Base-Promoted Hydroalkylation Reactions of 1,3,5-$Me_3C_6H_3$, *p*-$MeC_6H_4CHMe_2$, C_6Me_6, *p*-MeC_6H_4Me, and MeC_6H_5 Ligands Coordinated to Ruthenium(II)

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The $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = 1,3,5-$Me_3C_6H_3$ (**1**), *p*-$MeC_6H_4CHMe_2$ (**2**), C_6Me_6 (**3**), *p*-MeC_6H_4Me (**4**), MeC_6H_5 (**5**)) dimers react with diphenylvinylphosphine (DPVP) to produce $[(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)Ru(DPVP)Cl_2]$ (**1a**), $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)Ru(DPVP)\ Cl_2]$ (**2a**), $[(\eta^6\text{-}C_6Me_6)\text{-}Ru(DPVP)Cl_2]$ (**3a**), $[(\eta^6\text{-}p\text{-}MeC_6H_4Me)Ru(DPVP)Cl_2]$ (**4a**), and $[(\eta^6\text{-}MeC_6H_5)Ru(DPVP)\text{-}Cl_2]$ (**5a**). In acetonitrile, compounds **1**−**5** undergo base-promoted hydroalkylation reactions with potassium *tert*-butoxide and diphenylvinylphosphine to produce $[\{\eta^6\text{-}3,5\text{-}Me_2C_6H_3\text{-}1\text{-}CH_2CH_2CH_2P(C_6H_5)_2\}RuCl_2]$ (**1b**), $[\{\eta^6\text{-}p\text{-}Me_2CHC_6H_4CH_2CH_2CH_2P(C_6H_5)_2\}RuCl_2]$ (**2b**), $[\{\eta^6\text{-}C_6Me_5CH_2CH_2CH_2P(C_6H_5)_2\}RuCl_2]$ (**3b**), $[\{\eta^6\text{-}p\text{-}MeC_6H_4CH_2CH_2CH_2P(C_6H_5)_2\}RuCl_2]$ (**4b**), and $[\{\eta^6\text{-}C_6H_5CH_2CH_2CH_2P(C_6H_5)_2\}RuCl_2]$ (**5b**). The reaction with the *p*-$MeC_6H_4CHMe_2$ complex proceeds regioselectively at the methyl group to produce the most stable product. All the complexes have been characterized spectroscopically and the crystal structures of several of them have been obtained.

Introduction

π-Complexation of aromatics by transition-metal moieties has a powerful effect on the reactivity of the arene.[1−9] Exploitation of this effect has led to significant advances in transition-metal-mediated aromatic chemistry.[10] One major feature is the enhancement of the acidity of benzylic protons, which could lead to the alkylation and functionalization of methylated aromatic compounds.[11−13] Extensive work has been done on substitution and addition reactions with arenes complexed to the $Cr(CO)_3$[1,3,14−19] or $Mn(CO)_3^+$ [20,21] moieties. More recently reactions of other transition-metal arene complexes have been studied. Among these, the $[Fe(\eta^6\text{-arene})_2]^{2+}$,[22−29] $[Fe(arene)Cp]^+$,[4] and $[Ru(arene)Cp]^+$ [30] complexes offer the possibility of synthesizing functionalized cyclohexadienes and polyalkylated and polyfunctionalized aromatics.[22,23,26] The most studied reactions consist of deprotonation of a methyl substituent with an excess of a base and subsequent alkylation of the methylene group by alkyl or aryl halides.

Despite the aforementioned work for functionalizing coordinated arene ligands, to our knowledge, few reports of intramolecular C−H hydroalkylations have appeared. We have recently found that, in refluxing acetonitrile, the rhodium complex $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$[31,32] undergoes a base-promoted hydroalkylation with potassium *tert*-butoxide and diphenylvinylphosphine. We now have extended these studies to the reactions of $[(\eta^6\text{-arene})\text{-}RuCl_2]_2$ complexes under similar conditions. In this

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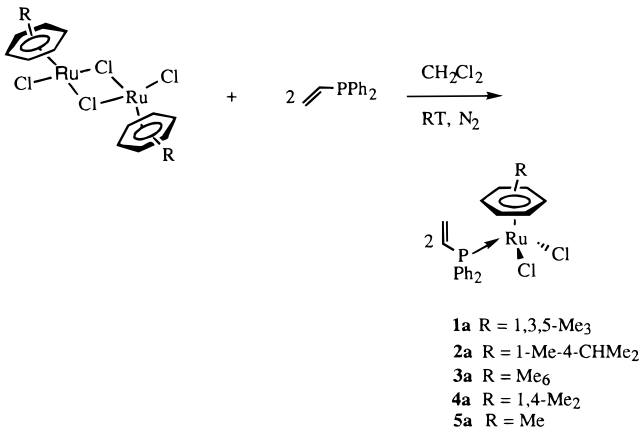
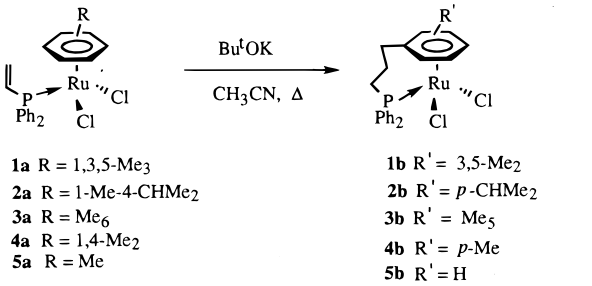
Scheme 1



Scheme 2



paper, details of the synthesis and characterization of novel ruthenium complexes containing chelating (phosphinopropyl)arene ligands, which are formed by base-promoted intramolecular hydroalkylations, are described. Our chief aim in this work is to put a functionality onto the methyl substituent which will act as a hand to grasp and rigidly hold the arene moiety to the metal in such a way that ring loss during reactions and catalytic cycles is less of a problem.

