Kinetics and Mechanism of Nucleophilic Substitutions on Coordinated Polyenes and Polyenyls. 3.1 Activation of η^5 -Cyclopentadienyl Ligands toward Nucleophilic Attack through $\eta^5 \rightarrow \eta^3$ Ring Slippage and a Comparison with Reaction at C₅H₄O in $[Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)(L)]^+$ (L = CH₃CN, Pyridine, Thiourea)

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Complexes of the types $[Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)]_2(CF_3SO_3)_2$ (1) and $[Ru(\eta^5-C_5H_5)(\eta^4-C_5$ $C_{5}H_{4}O(L)$ [CF₃SO₃ (L = CH₃CN (2), pyridine (3), thiourea (4)) react with tertiary phosphines to give (i) 1,1'- (12) or (ii) 1,2-disubstituted ruthenocenes (13) depending primarily on the basicity of the entering phosphine and the nature of L. Path i proceeds via the intermediacy of $[\operatorname{Ru}(\eta^3 - \operatorname{C}_5H_5)(\eta^4 - \operatorname{C}_5H_4O)(\operatorname{PR}_3)]_2^{2+}$ (5) and $[\operatorname{Ru}(\eta^3 - \operatorname{C}_5H_5)(\eta^4 - \operatorname{C}_5H_4O)(\operatorname{PR}_3)(L)]^+$ (6-8); i.e., the hapticity of the C₅H₅ ligand is changed from η^5 to η^3 while forming an additional Ru–P bond. The η^3 bonding mode was established by ¹H and ¹³C{¹H} NMR spectroscopies. The kinetics of these reactions were studied in detail, providing enthalpies and entropies of both activation and reaction. The conversions to **6**–**8** are exothermic ($\Delta H^{\circ} = -5.5$ to -16.9 kcal mol⁻¹) but entropically unfavorable ($\Delta S^\circ = -44.8$ to -19.0 cal K⁻¹ mol⁻¹). The activation parameters and rate constants vary little with the phosphine, suggesting a preequilibrium between η^5 and η^3 species of the starting complexes where the latter reacts with the entering phosphine in the rate-determining step. The new η^3 -C₅H₅ complexes are, with the exception of 5, fluxional in solution due to an intramolecular enantiomeric equilibrium likely proceeding through a five-coordinate η^1 -C₅H₅ intermediate. Path ii proceeds via η^3 -cyclopentenovl complexes of the type $[Ru(\eta^5-C_5H_5)(\eta^3-C_5H_4O-2-PR_3)(L)]^+$ (9–11). Furthermore, 3 and 4 react with small and basic phosphines $PR_3 = PMe_3$ and $Me_2PCH_2PMe_2$ to give the half-sandwich complexes $[Ru(\eta^5-C_5H_4OH)(PR_3)_2L]^+$ (14, 15) together with free $C_5H_4PR_3$ (16).

Introduction

Nucleophilic attack at metal-coordinated ligands constitutes one of the most useful procedures in synthetic organic chemistry for obtaining new regio- and stereoselectively functionalized molecules. Such processes are particularly facile if the metal center is coordinatively saturated, substitutionally inert, and sufficiently electrondeficient. For the ligands, nonconjugated and conjugated olefins are among the most reactive substrates, while aromatic ligands, in particular the cyclopentadienyl anion, are among the least reactive.² It was thus a surprise to find that tertiary phosphines react with the

cationic 18-electron complexes $[Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)]_2^{2+}$ (1) and $[\operatorname{Ru}(\eta^5 - \operatorname{C}_5 H_5)(\eta^4 - \operatorname{C}_5 H_4 O)(L)]^+$ (L = CH₃CN (2), pyridine (3), thiourea (4)) to give 1,1'-disubstituted ruthenocenes $[Ru(\eta^{5}-C_{5}H_{4}PR_{3})(\eta^{5}-C_{5}H_{4}OH)]^{+}$ (12) (paths i and ii, Scheme 1) as well as the anticipated 1,2disubstituted ruthenocenes (13), formed via η^3 -cyclopentenoyl complexes $[Ru(\eta^5-C_5H_5)(\eta^3-C_5H_4O-PR_3)(L)]^+$ (path iii, Scheme 1).^{1,3} Scheme 1 gives an overview of the reactions hitherto analyzed on a synthetic level. Thus, **1** yields only **12** irrespective of the nature of the phosphine, whereas complexes 2-4 give 13 as well. Preliminary kinetic studies with PMe₃ as the nucleophile have shown¹ that the formation of **12** is far more complex than that of 13. In the initial step, PMe₃ attacks the metal center to give the η^3 -C₅H₅ intermediate [Ru-

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 $(\eta^3\text{-}C_5\text{H}_5)(\eta^4\text{-}C_5\text{H}_4\text{O})(\text{PMe}_3)(\text{L})]^+$ which then undergoes an endo migration of PMe_3 to give $[\text{Ru}(\eta^5\text{-}C_5\text{H}_4\text{PMe}_3)\text{-}(\eta^5\text{-}C_5\text{H}_4\text{OH})]^+$ (**12a**) and/or free $C_5\text{H}_4\text{PMe}_3$ together with the half-sandwich complex $[\text{Ru}(\eta^5\text{-}C_5\text{H}_4\text{OH})\text{-}(\text{PMe}_3)_2\text{L}]^+$ (**14a**, **15**), depending on L (Schemes 1 and 2).^{1,3}

The process of η^5 to η^3 ring slippage of η^5 -C₅H₅ ligands (possibly also η^3 to η^1 ring slippage) is an appealing way of activating C₅H₅ systems toward nucleophilic attack. The occurrence of η^3 intermediates appears to be of more general importance. Such species have been postulated frequently as a mechanistic rationale for a number of stoichiometric⁴ and catalytic⁵ organometallic reactions. These include α - and β -hydrogen abstractions,^{6,7} photochemically induced C–H, Si–H, and C–C bond cleavages,⁸ cyclopentadienyl ligand transfers,⁹ and ligand

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substitutions.¹⁰ Unfortunately, the few reports dealing with additions, substitutions, and migrations of nucleophiles onto the C₅H₅ ligand do not allow definite conclusions to be drawn regarding the involvement of ring slippage.¹¹ Herein we report the kinetics and mechanism of nucleophilic addition and substitution reactions of tertiary phosphines with 1-4. In particular, we present kinetic and thermodynamic data for the formation of the 1,1'-disubstituted products via reversible formation of η^3 -C₅H₅ intermediates (Scheme 2). In addition, the facile and reversible η^5 to η^3 transformations to the novel η^3 -C₅H₅ complexes [Ru(η^3 -C₅H₅)(η^4 - $C_5H_4O(PR_3)]_2^{2+}$ (5) and $[Ru(\eta^3-C_5H_5)(\eta^4-C_5H_4O)(PR_3)-$ (L)]⁺ (**6**-**8**) have been studied by low-temperature NMR spectroscopy. Our mechanistic investigations are supported by extended Hückel molecular orbital calculations. Further data on the reactions that lead to the 1,2disubstituted ruthenocenes are presented, and the origin of the selectivity between the two ruthenocene products is discussed.

Results and Discussion

Syntheses and Spectroscopic Studies. We have previously shown that the dimeric complex $[\text{Ru}(\eta^5-C_5H_5)(\eta^4-C_5H_4O)]_2(\text{CF}_3\text{SO}_3)_2$ (1) reacts with tertiary phosphines to give exclusively 1,1'-disubstituted ruthenocenes 12 in essentially quantitative yield (Scheme 1).³ To detect and identify intermediates, this reaction with the tertiary phosphines PMe₃, PCy₃, P{(2,4,6-OMe)_3C_6H_2}_3, and PPh_3 has been monitored by NMR spectroscopy. These phosphines have been chosen since they cover a large range of nucleophilicity and size. The nucleophilicity is taken to increase in the order of increasing pK_a^{12} PPh₃ (2.73) < PMe₃ (8.65) < PCy₃ (9.70)

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 $< P\{(2,4,6-OMe)_{3}C_{6}H_{2}\}_{3}$ (11.02), while the bulkiness of the phosphines, as expressed by their cone angles,¹³ increases in the order PMe₃ (118°) < PPh₃ (145°) < PCy₃ $(170^{\circ}) < P\{(2,4,6\text{-OMe})_3C_6H_2\}_3 (184^{\circ}). Below -70 \, ^{\circ}C,$ the dimeric complexes $[Ru(\eta^3-C_5H_5)(\eta^4-C_5H_4O)(PR_3)]_2^{2+}$ (5a-c) are formed quantitatively (Scheme 3), except for the weakly nucleophilic PPh₃, for which about 70% unreacted 1 was observed at equilibrium. Upon an increase in the temperature above -70 °C, all of these complexes are cleanly converted to complexes 12a,e,f,g with no other intermediates detectable. The identity of **5a**-**d** has been unequivocally established by ¹H and ³¹P-¹H} NMR spectroscopies and in the case of **5a** also by ¹³C{¹H} NMR spectroscopy. The ¹H NMR spectra of **5a**-**d** are consistent with both the ketonic oxygen of the C_5H_4O moiety and the phosphine attached at the metal center; i.e., the complex is both dimeric and chiral. Complexes 5 are not fluxional (vide infra), and consequently, in the ¹H NMR spectrum the protons of the C_5H_5 and C_5H_4O ligands give rise to nine individual resonances. The ${}^{13}C{}^{1}H$ NMR spectrum of **5a** exhibits altogether 10 individual resonances for the C₅H₅ and C₅H₄O ligands. The resonance of the "ketonic" carbonyl carbon at 166.3 ppm is high-field shifted with respect to the corresponding resonance in **1** (cf. 183.3 ppm in 1), indicating that the C₅H₄O ligand has become somewhat more electron rich (partially reduced). Note that, for the final products **12**, where the η^4 -bound cyclopentadienone ligand is already fully reduced to an η^5 -bound hydroxycyclopentadienyl system, the resonance of the C–O carbon atom is found in the range 127–129 ppm.

Surprisingly, the dimeric nature of **5** is maintained even if **1** is treated with the strongly basic bidentate ligand Me₂PCH₂PMe₂. Instead of the expected monomeric complex [Ru(η^3 -C₅H₅)(η^4 -C₅H₄O)(η^2 (P,P)-Me₂PCH₂-PMe₂)]CF₃SO₃, the dimeric complex [Ru(η^3 -C₅H₅)(η^4 -C₅H₄O)(η^1 (P)-Me₂PCH₂PMe₂)]₂(CF₃SO₃)₂ (**5e**) is obtained with the Me₂PCH₂PMe₂ ligand coordinated in η^1 (P)fashion (cf. Scheme 4). Due to the η^1 (P) coordination mode of the Me₂PCH₂PMe₂ ligand, in the ³¹P{¹H} NMR spectrum the resonance of the coordinated PMe₂ group is significantly downfield shifted with respect to the noncoordinated PMe₂ moiety, giving rise to a doublet

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centered at 29.5 ppm (${}^{2}J_{PP} = 35.9$ Hz). The signal of the noncoordinated PMe₂ moiety exhibits a doublet centered at -43.4 ppm (${}^{2}J_{PP} = 35.9$ Hz).

The monomeric complex $[Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)(CH_3-$ CN) CF₃SO₃ (2) reacts with PR₃ (PMe₃, PBuⁿ₃, PMe₂-Ph) in acetone at -90 °C to afford the complexes [Ru(η^3 - C_5H_5)(η^4 - C_5H_4O) (PR₃)(CH₃CN)]CF₃SO₃ (**6a**-**c**) in quantitative yield (Scheme 2). Upon an increase in the temperature, complexes **6a**-**c** are quantitatively converted to complexes 12a-c. In the course of this reaction, no other intermediates could be detected. The reaction of 2 with PMePh₂ is less selective, as revealed by ¹H NMR spectroscopy. At -90 °C, two competing reactions take place to give the complexes $[Ru(\eta^3-C_5H_5)(\eta^4-C_5H_4O) (PMePh_2)(CH_3CN)]CF_3SO_3$ (6d) and $[Ru(\eta^5-C_5H_5)(\eta^3-$ C₅H₄O-PMePh₂) (CH₃CN)]CF₃SO₃ (9a) in a 1.3:1 ratio with complete consumption of 2. At higher temperatures, **9a** and **6d** (**6d** via the intermediacy of **2** and **9a**) are cleanly converted to the 1,2-disubstituted ruthenocene [Ru(η^5 -C₅H₅)(η^5 -C₅H₃OH-2-PMePh₂)]CF₃SO₃ (13d) with no evidence found for the formation of the 1,1'-disubstituted ruthenocene [Ru(η^5 -C₅H₄PMePh₂)(η^5 - C_5H_4OH (CF₃SO₃ (**12d**) (Scheme 2). It is noteworthy that, at low temperature, 2 does not react with PPh₃, while, at ambient temperature, $[Ru(\eta^5-C_5H_5)(\eta^5-C_5H_3-$ OH-2-PPh₃)]CF₃SO₃ (13e) is exclusively formed. In the case of the bulky phosphine $P\{(2,4,6-OMe)_3C_6H_2\}_3$, no evidence for the formation of an η^3 -C₅H₅ complex is found even at -90 °C, and the 1,2-disubstituted ruthenocene [Ru(η^{5} -C₅H₅)(η^{5} -C₅H₃OH-2-P{(2,4,6-OMe)₃- C_6H_2 ₃)]CF₃SO₃ (**13g**) is formed exclusively.

