

Structure, Synthesis, and Chemistry of $(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-benzyne})$. Reactions with Arenes, Alkenes, and Heteroatom-Containing Organic Compounds. Synthesis and Structure of a Monomeric Hydroxide Complex

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Abstract: Thermolysis of $(\text{PMe}_3)_4\text{Ru}(\text{Ph})(\text{Me})$ or $(\text{PMe}_3)_4\text{Ru}(\text{Ph})_2$ leads to the ruthenium benzyne complex $(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-C}_6\text{H}_4)$ (**1**) by a mechanism that involves initial reversible dissociation of phosphine. In many ways, its chemistry is analogous to that of early rather than late organo-transition-metal complexes. Thus, compound **1** undergoes apparent σ -bond metathesis reactions with the C-H bonds of benzene or toluene solvent (the reverse of the formation of **1**), the N-H bond in aniline, and O-H bonds of *p*-cresol, 2-propanol, and water. The monomeric hydroxide complex resulting from addition of water has been structurally characterized. Compound **1** also undergoes insertion reactions with a variety of unsaturated organic molecules, including ethylene, di-*p*-tolylacetylene, benzaldehyde, and benzonitrile. Qualitative mechanistic studies on the O-H addition of *p*-cresol and the insertion of benzaldehyde and benzonitrile are reported.

Introduction

Many organic and main-group organometallic reactive intermediates are stable when coordinated to transition-metal fragments. The most extensively studied example is probably the transition-metal carbene complex.¹ Molecules possessing unstable double or triple bonds have been generated at transition-metal centers and have been shown to be stabilized by this interaction; silene², disilene³, ketene⁴, benzyne, and cycloalkyne^{5,6} transition-metal complexes are a few examples. In most cases, the complexes do not display reactivity similar to that of the free molecule. Yet, studies are beginning to indicate that these complexes are more reactive than those containing typical M-X bonds. One type of molecule for which the reactivity has been recently developed is the transition-metal benzyne complex.

Much of the study of the early-transition-metal benzyne complexes has involved addition and insertion reactions with functionalized organic molecules. These overall transformations cleave a metal-carbon bond of the benzyne complex and form a new metal-nitrogen or metal-oxygen bond in the product, processes that are typically favorable for early-transition-metal complexes. In contrast, late-transition-metal benzyne and cycloalkyne complexes have shown more limited reactivity. They undergo addition reactions with acidic reagents such as alcohols and ketones, but not with amines; they undergo insertion reactions with CO, CO₂, and unsaturated hydrocarbons, but not with ketones, aldehydes, or nitriles.^{6b,c} The lack of reactivity of these complexes toward these reagents is consistent with the well-established reactivity of late-transition-metal alkyl and aryl complexes.⁷

We report the isolation of a benzyne complex of ruthenium that is generated by the same overall transformation used to form early-transition-metal benzyne complexes,^{6f-i} but by a mechanism typical of late-transition-metal compounds.⁷ The ruthenium complex displays reactivity more characteristic of early than late-transition-metal-carbon bonds; it readily undergoes addition reactions with weak acids and insertion reactions with aldehydes and nitriles, forming ruthenium-oxygen or ruthenium-nitrogen bonds. Thus, this material provides an easily accessible and versatile starting material for entry into the study of late-transition-metal heteroatom-containing molecules.⁸

Results

Formation of Benzyne Complex 1. Crystal Structure and Kinetic Analysis. Synthesis of the ruthenium benzyne complex $(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-C}_6\text{H}_4)$ is shown in Scheme I. Two methods were developed. Method B was a more convenient preparative scale

reaction of **1**, while method A allowed isolation of the intermediate complex $(\text{PMe}_3)_4\text{Ru}(\text{Me})(\text{Ph})$. A typical preparative scale reaction involved addition of 2.2 equiv of PhMgBr to 1.5 g of

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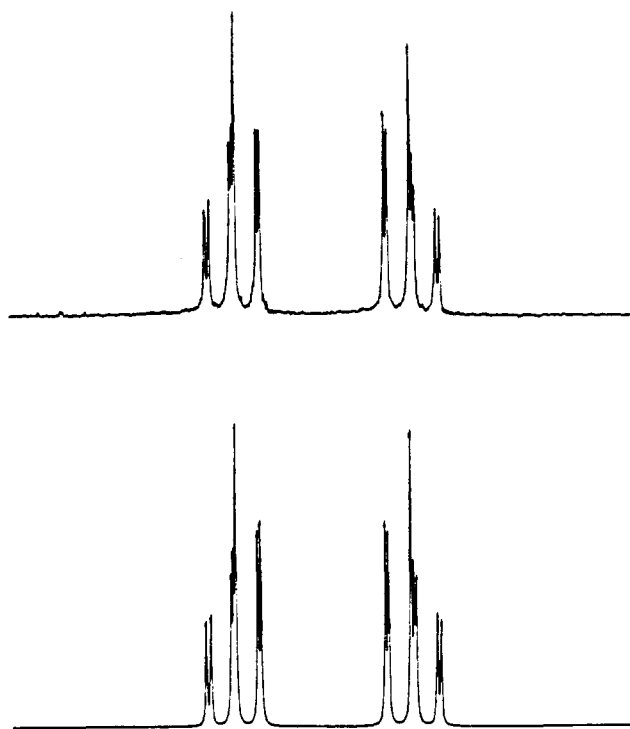
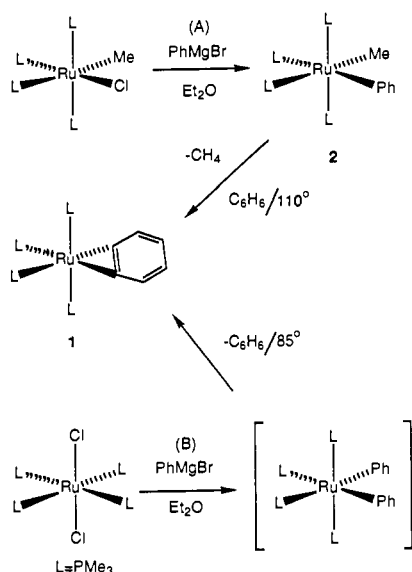


Figure 1. Experimental (top) and calculated (bottom) $^{31}P\{^1H\}$ NMR spectra of **1**.

Scheme 1



$(PMe_3)_4Ru(Cl)_2$ in ether, followed by heating of the resulting solution at $85^\circ C$ for 8 h. This provided samples of **1** in 55–70% yield that were pure enough without crystallization for synthetic purposes. Complex **1** was isolated in analytically pure form by crystallization from pentane at $-40^\circ C$. Alternatively, **1** could be prepared by the addition of $PhMgBr$ to the known $(PMe_3)_4Ru(Me)(Cl)_2$ ^{11a} to provide $(PMe_3)_4Ru(Me)(Ph)$ (**2**) in 20% yield after crystallization. Thermolysis of **2** in benzene- d_6 at $110^\circ C$ for 12 h provided **1** in 95–100% yield by 1H NMR spectroscopy.

The benzyne complex **1** is a white crystalline solid that is extremely air-sensitive but can be stored in a drybox at room temperature for months without decomposition. Full 1H , ^{13}C , and ^{31}P data on complex **1** (as well as on other complexes prepared in this research) are given in Tables VIII–X. The 1H NMR spectrum of **1** showed two broad resonances in the aromatic region at δ 7.26 and 7.31, while the $^{31}P\{^1H\}$ NMR spectrum consisted of a second-order A_2B_2 spectrum; this spectrum along with a

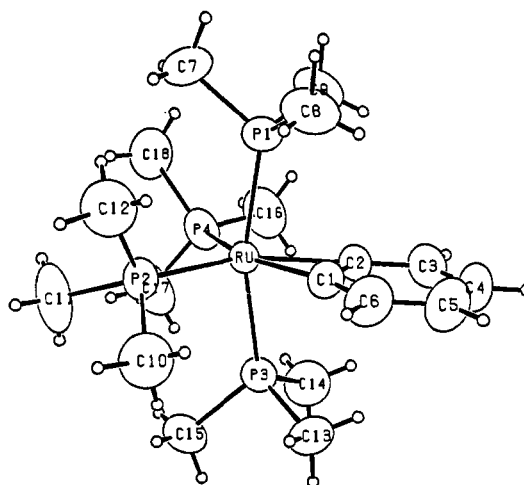


Figure 2. ORTEP drawing of **1**.

Table I. Crystal and Data Collection Parameters^a

	1	9	15
temperature ($^\circ C$)	25	-118	-89
empirical formula	$RuP_4C_{18}H_{40}$	$RuP_4OC_{18}H_{42}$	$RuP_4NC_{25}H_{45}$
formula weight (amu)	481.5	499.5	584.6
crystal size (mm)	0.20 × 0.25 × 0.50	0.25 × 0.29 × 0.30	0.15 × 0.15 × 0.25
space group	$P2_1/n$	$P\bar{1}$	$P2_12_1$
<i>a</i> (Å)	9.4492 (10)	8.698 (1)	9.722 (3)
<i>b</i> (Å)	15.9489 (17)	16.423 (3)	14.191 (6)
<i>c</i> (Å)	16.3007 (19)	17.097 (3)	20.462 (6)
α (deg)	90.0	80.858 (13)	90.0
β (deg)	91.528 (9)	84.741 (12)	90.0
γ (deg)	90.0	88.540	90.0
<i>V</i> (Å ³)	2455.7 (8)	2400.9 (9)	2823.0 (0)
<i>Z</i>	4	4	4
<i>d</i> _{calc} (g cm ⁻³)	1.30	1.38	1.38
μ _{calc} (cm ⁻¹)	8.8	9.1	7.8
reflections measured	$+h, +k, \pm l$	$+h, \pm k, \pm l$	$+h, +k, +l$
scan width	$\Delta\theta = 0.65 +$ $0.35 \tan \theta$	$\Delta\theta = 0.65 +$ $(0.35 \tan \theta)$	$\Delta\theta = 1.20 +$ $0.35 \tan \theta$
scan speed (θ , deg/min)	6.70	6.70	6.70
setting angles (2θ , deg) ^b	24–28	24–28	24–28

^aParameters common to all structures: radiation, Mo $K\alpha$; monochromator, highly oriented graphite ($2\theta = 12.2^\circ$); detector, crystal scintillation counter, with PHA; 2θ range, $3 \rightarrow 45^\circ$, scan type, θ - 2θ ; background, measured over 0.25 ($\Delta\theta$) added to each end of the scan; intensity standards, measured every hour of X-ray exposure time; orientation, 3 reflections were checked after every 200 measurements; crystal orientation was redetermined if any of the reflections were off-set from their predicted positions by more than 0.1° , reorientation was required twice for **1** and once for **15**. ^bUnit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo $K\alpha$ components of 24 reflections with the given 2θ range. In this and all subsequent tables, the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) of the reported value.

simulation is shown in Figure 1. In the ^{13}C NMR, the benzyne carbon atoms appear at δ 142.07. This chemical shift is comparable to those of corresponding carbon atoms in related complexes.^{5,6} Perhaps equally relevant are M–C carbon signals for aryl complexes in this series, which typically appear between δ 160 and 170.

Slow cooling of a pentane solution of **1** provided crystals that were suitable for an X-ray diffraction study. The complex crystallized in space group $P2_1/n$ and showed no unusually short intermolecular contacts. An ORTEP drawing of **1** is shown in Figure 2; acquisition parameters, intramolecular distances, and intramolecular angles are provided in Tables I–III. The coordination of the ruthenium atom can be described as a trigonal bipyramid or a distorted octahedron. The atoms P2, P4, Ru, C1, and C2

Table II. Intramolecular Distances for 1

atom 1-atom 2	distance	atom 1-atom 2	distance
Ru-P1	2.354 (1)	P1-C7	1.854 (3)
Ru-P2	2.303 (1)	P1-C8	1.827 (3)
Ru-P3	2.328 (1)	P1-C9	1.823 (3)
Ru-P4	2.319 (1)	P2-C10	1.840 (3)
Ru-C1	2.072 (2)	P2-C11	1.816 (3)
Ru-C2	2.111 (2)	P2-C12	1.827 (3)
C1-C2	1.355 (3)	P3-C13	1.820 (3)
C1-C6	1.382 (3)	P3-C14	1.826 (3)
C2-C3	1.372 (3)	P3-C15	1.844 (3)
C3-C4	1.411 (4)	P4-C16	1.831 (3)
C4-C5	1.363 (4)	P4-C17	1.839 (3)
C5-C6	1.398 (4)	P4-C18	1.834 (3)

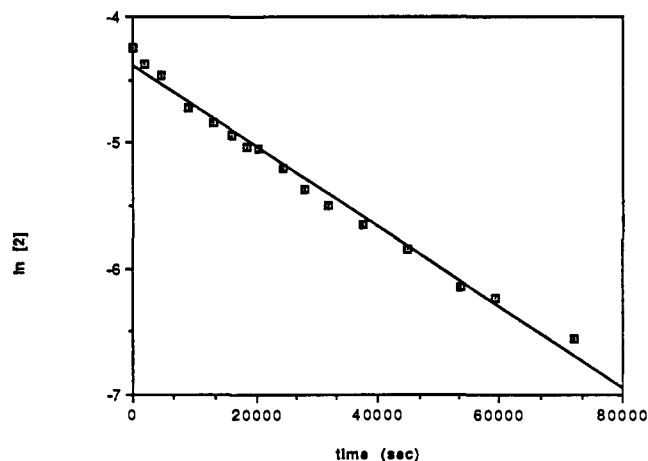
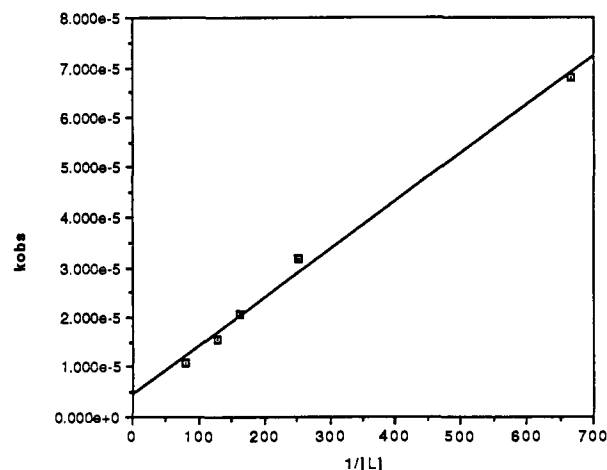
Table III. Intramolecular Angles for 1

atom 1-atom 2-atom 3	angle	atom 1-atom 2-atom 3	angle
P1-Ru-P2	98.01 (2)	Ru-P1-C7	123.90 (11)
P1-Ru-P3	165.13 (2)	Ru-P1-C8	116.23 (10)
P1-Ru-P4	92.18 (2)	Ru-P1-C9	114.35 (10)
P2-Ru-P3	95.11 (2)	C7-P1-C8	98.7 (2)
P2-Ru-P4	103.35 (2)	C7-P1-C9	100.4 (2)
P3-Ru-P4	91.57 (2)	C8-P1-C9	99.3 (2)
P1-Ru-C1	85.40 (6)	Ru-P2-C10	113.68 (11)
P1-Ru-C2	83.33 (6)	Ru-P2-C11	124.15 (11)
P2-Ru-C1	101.79 (6)	Ru-P2-C12	118.73 (11)
P2-Ru-C2	139.53 (6)	C10-P2-C11	99.6 (2)
P3-Ru-C1	85.09 (6)	C10-P2-C12	96.7 (2)
P3-Ru-C2	82.15 (6)	C11-P2-C12	99.1 (2)
P4-Ru-C1	154.83 (7)	Ru-P3-C13	116.59 (10)
P4-Ru-C2	117.06 (6)	Ru-P3-C14	115.35 (9)
C1-Ru-C2	37.78 (8)	Ru-P3-C15	122.52 (9)
Ru-C1-C2	72.71 (13)	C13-P3-C14	98.44 (14)
Ru-C1-C6	164.9 (2)	C13-P3-C15	98.93 (13)
Ru-C2-C1	69.52 (12)	C14-P3-C15	101.03 (13)
Ru-C2-C3	168.4 (2)	Ru-P4-C16	115.66 (10)
C2-C1-C6	122.2 (2)	Ru-P4-C17	120.99 (10)
C1-C2-C3	121.8 (2)	Ru-P4-C18	120.64 (11)
C2-C3-C4	116.9 (3)	C16-P4-C17	99.11 (14)
C3-C4-C5	121.1 (2)	C16-P4-C18	99.02 (14)
C4-C5-C6	121.1 (3)	C17-P4-C18	96.9 (2)
C1-C6-C5	116.8 (3)		