Results and Discussion

Synthesis and Characterization of 1a−5a. The $[(\eta^6\text{-arene})RuCl_2]_2$ dimers[33] (arene = 1,3,5-$Me_3C_6H_3$ (**1**), *p*-$MeC_6H_4CHMe_2$ (**2**), C_6Me_6 (**3**), *p*-MeC_6H_4Me (**4**), MeC_6H_5 (**5**)) were treated with 2.1 equiv of diphenylvinylphosphine (DPVP) under a nitrogen atmosphere, in dichloromethane at ambient temperature. After 4 h of stirring the ruthenium phosphine complexes **1a−5a** were isolated as microcrystalline red solids (Scheme 1).

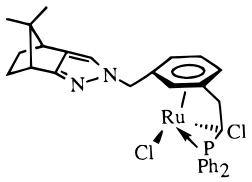
In chloroform-*d*, the $^{31}P\{^1H\}$ NMR spectra of the complexes show a singlet at δ 34.02 (**1a**), 21.77 (**2a**), 29.28 (**3a**), 29.33 (**4a**) and 25.17 ppm (**5a**), respectively, corresponding to the coordinated DPVP. The ^1H NMR spectra (see Experimental Section) show three multiplets in the olefinic region. The relative ratios of these resonances to those of the η^6-arene protons confirmed that there is only one DPVP coordinated to ruthenium and the vinyl group has not undergone a hydroalkylation reaction with the η^6-arene ligands.

Reactions of 1a−5a with Bu^{t}OK. The reactions of the complexes **1a−5a** with 1.0 equiv of Bu^{t}OK in acetonitrile led to the formation of hydroalkylated products **1b−5b** (Scheme 2). Moreover, if isolation of the complexes **1a−5a** was avoided, and the base was added 15 min after the dimers were treated with DPVP, complexes **1b−5b** were obtained in good yields, in one-pot reactions, after 48 h of reflux in acetonitrile. Following workup and isolation of the products, the ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra revealed the formation of complexes **1b−5b**. These results establish that the reaction is facilitated by a base to initiate the hydroalkylation reaction. The use of excess base has been avoided, since it seems to promote excessive decomposition of the complexes **1a−5a**. The reaction mixtures turned from a clear red to a dark red upon addition of the base.

The novelty of this reaction is the unusual reaction between the vinyl moiety on the coordinated phosphorus and the methyl groups of the η^6-arene ligands coordinated to ruthenium(II). The terminal vinylic carbon atom forms a new C−C bond to the methyl group with a concomitant C−H bond cleavage and formation of a new C−H bond on the carbon α to the phosphorus atom. Thus, a common feature of these reactions is the prior generation of a metal-stabilized benzyl carbanion that adds to the β-carbon of the vinyl group to form a new C−C bond and a carbanion α to the phosphorus that is subsequently protonated. This reaction is formally a base-catalyzed hydroalkylation of a C−C double bond.

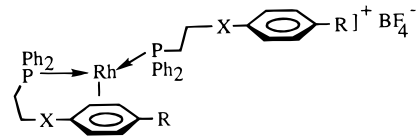
A notable feature of the products of these reactions is the simultaneous coordination of both the phosphine and the η^6-arene ligands to the ruthenium center. Thus, even though there may be an alternative route for synthesizing the phosphinopropyl substituted arene rings, it would be very difficult if not impossible to coordinate both the arene and the phosphine moieties to the ruthenium center. Moreover, the reaction with the *p*-$MeC_6H_4CHMe_2$ arene ligand proceeds regioselectively at the methyl group to produce the most stable product.

As far we are aware, only one similar ruthenium complex (**6**) has been previously reported.[34] Rhodium-



(6)

(I) complexes of $ArX(CH_2)_2PPh_2$ (X = O, CH_2; **7**) in which both the arene and phosphine are coordinated to the metal have also been described.[35] These complexes are



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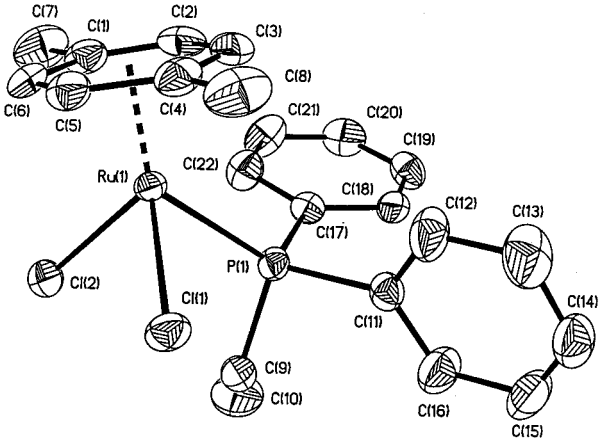

Figure 1. Structural drawing of **4a** with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

