R.B.N. thanks the National Science Foundation and Arthur D. Little for graduate fellowships.

Registry No. **1**, 116052-40-5; **3**, 11087-28-8; **4**, 12109-84-1; **5**, 116025-27-5; **6**, 116025-28-6; **7**, 116025-29-7; Bu_3SnH, 688-73-3; $CH_3CH(Cl)OCH_2CH_3$, 7081-78-9; Cp_2ZrCl_2, 1291-32-3; $CH_2{=}C{-}HOCH_2CH_3$, 109-92-2; Cp_2ZrHCl, 37342-97-5; $Cp_2Zr(OCH_2CH_3)_2$, 11087-35-7; (1-ethoxyethyl)tri-*n*-butylstannane, 116005-05-1.

Supplementary Material Available: A table of final thermal parameters for **1** (1 page); a listing of final observed and calculated structure factors for **1** (8 pages). Ordering information is given on any current masthead page.

Pentadienyl–Metal–Phosphine Chemistry. 17.[1] Syntheses, Structures, and Spectroscopy of Pentadienyl–Ruthenium–Phosphine Complexes

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Received March 29, 1988

The reaction of $RuCl_2(PPh_3)_3$ with pentadienyltributyltin produces (η^5-pentadienyl)$RuCl(PPh_3)_2$ (**1**), which serves as a convenient starting material for the synthesis of a large family of new pentadienyl–ruthenium–phosphine complexes. Treatment of **1** with 1 equiv of PMe_3, PMe_2Ph, PEt_3, or PEt_2Ph produces the mixed-phosphine complexes (η^5-pentadienyl)$RuCl(PR_3)(PPh_3)$ (**2a**, $PR_3 = PMe_3$; **2b**, $PR_3 = PMe_2Ph$; **2c**, $PR_3 = PEt_3$; **2d**, $PR_3 = PEt_2Ph$). Compound **2c** crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.435$ (2) Å, $b = 13.770$ (4) Å, $c = 18.237$ (5) Å, $\beta = 109.04$ (2)°, $V = 2715$ (1) Å^3, and $Z = 4$. This complex adopts a pseudooctahedral coordination geometry with the PEt_3 ligand residing under the open "mouth" of the pentadienyl ligand and the PPh_3 and Cl groups lying under the pentadienyl "edges". Treatment of **1** with 2 equiv of PEt_3, PEt_2Ph, or $PEtPh_2$ produces (η^5-pentadienyl)$RuCl(PR_3)_2$ (**3c**, $PR_3 = PEt_3$; **3d**, $PR_3 = PEt_2Ph$; **3e**, $PR_3 = PEtPh_2$). (η^5-Pentadienyl)$RuCl(PMe_2Ph)_2$ (**3b**) is obtained cleanly by reacting **2b** with one additional equivalent of PMe_2Ph. (η^5-Pentadienyl)$RuCl(PEt_3)_2$ (**3c**) [monoclinic, *Cc*, $a = 28.094$ (7) Å, $b = 10.003$ (2) Å, $c = 15.134$ (3) Å, $\beta = 98.54$ (2)°, $V = 4205$ (2) Å^3, $Z = 8$] and (η^5-pentadienyl)$RuCl(PEt_2Ph)_2$ (**3d**) [orthorhombic, $P2_12_12_1$, $a = 16.848$ (7) Å, $b = 19.409$ (4) Å, $c = 7.867$ (1) Å, $V = 2572$ (1) Å^3, $Z = 4$] have been structurally characterized. Both complexes adopt pseudooctahedral coordination geometries in which one phosphine resides under the pentadienyl "mouth" while the other phosphine and the chloro ligand lie under the pentadienyl "edges". Treatment of **1** with 3 equiv of PMe_3 produces (η^3-pentadienyl)$RuCl(PMe_3)_3$ (**4a**). (η^3-Pentadienyl)$RuCl(PMe_2Ph)_3$ (**4b**) is obtained upon treatment of **2b** with 2 equiv of PMe_2Ph. **4a** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.628$ (3) Å, $b = 13.662$ (3) Å, $c = 15.667$ (4) Å, $\beta = 91.59$°, $V = 2060$ (1) Å^3, and $Z = 4$. **4a**'s coordination geometry is pseudooctahedral with C1 and C3 of the pentadienyl ligand, the three phosphorus atoms, and the chlorine atom occupying the six coordination sites. The η^3-pentadienyl ligand adopts a W-shaped syn geometry. Both **4a** and **4b** react with $Ag^+O_3SCF_3^-$ or $Me^+O_3SCF_3^-$ to yield $[(\eta^5\text{-pentadienyl})Ru(PR_3)_3]^+O_3SCF_3^-$ (**5a**, $PR_3 = PMe_3$; **5b**, $PR_3 = PMe_2Ph$). **5a** crystallizes in the monoclinic space group $P2_1/m$ with $a = 8.622$ (2) Å, $b = 11.302$ (4) Å, $c = 12.676$ (2) Å, $\beta = 103.22$ (1)°, $V = 1202.6$ (6) Å^3, and $Z = 2$. It exhibits pseudooctahedral coordination geometry with one PMe_3 ligand under the open pentadienyl "mouth" and the other PMe_3 ligands under the pentadienyl "edges". Compounds **1**, **3**, and **5** undergo dynamic processes in solution involving rotation of their pentadienyl groups with respect to the metal–ligand framework. $\Delta G^{\ddagger}$'s for these processes have been determined from line-shape simulations of the variable-temperature ^{31}P NMR spectra.

Introduction

During the past several years, increased attention has been directed toward the synthesis and reactivity of transition-metal complexes containing the acyclic pentadienyl ligand.[2] Motivating this work has been the desire to exploit the unique features of the pentadienyl ligand, namely, (a) its ability to interconvert readily between η^5-, η^3-, and η^1-bonding modes and (b) its susceptibility to attack, both external nucleophilic attack and internal migratory attack.

Our own efforts in this area have focused on pentadienyl–metal–phosphine complexes of the late transition metals.[1] These electron-rich molecules may ultimately function as catalysts for the activation and functionalization of small molecules such as CH_4 and CO_2.[3] Further-

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[1] The previous papers in this series are the following: (a) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1983**, *2*, 1263. (b) Bleeke, J. R.; Hays, M. K. *Ibid.* **1984**, *3*, 506. (c) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1984**, *3*, 1422. (d) Bleeke, J. R.; Kotyk, J. J. *Ibid.* **1985**, *4*, 194. (e) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1986**, *5*, 635. (f) Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Ibid.* **1986**, *5*, 1642. (g) Bleeke, J. R.; Moore, D. A. *Inorg. Chem.* **1986**, *25*, 3522. (h) Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1986**, *5*, 2401. (i) Bleeke, J. R.; Hays, M. K. *Ibid.* **1987**, *6*, 486. (j) Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417. (k) Bleeke, J. R.; Hays, M. K. *Organometallics* **1987**, *6*, 1367. (l) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1987**, *6*, 1576. (m) Bleeke, J. R.; Donaldson, A. J.; Peng, W.-J. *Ibid.* **1988**, *7*, 33. (n) Bleeke, J. R.; Rauscher, D. J.; Moore, D. A. *Ibid.* **1987**, *6*, 2614. (o) Bleeke, J. R.; Hays, M. K.; Wittenbrink, R. J. *Ibid.*, **1988**, *7*, 1417. (p) Bleeke, J. R.; Donaldson, A. J. *Ibid.* **1988**, *7*, 1588.

[2] (a) Ernst, R. D. *Acct. Chem. Res.* **1985**, *18*, 56. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15. (c) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125. (d) Lush, S.-F.; Liu, R.-S. *Organometallics* **1986**, *5*, 1908.

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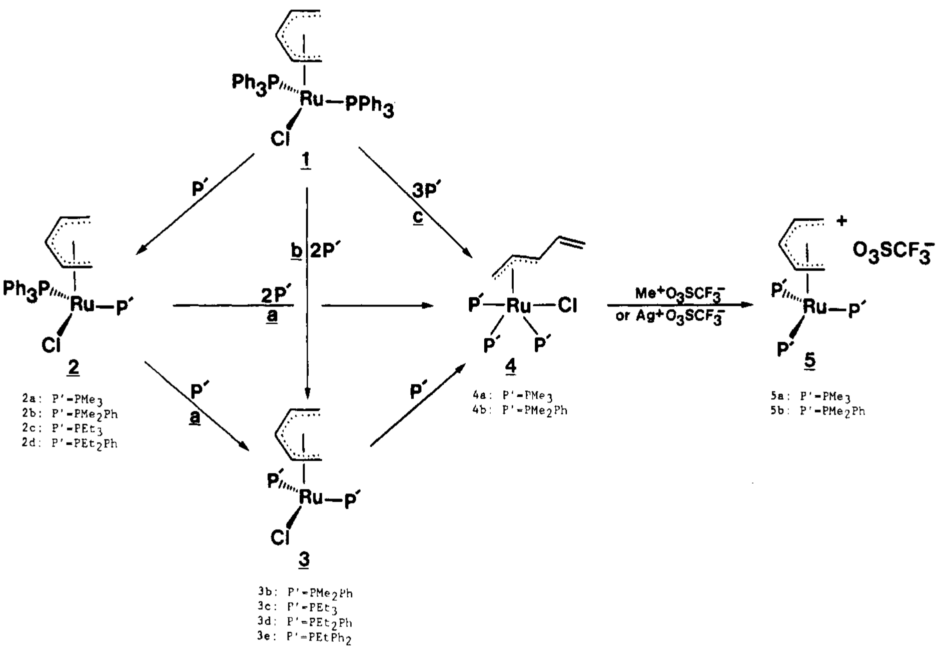
Scheme I[a]



[a] (a) preferred route for P′ = PMe_2Ph; (b) preferred route for P′ = PEt_3, PEt_2Ph, or $PEtPh_2$; (c) preferred route for P′ = PMe_3.

more, these complexes have potential utility in organic synthesis because their electron richness influences the regiochemistry of nucleophilic addition to the dienyl ligand.[1k,4]

In this contribution, we report syntheses, structures, and full spectral characterization of a new family of pentadienyl–ruthenium–phosphine complexes.

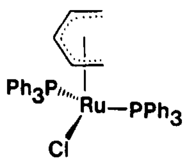
Results and Discussion

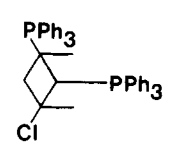
Synthesis and Spectroscopy of (η^5-Pentadienyl)RuCl(PPh_3)$_2$ (1). (η^5-Cyclopentadienyl)RuCl(PPh_3)$_2$ has been utilized very successfully as the synthetic precursor to a large family of cyclopentadienyl–ruthenium–phosphine complexes of formulae (η^5-cyclopentadienyl)RuCl(PR_3)(PPh_3), (η^5-cyclopentadienyl)RuCl(PR_3)$_2$, and [(η^5-cyclopentadienyl)Ru(PR_3)$_2$L]$^+$X$^-$.[5] For this reason, we decided to synthesize (η^5-pentadienyl)RuCl(PPh_3)$_2$ (1) and investigate its utility as a precursor to the analogous classes of pentadienyl complexes.

When we initiated this work, 1 had already been reported by Mann[6] as an intermediate in the reaction of Ru(H)(Cl)(PPh_3)$_3$ with 1,4-pentadiene in acetone. However, Mann reported that 1 could not be isolated under the reaction conditions because of its propensity to undergo coupling and dehydrogenation, producing (η^5-cyclopentadienyl)RuCl(PPh_3)$_2$. We, therefore, sought to synthesize 1 by a different route. Following the lead of Powell,[7] who had earlier synthesized (η^3-pentadienyl)RuCl(PMe_2Ph)$_2$(CO) by treating [$RuCl_2$(PMe_2Ph)$_2$CO]$_2$ with pentadienyltributyltin, we reacted $RuCl_2$(PPh_3)$_3$[8] with pentadienyltributyltin[9] and produced 1 in good yield. Under our reaction conditions, 1 was stable and exhibited no tendency toward coupling/dehydrogenation.

The NMR spectra of 1 were essentially identical with those reported by Mann.[6] However, Mann's contention that the high-field ^1H NMR shifts (δ −1.62, −0.33) of the anti (inner) protons on pentadienyl carbons C1 and C5 indicate an agostic interaction is clearly mistaken. Actually, these hydrogen atoms are probably pushed up and *away from* the ruthenium atom as a result of the atomic p_z orbitals on C1 and C5 bending toward the metal center to achieve better overlap (see, for example, the structure of (η^5-pentadienyl)RuCl(PEt_3)(PPh_3), which is reported herein). We have found that chemical shifts upfield from TMS are not uncommon for $H1_{anti}$ and $H5_{anti}$ in η^5-pentadienyl–metal–phosphine complexes.[1f–h]

The unsymmetrical ground-state structure of 1 (see side-on and overhead views below),





in which one PPh_3 ligand is situated under the open "mouth" of the pentadienyl group and the other PPh_3 ligand resides under a pentadienyl "edge", is clearly manifested in the low-temperature (−40 °C) ^{31}P, ^{13}C, and ^1H NMR spectra of 1.[10] Hence, 1 exhibits two phosphine ^{31}P NMR signals, five pentadienyl ^{13}C NMR signals, and

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(3) Other electron-rich polyenyl-metal complexes have recently been shown to activate C-H bonds in methane and C-O bonds in carbon dioxide. See, for example, (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (b) Jones, W. D.; Feher, F. *Ibid.* **1984**, *106*, 1650. (c) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *Ibid.* **1985**, *107*, 4358. (d) Green, M. L. H.; Joyner, D. S.; Wallis, J.; Bell, J. P. 190th National Meeting, American Chemical Society, Chicago, IL (Sept. 1985).

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(8) (a) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945. (b) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

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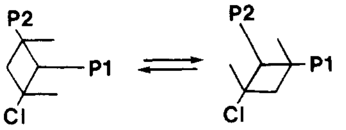
(10) We have observed similar unsymmetrical ground states in the structures of isoelectronic [(η^5-2,4-dimethylpentadienyl)Rh(PEt_3)$_2$Me]$^+$ (ref 1p) and [(η^5-2,4-dimethylpentadienyl)Ir(PEt_3)$_2$H]$^+$ (Bleeke, J. R.; Peng, W.-J., to be submitted for publication.

