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Synthesis and Chemistry of Ruthenium Hydrido Aryloxides and Arylamides. An Investigation of Structure, N–H and O–H Elimination Processes, Proton-Catalyzed Exchange Reactions, and Relative Ru–X Bond Strengths

John F. Hartwig, Richard A. Andersen,* and Robert G. Bergman*

Department of Chemistry, University of California, Berkeley, California 94720

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The synthesis and reactivity of ruthenium complexes containing a hydride and an aryloxide or arylamide ligand are reported. The arylamide complex $(PMe_3)_4Ru(H)(NHC_6H_5)$ (1) was prepared by the addition of aniline to the ethylene complex $(PMe_3)_4Ru(C_2H_4)$ (3) or to the cyclometalated hydride complex $(PMe_3)_4Ru(CH_2PMe_2)(H)$ (4). Monitoring of the reaction showed that the addition of aniline to 3 proceeds by initial conversion of 3 to 4. Moreover, H/D-exchange reactions between a series of arylamines and organic acids showed that this process is catalyzed by trace amounts of water and we believe that the addition of aniline to 4 may also be catalyzed by water or another trace acid, although the rate-determining step is clearly opening of the metallacycle. Addition of *p*-cresol to 3 or 4 formed the complex $(PMe_3)_4Ru(H)(OC_6H_4\text{-}p\text{-}Me)$ (2). This reaction proceeded faster than exchange of phosphine, indicating that the O–H bond of this substrate reacts directly with the ruthenium center. Addition of CO to 2 led to formation of the CO substitution product $(PMe_3)_3(CO)Ru(H)(OC_6H_4\text{-}p\text{-}Me)$ (5). X-ray structural analysis of 1, 2, and 5 showed that CO substitution has a marked effect on the Ru–O bond length. In addition variable-temperature NMR studies indicated that the ancillary ligands affect the barrier to aryl ring rotation, presumably due to a difference in the double-bond character of the X–Ar bond. Addition of H_2 and CO led to extrusion of *p*-cresol and aniline. Reaction of CO with 1 formed free aniline and $(PMe_3)_2Ru(CO)_3$ (7) after 8 h at 85 °C, while reaction of CO with 2 formed free *p*-cresol and 7 after 4 days at 135 °C. Addition of *p*-cresol to 1 cleanly formed 2, demonstrating that the Ru–O bond is stronger than the Ru–N bond in these compounds. In separate studies it has been shown that the precursor to these compounds, cyclometalated hydride 4, forms from thermolysis of benzyl hydride $(PMe_3)_4Ru(H)(CH_2Ph)$ (8), and the reaction of hydrogen with 1 and 2 forms dihydride $(PMe_3)_4Ru(H)_2$. Therefore these Ru–O and Ru–N bonds are stronger than the Ru–C bond in benzyl hydride 8, and the Ru–H bond in dihydride 4 is stronger than either the Ru–O or Ru–N bond. The following trend in Ru–X bond energies results: $L_4(H)Ru{-}H > L_4(H)Ru{-}OAr > L_4(H)Ru{-}NHPh > L_4(H)Ru{-}CH_2Ph$.

Introduction

Processes such as reductive elimination and oxidative addition, although well studied for the formation and cleavage of C–H bonds at transition-metal centers,[1] remain relatively unexplored for the formation and cleavage of N–H and O–H bonds. In fact, few monomeric complexes have been prepared which contain both a metal hydride and an η^1-metal–OR or metal–NHR (R = alkyl or aryl) linkage. Examples of such compounds in the late-transition-metal series include $Cp^*Ir(PPh_3)(H)(OEt)$,[2] *trans*-$(PR_3)_2Pt(H)(XAr)$ where X = O and NH,[3] $(PEt_3)Pd(H)(OPh)$,[4] and $[(PMe_3)_4Ir(H)(OMe)]PF_6$.[5] Early-transition-metal examples include $Cp_2Hf(H)(XR)$ where X = NH and O[6] and $Cp^*_2Th(H)(OR)$.[7]