The ¹H and ¹³C{¹H} NMR spectra of **6** are consistent with binding of the cyclopentadienyl ligand in an η^3 fashion. In the ¹H NMR spectra of **6**, the olefinic hydrogens H^{3,4} absorb at about 5.6 ppm, the terminal allylic hydrogen atoms H^{2,5} absorb at about 3.8 ppm, and the central allyl hydrogen H1 absorbs at about 4.4 ppm. Complexes 6 are chiral. In contrast to 5, complex **6** is fluxional in solution, and thus, the η^3 -C₅H₅ ligand exhibits only three proton and carbon resonances (in a 2:1:2 ratio) and the C_5H_4O ring shows only two hydrogen and three carbon resonances. This process is in the fast exchange region for 250 MHz ¹H NMR, even at -90 °C in acetone- d_6 . Even though **6** is fluxional, the CH₃CN ligand is substitutionally inert (vide infra). Accordingly, the reaction of 2 with either Me₂PCH₂PMe₂ or Me₂-PCH₂CH₂PMe₂ does not lead to the formation of [Ru-

 $(\eta^{3}-C_{5}H_{5})(\eta^{4}-C_{5}H_{4}O)(\eta^{2}(P,P)-Me_{2}PCH_{2}PMe_{2})]CF_{3}SO_{3}$ and $[Ru(\eta^3-C_5H_5)(\eta^4-C_5H_4O)(\eta^2(P,P)-Me_2PCH_2CH_2PMe_2)]CF_3$ -SO₃, respectively, but instead gives $[Ru(\eta^3-C_5H_5)(\eta^4 C_5H_4O$)($\eta^1(P)$ -Me₂PCH₂PMe₂)(CH₃CN)]CF₃SO₃ (**6e**) and $[Ru(\eta^3-C_5H_5)(\eta^4-C_5H_4O)(\eta^1(P)-Me_2PCH_2CH_2PMe_2)(CH_3-$ CN)]CF₃SO₃ (6f) with the phosphine ligands bound in an $\eta^1(P)$ -fashion (Scheme 4). Similarly to **2**, but at higher temperatures (≤ -20 °C), [Ru(η^{5} -C₅H₅)(η^{4} -C₅H₄O)(py)]CF₃- SO_3 (3) reacts with PR_3 (PMe₃, PBu^n_3 , PMe_2Ph , or PCy_3) to yield quantitatively $[Ru(\eta^3-C_5H_5)(\eta^4-C_5H_4O)(PR_3)-$ (py)]CF₃SO₃ (7**a**-**d**) (Scheme 2). Complexes 7 are formed quantitatively even at room temperature but are unstable under this condition, being readily converted to complexes **13a**-**c** and **13f**.^{3d} This reaction proceeds via the intermediacy of the η^3 -cyclopentenoyl complexes $[Ru(\eta^{5}-C_{5}H_{5})(\eta^{3}-C_{5}H_{4}O-PR_{3})(py)]CF_{3}SO_{3}$ (10).³ Complex 7a reacts in a less selective way to give a mixture of **12a** and **13a**. With the phosphines PMePh₂ and PPh₃, no reaction takes place at low temperature. At ambient temperature, PMePh₂ reacts with **3** to yield quantitatively **13d**. This reaction proceeds via the η^3 -cyclopentenoyl complex 10d. The strongly basic chelating bis-(phosphines) Me₂PCH₂PMe₂ and Me₂PCH₂CH₂PMe₂, on the other hand, react with 2 to give complexes of the $[Ru(\eta^{3}-C_{5}H_{5})(\eta^{4}-C_{5}H_{4}O)(\eta^{1}(P)-Me_{2}PCH_{2}PMe_{2})$ type (py)]CF₃SO₃ (7e) and [Ru(η^3 -C₅H₅)(η^4 -C₅H₄O)(η^1 (P)-Me₂-PCH₂CH₂PMe₂)(py)|CF₃SO₃ (7f), respectively (Scheme 4).

Interestingly, in the presence of >2 equiv of PMe₃, an alternative mode of reaction, which again is highly selective, is observed. Complex **7a** is slowly converted to the half-sandwich complex [Ru(η^{5} -C₅H₄OH)(PMe₃)₂-(py)]CF₃SO₃ (**14a**) and free C₅H₄PMe₃ (**16a**)¹⁴ in essentially quantitative yield as monitored by ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopies. The same reaction occurs with Me₂PCH₂PMe₂, leading to the formation of [Ru(η^{5} -C₅H₄OH)(η^{2} (P,P)-Me₂PCH₂PMe₂)(py)]CF₃SO₃ (**14b**) and free C₅H₄PMe₂CH₂PMe₂ (**16b**). This pathway, however, was not observed even with PBuⁿ₃ and thus appears to be limited to phosphines with small cone angles.

Attempts to isolate 7 in pure form usually failed due to equilibria with other species. However, addition of PMe₃ to a solution of **3** in acetone afforded **7a** as a pale yellow solid in essentially quantitative yield due to its insolubility in this solvent. In the solid state, 7a can be handled for a short period of time. The IR spectrum of **7a** exhibits a strong C=O stretching frequency at 1593 cm^{-1} (cf. 1682 cm^{-1} for $\mathbf{3}^{15}$ and $\bar{1}709\ cm^{-1}$ for free $C_5H_4O^{16}$) indicating loss of π -electron density from this group to the ring and metal and, thus, a substantial decrease in bond order. This observation suggests that in complexes containing the $[Ru(\eta^3-C_5H_5)(\eta^4-C_5H_4O)]^+$ moiety, there is a strong resonance interaction with the carbonyl group leading to the limiting structure **II**. Thus, the loss of aromaticity of the C₅H₅ ring as a result of the $\eta^5 \rightarrow \eta^3$ ring slippage process may be partially compensated for by the aromaticity gain of the C₅H₄O ring, a ground-state effect, although the crystal struc-

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tures of $1-4^{15}$ (Figures 1 and 2) show the C_5H_4O ring to be nonplanar and folded away from Ru by 13.7, 18.0, 18.8, and 18.9°, respectively. The identities of the intermediates 7 were established by ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopies and in the case of 7a also by elemental analysis. Complexes 7 are also fluxional in solution with the overall NMR spectroscopic features similar to those of 6 excepting the resonance of the hydrogen atom H¹. The latter experiences a shift of about -1.1 ppm relative to that of the analogous complexes 6 due to anisotropic shielding by the aromatic ring current of the pyridine placing the η^3 -C₅H₅ ligand in an endo orientation (as drawn in the schemes). Only in this conformation is H¹ situated above the pyridine ring.

Likewise, $[Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)(tu)]CF_3SO_3$ (4) is found to react with PMe₃, PBuⁿ₃, PMe₂Ph, Me₂PCH₂-PMe₂, and Me₂PCH₂CH₂PMe₂ to yield the respective complexes $[Ru(\eta^3-C_5H_5)(\eta^4-C_5H_4O)(PR_3)(tu)]CF_3SO_3$ (8ae) in quantitative yield as monitored by NMR spectroscopy (Scheme 2). In the case of PMePh₂ and PPh₃, no reaction takes place at low temperatures. When the temperature is raised, PMePh₂ is converted to the η^3 cyclopentenoyl complex 11d. In the further course of reaction, however, 11d decomposes to several intractable materials. The NMR spectra of complexes 8a-e are similar to those of 6 and 7 and are not discussed here. It is interesting to note, however, that in contrast to the cases of $\mathbf{6}$ and $\mathbf{7}$, when the temperature is lowered below about 0 °C, the signals of $H^{2,5}$, $H^{3,4}$, $H^{6,9}$, and $H^{7,8}$ broaden and eventually reemerge as eight distinct signals defining 8 as a chiral metal complex. The signal of the allylic proton H^1 remains unaffected by the exchange process, thus arguing against an exo/endo equilibrium. The same conclusion is drawn from ¹³C-¹H} NMR spectroscopy. This has been demonstrated previously for **8a**.¹ The dynamic behavior of complexes 6-8 has been rationalized by an intramolecular enantiomeric equilibrium leading to an inversion of ruthenium as shown in Scheme 5. Site exchange by a dissociative process is excluded by the observation that the temperature dependence of the line shapes is unaffected by addition of thiourea or PMe₃. From the variable-temperature NMR studies, exchange rate constants were determined by visual comparison of the observed and computer-simulated spectra.¹⁷ The rate constants derived from the different sets of coalescing resonances gave the same activation parameters. This points to the operation of a single exchange mechanism with $\Delta H^{\ddagger} = 12.3 \pm 0.4$ kcal mol⁻¹ and $\Delta S^{\ddagger} = -0.3 \pm 1.3$ cal mol⁻¹ K⁻¹. The rate constant (extrapolated to 298 K) of 5080 s⁻¹ is about 2500 times greater than k_{2m} in Table 1, again signaling the absence of ligand dissociation in the enantiomeric conversion. Further support of



Figure 1. Structural view of $[Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)-(py)]CF_3SO_3$ (**3**) showing 20% thermal ellipsoids (CF₃SO₃⁻ omitted for clarity). Selected bond lengths (Å): Ru-C(1-5)_{av} 2.187(4), Ru-C(7) 2.240(3), Ru-C(8) 2.162(3), Ru-C(9) 2.159(3), Ru-C(10) 2.237(4), Ru-N 2.127(3), C(7)-C(8) 1.392(5), C(8)-C(9) 1.410(5), C(9)-C(10) 1.390(5), O(1)-C(6) 1.221(4).



Figure 2. Structural view of $[\text{Ru}(\eta^5-\text{C}_5\text{H}_5)(\eta^4-\text{C}_5\text{H}_4\text{O})-(\text{tu})]\text{CF}_3\text{SO}_3\cdot\text{CH}_3\text{CN}$ (**4**·CH₃CN) showing 20% thermal ellipsoids (CF₃SO₃⁻ and CH₃CN omitted for clarity). Selected bond lengths (Å) and angle (deg): Ru-C(1-5)_{av} 2.207(4), Ru-C(7) 2.259(2), Ru-C(8) 2.160(3), Ru-C(9) 2.151(3), Ru-C(10) 2.249(2), C(7)-C(8) 1.394(4), C(8)-C(9) 1.426(5), C(9)-C(10) 1.407(4), Ru-S(1) 2.399(1), O(1)-C(6) 1.229(3); Ru-S(1)-C(11) 110.6(1).

Scheme 5



this interpretation follows from the observations that the dimer **5** is not dynamic in nature and that in the intermediates of Scheme 4 the ligand L is nonlabile. An intramolecular isomerization process requires a vacant coordination site with appropriate orbital geometry which may be brought about by rearranging **6**–**8** toward a five-coordinate pseudo four-legged piano stool complex containing an η^{1} -C₅H₅ ligand (as drawn in Scheme 5) where the ligands L and PR₃ change their positions in a pseudorotational fashion.¹⁸ For comparison, the activation enthalpies for such intramolecular ligand rear-

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Table 1. Activation Parameter and Rate Constant Data at 25 °C for the Reactions of $[Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)(L)]CF_3SO_3$ (L = CH₃CN (2), Pyridine (3), Thiourea (4)) with Tertiary Phosphines in Acetone To Give $[Ru(\eta^5-C_5H_4PR_3)(\eta^5-C_5H_4OH)]$ (12) via $[Ru(\eta^3-C_5H_5)(\eta^4-C_5H_4O)(PR_3)(L)]^+$ (6, 7, or 8)

PR ₃ p <i>K</i> _a ; cone angle, deg ^c	CH ₃ CN						pyridine			thiourea
	TTP ^a 11.0; 184	PMe ₃ ^b 8.65; 118	PPr ⁿ 3 8.65; 131	PBu ⁿ 3 8.43; 132	PMe ₂ Ph 6.50; 122	PMePh ₂ 4.57; 136	PMe ₃ ^b 8.65; 118	PBu ⁿ 3 8.43; 132	PMe ₂ Ph 6.50; 122	PMe ₃ ^b 8.65; 118
		$\begin{array}{c} 4.9\pm 0.2 \\ -27.8\pm 0.6 \\ 1400 \end{array}$	$\begin{array}{c} 4.8\pm 0.1\\ -30.2\pm 0.4\\ 494\end{array}$	$\begin{array}{c} 5.7 \pm 0.2 \\ -26.3 \pm 0.5 \\ 756 \end{array}$	$\begin{array}{c} 5.1 \pm 0.4 \\ -29.2 \pm 1.4 \\ 484 \end{array}$	$\begin{array}{c} 8.5\pm 0.1 \\ -18.2\pm 0.4 \\ 418 \end{array}$	$\begin{array}{c} 6.5\pm 0.2 \\ -24.8\pm 0.7 \\ 420 \end{array}$	$\begin{array}{c} 6.3\pm 0.1 \\ -27.5\pm 0.4 \\ 149 \end{array}$	$\begin{array}{c} 10.4\pm 0.3\\ -13.0\pm 1.2\\ 206\end{array}$	$\begin{array}{c} 7.5 \pm 1.2 \\ -26.5 \pm 4.0 \\ 33 \end{array}$
$\begin{array}{c} \Delta H_{2\mathrm{m}}^{*} \\ \Delta S_{2\mathrm{m}}^{*} \\ k_{2\mathrm{m}}, \ \mathrm{s}^{-1} \end{array}$		$\begin{array}{c} 20.1 \pm 1.0 \\ 9.8 \pm 3.1 \\ 1.4 \end{array}$	$\begin{array}{c} 21.7 \pm 1.8 \\ 14.6 \pm 5.9 \\ 1.2 \end{array}$	$\begin{array}{c} 19.6 \pm 0.8 \\ 9.9 \pm 2.6 \\ 3.8 \end{array}$	$\begin{array}{c} 19.1 \pm 0.8 \\ 11.0 \pm 2.7 \\ 15.4 \end{array}$	$\begin{array}{c} 14.0 \pm 0.1 \\ 0.9 \pm 0.6 \\ 546 \end{array}$	$\begin{array}{c} 22.8 \pm 1.2 \\ 18.4 \pm 3.7 \\ 1.2 \end{array}$	$\begin{array}{c} 17.0 \pm 1.5 \\ 4.4 \pm 5.3 \\ 20 \end{array}$	$\begin{array}{c} 19.1 \pm 0.3 \\ 16.2 \pm 1.1 \\ 207 \end{array}$	$\begin{array}{c} 20.2 \pm 2.6 \\ 10.8 \pm 8.9 \\ 2 \end{array}$
$\Delta H_{ m m}^{\circ}$ $\Delta S_{ m m}^{\circ}$ $K_{ m m}, { m M}^{-1}$	$\begin{array}{c} -8.6\pm 0.3\\ -21.1\pm 1.1\\ 53\end{array}$	-15.2 -37.6 1000	$-16.9 \\ -44.8 \\ 411$	-13.9 -36.2 199	$-14.0 \\ -40.2 \\ 31$	-5.5 -19.0 0.8	$-16.3 \\ -43.2 \\ 350$	$-10.7 \\ -31.8 \\ 8$	$-8.7 \\ -29.2 \\ 1$	-12.7 -37.3 17
ΔH_{3m}^{\dagger} ΔS_{3m}^{\dagger} k_{3m} , s ⁻¹		$\begin{array}{c} 20.8 \pm 0.2 \\ 12.6 \pm 0.7 \\ 2.1 \end{array}$	$\begin{array}{c} 19.2 \pm 0.1 \\ 7.9 \pm 0.4 \\ 2.7 \end{array}$	$\begin{array}{c} 21.1 \pm 0.2 \\ 15.3 \pm 0.7 \\ 4.6 \end{array}$	$\begin{array}{c} 20.5 \pm 0.4 \\ 10.6 \pm 1.4 \\ 1.2 \end{array}$	$<2 \times 10^{-2}$ f			<10 ^{-3 f}	