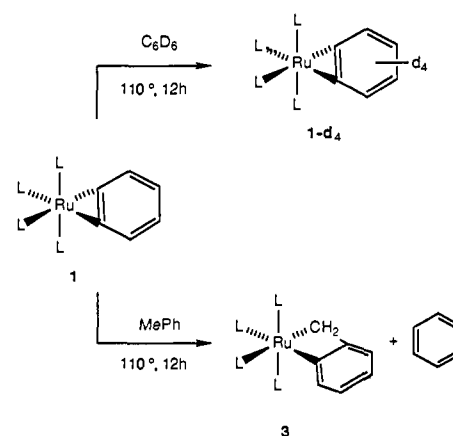
all lie in a plane with deviations of ± 0.02 Å. This plane forms an angle of less than 4° to the plane of the benzyne ligand. The angle P1-Ru-P3 is 165° and is bent away from the other two phosphorus atoms. The angles from the axial to the equatorial phosphorus atoms range from 91.6° to 98.0° , and the P-Ru-P angle in the equatorial plane is 103.4° . The four Ru-P distances are unequal, though they fall into a pattern. The mutually trans phosphorus distances are longer than those trans to the benzyne ligand. The average Ru-P1,3 distance is 2.341 ± 0.013 Å, and the average Ru-P2,4 distance is 2.311 ± 0.004 Å. The Ru-C distances are different in the solid state (Ru-C1 = 2.072 (2) Å and Ru-C2 = 2.111 (2) Å), as are the P-Ru-C angles (P2-Ru-C1 = 139.53 (6) $^\circ$ and P4-Ru-C2 = 117.06 (6) $^\circ$), although no asymmetry is observed in the solution spectroscopy. The source of this asymmetry does not seem to be steric crowding since there are no short intramolecular contacts within the coordination sphere; we are inclined to the view that the asymmetry is due to solid-state effects and that these two bonds are not chemically different. These two Ru-C bond distances are slightly shorter than the Ru-aryl bond in $(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-CH}_2\text{C}_6\text{H}_4)$.⁹ The average of the C-C bond distances in the benzyne ligand (1.385 ± 0.015 Å) is close to that found for free benzene (1.392 Å by X-ray diffraction),¹⁰ as has been the case for the other structurally

(9) Calabrese, J. C.; Colton, M. C.; Herskovitz, T.; Klabunde, U.; Parshall, G. W.; Thorn, D. L.; Tulip, T. H. *Ann. N. Y. Acad. Sci.* **1983**, *415*, 302. An ORTEP diagram is included in this reference but bond distances are not provided. The Ru-aryl bond length is 2.118 (3) Å; Tulip, T. H. Personal communication.

(10) Recent values are provided in Jeffrey, G. A.; Ruble, J. R.; McMullan, R. K.; Pople, J. A. *Proc. R. Soc. London, A* **1987**, *414*, 47.

Figure 3. Typical first-order plot ($[L] = 3.97$ mM) for the formation of 1 from 2.Figure 4. k_{obs} versus $1/[L]$ for the formation of 1 from 2.

Scheme II

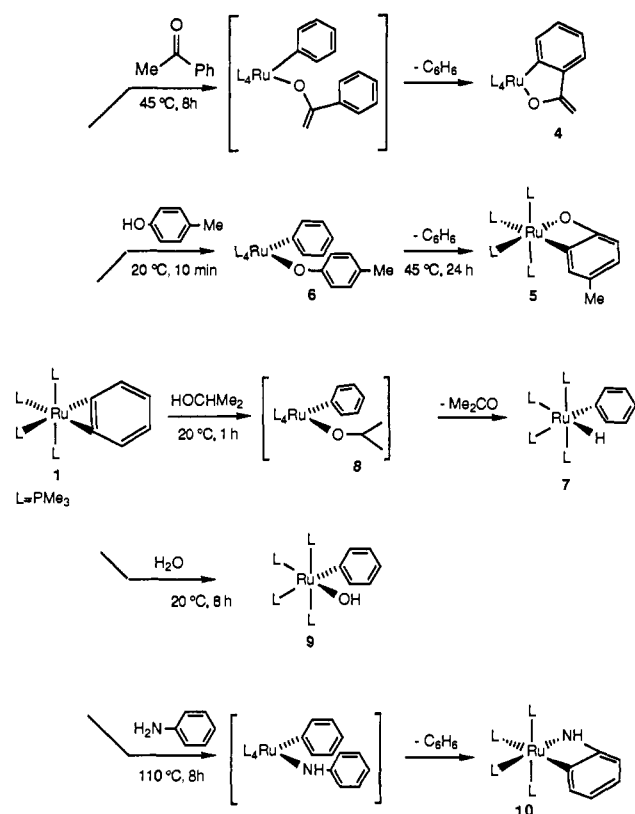


characterized benzyne complexes.⁵ Therefore, the structure of 1 can be considered to be a Ru(II) complex with two short metal-carbon σ bonds.

The rate of formation of benzyne complex 1 from the methyl phenyl complex 2 was measured at 110°C in benzene. The reaction was followed by monitoring the disappearance of the phosphine resonance of 2 at $\delta 0.96$ in samples containing between 1.70×10^{-3} and 1.87×10^{-2} M concentrations of phosphine. At all concentrations of phosphine, the reaction displayed clean

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Scheme III

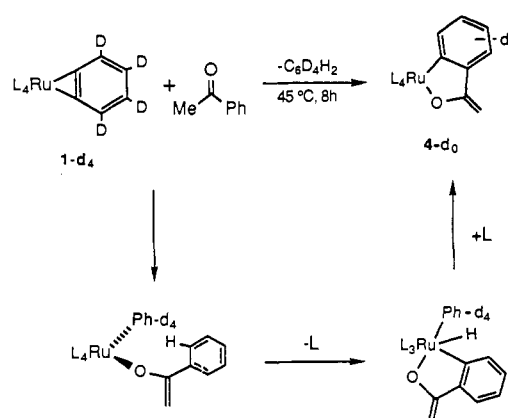


pseudo-first-order kinetic behavior. The plot of a typical kinetic run (0.0085 M PMe_3) is shown in Figure 3, and a plot of k_{obs} vs $1/[P]$ is shown in Figure 4, clearly demonstrating an inverse dependence of rate on phosphine concentration.

Addition of C-H, N-H, and O-H Bonds. The reactions of **1** with C-H bonds are shown in Scheme II. Thermolysis of **1** in C_6D_6 provided the deuterated benzyne complex $(PMe_3)_4Ru(\eta^2-C_6D_4)$, indicating that the formation of the benzyne complex by method B (Scheme I) is reversible. This reaction is reminiscent of a similar reversible formation of $Cp_2Zr(\eta^2\text{-benzyne})$ by Erker.^{6t} Complex **1-d₄** was identified by the absence of aromatic resonances in the 1H NMR spectrum of the reaction mixture and the presence of the benzyne resonances in the 2H NMR spectrum. The appearance of the $^{31}P\{^1H\}$ NMR spectrum of the deuterated complex was the same as that of the undeuterated sample. A simulation of the electron impact (EI) mass spectrum of the final reaction mixture showed that the starting complex **1** had been converted to 80–90% **1-d₄**. A more accurate simulation was made difficult by the large number of ruthenium isotopes. Thermolysis of **1** in toluene at 110 °C for 1–2 days resulted in formation of the known orthometalated benzyl compound **3¹¹** in essentially quantitative yield by $^{31}P\{^1H\}$ NMR spectroscopy. Complex **1** was extremely thermally stable in alkane solvents. Thermolysis in pentane at 145 °C for 8 h resulted in no detectable decomposition or reaction with solvent.

Addition reactions of functionalized organic compounds to **1** are shown in Scheme III. Acetophenone (1 equiv) reacted with **1** at 45 °C for 8 h to form the orthometalated, O-bound, enolate complex **4** in 45% yield. This complex was also the product of the addition of acetone to **1**, a reaction that will be reported in detail in a separate publication. Addition of acetophenone to **1-d₄** yielded **4-d₀**, as determined by integration of the 1H NMR spectrum of the product (Scheme IV). Treatment of **1** with 1 equiv of *p*-cresol in toluene, followed by heating to 45 °C for 24 h, provided the previously reported orthometalated cresolate complex **5¹²** in 70% yield. This reaction was monitored after the

Scheme IV



addition of the *p*-cresol. *p*-Cresol was added to **1** at room temperature, and the reaction was quickly cooled to -78 °C. 1H and $^{31}P\{^1H\}$ NMR spectroscopies showed that all of the benzyne complex **1** had reacted to form a complex that was stable at this temperature. This intermediate was not isolated, but the 1H and $^{31}P\{^1H\}$ NMR spectra were consistent with a compound of structure $(PMe_3)_4Ru(Ph)(OC_6H_4Me)$ (**6**). The formation of **5** from **6** required 24 h at 45 °C.

The qualitative rates of reaction of benzyne complex **1** with *p*-cresol and of phosphine dissociation from **1** were evaluated. $PMe_3\text{-}d_9$ (4 equiv) was added to **1**, and a $^{31}P\{^1H\}$ NMR spectrum was obtained after 10 min, 2 h, and 24 h at 25 °C. After 10 min, the ratio of free $PMe_3\text{-}d_9$ to $PMe_3\text{-}d_0$ was 36:1; after 2 h, the ratio was roughly 2:1; after 24 h, it was 1:1. These results demonstrate that the reaction of *p*-cresol with **1** to form **6** occurred much faster than phosphine dissociation.

Less acidic O-H bonds such as those in 2-propanol and water also formally add across the Ru-C bond in **1**. Treatment of **1** with 1 equiv of 2-propanol led to the phenyl hydride complex **7** in 56% isolated yield. This reaction presumably proceeds by initial addition of the alcohol to **1**, forming a phenyl isopropoxide intermediate **8**, similar to the intermediate observed with the addition of *p*-cresol. Intermediate **8** then leads to **7** by β -hydrogen elimination. Reaction of **1** with water does not afford the possibility of β -hydrogen elimination, and addition of 1 equiv of water yielded the phenyl hydroxide complex **9** in 62% yield after crystallization from pentane. Solution spectroscopic analysis of this complex was complicated by broad aryl resonances due to hindered rotation of the phenyl group at room temperature. Therefore, 1H and $^{13}C\{^1H\}$ NMR spectra were obtained at -40 °C. At this temperature, rotation of the ring was slow, compared to the NMR time scale, and all aryl protons and carbon atoms were inequivalent. The hydroxide moiety was identified by a sharp resonance in the 1H NMR spectrum at δ -4.47 and a sharp band in the solid-state infrared spectrum (Nujol) at 3636 cm^{-1} . Similar spectroscopic features are found in related iridium¹³ and platinum hydroxide¹⁴ complexes. The structural assignment was confirmed by the $^{31}P\{^1H\}$ NMR spectrum, which displayed an A_2BC pattern with one *cis* phosphine resonating upfield and one resonating downfield from the mutually *trans* phosphines, indicating that one PMe_3 is located *trans* to the aryl ring and the other is *trans* to the hydroxide.

Because few monomeric hydroxo complexes have been structurally characterized, an X-ray diffraction study was performed on a single crystal of **9**. Suitable crystals were obtained by slow cooling of a pentane solution of **9**. The crystal contained two molecules in the asymmetric unit; an ORTEP drawing of one of the molecules is shown in Figure 5, and acquisition parameters, intramolecular distances, and intramolecular angles are provided in Tables I, IV, and V. The crystal contained discrete monomers.

(12) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Organomet. Chem.* **1990**, *394*, 417.

(13) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387. Reference 27 lists metal-oxygen bond distances in monomeric metal hydroxide complexes.

(14) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.

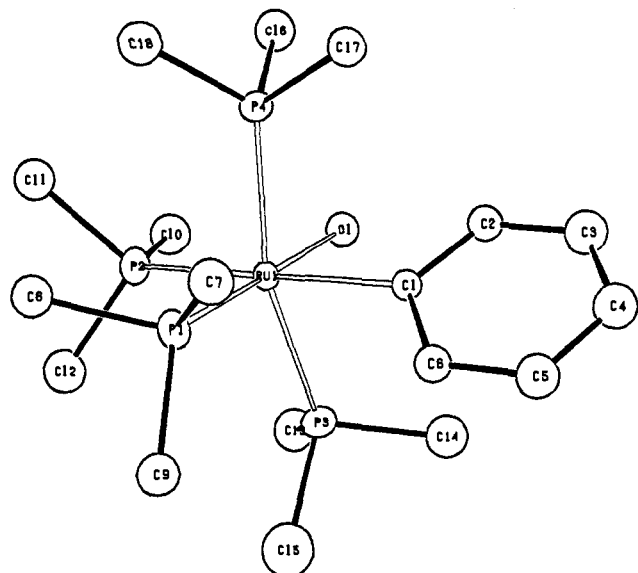


Figure 5. ORTEP drawing of 9. The hydrogen atoms have been removed for clarity.