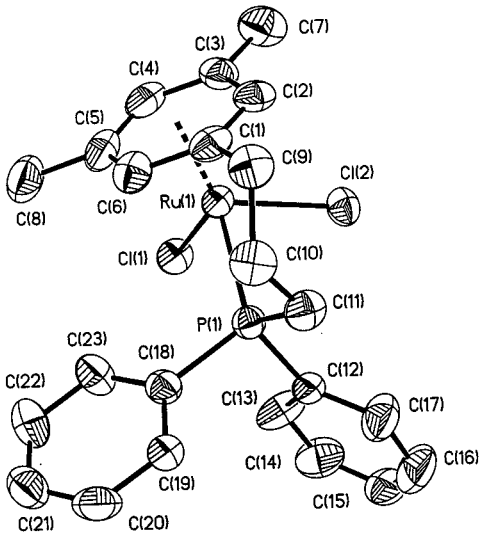

Figure 2. Structural drawing of **1b** with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

hemilabile[36] and undergo facile novel intramolecular arene exchange reactions.

X-ray crystallographic analysis confirmed the structures of both the precursors (**1a** and **4a**) and the hydroalkylated products (**1b**, **2b, 4b**, and **5b**). The quality of the crystals of **1a** was poor but was sufficient to establish the atom connectivity. The molecular structure for **4a** and those of the hydroalkylated products are illustrated in Figures1−5. Figures 4 and 5 appear in the Supporting Information. The structures of the precursors possess a pseudo-octahedral geometry around the ruthenium center. For the hydroalkylated products, the analysis revealed a pseudo-octahedral geometry at ruthenium with η^6-coordinated arene rings, one propyldiphenylphosphine moiety and two chlorides completing the metal coordination sphere. Each ruthenium bound diphenylphosphine group is connected to the arene rings via three methylene carbons. A similar linkage was observed for the analogous rhodium complex $[\{\eta^5\text{-}C_5Me_3\text{-}1,3\text{-}CH_2CH_2CH_2P(C_6H_5)_2\}_2RhCl]PF_6$.[31] For **1b** there are two inequivalent molecules in the asymmetric unit with very small differences in their

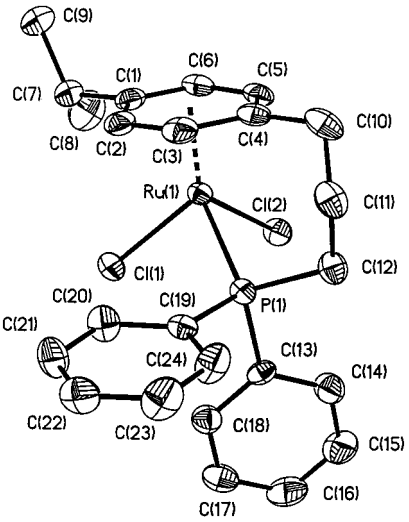

Figure 3. Structural drawing of **2b** with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

overall structures. They differ mainly in the orientations of the phenyl groups attached to phosphorus. None of the Ru−P and Ru−Cl bond distances of the hydroalkylated products differ significantly from those of their precursors.[33] This indicates that there is no steric encumbrance upon formation of the hydroalkylated products. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopic data for the precursors **1a** and **4a** as well as the hydroalkylated products **1b**−**5b** are in accord with the assigned structures. Crystallographic data are summarized in Table 1, and selected bond distances and angles are given in Table 2.

The electron density at the ruthenium atom for the precursors [(η^6-arene)$RuCl_2$(DPVP)] and the hydroalkylated products were estimated from the $^{31}P\{^1H\}$ chemical shifts and the oxidation potentials for the Ru^{II}/Ru^{III} couples, assuming that these data reflect the electron density at the metal center. For both types of complexes a reversible Ru^{II}/Ru^{III} oxidation was observed. The cyclic voltammograms in CH_2Cl_2 solution show that the oxidation of the precursors and the hydroalkylated products occur at the same potentials within experimental error. The trends in Ru^{II}/Ru^{III} potentials as a function of the arene for both the precursors and the hydroalkylated products follow the expected decrease in the electron-donating ability of the arene ligands. The $^{31}P\{^1H\}$ chemical shifts generally move upfield by 6−8 ppm upon formation of the hydroalkylated products. This indicates that there is a slight increase in electron density around the metal center upon formation of the hydroalkylated products. This may be attributed to the relatively higher electron-donating ability of the propylene than the vinyl functionality.[37] Electrochemical and $^{31}P\{^1H\}$ data for the complexes **1a**−**5a** and **1b**−**5b** are summarized in Table 3.

Conclusion

Intramolecular base-promoted hydroalkylation of η^6-coordinated methyl arenes to diphenylvinylphosphine occurs readily. The novel products of these reactions contain a tethered phosphinopropyl-η^6-arene ligand.