Most of the late-transition-metal examples have been prepared by the metathetical replacement of a late transition metal halide or pseudohalide by an alkali metal–amide or –alkoxide. Although the preparation of aryloxide complexes has been achieved by the reaction of phenols or substituted phenols with late-transition-metal complexes,[8] few hydrido alkoxides or amides have been made by this route.[3a,5] The formation of transition-metal amides by addition of the N–H bond of alkyl- or arylamines is less common than reactions with the fairly acidic O–H bond of phenols or alcohols. Reaction of amines to provide monomeric late-transition-metal alkyl- or arylamides has been reported in only a few cases.[9] Rather, addition of these unactivated N–H bonds has been reported with trinuclear osmium compounds, with a monomeric iridium complex to form products with bridging amides, and with an iridium complex containing a chelated amine.[10]

A study of ligand-induced O–H reductive elimination of ethanol from the ethoxy hydride $Cp^*Ir(PPh_3)(OEt)(H)$[2] was reported from this laboratory. This work has recently been extended to include the N–H reductive elimination of aniline from $Cp^*Ir(PPh_3)(NHPh)(H)$.[11] Only a few

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* To whom correspondence should be addressed.

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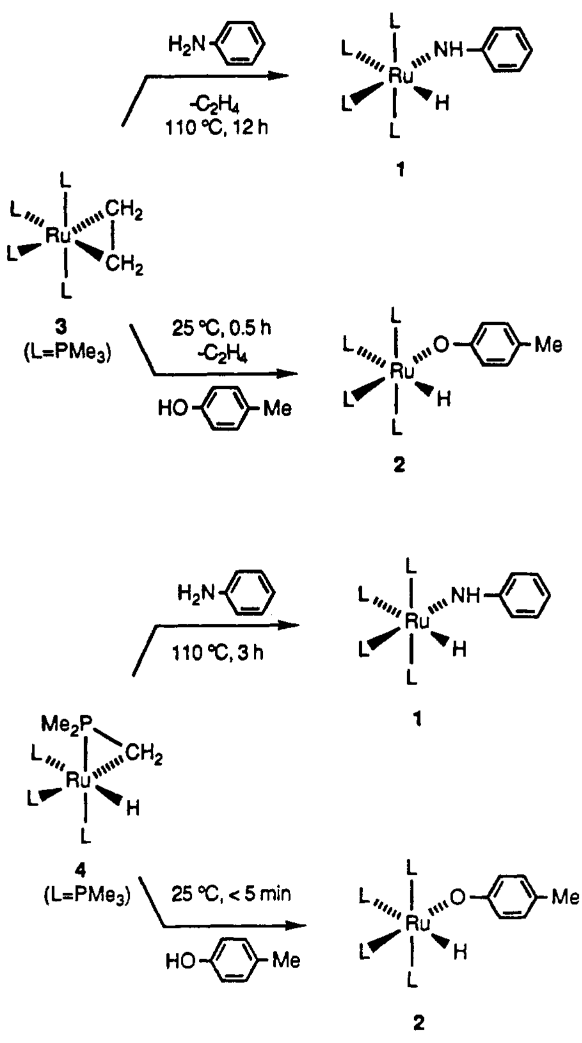
Scheme I



other cases of N–H and O–H reductive elimination reactions have been observed, all of them ligand induced.[3b,4,12]

We have investigated the reactions of an electron-rich ruthenium system with N–H and O–H bonds in the hope that such a metal system would favor oxidative addition of these bonds as it does for the oxidative addition of C–H bonds. Formation of the hydrido and aryloxide and arylamide complexes by these processes has allowed a comparison of the stability of these compounds with the analogous hydrido benzyl complex.[13] In addition, the reversible addition of hydrogen has provided both mechanistic information and relative thermodynamic stabilities of the M–O, M–N, and M–H linkages in these compounds. Finally, substitution of the poor σ-donating and strong π-accepting ligand CO for one of the σ-donating phosphine ligands has allowed us to determine the solid-state structure and the solution-state reactivity changes that occur when the electron density at the metal center is reduced.