^{*a*} TTP = P{(2,4,6-OMe)₃C₆H_{2}₃. ^{*b*} Reference 1. ^{*c*} References 11 and 12. ^{*d*} All ΔH values in kcal mol⁻¹. ^{*e*} All ΔS values in cal mol⁻¹ K⁻¹. ^{*f*} Estimated from product distribution.}

rangements in the five-coordinate d^6 ruthenium complexes $Ru(PPh_3)_3Cl_2$ and $Ru(PPh_3)_3(H)(Cl)$ have been reported to be 10.0 ± 0.4 and 13.4 ± 0.6 kcal mol $^{-1}$, respectively.¹⁹

Finally, if PMe₃ is present in excess, **8a** reacts analogously to **7a** to give the half-sandwich complex $[Ru(\eta^5-C_5H_4OH)(PMe_3)_2(tu)]CF_3SO_3$ (**15**) together with free $C_5H_4PMe_3$ (**16a**) in quantitative yield as monitored by ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopies (Scheme 2).

Cyclopentadienone is able to act, in addition to its simple diene function, both as a 2e⁻ oxidizing agent and as a one-proton acceptor while remaining coordinated. In this way it promotes the formation of substituted hydroxyruthenocenes in the final reaction step, i.e., the formation of complexes 12 and 13. With respect to C₅H₅ ring activation, however, its role is less clear, and therefore, we prepared the cationic 1,3-butadiene complex $[Ru(\eta^5-C_5H_5)(\eta^4-C_4H_6)(CH_3CN)]CF_3SO_3$ (17) for comparison with the analogous cyclopentadienone complex 2. Complex 17 has been prepared by the reaction of $[Ru(\eta^5-C_5H_5)(CH_3CN)_3]CF_3SO_3$ with 1,3-butadiene in moderate yield. Treatment of **17** with PMe₃ (>2 equiv) in acetone at room temperature gives the η^3 -allyl complex $[Ru(\eta^{5}-C_{5}H_{5})(\eta(1,2,3)-1-PMe_{3}-2-buten-1-yl) (PMe_3)]PF_6$ (18) in 95% yield (Scheme 6). ¹H NMR monitoring indicated essentially quantitative conversion. However, with equimolar amounts of each reagent, the reaction is incomplete, but no complexes other than 17 and 18 together with free CH₃CN are observed. At lower temperatures, no reaction at all takes place, and there is no indication for the formation of an η^3 cyclopentadienyl complex. These observations suggest that the C₅H₄O ligand plays an important role in the ring slippage of C_5H_5 . The formation of **18** involves regioselective addition of PMe₃ at the terminal carbon atom, as one would expect on the basis of the Davies-Green-Mingos rules.² Under these conditions, the addition is kinetically controlled, resulting in the sole formation of the anti η^3 -allyl isomer (as drawn). However, the $\eta(1,2,3)$ -4-PMe₃-2-buten-1-yl (anti CH₂PMe₃)



intermediate, which is not observed in the ¹H NMR spectrum, apparently undergoes a 1,4 hydrogen shift to give the more stable $\eta(1,2,3)$ -1-PMe₃-2-buten-1-yl isomer **18** (anti Me, syn PMe₃ complex). In the course of this rearrangement, PMe₃ is also substituted for CH₃CN. A structural view of **18**, as determined by X-ray crystallography, is shown in Figure 3 with selected bond distances and angles given in the caption. The allyl moiety adopts an exo conformation with respect to the metal-coordinated PMe₃ ligand. This conformation is also maintained in solution, and no evidence for an endo/exo equilibrium is found. Complex **18** has been characterized by a combination of ¹H and ³¹P NMR spectroscopies and elemental analysis.

Mechanistic Considerations. A mechanistic rationale for the transformation of the η^3 -C₅H₅ intermediates **6**–**8** to the various products is given in Scheme 7. The activation of the already slipped C₅H₅ ligand in **6**–**8** may proceed via a further $\eta^3 \rightarrow \eta^1$ ring slippage process to give the coordinatively unsaturated species **A**. The presence of **A** is inferred from ¹H NMR spectroscopy. In an α -H elimination/H migration sequence (steps **A** \rightarrow **B** \rightarrow **C**) the 18-electron cyclopentadienylidene complex **C** is formed. It has to be noted that mononuclear complexes with a terminal cyclopentadienylidene ligand

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Figure 3. Structural view of $[Ru(\eta^{5}-C_{5}H_{5})(\eta(1,2,3)-1-PMe_{3}-2-buten-1-yl)(PMe_{3})]PF_{6}$ (**18**) showing 20% thermal ellipsoids (only one of the two crystallographically independent complexes shown; PF₆⁻ omitted for clarity). Selected bond lengths (Å) and angle (deg): Ru(1)-C(1-5)_{av} 2.207(5), Ru(1)-C(6) 2.187(4), Ru(1)-C(7) 2.101(4), Ru(1)-C(8) 2.220(4), Ru(1)-P(2) 2.304(1), C(6)-C(7) 1.431(5), C(7)-C(8) 1.430(6), C(8)-C(9) 1.505(6), C(6)-P(1) 1.767(4); C(6)-C(7)-C(8) 118.0(4).

are as yet unknown²⁰ but have been trapped by the formation of a [2+2] cycloaddition dimer²¹ and have been postulated as intermediates in the decomposition of titanocene.²² Subsequent migration of the coordinated phosphine to the α -carbon atom of the carbene moiety produces **D**. The latter, again a coordinatively unsaturated species, can generate the 1,1'-disubstituted product via **E** and release of L. This reaction is restricted to complexes with comparatively weak Ru–L bonds, viz. Ru–(μ)O=C₅H₄ (1) and Ru–NCCH₃ (2). Alternatively, if phosphine is present in excess (>2 equiv) and attack of a second phosphine molecule at Ru intercepts the formation of **E**, due to a stronger Ru–L bond (L = pyridine, thiourea), intermediate **F** and eventually, via interaction of another PR₃ molecule, the half-sandwich

complex $[Ru(\eta^5-C_5H_4OH)(PR_3)_2L]^+$ (14, 15) together with free $C_5H_4PR_3$ (16) will be formed.

Kinetic Studies. The reactions shown in Scheme 3 have been studied in detail by means of stopped-flow spectrophotometry and ¹H NMR spectroscopy, with the results summarized in Tables 1 and 2. The kinetic and NMR spectroscopic studies allow observation of two reaction pathways: reversible nucleophilic attack of PR₃ at the metal center providing the intermediate [Ru(η^3 -C₅H₅)(η^4 -C₅H₄O)(L)(PR₃)]⁺ (**6**–**8**) (pathway 1) and reversible nucleophilic attack at the cyclopentadienone ligand giving an η^3 -cyclopentenoyl complex [Ru(η^5 -C₅H₅)(η^3 -C₅H₄O–PR₃)(L)]⁺ (**9**–**11**) (pathway 2).

The majority of the new kinetic results presented here involve attack of the nucleophile at Ru, leading to modification of the C_5H_5 ring and producing **12**. The details of the data collection and establishment of the rate laws are presented in the Experimental Section. A standard for comparison is the reaction of 2 with PPrⁿ₃. The data fit a two-term rate law involving reversible formation of an intermediate 6 followed by irreversible formation of the product 12. The rate constants are identified in Scheme 3 as k_{1m} and k_{2m} for the first step and k_{3m} for the product formation step. An example of the data is presented in Figure 4. The data points are the high and low pseudo-first-order rate constants observed and the amplitude ratio, all at 25 °C. The solid lines represent the fit to all of the data (85 observations at 28 different conditions of temperature and PPrⁿ₃ concentration). The rate constants at 25 °C and their associated activation parameters for all reactions involving attack at Ru are presented in Table 1. The PPrⁿ₃ reaction is typical in showing a small activation enthalpy (4.8 kcal mol⁻¹) along with a large, negative entropy of activation (-30 cal mol⁻¹ K⁻¹) for k_{1m} , characteristic of a bimolecular process. The two unimolecular processes, k_{2m} leading back to the reactants and k_{3m} leading to products, both have much larger activation enthalpies (21.7 and 19.2 kcal mol⁻¹, respectively) and positive activation entropies (15 and 8 cal mol⁻¹ K⁻¹). The rest of the data in Table 1 were collected similarly, or with some variation when the apparent

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Table 2. Activation Parameter and Rate Constant Data at 25 °C for the Reactions of $[\operatorname{Ru}(\eta^5-\operatorname{C}_5\operatorname{H}_5)(\eta^4-\operatorname{C}_5\operatorname{H}_4\operatorname{O})(L)]\operatorname{CF}_3\operatorname{SO}_3$ (L = CH₃CN (2), Pyridine (3), Thiourea (4)) with Tertiary Phosphines in Acetone To Give $[\operatorname{Ru}(\eta^5-\operatorname{C}_5\operatorname{H}_5)(\eta^5-\operatorname{C}_5\operatorname{H}_4\operatorname{OH}-2-\operatorname{PR}_3)]$ (13) via $[\operatorname{Ru}(\eta^5-\operatorname{C}_5\operatorname{H}_4\operatorname{O}-2-\operatorname{PR}_3)(L)]^+$ (9, 10, or 11)

$PR_{2} nK_{2}$	CH ₃ CN				pyridine			thiourea		
cone angle, deg ^c	TTP ^a 11.0; 184	PMePh ₂ ^b 4.57; 136	P(PhOMe) ₃ ^b 4.59; 145	PPh_{3}^{b} 2.73; 145	TTP 11.0; 184	PMe ₂ Ph 6.50; 122	PMePh ₂ 4.57; 136	TTP 11.0; 184	PMe ₂ Ph 6.50; 122	PMePh ₂ 4.57; 136
$ \frac{\Delta H_{1c}^{\dagger d}}{\Delta S_{1c}^{\dagger e}} \\ k_{1c}, \mathbf{M}^{-1} \mathbf{s}^{-1} $	$\begin{array}{c} 8.7\pm 0.2\\-15.4\pm 0.7\\1241\end{array}$	$\begin{array}{c} 13.1\pm 0.1\\-13.9\pm 0.5\\1.4\end{array}$	$\begin{array}{c} 11.6\pm 0.1 \\ -18.6\pm 0.2 \\ 1.7 \end{array}$	$\begin{array}{c} 11.6\pm 0.1\\ -22.5\pm 0.5\\ 0.22\end{array}$	$\begin{array}{c} 11.2 \pm 0.2 \\ -13.6 \pm 0.7 \\ 38 \end{array}$	$\begin{array}{c} 14.8\pm 0.8\\ -12.6\pm 2.5\\ 0.17\end{array}$	$\begin{array}{c} 9.8\pm 0.5\\ -31.5\pm 1.6\\ 5.0\times 10^{-2}\end{array}$	$\begin{array}{c} 10.3\pm 0.6\\-22.4\pm 2.0\\2.1\end{array}$	$\begin{array}{c} 14.2\pm 0.1\\-15.7\pm 0.3\\8.8\times 10^{-2}\end{array}$	$\begin{array}{c} 15.9\pm1.1\\-12.3\pm3.5\\2.8\times10^{-2}\end{array}$
$\begin{array}{l} \Delta H_{2c}^{ \dagger} \\ \Delta S_{2c}^{ \dagger} \\ k_{2c}, \ \mathrm{s}^{-1} \end{array}$		$\begin{array}{c} 23.4\pm 0.5\\ 9.7\pm 1.7\\ 6.1\times 10^{-3}\end{array}$	$\begin{array}{c} 20.9\pm 0.4\\ 0.9\pm 1.0\\ 4.2\times 10^{-3} \end{array}$	$\begin{array}{c} 20.6 \pm 0.1 \\ 5.3 \pm 0.4 \\ 0.074 \end{array}$						
$\Delta H_{\rm c}^{\circ}$ $\Delta S_{\rm c}^{\circ}$ $K_{\rm c}, {\rm M}^{-1}$		$-10.3 \\ -23.6 \\ 230$	$-9.3 \\ -19.5 \\ 405$	-9.0 -27.8 3.0						
ΔH_{3c}^{\dagger} ΔS_{3c}^{\dagger} k_{3c} , s ⁻¹	$\begin{array}{c} 19.9 \pm 0.1 \\ 8.4 \pm 0.2 \\ 1.13 \end{array}$	$\begin{array}{c} 21.3 \pm 0.2 \\ 6.1 \pm 0.6 \\ 3.2 \times 10^{-2} \end{array}$	$\begin{array}{c} 23.3 \pm 0.1 \\ 13.6 \pm 0.2 \\ 5.0 \times 10^{-2} \end{array}$	$\begin{array}{c} 23.7\pm 0.2\\ 13.9\pm 0.5\\ 2.9\times 10^{-2}\end{array}$	f	$\begin{array}{c} 24.3 \pm 0.6 \\ 9.1 \pm 2.1 \\ 9.2 \times 10^{-4} \end{array}$	$\begin{array}{c} 23.5\pm 0.2\\ 6.6\pm 0.7\\ 1.0\times 10^{-3} \end{array}$	f	$\begin{array}{c} 27.4 \pm 0.8^{\it b} \\ 12.8 \pm 0.5 \\ 3.05 \times 10^{-5} \end{array}$	f

^{*a*} TTP = P{(2,4,6-OMe)₃C₆H₂}. ^{*b*} Reference 1d. ^{*c*} References 11 and 12. ^{*d*} All ΔH values in kcal mol⁻¹. ^{*e*} All ΔS values in cal mol⁻¹ K⁻¹. ^{*f*} Decomposition occurred.