Table I. Positional Parameters and Their Estimated Standard Deviations for Non-Hydrogen Atoms in (η^5-Pentadienyl)RuCl(PEt$_3$)(PPh$_3$) (2c)

atom	*x*	*y*	*z*
Ru	0.13614 (1)	0.18552 (1)	0.12713 (1)
Cl	−0.00443 (5)	0.30747 (4)	0.15066 (4)
P1	0.16805 (5)	0.10794 (4)	0.24730 (3)
P2	0.29520 (5)	0.30195 (4)	0.16706 (3)
C1	0.2338 (2)	0.0693 (2)	0.0899 (2)
C2	0.2051 (2)	0.1454 (2)	0.0348 (2)
C3	0.0839 (3)	0.1817 (2)	−0.0019 (2)
C4	−0.0190 (3)	0.1567 (2)	0.0211 (2)
C5	−0.0215 (2)	0.0851 (2)	0.0746 (2)
C1P1	0.3283 (2)	0.1027 (2)	0.3146 (2)
C2P1	0.0827 (2)	0.1577 (2)	0.3091 (2)
C3P1	0.1237 (3)	−0.0210 (2)	0.2449 (2)
C4P1	0.3514 (3)	0.0566 (3)	0.3938 (2)
C5P1	−0.0540 (3)	0.1377 (3)	0.2828 (2)
C6P1	0.2061 (4)	−0.0951 (3)	0.2241 (2)
C1P2	0.2612 (2)	0.4213 (2)	0.1193 (1)
C2P2	0.3349 (2)	0.5019 (2)	0.1504 (2)
C3P2	0.3154 (3)	0.5893 (2)	0.1104 (2)
C4P2	0.2243 (2)	0.5975 (2)	0.0400 (2)
C5P2	0.1496 (2)	0.5192 (2)	0.0088 (2)
C6P2	0.1687 (2)	0.4314 (2)	0.0486 (1)
C7P2	0.4376 (2)	0.2694 (2)	0.1466 (1)
C8P2	0.4759 (2)	0.3185 (2)	0.0920 (1)
C9P2	0.5805 (2)	0.2883 (3)	0.0755 (2)
C10P2	0.6473 (2)	0.2090 (3)	0.1125 (2)
C11P2	0.6097 (3)	0.1586 (2)	0.1656 (2)
C12P2	0.5055 (2)	0.1880 (2)	0.1831 (2)
C13P2	0.3526 (2)	0.3425 (2)	0.2690 (1)
C14P2	0.2644 (2)	0.3748 (2)	0.3006 (1)
C15P2	0.2998 (3)	0.4047 (2)	0.3782 (2)
C16P2	0.4206 (3)	0.4010 (3)	0.4234 (2)
C17P2	0.5109 (3)	0.3717 (3)	0.3926 (2)
C18P2	0.4771 (2)	0.3424 (2)	0.3148 (2)

seven pentadienyl ^{1}H NMR signals at −40 °C. However, upon heating, the pentadienyl ligand begins to rotate with respect to the RuClP$_2$ framework (see below),



exchanging the two phosphines as well as the two sides of the pentadienyl ligand. The variable-temperature ^{31}P{^{1}H} NMR spectra of 1 are shown in Figure 1. Line-shape

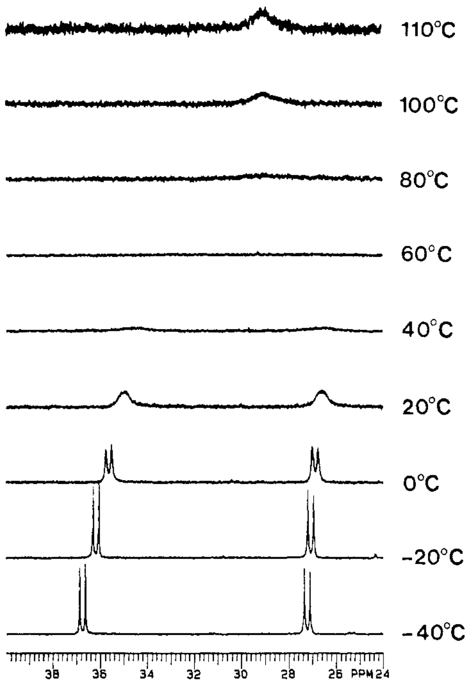


Figure 1. Variable-temperature ^{31}P{^{1}H} NMR spectra of (η^5-pentadienyl)RuCl(PPh$_3$)$_2$ (1).

analysis of these spectra yields a $\Delta G^‡$ for rotation of 14.3 ± 0.4 kcal/mol. This number compares favorably with Mann's reported barrier of 15 kcal/mol.[6]

Synthesis and Spectroscopy of (η^5-Pentadienyl)-RuCl(PR$_3$)(PPh$_3$) (2). Structure of (η^5-Pentadienyl)RuCl(PEt$_3$)(PPh$_3$) (2c). As shown in Scheme I, (η^5-pentadienyl)RuCl(PPh$_3$)$_2$ (1) reacts cleanly with 1 equiv of PMe$_3$, PMe$_2$Ph, PEt$_3$, or PEt$_2$Ph in toluene or tetrahydrofuran at 20 °C to produce (η^5-pentadienyl)RuCl-(PR$_3$)(PPh$_3$) (**2a**, PR$_3$ = PMe$_3$; **2b**, PR$_3$ = PMe$_2$Ph; **2c**, PR$_3$ = PEt$_3$; **2d**, PR$_3$ = PEt$_2$Ph). The solid-state structure of **2c** (see Figure 2) has been determined by X-ray crystallography. Positional parameters of non-hydrogen atoms are listed in Table I, while selected bond distances and angles are given in Table II. Perhaps the most striking feature of this pseudooctahedral complex is the relative orientation of the two phosphine ligands. The smaller PEt$_3$ ligand (cone angle = 132°)[11] is situated under the open

Table II. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (η^5-Pentadienyl)RuCl(PEt)$_3$(PPh$_3$) (2c)

		Bond Distances			
Ru–Cl	2.4572 (6)	P2–C13P2	1.844 (2)	C5P2–C6P2	1.391 (4)
Ru–P1	2.3570 (6)	C1–C2	1.414 (4)	C7P2–C8P2	1.387 (3)
Ru–P2	2.3547 (6)	C2–C3	1.420 (5)	C7P2–C12P2	1.402 (3)
Ru–C1	2.182 (3)	C3–C4	1.414 (5)	C8P2–C9P2	1.387 (4)
Ru–C2	2.151 (3)	C4–C5	1.394 (5)	C9P2–C10P2	1.377 (5)
Ru–C3	2.232 (3)	C1P1–C4P1	1.520 (4)	C10P2–C11P2	1.370 (5)
Ru–C4	2.192 (3)	C2P1–C5P1	1.514 (5)	C11P2–C12P2	1.389 (4)
Ru–C5	2.226 (3)	C3P1–C6P1	1.518 (6)	C13P2–C14P2	1.387 (4)
P1–C1P1	1.844 (3)	C1P2–C2P2	1.396 (3)	C13P2–C18P2	1.396 (3)
P1–C2P1	1.847 (3)	C1P2–C6P2	1.383 (3)	C14P2–C15P2	1.401 (4)
P1–C3P1	1.843 (3)	C2P2–C3P2	1.387 (4)	C15P2–C16P2	1.360 (5)
P2–C1P2	1.841 (2)	C3P2–C4P2	1.370 (5)	C16P2–C17P2	1.386 (5)
P2–C7P2	1.842 (2)	C4P2–C5P2	1.378 (4)	C17P2–C18P2	1.403 (4)
		Bond Angles			
Cl–Ru–P1	93.38 (2)	P1–Ru–C5	88.66 (9)	Ru–P1–C2P1	116.6 (1)
Cl–Ru–P2	87.94 (2)	P2–Ru–C1	99.99 (8)	Ru–P1–C3P1	117.2 (1)
Cl–Ru–C1	170.26 (8)	P2–Ru–C3	104.86 (8)	Ru–P2–C1P2	116.04 (7)
Cl–Ru–C3	103.58 (9)	P2–Ru–C5	172.60 (9)	Ru–P2–C7P2	114.61 (8)
Cl–Ru–C5	90.89 (8)	C1–Ru–C3	69.1 (1)	Ru–P2–C13P2	120.19 (7)
P1–Ru–P2	98.70 (2)	C1–Ru–C5	80.5 (1)	C1–C2–C3	124.1 (3)
P1–Ru–C1	90.99 (9)	C3–Ru–C5	68.3 (1)	C2–C3–C4	123.5 (3)
P1–Ru–C3	151.25 (7)	Ru–P1–C1P1	117.07 (9)	C3–C4–C5	126.1 (3)

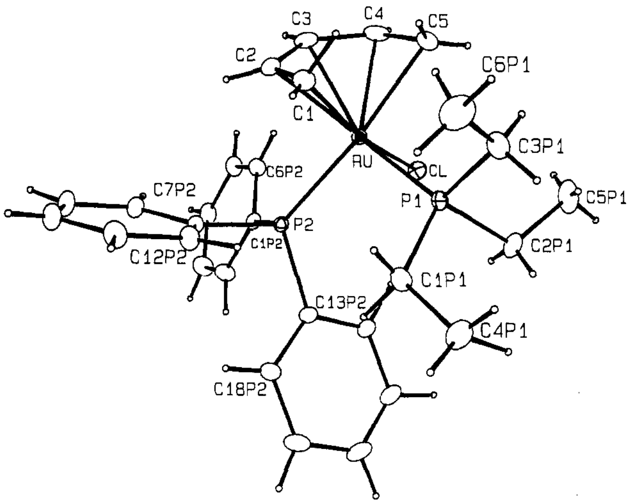


Figure 2. ORTEP drawing of (η^5-pentadienyl)RuCl(PEt$_3$)(PPh$_3$) (**2c**) with 15% thermal ellipsoids.

pentadienyl "mouth" while the larger PPh$_3$ ligand (cone angle = 145°)[11] occupies an "edge" position. Although one might naively expect the larger ligand (PPh$_3$) to reside in the roomier "mouth" site, the observed orientation allows the PEt$_3$ ligand to bend up into the "mouth"; hence, P1 (PEt$_3$) resides 2.322 (1) Å from the pentadienyl plane while P2 (PPh$_3$) is situated 3.171 (1) Å from that plane. The pronounced twisting of H1$_{anti}$ and H5$_{anti}$ up and away from the ruthenium atom (vide supra) can be seen quite clearly in Figure 2. These atoms reside 0.82 (4) and 0.58 (4) Å, respectively, out of the pentadienyl plane.

The similarity of the NMR spectra of **2a**, **2b**, and **2d** to those of **2c** lead us to believe that all of these mixed-phosphine complexes have the same pentadienyl orientation—PPh$_3$ in an "edge" site and PR$_3$ in the "mouth" site. The ^{31}P NMR chemical shifts of the PPh$_3$ ligands in these four compounds vary by only 4.7 ppm.

Attempts to synthesize (η^5-pentadienyl)RuCl(PEtPh$_2$)(PPh$_3$) (**2e**) by reacting **1** with 1 equiv of PEtPh$_2$ at 20 °C resulted in complex mixtures of products. Examination of these mixtures by NMR revealed the presence of two isomers of **2e** (probably one with PEtPh$_2$ under the pentadienyl "mouth" and the other with PPh$_3$ under the "mouth"), together with smaller quantities of unreacted **1** and the disubstituted product (η^5-pentadienyl)RuCl(PEtPh$_2$)$_2$ (**3e**). Apparently, the size difference between PEtPh$_2$ and PPh$_3$ is not sufficient to produce a strong preference for just one rotational isomer of **2e**.

Synthesis and Spectroscopy of (η^5-Pentadienyl)RuCl(PR$_3$)$_2$ (3). Structures of (η^5-Pentadienyl)RuCl(PEt$_3$)$_2$ (3c) and (η^5-Pentadienyl)RuCl(PEt$_2$Ph)$_2$ (3d). As shown in Scheme I, the fully phosphine-substituted complexes (η^5-pentadienyl)RuCl(PR$_3$)$_2$ (**3b**, PR$_3$ = PMe$_2$Ph; **3c**, PR$_3$ = PEt$_3$; **3d**, PR$_3$ = PEt$_2$Ph; **3e**, PR$_3$ = PEtPh$_2$) can be synthesized in two ways: (a) treatment of (η^5-pentadienyl)RuCl(PPh$_3$)$_2$ (**1**) with 2 equiv of PR$_3$ in refluxing tetrahydrofuran or toluene or (b) treatment of (η^5-pentadienyl)RuCl(PR$_3$)(PPh$_3$) (**2**) with 1 equiv of PR$_3$ in refluxing tetrahydrofuran or toluene. For **3c**, **3d**, and **3e**, method a works well and is the procedure of choice. For **3b**, method b leads cleanly to the desired product while method a produces some (η^3-pentadienyl)RuCl(PMe$_2$Ph)$_3$ (**4b**) (vide infra) and [(η^5-pentadienyl)Ru(PMe$_2$Ph)$_3$]$^+$Cl$^-$ as contaminants. Neither method leads to the clean synthesis of (η^5-pentadienyl)RuCl(PMe$_3$)$_2$ (**3a**), although a small quantity of **3a** has been observed by NMR in situ upon treatment of (η^5-pentadienyl)RuCl(PMe$_3$)(PPh$_3$) (**2a**) with 1 equiv of PMe$_3$.[12]

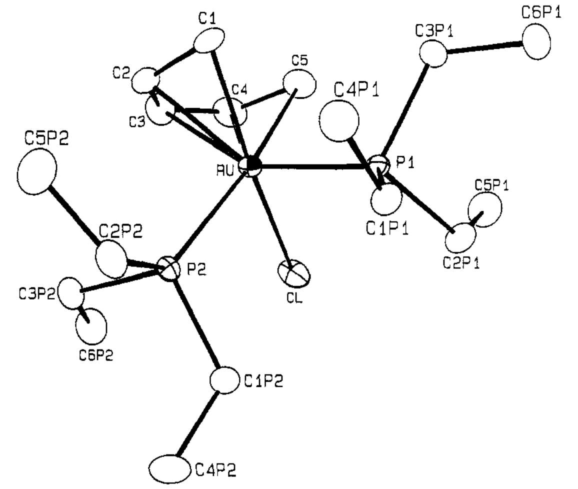


Figure 3. ORTEP drawing of (η^5-pentadienyl)RuCl(PEt$_3$)$_2$ (**3c**) with 15% thermal ellipsoids. There were two independent molecules per asymmetric unit. Molecule 1 is shown.

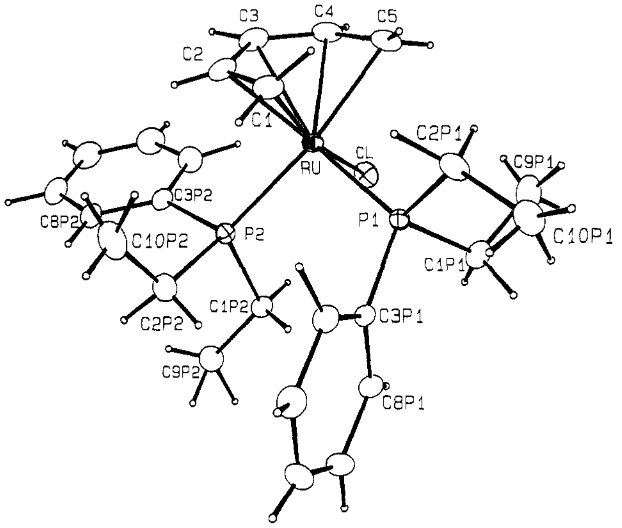


Figure 4. ORTEP drawing of (η^5-pentadienyl)RuCl(PEt$_2$Ph)$_2$ (**3d**) with 15% thermal ellipsoids.

