5)
C(12)–C(13)–C(14)	108.1(5)	C(13)–C(14)–C(15)	108.2(5)
C(11)–C(15)–C(14)	107.5(5)	C(11)–C(15)–C(16)	126.1(6)
C(14)–C(15)–C(16)	126.3(5)	C(25)–C(21)–C(22)	110.2(5)
C(21)–C(25)–C(24)	106.1(4)	C(21)–C(25)–C(26)	127.3(5)
C(24)–C(25)–C(26)	126.4(5)	C(25)–C(24)–C(23)	108.5(5)
C(24)–C(23)–C(22)	109.0(5)	C(21)–C(22)–C(23)	106.2(4)
C(21)–C(22)–C(27)	126.9(5)	C(23)–C(22)–C(27)	126.7(5)

Synthetic Results and Discussion

Reaction of ruthenium trichloride hydrate with excess 6,6-dimethylcyclohexadiene and zinc in refluxing ethanol afforded bis(6,6-dimethylcyclohexadienyl)ruthenium (**3**) in 28% yield, comparable to yields reported for (2,4-$Me_2C_5H_7$)$_2$Ru (reaction 1). Compound **3** was isolated as a pale yellow, air stable solid but could not be sublimed at temperatures up to 150 °C/10^{-2} Torr. Two new ruthenium compounds, (pentamethylcyclopentadienyl)(2,4-di-*tert*-butylpentadienyl)ruthenium (**4**) and (pentamethylcyclopentadienyl)(6,6-dimethylcyclohexadienyl)ruthenium (**5**) were prepared in 10–36% yields by the recently reported reduction of [Cp*$RuCl_2$]$_n$ with zinc in



(1)

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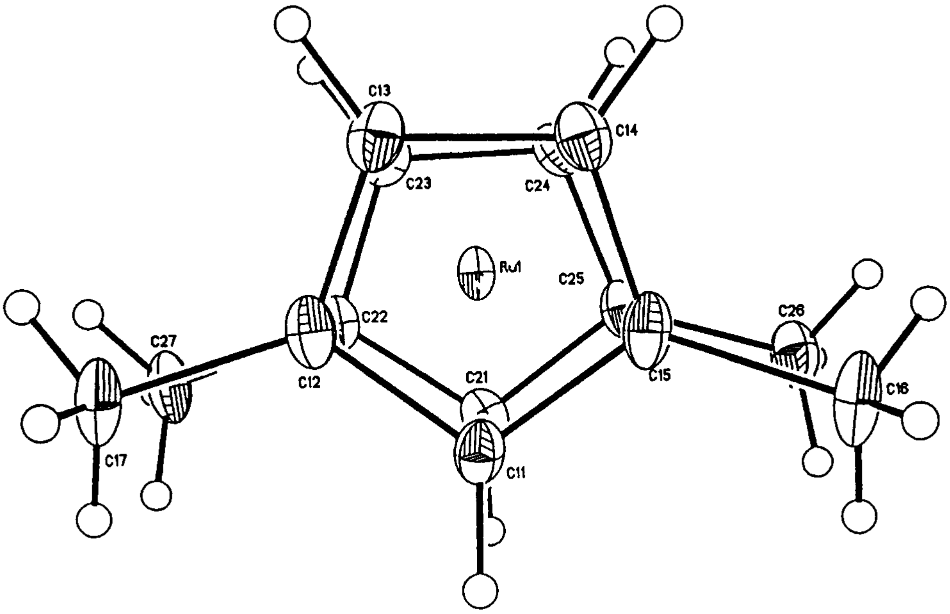
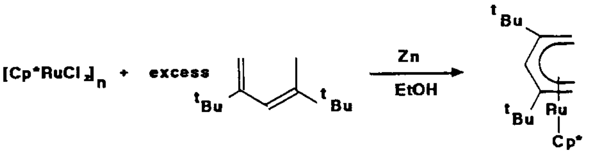


Figure 4. Crystal structure of Ru(η^5-1,3-$Me_2C_5H_3$)$_2$ (11) showing the cis-eclipsed conformation.

the presence of pentadiene derivatives (reactions 2 and 3).[10] The yields were not optimized in either case.