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Table 1. Crystallographic Data for 4a, 1b, 2b, 4b and 5b

	4a	1b	2b	4b	5b
empirical formula	$C_{22}H_{23}Cl_2PRu$	$C_{23}H_{25}Cl_2PRu$	$C_{24}H_{27}Cl_2PRu$	$C_{22}H_{23}Cl_2PRu$	$C_{21}H_{21}Cl_2PRu$
M_w	490.34	504.37	518.40	490.34	476.32
cryst syst	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	16.7533(11)	12.0231(7)	7.8102(5)	7.8483(10)	8.2080(6)
b (Å)	7.2475(5)	14.9360(13)	9.9985(5)	10.4983(8)	8.4318(4)
c (Å)	17.4702(14)	18.37229(12)	14.3465(11)	12.5892(13)	14.8847(11)
Z	4	4 [a]	2	2	2
α (deg)	90	100.337(6)	96.407(7)	79.294(8)	81.858(8)
β (deg)	99.639(4)	92.587(5)	91.310(6)	79.635(9)	79.742(8)
γ (deg)	90	106.386(6)	93.041(5)	88.685(9)	73.636(5)
V (Å^3)	2091.3(3)	3097.8(4)	1111.29(12)	1002.53(18)	968.04(11)
ρ_{calcd} (Mg/m^3)	1.557	1.593	1.549	1.624	1.634
no. of rflns collcd	4788	12574	4851	4368	4174
no. of indep rflns	3687	10878	3918	3520	3400
R1(F)[a,b]	0.0456	0.0643	0.0387	0.0305	0.0371
wR2(F^2)[a,b]	0.0848	0.1482	0.0665	0.0653	0.0757
GOF	1.003	1.043	1.009	1.005	1.065

[a] The data were refined by the method of full-matrix least squares on F^2, with the final R indices having $I > 2\sigma(I)$. [b] $R1(F) = \sum(|F_o| - |F_c|)^2/\sum(|F_o|)$; $wR2(F^2) = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_c^2|]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for the Complexes

	4a	1b	2b	4b	5b
Ru−P	2.3529(14)	2.326(2)	2.3226(11)	2.3127(9)	2.3243(11)
Ru−Cl(1)	2.4129(14)	2.420(2)	2.4040(10)	2.4108(9)	2.4183(12)
Ru−Cl(2)	2.4065(15)	2.397(2)	2.4073(11)	2.4179(10)	2.4002(11)
Ru−(C_1−C_6)[a]	2.2103(6)	2.208(7)	2.2041(6)	2.2103(3)	2.2105(9)
P−Ru−Cl(1)	81.18(5)	93.13(7)	88.60(4)	84.38(3)	90.63(4)
P−Ru−Cl(2)	87.23(5)	84.43(7)	84.87(4)	89.75(9)	84.26(4)
Cl(1)−Ru−l(2)	88.24(6)	88.39(7)	89.75(2)	89.36(2)	88.79(5)

[a] C_1−C_6 denotes the average Ru−C distances.

Table 3. $^{31}P\{^1H\}$ NMR Data and Ru^{II}/Ru^{III} Potentials for 1a−5a and 1b−5b

compd	$\delta(^{31}P\{^1H\})$ (ppm)	$E_{1/2}(Ru^{II}/Ru^{III})$ (V)[a]	ΔE_p (mV)
1a	34.02	0.61	105
2a	21.77	0.68	91[b]
3a	29.28	0.47	75[b]
4a	29.33	0.67	138
5a	25.17	0.74	107[b]
1b	27.74	0.61	137
2b	21.13	0.66	128
3b	25.17	0.47	96
4b	20.46	0.67	130
5b	20.10	0.74	102

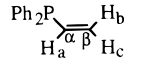
[a] Measured in CH_2Cl_2 solution at a glassy-carbon working electrode, with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. All potentials are vs Fc/Fc^+. The scan rate was 250 mV/s. [b] Data from ref 33.

These complexes probably could not be prepared by any other route. The new complexes are stable and are electronically and structurally very similar to their precursors. The chelate ring in these complexes is strain-free. Their reactivity, which is expected to be somewhat different from that of their precursors, is presently under investigation.

Experimental Section

Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or synthesized as described below. Acetonitrile was dried over CaH_2 and distilled immediately before use. 1,3,5-Trimethylcyclohexa-1,4-diene, 3,6-dimethylcyclohexa-1,4-diene,[38,39] and [(η^6-arene)-$RuCl_2]_2$[39] were synthesized by literature procedures. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were obtained using a Mel-Temp apparatus and are uncorrected. NMR spectra were recorded on a Varian Unity Plus-500 FT-NMR spectrometer operating at 500 MHz for ^1H, 125.7 MHz for ^{13}C, and 202.3 MHz for ^{31}P. Proton and carbon chemical shifts are relative to internal Me_4Si, while phosphorus chemical shifts are relative to external 85% H_3PO_4 (aqueous) with positive values being downfield of the respective reference. Cyclic voltammograms were recorded at 25 °C in freshly distilled CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate using a BAS CV 50 W voltammetric analyzer. A three-electrode system was used. The working electrode was a glassy-carbon disk; the auxiliary electrode was a platinum electrode, and the reference electrode was an aqueous Ag^+/AgCl electrode separated from the cell by a Luggin capillary. The Fc/Fc^+ couple occurred at 509 mV [40]under the same conditions.

Synthesis. Preparations of 1a−5a. Complexes **1a**−**5a** were synthesized from the appropriate [(η^6-arene)$RuCl_2]_2$ dimers as follows.[33] A suspension of 1.0 mmol of the dimer in 40 mL of dichloromethane was purged with dry nitrogen for 15 min; then 2.1 mmol of diphenylvinylphosphine was added via syringe. The mixture was stirred under dry nitrogen at ambient temperature for 4 h. The solution volume was reduced to about 10 mL on a rotary evaporator, and then ether was added. The products were isolated by filtration, washed with ether, and dried under vacuum to give the pure products as microcrystalline solids (percent yield and melting point (°C)): **1a,** 70 and 209−211; **2a,** 95 and 195−196; **3a,** 68 and 226−228; **4a,** 92 and 223−225; **5a**, 85 and 207−209.