Figure 4. Dependence of the observed rate constants and the amplitude ratio on phosphine concentration for the reaction of **2** with PPr_3^n at 25 °C. Squares represent the lower rate constant, circles represent the higher rate constant, and triangles represent the ratio of the amplitudes. The solid line depicts the calculated fit to all of the points, based on the parameters in Table 1.

rate constants for the two steps greatly diverged, as described in the Experimental Section. A variety of patterns can be observed in the data in Table 1. The dependence on phosphine is demonstrated most extensively for the reactions of **2**. The values of k_{1m} and its attendant activation parameters vary little. Considering only $k_{1m}(25 \text{ °C})$, PMe₃ is somewhat more reactive than the other phosphines, but there is little variation in the activation parameters. When there is some variation in the activation parameters, as with PMePh₂, they compensate, leaving the $k_{1m}(25 \text{ °C})$ values little different. There is a significant increase in k_{2m} , due to a decrease in ΔH^{\ddagger} , with decreasing p K_a of the phosphine. This trend is most clearly seen when k_{1m} and k_{2m} are combined to give $K_{\rm m}$, the equilibrium constant for the formation of the intermediate from the reactants. Excluding the exceptionally bulky and generally differently reacting ortho-substituted phenylphosphine $P\{(2,4,6-OMe)_3 C_6H_2$ ₃,²³ there is a decrease in stability of the intermediate with decreasing basicity of the ligand. The origin of this trend is primarily in $\Delta H_{\rm m}^{\circ}$. The fact that



the k_{1m} step is hardly affected by both size and basicity of the entering phosphine suggests that ring slippage and concomitant ligand rearrangements occur to a large extent prior to Ru-P bond formation. This may be interpreted as a rapid preequilibrium between η^5 and η^3 forms of the starting complexes **2**–**4**, where the latter react in a rate-determining step with the entering phosphine to give the stable η^3 complexes **6**–**8** (Scheme 8). Thus, the unsaturated η^3 species $[\text{Ru}(\eta^3\text{-}\text{C}_5\text{H}_5)(\eta^4\text{-}$ $C_5H_4O(L)$]⁺ lies near in energy to the transition state where, as depicted in Figure 5, Ru-P bond formation is incomplete. Similar observations have been made in ring slippage processes involving the indenyl ligand.^{24,31} The k_{2m} pathway, on the other hand, requires the cleavage of a strong Ru-P bond. Although there are no absolute Ru-P bond dissociation energies available in the literature, the activation enthalpies for PMe₃ dis-

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Figure 5. Reaction coordinate diagram for the conversion of 2 to 6a.

sociation from $Ru(\eta^5-C_5Me_5)(PMe_3)_2X$ (X = various anionic N, S, and C donor ligands and halides) provide approximate minimum Ru-P bond strengths which are on the order of 23–47 kcal mol⁻¹.²⁵ The strength of the Ru-P bond in **6–8** appears to follow the order $PMe_3 \approx PBu^n_3 > PMe_2Ph > PMePh_2 > PPh_3$, which parallels their basicities.

The product formation step, like the initial bimolecular attack, is little affected by changes in the ligand for the four ligands that give this rate constant. However, the upper limit on the rate constant estimated for k_{3m} from PMePh₂ indicates that this process is much slower for the least basic ligand for which attack at Ru is observed.

The dependence of the reactivity on the ancillary ligand L is demonstrated most completely for the reactions of **3**. The bimolecular step, k_{1m} , has a lower rate constant primarily due to an increased activation enthalpy. The values of k_{2m} and K_m are quite similar to those for the reactions of 2, with the trend to decreased stability of the intermediate with decreasing basicity slightly more pronounced than in the first case. These compounds do not continue to product, thus showing a large but unmeasurable decrease in k_{3m} . The change of L from pyridine to thiourea gives a further decrease in reactivity with PMe₃ (k_{1m}) and a similar k_{2m} , thus a yet less stable intermediate. The observed effect of the ligands L may be explained by their nucleophilicity with respect to the $[Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)]^+$ fragment taken to increase in the order C_5H_4O (1) < CH_3CN (2) < pyridine (3) < thiourea (4).¹⁵ It should be noted that none of these ancillary ligands are sterically demanding (Figures 1 and 2). Therefore, the reactivity of 1-4toward phosphines in the order 1 > 2 > 3 > 4 is probably not due to significant steric contributions.

This study has also produced further kinetic data on phosphines that attack directly at the C₄H₄O ligand, producing 1,2-disubstituted ruthenocenes **13**. The new results and those from the first paper in this series^{3d} are presented in Table 2. The addition of the bulky and basic P{(2,4,6-OMe)₃C₆H₂}₃ demonstrates a trend in the bimolecular process, k_{1c} , that was not present in the bimolecular attack at Ru, k_{1m} . The rate constant decreases as the basicity of the phosphine decreases with no sensitivity to cone angle. This is true for all three ancillary ligands. The change from CH_3CN to pyridine and then to thiourea produces a progressive decrease in the rate constant due to changes in both enthalpy and entropy of activation, with the enthalpy effect usually dominating, but $P\{(2,4,6-OMe)_3C_6H_2\}_3$ shows more complex changes. New data on the product formation step, k_{3c} , also demonstrate some trends. The largest and most basic phosphine, $P\{(2,4,6-OMe)_3C_6H_2\}_3$, leads to the fastest reaction when CH_3CN is being expelled. For the comparisons that can be made, in reactions with PMe_2Ph and $PMePh_2$, the ancillary ligands pyridine and thiourea slow the reaction compared to CH_3CN .

A major question to be answered is the origin of the change in product with a change in the entering phosphine. Only the more basic phosphines react to produce the C₅H₅-modified 1,1'-disubstituted ruthenocene. The question remains as to why the more basic phosphines do not also produce the product of attack at C₅H₄O, the 1,2-disubstituted product. Some indication comes from the reaction of PMePh₂, which produces both intermediates but only the 1,2-disubstituted product. These data were obtained by studying the reactions at different temperatures. Considering the rate constants at 25 °C, the reaction to form intermediate 6d, the result of attack at Ru, is 300-fold faster than the reaction to form intermediate 9d, in which attack has occurred at C₅H₄O. However, the reverse reactions of these two processes show an even greater disparity. Thus the equilibrium constant for the formation of 6d is only 0.8 M^{-1} , while for the formation of **9d** it is 230 M^{-1} . The conversion of **6d** to product could not be observed, while **9d** is converted to product with a rate constant (k_{3c}) similar to that of all phosphines showing this reactivity. The trend in k_{3m} with phosphine basicity, if it extrapolates to PMePh₂, would give a rate constant lower than that of the other phosphines but comparable to k_{3c} . Thus the kinetics indicate that both the stability of the intermediate and, to a lesser extent, the lower reactivity in the product-forming step prevents the less basic phosphines from giving the 1,1'-product. Conversely, the enhanced stability of the intermediate formed from phosphine attack at Ru and the enhanced reactivity in the product-forming step for the more basic phosphines lead to the 1,1'-disubstituted product from these nucleophiles.

In the presence of excess $PR_3 = PMe_3$ and Me_2PCH_2 -PMe₂, the η^3 -intermediates **7** and **8** proceed by a different pathway to yield **14** and **15**, respectively, together with free $C_5H_4PR_3$ (Scheme 3). The kinetics of the reaction of **7a** with PMe₃ have been studied by means of ¹H NMR spectroscopy as described in the Experimental Section. A simple second-order rate law, first order in each reactant, was obtained. The apparent second-order rate constant k_{4m} at 25 °C is 2.4 × 10⁻² M^{-1} s⁻¹ with ΔH^{\ddagger} of 13.8 ± 1.2 kcal mol⁻¹ and ΔS^{\ddagger} of -19.8 ± 4.5 cal mol⁻¹ K⁻¹. The activation parameters are indicative of an associative process. However, the overall process requires two phosphines, and thus it is unclear what process or combination of processes is actually being observed.

As has been previously shown,¹⁵ CH₃CN in 2 is readily substituted by pyridine to give 3 quantitatively. To establish whether this reaction proceeds via an



associative pathway, i.e., via an η^3 -C₅H₅ intermediate, the kinetics of this reaction were studied by ¹H NMR spectroscopy (Scheme 9). A simple second-order rate law, first order in each reactant was obtained. The apparent second-order rate constant at 25 °C is 1.6 × 10^{-3} M⁻¹ s⁻¹ with a ΔH^{\pm} of 18.3 ± 0.4 kcal mol⁻¹ and ΔS^{\pm} of -10.0 ± 1.4 cal mol⁻¹ K⁻¹. These data are consistent with a bimolecular mechanism involving coordination of pyridine- d_5 to the ruthenium center concomitant with an η^5 to η^3 ring slip of the C₅H₅ ligand, followed by dissociation of the CH₃CN ligand (Scheme 7). Again the simplicity of the rate law does not allow further information concerning the individual rate constants to be obtained from the data.

EHMO Calculations. An insight into a possible mechanism of the two reaction pathways is provided by extended Hückel molecular orbital calculations. The LUMO and SLUMO of $[\operatorname{Ru}(\eta^3-\operatorname{C}_5\operatorname{H}_5)(\eta^4-\operatorname{C}_5\operatorname{H}_4\operatorname{O})(L)]^+$ having the characteristics of the π^* MO of C₅H₄O and that of the second e_{1g} of C_5H_5 , respectively, are relevant to nucleophilic attack by PR3 at the C5H4O ligand and at the metal. In the ground state, however, both modes of attack are not possible without a prior change in orbital symmetries through ligand rearrangement. Furthermore, the LUMO (for attack at C_5H_4O) and the SLUMO (for attack at the metal) lie too high in energy and the overlap integral between these MO's and the σ PR₃ orbital is too small. It has to be noted also that the reactivity of $[Ru(\eta^5-C_5H_5)(\eta^3-C_5H_4O-PR_3)(L)]^+$ is affected by L since its π^* and/or σ orbitals participate in the SLUMO and the LUMO, respectively. Thus, strong π -acceptor and σ -donor ligands disfavor both modes of nucleophilic attack in agreement with the kinetic data.

To provide better interactions between the nucleophile and the C₅H₄O ring, the LUMO of the Ru complex must be altered to include the p_z orbital of the C₅H₄O α -carbons and to lower its energy. This is affected by η^4 to η^3 ring slippage and subsequent gauche deformation of the C₅H₄O ligand similar to the transition state suggested by us previously for the nucleophilic attack at acyclic 1,3-diene ligands.²⁶ For free 1,3-butadiene, it is noteworthy that the gauche structure is only about 0.4 kcal mol⁻¹ higher in energy than the s-cis structure.²⁷ In the case of hexafluoro-1,3-butadiene, the gauche conformer was even shown to be the groundstate structure.²⁸ This interaction should be little affected by the shape and size of PR3 but should be sensitive to the nucleophilicity of the phosphine (see kinetics data). It should be re-emphasized here that



Figure 6. $\eta^5 \rightarrow \eta^3$ ring slippage and concomitant ligand rearrangements of **2**: CACAO drawing for the SLUMO–LUMO inversion (in the absence of the nucleophile).

attack at C_5H_4O does not need prior reduction in the metal valence electron count.

Attack at the metal center requires geometric changes toward a 16-electron intermediate in which the SLUMO has lower energy. Otherwise, an energetically unfavorable 20-electron complex has to be formed. The following proposal, shown in Figure 6, is appealing: The sixelectron donor C5H5 can be transformed into a fourelectron donor through $\eta^5 \rightarrow \eta^3$ ring slippage, thus affording a 16-electron complex and promoting metal attack. For the formation of $[Ru(\eta^3-C_5H_5)(\eta^4-C_5H_4O)(CH_3 (PR_3)$]⁺, in addition to formation of the 16e complex and the decrease in the SLUMO level, of primary importance is the availability of a vacant low-lying metal-centered orbital for the entry of PR₃. Computer simulations of the positional changes of the ligands C_5H_4O and $CH_3CN^{\mbox{-}}\mbox{(slipping, folding, bending)}$ show that the change in the orbital symmetry at the metal center is highly unfavorable energetically. For the C₅H₅ ligand, both rotation and $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1 \rightarrow \eta^3 \rightarrow \eta^5$ ringslippage barriers are known to be very low (at least in the absence of any ring deformations²⁹) but to be ineffective as regards orbital symmetry changes. However, $\eta^5 \rightarrow \eta^3$ slippage can provoke ring deformation affording an allyl system that typically leads to a bent η^3 -C₅H₅ ligand with a dihedral angle of about 20°.³⁰ Such a rearrangement creates a vacant orbital at the metal and may provide a low-energy associative reaction path.³¹ This is also characteristic of the indenvl system.^{24,32} In the present case, the 16e complex is formed with SLUMO-LUMO inversion. Although the new LUMO level is lowered by C₅H₅–Ru bond weakening, there is no orbital of suitable symmetry for nucleophilic attack at Ru to occur unless there are a horizontal swing of CH₃CN and concomitant rotation of the η^3 -C₅H₅ system to improve the conjugation in the final complex fragment (in the absence of the nucleophile). The new MO (the LUMO of the 16e complex) is a low-lying metalcentered orbital suitable for attack by PR₃.