The solid-state structures of both **3c** and **3d** have been determined by X-ray diffraction (Figures 3 and 4). Positional parameters of non-hydrogen atoms are listed in Tables III and V, while significant bond distances and angles are given in Tables IV and VI. Like **1**, compounds **3c** and **3d** have unsymmetrical structures in which one phosphine resides under the pentadienyl "mouth" while the other lies under a pentadienyl "edge". The solution-phase NMR spectra of **3b–e** at −40 °C reflect this unsymmetrical ground-state structure. However, as with **1**, heating causes the pentadienyl ligand to rotate with respect to the RuClP$_2$ framework. This, in turn, exchanges the phosphines and the sides of the pentadienyl ligand. Simulations of the variable-temperature ^{31}P{^{1}H} NMR spectra of **3b**, **3c**, **3d**, and **3e** yield $\Delta G^{\ddagger}$'s for the rotational process of 16.2 (3), 17.8 (4), 16.9 (4), and 14.4 (4) kcal/mol, respectively.

Synthesis and Spectroscopy of (η^3-Pentadienyl)RuCl(PR$_3$)$_3$ (4). Structure of (η^3-Pentadienyl)RuCl(PMe$_3$)$_3$ (4a). Addition of 3 equiv of PMe$_3$ to (η^5-pentadienyl)RuCl(PPh$_3$)$_2$ (**1**) in refluxing tetrahydrofuran pro-

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(11) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(12) (η^3-Pentadienyl)RuCl(PMe$_3$)$_3$ (**4a**) and unreacted **2a** are the principal products of this reaction.

Table III. Positional Parameters and Their Estimated Standard Deviations for Non-Hydrogen Atoms in (η^5-Pentadienyl)RuCl(PEt_3)$_2$ (3c)[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ru	0.000	0.19141 (3)	0.000	Ru′	0.25056 (1)	0.20765 (3)	−0.29040 (2)
Cl	0.01803 (6)	0.0265 (2)	0.1226 (1)	Cl′	0.27030 (5)	0.1844 (1)	−0.44377 (8)
P1	−0.02979 (4)	0.3497 (1)	0.08949 (7)	P1′	0.22362 (4)	−0.0122 (1)	−0.28649 (7)
P2	−0.07186 (4)	0.0763 (1)	−0.04265 (8)	P2′	0.17742 (4)	0.2994 (1)	−0.35511 (8)
C1	−0.0006 (2)	0.3398 (6)	−0.1066 (3)	C1′	0.2487 (2)	0.2332 (6)	−0.1480 (3)
C2	0.0078 (2)	0.2113 (6)	−0.1395 (4)	C2′	0.2570 (2)	0.3567 (5)	−0.1880 (3)
C3	0.0449 (2)	0.1242 (7)	−0.1010 (5)	C3′	0.2938 (2)	0.3834 (6)	−0.2385 (4)
C4	0.0748 (2)	0.1495 (8)	−0.0205 (6)	C4′	0.3248 (2)	0.2816 (6)	−0.2642 (4)
C5	0.0763 (2)	0.2678 (8)	0.0304 (6)	C5′	0.3275 (2)	0.1497 (7)	−0.2361 (4)
C1P1	−0.0937 (2)	0.3982 (6)	0.0696 (3)	C1P1′	0.1611 (2)	−0.0491 (6)	−0.2731 (4)
C2P1	−0.0221 (2)	0.3112 (6)	0.2091 (4)	C2P1′	0.2285 (2)	−0.1145 (5)	−0.3857 (3)
C3P1	−0.0002 (2)	0.5137 (5)	0.0867 (4)	C3P1′	0.2572 (2)	−0.1114 (5)	−0.1951 (3)
C4P1	−0.1102 (2)	0.4770 (6)	−0.0149 (4)	C4P1′	0.1484 (2)	−0.0119 (8)	−0.1818 (5)
C5P1	0.0292 (3)	0.3116 (9)	0.2558 (4)	C5P1′	0.2793 (2)	−0.1525 (7)	−0.3973 (4)
C6P1	−0.0146 (3)	0.6224 (7)	0.1479 (4)	C6P1′	0.2427 (3)	−0.2558 (6)	−0.1873 (4)
C1P2	−0.0997 (2)	0.0128 (6)	0.0511 (4)	C1P2′	0.1509 (2)	0.2180 (6)	−0.4594 (4)
C2P2	−0.1245 (2)	0.1487 (7)	−0.1137 (4)	C2P2′	0.1247 (2)	0.3096 (6)	−0.2958 (5)
C3P2	−0.0647 (2)	−0.0749 (6)	−0.1092 (4)	C3P2′	0.1817 (2)	0.4747 (6)	−0.3896 (4)
C4P2	−0.1445 (3)	−0.071 (1)	0.0295 (6)	C4P2′	0.1062 (3)	0.2807 (9)	−0.5134 (6)
C5P2	−0.1167 (3)	0.1937 (9)	−0.2067 (5)	C5P2′	0.1307 (2)	0.3933 (8)	−0.2105 (5)
C6P2	−0.348 (3)	−0.1829 (7)	−0.0606 (6)	C6P2′	0.2131 (3)	0.5002 (7)	−0.4617 (5)

[a] There were two independent molecules per asymmetric unit. Atoms in molecule 1 have unprimed labels, while those in molecule 2 have primed labels.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (η^5-Pentadienyl)RuCl(PEt_3)$_2$ (3c)[a]

		Bond Distances			
Ru–Cl	2.478 (2)	C3–C4	1.40 (1)	P1′–C1P1′	1.834 (6)
Ru–P1	2.319 (1)	C4–C5	1.41 (1)	P1′–C2P1′	1.839 (5)
Ru–P2	2.330 (1)	C1P1–C4P1	1.514 (9)	P1′–C3P1′	1.843 (5)
Ru–C1	2.191 (6)	C2P1–C5P1	1.51 (1)	P2′–C1P2′	1.832 (6)
Ru–C2	2.164 (7)	C3P1–C6P1	1.522 (9)	P2′–C2P2′	1.845 (7)
Ru–C3	2.227 (7)	C1P2–C4P2	1.51 (1)	P2′–C3P2′	1.839 (7)
Ru–C4	2.210 (6)	C2P2–C5P2	1.52 (1)	C1′–C2′	1.41 (1)
Ru–C5	2.257 (8)	C3P2–C6P2	1.49 (1)	C2′–C3′	1.40 (1)
P1–C1P1	1.842 (6)	Ru′–Cl′	2.476 (1)	C3′–C4′	1.43 (1)
P1–C2P1	1.832 (6)	Ru′–P1′	2.329 (1)	C4′–C5′	1.38 (1)
P1–C3P1	1.843 (6)	Ru′–P2′	2.329 (1)	C1P1′–C4P1′	1.52 (1)
P2–C1P2	1.833 (6)	Ru′–C1′	2.178 (7)	C2P1′–C5P1′	1.51 (1)
P2–C2P2	1.844 (7)	Ru′–C2′	2.139 (6)	C3P1′–C6P1′	1.510 (9)
P2–C3P2	1.845 (7)	Ru′–C3′	2.213 (6)	C1P2′–C4P2′	1.528 (9)
C1–C2	1.41 (1)	Ru′–C4′	2.192 (7)	C2P2′–C5P2′	1.53 (1)
C2–C3	1.42 (1)	Ru′–C5′	2.271 (6)	C3P2′–C6P2′	1.52 (1)
		Bond Angles			
Cl–Ru–P1	93.93 (6)	Ru–P1–C2P1	115.7 (3)	P1′–Ru′–C5′	92.6 (2)
Cl–Ru–P2	87.17 (6)	Ru–P1–C3P1	113.0 (2)	P2′–Ru′–C1′	102.7 (2)
Cl–Ru–C1	168.8 (2)	Ru–P2–C1P2	114.1 (2)	P2′–Ru′–C3′	103.9 (2)
Cl–Ru–C3	103.9 (2)	Ru–P2–C2P2	123.7 (2)	P2′–Ru′–C5′	170.3 (2)
Cl–Ru–C5	89.5 (3)	Ru–P2–C3P2	113.3 (2)	C1′–Ru′–C3′	69.4 (3)
P1–Ru–P2	97.25 (5)	C1–C2–C3	124.6 (7)	C1′–Ru′–C5′	80.4 (3)
P1–Ru–C1	90.2 (2)	C2–C3–C4	123.9 (7)	C3′–Ru′–C5′	68.4 (3)
P1–Ru–C3	153.9 (2)	C3–C4–C5	126.4 (8)	Ru′–P1′–C1P1′	120.9 (2)
P1–Ru–C5	93.7 (3)	Cl′–Ru′–P1′	93.10 (5)	Ru′–P1′–C2P1′	116.1 (2)
P2–Ru–C1	102.6 (2)	Cl′–Ru′–P2′	87.10 (5)	Ru′–P1′–C3P1′	113.3 (2)
P2–Ru–C3	102.5 (2)	Cl′–Ru′–C1′	168.5 (2)	Ru′–P2′–C1P2′	114.0 (2)
P2–Ru–C5	168.8 (3)	Cl′–Ru′–C3′	102.7 (2)	Ru′–P2′–C2P2′	122.6 (3)
C1–Ru–C3	69.0 (3)	Cl′–Ru′–C5′	88.9 (2)	Ru′–P2′–C3P2′	113.8 (2)
C1–Ru–C5	79.9 (3)	P1′–Ru′–P2′	96.48 (5)	Cl′–C2′–C3′	125.6 (7)
C3–Ru–C5	67.9 (3)	P1′–Ru′–C1′	91.7 (2)	C2′–C3′–C4′	122.8 (7)
Ru–P1–C1P1	120.8 (2)	P1′–Ru′–C3′	154.7 (2)	C3′–C4′–C5′	127.1 (7)

[a] There were two independent molecules per asymmetric unit. The unprimed atom labels refer to molecule 1, while the primed labels refer to molecule 2.

duces (η^3-pentadienyl)RuCl(PMe_3)$_3$ (**4a**) (see Scheme I). The PMe_2Ph analogue of **4a**, (η^3-pentadienyl)RuCl(PMe_2Ph)$_3$ (**4b**), can be obtained cleanly from the reaction of (η^5-pentadienyl)RuCl(PMe_2Ph)(PPh_3) (**2b**) with 2 equiv of PMe_2Ph or from the reaction of (η^5-pentadienyl)RuCl(PMe_2Ph)$_2$ (**3b**) with 1 equiv of PMe_2Ph in hot (100 °C) toluene. NMR monitoring of these PMe_2Ph reaction solutions indicates that at 100 °C, **4b** and **3b** exist in a ~40:60 equilibrium mixture. However, upon cooling to 20 °C and standing for several days, the equilibrium gradually shifts to ~80:20 (**4b**:**3b**), allowing isolation of **4b**.

The solid-state structure of **4a**, determined by X-ray crystallography, is shown in Figure 5. Positional parameters of the non-hydrogen atoms are listed in Table VII, while significant bond distances and angles are given in Table VIII. The complex is pseudooctahedral with the three phosphorus atoms, the chlorine atom, and the pen-

Table V. Positional Parameters and Their Estimated Standard Deviations for Non-Hydrogen Atoms in (η^5-Pentadienyl)RuCl(PEt_2Ph)$_2$ (3d)

atom	*x*	*y*	*z*
Ru	−0.01073 (2)	−0.18262 (2)	−0.10643 (4)
Cl	−0.04581 (9)	−0.16772 (8)	−0.4091 (2)
P1	−0.11418 (7)	−0.11256 (6)	−0.0151 (2)
P2	0.08553 (7)	−0.09642 (6)	−0.1418 (1)
C1	0.0095 (4)	−0.2144 (3)	0.1557 (7)
C2	0.0726 (4)	−0.2375 (3)	0.0486 (7)
C3	0.0602 (4)	−0.2781 (3)	−0.0983 (8)
C4	−0.0144 (4)	−0.2924 (3)	−0.1690 (8)
C5	−0.0869 (4)	−0.2776 (3)	−0.0968 (9)
C1P1	−0.1886 (4)	−0.0881 (4)	−0.1723 (9)
C2P1	−0.1753 (3)	−0.1523 (3)	0.1514 (8)
C3P1	−0.0903 (3)	−0.0291 (2)	0.0805 (6)
C4P1	−0.0685 (3)	−0.0258 (3)	0.2535 (7)
C5P1	−0.0491 (4)	0.0371 (3)	0.3277 (8)
C6P1	−0.0490 (4)	0.0965 (3)	0.231 (1)
C7P1	−0.0713 (4)	0.0941 (3)	0.062 (1)
C8P1	−0.0927 (3)	0.0314 (3)	−0.0122 (7)
C9P1	−0.2377 (5)	−0.1480 (5)	−0.238 (1)
C10P1	−0.2465 (4)	−0.1117 (4)	0.214 (1)
C1P2	0.0588 (3)	−0.0294 (3)	−0.2975 (7)
C2P2	0.1221 (3)	−0.0427 (3)	0.0356 (7)
C3P2	0.1772 (3)	−0.1294 (3)	−0.2391 (6)
C4P2	0.1680 (4)	−0.1758 (3)	−0.3774 (7)
C5P2	0.2352 (5)	−0.1990 (4)	−0.4633 (9)
C6P2	0.3094 (4)	−0.1793 (4)	−0.4167 (9)
C7P2	0.3188 (4)	−0.1351 (4)	−0.2841 (9)
C8P2	0.2533 (3)	−0.1094 (3)	−0.1921 (8)
C9P2	0.1213 (4)	0.0254 (3)	−0.343 (1)
C10P2	0.1533 (5)	−0.0799 (5)	−0.1895 (9)

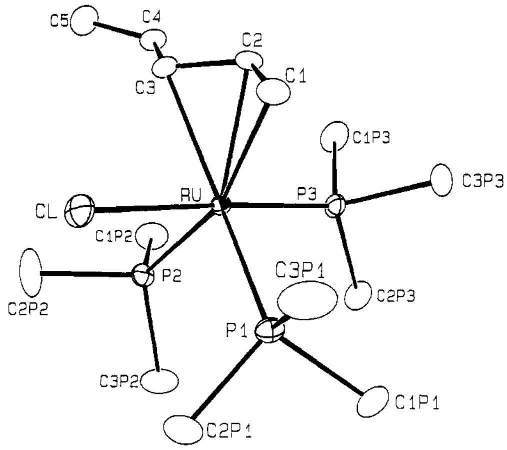

Figure 5. ORTEP drawing of (*syn*-η^3-pentadienyl)RuCl(PMe_3)$_3$ (**4a**) with 15% thermal ellipsoids.