1a: ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.81 (m, 4H, H_m), 7.45 (m, 6H, H_o, H_p), 6.75 (ddd, $^2J(PH) = 24.5$ Hz, $^3J(H_aH_b) =$

(38) Birch, A. J. *Adv. Org. Chem.* **1972**, *8*, 1.
(39) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.
(40) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

18.5 Hz, $^3J(H_aH_c)$ = 12.0 Hz, 1H, H_a), 5.91 (ddd, $^3J(PH)$ = 38.5 Hz, $^3J(H_aH_c)$ = 12.0 Hz, $^2J(H_bH_c)$ = 1.0 Hz, 1H, H_c), 5.31 (ddd, $^3J(PH)$ = 19.0 Hz, $^3J(H_aH_b)$ = 18.5 Hz, $^2J(H_bH_c)$ = 1.0 Hz, 1H, H_b), 4.71 (s, 3H, CH_{ring}), 1.98 (s, 9H, $3CH_3$); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C) δ 134.33 (d, $^2J(PC)$ = 9.6 Hz, C_o), 132.57 (d, $^2J(PC)$ = 49.0 Hz, C_i), 131.35 (d, $^1J(PC)$ = 46.2 Hz, C_α), 130.61 (d, $^4J(PC)$ = 2.5 Hz, C_p), 128.35 (d, $^2J(PC)$ = 4.4 Hz, C_β), 128.11 (d, $^3J(PC)$ = 9.7 Hz, C_m), 103.42 (d, $J(PC)$ = 2.5 Hz, C_{ring}), 85.08 (d, $J(PC)$ = 4.1 Hz, C_{ring}), 1.98 (s, CH_3). Anal. Calcd for $C_{23}H_{25}Cl_2PRu$ (**1a**): C, 54.77; H, 4.99; Cl, 14.06. Found: C, 54.69; H, 4.87; Cl, 13.92.

2a:^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.78 (m, 4H, H_m), 7.44 (m, 6H, H_o, H_p), 6.96 (ddd, $^2J(PH)$ = 25.0 Hz, $^3J(H_aH_b)$ = 18.0 Hz, $^3J(H_aH_c)$ = 12.0 Hz, 1H, H_a), 5.92 (ddd, $^3J(PH)$ = 38.0 Hz, $^3J(H_aH_c)$ = 12.0 Hz, $^2J(H_bH_c)$ = 1.0 Hz, 1H, H_c), 5.17 (ddd, $^3J(PH)$ = 18.0 Hz, $^3J(H_aH_b)$ = 18.0 Hz, $^2J(H_aH_c)$ = 1.0 Hz, 1H, H_b), 5.25 (m, 4H, CH_{ring}), 2.58 (septet, $^3J(HH)$ = 7.0 Hz, 1H, CH), 1.87 (s, 3H, CH_3), 0.93 (d, $^3J(HH)$ = 7.0 Hz, 6H, $2CH_3$); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C) δ 133.73 (d, $^2J(PC)$ = 9.0 Hz, C_o), 132.85 (d, $^1J(PC)$ = 46.8 Hz, C_i), 131.05 (d, $^1J(PC)$ = 49.1 Hz, C_α), 130.56 (d, $^4J(PC)$ = 2.4 Hz, C_p), 129.96 (d, $^2J(PC)$ = 4.5 Hz, C_β), 128.19 (d, $^3J(PC)$ = 9.8 Hz, C_m), 108.73 (d, $J(PC)$ = 1.3 Hz, C_{ring}) 94.92 (s, C_{ring}), 89.24 (d, $J(PC)$ = 4.1 Hz, C_{ring}), 85.87 (d, $J(PC)$ = 5.8 Hz, C_{ring}), 30.03 (s, CH), 21.49 (s, $2CH_3$), 17.39 (s, CH_3). Anal. Calcd for $C_{24}H_{27}Cl_2PRu$ (**2a**): C, 55.60; H, 5.25; Cl, 13.68. Found: C, 55.35; H, 5.18; Cl, 13.54.

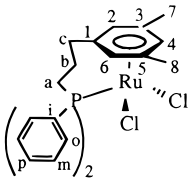
3a: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.77 (m, 4H, H_m), 7.43 (m, 6H, H_o, H_p), 6.79 (ddd, $^2J(PH)$ = 25.0 Hz, $^3J(H_aH_c)$ = 18.0 Hz, $^3J(H_aH_b)$ = 12.5 Hz, 1H, H_a), 5.77 (dd, $^3J(PH)$ = 37.2 Hz, $^3J(H_aH_b)$ = 12.5 Hz, 1H, H_c), 5.28 (dd, $^3J(PH)$ = 18.0 Hz, $^3J(H_aH_b)$ = 18.0 Hz, 1H, H_b), 1.78 (s, 18H, CH_3); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C) δ 134.82 (d, $^2J(PC)$ = 9.2 Hz, C_o), C_i unresolved, 130.40 (d, $^1J(PC)$ = 50.0 Hz, C_α), 130.29 (d, $^4J(PC)$ = 2.3 Hz, C_p), 128.63 (d, $^2J(PC)$ = 12.1 Hz, C_β), 127.91 (d, $^3J(PC)$ = 9.7 Hz, C_m), 96.15 (d, $J(PC)$ = 3.3 Hz, C_{ring}), 15.17 (s, CH_3). Anal. Calcd for $C_{26}H_{31}Cl_2PRu$ (**3a**): C, 57.14; H, 5.72; Cl, 12.97. Found: C, 57.02; H, 5.57; Cl, 12.68.