Table IV. Intramolecular Distances for 9

atom 1-atom 2	distance	atom 1-atom 2	distance
Ru1-P1	2.286 (1)	P1-C7	1.844 (6)
Ru1-P2	2.354 (1)	P1-C8	1.851 (5)
Ru1-P3	2.379 (1)	P1-C9	1.851 (6)
Ru1-P4	2.332 (1)	P2-C10	1.851 (6)
Ru1-O1	2.168 (3)	P2-C11	1.866 (6)
Ru1-C1	2.159 (5)	P2-C12	1.834 (6)
C1-C2	1.384 (7)	P3-C13	1.839 (6)
C1-C6	1.426 (7)	P3-C14	1.834 (6)
C2-C3	1.412 (7)	P3-C15	1.845 (7)
C3-C4	1.380 (8)	P4-C16	1.829 (6)
C4-C5	1.414 (8)	P4-C17	1.833 (5)
C5-C6	1.417 (7)	P4-C18	1.857 (6)

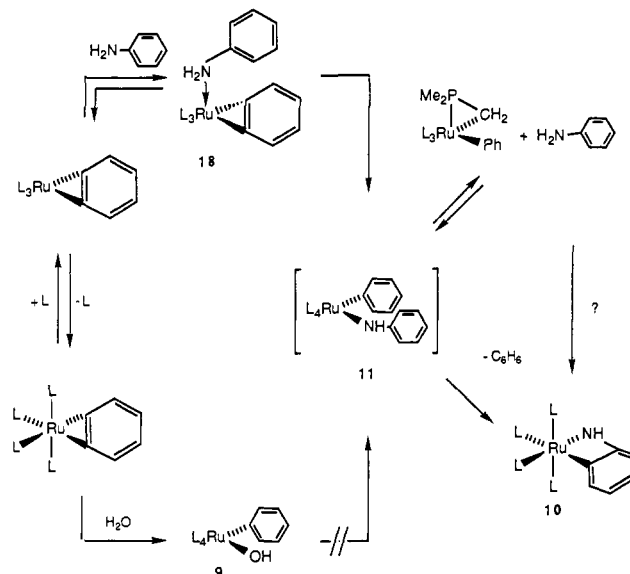
No hydrogen bonding was observed between the ruthenium complexes and no water of solvation was observed, confirming that this synthesis is particularly useful since it provides a hydroxide complex that is free of hydrogen-bound water. The coordination at ruthenium is pseudooctahedral, with the phenyl ring and hydroxide group occupying mutually cis sites. The hydrogen atom of the hydroxide moiety was not located. The ruthenium-oxygen distance is 2.168 (3) Å, slightly longer than the iridium-oxygen distance of 2.119 (5) Å in [(PMe₃)₄Ir(H)(OH)]PF₆,¹³ the ruthenium-aryl distance is 2.159 (5) Å, slightly longer than the (PMe₃)₄Ru-aryl bonds contained in the metallacycles described in this paper and in (PMe₃)₄Ru(η²-CH₂C₆H₄).⁸ The Ru1-P1 bond length, the metal-phosphorus distance corresponding to the ligand located trans to the hydroxide substituent, is significantly shorter than the other ruthenium-phosphorus distances, consistent with a hydroxide ligand having a weak trans influence. The weaker trans influence of the hydroxide substituent in [(PMe₃)₄Ir(H)(OH)]⁺ relative to that of the hydride or phosphine ligands is also demonstrated by the metal-phosphorus distances, (2.259 (2) Å trans to the hydroxide, 2.369 (2) Å trans to the hydride, and 2.337 Å for the mutually trans phosphines.

Addition of aniline to the ruthenium benzyne complex 1 resulted in the formation of the orthometallated anilide complex 10 in 98% yield by ¹H NMR spectroscopy and 68% isolated yield. Complex 10 was identified by conventional spectroscopic techniques and microanalysis. The ¹H NMR spectrum showed four aromatic resonances, and the ¹³C/¹H NMR spectrum contained a doublet of doublet of quartets resonance, corresponding to a quaternary aryl carbon atom, indicating that metalation of the ring had occurred. The ³¹P/¹H NMR spectrum displayed an A₂BC pattern, with one phosphine resonating upfield and one downfield of the mutually trans phosphines, similar to the spectrum observed for the phenyl hydroxide complex 9. The infrared spectrum contained

Table V. Intramolecular Angles for 9

atom 1-atom 2-atom 3	angle	atom 1-atom 2-atom 3	angle
P1-Ru1-P2	94.71 (5)	Ru1-P1-C7	117.99 (18)
P1-Ru1-P3	103.82 (5)	Ru1-P1-C8	120.70 (18)
P1-Ru1-P4	91.65 (5)	Ru1-P1-C9	120.82 (19)
P1-Ru1-O1	179.27 (10)	C7-P1-C8	96.89 (25)
P1-Ru1-C1	93.37 (13)	C7-P1-C9	99.1 (3)
P2-Ru1-P3	93.01 (5)	C8-P1-C9	96.24 (25)
P2-Ru1-P4	94.10 (5)	Ru1-P2-C10	114.02 (19)
P2-Ru1-O1	84.58 (9)	Ru1-P2-C11	123.58 (19)
P2-Ru1-C1	171.58 (13)	Ru1-P2-C12	118.58 (19)
P3-Ru1-P4	162.37 (5)	C10-P2-C11	97.9 (3)
P3-Ru1-O1	76.07 (10)	C10-P2-C12	102.1 (3)
P3-Ru1-C1	82.75 (13)	C11-P2-C12	96.6 (3)
P4-Ru1-O1	88.57 (10)	Ru1-P3-C13	116.53 (20)
P4-Ru1-C1	88.03 (13)	Ru1-P3-C14	114.79 (20)
O1-Ru1-C1	87.34 (15)	Ru1-P3-C15	125.49 (23)
Ru1-C1-C2	121.2 (4)	C13-P3-C14	97.8 (3)
Ru1-C1-C6	122.5 (3)	C13-P3-C15	98.5 (3)
C2-C1-C6	116.0 (4)	C14-P3-C15	98.9 (3)
C1-C2-C3	123.2 (5)	Ru1-P4-C16	111.89 (19)
C2-C3-C4	120.5 (5)	Ru1-P4-C17	120.03 (18)
C3-C4-C5	118.8 (5)	Ru1-P4-C18	123.86 (19)
C4-C5-C6	119.8 (5)	C16-P4-C17	101.14 (25)
C1-C6-C5	121.7 (5)	C16-P4-C18	99.7 (3)
		C17-P4-C18	96.23 (25)

Scheme V



an O-H stretching band at 3336 cm⁻¹.

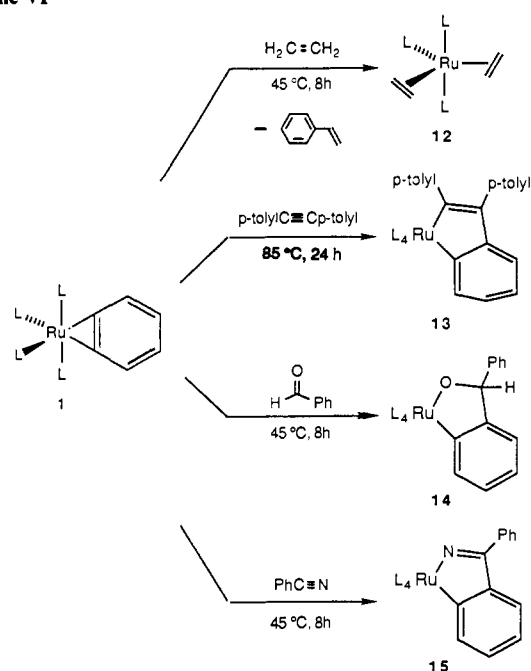
In light of the results reported for H/D exchange reaction of arylamines with (PMe₃)₄Ru(D)₂, which were shown to be catalyzed by trace amounts of water, we were concerned that the addition of aniline to 1 might also be catalyzed by water. As noted above, water adds to 1 to form phenyl hydroxide complex 9, and addition of aniline to 9 may lead to a phenyl anilide intermediate 11, as is the case for another ruthenium hydroxide complex.¹⁵ Intermediate 11 could form benzene and 10 by orthometalation as shown in Scheme V. To probe this possibility, 1 equiv of aniline was added to phenyl hydroxide 9, followed by heating to 110 °C for 8 h. No formation of 10 was detected. Rather, the bridging hydroxide complexes resulting from thermolysis of phenyl hydroxide 9 in the absence of aniline were observed.¹⁶ Although these results suggest that orthometallated anilide 10 does not form directly from 9, water could be catalyzing this reaction by another mechanism.

The reaction of aniline with 1 takes place at a temperature at which phosphine is rapidly exchanging, and therefore the reaction

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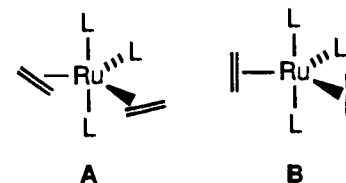
Scheme VI



could proceed by coordination of the amine nitrogen atom to the ruthenium prior to N–H addition. Unfortunately, when monitoring the reaction at 95°C for 1.5 h in the presence of 5 equiv of phosphine (0.16 M), the added phosphine appeared to prevent orthometalation of the aryl ring from occurring and led to several reaction products, none of which was **10**. These compounds contained resonances between δ –35 and –40¹⁷ in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, indicating that cyclometalation of one of the phosphine ligands had occurred to form a metallaphosphacyclopropane ring (Scheme V). However, heating this sample for an additional 24 h at 110°C led to clean formation (81% yield by ^1H NMR spectroscopy) of **10**, indicating that these intermediates may be involved in the reactions run in the absence of added phosphine.

Insertion Reactions. The insertion chemistry we have observed with **1** is shown in Scheme VI. Addition of 5–10 equiv of ethylene to a benzene solution of **1** followed by heating to 85°C for 8 h resulted in formation of styrene (identified by ^1H NMR spectroscopy and GC retention time) and the diethylene complex **12**. The organometallic product was independently synthesized by the addition of ethylene to the previously reported complex $(\text{PMe}_3)_4\text{Ru}(\text{C}_2\text{H}_4)$ ¹⁸ and was characterized by conventional spectroscopic techniques. The compound was most clearly identified by its A_2B pattern in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and its two multiplet resonances at δ 1.41 and 1.80 in the ^1H NMR spectrum and the two doublet of triplet resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at δ 21.14 and 23.47. The observation of two ethylene resonances in both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra is consistent with a rigid structure **A** containing two ethylene molecules oriented perpendicular to the axis containing the two trans phosphines and is inconsistent with structure **B** containing two ethylene molecules coordinated parallel to the trans axis (Figure 6).¹⁹ The reaction was run with 5 equiv of ethylene-*1,1-d*₂ and a 1:1:1 ratio of the vinylic resonances of the styrene in the final reaction mixture was observed by integration of the ^1H and ^2H NMR spectra of the final reaction mixture.

Insertion of a substituted alkyne would prevent β -hydrogen elimination from occurring. The reaction of 1 equiv of di-*p*-

Figure 6. Two possible geometries for $(\text{PMe}_3)_3\text{Ru}(\text{C}_2\text{H}_4)_2$ (**12**).

tolylacetylene with **1** for 24 h at 85°C gave rise to the single insertion product **13** in 56% isolated yield. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra indicated the presence of an ortho-substituted aryl ring and two para-substituted rings. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consisted of an A_2BC pattern, with both mutually cis phosphine ligands resonating upfield from the mutually trans ones, indicating that they are located trans to two different metal–carbon bonds. A few preliminary experiments were carried out with terminal alkynes. These were not pursued extensively, but cursory spectroscopic investigation indicated that protonation rather than insertion processes occur in these cases, leading ultimately to benzene and σ -alkynyl complexes $\text{L}_4\text{Ru}(\text{C}\equiv\text{CR})_2$.

Addition of 1 equiv of benzaldehyde to a benzene solution of **1** followed by heating to 45°C for 8 h led to formation of the single insertion product **14** in 93% yield by ^1H NMR spectroscopy and 32% isolated yield. This product was characterized by conventional spectroscopic techniques and microanalysis. The observation of signals due to one ortho-substituted aryl ring in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, a resonance at δ 5.45 in the ^1H NMR spectrum, and the absence of bands between 1500 and 1800 cm^{-1} in the infrared spectrum indicated most clearly that **14** was the insertion product. The inequivalence of the mutually trans phosphines in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was also consistent with this assignment. A second-order ABCD pattern was observed, with one of the cis phosphines resonating downfield and one upfield from the mutually trans phosphines, confirming the presence of one ruthenium–oxygen and one ruthenium–carbon bond. The identity of this spin system was confirmed by simulation, which included a trans P–P coupling constant of 332 Hz. The calculated and experimental spectra are shown in Figure 7.

In contrast to these observations, addition of a 5–10-fold excess of pivaldehyde to **1** resulted in no reaction upon heating to 85°C for 8 h, and addition of acetaldehyde did not lead to a clean reaction. Benzophenone (a ketone without α -hydrogens) did not react with **1** upon heating to 85°C for 8 h.

Reaction of **1** with 3 equiv of benzonitrile did lead cleanly to the insertion product **15** in quantitative yield by ^1H NMR spectroscopy and 46% isolated yield. The structure of **15** was inferred from solution NMR and solid-state infrared spectroscopy and microanalysis. An infrared absorption band at 1436 cm^{-1} was observed, but we do not know whether this should be assigned to an unusually low frequency C=N stretch or to an aromatic vibration. Unlike the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound **14**, the spectrum of **15** showed both of the cis phosphine resonances upfield from the resonances corresponding to the mutually trans phosphines, perhaps due to the inability of the metallamine to act as a π donor since it is constrained in the metallacycle.