tadienyl carbon atoms C1 and C3 occupying the six coordination sites. P1 and P2 reside trans to the pentadienyl ligand while P3 is trans to the chloro ligand. The η^3-pentadienyl ligand, whose "mouth" opens toward the chloro ligand, has a W-shaped syn geometry. Pentadienyl carbon atoms C1, C2, C3, and C4 are essentially coplanar, while C5 lies 0.374 (6) Å out of that plane and away from the ruthenium atom. Torsional angle C2–C3–C4–C5 is 158.1 (5)°.[13]

The solution-phase NMR spectra of both **4a** and **4b** are consistent with a *syn*-η^3-pentadienyl geometry. Particularly diagnostic is the relatively large anti coupling between H2 and H3, 10.5 Hz. In contrast, the syn coupling of $H1_{syn}$ to H2 is only 7 Hz. Powell's complex, (η^3-pentadienyl)RuCl(PMe_2Ph)$_2$(CO), also exhibits a large J_{H2-H3} (11 Hz) and, although not structurally characterized, is almost certainly a *syn*-η^3-pentadienyl complex.[7] The $^{31}P\{^1H\}$ NMR spectra of **4a** and **4b** each consist of three signals which do not broaden upon heating.[14]

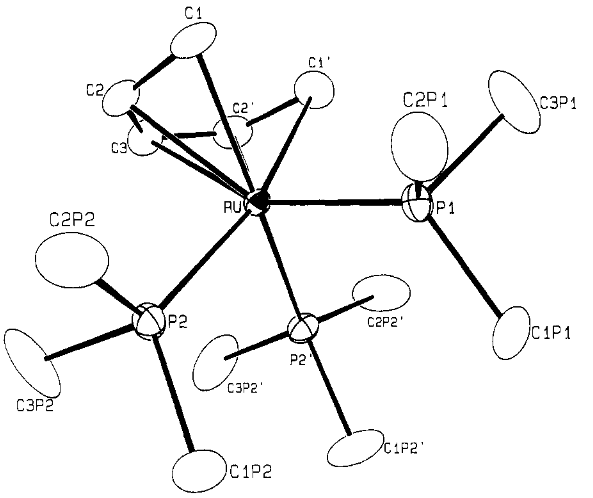

Figure 6. ORTEP drawing of the cation of [(η^5-pentadienyl)Ru(PMe_3)$_3$]$^+O_3SCF_3^-$ (**5a**) with 15% thermal ellipsoids. The molecule resided on a crystallographically imposed mirror plane which included atoms Ru, P1, C3, S, O1, C and F1. The primed atoms are located in the symmetry-generated portion of the molecule. The carbon atoms on phosphorus atom P1 were disordered about the mirror plane (two symmetry-related rotamers, each with one-half occupancy, were observed in the difference Fourier maps). One unique set of phosphine carbon atoms (C1P1, C2P1, C3P1) is shown.

Products of general formula (η^3-pentadienyl)RuCl(PR_3)$_3$ cannot be obtained with large phosphines (cone angle > 130°)[11] such as PEt_3, PEt_2Ph, or $PEtPh_2$. Apparently, steric crowding prevents three large phosphine ligands from coordinating to a single metal center.

Synthesis and Spectroscopy of [(η^5-Pentadienyl)Ru(PR_3)$_3$]$^+O_3SCF_3^-$ (5). Structure of [(η^5-Pentadienyl)Ru(PMe_3)$_3$]$^+O_3SCF^-$ (5a). As indicated in Scheme I, treatment of (η^3-pentadienyl)Ru(PR_3)$_3$Cl (**4a**, PR_3 = PMe_3; **4b**, PR_3 = PMe_2Ph) with $Ag^+O_3SCF_3^-$ or $Me^+O_3SCF_3^-$ in tetrahydrofuran results in removal of the chloro ligand and production of [(η^5-pentadienyl)Ru(PR_3)$_3$]$^+O_3SCF_3^-$ (**5a**, PR_3 = PMe_3; **5b**, PR_3 = PMe_2Ph). The solid-state structure of **5a** (see Figure 6) has been determined by X-ray crystallography. Positional parameters of non-hydrogen atoms are listed in Table IX while significant bond distances and angles are given in Table X. As expected, the cation's overall coordination geometry is pseudooctahedral with pentadienyl carbon atoms C1, C3, and C5 and phosphine atoms P1, P2, and P3 occupying the six coordination sites.

The $^{31}P\{^1H\}$ NMR spectra of **5a** and **5b** at 20 °C are A_2B patterns, which arise from the presence of two equivalent phosphines under the "edges" of the pentadienyl ligand and one unique phosphine under the "mouth". Upon heating, these signals coalesce to a single peak as a result of pentadienyl rotation. The $\Delta G^{\ddagger}$'s for rotation in **5a** and **5b**, as calculated from line-shape simulations of the variable-temperature $^{31}P\{^1H\}$ NMR spectra, are both 18 (1) kcal/mol.[15]

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres

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[13] Similar features are exhibited by other *syn*-η^3-pentadienyl ligands. See, for example, ref 1b, 1d, and 1o. See also: (a) Lee, G.-H.; Peng, S.-M.; Liao, M.-Y.; Liu, R.-S. *J. Organomet. Chem.* **1986**, *312*, 113. (b) Lee, G.-H.; Peng, S.-M.; Lee, T.-W.; Liu, R.-S. *Organometallics* **1986**, *5*, 2379.

[14] However, upon heating, **4b** establishes an equilibrium with **3b**.

[15] Isoelectronic complexes (η^5-pentadienyl)MnP_3, (η^5-pentadienyl)ReP_3, and (η^5-pentadienyl)FeP_3^+ undergo analogous pentadienyl ligand rotation. See ref 1f, 1g, and 1o.

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (η^5-Pentadienyl)RuCl($PEt_2Ph)_2$ (3d)

		Bond Distances			
RuCl	2.471 (2)	P2–C1P2	1.843 (6)	C4P1–C5P1	1.39 (1)
Ru–P1	2.324 (1)	P2–C2P2	1.848 (7)	C5P1–C6P1	1.38 (1)
Ru–P2	2.347 (1)	P2–C3P2	1.839 (6)	C6P1–C7P1	1.38 (1)
Ru–C1	2.180 (6)	C1–C2	1.43 (1)	C7P1–C8P1	1.40 (1)
Ru–C2	2.144 (6)	C2–C3	1.42 (1)	C1P2–C9P2	1.539 (9)
Ru–C3	2.206 (6)	C3–C4	1.40 (1)	C2P2–C10P2	1.50 (1)
Ru–C4	2.187 (6)	C4–C5	1.38 (1)	C3P2–C4P2	1.421 (9)
Ru–C5	2.247 (9)	C1P1–C9P1	1.52 (1)	C3P2–C8P2	1.390 (9)
P1–C1P1	1.825 (8)	C2P1–C10P1	1.52 (1)	C4P2–C5P2	1.39 (1)
P1–C2P1	1.835 (7)	C3P1–C4P1	1.412 (9)	C5P2–C6P2	1.36 (1)
P1–C3P1	1.831 (5)	C3P1–C8P1	1.382 (8)	C6P2–C7P2	1.36 (1)
				C7P2–C8P2	1.41 (1)
		Bond Angles			
Cl–Ru–P1	92.88 (6)	P1–Ru–C5	92.3 (3)	Ru–P1–C2P1	113.3 (2)
Cl–Ru–P2	88.14 (5)	P2–Ru–C1	101.9 (2)	Ru–P1–C3P1	118.7 (2)
Cl–Ru–C1	169.3 (2)	P2–Ru–C3	103.2 (2)	Ru–P2–C1P2	114.4 (2)
Cl–Ru–C3	104.8 (3)	P2–Ru–C5	169.6 (3)	Ru–P2–C2P2	122.9 (3)
Cl–Ru–C5	89.5 (3)	C1–Ru–C3	69.5 (3)	Ru–P2–C3P2	112.4 (2)
P1–Ru–P2	97.93 (5)	C1–Ru–C5	79.9 (4)	C1–C2–C3	123.1 (7)
P1–Ru–C1	89.4 (2)	C3–Ru–C5	67.6 (4)	C2–C3–C4	124.6 (6)
P1–Ru–C3	152.7 (2)	Ru–P1–C1P1	117.3 (3)	C3–C4–C5	126.1 (7)

Table VII. Positional Parameters and Their Estimated Standard Deviations for Non-Hydrogen Atoms in (*syn*-η^3-Pentadienyl)RuCl($PMe_3)_3$ (4a)

atom	*x*	*y*	*z*
Ru	0.23958 (3)	0.28971 (2)	0.41925 (2)
P1	0.0270 (1)	0.22204 (8)	0.45161 (8)
P2	0.3416 (1)	0.15848 (8)	0.34968 (7)
P3	0.3428 (1)	0.25290 (9)	0.54668 (7)
Cl	0.1038 (1)	0.3307 (1)	0.28287 (8)
C1	0.1773 (5)	0.4412 (3)	0.4561 (4)
C2	0.3210 (5)	0.4368 (3)	0.4461 (3)
C3	0.3856 (5)	0.4107 (3)	0.3686 (3)
C4	0.5351 (5)	0.4056 (3)	0.3631 (3)
C5	0.6041 (6)	0.4120 (5)	0.2916 (4)
C1P1	−0.0058 (6)	0.1484 (5)	0.5481 (3)
C2P1	−0.0565 (5)	0.1420 (4)	0.3717 (4)
C3P1	−0.1062 (5)	0.3148 (4)	0.4654 (5)
C1P2	0.5280 (5)	0.1408 (4)	0.3660 (4)
C2P2	0.3352 (8)	0.1643 (6)	0.2340 (3)
C3P2	0.2844 (6)	0.0329 (4)	0.3673 (4)
C1P3	0.5262 (5)	0.2845 (5)	0.5659 (3)
C2P3	0.3519 (6)	0.1258 (4)	0.5833 (3)
C3P3	0.2672 (7)	0.3130 (5)	0.6400 (3)

drybox or by standard vacuum or Schlenk techniques. Solvents were stored under nitrogen after being distilled from appropriate drying agents (tetrahydrofuran and diethyl ether, sodium and benzophenone; pentane, calcium hydride; dichloromethane and acetone, anhydrous magnesium sulfate; toluene, fresh cut sodium). Triphenylphosphine, tributyltin chloride, silver trifluoromethanesulfonate, methyl trifluoromethanesulfonate (Aldrich), 1,4-pentadiene (Wiley), deuteriated NMR solvents (1-g or 1-mL sealed ampules; MSD Isotopes and/or Cambrdige Isotope Laboratories), trimethylphosphine (Strem), ruthenium trichloride trihydrate, and the remaining phosphine ligands (Pressure Chemical) were all used without further purification. $RuCl_2(PPh_3)_3$[8] and pentadienyltributyltin[9] were prepared by the literature methods.

NMR experiments were performed on a Varian XL-300 or VXR-500 NMR spectrometer. All variable-temperature and 2D experiments were performed on the Varian XL-300. ^1H (300- and 500-MHz) and ^{13}C (75- and 125-MHz) spectra are referenced to TMS, while ^{31}P (120- and 200-MHz) spectra are referenced to H_3PO_4. Probe temperatures were calibrated by using the temperature dependence for the frequency separation of the ^1H resonances of the methyl and hydroxyl groups of neat methanol below ambient temperatures, and the ^1H resonances of the methylene and hydroxyl groups of neat ethylene glycol above ambient temperatures.[16]

In general, ^1H connectivities were determined from ^1H–^1H shift-correlated (COSY) 2D spectra; ^1H and ^{13}C peak assignments were made by using ^{13}C gated-decoupled spectra and ^{13}C–^1H shift-correlated (HETCOR) 2D spectra. In some cases, ^1H–^1H and ^1H–^{31}P coupling constants were determined by using ^1H *J*-resolved (HOM2DJ) 2D spectra and are so noted. Infrared spectra were recorded on a Perkin-Elmer 283B spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

All of the neutral compounds described below (**1**–**4**) are relatively air-stable as solids; however, exposure of their solutions to air causes decomposition after a few minutes. The cationic compounds (**5**) are air-stable both in the solid state and in solution.

(η^5-Pentadienyl)RuCl($PPh_3)_2$ (1). In a typical reaction, pentadienyltributyltin (0.95 g, 2.7 × 10^{-3} mol) was added to a dark red-brown filtered solution of $RuCl_2(PPh_3)_3$ (2.00 g, 2.09 × 10^{-3} mol) in 200 mL of tetrahydrofuran and refluxed for 1.0 h to yield a bright orange solution. The tetrahydrofuran was removed in vacuo to yield an oily orange solid which was taken up in 75 mL of diethyl ether and passed through on alumina column to remove any residual $RuCl_2(PPh_3)_3$. The diethyl ether was removed in vacuo, and the oily was vigorously washed with four aliquots of pentane (20 mL each), then dried, and filtered to yield 1.3–1.4 g (85–92% based on $RuCl_2(PPh_3)_3$) of crude **1** as a bright yellow-orange powder. This crude product often contained small amounts of tributyltin chloride as an impurity but was of sufficient quality for further reactions and was generally used without further purification. Analytically pure **1** was obtained by crystallizing from diethyl ether: ^1H NMR (stopped exchange, dichloromethane-d_2, −40 °C) δ 7.5–7.0 (multiplets, 30, PPh_3), 5.75 (unresolved dt, 1, H3), 5.16 (m, 1, H4), 4.16 (m, 1, H2), 3.08 (d, 1, $H5_{syn}$), 0.51 (d, 1, $H1_{syn}$), −0.33 (d, 1, $H5_{anti}$), −1.62 (d, 1, $H1_{anti}$); ^1H NMR (fast exchange, toluene-d_8, 100 °C) δ 7.60, 6.95 (br, 30, PPh_3), 5.41 (t, 1, H3), 4.75 (br, 2, H2 = H4), 2.1 (br, 2, $H1_{syn}$ = $H5_{syn}$), −0.50 (br, 2, $H1_{anti}$ = $H5_{anti}$); $^{13}C\{^1H\}$ NMR (stopped exchange, dichloromethane-d_2, −40 °C) δ 138.16 (d, J_{C-P} = 39 Hz, PPh_3), 134.04 (d, J_{C-P} = 10 Hz, PPh_3), 133.39 (d, J_{C-P} = 10 Hz, PPh_3), 129.14 (s, PPh_3), 128.73 (s, PPh_3), 127.78 (d, J_{C-P} = 9 Hz, PPh_3), 127.20 (d, J_{C-P} = 9 Hz, PPh_3), 109.50 (s, C4), 93.80 (d, J_{C-P} = 12 Hz, C3), 87.68 (s, C2), 55.26 (d, J_{C-P} = 22 Hz, C5), 42.03 (s, C1); $^{31}P\{^1H\}$ NMR (stopped exchange, dichloromethane-d_2, −40 °C) δ 38.0, 27.4 (doublets, J_{P-P} = 30 Hz); $^{31}P\{^1H\}$ NMR (fast exchange, toluene-d_8, 100 °C) δ 27.2 (br s). Anal. Calcd for $H_{37}C_{41}ClP_2Ru$: C, 67.62; H, 5.12. Found: C, 67.09; H, 5.67.