4a: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.80 (m, 4H, H_m), 7.45 (m, 6H, H_o, H_p), 6.90 (ddd, $^3J(PH)$ = 25.0 Hz, $^3J(H_aH_b)$ = 18.5 Hz, $^3J(H_aH_c)$ = 12.3 Hz, 1H, H_a), 5.95 (ddd, $^3J(PH)$ = 26.5 Hz, $^3J(H_aH_c)$ = 12.0 Hz, $^2J(H_bH_c)$ = 1.0 Hz, 1H, H_c), 5.30 (ddd,$^3J(PH)$ = 19.0 Hz, $^3J(H_aH_b)$ = 18.5 Hz, $^2J(H_bH_c)$ = 1.0 Hz, 1H, H_b), 5.16 (d, $J(PH)$ = 1.0 Hz, 4H, CH_{ring}), 1.85 (s, 6H, $2CH_3$); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C) δ 133.76 (d, $^2J(PC)$ = 9.3 Hz, C_o), 132.73 (d, $^1J(PC)$ = 47.3 Hz, C_i), 131.08 (d, $^1J(PC)$ = 49.3 Hz, C_α), 130.67 (d, $^4J(PC)$ = 2.3 Hz, C_p), 129.76 (d, $^2J(PC)$ = 4.7 Hz, C_β), 128.28 (d, $^3J(PC)$ = 9.8 Hz, C_m), 95.99 (s, C_{ring}), 89.71 (d, $J(PC)$ = 5.0 Hz, CH_{ring}), 17.52 (s, 2C, $2CH_3$). Anal. Calcd for $C_{22}H_{23}Cl_2PRu$ (**4a**): C, 53.88; H, 4.73; Cl, 14.46. Found: C, 53.69; H, 4.67; Cl, 14.38.

5a: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.75 (m, 4H, H_m), 7.46 (m, 6H, H_o, H_p), 6.83 (ddd, $^2J(PH)$ = 25.0 Hz, $^3J(H_aH_b)$ = 18.5 Hz, $^3J(H_aH_c)$ = 12.5 Hz, 1H, H_a), 5.99 (dd, $^3J(PH)$ = 39.0 Hz, $^3J(H_aH_c)$ = 12.5 Hz, 1H, H_c), 5.38 (dd, $^3J(PH)$ = 18.5 Hz, $^3J(H_aH_b)$ = 18.5 Hz, 1H, H_b), 5.33 (td, $^3J(HH)$ = 6.0 Hz, $^2J(PH)$ = 2.0 Hz, 2H, H_m), 5.19 (d, $^3J(HH)$ = 6.0 Hz, 2H, H_o), 4.68 (t, $^3J(HH)$ = 6.0 Hz, 1H, H_p), 2.16 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C) δ 133.65 (d, $^2J(PC)$ = 9.3 Hz, C_o), 132.73 (d, $^1J(PC)$ = 48.6 Hz, C_i), 130.91 (d, $^1J(PC)$ = 50.3 Hz, C_α), 130.72 (d, $^4J(PC)$ = 2.4 Hz, C_p), 129.96 (d, $^2J(PC)$ = 4.4 Hz, C_β), 128.38 (d, $^3J(PC)$ = 9.9 Hz, C_m), 108.05 (d, $J(PC)$ = 5.0 Hz, C_{ring}), 88.60 (d, $J(PC)$ = 1.6 Hz, CH_{ring}), 87.85 (d, $J(PC)$ = 6.2 Hz, CH_{ring}), 80.11 (s, CH_{ring}), 18.72 (s, CH_3). Anal. Calcd for $C_{21}H_{21}Cl_2PRu$ (**5a**): C, 52.95; H, 4.44; Cl, 14.88. Found: C, 52.76; H, 4.25; Cl, 14.67.

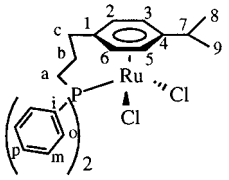
Preparations of 1b−5b. General Procedure. These complexes were all prepared by the same general procedure as follows. A suspension of the $[(\eta^6\text{-arene})RuCl_2]_2$ dimer (0.20 g) in 25 mL of CH_3CN was purged with dry nitrogen for 15 min, after which diphenylvinylphosphine (0.13−0.17 mL) was added via syringe, and then the clear red mixture was stirred at room temperature for 15 min. To this solution was added Bu^{t}OK (0.03−0.04 g) and 5 mL of CH_3CN. The clear red solution turned dark red upon addition of the base. The solution was refluxed for 48 h. Then the solvent was removed on a rotary evaporator. The residue was dissolved in a minimum amount of dichloromethane, and ether was added. The mixture was then filtered and recrystallized from dichloromethane/ether or dichloromethane/hexane solvent mixtures. Drying the resulting solid in vacuo gave the pure products as red crystals (% yield and melting point (°C)): **1b**, 70 and 226−228; **2b**, 67 and 190−192; **3b**, 48 and 220−222; **4b**, 60 and 216−218; **5b**, 52 and 198−200.