Because of its anomalous IR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, the structure of **15** was confirmed by X-ray crystallography. Compound **15** crystallized from pentane in space group $P2_12_12_1$; no close intermolecular contacts were observed. An ORTEP drawing of **15** is shown in Figure 8; acquisition parameters are provided in Table I. Intramolecular distances and angles are given in Tables VI and VII. The coordination at ruthenium is pseudooctahedral, the ruthenium–carbon bond distance is 2.123 (13) Å, in the range found in other ruthenium aryl compounds,⁸ and the metal–nitrogen bond length is 2.108 (13) Å. The metal–phosphine distance trans to the nitrogen is significantly shorter than that trans to the aryl group, as is expected from conventional trans influences.⁷

Addition of other nitriles did not lead to clean reactions. For example, 2-methyl-2-propanecarbonitrile did not react with **1** at 85°C for 12 h and acetonitrile reacted with **1** under these conditions to yield several products. Several pathways for the reaction

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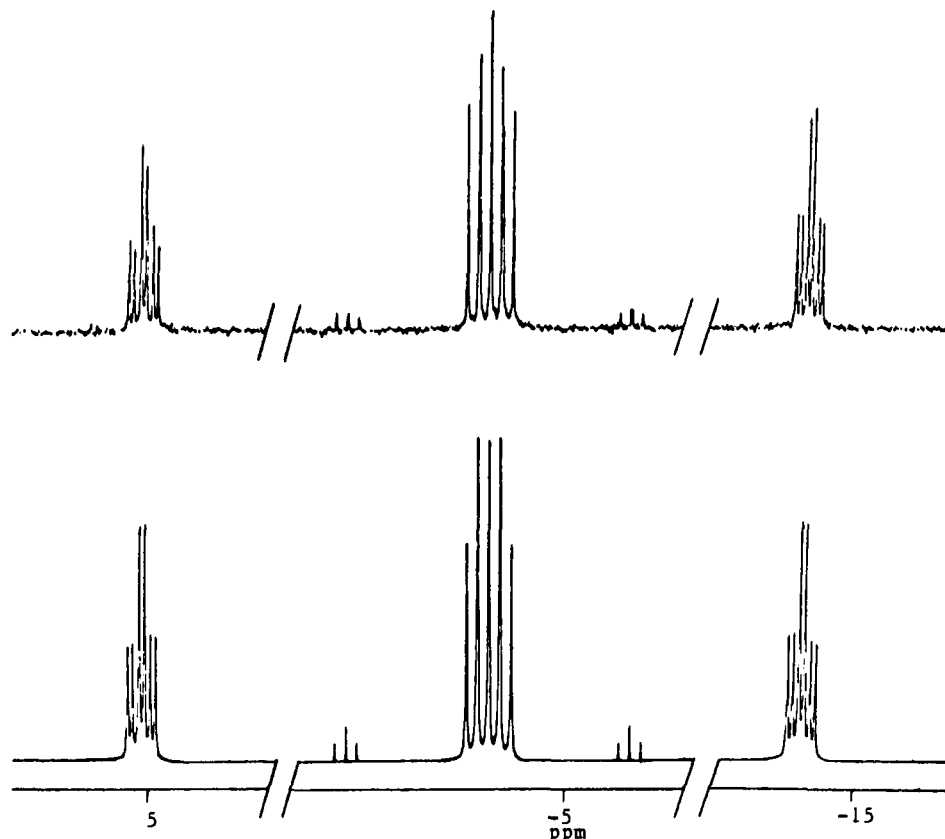


Figure 7. Experimental (top) and calculated (bottom) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 14.

Table VI. Intramolecular Distances for 15

atom 1-atom 2	distance	atom 1-atom 2	distance
Ru-P1	2.366 (4)	C9-C10	1.45 (2)
Ru-P2	2.323 (4)	C10-C11	1.47 (2)
Ru-P3	2.373 (4)	C11-C12	1.41 (2)
Ru-P4	2.317 (4)	C12-C13	1.50 (2)
Ru-N	2.108 (13)	P1-C14	1.845 (14)
Ru-C1	2.123 (13)	P1-C15	1.88 (2)
N-C7	1.26 (2)	P1-C16	1.83 (2)
C1-C2	1.43 (2)	P2-C17	1.836 (13)
C1-C6	1.37 (2)	P2-C18	1.90 (2)
C2-C3	1.41 (2)	P2-C19	1.86 (2)
C3-C4	1.41 (2)	P3-C20	1.86 (2)
C4-C5	1.45 (2)	P3-C21	1.88 (2)
C5-C6	1.42 (2)	P3-C22	1.85 (2)
C6-C7	1.49 (2)	P4-C23	1.86 (2)
C7-C8	1.49 (2)	P4-C24	1.839 (15)
C8-C9	1.38 (2)	P4-C25	1.91 (2)
C8-C13	1.44 (2)		

of acetonitrile are possible, including exchange of acetonitrile for phosphine ligands, addition of the activated C-H bond, and insertion of the C-N bond (a reviewer has suggested that methyl to nitrogen proton transfer may occur in the initially formed insertion product). No products were isolated from the reaction with acetonitrile, but $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of the crude reaction mixture showed one product with an A_2B pattern and others with A_2BC patterns, suggesting that ligand substitution may compete with C-H addition and C-N insertion pathways.

In order to determine if phosphine dissociation played a role in the unusual aldehyde and nitrile insertion reactions, these reactions were run in the presence of added phosphine (5 equiv, 0.16 M). A marked inhibition of the reaction rate for the samples containing added phosphine was observed. The insertion of benzaldehyde was complete after 2.5 h at 45 °C for the sample containing no added phosphine, while the reaction had run to only 28% completion for the reaction run in a 0.16 M solution of PMe_3 in benzene- d_6 . Similarly, the nitrile insertion reaction was complete after 2.5 h at 55 °C for the sample containing no added phosphine,

Table VII. Intramolecular Angles for 15

atom 1-atom 2-atom 3	angle	atom 1-atom 2-atom 3	angle
P1-Ru-P2	164.32 (15)	C9-C8-C13	121.5 (16)
P1-Ru-P3	98.24 (16)	C8-C9-C10	120.6 (16)
P1-Ru-P4	91.28 (16)	C9-C10-C11	120.8 (16)
P1-Ru-N	87.7 (4)	C10-C11-C12	117.2 (16)
P1-Ru-C1	81.8 (4)	C11-C12-C13	121.8 (16)
P2-Ru-P3	96.64 (16)	C8-C13-C12	117.7 (15)
P2-Ru-P4	92.19 (16)	Ru-P1-C14	115.7 (5)
P2-Ru-N	90.4 (4)	Ru-P1-C15	115.2 (5)
P2-Ru-C1	82.6 (4)	Ru-P1-C16	126.1 (6)
P3-Ru-P4	95.58 (15)	C14-P1-C15	98.2 (7)
P3-Ru-N	78.4 (3)	C14-P1-C16	97.8 (7)
P3-Ru-C1	156.7 (4)	C15-P1-C16	99.0 (8)
P4-Ru-N	173.7 (4)	Ru-P2-C17	115.8 (4)
P4-Ru-C1	107.7 (4)	Ru-P2-C18	114.6 (5)
N-Ru-C1	78.4 (5)	Ru-P2-C19	125.2 (5)
Ru-N-C7	114.9 (10)	C17-P2-C18	99.7 (7)
Ru-C1-C2	128.5 (11)	C17-P2-C19	99.7 (7)
Ru-C1-C6	112.8 (10)	C18-P2-C19	97.6 (7)
C2-C1-C6	118.2 (14)	Ru-P3-C20	113.5 (6)
C1-C2-C3	120.2 (14)	Ru-P3-C21	114.3 (5)
C2-C3-C4	121.3 (14)	Ru-P3-C22	125.8 (6)
C3-C4-C5	119.0 (14)	C20-P3-C21	97.6 (6)
C4-C5-C6	117.3 (14)	C20-P3-C22	102.7 (8)
C1-C6-C5	123.9 (14)	C21-P3-C22	98.6 (7)
C1-C6-C7	114.1 (15)	Ru-P4-C23	117.1 (5)
C5-C6-C7	121.9 (15)	Ru-P4-C24	120.0 (5)
N-C7-C6	119.2 (15)	Ru-P4-C25	122.6 (6)
N-C7-C8	120.8 (13)	C23-P4-C24	97.3 (7)
C6-C7-C8	120.0 (14)	C23-P4-C25	98.6 (8)
C7-C8-C9	123.2 (15)	C24-P4-C25	96.1 (7)
C7-C8-C13	114.4 (14)		

but had run to only 57% completion in a 0.16 M solution of PMe_3 in C_6D_6 .

Discussion

Mechanism of the Benzyne-Formation Reaction. Two possible pathways for the generation of benzyne complex 1 from the methyl

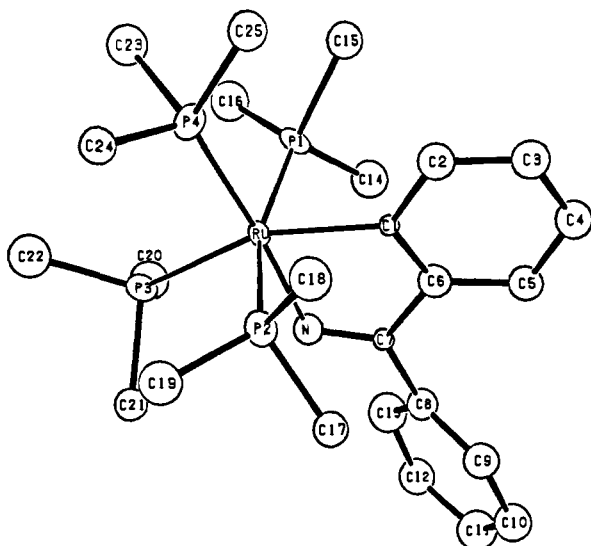
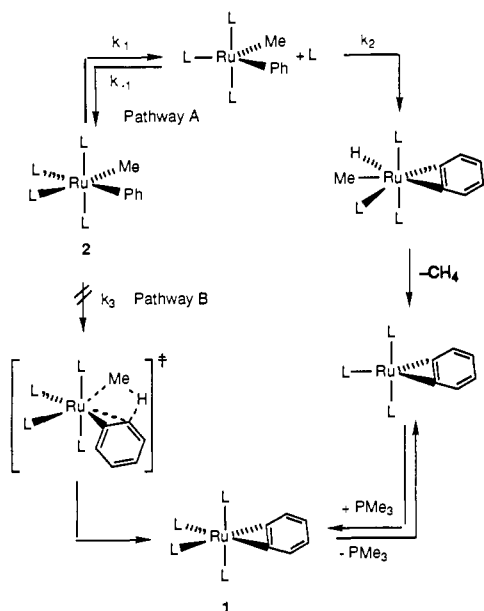


Figure 8. ORTEP drawing of 15. The hydrogen atoms have been removed for clarity.

Scheme VII



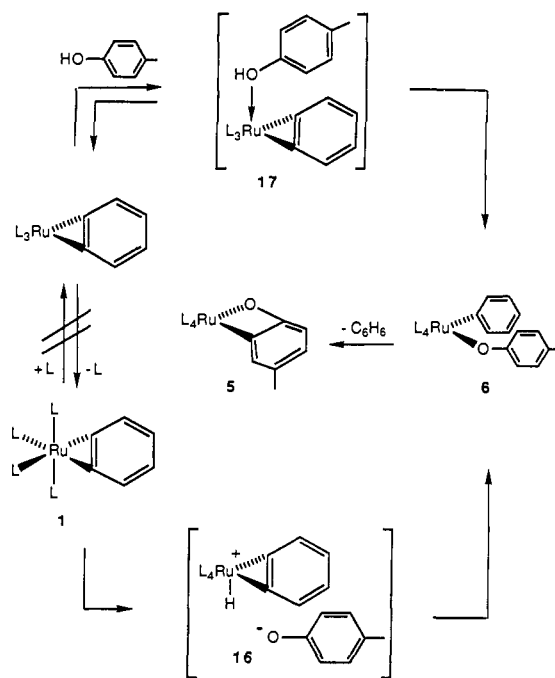
phenyl complex **2** are shown in Scheme VII. Pathway A in this scheme is a typical one for orthometalation of γ -elimination reactions of late-transition-metal complexes²⁰ and consists of phosphine dissociation to open a coordination site, followed by oxidative addition of the ortho C-H bond, reductive elimination of methane or benzene, and recoordination of phosphine. Pathway B is the route thought to be followed by early-transition-metal systems that form benzyne complexes^{6f-i,21} and presumably would not require phosphine loss; four-centered addition of the ortho C-H bond across the metal-alkyl bond would lead directly to product.

The rate laws for these two mechanisms are provided in eqs 1 and 2 for pathways A and B, respectively. We observed a linear inverse dependence of k_{obs} on phosphine concentration, consistent

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(21) For mechanistic studies of cyclometalations and β -hydride eliminations at the Cp_2Zr^{IV} center, see: Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171 and references therein.

Scheme VIII



with the rate law corresponding to pathway A. Although C-H orthometalation reactions are fairly common, **2** is a rare example of a metal system that forms a benzyne complex by this route.

$$A: \frac{d[1]}{dt} = \frac{k_1 k_2 [1]}{k_2 + k_{-1} [L]} \quad k_{\text{obs}} = \frac{k_1 k_2}{k_2 + k_{-1} [L]} \quad (1)$$

$$B: \frac{d[1]}{dt} = k_3 [1] \quad k_{\text{obs}} = k_3 \quad (2)$$

The only other possible example is the rhenium benzyne complex recently prepared.^{6d,e} This reaction is favorable, despite generating the unusually reactive organometallic species $(PMe_3)_4Ru(\eta^2-C_6H_4)$ because a strong C-H bond in the methane or benzene byproduct is formed along with **1**. Benzyne or cycloalkyne complexes of other late-transition-metal systems (i.e., in the nickel triad) have been formed by the reduction of a metal halide bound to an *o*-haloaryl or α -halovinyl group.^{6b,c}

Mechanism of Addition Reactions. The exchange of the aryl ring in **1** with solvent benzene and the addition of toluene to **1** presumably occur by the microscopic reverse of the benzyne formation reaction. More specifically, dissociation of phosphine followed by addition of the C-H bond of benzene regenerates diphenyl complex **3**, which is the precursor to **1** by method A (Scheme I). We have no experimental evidence to distinguish between the initial reaction of **1** with a benzylic C-H bond of toluene followed by orthometalation and initial reaction with the ortho position of the toluene followed by metalation of the benzylic methyl group.

The result of the addition of acetophenone to **1-d**₄ is consistent with initial addition of the C-H bond of acetophenone or the O-H bond of its enol form. The mechanism in Scheme IV accounts for the formation of protiated product. Addition of the α -C-H bond of the ketone to **1** results in the formation of the O-bound phenyl enolate intermediate.²² Oxidative addition of the ortho C-H bond followed by reductive elimination of benzene and

(22) Addition of acetone to the platinum cyclohexyne complex $(Ph_2PCH_2CH_2PPh_2)Pt(\eta^2-C_6H_8)$ led to formation of the C-bound enolate $(Ph_2PCH_2CH_2PPh_2)Pt(C_6H_9)(CH_3C(O)CH_3)$ (ref 6b). We have reported the observation of only the O-bound form for the $(PMe_3)_4Ru$ enolate complexes we have prepared, with the exception of one example, which exists as an equilibrium mixture of the O- and C-bound forms: Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 3234. Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 5670.

recoordination of phosphine forms the undeuterated final product 4.