(η^5-Pentadienyl)RuCl(PMe_3)(PPh_3) (2a). Trimethylphosphine (0.24 g, 3.2 × 10^{-3} mol) was added to a solution of **1**

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(16) Von Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227.

(17) $J = |^2J_{P-H} + {}^4J_{P-H}|$ for methylated phosphine $H_nPP'H_n'$ spin systems. See: Bertrand, R. D.; Ogilvie, F. B.; Verkade, J. G. *J. Am. Chem. Soc.* **1970**, *92*, 1908 and references therein.

Table VIII. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (*syn*-η^3-Pentadienyl)RuCl(PMe_3)$_3$ (4a)

		Bond Distances			
Ru–P1	2.315 (1)	P1–C1P1	1.850 (5)	P3–C2P3	1.830 (4)
Ru–P2	2.329 (1)	P1–C2P1	1.832 (5)	P3–C3P3	1.844 (5)
Ru–P3	2.2619 (9)	P1–C3P1	1.820 (5)	C1–C2	1.398 (6)
Ru–Cl	2.536 (1)	P2–C1P2	1.823 (4)	C2–C3	1.424 (5)
Ru–C1	2.236 (4)	P2–C2P2	1.814 (5)	C3–C4	1.446 (6)
Ru–C2	2.194 (3)	P2–C3P2	1.825 (5)	C4–C5	1.321 (6)
Ru–C3	2.324 (4)	P3–C1P3	1.835 (4)		
		Bond Angles			
P1–Ru–P2	100.48 (4)	P3–Ru–Cl	175.01 (4)	Ru–P2–C1P2	117.6 (2)
P1–Ru–P3	95.00 (4)	P3–Ru–C1	95.3 (1)	Ru–P2–C2P2	115.5 (2)
P1–Ru–Cl	80.47 (4)	P3–Ru–C3	101.8 (1)	Ru–P2–C3P2	121.3 (2)
P1–Ru–C1	93.9 (1)	Cl–Ru–C1	83.0 (1)	Ru–P3–C1P3	119.3 (2)
P1–Ru–C3	154.9 (1)	Cl–Ru–C3	81.8 (1)	Ru–P3–C2P3	120.3 (2)
P2–Ru–P3	93.52 (4)	C1–Ru–C3	66.3 (1)	Ru–P3–C3P3	115.3 (2)
P2–Ru–Cl	89.41 (4)	Ru–P1–C1P1	124.6 (2)	C1–C2–C3	124.3 (4)
P2–Ru–C1	162.4 (1)	Ru–P1–C2P1	117.5 (2)	C2–C3–C4	121.5 (4)
P2–Ru–C3	96.9 (1)	Ru–P1–C3P1	112.2 (2)	C3–C4–C5	124.9 (5)

Table IX. Positional Parameters and Their Estimated Standard Deviations for Non-Hydrogen Atoms in [(η^5-Pentadienyl)Ru(PMe_3)$_3$]$^+$$O_3SCF_3^-$ (5a)[a]

atom	*x*	*y*	*z*
Ru	0.03575 (4)	0.250	0.30740 (3)
P1	−0.1146 (2)	0.250	0.1311 (1)
P2	0.2096 (1)	0.3998 (1)	0.28328 (8)
C1	−0.1362 (5)	0.3746 (5)	0.3641 (4)
C2	0.0059 (5)	0.3588 (5)	0.4465 (3)
C3	0.0739 (8)	0.250	0.4871 (4)
C1P1	−0.036 (1)	0.201 (1)	0.0163 (7)
C2P1	−0.201 (1)	0.3910 (9)	0.0819 (9)
C3P1	−0.297 (1)	0.162 (1)	0.110 (1)
C1P2	0.3057 (6)	0.4052 (6)	0.1709 (4)
C2P2	0.1292 (8)	0.5480 (5)	0.2727 (7)
C3P2	0.3820 (7)	0.4167 (7)	0.3940 (6)
S	0.4451 (2)	0.250	0.7484 (1)
O1	0.6018 (6)	0.250	0.8163 (5)
O2	0.3960 (6)	0.3574 (4)	0.6890 (4)
C	0.3221 (8)	0.250	0.8414 (7)
F1	0.1714 (5)	0.250	0.7915 (6)
F2	0.3486 (5)	0.3407 (4)	0.9070 (3)

[a] The molecule resided on a crystallographically imposed mirror plane which included atoms Ru, P1, C3, S, O1, C, and F1. The carbon atoms on phosphorus atom P1 were disordered about the mirror plane (two symmetry-related rotamers were observed in the difference Fourier maps). One unique set (C1P1, C2P1, C3P1) was refined at a multiplicity of $^1/_2$.

(1.42 g, 1.95×10^{-3} mol) in 50 mL of toluene and stirred at room temperature for 0.5 h during which the solution changed in color from orange to bright yellow and **2a** began to precipitate as a yellow powder. The toluene was removed in vacuo, and the yellow solid was washed with four aliquots of pentane (20 mL each) to yield crude **2a** as a yellow powder, crude yield 0.84 g (80%, based on **1**). The crude **2a** was recrystallized from warm toluene, yielding 0.60 g (57%) of bright yellow needlelike microcrystals: ^{1}H (dichloromethane-d_2, 20 °C) δ 7.5–7.3 (multiplets, 15, PPh_3), 6.22 (unresolved dt, 1, H3), 4.94 (m, 1, H4), 3.08 (m, 1, H2), 2.54 (d, 1, $H5_{syn}$), 1.51 (d, J_{P-H} = 9 Hz, 9, PMe_3), 0.96 (d, 1, $H1_{syn}$), 0.25 (dd, 1, $H5_{anti}$), −0.58 (d, 1, $H1_{anti}$); $^{13}C\{^1H\}$ (dichloromethane-d_2, 20 °C) δ 136.50 (d, J_{P-C} = 35 Hz, PPh_3), 134.00 (d, J_{P-C} = 10 Hz, PPh_3), 129.13 (s, PPh_3), 128.12 (d, J_{P-C} = 9 Hz, PPh_3), 107.56 (s, C4), 92.49 (d, J_{P-C} = 13 Hz, C3), 86.17 (s, C2), 51.74 (d, J_{P-C} = 26 Hz, C5), 35.43 (d, J_{P-C} = 6 Hz, C1), 20.98 (d, J_{P-C} = 29 Hz, PMe_3); $^{31}P\{^1H\}$ (dichloromethane-d_2, 20 °C) δ 38.6, −0.50 (doublets, J_{P-P} = 29 Hz). Anal. Calcd for $H_{31}C_{26}ClP_2Ru$: C, 57.62; H, 5.76. Found: C, 57.60; H, 5.88.

(η^5-Pentadienyl)RuCl(PMe_2Ph)(PPh_3) (2b). **2b** was prepared in a manner similar to **2a** using dimethylphenylphosphine (0.38 g, 2.7×10^{-3} mol) and **1** (2.00 g, 2.75×10^{-3} mol) and a 1.0-h reaction time to yield crude **2b** as a yellow-orange powder, yield of crude **2b**, 1.49 g (90%, based on **1**). Crude **2b** was recrystallized from warm tetrahydrofuran, yielding 1.12 g (68%) of orange crystals: ^{1}H (dichloromethane-d_2, 20 °C) δ 7.4–7.0 (multiplets, 20, PPh), 6.20 (unresolved dt, 1, H3), 4.95 (m, 1, H4), 3.07 (m, 1, H2), 2.52 (d, 1, $H5_{syn}$), 2.01 (d, J_{P-H} = 9 Hz, 3, PMe), 1.71 (d, J_{P-H} = 9 Hz, 3, PMe), 0.82 (d, 1, $H1_{syn}$), −0.02 (unresolved dd, 1, $H5_{anti}$), −0.60 (d, 1, $H1_{anti}$); $^{13}C\{^1H\}$ (dichloromethane-d_2, 20 °C) δ 141.80 (d, J_{P-C} = 30 Hz, PPh), 135.80 (d, J_{P-C} = 30 Hz, PPh), 134.04 (d, J_{P-C} = 10 Hz, PPh), 129.72 (d, J_{P-C} = 8 Hz, PPh), 129.43 (s, PPh), 128.24 (s, PPh), 128.03 (d, J_{P-C} = 9 Hz, PPh), 127.95

Table X. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for [(η^5-Pentadienyl)Ru(PMe_3)$_3$]$^+$$O_3SCF_3^-$ (5a)[a]

		Bond Distances			
Ru–P1	2.313 (1)	P1–C2P1	1.81 (1)	C2–C3	1.408 (6)
Ru–P2	2.327 (1)	P1–C3P1	1.83 (1)	S–O1	1.427 (5)
Ru–C1	2.276 (4)	P2–C1P2	1.805 (5)	S–O2	1.439 (5)
Ru–C2	2.212 (4)	P2–C2P2	1.807 (6)	S–C	1.758 (8)
Ru–C3	2.226 (5)	P2–C3P2	1.805 (6)	C–F1	1.309 (8)
P1–C1P1	1.82 (1)	C1–C2	1.428 (7)	C–F2	1.307 (6)
		Bond Angles			
P1–Ru–P2	96.23 (4)	C1–Ru–C3	68.4 (2)	O1–S–O2	116.1 (2)
P1–Ru–C1	92.5 (1)	Ru–P1–C1P1	122.9 (3)	O1–S–C	103.2 (4)
P1–Ru–C2	128.9 (2)	Ru–P1–C2P1	115.4 (4)	O2–S–O2′	114.9 (4)
P1–Ru–C3	155.2 (2)	Ru–P1–C3P1	114.7 (5)	O2–S–C	101.5 (3)
P2–Ru–P2′	93.32 (6)	Ru–P2–C1P2	123.6 (2)	S–C–F1	111.1 (6)
P2–Ru–C1	94.4 (2)	Ru–P2–C2P2	115.9 (2)	S–C–F2	112.5 (4)
P2–Ru–C1′	167.6 (1)	Ru–P2–C3P2	114.5 (2)	F1–C–F2	108.5 (5)
P2–Ru–C3	100.7 (1)	C1–C2–C3	126.4 (5)	F2–C–F2′	103.4 (8)
C1–Ru–C1′	76.4 (3)	C2–C3–C2′	121.6 (6)		

[a] The molecule resided on a crystallographically imposed mirror plane which included atoms Ru, P1, C3, S, O1, C, and F1. The primed atoms are located in the symmetry-generated portion of the molecule. The carbon atoms on phosphorus atom P1 were disordered about the mirror plane (two symmetry-related rotamers were observed in the difference Fourier maps). One unique set (C1P1, C2P1, C3P1) was refined at a multiplicity of $^1/_2$.

(d, $J_{\mathrm{P-C}}$ = 9 Hz, PPh), 108.14 (s, C4), 92.02 (d, $J_{\mathrm{P-C}}$ = 13 Hz, C3), 86.78 (s, C2), 53.96 (d, $J_{\mathrm{P-C}}$ = 27 Hz, C5), 38.09 (d, $J_{\mathrm{P-C}}$ = 6 Hz, C1), 20.04 (d, $J_{\mathrm{P-C}}$ = 31 Hz, PMe), 17.31 (d, $J_{\mathrm{P-C}}$ = 9 Hz, PMe); ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ (dichloromethane-d_2, 20 °C) 36.4, 9.8 (doublets, $J_{\mathrm{P-P}}$ = 27 Hz). Anal. Calcd for $\mathrm{H_{33}C_{31}ClP_2Ru}$: C, 61.64; H, 5.51. Found: C, 61.00; H, 5.56.

(η^5-Pentadienyl)RuCl(PEt$_3$)(PPh$_3$) (2c). **2c** was prepared in a manner similar to **2a** using triethylphosphine (0.31 g, 2.6 × 10^{-3} mol) and **1** (1.40 g, 1.92 × 10^{-3} mol) and a 1.0-h reaction time to yield crude **2c** as an orange solid; yield of crude **2c**, 0.97 g (86%, based on 1). Crude **2c** was recrystallized from warm toluene, yielding 0.54 g (48%) of orange microcrystals: ${}^{1}\mathrm{H}$ (dichloromethane-d_2, 20 °C) δ 7.4–7.2 (multiplets, 15, PPh$_3$), 5.92 (dt, 1, H3), 4.88 (m, 1, H4), 3.53 (m, 1, H2), 2.75 (d, 1, $\mathrm{H5_{syn}}$), 2.08, 1.86 (m, $J_{\mathrm{P-H}}$ = 5 Hz, $J_{\mathrm{H-C-C-H}}$ = 7.5 Hz, $J_{\mathrm{H-C-H}}$ = 15 Hz, 6, phosphine CH$_2$), 1.34 (d, 1, $\mathrm{H1_{syn}}$), 1.01 (dt, $J_{\mathrm{P-H}}$ = 14 Hz, 9, phosphine CH$_3$), 0.04 (unresolved dd, 1, $\mathrm{H5_{anti}}$), −0.64 (d, 1, $\mathrm{H1_{anti}}$); ${}^{13}\mathrm{C}\{{}^{1}\mathrm{H}\}$ (dichloromethane-d_2, 20 °C) δ 136.77 (d, $J_{\mathrm{P-C}}$ = 36 Hz, PPh$_3$), 134.04 (d, $J_{\mathrm{P-C}}$ = 10 Hz, PPh$_3$), 129.51 (s, PPh$_3$), 128.07 (d, $J_{\mathrm{P-C}}$ = 9 Hz, PPh$_3$), 107.73 (s, C4), 94.32 (d, $J_{\mathrm{P-C}}$ = 12.5 Hz, C3), 84.99 (s, C2), 48.46 (dd, $J_{\mathrm{P-C}}$ = 25, 3 Hz, C5), 32.96 (d, $J_{\mathrm{P-C}}$ = 6 Hz, C1), 20.99 (d, $J_{\mathrm{P-C}}$ = 24 Hz, phosphine CH$_2$), 8.39 (d, $J_{\mathrm{P-C}}$ = 4 Hz, phosphine CH$_3$); ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ (dichloromethane-d_2, 20 °C) δ 35.7, 24.3 (doublets, $J_{\mathrm{P-P}}$ = 28 Hz). Anal. Calcd for $\mathrm{H_{37}C_{29}ClP_2Ru}$: C, 59.64; H, 6.38. Found: C, 59.84; H, 6.35.