1b:



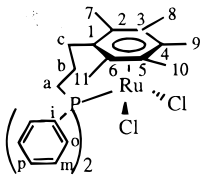
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.59 (m, 4H, H_o), 7.33 (m, 2H, H_p), 7.28 (m, 4H, H_m), 5.79 (s, 1H, H_4), 4.67 (t, $^4J(HH)$ = 1.5 Hz, 2H, $H_{2,6}$), 2.49 (m, 2H, H_c), 2.46 (m, 2H, H_a), 2.27 (s, 6H, $H_{7,8}$), 2.04 (appdquin, $^3J(PH)$ = 23.0 Hz, $^3J(HH)$ = 5.0 Hz, 2H, H_b); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C) δ 133.66 (d, $^2J(PC)$ = 8.7 Hz, C_o), 132.81 (d, $^1J(PC)$ = 48.1 Hz, C_i), 130.00 (d, $^4J(PC)$ = 1.8 Hz, C_p), 127.63 (d, $^3J(PC)$ = 10.1 Hz, C_m), 104.65 (d, $J(PC)$ = 3.8 Hz, C_1), 98.33 (d, $J(PC)$ = 12.1 Hz, C_4), 90.5 (d, $J(PC)$ = 0.9 Hz, $C_{3,5}$), 80.3 (s, $C_{2,6}$), 30.44 (d, $^3J(PC)$ = 2.0 Hz, C_c), 23.00 (d, $^1J(PC)$ = 30.3 Hz C_a), 20.22 (d, $^2J(PC)$ = 1.8 Hz, C_b), 18.01 (s, $C_{7,8}$). Anal. Calcd for $C_{23}H_{25}Cl_2PRu$ (**1b**): C, 54.77; H, 4.99; Cl, 14.06. Found: C, 54.64; H, 4.91; Cl, 13.86.

2b:



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.61 (m, 4H, H_o), 7.34 (m, 2H, H_p), 7.31 (m, 4H, H_m), 5.48 (d, $^3J(HH)$ = 6.0 Hz, 2H, $H_{3,5}$), 5.05 (dd, $^3J(HH)$ = 6.0 Hz, $J(PH)$ = 1.5 Hz, 2H, $H_{2,6}$), 3.21 (septet, $^3J(HH)$ = 7.0 Hz, 1H, H_7), 2.59 (t, $^3J(HH)$ = 5.5 Hz, 2H, H_c), 2.57 (dt, $^2J(PH)$ = 12.0 Hz, $^3J(HH)$ = 4.5 Hz, 2H, H_a), 2.15 (dtt, $^3J(PH)$ = 23.0 Hz, $^3J(HH)$ = 5.5 Hz, $^3J(HH)$ = 4.5 Hz, 2H, H_b), 1.39 (d, $^3J(HH)$ = 7.0 Hz, 6H, $H_{8,9}$); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C) δ 133.82 (d, $^2J(PC)$ = 8.5 Hz, C_o), 132.17 (d, $^1J(PC)$ = 48.6 Hz, C_i), 130.14 (d, $^4J(PC)$ = 2.6 Hz, C_p), 127.79 (d, $^3J(PC)$ = 9.9 Hz, C_m), 122.34 (d, $J(PC)$ = 9.3 Hz, C_1), 87.32 (s, C_4), 86.79 (s, $C_{3,5}$), 84.16 (s, $C_{2,6}$), 30.78 (s, C_7), 30.12 (d, $^3J(PC)$ = 0.6 Hz, C_c), 22.70 (d, $^1J(PC)$ = 31.0 Hz, C_a), 21.70 (s, $C_{8,9}$), 20.33 (d, $^2J(PC)$ = 1.0 Hz, C_b). Anal. Calcd for $C_{24}H_{27}Cl_2PRu$ (**2b**): C, 55.60; H, 5.25; Cl, 13.68. Found: C, 55.44; H, 5.22; Cl, 13.61.

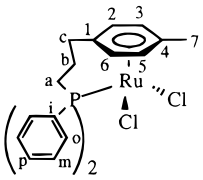
3b:



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.64 (m, 4H, H_o), 7.30 (m, 6H, H_m, H_p), 2.59 (t, $^3J(HH)$ = 6.5 Hz, 2H, H_c), 2.43 (m, 2H, H_a), 2.24 (d, $J(PH)$ = 2.5 Hz, 3H, H_9), 2.19 (dquin, $^3J(HH)$ =

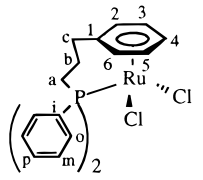
4.5 Hz, ^3J(PH) = 24.0 Hz, 2H, H_b), 2.09 (s, 6H, $H_{8,10}$), 1.76 (s, 6H, $H_{7,11}$); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C) δ 133.31 (d, ^2J(PC) = 8.5 Hz, C_o), 132.75 (d, ^1J(PC) = 46.4 Hz, C_i), 129.58 (d, ^4J(PC) = 1.9 Hz, C_p), 127.54 (d, ^3J(PC) = 9.8 Hz, C_m), 106.19 (d, J(PC) = 10.9 Hz, C_1), 101.18 (d, J(PC) = 4.5 Hz, C_4), 91.55 (s, $C_{3,5}$), 85.48 (d, J(PC) = 1.4 Hz, $C_{2,6}$), 24.91 (d, ^3J(PC) = 1.9 Hz, C_c), 22.58 (d, ^2J(PC) = 3.0 Hz, C_b), 21.66 (d, ^1J(PC) = 30.7 Hz, C_a), 16.01 (s, $C_{7,11}$), 15.51 (s, $C_{8,10}$), 14.88 (d, J(PC) = 1.3 Hz, C_9). Anal. Calcd for $C_{26}H_{31}Cl_2PRu$ (**3b**): C, 57.14; H, 5.72; Cl, 12.97. Found: C, 57.15; H, 5.60; Cl, 12.73.