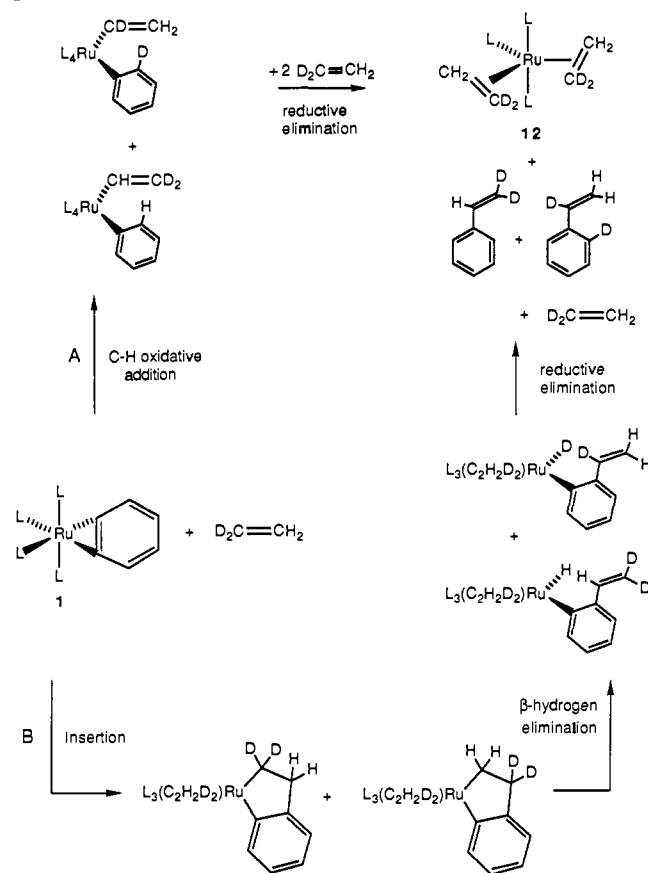
In contrast to the aryl C–H addition reactions, the O–H addition reaction with *p*-cresol occurs without prior phosphine dissociation. Reaction of *p*-cresol with the benzyne complex occurred faster than phosphine exchange in 1, ruling out the possibility (illustrated in Scheme VIII) that the unsaturated intermediate resulting from phosphine dissociation undergoes oxidative addition of the O–H bond in *p*-cresol or that the oxygen of the *p*-cresol forms a complex such as 17 with the unsaturated metal center before addition of the O–H bond. Instead we propose that reaction of the acidic O–H bond with the highly basic metal center occurs directly to form an intermediate 7-coordinate species 16 (Scheme VIII). This then undergoes reductive elimination and ion pair collapse to form the phenyl cresolate intermediate 6, which can be observed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Finally, orthometalation of 6 and reductive elimination of benzene leads to 5. Results from the reaction of $(\text{DMPE})_2\text{Fe}(\text{H})_2$ (DMPE = 1,2-bis(dimethylphosphino)ethane) with ethanol have shown that even aliphatic alcohols are acidic enough to protonate an L_4M (L = phosphine) metal center. The authors provide low-temperature NMR spectroscopic evidence for the ionic species $[(\text{DMPE})_2\text{Fe}(\text{H})_2(\text{H})]\text{OEt}$.²³

Although we have not obtained mechanistic data on the reaction of aniline with 1, it seems likely that this organic substrate is not acidic enough to react with 1 directly. Consistent with this notion, the H/D exchange reactions of arylamines with $(\text{PMe}_3)_4\text{Ru}(\text{D})_2$ at room temperature were shown to be catalyzed by water.²⁴ Although addition of aniline to phenyl hydroxide 9 did not lead to formation of orthometalated anilide 10, an acid catalyst formed under the 110 °C reaction conditions could promote the addition of the aniline N–H bond. Alternatively, initial dissociation of phosphine and coordination of the aniline nitrogen atom to the metal center to form an intermediate such as 18 would enhance the acidity of the N–H proton as shown in Scheme V, and the reaction of 1 with aniline does occur only at temperatures at which phosphine rapidly dissociates. Coordination of the aniline could promote either direct protonation of the metal–aryl bond or protonation of the metal center followed by C–H reductive elimination from one side of the benzyne moiety to form the phenyl (anilide) intermediate 11 that gives rise to 10. Evidence for a similar mechanism was reported for the reaction of phenols with a coordinatively saturated octahedral dialkyliron compound.²⁵

Mechanism of the Reaction of 1 with Ethylene. Two likely pathways for reaction of 1 with ethylene are depicted in Scheme IX. Pathway A involves initial C–H oxidative addition of the C–H bond of ethylene,²⁶ while pathway B involves initial insertion of ethylene into the M–C bond.^{6b,c} The oxidative addition step in pathway A would give rise to a primary isotope effect and would favor formation of the styrene- β , β - d_2 over formation of styrene- α , α - d_2 . In addition, the rate-determining step in a mechanism involving reversible insertion of ethylene would involve cleavage of the β -C–H bond and, again, would give rise to a primary isotope effect. In contrast, *irreversible* insertion of ethylene via pathway B would involve cleavage of the C–C double bond in the rate-determining step and would give rise to a secondary isotope effect. The observation of a 1:1:1 integrated ratio of vinyl resonances in the ^1H NMR spectrum of the reaction mixture is consistent only with pathway B, involving irreversible insertion of ethylene.

We have not investigated the mechanism of the other three insertion reactions in detail but have obtained qualitative information that indicates that they proceed by initial coordination of the unsaturated substrate, followed by migration of the benzyne carbon to the electrophilic site of the coordinated molecule. This

Scheme IX



coordination and migration mechanism, which requires initial dissociation of phosphine, would lead to a dependence of rate on phosphine concentration if the phosphine reassociation step is competitive with the addition and migration processes (similar to the kinetic behavior for the benzyne-formation reaction). Our observations are consistent with these predictions: each of the insertion reactions proceeds at a rate that is much slower than the rate of phosphine exchange with 1, and addition of 1 equiv of phosphine to the reaction mixture markedly inhibits the rate of the reaction. Although a coordination and migration mechanism are usually invoked for the insertion reactions of carbon monoxide and ethylene into metal–alkyl bonds,⁷ little mechanistic data is available to support this mechanism for other substrates such as aldehydes and nitriles.

Comparison of Reactivity to That of Other Transition-Metal–Carbon Bonds. Benzyne complex 1 displays reactivity that is markedly different from that which has previously been observed for late-transition-metal–carbon bonds. Addition and insertion reactions with late-transition-metal–carbon bonds that result in the formation of new M–O or M–N bond are rare.^{12,19,27} Transformations such as the reaction of 1 with aniline, which converts a late-transition-metal–carbon σ bond to a late-transition-metal–nitrogen bond of an aryl- or alkylamide substituent, have not previously been observed.²⁸ The reactions observed here

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Table VIII. 1H NMR Spectroscopic Data^a

δ	mult	$J(\text{Hz})$	int	assgnt	δ	mult	$J(\text{Hz})$	int	assgnt
$(PMe_3)_4Ru(\eta^2\text{-C}_6\text{H}_4)$ (1) ^b					$(PMe_3)_4Ru(\text{OH})(\text{Ph})$ (9) ^f				
0.78	t	4.4	18	trans PMe_3	-4.47	m		1	Ru-OH
1.28	d	2.6	18	cis PMe_3	1.06	t	5.6	18	trans PMe_3
7.26	br s		2	aromatic	1.37	d	7.3	9	cis PMe_3
7.31	br s		2		1.40	d	6.0	9	
$(PMe_3)_4Ru(\eta^2\text{-C}_6\text{D}_4)$ (1-d ₄) ^b					$(PMe_3)_4Ru(\eta^2\text{-NHC}_6\text{H}_4)$ (10) ^b				
0.78	t	4.4	18	trans PMe_3	0.98	d	5.7	9	cis PMe_3
1.28	d	2.6	18	cis PMe_3	1.06	d	6.7	9	
$(PMe_3)_4Ru(\text{Me})(\text{Ph})$ (2) ^b					$(PMe_3)_3Ru(\text{C}_2\text{H}_4)_2$ (12) ^b				
-0.033	dq	7.7, 3.5	3	Ru-Me	0.66	t	2.3	18	trans PMe_3
0.96	t	5.2	18	trans PMe_3	1.25	d	6.1	9	cis PMe_3
1.04	d	5.0	9	cis PMe_3	1.41	m		4	C_2H_4
1.22	d	4.7	9		1.80	m		4	
7.13	m		1	aromatic	$(PMe_3)_4Ru(\eta^2\text{-C}(p\text{-tolyl})\text{C}(p\text{-tolyl})\text{C}_6\text{H}_4)$ (13) ^b				
7.19	m		2		0.82	d	4.9	9	cis PMe_3
7.88	br s		2		1.25	d	4.6	9	
$(PMe_3)_4Ru(\eta^2\text{-OC}(\text{CH}_2)\text{C}_6\text{H}_4)$ (4) ^c					$(PMe_3)_4Ru(\eta^2\text{-OC}(p\text{-tolyl})\text{C}(p\text{-tolyl})\text{C}_6\text{H}_4)$ (13) ^b				
1.02	t	6.0	18	trans PMe_3	1.17	t	2.7	18	trans PMe_3
1.42	d	6.9	9	cis PMe_3	2.14	s		3	<i>p</i> -Me
1.45	d	6.0	9		2.18	s		3	
3.39	d	1.2	1	$\text{OC}(\text{CH}_2)\text{C}_6\text{H}_4$	6.91	d	7.8	2	<i>p</i> -tolyl
3.95	br s		1		7.03	d	7.9	2	
6.61	tq	7.3, 1.0	1	$\text{OC}(\text{CH}_2)\text{C}_6\text{H}_4$	7.10	d	7.8	2	
6.63	t	7.1	1		7.30	d	7.9	2	
7.11	dt	7.6, 1.6	1		7.20	m		3	C_6H_4
7.46	m		1		8.07	br s		1	
$(PMe_3)_4Ru(\eta^2\text{-OC}_6\text{H}_3\text{Me})$ (5) ^b					$(PMe_3)_4Ru(\eta^2\text{-OC}(\text{H})(\text{Ph})\text{C}_6\text{H}_4)$ (14) ^b				
1.00	d	7.4	9	cis PMe_3	1.03	dd	4.8, 0.5	9	PMe_3
1.09	d	6.0	9		1.27	d	4.9	9	
1.15	t	5.8	18	trans PMe_3	1.38	d	5.7	9	
2.58	s		3	<i>p</i> -Me	1.45	d	6.6	9	
6.06	d	7.6	1	aromatic	5.45	t	3.7	1	$\text{C}(\text{H})(\text{Ph})\text{C}_6\text{H}_4$
6.96	d	7.2	1		6.22	d	7.4	1	aromatic
7.30	br s		1		6.46	t	7.4	1	
$(PMe_3)_4Ru(\text{OC}_6\text{H}_4\text{Me})(\text{Ph})$ (6) ^d					$(PMe_3)_4Ru(\eta^2\text{-NC}(\text{Ph})\text{C}_6\text{H}_4)$ (15) ^b				
0.88	t	2.6	18	trans PMe_3	0.92	t	2.8	18	trans PMe_3
0.90	d	6.8	9	cis PMe_3	1.48	d	5.4	9	cis PMe_3
1.08	d	5.6	9		1.54	d	5.8	9	
2.49	s		3	<i>p</i> -Me	6.70	m		2	aromatic
6.67	d	8.2	2	<i>p</i> -cresolate	7.01	dt	7.1, 1.9	1	
7.22	d	8.3	2		7.11	t	7.3	1	
7.31	m		2	phenyl	7.22	t	5.6	2	
7.45	t	7.0	1		7.44	d	6.9	2	
7.87	br s		1		7.70	br t	6	1	
8.73	br d	7.2	1		$(PMe_3)_4Ru(\text{H})(\text{Ph})$ (7) ^e				
$(PMe_3)_4Ru(\text{H})(\text{Ph})$ (7) ^e					$(PMe_3)_4Ru(\text{H})(\text{Ph})$ (7) ^e				
-9.50	ddt	92.6, 18.3	1	Ru-H					
1.10	t	2.6	18	trans PMe_3					
1.35	d	5.8	9	cis PMe_3					
1.38	d	5.4	9						
6.60	m		3	aromatic					
7.45	m		1						
7.75	m		1						

^a The multiplicities d and t, when applied to the PMe_3 resonances, refer to apparent splitting patterns. Accordingly, the values reported for J do not reflect true coupling constants. ^b C_6D_6 , 20 °C. ^c THF-d_8 , 20 °C. ^d PhMe-d_8 , -60 °C. ^e THF-d_8 , -55 °C. ^f THF-d_8 , -45 °C.

proceed more slowly than analogous processes that are common in early-transition-metal systems, but the fact that they proceed at all with low-valent ruthenium is noteworthy.