(2)

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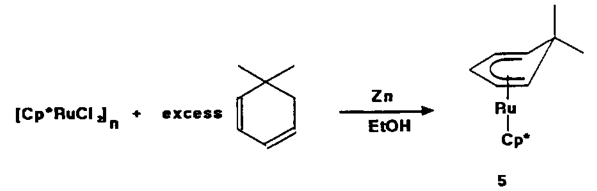

(3)

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Compounds 4 and 5 were found to be relatively air stable as solids and could be readily sublimed (80 °C/10^{-2} Torr). Thermolysis of compounds 1, 2, and 4 by passage through a hot tube at 400–450 °C and 0.1 Torr led to the isolation of three unsymmetrical ruthenocene derivatives 6–8 (reactions 4–6) as white, air stable solids in yields ranging from 17 to 53%.

The validity of Woodward–Hoffman rules for predicting the course of electrocyclic carbon–carbon bond forming reactions is well established. For similar reactions at transition metal centers, considerably fewer data are available. The formation of (η^5-1,3-$Me_2C_5H_5$)$_2$M (M = Ru, Os) from thermolysis of (η^5-2,4-$Me_2C_5H_7$)$_2$M was consistent with a thermally allowed, disrotatory C–C bond forming step, followed by C–H activation and loss of H_2 (Figure 6).

The crystal structures of (η^5-2,3,4-$Me_3C_5H_4$)$_2$Ru, (η^5-2,4-$Me_2C_5H_4$)$_2$Ru (9), and (η^5-2,4-$Me_2C_5H_4$)$_2$V indicated that the exo hydrogens of the terminal vinyl groups were pointed toward the ruthenium while the endo hydrogens were pointed away from the metal center. We have argued that during thermolysis of 9, it is the exo hydrogens of the terminal vinyl groups that are lost during formation of the 1,3-dimethylcyclopentadienyl rings of (η^5-1,3-$Me_2C_5H_3$)$_2$Ru (11). The observation of a similar reaction with (pentamethylcyclopentadienyl)(2,4-dimethylpentadienyl) ruthenium (1) forming 6 is not surprising, as 1 is closely related to the mixed (1,3-dimethylcyclopentadienyl)(2,4-dimethylpentadienyl)ruthenium (10). Our earlier work on the pyrolysis of 9 showed that 10 could be converted to 11. In structurally similar compounds, replacement of the endo hydrogens with alkyl groups was predicted to have little effect on a disrotatory reaction pathway.

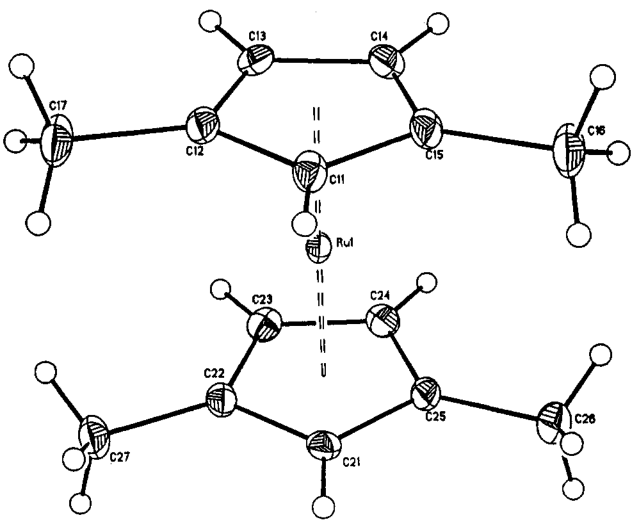


Figure 5. Perspective view and numbering scheme of Ru(η^5-1,3-$Me_2C_5H_3$)$_2$ (11) showing the tilt angle between the two dimethylcyclopentadienyl ligand planes.