Conclusion

There is an increasing awareness of the importance of haptotropic rearrangement reactions of polyenyl

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ligands which become facile processes when certain conditions are met. In the present case, the $\eta^5 \rightarrow \eta^3$ ring slippage of the C₅H₅ ligand is promoted with the aid of the coligand cyclopentadienone, which acts as a "built-in" oxidizing agent converting into an η^5 -bound oxocyclopentadienyl ligand. This may be called the cyclopentadienone effect, similar to the known indenyl effect. The energy barrier for $\eta^5 \rightarrow \eta^3$ ring slippage of the indenyl ligand is extremely low since the fused benzo ring regains its full aromaticity in the η^3 coordination mode.

At first glance, one would surmise that the present conversion of the 18-electron complex $[Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)(L)]^+$ with tertiary phosphines to give stable $\eta^3-C_5H_5$ complexes of $[Ru(\eta^3-C_5H_5)(\eta^4-C_5H_4O)(L)(PR_3)]^+$ is driven by the Ru–P bond formation. However, the kinetic analysis shows that the ring slippage reaction is little affected by the entering nucleophile. This finding suggests ligand rearrangements to occur prior to Ru–P bond formation. As we have shown here, $\eta^3-C_5H_5$ and possibly $\eta^1-C_5H_5$ complexes are intermediates in the formation of substituted cyclopentadienyl products; i.e., ring slippage is a feasible way to activate C_5H_5 ligands toward nucleophilic attack.

Experimental Section

General Information. Manipulations were performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and/or a glovebox. All chemicals were standard reagent grade and were used without further purification. The solvents were purified according to standard procedures.³³ The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. [Ru(η^{5} -C₅H₅)(η^{4} - C_5H_4O]₂(CF₃SO₃)₂ (1), [Ru(η^5 -C₅H₅)(η^4 -C₅H₄O)(CH₃CN)]CF₃-SO₃ (2), $[Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)(py)]CF_3SO_3$ (py = pyridine) (3), $[\operatorname{Ru}(\eta^5 - \operatorname{C}_5 \operatorname{H}_5)(\eta^4 - \operatorname{C}_5 \operatorname{H}_4 O)(\operatorname{tu})] \operatorname{CF}_3 \operatorname{SO}_3$ (tu = thiourea) (4), $[Ru(\eta^5-C_5H_5)(CH_3CN)_3]PF_6$, and $NaBAr'_4$ (Ar' = 3,5-C₆H₃(CF₃)₂) were prepared according to the literature.^{3,15,34} The intermediates $[Ru(\eta^5-C_5H_5)(\eta^3-C_5H_4O-PR_3)(CH_3CN]^+$ (9), with the exception of $[Ru(\eta^5-C_5H_5)(\eta^3-C_5H_4O-PMePh_2)(CH_3CN]^+$ (9a), were detected only kinetically. The NMR spectra of the intermediates $[Ru(\eta^{5}-C_{5}H_{5})(\eta^{3}-C_{5}H_{4}O-PR_{3})(py)]^{+}$ (PR₃ = PMe₃ (**10a**), PBuⁿ₃ (10b), PMe₂Ph (10c), PMePh₂ (10d)) and [Ru(η^{5} -C₅H₅)- $(\eta^3 - C_5 H_4 O - PR_3)(tu)]^+$ (PR₃ = PMe₃ (**11a**), PBuⁿ₃ (**11b**), PMe₂-Ph (11c), PMePh₂ (11d)) have been described previously.^{3d} Syntheses and NMR spectra of $[Ru(\eta^5-C_5H_4PR_3)(\eta^5-C_5H_4OH)]^+$ $(PR_3 = PMe_3 (12a), PBu^n_3 (12b), PMe_2Ph (12c), PMePh_2 (12d),$ PPh₃ (12e), PCy₃ (12f)) and $[Ru(\eta^5-C_5H_5)(\eta^5-C_5H_3-2-PR_3-OH)]^+$ $(PR_3 = PMe_3 (13a), PBu^n_3 (13b), PMe_2Ph (13c), PMePh_2 (13d),$ PPh₃ (13e), PCy₃ (13f)) have been reported elsewhere.³ Infrared spectra were recorded on a Perkin-Elmer 16PC FT IR spectrometer. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Bruker AC 250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to $SiMe_4$ and to H_3PO_4 (85%). Temperature readings were calibrated by using the method of Raiford et al.,35 corrected to 250.13 MHz, by adding a capillary of methanol to the experimental sample. The assignments of the proton resonances were aided by double-resonance experiments and ¹H-¹H shift correlated (COSY) spectra. Microanalyses were carried out by the Microanalytical Laboratories, University of Vienna.

Syntheses. [**Ru**(η^5 -**C**₅**H**₅)(η^4 -**C**₅**H**₄**O**)(**py**)]**B**Ar'₄ (**3**'). **3** (155 mg, 0.327 mmol) and NaBAr'₄ (320 mg, 0.361 mmol) were dispersed in CH₂Cl₂ (15 mL), and the mixture was stirred for 1 h at room temperature, whereupon a precipitate of NaCF₃-SO₃ formed. Solid materials were removed by filtration, and the solution was evaporated to dryness. The pale yellow solid was washed several times with diethyl ether to remove unreacted NaBAr'₄ and then dried under vacuum. Yield: 318 mg (82%). ¹H NMR (δ , CD₃CN, -35 °C): 8.70 (d, 2H, py), 7.59 (t, 1H, py), 7.72 (b s, 8H, Ar'), 7.65 (s, 4H, Ar'), 7.47 (t, 2H, py), 6.15 (t, 2H), 5.44 (s, 5H, C₅H₅), 4.51 (t, 2H).

[Ru(η^{5} -C₅H₅)(η^{4} -C₅H₄O)(tu)]BAr'₄ (4'). This compound was synthesized analogously to 3' by treatment of 4 with NaBAr'₄ in CH₂Cl₂. ¹H NMR (δ , CD₃CN, -35 °C): 7.70 (b s, 8H, Ar'), 7.64 (s, 4H, Ar'), 7.30 (b s, 2H, tu), 6.84 (b s, 2H, tu), 5.96 (b s, 2H), 5.46 (s, 5H, C₅H₅), 4.13 (b s, 2H).

NMR Spectroscopic Studies. Typically, a 5 mm NMR tube was charged with a solution of either **1**, **2**, **3** (**3**), or **4** (**4**) (ca. 20-30 mg) in neat acetone- d_6 , CD₃NO₂, or a mixture thereof (0.5 mL) and was capped with a septum. The tube was then cooled to an appropriate temperature, and the tertiary phosphine (ca. 1 equiv) was added by syringe. In the case of solid phosphines, the NMR tube was charged with complexes **1**–**4** and the tertiary phosphine and the sample was cooled to an appropriate temperature. Deuterated solvent was then added slowly by syringe. The sample was transferred to a precooled NMR probe, and ¹H and ³¹P{¹H} NMR spectra were immediately recorded. ¹³C{¹H} NMR spectra were recorded when the stability of the complexes allowed.

Reaction of 1 with PMe₃. Formation of [Ru(η³-C₅H₃)-(η⁴-C₅H₄O)(PMe₃)]₂(CF₃SO₃)₂ (5a). ¹H NMR (δ, acetone-d₆, -70 °C): 5.68 (m, 2H), 4.76 (m, 1H), 4.66 (m, 1H), 4.60 (m, 1H), 4.43 (m, 1H), 4.32 (m, 1H), 4.08 (m, 1H), 3.84 (m, 1H), 1.83 (d, 9H, ²J_{HP} = 14.3 Hz). ¹³C{¹H} NMR (δ, CD₃NO₂/acetoned₆ (1:1), -70 °C): 166.3 (C=O), 80.1, 79.6, 76.1, 75.5, 73.1, 71.4, 56.8, 56.3, 48.9 (d, J_{CP} = 20.8 Hz), 6.3 (d, J_{CP} = 50.3 Hz, PMe₃). ³¹P{¹H} NMR (δ, acetone-d₆, -70 °C): 26.4. At temperatures above -50 °C, quantitative formation of **12a** was observed.

Reaction of 1 with PCy₃. Formation of [Ru(η^3 -C₅H₃)-(η^4 -C₅H₄O)(PCy₃)]₂(CF₃SO₃)₂ (5b). ¹H NMR (δ , acetone- d_6 , -78 °C): 5.79 (m, 2H), 4.80 (m, 1H), 4.65 (m, 2H), 4.52 (m, 1H), 4.46 (m, 1H), 4.28 (m, 1H), 3.99 (m, 1H), 2.63 (m, 3H), 2.00–1.20 (m, 30H). ³¹P{¹H} NMR (δ , acetone- d_6 , -78 °C): 31.9. At temperatures above -50 °C, quantitative formation of **12f** was observed.

Reaction of 1 with P{(**2**,**4**,**6**-OMe)₃C₆H₂}. Formation of [Ru(η^3 -C₅H₅)(η^4 -C₅H₄O)(P{(**2**,**4**,**6**-OMe)₃C₆H₂}₃)]₂(CF₃-SO₃)₂ (**5c**). ¹H NMR (δ , acetone- d_6 , -78 °C): 6.35-6.10 (m, 6H), 5.66 (m, 2H), 5.04 (m, 1H), 4.89 (m, 1H), 4.72 (m, 1H), 4.60 (m, 1H), 4.46 (m, 1H), 4.33 (m, 1H), 3.90-3.30 (m, 28H). The resonance of one of the η^3 -C₅H₅ protons was obscured by those of the P{(2,4,6-OMe)₃C₆H₂} ligand. ³¹P{¹H} NMR (δ , acetone- d_6 , -78 °C): 6.5. At temperatures above -50 °C, quantitative formation of [Ru(η^5 -C₅H₄P{(2,4,6-OMe)₃C₆H₂})(η^5 -C₅H₄OH)]⁺ (**12g**) was observed. ¹H NMR for **12g** (δ , acetone- d_6 , 20 °C): 6.31 (d, 9H, J = 4.6 Hz), 4.63 (m, 2H), 4.58 (m, 2H), 4.51 (m, 4H), 3.91 (s, 18H), 3.83 (s, 9H). ³¹P{¹H} NMR for **12g** (δ , acetone- d_6 , 20 °C): 1.0.

Reaction of 1 with PPh₃. Formation of [Ru(η^3 -C₅H₄)-(η^4 -C₅H₄O)(**PPh₃**)]₂(**CF**₃**SO**₃)₂ (**5d**). ¹H NMR (δ , acetone- d_6 , -90 °C): 5.51 (m, 1H), 5.46 (m, 1H), 5.38 (m, 1H), 4.95 (m, 1H), 4.89 (m, 1H), 4.82 (m, 1H), 4.74 (m, 1H), 4.54 (m, 1H), 4.48 (m, 1H). The resonances of the PPh₃ ligand are superimposed by the resonances of the free PPh₃ ligand. ³¹P{¹H} NMR (δ , acetone- d_6 , -90 °C): 19.5. At temperatures above -50 °C, quantitative formation of **12e** was observed.

Reaction of 1 with Me₂PCH₂PMe₂. Formation of [Ru-(η^3 -C₅H₅)(η^4 -C₅H₄O)(η^1 (P)-Me₂PCH₂PMe₂)]₂(CF₃SO₃)₂ (5e). ¹H NMR (δ, acetone- d_6 , -81 °C): 5.65 (m, 2H), 4.73 (m, 1H), 4.67 (m, 1H), 4.60 (m, 1H), 4.45 (m, 1H), 4.28 (m, 1H), 4.10

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(m, 1H), 3.81 (m, 1H), 1.76 (d, 6H, ${}^{2}J_{HP} = 13.5$ Hz, PMe₂), 1.34 (t, 2H, ${}^{2}J_{HP} = 3.2$ Hz, PCH₂P), 0.97 (d, 6H, ${}^{2}J_{HP} = 8.4$ Hz, PMe₂). ${}^{31}P{}^{1}H{}$ NMR (δ , acetone- d_{6} , -81 °C): 29.5 (d, ${}^{2}J_{PP} = 35.9$ Hz), -43.4 (d, ${}^{2}J_{PP} = 35.9$ Hz).

Reaction of 2 with PMe₃. Formation of [Ru(η³-C₅H₅)-(η⁴-C₅H₄O)(PMe₃)(CH₃CN)]CF₃SO₃ (6a). ¹H NMR (δ , acetone d_6 , -90 °C): 5.63 (m, 2H, H^{3,4}), 4.95 (m, 2H, H^{7,8}), 4.32 (m, 1H, H¹), 3.93 (m, 2H, H^{6,9}), 3.81 (m, 2H, H^{2,5}), 3.66 (s, 3H), 1.76 (d, 9H, ²J_{HP} = 14.4 Hz).¹³C{¹H} NMR (δ , acetone- d_6 , -90 °C): 173.7 (C=O), 129.4 (CN), 78.3, 75.6, 65.8, 52.4 (d, J_{CP} = 5.3 Hz), 50.4 (d, J_{CP} = 14.8 Hz), 5.4 (d, J_{CP} = 54.1 Hz, PMe₃). ³¹P{¹H} NMR (δ , acetone- d_6 , -90 °C): 24.6. At temperatures above -50 °C, quantitative formation of **12a** was observed.

Reaction of 2 with PBuⁿ3. Formation of [Ru(η³-C₅H₃)-(η⁴-C₅H₄O)(PBuⁿ3)(CH₃CN)]CF₃SO₃ (6b). ¹H NMR (δ , acetone- d_6 , -90 °C): 5.66 (m, 2H, H^{3.4}), 4.92 (m, 2H, H^{7.8}), 4.35 (s, 1H, H¹), 3.96 (m, 2H, H^{6.9}), 3.80 (m, 2H, H^{2.5}), 2.18 (m, 6H), 1.60-1.20 (m, 12H), 0.87 (t, 9H).¹³C{¹H} NMR (δ , acetone- d_6 , -90 °C): 173.8 (C=O), 129.8 (CN), 78.3, 75.9, 66.1, 53.0, 49.2 (d, $J_{CP} = 13.9$ Hz), 25.3 (d, $J_{CP} = 15.3$ Hz, PBu₃), 24.5, 17.8, 17.1, 5.4 (CH₃CN). ³¹P{¹H} NMR (δ , acetone- d_6 , -90 °C): 27.5. At temperatures above -50 °C, quantitative formation of **12b** was observed.