The insertions of benzaldehyde and benzonitrile are also unusual. Insertion reactions of aldehydes and ketones with M-C bonds have typically been limited to early-transition-metal alkyl complexes.²⁹ Decarbonylation reactions with aldehydes, which proceed by initial addition of the aldehyde C-H bond, are more characteristic of the reactivity of late-transition-metal complexes.³⁰ Only

recently has the insertion of formaldehyde into a Pt-C bond been observed;³¹ prior to this, only insertions involving fluorinated ketones and aldehydes had been reported.³² The lack of insertion chemistry of aldehydes and ketones with late-transition-metal complexes has been attributed to the strong C=O bond strength and formation of a metal alkoxide which would be unstable relative to the starting metal alkyl. To our knowledge, the reaction of **1** with benzonitrile is the first nitrile insertion into a late-tran-

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Table IX. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectroscopic Data^a

δ	mult	$J(\text{Hz})$	assgnt	δ	mult	$J(\text{Hz})$	assgnt
(PMe ₃) ₄ Ru(η^2 -C ₆ H ₄) (1) ^b				(PMe ₃) ₄ Ru(η^2 -NHC ₆ H ₄) (10) ^b			
21.32	tt	13.1, 3.6	trans PMe ₃	19.57	tm	11.8	trans PMe ₃
27.64	m		cis PMe ₃	23.36	dt	16.9, 2.2	cis PMe ₃
125.09	t	2.4	aromatic	25.31	dm	21.4	
126.12	d	4.6		105.28	m		aromatic
142.07	dq	52, 9.7		111.12	dt	5.4, 1.8	
(PMe ₃) ₄ Ru(Me)(Ph) (2) ^b				(PMe ₃) ₃ Ru(C ₂ H ₄) ₂ (12) ^b			
-2.64	dtd	55.5, 13.2, 7.9	Ru-Me	122.78	s		
20.27	t	12.4	trans PMe ₃	136.38	m		
23.73	d	17.0	cis PMe ₃	143.46	dtd	64.2, 15.7, 7.5	
24.89	d	19.9		178.80	q	4.1	
119.92	s		aromatic	(PMe ₃) ₃ Ru(C ₂ H ₄) ₂ (12) ^b			
123.92	s			14.69	td	11.4, 3.0	trans PMe ₃
124.95	s			23.03	dt	18.3	cis PMe ₃
143.22	s			21.14	dt	10.8, 4.2	C ₂ H ₄
147.59	d	15.6		23.47	dt	8.0, 2.4	
173.50	dq	75.8, 10		(PMe ₃) ₄ Ru(η^2 -C(<i>p</i> -tolyl)C(<i>p</i> -tolyl)C ₆ H ₄) (13) ^b			
(PMe ₃) ₄ Ru(η^2 -OC(CH ₂)C ₆ H ₄) (4) ^c				(PMe ₃) ₄ Ru(η^2 -OC(H)(Ph)C ₆ H ₄) (14) ^b			
19.40	td	12.6, 2.6	trans PMe ₃	21.24	tt	12.9, 3.5	trans PMe ₃
22.28	dt	17.0, 1.7	cis PMe ₃	24.90	dq	16.0, 2.1	cis PMe ₃
25.23	dm	23.6		25.71	dq	15.2, 2.6	
72.90	s		C(CH ₂)C ₆ H ₄	21.16	s		<i>p</i> -Me
120.68	d	1.3	C(CH ₂)C ₆ H ₄	21.28	s		
122.61	d	1.4	and	121.63	s		aromatic
125.23	m		aromatic	121.73	s		and
141.27	m			122.73	s		vinyl
152.86	d	3.1		127.88	s		
176.60	dm	7.7		128.41	s		
1777.71	dq	65.0, 8.2		128.48	s		
(PMe ₃) ₄ Ru(η^2 -OC ₆ H ₃ Me) (5) ^c				131.28	s		
18.65	td	13.5, 3.0	trans PMe ₃	133.03	s		
22.44	dt	18.1, 2.6	cis PMe ₃	130.98	s		
25.32	dq	25.0, 3.4		143.01	s		
21.88	s		<i>p</i> -Me	143.16	s		
105.55	s		aromatic	149.54	s		
120.44	s			156.34	s		
122.00	s			163.31	d	6.6	
137.80	s			174.40	dm	56.5	
142.69	dtd	65, 16, 6		184.43	dm	57.5	
182.41	s			(PMe ₃) ₄ Ru(η^2 -NC(Ph)C ₆ H ₄) (15) ^b			
(PMe ₃) ₄ Ru(H)(Ph) (7) ^d				19.17	ddd	18.3, 7.0, 2.7	PMe ₃
23.59	t	12.2	trans PMe ₃	19.88	ddd	16.8, 7.2, 2.9	
24.67	m		cis PMe ₃	21.60	dt	16.8, 1.4	
27.96	d	18		25.25	dt	23.4, 1.5	
119.69	s		aromatic	90.12	d	8.5	OC(H)(Ph)C ₆ H ₄
124.84	s			120.48	s		aromatic
125.32	s			122.84	s		
146.55	d	8.8		123.73	s		
153.10	s			125.61	s		
174.20	m			127.86	s		
(PMe ₃) ₄ Ru(OH)(Ph) (9) ^e				129.64	s		
18.53	td	12.5, 2	trans PMe ₃	139.32	s		
22.02	d	17.4	cis PMe ₃	152.86	s		
25.54	d	24		161.22	s		
120.51	s		aromatic	178.13	dm	68.8	
124.70	s			(PMe ₃) ₄ Ru(η^2 -NC(Ph)C ₆ H ₄) (15) ^b			
125.15	s			19.95	t	14.0	trans PMe ₃
139.83	s			22.34	d	17.9	cis PMe ₃
145.77	d	8.0		25.92	d	15.7	
174.55	dtd	74.2, 16.1, 10.0		120.20	s		aromatic
				123.20	s		and
				124.85	s		imine
				125.84	s		
				127.82	s		
				128.34	s		
				142.84	t	2.0	
				146.37	d	9.1	
				155.20	d	12.6	
				175.46	m		
				187.30	dq	67.8, 6.8	

^aThe multiplicities d and t, when applied to the PMe₃ resonances, refer to apparent splitting patterns. Accordingly, the values reported for *J* do not reflect true coupling constants. ^bC₆D₆, 20 °C. ^cTHF-*d*₈, 20 °C. ^dTHF-*d*₈, -55 °C. ^eTHF-*d*₈, -45 °C.

sition-metal-alkyl or -aryl bond.

Experimental Section

General Procedure. Unless otherwise noted, all manipulations were carried out under an inert atmosphere in a Vacuum Atmospheres 553-2

drybox with attached M6-40-1H DriTrain or with use of standard Schlenk or vacuum line techniques. ¹H NMR spectra were obtained on either the 250-, 300-, 400-, or 500-MHz Fourier transform spectrometers at the University of California, Berkeley (UCB), NMR facility. The 250- and 300-MHz instruments were constructed by Mr. Rudi Nunlist and in-

Table X. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectroscopic Data

spin system	δ	$J(\text{Hz})$
A_2B_2	$(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-C}_6\text{H}_4)$ (1) ^a	
	$\delta_{\text{A}} = -6.84$	$J_{\text{AB}} = 31.5$
	$\delta_{\text{B}} = -8.15$	
A_2BC	$(\text{PMe}_3)_4\text{Ru}(\text{Me})(\text{Ph})$ (2) ^a	
	$\delta_{\text{A}} = -2.76$	$J_{\text{AB}} = 25.5$
	$\delta_{\text{B}} = -9.99$	$J_{\text{AC}} = 23.7$
A_2BC	$(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-OC}(\text{CH}_2)\text{C}_6\text{H}_4)$ (4) ^b	
	$\delta_{\text{A}} = 0.69$	$J_{\text{AB}} = 25.3$
	$\delta_{\text{B}} = -13.71$	$J_{\text{AC}} = 32.2$
A_2BC	$(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-OC}_6\text{H}_3\text{Me})$ (5) ^a	
	$\delta_{\text{A}} = -2.73$	$J_{\text{AB}} = 34$
	$\delta_{\text{B}} = 15.78$	$J_{\text{AC}} = 24$
A_2BC	$(\text{PMe}_3)_4\text{Ru}(\text{OC}_6\text{H}_4\text{Me})(\text{Ph})$ (6) ^c	
	$\delta_{\text{A}} = -4.07$	$J_{\text{AB}} = 36.7$
	$\delta_{\text{B}} = 9.03$	$J_{\text{AC}} = 22.0$
A_2BC	$(\text{PMe}_3)_4\text{Ru}(\text{H})(\text{Ph})$ (7) ^d	
	$\delta_{\text{A}} = -1.32$	$J_{\text{AB}} = 24.5$
	$\delta_{\text{B}} = -10.59$	$J_{\text{AC}} = 26.7$
A_2BC	$(\text{PMe}_3)_4\text{Ru}(\text{OH})(\text{Ph})$ (9) ^e	
	$\delta_{\text{A}} = -3.34$	$J_{\text{AB}} = 31.2$
	$\delta_{\text{B}} = 3.97$	$J_{\text{AC}} = 25.2$
A_2BC	$(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-NHC}_6\text{H}_4)$ (10) ^a	
	$\delta_{\text{A}} = -4.01$	$J_{\text{AB}} = 32.7$
	$\delta_{\text{B}} = 6.56$	$J_{\text{AC}} = 23.9$
A_2B	$(\text{PMe}_3)_3\text{Ru}(\text{C}_2\text{H}_4)_2$ (12) ^a	
	$\delta_{\text{A}} = 1.80$	$J_{\text{AB}} = 25.1$
	$\delta_{\text{B}} = -0.94$	
A_2BC	$(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-C}(\text{p-tolyl})\text{C}(\text{p-tolyl})\text{C}_6\text{H}_4)$ (13) ^a	
	$\delta_{\text{A}} = -8.81$	$J_{\text{AB}} = 30.7$
	$\delta_{\text{B}} = -19.23$	$J_{\text{AC}} = 23.1$
ABCD	$(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-OC}(\text{H})(\text{Ph})\text{C}_6\text{H}_4)$ (14) ^a	
	$\delta_{\text{A}} = 4.75$	$J_{\text{AB}} = 29.0$
	$\delta_{\text{B}} = -3.46$	$J_{\text{AC}} = 30.6$
A_2BC	$(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-NC}(\text{Ph})\text{C}_6\text{H}_4)$ (15) ^a	
	$\delta_{\text{A}} = 5.53$	$J_{\text{AB}} = 29.4$
	$\delta_{\text{B}} = -11.57$	$J_{\text{AC}} = 28.0$
	$\delta_{\text{C}} = -13.67$	$J_{\text{BC}} = 9.1$

^a C_6D_6 , 20 °C. ^bTHF- d_8 , 20 °C. ^cPhMe- d_8 , -60 °C. ^dTHF- d_8 , -55 °C. ^eTHF- d_8 , -45 °C.

terfaced with either a Nicolet 1180 or 1280 computer. The 400- and 500-MHz instruments were commercial Bruker AM series spectrometers. ^1H NMR spectra were recorded relative to residual protiated solvent. ^{13}C NMR spectra were obtained at either 75.4 or 100.6 MHz on the 300- or 500-MHz instruments, respectively, and chemical shifts were recorded relative to the solvent resonance. Chemical shifts are reported in δ downfield from tetramethylsilane, and all coupling constants are reported in hertz. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic data are given in Tables VIII-X. IR spectra were obtained on a Perkin-Elmer Model 283 infrared spectrometer or on a Perkin-Elmer Model 1550 or 1750 FT-IR spectrometer with potassium bromide ground pellets. Mass spectroscopic (MS) analyses were obtained at the UCB mass spectrometry facility on AEI MS-12 and Kratos MS-50 mass spectrometers. Elemental analyses were obtained from the UCB Microanalytical Laboratory. Sealed NMR tubes were prepared by fusing Wilmad 505-PP and 504-PP tubes to ground-glass joints that were then attached to a vacuum line with Kontes stopcocks, or alternatively, the tubes were attached via Cajon adapters

directly to Kontes vacuum stopcocks.³³ Known-volume bulb vacuum transfers were accomplished with an MKS Baratron attached to a high-vacuum line. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. PMe_3 (Strem) was dried over NaK or a Na mirror and vacuum transferred prior to use. Acetophenone and benzaldehyde were distilled under nitrogen prior to use. Benzonitrile was purchased from Alfa and used as received. Aniline was dried over a small piece of sodium and distilled under argon. A benzene solution of *p*-cresol was azeotroped with a Dean-Stark trap and the *p*-cresol distilled under argon. Ethylene was purchased from Matheson. Ethylene-*1,1-d_2* was purchased from MSD Isotopes and was stated to be 99.6% isotopically pure. Deionized water was degassed by bubbling nitrogen through it for 15 min. PhMgBr and AlMe_3 were purchased from Aldrich and used as received. Pentane and hexane (UV grade, alkene-free) were distilled from LiAlH_4 under nitrogen. Benzene and toluene were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was either distilled under N_2 or vacuum transferred from CaH_2 . Deuterated solvents for use in NMR experiments were dried as their protiated analogues but were vacuum transferred from the drying agent.

$(\text{PMe}_3)_4\text{Ru}(\text{Me})(\text{Cl})$. We found the procedure provided here to be more convenient than the published procedure.^{11a} In a 250-mL round-bottom flask, 1.50 g of $(\text{PMe}_3)_4\text{Ru}(\text{OAc})(\text{Cl})$ was dissolved in 100 mL of toluene. To this stirred solution was added, at room temperature over 3 min, 0.50 mL (0.33 equiv) of AlMe_3 as a 2.0 M solution in toluene. The solution was stirred for 1 h at room temperature over which time a fine white powder formed. The volume of the solution was reduced to 5–10 mL and filtered while still cold from solvent removal in order to remove all aluminum salts. The resulting yellow solution was then layered with pentane to yield 0.629 g (46%) of yellow blocks. The supernatant was then cooled to -40 °C to yield an additional 0.246 g (18%) of product.

$(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-C}_6\text{H}_4)$ (1). In a typical preparative scale reaction, a 250-mL flask equipped with a side arm was charged with 1.50 g (3.15 mmol) of $\text{Ru}(\text{PMe}_3)_4(\text{Cl})_2$,³⁴ 100 mL of ether, and a magnetic stir bar. To a Schlenk tube were added 2.31 mL (2.2 equiv, 6.93 mmol) of PhMgBr as a 3.0 M solution in ether and 5 mL of additional ether. Both vessels were brought out of the drybox, carefully degassed, and charged with argon. It is essential that all solutions be nitrogen-free because $\text{Ru}(\text{PMe}_3)_4(\text{Ph})_2$ forms a complex with nitrogen. The Grignard reagent was added by cannula to the ether slurry of $\text{Ru}(\text{PMe}_3)_4(\text{Cl})_2$ at room temperature over a 5–10-min period. The solution was then stirred under argon for ~3 h at room temperature until no orange, solid $\text{Ru}(\text{PMe}_3)_4(\text{Cl})_2$ remained. The resulting solution, including magnesium salts, was transferred by cannula to a glass reaction vessel fused to a Kontes vacuum adaptor. The vessel was partially degassed. The vessel was then closed and heated to 85 °C for 8 h. The solution turned a dark brown color upon heating; the reaction was complete when the solution became light brown in color while at 85 °C. After this time, the solvent was removed under reduced pressure and the residue extracted three times with a total of 150 mL of pentane, stirring for 5 min after each addition of pentane. Removal of the pentane solvent provided a pale yellow or white solid in 55–70% yield, which is pure enough (~95%) for synthetic purposes. Crystallization from pentane provided analytically pure samples of 1 in 35–50% yield. IR (Nujol): group of very weak absorptions (probably aromatic overtone bands) centered at 1886, 1570 (s), 1420 (w), 1412 (w), 1402 (m), 1316 (w), 1295 (m), 1277 (m), 1188 (w), 1140 (w), 1115 (w), 966 (m), 934 (s), 853 cm^{-1} (m). MS (EI), *m/e*: 482 (M^+). Anal. Calcd for $\text{C}_{18}\text{H}_{40}\text{P}_4\text{Ru}$: C, 44.90; H, 8.37. Found: C, 45.17; H, 8.38.