(η^5-Pentadienyl)RuCl(PEt$_2$Ph)(PPh$_3$) (2d). **2d** was prepared in a manner similar to **2a** using diethylphenylphosphine (0.33 g, 2.0 × 10^{-3} mol) and **1** (1.35 g, 1.85 × 10^{-3} mol) and a 3.0-h reaction time to yield crude **2d** as a yellow powder; yield of crude **2d**, 1.02 g (87%, based on **1**). Crude **2d** was recrystallized from warm dichloromethane to yield red-orange crystals of **2d** with 0.5 mol of dichloromethane of solvation (as determined by ${}^{1}\mathrm{H}$ NMR): 0.77 g (62%) (the dichloromethane of solvation was removed by prolonged evacuation); ${}^{1}\mathrm{H}$ (dichloromethane-d_2, 20 °C) δ 7.4–7.1, 6.81 (multiplets, 20, PPh), 6.22 (dt, 1, H3), 4.94 (m, 1, H4), 3.11 (m, 1, H2), 2.83 (d, 1, $\mathrm{H5_{syn}}$), 2.7–2.5 (overlapping multiplets, 3, phosphine $\mathrm{CH_2^{A}}$, $\mathrm{CH_2^{A'}}$, and $\mathrm{CH_2^{B}}$), 2.02 (m, 1, phosphine $\mathrm{CH_2^{B'}}$), 1.28 (dt, $J_{\mathrm{P-H}}$ = 15 Hz, $J_{\mathrm{H-C-C-H}}$ = 7.5 Hz, 3, phosphine $\mathrm{CH_3^{B}}$), 0.94 (dt, $J_{\mathrm{P-H}}$ = 14 Hz, $J_{\mathrm{H-C-C-H}}$ = 7 Hz, 3, phosphine $\mathrm{CH_3^{A}}$), 0.78 (d, 1, $\mathrm{H1_{syn}}$), 0.17 (unresolved dd, 1, $\mathrm{H5_{anti}}$), −0.40 (d, 1, $\mathrm{H1_{anti}}$); ${}^{13}\mathrm{C}\{{}^{1}\mathrm{H}\}$ (dichloromethane-d_2, 20 °C) δ 134.05 (br, PPh), 130.72 (d, $J_{\mathrm{P-C}}$ = 7 Hz, PPh), 129.28 (s, PPh), 128.98 (s, PPh), 128.75 (d, $J_{\mathrm{P-C}}$ = 7 Hz, PPh), 128.2–128.0 (overlapping peaks, PPh), 127.81 (d, $J_{\mathrm{P-C}}$ = 9 Hz, PPh), 107.40 (s, C4), 92.52 (d, $J_{\mathrm{P-C}}$ = 12 Hz, C3), 86.60 (s, C2), 50.08 (dd, $J_{\mathrm{P-C}}$ = 28, 3 Hz, C5), 37.37 (d, $J_{\mathrm{P-C}}$ = 5 Hz, C1), 22.61 (dd, $J_{\mathrm{P-C}}$ = 30, 3 Hz, phosphine $\mathrm{CH_2^{A}}$), 17.84 (d, $J_{\mathrm{P-C}}$ = 21 Hz, phosphine $\mathrm{CH_2^{B}}$), 8.58 (d, $J_{\mathrm{P-C}}$ = 7 Hz, phosphine $\mathrm{CH_3^{A}}$), 8.32 (d, $J_{\mathrm{P-C}}$ = 2 Hz, phosphine $\mathrm{CH_3^{B}}$); ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ (dichloromethane-d_2, 20 °C) δ 33.9, 27.6 (doublets, $J_{\mathrm{P-P}}$ = 27 Hz). Anal. Calcd for $\mathrm{H_{37}C_{33}ClP_2Ru}$: C, 62.70; H, 5.90. Found: C, 62.33; H, 5.66.

(η^5-Pentadienyl)RuCl(PMe$_2$Ph)$_2$ (3b). Dimethylphenylphosphine (0.30 g, 2.2 × 10^{-3} mol) was added to crystalline **2b** (1.26 g, 2.08 × 10^{-3} mol) in 100 mL of toluene and refluxed for 0.5 h during which there was no obvious color change. The toluene was removed in vacuo to yield an orange oil. The oil was taken up in a minimal amount of tetrahydrofuran and introduced onto a neutral alumina column which was then washed with 100 mL of pentane followed by 50 mL of tetrahydrofuran to elute **3b** as a bright yellow solution. This solution was dried in vacuo to yield an orange oil, which was dissolved in 5 mL of diethyl ether and, upon sitting at ambient temperature (ca. 1 h), yielded 0.58 g (58%, based on **2b**) of orange crystals of **3b**: ${}^{1}\mathrm{H}$ (dichloromethane-d_2, 20 °C) δ 7.6–7.3 (multiplets, 10, PPh), 4.93 (dt, 1, H3), 4.84 (m, 1, H4), 3.71 (m, 1, H2), 2.52 (d, 1, $\mathrm{H5_{syn}}$), 2.09 (overlapping doublets, $J_{\mathrm{P-H}}$ = ca. 9 Hz, 6, PMe), 1.24 (d, $J_{\mathrm{P-H}}$ = 9 Hz, 3, PMe), 1.16 (d, 1, $\mathrm{H1_{syn}}$), 0.90 (d, $J_{\mathrm{P-H}}$ = 8 Hz, 3, PMe), 0.23 (dd, 1, $\mathrm{H5_{anti}}$), −0.48 (d, 1, $\mathrm{H1_{anti}}$); ${}^{13}\mathrm{C}\{{}^{1}\mathrm{H}\}$ (dichloromethane-d_2, 20 °C) δ 129.78 (d, $J_{\mathrm{P-C}}$ = 8 Hz, PPh), 128.74 (s, PPh), 128.47 (d, $J_{\mathrm{P-C}}$ = 9 Hz, PPh), 127.91 (d, $J_{\mathrm{P-C}}$ = 9 Hz, PPh), 110.24 (s, C4), 91.12 (d, $J_{\mathrm{P-C}}$ = 12 Hz, C3), 86.09 (s, C2), ca. 53.6 (obscured by dichloromethane-d_2, C5), 35.97 (d, $J_{\mathrm{P-C}}$ = 5 Hz, C1), 20.90 (d, $J_{\mathrm{P-C}}$ = 31 Hz, PMe), 19.02 (d, $J_{\mathrm{P-C}}$ = 27 Hz, PMe), 15.32 (d, $J_{\mathrm{P-C}}$ = 28 Hz, PMe), 11.89 (d, $J_{\mathrm{P-C}}$ = 28 Hz, PMe); ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ (dichloromethane-d_2, 20 °C) δ 9.2, 5.7 (doublets, $J_{\mathrm{P-P}}$ = 31 Hz). Anal. Calcd for $\mathrm{H_{29}C_{21}ClP_2Ru}$: C, 52.56; H, 6.09. Found: C, 52.47; H, 6.14.

(η^5-Pentadienyl)RuCl(PEt$_3$)$_2$ (3c). Triethylphosphine (0.48 g, 4.1 × 10^{-3} mol) was added to a solution of **1** (1.46 g, 2.00 × 10^{-3} mol) in 100 mL of toluene and refluxed for 0.5 h during which the solution's color changed from orange to yellow. The toluene was removed in vacuo to yield a yellow-orange oil. This was taken up in pentane and introduced onto a neutral alumina column which was washed with 100 mL of pentane followed by 20 mL of tetrahydrofuran to elute **3c** as a yellow solution. The solution was dried in vacuo to yield a yellow-orange oily solid which was dissolved in 5 mL of pentane and cooled to −30 °C to yield 0.62 g (70%, based on 1) of orange crystals of **3c**: ${}^{1}\mathrm{H}$ (dichloromethane-d_2, 20 °C, couplings from HOM2DJ spectra) δ 5.79 (dt, $J_{\mathrm{P-H}}$ = 3 Hz, $J_{\mathrm{H3-H2}}$ = 6 Hz, $J_{\mathrm{H3-H4}}$ = 6 Hz, 1, H3), 4.73 (m, $J_{\mathrm{H4-H5_{syn}}}$ = 10 Hz, $J_{\mathrm{H4-H5_{anti}}}$ = 12 Hz, 1, H4), 4.27 (m, $J_{\mathrm{P-H}}$ = 8 Hz, $J_{\mathrm{H2-H1_{syn}}}$ = 9 Hz, $J_{\mathrm{H2-H1_{anti}}}$ = 9 Hz, 1, H2), 2.63 (dd, $J_{\mathrm{H5_{syn}-H5_{anti}}}$ = 3 Hz, 1, $\mathrm{H5_{syn}}$), 2.19 (m, $J_{\mathrm{P-H}}$ = 8 Hz, $J_{\mathrm{H-C-C-H}}$ = 7.5 Hz, $J_{\mathrm{H-C-H}}$ = 15 Hz, 3, phosphine $\mathrm{CH_2^{B}}$), 2.02 (m, $J_{\mathrm{P-H}}$ = 8 Hz, $J_{\mathrm{H-C-C-H}}$ = 7.5 Hz, 3, phosphine $\mathrm{CH_2^{B'}}$), 1.90 (m, $J_{\mathrm{P-H}}$ = 9 Hz, $J_{\mathrm{H-C-C-H}}$ = 8 Hz, $J_{\mathrm{H-C-H}}$ = 15 Hz, 3, phosphine $\mathrm{CH_2^{A}}$), 1.55 (dd, $J_{\mathrm{H1_{syn}-H1_{anti}}}$ = 2 Hz, 1, $\mathrm{H1_{syn}}$), 1.51 (m, $J_{\mathrm{P-H}}$ = 5 Hz, $J_{\mathrm{H-C-C-H}}$ = 8 Hz 3, phosphine $\mathrm{CH_2^{A'}}$), 1.17 (dt, $J_{\mathrm{P-H}}$ = 14 Hz, 9, phosphine $\mathrm{CH_3^{B}}$), 1.03 (dt, $J_{\mathrm{P-H}}$ = 13 Hz, 9, phosphine $\mathrm{CH_3^{A}}$), −0.03 (dd, 1, $\mathrm{H5_{anti}}$), −0.74 (dd, 1, $\mathrm{H1_{anti}}$); ${}^{13}\mathrm{C}\{{}^{1}\mathrm{H}\}$ (dichloromethane-d_2, 20 °C) δ 108.52 (s, C4), 90.18 (d, $J_{\mathrm{P-C}}$ = 12.5 Hz, C3), 82.50 (s, C2), 49.94 (d, $J_{\mathrm{P-C}}$ = 29 Hz, C5), 31.13 (d, $J_{\mathrm{P-C}}$ = 6 Hz, C1), 21.92 (d, $J_{\mathrm{P-C}}$ = 22 Hz, phosphine $\mathrm{CH_2^{B}}$), 19.14 (d, $J_{\mathrm{P-C}}$ = 22 Hz, phosphine $\mathrm{CH_2^{A}}$), 8.72 (d, $J_{\mathrm{P-C}}$ = 3 Hz, phosphine $\mathrm{CH_3^{A}}$), 8.49 (d, $J_{\mathrm{P-C}}$ = 3.5 Hz, phosphine $\mathrm{CH_3^{B}}$); ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ (dichloroethane-d_2, 20 °C) δ 26.0, 14.7 (doublets, $J_{\mathrm{P-P}}$ = 32 Hz). Anal. Calcd for $\mathrm{H_{37}C_{17}ClP_2Ru}$: C, 46.41; H, 8.48. Found: C, 46.40; H, 8.31.

(η^5-Pentadienyl)RuCl(PEt$_2$Ph)$_2$ (3d). Diethylphenylphosphine (0.65 g, 3.9 × 10^{-3} mol) was added to a solution of **1** (1.35 g, 1.85 × 10^{-3} mol) in 100 mL of toluene and refluxed for 1.0 h during which the color changed from orange to bright yellow. The toluene was removed in vacuo to yield a bright yellow solid which was washed with four aliquots of pentane (20 mL each) to yield crude **3d**, crude yield 0.84 g (84%, based on **1**). Crude **3d** was recrystallized from tetrahydrofuran (−30 °C) to yield 0.60 g (60%) of yellow-orange crystals: ${}^{1}\mathrm{H}$ (dichloromethane-d_2, 20 °C) δ 7.59, 7.5–7.3, 7.27 (multiplets, 10, PPh), 5.03 (dt, 1, H3), 4.77 (m, 1, H4), 3.84 (m, 1, H2), 2.67 (d, $\mathrm{H5_{syn}}$; partially obscured by phosphine CH$_2$), 2.7–2.4 (overlapping multiplets, 4, phosphine $\mathrm{CH_2^{D}}$, $\mathrm{CH_2^{D'}}$, $\mathrm{CH_2^{C}}$, $\mathrm{CH_2^{C'}}$), 2.21 (m, 1, phosphine $\mathrm{CH_2^{A}}$), 1.55 (m, 1, phosphine $\mathrm{CH_2^{B}}$), 1.32 (m, phosphine $\mathrm{CH_2^{A'}}$, partially overlapping $\mathrm{CH_3^{D}}$), 1.22 (dt, $J_{\mathrm{P-H}}$ = 15 Hz, $J_{\mathrm{H-C-C-H}}$ = 8 Hz, phosphine $\mathrm{CH_3^{D}}$, overlapping $\mathrm{H1_{syn}}$ and $\mathrm{CH_2^{A'}}$), 1.18 (obscured by $\mathrm{CH_3^{D}}$, shift from ${}^{1}\mathrm{H}$ COSY, $\mathrm{H1_{syn}}$), 1.06 (dt, $J_{\mathrm{P-H}}$ = 14 Hz, $J_{\mathrm{H-C-C-H}}$ = 7 Hz, 3, phosphine $\mathrm{CH_3^{C}}$), 0.92 (m, 1, phosphine $\mathrm{CH_2^{B'}}$), 0.70 (dt, $J_{\mathrm{P-H}}$ = 14 Hz, $J_{\mathrm{H-C-C-H}}$ = 7 Hz, 3, phosphine $\mathrm{CH_3^{B}}$), 0.68 (dt, $J_{\mathrm{P-H}}$ = 14 Hz, $J_{\mathrm{H-C-C-H}}$ = 7 Hz, 3, phosphine $\mathrm{CH_3^{A}}$), 0.12 (dd, 1, $\mathrm{H5_{anti}}$), −0.56 (d, 1, $\mathrm{H1_{anti}}$); ${}^{13}\mathrm{C}\{{}^{1}\mathrm{H}\}$ (dichloromethane-d_2, 20 °C) δ 131.1–127.7 (overlapping peaks, PPh), 108.99 (s, C4), 91.55 (d, $J_{\mathrm{P-C}}$ = 12 Hz, C3), 84.90 (s, C2), 50.35 (d, $J_{\mathrm{P-C}}$ = 25 Hz, C5), 34.98 (d, $J_{\mathrm{P-C}}$ = 5 Hz, C1), 22.92 (d, $J_{\mathrm{P-C}}$ = 28 Hz, phosphine CH$_2$), 19.69 (d, $J_{\mathrm{P-C}}$ = 23 Hz, phosphine CH$_2$), 18.37 (d, $J_{\mathrm{P-C}}$ = 24 Hz, phosphine CH$_2$), 16.45 (d, $J_{\mathrm{P-C}}$ = 22 Hz, phosphine CH$_2$), 8.7–8.5 (overlapping peaks, phosphine CH$_3$); ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ (dichloromethane-d_2, 20 °C) δ 28.7, 21.0 (doublets, $J_{\mathrm{P-P}}$ = 30 Hz). Anal. Calcd for $\mathrm{H_{37}C_{25}ClP_2Ru}$: C, 56.02; H, 6.96. Found: C, 56.38; H, 7.05.