Reaction of 2 with PMe₂Ph. Formation of [Ru(\eta^3-C₅H₅)(\eta^4-C₅H₄O)(PMe₂Ph)(CH₃CN)]CF₃SO₃ (6c). ¹H NMR (\delta, acetone-d_6, -70 °C): 8.00-7.60 (m, 5H), 5.19 (m, 2H, H^{3,4}), 4.80 (m, 2H, H^{7.8}), 4.45 (m, 1H, H¹), 3.85 (m, 2H, H^{6.9}), 3.71 (m, 2H, H^{2.5}), 2.60 (s, 3H), 2.21 (d, 6H, ²J_{HP} = 13.7 Hz). ³¹P-{¹H} NMR (\delta, acetone-d_6, -70 °C): 22.2. At temperatures above -50 °C, quantitative formation of 12c was observed.

Reaction of 2 with PMePh₂. Formation of [Ru(η³-C₅H₅)(η⁴-C₅H₄O)(PMePh₂)(CH₃CN)]CF₃SO₃ (6d) and [Ru-(η⁵-C₅H₅)(η³-C₅H₄O-2-PMePh₂)(CH₃CN)]CF₃SO₃ (9a). The ¹H NMR spectrum was immediately recorded showing the formation of both [Ru(η³-C₅H₅)(η⁴-C₅H₄O)(PMePh₂)(CH₃CN)]-CF₃SO₃ (6d) and [Ru(η⁵-C₅H₅)(η³-C₅H₄O-2-PMePh₂)(CH₃CN)]-CF₃SO₃ (9a). ¹H NMR for 6d (\delta, acetone-*d***₆, -90 °C): 8.00-7.60 (m, 10H, PMePh₂), 5.22 (m, 2H), 5.13 (m, 1H), 4.86 (m, 2H), 3.92 (m, 2H), 3.80 (m, 2H), 2.70 (s, 3H), 2.54 (d, 3H,** *J***_{HP} = 13.9 Hz, PMePh₂). ¹H NMR for 9a (\delta, acetone-***d***₆, -90 °C): 8.00-7.60 (m, 10H), 5.49 (m, 1H), 4.70 (s, 5H), 4.11 (d, 1H,** *J***_{HP} = 10.5 Hz), 3.67 (m, 1H), 3.52 (m, 1H), 2.61 (s, 3H), 2.60 (d, 3H,** *J***_{HP} = 13.9 Hz, PMePh₂). When the solution was warmed to ambient temperature, only the resonances of 13d and free CH₃CN were observed.**

Reaction of 2 with P{(2,4,6-OMe)₃C₆H₂}₃. Formation of [Ru(η^{5} -C₅H₅)(η^{5} -C₅H₃OH-2-P{(2,4,6-OMe)₃C₆H₂}₃)]CF₃-SO₃ (13g). ¹H NMR (δ , CD₃CN, 20 °C): 6.21 (d, 6H, J = 4.6 Hz), 4.70 (m, 1H), 4.41 (s, 5H), 4.39 (m, 1H), 4.25 (m, 12H), 3.87 (s, 9H), 3.45 (s, 18H). ³¹P{¹H} NMR (δ , CD₃CN, 20 °C): -3.7.

Reaction of 2 with Me₂PCH₂PMe₂. Formation of [Ru-(η³-C₅H₅)(η⁴-C₅H₄O)(η¹(P)-Me₂PCH₂PMe₂)(CH₃CN)]-CF₃SO₃ (6e). ¹H NMR (δ, acetone-d₆, -70 °C): 5.59 (m, 2H, H^{3,4}), 4.91 (m, 2H, H^{7,8}), 4.28 (s, 1H, H¹), 3.94 (m, 2H, H^{6,9}), 3.81 (m, 2H, H^{2.5}), 2.65 (s, 3H), 2.37 (d, 2H, J_{HP} = 14.5 Hz, PCH₂P), 1.76 (d, 6H, J_{HP} = 13.7 Hz, PMe₂), 1.17 (d, 6H, J_{HP} = 3.3 Hz, PMe₂). ¹³C{¹H} NMR (δ, acetone-d₆, -70 °C): 173.8 (C=O), 129.5 (CN), 78.4, 75.8, 66.0, 52.5, 51.7 (d, J_{CP} = 17.6 Hz), 21.2 (dd, J_{CP} = 44.9 Hz, J_{CP} = 33.3 Hz, P*C*H₂P), 15.8 (dd, J_{CP} = 13.2 Hz, J_{CP} = 7.26 Hz, P*M*e₂), 5.2 (CH₃CN), 5.1 (dd, J_{CP} = 49.9 Hz, J_{CP} = 5.6 Hz, P*M*e₂). ³¹P{¹H} NMR (δ, acetoned₆, -70 °C): 27.5 (d, ²J_{PP} = 41.3 Hz), -51.7 (d, ²J_{PP} = 41.3 Hz).

Reaction of 2 with Me₂PCH₂CH₂PMe₂. Formation of [Ru(η³-C₅H₅)(η⁴-C₅H₄O)(η¹(P)-Me₂PCH₂CH₂PMe₂)(CH₃CN)]-CF₃SO₃ (6f). ¹H NMR (δ, acetone-d₆, -70 °C): 5.61 (m, 2H, H^{3.4}), 4.91 (m, 2H, H^{7.8}), 4.31 (s, 1H, H¹), 3.96 (m, 2H, H^{6.9}), 3.80 (m, 2H, H^{2.5}), 2.63 (s, 3H), 2.22 (b, 2H, PCH₂CH₂P), 1.76 (d, 6H, J_{HP} = 14.1 Hz, PMe₂), 1.58 (b, 2H, PCH₂CH₂P), 0.99 (s, 6H, PMe₂). ¹³C{¹H} NMR (δ, acetone-d₆, -70 °C): 173.8 (C=O), 129.5 (CN), 78.3, 75.8, 66.0, 52.5, 50.4 (d, $J_{CP} = 17.8$ Hz), 20.9 (d, $J_{CP} = 47.7$ Hz, P CH_2CH_2P), 17.0 (dd, $J_{CP} = 44.5$ Hz, $J_{CP} = 15.9$ Hz, PCH₂ CH_2P), 13.4 (d, $J_{CP} = 13.4$ Hz, P Me_2), 5.2 (CH₃CN), 3.6 (d, $J_{CP} = 48.3$ Hz, P Me_2). ³¹P{¹H} NMR (δ , acetone- d_6 , -70 °C):. 29.1 (d, ³ $J_{PP} = 34.1$ Hz), -43.7 (d, ³ $J_{PP} = 34.1$ Hz).

Reaction of 3 with PMe₃. Formation of $[Ru(\eta^3-C_5H_5) (\eta^4-C_5H_4O)(PMe_3)(py)]CF_3SO_3$ (7a). To a solution of 3 (200 mg, 0.422 mmol) in acetone- d_6 (5 mL) was added PMe₃ (0.86 mL, 0.844 mmol), resulting in the immediate formation of a pale yellow precipitate, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 230 mg (99%). Anal. Calcd for C₁₉H₂₃F₃NO₄RuS: C, 41.46; H, 4.21; N, 2.54; P, 5.82. Found: C, 42.41; H, 4.30; N, 2.42; P, 5.63. ¹H NMR (ô, CD₃NO₂, -20 °C): 9.17 (m, 2H, py), 7.91 (m, 1H, py), 7.44 (m, 2H, py), 5.49 (m, 2H, H^{3,4}), 4.83 (m, 2H, H^{7,8}), 3.79 (m, 2H, H^{6,9}), 3.70 (m, 2H, H^{2,5}), 3.10 (m, 1H, H¹), 1.58 (d, 9H, ${}^{2}J_{HP} = 14.0$ Hz). ${}^{13}C{}^{1}H$ NMR (δ , CD₃NO₂/acetoned₆ (1:3), -20 °C): 173.7 (C=O), 160.6 (py), 139.1 (py), 127.3 (py), 78.0, 76.4, 68.3, 52.6 (d, $J_{CP} = 5.1$ Hz), 51.2 (d, $J_{CP} =$ 19.9 Hz), 6.0 (d, $J_{CP} = 49.5$ Hz, PMe₃). ³¹P{¹H} NMR (δ , CD₃-NO, -20 °C): 30.7. At room temperature, formation of 12a and 13a was observed.

Reaction of 3 with PBuⁿ₃. Formation of [Ru(η³-C₅H₅)-(η⁴-C₅H₄O)(PBuⁿ₃)(py)]CF₃SO₃ (7b). ¹H NMR (δ , CD₃NO₂/ acetone-*d*₆ (1:3), -66 °C): 9.18 (m, 2H, py), 7.94 (m, 1H, py), 7.47 (m, 2H, py), 5.56 (m, 2H, H^{3.4}), 4.86 (m, 2H, H^{7.8}), 3.79 (m, 2H, H^{6.9}), 3.75 (m, 2H, H^{2.5}), 3.17 (m, 1H, H¹), 2.02 (m, 6H, PBu₃), 1.36 (m, 12H, PBu₃), 0.85 (m, 9H, PBu₃). ¹³C{¹H} NMR (δ , CD₃NO₂/acetone-*d*₆ (1:3), -66 °C): 173.9 (C=O), 160.5 (py), 139.3 (py), 127.4 (py), 78.1, 76.5, 68.3, 53.2, 49.3 (d, *J*_{CP} = 12.5 Hz), 25.4 (d, *J*_{CP} = 15.3 Hz, PBu₃), 15.3 (s, PBu₃), 17.8 (d, *J*_{CP} = 42.5 Hz, PBu₃), 114.3 (s, PBu₃). ³¹P{¹H} NMR (δ , CD₃NO₂/acetone-*d*₆ (1:3), -66 °C): 26.7. At room temperature, quantitative formation of **13b** was observed.

Reaction of 3 with PMe₂Ph. Formation of [Ru(η³-C₅H₃)(η⁴-C₅H₄O)(PMe₂Ph)(py)]CF₃SO₃ (7c). ¹H NMR (\delta, acetone-d_6, -70 °C): 9.15 (m, 2H, py), 8.0-7.5 (m, 8H, py and PMe₂Ph), 5.19 (m, 2H, H^{3.4}), 4.83 (m, 2H, H^{7.8}), 3.72 (m, 2H, H^{6.9}), 3.65 (m, 2H, H^{2.5}), 3.57 (m, 1H, H¹), 2.08 (m, 9H, PMe₂-Ph). ¹³C{¹H} NMR (\delta, acetone-d_6, -70 °C): 174.3 (C=O), 160.8 (py), 144.4 (d, J_{CP} = 13.9 Hz, PMe₂Ph), 139.2 (py), 135.5 (s, PMe₂Ph), 134.0 (d, J_{CP} = 9.3 Hz, PMe₂Ph), 130.8 (d, J_{CP} = 11.6 Hz, PMe₂Ph), 127.5 (py), 77.8, 76.5, 68.5, 53.4 (d, J_{CP} = 11.1 Hz), 51.9 (d, J_{CP} = 5.1 Hz), 5.1 (d, J_{CP} = 49.5 Hz, PMe₂Ph). ³¹P{¹H} NMR (\delta, acetone-d_6, -70 °C): 22.0. At room temperature, quantitative formation of 13c was observed.

Reaction of 3 with PCy₃. Formation of [Ru(η³-C₅H₃)-(η⁴-C₅H₄O)(PCy₃)(py)]CF₃SO₃ (7d). ¹H NMR (δ , acetone- d_6 , -97 °C): 9.35 (m, 2H, py), 8.05 (m, 1H, py), 7.60 (m, 2H, py), 5.68 (m, 2H), 4.96 (m, 2H), 3.92 (m, 2H), 3.78 (m, 2H), 3.12 (m, 1H, H¹), 2.55 (m, 3H, PCy₃). The other resonances of PCy₃ were obscured by those of free PCy₃. ³¹P{¹H} NMR (δ , acetone d_6 , -97 °C): 20.0. At room temperature, quantitative formation of **13f** was observed.

Reaction of 3 with Me₂PCH₂PMe₂. Formation of [Ru- $(\eta^{3}-C_{5}H_{5})(\eta^{4}-C_{5}H_{4}O)(\eta^{1}(P)-Me_{2}PCH_{2}PMe_{2})(py)]BAr'_{4}(7e).$ ¹H NMR (δ, acetone-d₆, -47 °C): 9.20 (m, 2H, py), 7.95 (m, 1H, py), 7.82 (m, 8H, BAr'₄), 7.73 (m, 4H, BAr'₄), 7.48 (m, 2H, py), 5.57 (m, 2H, H^{3,4}), 4.91 (m, 2H, H^{7,8}), 3.77 (m, 2H, H^{6,9}), 3.72 (m, 2H, $H^{2.5}$), 3.34 (m, 1H, H^1), 2.29 (d, 2H, $J_{HP} = 14.6$ Hz, PCH₂P), 1.67 (d, 6H, $J_{HP} = 13.6$ Hz, PMe₂), 1.11 (d, 6H, $J_{\rm HP} = 3.4$ Hz, PMe₂). ¹³C{¹H} NMR (δ , acetone- d_6 , -47 °C): 174.0 (C=O), 163.0 (BAr'₄, $J_{CB} = 49.6$ Hz), 160.6 (py), 139.0 (py), 135.9 (BAr'₄), 130.3 (BAr'₄, $J_{CF} = 32.4$ Hz), 127.2 (py), 125.7 (BAr'₄, $J_{CF} = 272.0$ Hz), 118.5 (BAr'₄), 77.5, 76.4, 68.4, 52.0, 51.8 (d, $J_{CP} = 11.6$ Hz), 21.9 (dd, $J_{CP} = 44.6$ Hz, $J_{CP} =$ 32.6 Hz, PCH_2P), 16.0 (dd, $J_{CP} = 13.2$ Hz, $J_{CP} = 7.2$ Hz, PMe_2), 5.6 (dd, $J_{CP} = 49.7$ Hz, $J_{CP} = 5.8$ Hz, PMe₂). ³¹P{¹H} NMR (δ , acetone- d_6 , -47 °C): 27.5 (d, $J_{PP} = 41.3$ Hz), -52.3 (d, $J_{PP} =$ 41.3 Hz).