X-ray Crystal Structure Determination of 1. Mounting Procedure. Clear colorless columnar air-sensitive crystals of 1 were obtained by slow crystallization from pentane at -40 °C. End fragments cleaved from some of these crystals were mounted in thin-wall quartz capillaries in an inert-atmosphere glovebox and then flame sealed. Preliminary precession photographs indicated monoclinic Laue symmetry and yielded approximate cell dimensions.

The crystal used for data collection was transferred to the Enraf-Nonius CAD-4 diffractometer and centered in the beam. Automatic peak search and indexing procedures yielded a monoclinic reduced

(33) Bergman, R. G.; Buchanan, J. M.; McGhee, W. D.; Periana, R. A.; Seidler, P. F.; Trost, M. K.; Wenzel, T. T. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darenbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987, p 227.

(34) (a) Schmidbaur, H.; Blaschke, Y. Z. *Naturforsch., Anorg. Chem., Org. Chem.* 1980, 35B, 584. (b) Sellmann, D.; Bohlen, E. Z. *Naturforsch., Anorg. Chem., Org. Chem.* 1982, 37, 1026.

primitive cell. The final cell parameters and specific data collection parameters for this data set are given in Table 1.

Structure Determination. The 3571 raw intensity data were converted to structure factor amplitudes and their estimated standard deviations (esd's) by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the intensity standards revealed a gradual reduction in intensity with a sudden jump of about 8% superimposed on it between the seventh and eighth hours of data collection. The data were corrected for this variation. Inspection of the azimuthal scan data showed a variation of $I_{\min}/I_{\max} = \pm 1\%$ for the average curve. No correction for absorption was applied. Inspection of the systematic absences indicated uniquely space group $P2_1/n$. Removal of systematically absent and redundant data left 3202 unique data in the final data set. The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to the positions of most of the hydrogen atoms. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.3 (1.2 for benzyne hydrogens) times the B_{eq} of the atoms to which they were attached. They were included in structure factor calculations but not refined. Before the final cycles of refinement, eight reflections that appeared to be affected by multiple diffraction were removed from the data set.

The final residuals for 208 variables refined against the 2761 accepted data for which $F^2 > 3\sigma F^2$ were $R = 2.11\%$, $wR = 2.99\%$, and GOF (goodness of fit) = 1.542. The R value of all 3194 accepted data were 3.40%.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in ranges of $\sin(\theta/\lambda)$, $|F_c|$, and parity and value of the individual indices showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of $0.36 \text{ e}/\text{\AA}^3$, located near the ruthenium atom. There was no indication of secondary extinction in the high-intensity low-angle data.

Positional and thermal parameters are available as supplementary material to ref 8. Thermal parameters of the non-hydrogen atoms, anisotropic thermal parameters, and the positions and thermal parameters of the hydrogen atoms are available as supplementary material.

(PMe₃)₄Ru(η^2 -C₆H₄) (1-d₄). Unlabeled benzyne complex 1 (65.4 mg) was dissolved in 1.7 mL of C₆D₆ in a 9-in. NMR tube. The sample was degassed and the tube sealed. The sample was heated at 110 °C for 3 days in order to provide complete conversion to 1-d₄. No decomposition products were observed by ¹H or ³¹P{¹H} NMR spectroscopies under these conditions. The tube was then opened, the solvent removed, and the residue crystallized from pentane at -40 °C to provide 35.6 mg (54% yield) of 1-d₄. MS (EI), m/e : 485 (M⁺).

Ru(PMe₃)₄(Ph)(Me) (2). A round-bottom flask was charged in the drybox with 0.708 g (1.55 mmol) of Ru(PMe₃)₄(Cl)(Me) and 100 mL of ether. While this solution was stirred, 0.518 mL of a 3.0 M solution of PhMgBr was added at room temperature over 5 min. The solution was stirred for an additional 3 h at room temperature. At this time, the solvent was removed under reduced pressure and the residue was extracted with pentane (3 × 50 mL). The solution was concentrated to a volume of 5–10 mL and cooled to -40 °C. The material recovered from this crystallization was then recrystallized to yield 153 mg (19.9%) of white crystals of 2, which were analytically pure and suitable for kinetic studies. IR (KBr): 3121 (m), 3101 (m), 3052 (s), 3038 (m), 3025 (s), 2969 (s), 2910 (s), 2471 (w), 2363 (w), 2343 (w), 1967 (w), 1925 (w), 1859 (w), 1637 (w), 1561 (s), 1462 (s), 1429 (w), 1296 (s), 1273 (s), 1237 (w), 1190 (s), 1178 (w), 1058 (w), 1010 (m), 964 (s), 934 (s), 849 (s), 735 (s), 699 (s), 670 (m), 656 (s), 629 (m), 492 cm⁻¹ (w). MS (EI), m/e : 482 (M - CH₄⁺). Anal. Calcd for C₁₉H₁₄P₄Ru: C, 45.87; H, 8.91. Found: C, 45.99; H, 9.05.

Kinetic Evaluation of the Thermolysis of Ru(PMe₃)₄(Ph)(Me) in C₆D₆. Into a 5.00 mL volumetric flask were weighed 35.6 mg (0.0716 mmol) of Ru(PMe₃)₄(Ph)(Me) and 28 mg of ferrocene as an internal standard. C₆D₆ was added to the flask, making a 0.0143 M solution. In a typical experiment, 0.70 mL of this solution was added by syringe to a thin-walled, 9-in. NMR tube. The tube was degassed, the appropriate amount of PMe₃ was added by vacuum transfer, and the tube was flame sealed to give a length of 8.5 in. The tubes were heated at 110 °C in a factory-calibrated Neslab Exocal Model 251 constant-temperature bath filled with Dow Corning 200 silicone fluid and frozen rapidly in ice-water after removal from the bath. All reactions were monitored to greater than 3 half-lives by ambient-temperature ¹H NMR spectrometry by integrating

the PMe₃ resonance of the starting material at 0.99 vs the ferrocene internal standard. The spectra were taken with a single acquisition and double checked with a second acquisition after a delay of at least 10T₁. All kinetic plots displayed excellent linearity with correlation coefficients of 0.98 or better. A plot of k_{obs} vs $1/[L]$ is shown in Figure 4 and displays a correlation coefficient of 0.99.

Ru(PMe₃)₄(η^2 -OC(CH₃)C₆H₄) (4). Into a glass reaction vessel fused to a Kontes vacuum adaptor was weighed 31.6 mg (0.0656 mmol) of 1. Benzene (5 mL) was added, and to the resulting solution was added 7.9 mg (1 equiv) of acetophenone. The vessel was heated to 45 °C for 8 h, after which time the initial clear solution had turned yellow. The solvent was then removed, and the product was crystallized from a pentane/toluene (10:1) solvent mixture to yield 13.6 mg (39.5%) of yellow product. An alternative preparation of this compound from the reaction of acetone and 1, along with a determination of its structure by X-ray diffraction, will be reported in a separate publication.³⁵ IR (KBr): 3103 (m), 3050 (s), 3043 (s), 3028 (m), 2969 (s), 2903 (s), 1977 (w), 1934 (w), 1624 (w), 1569 (s), 1548 (m), 1431 (s), 1395 (s), 1338 (s), 1316 (s), 1298 (s), 1279 (s), 1262 (s), 1238 (m), 1122 (s), 1021 (m), 990 (s), 938 (s), 854 (s), 841 (s), 784 (s), 736 (s), 712 (s), 700 (s), 662 (s), 647 (s), 634 (m), 498 cm⁻¹ (m). MS (FAB), m/e : 525 (MH⁺).

Ru(PMe₃)₄(η^2 -OC₆H₃Me) (5). Into a small vial with a stir bar were placed 20.4 mg of 1, 7 mg of ferrocene, and 1.0 mL of C₆D₆. This solution was divided into two equal portions. One sample was placed in an NMR tube. To the other sample was added 2.3 mg (1 equiv) of *p*-cresol in 0.4 mL of C₆D₆ while it was stirred. The solution, which immediately turned from clear to orange-yellow, was quickly transferred to an NMR tube. ¹H and ³¹P{¹H} NMR spectra obtained within 10 min after the addition showed that all of 1 had reacted and that it had been converted to at least two intermediates. The NMR tube was then brought into the drybox, equipped with a vacuum adaptor, and sealed. Heating the tube for 24 h at 45 °C provided conversion of the intermediates to Ru(PMe₃)₄(η^2 -OC₆H₃Me) in 70% yield by ¹H NMR spectroscopy, as determined by comparison of integrated ratios of the PMe₃ resonances in the starting material and product to those of the ferrocene internal standard.

Low-Temperature Observation of Ru(PMe₃)₄(Ph)(OC₆H₄Me) (6). In the drybox, 15.1 mg of 1 was dissolved in 0.7 mL of toluene-*d*₈ in an NMR tube equipped with a vacuum adaptor. To this stirred solution was added 3.4 mg (1 equiv) of *p*-cresol in 0.2 mL of toluene. Immediately after addition, the sample was brought out of the drybox and cooled in a -78 °C bath. The tube was sealed and placed into the probe of the NMR spectrometer, which had been precooled to -60 °C. ³¹P{¹H} and ¹H NMR spectra were taken at this temperature and indicated clean conversion to the phenyl cresolate intermediate.

Ru(PMe₃)₄(Ph)(H) (7). To a solution of 300 mg (0.627 mmol) of Ru(PMe₃)₄(η^2 -C₆H₄) in 5 mL of pentane was added 47.7 μ L (0.627 mmol) of 2-propanol in 0.5 mL of pentane at room temperature. After the mixture was allowed to react for 1 h, the volume was reduced under vacuum to 1 mL and cooled to -40 °C to yield 145 mg (48.2%) of white crystals. IR: 3060 (m), 2981 (m), 2966 (m), 1859 (M-H, s), 1561 (m), 1424 (m), 1419 (m), 1295 (s), 1278 (m), 940 cm⁻¹ (s). MS (EI), m/e : 406 (M - C₆H₆), 330 (M - C₆H₆ - PMe₃). Anal. Calcd for C₁₈H₁₄P₄Ru: C, 44.71; H, 8.62. Found: C, 44.82; H, 8.83.

Ru(PMe₃)₄(Ph)(OH) (9). In the drybox, 78.6 mg of 1 and 1 mL of benzene were added to a glass vessel fused to a Kontes vacuum adaptor. The vessel was brought out of the drybox, and 3.0 μ L (1 equiv) of water was added by syringe to the vessel on a Schlenk line. The solution was allowed to react for 8 h at room temperature, after which time the solvent was removed and the residue extracted with 25 mL of pentane. The clear solution was concentrated to 5–10 mL and cooled to -40 °C to provide 43.6 mg (54%) of product. IR (Nujol): 3636 (w), 1974 (w), 1933 (w), 1853 (w), 1562 (s), 1553 (m), 1523 (m), 1436 (s), 1423 (s), 1297 (s), 1279 (s), 1241 (m), 1180 (m), 1147 (m), 1060 (m), 1014 (s), 942 (s), 855 (s), 795 (s), 731 (s), 709 (s), 662 (s), 634 cm⁻¹ (m). MS (FAB), m/e : 482 (MH - H₂O⁺), 406 (M - OH₂ - PMe₃⁺). Anal. Calcd for C₁₈H₁₄OP₄Ru: C, 43.28; H, 8.48. Found: C, 43.02; H, 8.39.

Ru(PMe₃)₄(η^2 -NHC₆H₄) (10). Into a vial were placed 80.2 mg (0.167 mmol) of 1, 17.05 mg (1.1 equiv) of aniline, and 2 mL of benzene. The solution was then placed in a 9-in. NMR tube, which was degassed and sealed. The sample was heated to 110 °C for 8 h. When it had cooled, 56.4 mg (68.2%) of 3 had crystallized from the reaction solution and all of the starting material had been consumed as determined by ³¹P{¹H} NMR spectroscopy. The material that crystallized from solution was pure by ¹H NMR spectroscopy, but a portion of this sample was crystallized from ether for microanalysis. IR (KBr): 3337 (w), 3019 (m), 2989 (m), 2969 (m), 2906 (s), 1594 (m), 1560 (m), 1534 (m), 1435 (s),

1425 (s), 1297 (m), 1281 (m), 1266 (m), 942 (s), 705 (s), 665 cm^{-1} (s). Anal. Calcd for $C_{18}H_{41}NP_4Ru$: C, 43.55; H, 8.32; N, 2.82. Found: C, 43.35; H, 8.15; N, 2.82.

Addition of Aniline to 9. An NMR tube was charged with approximately 0.5 mL of a C_6D_6 solution containing 10.2 mg of **9**. To this solution was added 1 equiv of aniline. The tube was degassed and sealed. Heating the sample to 110 °C for 2 h led to the formation of bridging hydroxide complexes, which are formed from **9** in the absence of aniline.¹⁶ No formation of **10** was detected.

$Ru(PMe_3)_3(C_2H_4)_2$ (12). A 100-mL round-bottom flask was charged with 505 mg (1.06 mmol) of $Ru(PMe_3)_4(Cl)_2$ and 25 mL of ether. To this suspension was added 2.2 equiv of C_2H_5MgCl as a 1.5 M solution in ether. The reaction was stirred at room temperature until the all-orange $Ru(PMe_3)_4(Cl)_2$ ³⁴ had reacted and the suspension was milky white (2–3 h). At this time, the ether was removed under vacuum and the residue was extracted with pentane (3 × 20 mL). The volume of the extract was reduced to 5 mL and placed in a glass vessel fused to a Kontes vacuum adaptor. Ethylene (2.1 equiv) was condensed into the vessel, and the resulting solution was heated for 24 h at 85 °C. At this point, the volume of the solution was reduced under vacuum to 2 mL and filtered through a plug of Celite. Reducing the volume to 1 mL and cooling to –40 °C provided a 244-mg (59.7%) yield of clear blocks. IR (KBr): 3027 (m), 2964 (m), 2903 (m), 2896 (m), 1424 (m), 1298 (m), 1293 (m), 1279 (s), 1132 (s), 941 (s), 845 (m), 711 (m), 699 (m), 660 cm^{-1} (s).