(η^5-Pentadienyl)RuCl(PEtPh$_2$)$_2$ (3e). Ethyldiphenylphosphine (0.81 g, 3.8 × 10^{-3} mol) was added to a solution of **1** (1.37 g, 1.88 × 10^{-3} mol) in 100 mL of tetrahydrofuran and refluxed for 2.0 h during which the color changed from orange to yellow-orange. The tetrahydrofuran was removed in vacuo to yield an orange oil which was taken up in a minimal amount of diethyl ether and introduced onto a neutral alumina column. The column was washed with 50 mL of pentane, 50 mL of diethyl ether, and then 75 mL of tetrahydrofuran to elute **3e** as an orange solution. The solution was dried in vacuo to yield crude **3e** as a bright yellow solid, crude yield 0.85 g (71%, based on **1**). Crude **3e** was recrystallized from tetrahydrofuran (−30 °C) to yield bright yellow microcrystals with 1.0 mol of tetrahydrofuran of solvation (as determined by ${}^{1}\mathrm{H}$ NMR): 0.65 g (49%); ${}^{1}\mathrm{H}$ (stopped exchange, dichloromethane-d_2, −40 °C) δ 7.71, 7.5–7.1, 6.69, 6.23 (multiplets, 20, PPh), 5.1 (overlapping peaks, 2, H3, H4), 3.88 (m, 1, H2), 2.96 (m, 1, phosphine $\mathrm{CH_2^{B}}$), 2.84 (m, 1, phosphine $\mathrm{CH_2^{B'}}$), 2.64 (d, 1, $H5_{syn}$), 2.52 (m, 1, phosphine CH_2^{A}), 1.77 (m, 1, phosphine $CH_2^{A'}$), 0.68 (dt, J_{P-H} = 14 Hz, $J_{H-C-C-H}$ = 7 Hz, 3, phosphine CH_3^{B}), 0.47 (d, 1, $H5_{anti}$), 0.33 (dt, J_{P-H} = 14 Hz, $J_{H-C-C-H}$ = 7 Hz, 3, phosphine CH_3^{A}), 0.08 (d, 1, $H1_{syn}$), −1.16 (d, 1, $H1_{anti}$); ^1H (fast exchange, toluene-d_8, 100 °C) δ 7.5, 7.4, 7.2–7.0 (br, 20, PPh), 5.12 (t, 1, H3), 4.60 (br, 2, H2 = H4), 2.90 (br m, 2, phosphine CH_2), 2.44 (br, 2, phosphine CH_2), ca. 1.2 (br, obscured by tetrahydrofuran, $H1_{syn}$ = $H5_{syn}$), 0.68 (dt, J_{P-C} = 14 Hz, $J_{H-C-C-H}$ = 7 Hz, 6, phosphine CH_3), −0.09 (br, 2, $H1_{anti}$ = $H5_{anti}$); $^{13}C\{^1H\}$ (stopped exchange, dichloromethane-d_2, −40 °C) δ 135.2–127.1 (overlapping peaks, PPh), 109.88 (s, C4), 89.88 (d, J_{P-C} = 12 Hz, C3), 87.29 (s, C2), 51.78 (d, J_{P-C} = 24 Hz, C5), 43.67 (s, C1), 25.44 (dd, J_{P-C} = 23, 3 Hz, phosphine CH_2), 16.28 (d, J_{P-C} = 24 Hz, phosphine CH_2), 9.28 (d, J_{P-C} = 8 Hz, phosphine CH_3), 7.68 (d, J_{P-C} = 9 Hz, phosphine CH_3); $^{31}P\{^1H\}$ (stopped exchange, dichloromethane-d_2, −40 °C) δ 32.7, 28.2 (doublets, J_{P-P} = 30 Hz); $^{31}P\{^1H\}$ (fast exchange, toluene-d_8, 80 °C) δ 27.2 (br s). Anal. Calcd for $H_{37}C_{33}ClP_2Ru{\cdot}H_8C_4O$: C, 63.10; H, 6.45. Found: C, 62.81; H, 6.41.

(η^3-Pentadienyl)RuCl(PMe$_3$)$_3$ (4a). Trimethylphosphine (0.90 g, 1.2 × 10^{-2} mol) was added to a solution of 1 (2.00 g, 2.75 × 10^{-3} mol) in 100 mL of tetrahydrofuran and refluxed for 1.0 h during which the color changed from orange to bright yellow. The tetrahydrofuran was removed in vacuo to yield a yellow solid which was washed with four aliquots of pentane (20 mL each) to yield crude **4a** as a bright yellow powder, crude yield 1.13 g (95%, based on 1). Crude **4a** was recrystallized from tetrahydrofuran at −30 °C to yield 0.72 g (61%) of yellow crystals: ^1H (dichloromethane-d_2, 20 °C, couplings from HOM2DJ) δ 6.21 (dt, J_{H4-H3} = 10.5 Hz, $J_{H4-H5_{syn}}$ = 10.5 Hz, $J_{H4-H5_{anti}}$ = 17 Hz, 1, H4), 5.10 (dt, triplet coupling J = 2 Hz, 1, $H5_{anti}$), 4.83 (dt, triplet J = 2 Hz, 1, $H5_{syn}$), 4.30 (m, J_{P-H} = 8 Hz, J_{H2-H3} = 10.5 Hz, $J_{H2-H1_{syn}}$ = 7 Hz, $J_{H2-H1_{anti}}$ = 12 Hz, 1, H2), 3.69 (dt, J_{P-H} = 5 Hz, 1, H3), 2.63 (dt, triplet J_{P-H} = 3.5 Hz, 1, $H1_{syn}$), 1.81 (dd, J_{P-H} = 6 Hz, 1, $H1_{anti}$), 1.52, 1.45, 1.16 (doublets, J_{P-H} = 8 Hz, 9 (each), PMe_3); $^{13}C\{^1H\}$ (dichloromethane-d_2, 20 °C) δ 143.44 (s, C4), 108.97 (s, C5), 98.57 (s, C2), 72.87 (d, J_{P-C} = 23 Hz, C3), 46.14 (d, J_{P-C} = 24 Hz, C1), 22.91 (d, J_{P-C} = 26 Hz, PMe_3), 21.90 (d, J_{P-C} = 29 Hz, PMe_3), 20.03 (d, J_{P-C} = 24 Hz, PMe_3); $^{31}P\{^1H\}$ (dichloromethane-d_2, 20 °C) δ 23.0 (t, J_{P-P} = 38 Hz), −4.7 (dd, J_{P-P} = 10, 38 Hz), −11.2 (dd, J_{P-P} = 10, 38 Hz); characteristic IR peak (10 w/w %, dichloromethane) 1615 cm^{-1} (pentadienyl vinylic C═C stretch). Anal. Calcd for $H_{34}C_{14}ClP_3Ru$: C, 38.94; H, 7.93. Found: C, 39.11; H, 7.87.

(η^3-Pentadienyl)RuCl(PMe$_2$Ph)$_3$ (4b). Dimethylphenylphosphine (0.96 g, 6.9 × 10^{-3} mol) was added to crystalline **2b** (2.00 g, 3.31 × 10^{-3} mol) in 75 mL of toluene. The mixture was refluxed for 1 h during which the solution turned from orange to yellow-orange. The mixture was cooled to room temperature and stirred for 72 h, causing precipitation of a yellow solid. The toluene was removed in vacuo to yield a yellow-orange oil which was extracted with tetrahydrofuran and cooled to −30 °C. **4b** precipitated as a bright yellow powder. The product was filtered, washed liberally with pentane, and dried to yield 1.44 g (two crops, 70% based on **2b**) of **4b**: ^1H (dichloromethane-d_2, 20 °C) δ 7.7–7.6, 7.3–7.1 (multiplets, 15, PPh), 5.73 (dt, 1, H4), 5.16 (d, 1, $H5_{anti}$), 4.88 (d, 1, $H5_{syn}$), 4.40 (m, 1, H2), 3.74 (dt, 1, H3), 2.52 (dt, 1, $H1_{syn}$), 1.96 (dt, 1, $H1_{anti}$), 1.81, 1.74, 1.61, 1.51, 1.00, 0.87 (doublets, J_{P-H} = 8 Hz, 3 (each), PMe); $^{13}C\{^1H\}$ (dichloromethane-d_2, 20 °C) δ 142.81 (d, J_{P-C} = 4 Hz, C4), 131.6–127.7 (overlapping peaks, PPh), 110.86 (d, J_{P-C} = 4 Hz, C5), 98.16 (s, C2), 75.75 (d, J_{P-C} = 23 Hz, C3), 47.63 (d, J_{P-C} = 24 Hz, C1), 21.00 (d, J_{P-C} = 32 Hz, PMe), 20.42 (d, J_{P-C} = 29 Hz, PMe), 19.52 (d, J_{P-C} = 26 Hz, PMe), 18.38 (d, J_{P-C} = 30 Hz, PMe), 17.88 (d, J_{P-C} = 29 Hz, PMe), 17.52 (d, J_{P-C} = 26 Hz, PMe); $^{31}P\{^1H\}$ (dichloromethane-d_2, 20 °C) δ 29.80 (unresolved dd, J_{P-P} = 34, 37 Hz), 2.52 (dd, J_{P-P} = 7.5, 37 Hz), −8.12 (dd, J_{P-P} = 7.5, 34 Hz); characteristic IR peak (10 w/w %, dichloromethane) 1615 cm^{-1} (pentadienyl vinylic C═C stretch). Anal. Calcd for $H_{40}C_{29}ClP_3Ru$: C, 56.36; H, 6.52. Found: C, 56.37; H, 6.54.

[(η^5-Pentadienyl)Ru(PMe$_3$)$_3$]$^+$O$_3$SCF$_3^-$ (5a). (a) Silver trifluoromethanesulfonate (0.23 g, 9.0 × 10^{-4} mol) in 30 mL of dichloromethane was added while stirring to a cold (−78 °C) solution of **4a** (0.34 g, 7.9 × 10^{-4} mol) in 30 mL of dichloromethane. A white precipitate formed immediately. The mixture was stirred at −78 °C for 0.5 h and then allowed to warm to room temperature. The solution was filtered to give a pale yellow filtrate which was dried in vacuo to yield crude **5a** as a pale yellow solid. Recrystallization at −30 °C from acetone gave 0.22 g (51%, based on **4a**) of colorless crystals of **5a**.

(b) Methyl trifluoromethanesulfonate (0.12 g, 7.3 × 10^{-4} mol) was added to a solution of **4a** (0.17 g, 3.9 × 10^{-4} mol) in 10 mL of dichloromethane at −30 °C. The solution was warmed to room temperature during which the solution turned pale yellow. The dichloromethane was removed in vacuo to yield crude **5a** as a pale yellow powder. Recrystallization at −30 °C from acetone gave 0.15 g (70%, based on **4a**) of colorless crystals of **5a**: ^1H (dichloromethane-d_2, 20 °C, couplings from HOM2DJ spectra) δ 5.51 (dt, J_{P-H} = 2 Hz, J_{H3-H2} = 6 Hz, 1, H3), 4.86 (m, J_{P-H} = 6 Hz, $J_{H2-H1_{syn}}$ = 9 Hz, $J_{H2-H1_{anti}}$ = 11 Hz, 2, H2), 2.51 (dd, $J_{H1_{syn}-H1_{anti}}$ = 3 Hz, 2, $H1_{syn}$), 1.72 (d, J_{P-H} = 8 Hz, 9, "mouth" PMe_3), 1.36 ("filled in" d, J^{17} = 8 Hz, 18, "edge" PMe_3), 0.73 (dd, 2, $H1_{anti}$); $^{13}C\{^1H\}$ (dichloromethane-d_2, 20 °C) δ 101.12 (s, C2), 86.79 (d, J_{P-C} = 8 Hz, C3), 51.62 (virtual t, J_{P-C} = 16 Hz, C1), 24.49 (complex d, doublet J_{P-C} = 29 Hz, "mouth" PMe_3), 20.68 (complex virtual t, virtual J_{P-C} = 26 Hz, "edge" PMe_3's), $^{31}P\{^1H\}$ (dichloromethane-d_2, 20 °C) A_2B pattern, δ −9.85 (A, "edge" PMe_3's), −10.22 (B, "mouth" PMe_3), J_{A-B} = 30 Hz. Anal. Calcd for $H_{34}C_{15}O_3F_3P_3SRu$: C, 33.03; H, 6.28. Found: C, 33.10; H, 6.56.

[(η^5-Pentadienyl)Ru(PMe$_2$Ph)$_3$]$^+$O$_3$SCF$_3^-$ (5b). Silver trifluoromethanesulfonate (0.20 g, 7.8 × 10^{-4} mol) in 30 mL of dichloromethane was added to a cold (−78 °C), stirred solution of **4b** (0.43 g, 7.0 × 10^{-4} mol) in 30 mL of dichloromethane. Upon warming to 20 °C, the solution became bright red and then pale yellow as a white precipitate formed. The solution was filtered to give a pale yellow filtrate which was dried in vacuo to give crude **5b** as a pale yellow powder: yield of crude **5b**, 0.50 g (98% based on **4b**); ^1H (acetone-d_6, 20 °C) δ 7.79, 7.54, 7.5–7.4 (multiplets, 15, PPh), 5.78 (dt, 1, H3), 5.27 (m, 2, H2), 2.27 (d, J_{P-H} = 8 Hz, 6, "mouth" PMe), 2.23 (dd, 2, $H1_{syn}$), 1.60 ("filled in" d, J^{17} = 7 Hz, 6, "edge" PMe^{A}), 1.56 ("filled in" d, J^{17} = 8 Hz, 6, "edge" PMe^{B}), 0.76 (dd, 2, $H1_{anti}$); $^{13}C\{^1H\}$ (acetone-d_6, 20 °C) δ 144.42 (d, J_{P-C} = 40 Hz, PPh), 140.03 (virtual t, J_{P-C} = 42 Hz, PPh), 130.86 (virtual t, J_{P-C} = 8 Hz, PPh), 130.59 (s, PPh), 130.33 (d, J_{P-C} = 8 Hz, PPh), 130.07 (s, PPh), 129.55 (virtual t, J_{P-C} = 8 Hz, PPh), 129.45 (d, J_{P-C} = 9 Hz, PPh), 101.71 (s, C2), 88.98 (d, J_{P-C} = 9 Hz, C3), 54.88 (virtual dt, J_{P-C} = 4 Hz, virtual J_{P-C} = 10 Hz, C1), 23.20 (d, J_{P-C} = 30 Hz, "mouth" PMe), 18.99 (virtual t, J_{P-C} = 32 Hz, "edge" PMe^{A}), 18.70 (virtual t, J_{P-C} = 28 Hz, "edge" PMe^{B}); $^{31}P\{^1H\}$ (acetone-d_6, 20 °C) A_2B pattern, δ 3.23 (A, "edge" PMe_2Ph's), 2.49 (B, "mouth" PMe_2Ph), J_{A-B} = 28 Hz. Anal. Calcd for $H_{40}C_{30}O_3F_3P_3SRu$: C, 49.24; H, 5.51. Found: C, 49.16; H, 5.54.