4b:



^{1}H NMR (500 MHz, $CDCl_3$, 40 °C) δ 7.64 (m, 4H, H_o), 7.35 (m, 6H, H_m, H_p), 5.39 (d, ^3J(PH) = 5.5 Hz, 2H, $H_{3,5}$), 5.06 (d, J(PH) = 5.5 Hz, 2H, $H_{2,6}$), 2.61 (t, ^3J(HH) = 6.0 Hz, 2H, H_c), 2.59 (t, ^3J(HH) = 6.0 Hz, 2H, H_a) 2.19 (appdquin, ^3J(HH) = 5.5 Hz, ^3J(PH) = 24.0 Hz, 2H, H_b), 2.44 (s, 3H, H_7); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 40 °C) δ 133.81 (d, ^2J(PC) = 8.5 Hz, C_o), 132.46 (d, ^1J(PC) = 48.4 Hz, C_i), 130.26 (d, ^4J(PC) = 1.9 Hz, C_p), 127.95 (d, ^3J(PC) = 10.1 Hz, C_m), 88.90 (d, J(PC) = 6.3 Hz, C_1), 88.88 (s, C_4), 85.59 (s, $C_{3,5}$), 85.32 (s, $C_{2,6}$), 30.11 (d, ^3J(PC) = 1.4 Hz, C_c), 22.72 (d, ^1J(PC) = 31.7 Hz, C_a), 20.55 (d, ^2J(PC) = 0.88 Hz, C_b), 18.43 (s, C_7). Anal. Calcd for $C_{22}H_{23}Cl_2PRu$ (**4b**): C, 53.88; H, 4.73; Cl, 14.46. Found: C, 53.72; H, 4.65; Cl, 14.22.

5b:



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.63 (m, 4H, H_o), 7.38 (m, 2H, H_p), 7.32 (m, 4H, H_m) 6.40 (t, ^3J(HH) = 11.5 Hz, H_4), 5.78 (t, ^3J(HH) = 11.5 Hz, 2H, $H_{2,6}$), 5.15 (dd, ^3J(PH) = 5.0 Hz, ^3J(HH) = 3.5 Hz, 2H, $H_{3,5}$), 2.61 (t, ^3J(HH) = 6.0 Hz, 2H, H_c), 2.59 (t, ^3J(HH) = 6.0 Hz, 2H, H_a) 2.23 (dquin, ^3J(HH) = 5.0 Hz, ^3J(PH) = 23.0 Hz, 2H, H_b); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C) δ 133.91 (d, ^2J(PC) = 8.4 Hz, C_o), 131.87 (d, ^1J(PC) = 49.4 Hz, C_i), 130.41 (d, ^4J(PC) = 2.6 Hz, C_p), 127.97 (d, ^3J(PC) = 10.2 Hz, C_m), 100.98 (d, J(PC) = 10.3 Hz, C_1), 89.75 (s, C_4), 88.31 (s, $C_{3,5}$), 84.48 (s, $C_{2,6}$), 30.52 (d, ^3J(PC) = 1.5 Hz, C_c), 22.67 (d, ^1J(PC) = 31.3 Hz, C_a), 20.26 (d, ^2J(PC) = 1.3 Hz, C_b). Anal. Calcd for $C_{21}H_{21}Cl_2PRu$ (**5b**): C, 52.95; H, 4.44; Cl, 14.88. Found: C, 52.69; H, 4.28; Cl, 14.71.

X-ray Data Collection and Processing. Crystals of the complexes, obtained from CH_2Cl_2/ether mixtures were mounted on glass fibers coated with epoxy and placed on a Siemens P_4 diffractometer. Intensity data were taken in the ω-mode at 298 K with Mo Kα graphite-monochromated radiation (λ = 0.710 73 Å). Three check reflections monitored every 100 reflections showed random (<2%) variation during the data collections. The data were corrected for Lorentz, polarization effects, and absorption using an empirical model derived from azimuthal data collections. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[41] Calculations were performed with the Siemens SHELXTL plus version 5.10 software package on a personal computer. The structures were solved by Patterson methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C−H vector was fixed at 0.96 Å.

Acknowledgment. This research was supported by an award from the Research Corp., for which we are grateful.

Supporting Information Available: Structural drawings of **4a** and **5b** and tables of crystal data and structure refinement, atomic coordinates, isotropic and anisotropic displacement parameters, bond lengths and angles, and hydrogen coordinates for **4a**, **1b**, **2b, 4b**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000375T

(41) *International Tables for X-ray Crystallography*; D. Reidel: Boston, MA, 1992; Vol. C.