Reaction of Ethylene with 1. An NMR tube was charged with 6.9 mg (0.0143 mmol) of **1** and 0.7 mL of benzene- d_6 . The sample was degassed, and 10 equiv of ethylene was added by vacuum transfer. The tube was sealed and heated to 85 °C for 1.5 days, at which point the ¹H NMR spectrum of the final reaction mixture showed the formation of styrene (confirmed by GC/MS) in 70% yield. The ¹H and ³¹P{¹H} NMR spectra showed the formation of $(PMe_3)_4Ru(C_2H_4)_2$ in 68% yield by comparison with the independently prepared sample.

Reaction of Ethylene-1,1- d_2 with 1. Into an NMR tube were placed 8.0 mg (0.0143 mmol) of **1** and 0.7 mL of benzene- d_6 . The sample was degassed, and 7 equiv of ethylene-1,1- d_2 was added by vacuum transfer. The tube was sealed and heated to 85 °C for 16 h. The ¹H NMR spectrum of the final reaction mixture showed a 1:1:1 ratio of the vinylic resonances (to within the roughly 10% error of integration), indicating a 1:1 ratio of the two isomers styrene- β , β - d_2 and styrene- α ,2- d_2 . The experiment was conducted a second time following a similar procedure, except the reaction was run in benzene- d_0 and the final reaction mixture was analyzed by ²H NMR spectroscopy. Again, within the accuracy of the integration (roughly 10%), a 1:1:1 ratio of vinylic resonances was observed.

$Ru(PMe_3)_4(\eta^2\text{-C}(p\text{-tolyl)C}(p\text{-tolyl)C}_6H_4)$ (13). Into a glass reaction vessel fused to a Kontes vacuum adaptor were placed 121 mg (0.252 mmol) of **1** and 5 mL of toluene. To this solution was added 5 equiv of di-*p*-tolylacetylene. The reaction vessel was partially degassed by one freeze–pump–thaw cycle and heated to 85 °C for 24 h. After this time, the solution was concentrated under vacuum and filtered. Layering of the solution with pentane and cooling to –40 °C provided 79.4 mg (46%) of product, which was pure by ¹H NMR spectroscopy. This material was recrystallized from toluene/pentane vapor diffusion for microanalysis. IR (KBr): 2972 (m), 2911 (s), 1437 (m), 1434 (m), 1420 (m), 1298 (m), 965 (m), 942 (s), 855 (m), 728 (m), 701 (m), 662 cm^{-1} (m). Anal. Calcd for $C_{34}H_{54}P_4Ru$: C, 59.38; H, 7.91. Found: C, 59.28; H, 8.04.

$Ru(PMe_3)_4(\eta^2\text{-OC}(H)(Ph)C_6H_4)$ (14). Into a glass reaction vessel fused to a Kontes vacuum adaptor was placed 80.0 mg of **1**, along with the minimum amount of pentane (~2 mL) necessary to dissolve the material. To this solution was added 17.6 mg (1 equiv) of benzaldehyde at room temperature. The vessel was then heated to 45 °C for 1.5 days, during which period the solution turned dark brown. (When the reaction was run in tetrahydrofuran, the reaction solution turned green.) When it was cooled to room temperature, the product crystallized from the reaction solution as brown or green blocks (31.8 mg, 32.6%). MS (FAB), *m/e*: 589 (MH⁺). IR (KBr): 3078 (m), 3044 (m), 3025 (m), 2970 (s), 2906 (s), 2815 (m), 2708 (m), 2661 (m), 2504 (m), 1597 (m), 1578 (m), 1566 (m), 1542 (m), 1505 (m), 1490 (m), 1431 (m), 1397 (m), 1351 (s), 1298 (s), 1279 (s), 1233 (m), 1059 (s), 1042 (m), 1027 (m), 1017 (m), 964 (s), 941 (s), 854 (s), 763 (m), 736 (s), 702 (s), 664 (s), 629 cm^{-1} (m). Anal. Calcd for $C_{25}H_{46}OP_4Ru$: C, 51.10; H, 7.89. Found: C, 50.97; H, 7.95.

$Ru(PMe_3)_4(\eta^2\text{-NC}(Ph)C_6H_4)$ (15). Into a glass reaction vessel fused to a Kontes vacuum adaptor were placed 158 mg (0.328 mmol) of **1** and 8 mL of benzene. To this solution was added 5 equiv of benzonitrile. The reaction vessel was partially degassed by one freeze–pump–thaw cycle and heated to 85 °C for 24 h. After this time, the solvent was removed under reduced pressure. The residue was extracted with toluene, and the extracts were filtered, concentrated under vacuum, and crystallized by

layering the toluene solution with pentane and cooling to –40 °C to provide 88.6 mg (46%) of yellow blocks suitable for microanalysis and X-ray crystal structure analysis. IR (KBr): 653 (m), 656 (m), 665 (m), 698 (m), 709 (m), 714 (m), 731 (s), 788 (m), 853 (m), 942 (s), 963 (m), 1281 (m), 1298 (m), 1412 (m), 1436 (m), 2909 (s), 2966 (m), 2992 (m), 3048 cm^{-1} (w). Anal. Calcd for $C_{25}H_{40}N$: C, 51.39; H, 7.76; N, 2.40. Found: C, 51.21; H, 7.76; N, 2.37.

X-ray Crystal Structure Determination of Complexes 9 and 15. The procedure used in the determination of the structure of **1** was employed with the following modifications: (a) Mounting procedure: Orange, air-sensitive crystals of **15** were obtained by layering a toluene solution of **15** with pentane. Clear, air-sensitive crystals of **9** were obtained by cooling a pentane solution of **9**. End fragments cleaved from some of these crystals were mounted in a viscous oil. The final cell parameters and specific data collection parameters for the data sets are given in Table I.

(b) Structure determination: For **9**, 6274 raw intensity data were collected, and for **15**, 2135 were collected. These data were converted to structure factor amplitudes and their ends by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the azimuthal scan data showed a variation of $I_{\min}/I_{\max} = \pm 1\%$ for the average curve. No correction for absorption was applied. Inspection of the systematic absences indicated space group $P\bar{1}$ for **9** and $P2_1/n$ for **15**. Removal of systematically absent and redundant data left 2113 unique data in the final data set for **15**.

Each structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. The final refinement included anisotropic refinement of the ruthenium and phosphorus atoms and isotropic refinement of the carbon and nitrogen atoms. Hydrogen atoms were not included in the refinement.

The final residuals for **9** for the 243 variables refined against the 5021 accepted data for which $F^2 > 3\sigma F^2$ were $R = 5.8\%$, $wR = 9.2\%$, and $GOF = 3.86$. The R value for all 6274 data was 7.2%. For **15**, the final residuals for the 150 variables refined against the 1462 accepted data for **15** for which $F^2 > 3\sigma F^2$ were $R = 6.4\%$, $wR = 6.9\%$, and $GOF = 1.93$. The R value for all 2135 data was 11.0%.

Interatomic distances and angles for **9** are given in Tables IV and V and for **15** in Tables VI and VII. Positional and thermal parameters as well as listings of F_o and F_c are available as supplementary material.

Phosphine Inhibition Studies for the Reaction of 1 with Benzaldehyde and Benzonitrile. Into a vial were weighed 40.6 mg of **1** and 10 mg of ferrocene as an internal standard. Benzene- d_6 (3 mL) was added, and the solution was divided into two equal portions. To one of the samples was added 5 equiv of benzaldehyde and to the other 5 equiv of benzonitrile. Each of these samples was then further divided into two equal portions and placed into NMR tubes to make a total of four samples. Each NMR tube was degassed by three freeze–pump–thaw cycles. To one sample containing benzaldehyde and to another containing benzonitrile was added 5 equiv of PMe_3 by vacuum transfer before all of the tubes were sealed. ¹H and ³¹P{¹H} NMR spectra of the solutions were obtained before heating. The two samples containing benzaldehyde were heated to 45 °C for 2.5 h, and the two containing benzonitrile were heated to 55 °C for 2.5 h. Conversions and yields were determined by comparing ¹H and ³¹P{¹H} NMR spectra to those obtained before heating. The experiment was conducted twice and similar phosphine inhibition was observed during both runs.

Phosphine Exchange Studies for 1. Into an NMR tube was placed 0.7 mL of a C_6D_6 solution containing 12.4 mg of **1**. The tube was degassed, and 4 equiv of PMe_3-d_9 was condensed into the sample. The approximate amounts of phosphine exchange at 5 min, 2 h, and 24 h were determined by integrating the ³¹P{¹H} NMR signals for free PMe_3-d_9 and PMe_3-d_0 . The ratios were found to be 36:1 after 10 min, 2:1 after 2 h, and 1:1 after 24 h.

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Registry No. **1**, 119503-00-3; **1-d₄**, 119480-44-3; **2**, 119480-42-1; **4**, 119480-46-5; **5**, 131182-21-3; **6**, 132698-68-1; **7**, 132698-69-2; **9**, 119480-43-2; **10**, 132698-70-5; **12**, 132698-71-6; **13**, 132698-72-7; **14**, 119480-45-4; **15**, 132698-73-8; $(PMe_3)_4Ru(Me)Cl$, 93366-00-8;

(PMe₃)₄Ru₄(OAc)Cl, 88968-54-1; Ru(PMe₃)₄Cl₂, 96615-09-7; HOCHMe₂, 67-63-0; H₂C=CH₂, 74-85-1; PhC≡N, 100-47-0; PMe₃-d₃, 22529-57-3; acetophenone, 98-86-2; *p*-cresol, 106-44-5; aniline, 62-53-3; di-*p*-tolylacetylene, 2789-88-0; benzaldehyde, 100-52-7; ethylene-1,1-d₂, 6755-54-0; styrene-β,β-d₂, 934-85-0; styrene-α,α-d₂, 93185-51-4.

Supplementary Material Available: Tables of general tem-

perature factor expressions (*B*'s), positional parameters and their estimated standard deviations, and root mean square amplitudes of anisotropic displacements for **9** and **15** (4 pages). Ordering information is given on any current masthead page. Analogous data for the structure of **1** have been submitted as supplementary material with the previously published communication.⁸

Enantioselective Aldol Chemistry via Alkyl Enol Ethers. Scope of the Lewis Acid Catalyzed Condensation of Optically Active Trimethylsilyl and Methyl 2-[(*E*)-1-Alkenyloxy]ethanoates with Acetals

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Abstract: Optically active, mono- and disubstituted trimethylsilyl 2-[(*E*)-1-alkenyloxy]ethanoates of the type RR¹CH=CHOCHR²CO₂SiMe₃ (R = Me, PhCH₂, *n*-Bu, MeO₂CCMe₂CH₂, PhSCH₂; R¹ = H, Me; R² = Me, *c*-C₆H₁₁) undergo highly diastereoselective, Lewis acid catalyzed reactions with aliphatic and aromatic acetals R³CH(OR⁴)₂ (R³ = H, Me, *t*-Bu, Ph; R⁴ = Me, CH₂Ph) to afford *cis*-2-[RR¹CH(R³CHOR⁴)]-5-R²-1,3-dioxolanones corresponding to erythro-diastereoselective aldol reactions involving net *syn*-periplanar addition of the acetal-derived electrophile and trimethylsilyl ester oxygen across the enol ether double bond. Analysis of the alcohols RR¹C(R³CHOR⁴)CH₂OH obtained by reductive removal of the ethanoate auxiliary reveals the following points. (1) Enantiomeric excesses in the range 90–98% ee are possible with dimethyl and dibenzyl acetals derived from formaldehyde, acetaldehyde, pivalaldehyde, and benzaldehyde. (2) The aldol reactions are moderately to highly erythro diastereoselective (*e/t* = 4:1–99:1), even when quaternary and tertiary centers are juxtaposed (R¹ = Me; *e/t* = 13:1–32:1). (3) The highest diastereoselectivities are observed with a bulky cyclohexyl substituent at the primary chiral center (R² = Cy); however, diastereoselectivities as high as 88% ee are possible even with lactic acid derivatives (R² = Me). (4) The enantiomeric excesses are catalyst dependent, with Me₃SiOTf giving slightly better results than Ph₃CSbCl₆ in reactions with benzaldehyde dimethyl acetal but Ph₃CSbCl₆ giving much better results than Me₃SiOTf in reactions with acetaldehyde dimethyl acetal. (5) Perhaps most notably, the diastereoselectivities are remarkably insensitive to changes in substitution at the nucleophilic enol ether carbon, so that essentially identical results are observed regardless of whether R = PhCH₂, MeO₂CCMe₂CH₂, or PhSCH₂ and regardless of whether R¹ = H or Me. Reaction of the symmetrically disubstituted enol ether Me₂C=CHOCH(*c*-C₆H₁₁)CO₂SiMe₃ with PhCH(OMe)CO₂SiMe₃ affords, after reduction with LiAlH₄, Me₂C(PhCHOMe)CH₂OH of 94% ee. PhCHO and PhCH₂CH=CHOCH(*c*-C₆H₁₁)CO₂SiMe₃ undergo a similar reaction to afford, after aqueous workup and reduction, *threo*-PhCH₂CH(PhCHOH)CH₂OH (*e/t* = 1:13; 98% ee). The corresponding methyl ester, PhCH₂CH=CHOCH(*c*-C₆H₁₁)CO₂Me, undergoes related aldol condensation/transacetalization chemistry upon reaction with the same acetals and Me₃SiOTf to afford *erythro*-PhCH₂CH(R³CHOR⁴)CH(OR⁴)₂ products in 61–86% nonoptimized yield, with erythro/*threo* ratios and enantiomeric excesses identical with those observed for the corresponding trimethylsilyl ester reaction products.

Introduction

Enantioselective aldol reactions^{1–6} are among the most powerful and versatile means of introducing stereochemistry and func-

tionality in organic synthesis. A variety of metal enolate,² metallo enolate,³ allylborane,⁴ allylboronic ester,⁵ and other methods⁶ have been developed for this purpose; we report herein the first *alkyl* enol ether based approach,⁷ involving the Lewis acid catalyzed condensation of acetals with optically active trimethylsilyl and methyl 2-[(*E*)-1-alkenyloxy]ethanoates.⁸ Our interest in these reactions was stimulated, initially, by the ready availability of optically active 2-[(*E*)-1-alkenyloxy]ethanoic acid esters^{9,10} and, subsequently, by the potential of these enol ethers to undergo reactions analogous to the Lewis acid catalyzed reactions of silyl enol ethers with acetals¹¹ (eq 1).

In particular, we speculated that trimethylsilyl 2-[(*E*)-1-alkenyloxy]ethanoates would undergo oxocarbenium ion induced cyclization to give a charged intermediate, which would lose a trimethylsilyl cation from oxygen to afford a neutral, protected aldol product (eq 2).

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