Results

$(PMe_3)_4Ru(H)(NHPh)$. The synthesis of compounds $(PMe_3)_4Ru(H)(NHPh)$ (**1**) and $(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me) (**2**) is summarized in Scheme I. Addition of aniline to the ethylene complex (**3**)[14] followed by heating to 135 °C for 24 h led to clean formation of the hydrido anilide complex **1** in 66% isolated yield. Addition to the cyclometalated hydride $(PMe_3)_3Ru(CH_2PMe_2)(H)$ (**4**)[15] followed by heating to 110 °C for 24 h led to **1** in 93% yield by ^1H NMR spectroscopy. These reaction conditions reliably led to formation of **1**, but during some preparations from ethylene complex **3**, the reaction rate was markedly faster; heating to 110 °C for 3–12 h often gave complete conversion. Compound **1** was characterized by ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and IR spectroscopy, as well as microanalysis and X-ray diffraction (vide infra). The A_2BC pattern in the $^{31}P\{^1H\}$ NMR spectrum indicated a cis configuration of the σ-bound ligands. The other possible geometry, a trans relationship between the hydride and anilide substituents, would result in a singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum. The doublet of quartets hydride resonance (one large trans coupling and three nearly identical cis couplings) at δ −7.69 confirms this assignment. The Ru–H linkage was confirmed by an infrared absorption at 1845 cm^{-1}. The N–H proton was observed at δ 1.71 in the ^1H NMR spectrum (as a doublet with J = 7.3 Hz, presumably due to coupling with the phosphorus nucleus located trans to it) and at 3370 cm^{-1} in the infrared spectrum. The aryl region of the ^1H NMR spectrum contained five inequivalent resonances between δ 6.43 and 7.38, and the $^{13}C\{^1H\}$ NMR spectrum displayed five inequivalent C–H resonances between δ 107.39 and 129.83 and one quaternary resonance at δ 161.83. These signals fall in the region of normal, uncomplexed aryl rings; the inequivalence of the two sides of the ring indicate that it is not rotating on the NMR time scale.

The addition of aniline was conducted with and without added PMe_3. No rate inhibition was observed for the sample with added phosphine. Rather, qualitative studies showed that samples containing added PMe_3 reacted 10–20% faster than those with no added phosphine. In addition, the reaction of rigorously dried (vide infra) *p*-chloroaniline was run in the presence and absence of added water. The sample containing added water reacted at 2–3 times the rate as the sample containing no added water.

The dideuterated analogue of **1** was prepared in 38% yield by the addition of 0.25 equiv of lithium aluminum deuteride to a THF solution of the complex $(PMe_3)_4Ru(OAc)(Cl)$, followed by the addition of the deuterated lithium anilide, LiNDPh. No hydride or anilide resonance was observed in the ^1H NMR spectrum for a 0.06 M sample, indicating at least 95% isotopic purity. The deuteride resonance was observed at δ 7.67, and the anilide deuterium was observed at δ 1.66 in the ^2H NMR spectrum; no other resonances were observed. An infrared absorption band at 2497 cm^{-1} was assigned to the N–D stretch, and a shoulder at 1326 cm^{-1} corresponded to the Ru–D stretch.

Thermolysis of the labeled compound at 125 °C for 4 h led to scrambling of the deuterium into the phosphine and aryl groups (determined by ^2H NMR spectroscopy), preventing useful mechanistic results from deuterium labeling experiments. When aniline-*N*,*N*-d_2 was added to cyclometalated hydride **4** at 110 °C (the conditions used for formation of **1**) and the fate of the deuterium label was determined by ^2H NMR spectroscopy, signals were observed not only in the hydride and anilide N–H position but also in the aromatic and phosphine regions. Reversible cyclometalation of the anilide substituent would account for incorporation of deuterium into these positions, and orthometalation of the anilide substituent would account

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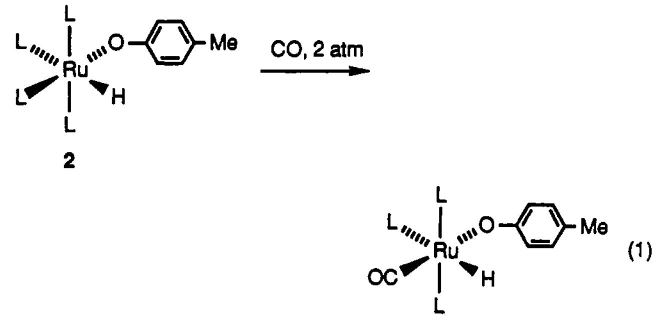
for the presence of aryl resonances.