Reaction of 3 with Me₂PCH₂CH₂PMe₂. Formation of $[Ru(\eta^{3}-C_{5}H_{5})(\eta^{4}-C_{5}H_{4}O)(\eta^{1}(P)-Me_{2}PCH_{2}CH_{2}PMe_{2})(py)]$ **BAr'₄ (7f).** ¹H NMR (δ , acetone- d_6 , -47 °C): 9.20 (m, 2H, py), 7.96 (m, 1H, py), 7.81 (m, 8H, BAr'₄), 7.72 (m, 4H, BAr'₄), 7.48 (m, 2H, py), 5.59 (m, 2H, H^{3,4}), 4.91 (m, 2H, H^{7,8}), 3.81 (m, 2H, H^{6,9}), 3.72 (m, 2H, H^{2,5}), 3.41 (m, 1H, H¹), 2.20 (m, 2H, PCH₂-CH₂P), 1.75 (d, 6H, J_{HP} = 13.9 Hz, PMe₂), 1.54 (m, 2H, PCH₂-CH₂P), 0.95 (d, 6H, $J_{HP} = 2.4$ Hz, PMe₂). ¹³C{¹H} NMR (δ , acetone-d₆, -47 °C): 174.1 (C=O), 163.0 (BAr'₄, J_{CB} = 49.8 Hz), 160.6 (py), 139.0 (py), 135.9 (BAr'₄), 130.3 (BAr'₄, $J_{CF} =$ 31.6 Hz), 127.9 (py), 125.7 (BAr'₄, $J_{CF} = 272.0$ Hz), 118.5 (BAr'₄), 77.6, 76.4, 68.4, 52.0 (d, $J_{CP} = 5.1$ Hz), 50.7 (d, $J_{CP} =$ 14.8 Hz), 23.0 (dd, $J_{CP} = 15.0$ Hz, $J_{CP} = 6.7$ Hz, PCH_2CH_2P), 17.6 (dd, $J_{CP} = 42.5$ Hz, $J_{CP} = 16.2$ Hz, PCH_2CH_2P), 13.6 (d, $J_{CP} = 13.9$ Hz, PMe₂), 4.1 (d, $J_{CP} = 48.6$ Hz, PMe₂). ³¹P{¹H} NMR (δ , acetone- d_6 , -47 °C): 27.9 (d, $J_{PP} = 34.1$ Hz), -43.9 (d, $J_{PP} = 34.1$ Hz).

Reaction of 4 with PMe₃. Formation of $[Ru(\eta^3-C_5H_5) (\eta^4-C_5H_4O)(PMe_3)(tu)]CF_3SO_3$ (8a). PMe₃ (7.0 μ L, 0.068 mmol) was added by syringe to a 5 mm NMR tube containing a sample of 4 (20 mg, 0.042 mmol) in CD₃NO₂ (0.5 mL) cooled at about -25 °C. The tube was placed into a precooled NMR probe at -20 °C, and quantitative formation of **7a** was observed. Attempts to isolate this complex in pure form, however, failed due to equilibrium reasons, and a mixture of 4 and 7a was obtained in a 2:1 ratio. ¹H NMR (δ , CD₃NO₂, -20 °C): 8.39 (b, 4H, NH₂), 5.56 (m, 2H, H^{3,4}), 4.90 (m, 2H, H^{7,8}), 4.52 (m, 1H, H¹), 4.01 (m, 2H, H^{6,9}), 3.60 (m, 2H, H^{2,5}), 1.65 (d, 9H, ${}^{2}J_{\text{HP}} = 13.7$ Hz). ${}^{1}\text{H}$ NMR (δ , CD₃NO₂, -20 °C): 8.40 (b, 4H, NH₂), 5.58 (m, 1H), 5.55 (m, 1H), 4.97 (m, 1H), 4.84 (m, 1H), 4.52 (m, 1H, H¹), 4.15 (m, 1H), 3.87 (m, 1H), 3.69 (m, 1H), 3.51 (m, 1H), 1.65 (d, 9H, ${}^{2}J_{HP} = 13.7$ Hz). ${}^{31}P$ -{¹H} NMR (δ , CD₃CN, -20 °C): 25.8. For solubility reasons, the ${}^{13}C{}^{1}H$ NMR (δ , CD₃CN, -20 °C) was recorded with [Ru- $(\eta^3-C_5H_5)(\eta^4-C_5H_4O)(PMe_3)(tu)]BAr'_4$ (8a'): 182.8 (C=S), 171.6 (C=O), 162.3 (BAr'₄, J_{CB} = 49.4 Hz), 135.2 (BAr'₄), 129.3 (BAr'₄, $J_{\rm CF} = 31.3$ Hz), 125.0 (BAr'₄, $J_{\rm CF} = 271.8$ Hz), 76.0, 75.7, 74.3, 73.2, 67.5, 64.8, 52.8 (d, $J_{CP} = 20.3$ Hz), 50.3 (d, $J_{CP} = 13.0$ Hz), 47.0 (d, $J_{CP} = 4.6$ Hz), 5.7 (d, $J_{CP} = 49.9$ Hz, PMe₃). At room temperature, formation of 12a and 13a was observed.

Reaction of 4 with PBuⁿ₃**. Formation of [Ru**(η^{3} -C₅H₅)-(η^{4} -C₅H₄O)(**PBu**ⁿ₃)(**tu**)]CF₃SO₃ (**8b**). ¹H NMR (δ , CD₃NO₂/ acetone- d_6 (1:1), -42 °C): 8.48 (b, 4H, NH₂), 5.58 (m, 1H, H^{3.4}), 5.53 (m, 1H, H^{3.4}), 4.92 (m, 1H), 4.81 (m, 1H), 4.73 (m, 1H, H¹), 4.13 (b, 1H), 3.81 (m, 1H), 3.67 (m, 1H), 3.51 (m, 1H). Resonances of the coordinated phosphine were obscured by those of free PBuⁿ₃. ³¹P{¹H} NMR (δ , CD₃NO₂/acetone- d_6 (1: 1), -42 °C): 27.2. At room temperature, quantitative formation of **13b** was observed.

Reaction of 4 with PMe₂Ph. Formation of [Ru(η³-C₅H₅)(η⁴-C₅H₄O)(PMe₂Ph)(tu)]CF₃SO₃ (8c). ¹H NMR (\delta, CD₃NO₂, -12 °C): 8.27 (b, 4H, NH₂), 7.65-7.90 (m, 5H), 5.35 (m, 2H, H^{3.4}), 4.82 (m, 2H), 4.72 (d, 2H, ²J_{HP} = 4.1 Hz), 3.90 (b, 2H), 3.54 (m, 2H), 2.02 (d, 6H, ²J_{HP} = 13.5 Hz). ³¹P{¹H} NMR (\delta, CD₃NO₂, -41 °C): 20.4. At room temperature, quantitative formation of 13c was observed.

Reaction of 4 with Me₂PCH₂PMe₂. Formation of [Ru-(η³-C₅H₅)(η⁴-C₅H₄O)(η¹(P)-Me₂PCH₂PMe₂)(tu)]CF₃SO₃ (8d). ¹H NMR (δ, CD₃NO₂, -41 °C): 8.43 (b, 4H, NH₂), 5.54 (m, 2H, H^{3,4}), 4.96 (m, 1H), 4.84 (m, 1H), 4.61 (m, 1H, H¹), 4.04 (b, 1H), 3.87 (m, 1H), 3.69 (m, 1H), 3.51 (m, 1H), 2.11 (d, 2H, ²J_{HP} = 13.5 Hz, PCH₂P), 1.69 (d, 6H, ²J_{HP} = 13.4 Hz, PMe₂), 1.40 (s, 6H, PMe₂). ³¹P{¹H} NMR (δ, CD₃NO₂, -41 °C): 26.5 (d, ²J_{PP} = 44.9 Hz), -54.8 (d, ²J_{PP} = 44.9 Hz).

Reaction of 4 with Me₂PCH₂CH₂PMe₂. Formation of [Ru(\eta^3-C₅H₅)(\eta^4-C₅H₄O)(\eta^1(P)-Me₂PCH₂CH₂PMe₂)(tu)]-CF₃SO₃ (8e). ¹H NMR (\delta, CD₃NO₂, -47 °C): 8.37 (b, 4H, NH₂), 5.59 (m, 1H, H^{3.4}), 5.55 (m, 1H, H^{3.4}), 4.97 (m, 1H), 4.85 (m, 1H), 4.62 (m, 1H, H¹), 4.05 (b, 1H), 3.87 (m, 1H), 3.70 (m, 1H), 3.52 (m, 1H), 2.08 (b, 2H, PCH₂CH₂P), 1.66 (d, 6H, ²*J***_{HP} = 13.3 Hz, PMe₂), 1.54 (b, 2H, PCH₂CH₂P), 0.99 (d, 6H, ²***J***_{HP} = 2.2**

Hz, PMe₂). ³¹P{¹H} NMR (δ , CD₃NO₂, -47 °C): 27.7 (d, ³J_{PP} = 34.1 Hz), -46.1 (d, ³J_{PP} = 34.1 Hz).

[Ru(η^{5} -C₅H₄OH)(**PMe₃**)₂(**py**)**]BAr'**₄ (**14a**). PMe₃ (20 μL, 0.20 mmol) was added by syringe to a 5 mm NMR tube containing a sample of **2** as the BAr'₄ salt (40 mg, 0.034 mmol) in acetone-*d*₆ (0.5 mL) cooled at about -30 °C. The tube was placed in a precooled NMR probe at -30 °C, and quantitative formation of **14a** and **16a** was observed within 12 h. ¹H NMR (δ , acetone-*d*₆, -30 °C): 8.72 (d, 2H, *J* = 5.14 Hz, py), 7.80 (m, 9H, BAr'₄, py), 7.70 (m, 4H, BAr'₄), 7.22 (t, 2H, *J* = 6.51 Hz, py), 4.14 (m, 4H, CPD), 1.54 (vt, 1H, *J*_{HP} = 3.77 Hz, PMe₃). The OH resonance was not observed. ¹³C{¹H} NMR (δ , acetone-*d*₆, -30 °C): 163.0 (BAr'₄, *J*_{CE} = 49.9 Hz), 159.1 (py), 136.9 (py), 135.8 (BAr'₄), 130.3 (BAr'₄, *J*_{CF} = 29.6 Hz), 126.1 (py), 125.7 (BAr'₄, *J*_{CF} = 271.9 Hz), 118.5 (BAr'₄), 71.5, 61.0, 21.8 (t, *J*_{CP} = 13.9 Hz, PMe₃). The CO resonance was not observed. ³¹P{¹H} NMR (δ , acetone-*d*₆, -30 °C): 9.1.

[Ru(η⁵-**C**₅**H**₄**OH**)(η²(**P**,**P**)-**Me**₂**PCH**₂**PMe**₂)(**py**)]**BAr'**₄ (14b). Me₂PCH₂PMe₂ (7 μL, 0.044 mmol) was added by syringe to a 5 mm NMR tube containing a sample of **2** as the BAr'₄ salt (25 mg, 0.021 mmol) in acetone-*d*₆ (0.5 mL) cooled at about -30 °C. The tube was kept at -30 °C for 12 h, after which it was transferred to a precooled NMR probe at -30 °C and quantitative formation of **14b** and **16b** was observed. ¹H NMR (δ , acetone-*d*₆, -30 °C): 8.88 (d, 2H, *J* = 5.4 Hz, py), 7.81 (m, 9H, BAr'₄, py), 7.73 (m, 4H, BAr'₄), 7.23 (t, 2H, *J* = 6.6 Hz, py), 4.17 (m, 4H), 3.66 (m, 2H, PCH₂P), 1.76 (vt, 6H, *J*_{HP} = 4.9 Hz, PMe₂), 1.54 (vt, 6H, *J*_{HP} = 4.9 Hz, PMe₂). The OH resonance was not observed. ³¹P{¹H} NMR (δ , acetone-*d*₆, -30 °C): -15.9.

[Ru(η^{5} -C₅H₄OH)(η^{2} (P,P)-Me₂PCH₂CH₂PMe₂)(py)]-CF₃SO₃ (14c). Monitoring of the formation of complex 14c was carried out analogously to that for 14b. ¹H NMR (δ , acetone d_{6} , -30 °C): 8.69 (m, 1H, py), 8.57 (m, 1H, py), 7.75 (m, 1H, py), 7.39 (m, 1H, py), 7.18 (m, 1H, py), 4.41 (m, 2H), 3.92 (m, 2H), 1.70 (m, 6H, PMe₂), 1.44 (m, 3H, PMe) 1.35 (vt, 3H, J_{HP} = 3.5 Hz, PMe). The OH resonance was not observed, and the resonances of the PCH₂CH₂P moiety were obscured by the resonances of 16c. ³¹P{¹H} NMR (δ , acetone- d_{6} , -30 °C): -15.9.

[**Ru**(η^{5} -**C**₅**H**₄**OH**)(**PMe**₃)₂(**S**=**C**(**NH**₂)₂)]**CF**₃**SO**₃ (15). Monitoring of the formation of complex 15 was carried out analogously to that for 14b. ¹H NMR (δ , CD₃NO₂, -20 °C): 4.26 (s, 2H), 4.19 (s, 2H), 1.46 (vt, 18H, $J_{HP} = 4.2$ Hz). The resonance of the OH proton could not be detected. ¹³C{¹H} NMR (δ , CD₃-NO₂, -20 °C): 185.8 (C=S), 126.4 (CO), 72.8, 61.3, 22.1 (t, $J_{CP} = 14.8$ Hz, PMe₃). ³¹P{¹H} NMR (δ , CD₃NO₂, -20 °C): 8.0.