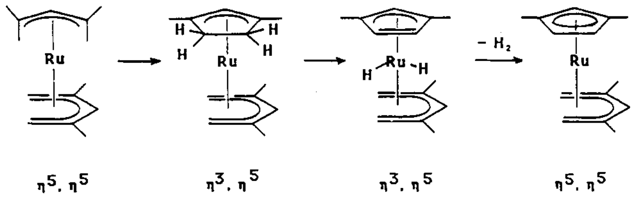
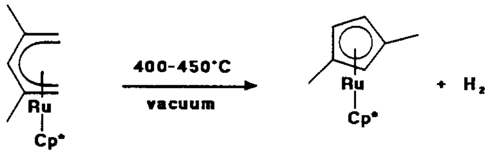


Figure 6. Proposed mechanism for electrocyclic reactions of pentadienylruthenium compounds.

(Pentamethylcyclopentadienyl)(cyclooctadienyl)ruthenium (2), bis(6,6-dimethylcyclohexadienyl)ruthenium (3), and (pentamethylcyclopentadienyl)(6,6-dimethylcyclohexadienyl)ruthenium (6) all have alkyl groups in the



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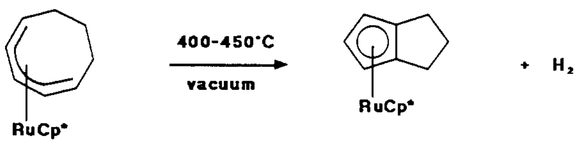

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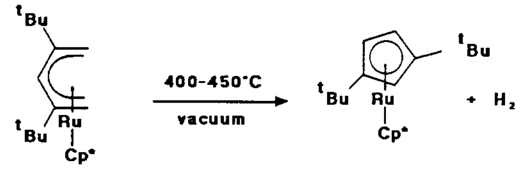

(6)

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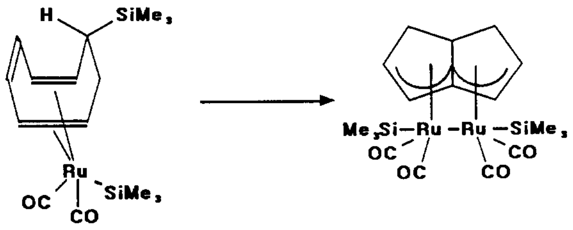
endo positions of the terminal carbon in the pentadienyl unit, presumably pointed away from the metal center, as judged by NMR spectroscopy. It was, therefore, not surprising to observe the ring closure of **2** to form (pentamethylcyclopentadienyl)(1,2-trihydropentalenyl)-ruthenium (**7**). The formation of two fused five membered rings is consistent with minimization of ring strain in five member rings. Organometallic compounds with trihydropentalene and related ligands have been isolated from reactions of $Re_2(CO)_{10}$ and $Co(acac)_3$ with cyclooctadiene.[13] Refluxing a substituted (η^4-cyclooctatriene)ruthenium complex, **12**, in hydrocarbon solvents produced also a pentalene bridged diruthenium compound **13** (reaction 7).[14] Pentamethylcyclopentadienyl(6,6-dimethylcyclohexadienyl)ruthenium (**5**) could be passed through a 450 °C oven unchanged and was recovered in ~80% yield from the exit of the oven. It is reasonable to expect that formation of a highly strained bicyclic system containing three and five membered fused ring systems is energetically unfavorable (reaction 8).



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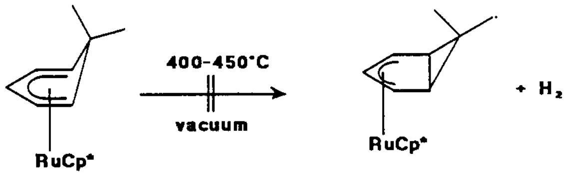

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Supplementary Material Available: Tables of crystal data, bond angles, thermal parameters, and atomic parameters and a crystal packing diagram (11 pages). Ordering information is given on any current masthead page. Crystal structure data are available from M.R.C.

OM9303461

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