$(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me). Addition of 1 equiv of *p*-cresol to the ethylene complex 3 at room temperature led to rapid formation of ethylene and $(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me) (2) in 64% isolated yield. Addition of *p*-cresol to the cyclometalated hydride 4 also occurred rapidly at room temperature and provided 2 in 62% isolated yield. Again, 3 proved to be the more convenient starting material. Compound 2 was characterized by ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and IR spectroscopy, as well as microanalysis. As observed for compound 1, the $^{31}P\{^1H\}$ NMR spectrum displayed an A_2BC pattern and the ^1H NMR spectrum contained a doublet of quartets pattern for the hydride resonance, indicating a cis orientation of the hydride and aryloxide ligands. The Ru–H infrared absorption was observed at 1836 cm^{-1}. In contrast to the anilide substituent in 1, the two sides of the aryl ring in the cresolate substituent of 2 were equivalent by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (an AA′BB′ pattern of the aryl region of the ^1H NMR spectrum, and two CH resonances in the aryl region of the $^{13}C\{^1H\}$ NMR spectrum). Therefore, either the aryl ring of 1 is located in the plane of the two mutually trans phosphine ligands and the oxygen atom of the aryloxide substituent or it is freely rotating on the NMR time scale. X-ray diffraction shows that the ring is located in the plane of the hydride, ruthenium, and oxygen atoms in the solid state (vide infra), suggesting that the two sides of the ring are inequivalent in the lowest energy conformation in solution but are rapidly exchanging on the NMR time scale.

$(PMe_3)_3(CO)Ru(H)(OC_6H_4$-*p*-Me). Addition of carbon monoxide (2 atm) to compound 2 at 65 °C for 8 h led to formation of the CO ligand substitution product $(PMe_3)_3(CO)Ru(H)(OC_6H_4$-*p*-Me) (5), in which the poor σ-donor and strong π-acceptor CO[16] is located trans to the aryloxide substituent (eq 1). Compound 5 was characterized by ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and IR spectroscopy, microanalysis, and X-ray diffraction (vide infra). Again, $^{31}P\{^1H\}$ and ^1H NMR spectroscopy demonstrated the stereochemistry. A doublet of triplets resonance with a large trans H–P coupling constant on the order of that observed for 2 (117.8 Hz versus 102.8 for 2) was observed at δ −5.92 for the hydride substituent, indicating that a phosphine ligand is located trans to it. Moreover, an A_2B pattern in the $^{31}P\{^1H\}$ NMR spectrum with P_B resonating upfield from P_A is consistent with P_B being located trans to a substituent with a stronger trans influence than phosphine.[17]



2

5

(1)

Table I. Crystal and Data Collection Parameters[a]

	1	2	5
temp, °C	−90	25	−89
emp formula	$RuP_4NC_{18}H_{43}$	$RuP_4OC_{19}H_{44}$	$RuP_3O_2C_{17}H_{35}$
fw	498.5	513.5	465.5
cryst size, mm	0.20 × 0.21 × 0.36	0.20 × 0.25 × 0.50	0.10 × 0.20 × 0.25
space group	$P\bar{1}$	$P2_1/n$	*Cmca*
a Å	12.364 (4)	13.539 (2)	13.300 (2)
b, Å	13.951 (6)	13.711 (2)	14.088 (3)
c, Å	15.062 (6)	29.302 (2)	24.960 (3)
α, deg	103.79 (3)	90.0	90.0
β, deg	96.10 (2)	102.50 (2)	90.0
γ, deg	90.02 (3)	90.0	90.0
V, Å^3	2507.9 (3)	5310.2 (3)	4676.9 (3)
Z	4	8	8
d_{calc}, g cm^{-3}	1.32	1.28	1.32
μ_{calc}, cm^{-1}	8.7	8.8	8.7
reflns measd	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,+l$
scan width	$\Delta\theta = 0.70 + 0.35 \tan\theta$	$\Delta\theta = 0.70 + 0.35 \tan\theta$	$\Delta\theta = 0.80 + 0.35 \tan\theta$
scan speed (θ), deg/min	6.70	6.70	6.70
setting angles (2θ), deg[b]	24–28	24–28	22–26