C₅**H**₄**PMe**₃ (16a). ¹H NMR (δ, acetone- d_6 , -30 °C): 6.06 (m, 2H), 5.93 (m, 2H), 1.81 (d, 9H, $J_{HP} = 13.7$ Hz, Me). ¹³C{¹H} NMR (δ, acetone- d_6 , -30 °C): 113.1 (d, $J_{CP} = 18.0$ Hz), 112.2 (d, $J_{CP} = 16.7$ Hz), 13.6 (d, $J_{CP} = 59.7$ Hz, PMe₃). The resonance of the quaternary carbon could not be detected. ³¹P{¹H} NMR (δ, acetone- d_6 , -30 °C): 4.0 (cf. ref 14).

C₅**H**₄**PMe**₂**CH**₂**PMe**₂ (16b). ¹H NMR (δ , acetone-*d*₆, -30 °C): 6.07 (m, 2H), 5.94 (m, 2H), 1.92 (d, 6H, *J*_{HP} = 13.6 Hz, PMe₂), 0.74 (d, 6H, *J*_{HP} = 3.1 Hz, PMe₂). The resonances of the PCH₂P moiety were obscured by those of 14b. ³¹P{¹H} NMR (δ , acetone-*d*₆, -30 °C): 31.2 (d, *J*_{PP} = 50.3 Hz), 6.2 (d, *J*_{PP} = 52.1 Hz).

[Ru(η^{5} -C₅H₅)(η^{4} -C₄H₆)(CH₃CN)]**PF**₆ (17). A solution of [Ru(η^{5} -C₅H₅)(CH₃CN)₃]**PF**₆ (2.98 g, 6.86 mmol) in acetonitrile (300 mL) was saturated with 1,3-butadiene, and the mixture was heated at reflux for 35 min. During that time, the solution was purged several times with 1,3-butadiene. On removal of the solvent, a bright yellow solid was obtained, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 1.26 g (45%). Anal. Calcd for C₁₁H₁₄F₆-NPRu: C, 32.52; H, 3.47; N, 3.45. Found: C, 32.41; H, 3.30; N, 3.50. ¹H NMR (δ, acetone-*d*₆, -30 °C): 5.88 (m, 2H), 5.41 (s, 5H), 4.13 (d, 2H, *J* = 7.5 Hz), 2.64 (s, 3H), 1.52 (d, 2H, *J* = 9.8 Hz).

Table 3. Crystallographic Data

	3	4 ⋅CH ₃ CN	18
formula	C ₁₆ H ₁₄ F ₃ NO ₄ RuS	$C_{14}H_{16}F_3N_3O_4RuS_2$	$C_{15}H_{29}F_6P_3R_4$
fw	474.41	512.49	517.36
cryst size, mm	0.11 imes 0.25 imes 0.70	0.26 imes 0.20 imes 0.10	0.50 imes 0.26 imes 0.25
space group	P1 (No. 2)	<i>P</i> 1 (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
a, Å	7.919(1)	7.835 (3)	22.134(4)
b, Å	10.477(2)	11.387 (4)	8.623(2)
<i>c</i> , Å	10.856(2)	11.447(4)	22.404(5)
α, deg	91.90(1)	83.99(1)	
β , deg	106.09(1)	78.70(1)	95.31(1)
γ , deg	97.71(1)	76.91(1)	
$V, Å^3$	855.2(3)	973.5(6)	4258(2)
F(000)	472	512	2096
Z	2	2	8
$\rho_{\rm calc}, {\rm g} {\rm cm}^{-3}$	1.842	1.748	1.614
Т, К	297	299	298
μ , mm ⁻¹ (Mo K α)	1.092	1.072	1.009
abs corr	none	empirical	empirical
transm factor: min/max		0.71/0.93	0.69/0.83
$\theta_{\rm max}$, deg	25	30	25
index ranges	$0 \le h \le 9$	$-11 \le h \le 11$	$-31 \le h \le 31$
-	$-12 \leq k \leq 12$	$-16 \leq k \leq 16$	$-12 \le k \le 12$
	$-12 \leq l \leq 12$	$-16 \leq l \leq 16$	$-31 \le l \le 31$
no. of rflns measd	3044	15 431	43 536
no. of unique rflns	3044	5625	7453
no. of rflns, $F > 4\sigma(F)$	2848	4359	6607
no. of params	242	251	453
no. of restraints	0	2	0
$R(F > 4\sigma(F)^a)$	0.029	0.031	0.039
$R(all data)^a$	0.032	0.049	0.045
$R_{\rm w}({\rm all \ data})^b$	0.074	0.075	0.102
diff Fourier peaks, min/max e ${ m \AA}^{-3}$	-0.37/0.64	-0.39/0.52	-1.074 /1.069

 $^{a}R = \sum ||F_{0}| - |F_{c}|| / \sum |F_{0}|$. $^{b}R_{w} = [\sum (w(F_{0}^{2} - F_{c}^{2})^{2}) / \sum (w(F_{0}^{2})^{2})]^{1/2}$

[**Ru**(η⁵⁻C₅H₅)(η(1,2,3)-1-PMe₃-2-buten-1-yl)(PMe₃)]**PF**₆ (18). A solution of 17 (100 mg, 0.246 mmol) in acetone (5 mL) was treated with PMe₃ (75 μL, 0.738 mmol), and the mixture was stirred for 2 h at room temperature. Upon addition of diethyl ether, a pale yellow precipitate was formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 113 mg (95%). Anal. Calcd for C₁₅H₂₉F₆P₃-Ru: C, 34.82; H, 5.65. Found: C, 34.81; H, 5.70. ¹H NMR (δ, acetone-*d*₆, 20 °C): 4.81 (s, 5H), 4.47 (m, 1H, H², *J*_{HP} = 10.6 Hz, *J*¹² = 8.8 Hz, *J*²³ = 7.3 Hz, *J* = 1.8 Hz), 3.51 (m, 1H, H³, *J*²³ = 7.3 Hz, *J*³⁴ = 6.6 Hz, *J* = 2.4 Hz), 1.97 (d, 9H, *J*_{HP} = 13.7 Hz), 1.49 (d, 9H, *J*_{HP} = 8.3 Hz), 1.21 (m, 1H, H¹, *J*_{HP} = 12.5 Hz, *J*_{HP} = 12.5 Hz, *J*¹² = 8.8 Hz, *J* = 3.1 Hz). ³¹P{¹H} NMR (δ, acetone-*d*₆, 20 °C): 30.3, 4.7, -142.7 (s t, PF₆⁻, *J*_{PF} = 707.3 Hz).

Kinetics. The stopped-flow kinetic data were obtained with Hi-Tech SF-40 and Hi-Tech SF-61 instruments. The optical signals at 400 nm (in the case of PPhMe₂) and at 355 nm (in the case of $P\{(2,4,6-OMe)_3C_6H_2\}_3$) were monitored. The data were collected as sets of 2.048 and 512 points, respectively, corresponding to 3-4 half-lives. The data were transferred to a DOS/Windows-based personal computer for data analysis. The data all involved pseudo-first-order conditions with the phosphine in large excess over the ruthenium complex. They were fit to one exponential or a sum of two exponentials (in one case, a third exponential was required) using the CURFIT nonlinear least-squares routine of Bevington³⁶ programmed in QuickBasic or the Hi-Tech IS-2 software suite. The nonlinear least-squares analysis of the dependence of the observed rate constants (k) and amplitudes (A) on phosphine concentration and temperature was performed using the Scientist data analysis package with the points weighted by $1/(k \text{ or } A)^2$. Typically 36 different conditions of phosphine concentration and temperature were utilized, with 3-8 replicate kinetic measurements at each condition.

Most reactions of $[Ru(\eta^5-C_5H_5)(\eta^4-C_5H_4O)(L)]CF_3SO_3$ where $L = CH_3CN$ showed two exponentials and were fit to a rate law for the reversible formation of an intermediate followed by the irreversible formation of the product, as described previously.^{3d} This leads to fit parameters (see Scheme 3) for k_{1m} , k_{2m} , and k_{3m} (pathway 1) and k_{1c} , k_{2c} , and k_{3c} (pathway 2). For PPhMe₂, a third exponential that was slower and of lower amplitude, and which showed no concentration dependence, was observed. This process was also observed when CH₃CN instead of acetone was the solvent, but its activation parameters were much different. In this case, the two faster processes were treated as for the previously discussed phosphines. For PPh₂Me, the steps were separated further in time so that the reversible first step was studied independently from the product-forming step. In such cases, the concentration dependence is of the form $k_{obs} = k_1$ [phosphine] + k_2 and the rate constants are identified with the slope and intercept of the plot of k_{obs} vs [phosphine] as obtained by weighted linear leastsquares regression.³⁶ In the single case of $P\{(2,4,6-OMe)_3C_6H_2\}_3$, two exponentials were observed and the data were fit to the fast preequilibrium formation of one dead end species (identified as the intermediate produced by attack at the metal) and the irreversible formation of a second intermediate (identified as the intermediate produced by attack at C₅H₄O) and then further irreversible formation of the 1,2-disubstituted product. The parameters produced from this treatment are identified as $K_{\rm m}$, $k_{\rm 1c}$, and $k_{\rm 3c}$. The assignment of the kinetic processes to mechanistic steps relied on the NMR results and the signs of the amplitudes of the optical changes.

The reaction of $[\operatorname{Ru}(\eta^5-\operatorname{C_5H_5})(\eta^4-\operatorname{C_5H_4O})(L)]\operatorname{CF_3SO_3}$ where L = pyridine or thiourea and the phosphine PMe₃ and the reaction where L = pyridine or PBuⁿ₃ showed a single exponential with a positive intercept in the concentration dependence plot. This was attributed to reversible formation of the intermediate formed by attack at the metal and allowed resolution of k_{1m} and k_{2m} . For the reactions with L = pyridine and PPh₂Me as well as for L = thiourea with PPhMe₂ and PBuⁿ₃, a single exponential was observed and attributed to

⁽³⁶⁾ Bevington, P. R. Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill: New York, 1969.

the irreversible formation of the intermediate formed by attack at C₅H₄O. The rate of the subsequent reaction to produce the 1,2-disubstituted product was measured by NMR methods. For the reaction with L = pyridine and $P\{(2,4,6-OMe)_3C_6H_2\}_3$ and for the reaction of L = thiourea with PPh₂Me, a similar situation was observed, but the subsequent product formation step could not be studied due to decomposition of the intermediate. The most complex case involves the reaction of PMe₂-Ph with the Ru complex in which L = pyridine. This reaction shows two exponentials. One is attributed to the reversible formation of the intermediate formed by attack at the Ru, and the slower one is assigned to the irreversible formation of the intermediate formed by attack at the C5H4O ligand. The latter intermediate goes on to the 1,2-disubstituted product at a yet much slower rate, as monitored by ¹H NMR spectroscopy. The reaction of 3 with PMePh₂ was also monitored by ¹H NMR spectroscopy in the temperature range from 0 to 36 °C. The concentration vs time curves were fit to a rate law for the reversible formation of an intermediate followed by the irreversible formation of the product.

The reaction of the η^3 intermediate **7a** with PMe₃ was studied by means of ¹H NMR spectroscopy in acetone- d_6 in the temperature range -15 to 0 °C. The rate of disappearance of **7a** and the rate of the appearance of **14a** were followed by integration of the pyridine resonances at 9.2 ppm (**7a**) and 8.7 ppm (**14a**). PMe₃ was in large excess (0.4–1.6 M) over the ruthenium complex (0.04 M) to ensure pseudo-first-order conditions. The linear dependence of the observed pseudo-firstorder rate constant on [PMe₃] indicates that the reaction is first order in PMe₃ and second order overall. There was no evidence for an intermediate or a reversible reaction.

The kinetics of the reaction of **2** with pyridine- d_5 in acetone d_6 as the solvent to give **3** (substitution of CH₃CN by pyridine) were studied by ¹H NMR spectroscopy. Pyridine- d_5 was used in large excess (0.4–1.6 M) over the ruthenium complex (0.04 M) to ensure pseudo-first-order conditions. The rate of disappearance of **2**, and the rate of appearance of **3** were followed by integration of the respective C₅H₅ proton resonances. The observed rate constant k_{obs} depended linearly on the concentration of pyridine- d_5 , and there was no evidence for an intermediate or reversibility of the reaction. Measurements over the temperature range 3–50 °C yielded the activation parameters.

EHMO Calculations. The extended Hückel molecular orbital calculations were conducted using the program devel-

oped by Hoffmann and Lipscomb,³⁷ as modified by Mealli and Proserpio.³⁸ The atomic parameters were taken from the CACAO program. All bond lengths and angles of the complexes analyzed were those determined from crystallography or from geometry optimization using a Walsh analysis with initial values taken from known structural data.

Crystallographic Structure Determinations. Crystal, data collection, and refinement parameters are given in Table 3. For **3**, a Philips PW1100 four-circle diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.710$ 73 Å) and a $\theta - 2\theta$ scan capability was used. For **4** CH₃CN and **18**, X-ray data were collected on a Siemens Smart CCD area detector diffractometer (graphite-monochromated Mo K α radiation, $\lambda = 0.710$ 73 Å, $0.3^{\circ} \omega$ -scan frames). Corrections for Lorentz and polarization effects, for crystal decay, and, in the case of **4** CH₃CN and **18**, for absorption were applied. The structures were solved by direct methods.³⁹ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. The structures were refined against $F^{2.40}$

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Supporting Information Available: Tables S1–S28, listing the kinetic conditions and all of the measured rate constants and amplitude ratios as well as the fit values, and Tables S29–S43, giving atomic coordinates and U_{eq} values, hydrogen coordinates and U_{iso} values, anisotropic temperature factors, complete bond lengths and angles, and least-squares planes for complexes **3**, **4**·CH₃CN, and **18** (47 pages). Ordering information is given on any current masthead page.

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