Single-Crystal X-ray Diffraction Studies. Suitable crystals of **2c**, **3c**, **3d**, and **4a** were mounted in glass capillaries under inert atmosphere; crystals of **5a** were mounted on glass fibers. Data was collected at room temperature on a Nicolet P3 diffractometer using graphite-monochromated Mo Kα radiation. Three standard reflections were measured every 100 events as check reflections for crystal deterioration and/or misalignment. Where necessary, corrections were made for linear decay. All data reduction (including standard Lorentz and polarization corrections) and refinement were done by using the Enraf-Nonius SDPVAX structure determination package (modified by B. A. Frenz and Assoc., Inc., College Station, TX) on a VAX 11/780 computer.[18] Crystal data and details of data collection and structure analysis are summarized in Table XI.

Single, dark orange crystals of **2c** were obtained by slow cooling to room temperature of a warm (40 °C) dichloromethane solution; orange crystals of **3c**, yellow-orange crystals of **3d**, and bright yellow crystals of **4a** were obtained by cooling tetrahydrofuran solutions to −30 °C; clear, colorless crystals of **5a** were obtained by cooling acetone solutions to −30 °C. The coordinates of the ruthenium atoms were determined from Patterson syntheses and checked via the use of direct methods (MULTAN). The remaining heavy atoms were found by successive full-matrix least-squares refinement and difference Fourier map calculations. **2c** and **4a** were corrected for absorption by using the DIFABS method based upon the heavy-atom (non-hydrogen) isotropic solution; **3c**, **3d**,

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(18) Atomic scattering factors were obtained from the: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table XI. X-ray Diffraction Structure Summary for Compounds 2c, 3c, 3d, 4a, and 5a

	2c	3c	3d	4a	5a
Crystal Parameters and Data Collection Summary					
formula	$RuC_{29}H_{37}P_2Cl$	$RuC_{17}H_{37}P_2Cl$	$RuC_{25}H_{37}P_2Cl$	$RuC_{14}H_{34}P_3Cl$	$RuC_{15}H_{34}P_3SO_3F_3$
fw	584.09	439.96	536.04	431.87	545.49
cryst system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	Cc	$P2_12_12_1$	$P2_1/n$	$P2_1/m$
a, Å	11.435 (2)	28.094 (7)	16.848 (7)	9.628 (3)	8.622 (2)
b, Å	13.770 (4)	10.003 (2)	19.409 (4)	13.662 (3)	11.302 (4)
c, Å	18.237 (5)	15.134 (3)	7.867 (1)	15.667 (4)	12.676 (2)
α, deg	90.0	90.0	90.0	90.0	90.0
β, deg	109.04 (2)	98.54 (2)	90.0	91.59 (2)	103.22 (1)
γ, deg	90.0	90.0	90.0	90.0	90.0
V, Å^3	2715 (1)	4205 (2)	2572 (1)	2060 (1)	1202.6 (6)
Z	4	8 (2 mol. in asym. unit)	4	4	2
cryst dimens, mm	0.75 × 0.50 × 0.50	0.73 × 0.25 × 0.38	0.65 × 0.50 × 0.45	0.50 × 0.18 × 0.50	0.50 × 0.35 × 0.25
d_{calcd}, g/cm^3	1.429	1.390	1.348	1.392	1.506
radiatn, Å	Mo Kα, 0.71069	Mo Kα, 0.71069	Mo Kα, 0.71069	Mo Kα, 0.71069	Mo Kα, 0.71069
scan type	θ:2θ	ω	θ:2θ	θ:2θ	θ:2θ
scan rate, deg/min	variable; 4.0–29.3	variable; 2.0–29.3	variable; 4.0–29.3	variable; 4.0–29.3	variable; 4.0–29.3
scan range	1.2° 2θ below Kα_1 to 1.2° 2θ above Kα_2	0.60° ω	1.2° 2θ below Kα_1 to 1.2° 2θ above Kα_2	1.2° 2θ below Kα_1 to 1.2° 2θ above Kα_2	1.2° 2θ below Kα_1 to 1.2° 2θ above Kα_2
2θ range, deg	4.0–55.0	4.0–55.0	4.0–55.0	4.0–55.0	4.0–55.0
data collected	$h,k,\pm l$	$h,k,\pm l(h + k = 2n)$	h,k,l	$h,k,\pm l$	$h,k,\pm l$
total decay	2.3%	1.3%	none detected	none detected	1.5%
Treatment of Intensity Data and Refinement Summary					
no. of data collected	6863	5035	3405	5141	2950
no. of unique data	6547	4846	3405	4971	2858
no. of data with $I > 3\sigma(I)$ (no. of data used in least squares)	5122	4327	2795	3518	2341
internal R values from averaging[a]					
on I	0.055	0.047		0.035	0.015
on F_o	0.030	0.024		0.021	0.011
Mo Kα linear abs coeff, cm^{-1}	7.969	10.044	8.343	10.972	9.530
abs correctn applied	DIFABS	ψ-scans	ψ-scans	DIFABS	ψ-scans
calcd trans factors min, max, av (%)		88.65, 99.90, 96.26	92.00, 99.85, 95.85		79.16, 99.86, 91.55
abs corrections min, max, av	0.8423, 1.0677, 0.9758	0.9415, 0.9995, 0.9811	0.9592, 0.9992, 0.9790	0.6897, 1.1818, 0.9897	0.8897, 0.9993, 0.9568
no. of parameters refined	409	377	337	172	142
R[b]	0.029	0.026	0.031	0.036	0.041
R$_w$[b]	0.044	0.037	0.043	0.049	0.057
GOF[c]	1.187	0.872	0.897	1.448	1.223
largest residual peak in diff Fourier, e/Å^3	0.62, 1.602 Å from Ru	0.31, 0.892 Å from Ru	0.64, 0.812 Å from Ru	0.70, 0.892 Å from Ru	0.61, between C1 and C1′

[a] For observed and accepted data: $R_I = \sum(|I - I_{av}|)/(|I|)$; $R_F = \sum(||F| - |F_{av}||)/(|F|)$. [b] $R = \sum(||F_o| - |F_c||)/\sum(|F_o|)$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(|F_o|)$. [c] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{variables})]^{1/2}$; the esd on an observation of unit weight.

and **5a** were corrected by using the psi-scan technique (see Table XI). Following anisotropic refinement of the heavy atoms, the hydrogen atoms in **2c** and **3d** were located in difference Fourier maps and refined for their positional parameters with fixed isotropic thermal parameters (**2c**, 8.0 for the methyl hydrogens and 6.0 for the rest; **3d**, 10.0 for the methyl hydrogens and 6.0 for the rest). The methyl hydrogens in **3d** did not refine well and were ultimately included at their difference Fourier positions with the above isotropic thermal parameters and used in the structure factor calculations but not refined. The hydrogen atoms for **3c**, **4a**, and **5a** were placed at idealized positions, riding upon their respective carbon atoms, and given fixed isotropic thermal parameters (**3c**, 11.0 for methyl hydrogens and 7.0 for the rest; **4a**, 10.0 for methyl hydrogens, 9.0 for pentadienyl C5 vinylic hydrogens, and 6.0 for the rest; **5a**, 15.0 for methyl hydrogens and 10.0 for pentadienyl hydrogens) and used in the structure factor calculations but not refined. The hydrogens on carbon atoms C1P1, C2P1, and C3P1 in **5a** were included at a multiplicity of 0.5 due to a disorder in the carbon atom positions (see below).

The absolute structures for **3c** and **3d** were determined by comparing the R factors (both weighted and unweighted) of the final structures and their enantiomorphs. In each case, the absolute structure was taken as the structure with the lower R factors. The ratios of the higher to lower R factors were 1.01 and 1.06 for the enantiomorphic structure pairs of **3c** and **3d**, respectively.

The systematic absences for **3c** were consistent with either Cc or $C2/c$. Successful structure refinement (see final R factors, Table XI) indicates that Cc is the correct space group; attempts to solve the structure in $C2/c$ were unsuccessful, and examination of the unit cell drawings and heavy-atom coordinates for the structure in Cc revealed no center of symmetry. Since there are eight molecules in the unit cell, Cc required that there be two molecules in the asymmetric unit; therefore, two molecules were located and refined concurrently.

The systematic absences for **5a** were consistent with either $P2_1$ or $P2_1/m$. The number of molecules in the unit cell (2) required that mirror plane symmetry be present in the molecule for space group $P2_1/m$. The $N(z)$ statistics were inconclusive; therefore, the structure was initially refined in each space group. The reported final structure was successfully refined in the space group $P2_1/m$ with an apparent disorder in the carbon atoms of the "mouth" phosphine, P1. Difference Fourier maps revealed two sets of three carbon atoms (total of six) related by the mirror plane and bonded to P1 with the expected bond distances and angles within each set. This was taken as a 1:1 disorder of the three carbon atoms on P1 about the mirror plane; therefore, one set (C1P1, C2P1, and C3P1) was included in the asymmetric unit with a given multiplicity of 0.5 and refined. In spite of lower R values ($R = 0.037$, $R_w = 0.051$ for 234 variables and 2341 observations for the lower R-value enantiomorph), the structure in $P2_1$ was rejected as the final solution because (1) there were large correlations between similar atoms on either side of the molecular plane, (2) the estimated standard deviations for bond distances and angles were two to three times those found in the $P2_1/m$ structure, and (3) the overall geometry of the molecule (cation and anion) appeared somewhat distorted. Although we have chosen to report the $P2_1/m$ structure, both structures exhibited the same gross features and provided structure proof for **5a**.

Dynamic NMR Studies. Determination of $\Delta G^{\ddagger}$. Theoretical line shapes were calculated for a series of rates using the method of C. S. Johnson.[19,20] The experimental spectra were matched against the theoretical spectra, and, in this way, exchange rate constants were determined for each temperature. These exchange rate constants, k, were then used to calculate the free energy of activation, $\Delta G^{\ddagger}$, at each temperature, T, using the Eyring equation.[21]

The $\Delta G^{\ddagger}$'s for η^5-pentadienyl ligand rotation were determined by line-shape analysis of the variable-temperature $^{31}P\{^1H\}$ NMR spectra (**1**, **3b**, **3c**, **3d**, and **3e** in toluene-d_8; **5a** and **5b** in DMSO-d_6). For **1**, **3b**, **3c**, **3d**, and **3e**, the reported $\Delta G^{\ddagger}$ is the average value over all the temperatures in the simulation and the uncertainty is the estimated standard deviation. (This deviation reflects the uncertainty in the average value but need not necessarily reflect the distribution of individual values.) It should be noted that coalescence was not achieved in the spectra of **3c** and **3d** and the $\Delta G^{\ddagger}$'s were obtained from the slow exchange spectra only. The values for **5a** and **5b** are approximated to within ±1 kcal, because our simulation program could not be applied to the A_2B pattern except near and after coalescence.

Summary

(η^5-Pentadienyl)RuCl(PPh_3)$_2$ (**1**) serves as a convenient precursor to a new family of pentadienyl–ruthenium–phosphine complexes. Treatment of **1** with 1 equivalent of PMe_3, PMe_2Ph, PEt_3, or PEt_2Ph yields the monosubstituted compounds (η^5-pentadienyl)RuCl(PR_3)(PPh_3) (**2a**, PR_3 = PMe_3; **2b**, PR_3 = PMe_2Ph; **2c**, PR_3 = PEt_3; **2d**, PR_3 = PEt_2Ph). Likewise, treatment of **1** with 2 equiv of PEt_3, PEt_2P, or $PEtPh_2$ leads to displacement of both PPh_3 ligands and production of (η^5-pentadienyl)RuCl(PR_3)$_2$ (**3c**, PR_3 = PEt_3; **3d**, PR_3 = PEt_2Ph; **3e**, PR_3 = $PEtPh_2$). The PMe_2Ph derivative (η^5-pentadienyl)RuCl(PMe_2Ph)(PPh_3) (**3b**) can be obtained cleanly from the reaction of **2b** with 1 equiv of PMe_2Ph.

Treatment of **1** with 3 equiv of PMe_3 produces (*syn*-η^3-pentadienyl)RuCl(PMe_3)$_3$ (**4a**). The PMe_2Ph analogue (*syn*-η^3-pentadienyl)RuCl(PMe_2Ph)$_3$ (**4b**) can be synthesized cleanly from the reaction of **2b** with 2 equiv of PMe_2Ph. Compounds **4a** and **4b** react with $Ag^+O_3SCF_3^-$ or $Me^+O_3SCF_3^-$ to produce the corresponding [(η^5-pentadienyl)Ru(PR_3)$_3$]$^+O_3SCF_3^-$ compounds (**5a**, PR_3 = PMe_3; **5b**, PR_3 = PMe_2Ph).

In solution, the η^5-pentadienyl ligands in compounds **1**, **3**, and **5** undergo rotation with respect to the metal–ligand framework. The $\Delta G^{\ddagger}$'s for these dynamic processes have been calculated from variable-temperature ^{31}P NMR spectroscopy and fall in the range of 14–18 kcal/mol.

Acknowledgment. Support from the National Science Foundation (Grant CHE-8520680) is gratefully acknowledged. Washington University's High Resolution NMR Service Facility was funded in part by National Institutes of Health Biomedical Research Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co.

Note Added in Proof. Recently, we have discovered that (η^5-pentadienyl)RuCl(PMe_3)$_2$ (**3a**) can be obtained cleanly via the procedure described below. Compound **1** is reacted with 2 equiv of PMe_3 in *methanol* to produce [(η^5-pentadienyl)Ru(PMe_3)$_2$(PPh_3)]$^+Cl^-$. After crystallization from methanol/diethyl ether, this salt is heated in acetonitrile solvent, producing **3a**.

Registry No. **1**, 110140-35-7; **2a**, 116026-05-2; **2b**, 116026-06-3; **2c**, 116026-07-4; **2d**, 116026-08-5; **3b**, 116026-09-6; **3c**, 116026-10-9; **3d**, 116026-11-0; **3e**, 116026-12-1; **4a**, 116026-13-2; **4b**, 116026-14-3; **5a**, 116026-16-5; **5b**, 116026-18-7; $RuCl_2(PPh_3)_3$, 15529-49-4; Pentadienyltributyltin, 87920-24-9.

Supplementary Material Available: Listing of final atomic coordinates, thermal parameters, bond lengths, bond angles, torsional angles, and significant least-squares planes for **2c**, **3c**, **3d**, **4a**, and **5a** and ORTEP drawings of molecule 2 of **3c**, the second of two independent molecules in the asymmetric unit, and of **5a**, showing both sets of disordered carbon atoms on phosphorus atom P1 (54 pages); listings of observed and calculated structure factor amplitudes (73 pages). Ordering information given on any current masthead page.

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