[a] Parameters common to all structures: Mo Kα radiation λ = 0.710 73 Å (except for 1c, λ = 0.709 30 Å; monochromator, highly-oriented graphite (2θ = 12.2°); detector, crystal scintillation counter, with PHA; 2θ range, 3–45° (except for 1c 2–45°); scan type, θ–2θ; background, measured over 0.25 (Δθ) added to each end of the scan; vertical aperture = 3.0 mm; horizontal aperture = 2.0 + 1.0 tan θ mm; intensity standards, measured every 1 h of X-ray exposure time; orientation, 3 reflections were checked after every 200 measurements. Crystal orientation was redetermined if any of the reflections were offset from their predicted positions by more than 0.1°. Reorientation was required twice for 1 and 2 and once for 5. [b] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα 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.

Table II. Selected Intramolecular Bond Distances for 1

Ru1–P1	2.268 (2)	P1–C7	1.838 (9)
Ru1–P2	2.363 (2)	P1–C8	1.858 (8)
Ru1–P3	2.325 (2)	P1–C9	1.845 (8)
Ru1–P4	2.331 (2)	P2–C10	1.861 (8)
Ru1–N1	2.160 (6)	P2–C11	1.856 (8)
Ru2–P5	2.354 (2)	P2–C12	1.877 (8)
Ru2–P6	2.271 (2)	P3–C13	1.858 (9)
Ru2–P7	2.318 (2)	P3–C14	1.844 (9)
Ru2–P8	2.343 (2)	P3–C15	1.831 (8)
Ru2–N2	2.163 (6)	P4–C16	1.845 (9)
N1–C1	1.340 (9)	P4–C17	1.844 (8)
C1–C2	1.475 (10)	P4–C18	1.804 (8)
C1–C6	1.475 (10)	P5–C27	1.861 (8)
C2–C3	1.324 (10)	P5–C28	1.844 (8)
C3–C4	1.417 (11)	P5–C29	1.858 (8)
C4–C5	1.376 (10)	P6–C30	1.875 (9)
C5–C6	1.403 (10)	P6–C31	1.865 (9)
N2–C21	1.355 (8)	P6–C32	1.834 (9)
C21–C22	1.431 (10)	P7–C33	1.853 (9)
C21–C26	1.438 (9)	P7–C34	1.851 (8)
C22–C23	1.353 (10)	P7–C35	1.861 (8)
C23–C24	1.392 (11)	P8–C36	1.834 (9)
C24–C25	1.482 (11)	P8–C37	1.885 (9)
C25–C26	1.326 (10)	P8–C38	1.841 (8)

X-ray Structural Analyses. A suitable single crystal of 1 was obtained by allowing a refluxing hexane solution to cool slowly to room temperature. The compound

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Table III. Selected Intramolecular Bond Angles for 1

P1–Ru1–P2	98.37 (7)	Ru1–N1–C1	134.1 (5)
P1–Ru1–P3	94.24 (7)	Ru2–N2–C21	135.6 (5)
P1–Ru1–P4	95.87 (7)	N1–C1–C2	125.4 (6)
P1–Ru1–N1	172.09 (15)	N1–C1–C6	119.4 (6)
P2–Ru1–P3	96.18 (7)	C2–C1–C6	115.1 (6)
P2–Ru1–P4	97.88 (7)	C1–C2–C3	118.5 (7)
P2–Ru1–N1	88.72 (15)	C2–C3–C4	128.1 (7)
P3–Ru1–P4	161.27 (8)	C3–C4–C5	114.1 (7)
P3–Ru1–N1	81.44 (16)	C4–C5–C6	123.9 (7)
P4–Ru1–N1	86.57 (16)	C1–C6–C5	120.0 (7)
P5–Ru1–P6	97.93 (7)	N2–C21–C22	122.4 (6)
P5–Ru2–P7	99.09 (7)	N2–C21–C26	123.7 (6)
P5–Ru2–P8	94.52 (7)	C22–C21–C26	113.9 (6)
P5–Ru2–N2	90.69 (16)	C21–C22–C23	122.6 (7)
P6–Ru2–P7	95.38 (8)	C22–C23–C24	123.5 (8)
P6–Ru2–P8	95.11 (8)	C23–C24–C25	115.0 (7)
P6–Ru2–N2	170.93 (16)	C24–C25–C26	120.5 (7)
P7–Ru2–P8	161.48 (8)	C21–C26–C25	124.4 (7)
P7–Ru2–N2	85.97 (16)		
P8–Ru2–N2	81.34 (16)		

Table IV. Selected Intramolecular Bond Distances for 2

Ru1–P1	2.229 (2)	P3–C16	1.811 (10)
Ru1–P2	2.327 (2)	P4–C17	1.820 (8)
Ru1–P3	2.329 (2)	P4–C18	1.803 (9)
Ru1–P4	2.364 (2)	P4–C19	1.794 (8)
Ru1–O1	2.152 (3)	O1–C1	1.308 (7)
Ru1–H1	1.734 (1)	C1–C2	1.413 (7)
P1–C8	1.803 (8)	C1–C6	1.399 (7)
P1–C9	1.831 (10)	C2–C3	1.375 (8)
P1–C10	1.791 (8)	C3–C4	1.364 (7)
P2–C11	1.828 (7)	C4–C5	1.384 (7)
P2–C12	1.802 (7)	C4–C7	1.524 (9)
P2–C13	1.841 (7)	C5–C6	1.387 (8)
P3–C14	1.825 (8)		
P3–C15	1.781 (8)		

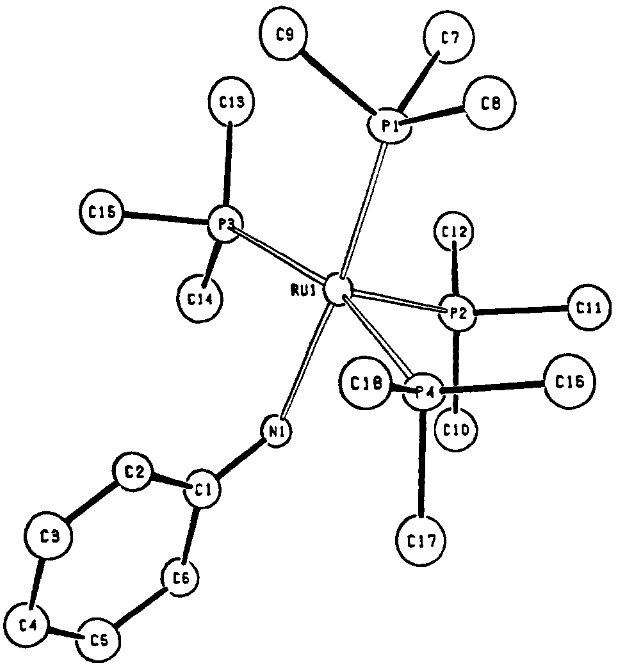

Figure 1. ORTEP drawing of 1. The ruthenium-bound hydrogen was not located.

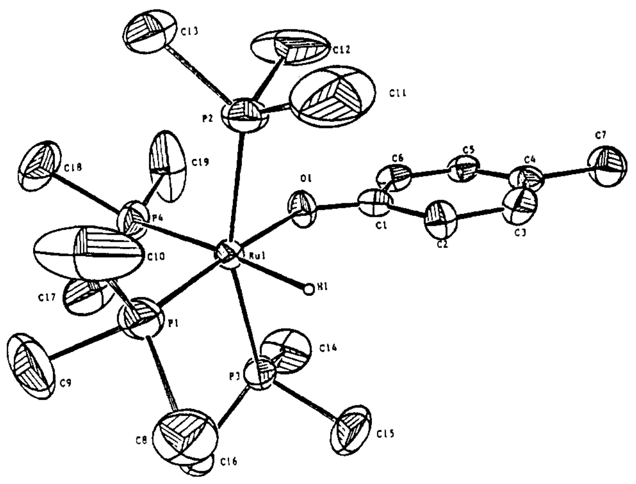

Figure 2. ORTEP drawing of 2. The ruthenium-bound hydrogen was located but not refined. Most of the other hydrogen atoms were also located but have been omitted for clarity.

Table V. Selected Intramolecular Bond Angles for 2

P1–Ru1–P2	94.48 (6)	C11–P2–C12	99.4 (4)
P1–Ru1–P3	96.16 (6)	C11–P2–C13	98.9 (3)
P1–Ru1–P4	99.49 (7)	C12–P2–C13	99.6 (3)
P1–Ru1–O1	176.96 (11)	Ru1–P3–C14	125.5 (3)
P1–Ru1–H1	76.31 (6)	Ru1–P3–C15	114.4 (3)
P2–Ru1–P3	160.97 (7)	Ru1–P3–C16	115.0 (3)
P2–Ru1–P4	96.97 (6)	C14–P3–C15	98.2 (4)
P2–Ru1–O1	83.47 (10)	C14–P3–C16	100.2 (4)
P2–Ru1–H1	82.44 (4)	C15–P3–C16	99.2 (6)
P3–Ru1–P4	96.76 (4)	Ru1–P4–C17	121.05 (23)
P3–Ru1–O1	85.21 (10)	Ru1–P4–C18	120.50 (25)
P3–Ru1–H1	84.82 (5)	Ru1–P4–C19	115.2 (3)
P4–Ru1–O1	83.01 (10)	C17–P4–C18	96.7 (4)
P4–Ru1–H1	175.68 (5)	C17–P4–C19	98.8 (4)
O1–Ru1–H1	101.15 (9)	C18–P4–C19	100.3 (5)
Ru1–P1–C8	117.2 (3)	Ru1–O1–C1	133.3 (3)
Ru1–P1–C9	119.4 (3)	O1–C1–C2	118.6 (4)
Ru1–P1–C10	121.4 (3)	O1–C1–C6	125.4 (4)
C8–P1–C9	96.8 (4)	C2–C1–C6	116.0 (5)
C8–P1–C10	99.2 (4)	C1–C2–C3	121.2 (5)
C9–P1–C10	98.0 (5)	C2–C3–C4	122.9 (4)
Ru1–P2–C11	114.46 (22)	C3–C4–C5	116.5 (5)
Ru1–P2–C12	115.18 (22)	C3–C4–C7	122.7 (4)
Ru1–P2–C13	125.15 (22)	C5–C4–C7	120.8 (5)
		C4–C5–C6	122.5 (5)

Table VI. Selected Intramolecular Bond Distances for 5

Ru–P1	2.334 (2)	C3–C4	1.399 (12)
Ru–P2	2.396 (3)	C4–C5	1.367 (13)
Ru–O1	2.108 (6)	C4–C7	1.621 (15)
Ru–C8	1.783 (10)	C5–C6	1.370 (13)
C8–O2	1.201 (11)	P1–C11	1.860 (8)
O1–C1	1.333 (10)	P1–C12	1.822 (7)
C1–C2	1.429 (12)	P1–C13	1.827 (7)
C1–C6	1.409 (13)	P2–C9	1.853 (11)
C2–C3	1.387 (13)	P2–C10	1.839 (8)

crystallized in space group $P\bar{1}$ with two independent molecules in the asymmetric unit. Crystal and data collection parameters are provided in Table I; intramolecular bond distances and angles are displayed in Tables II and III. An ORTEP drawing of the molecule is shown in Figure 1. Compound 2 crystallized in space group $P2_1/n$ with two crystallographically independent molecules in the asymmetric unit by cooling a solution of 1 in pentane to −40 °C. An ORTEP drawing of the molecule is provided in Figure 2. Crystal and data collection parameters are included in Table I; intramolecular distances and angles are provided in Tables IV and V. A suitable single crystal of 5 (space group *Cmca*) was obtained by slow cooling of a toluene/pentane (1:100) solution to −40 °C. An ORTEP drawing of the molecule is shown in Figure 3. Crystal and data collection parameters are included in Table I; intramolecular bond distances and angles are displayed in Tables VI and VII. The structures were solved by Patterson methods and refined by least-squares and Fourier techniques.

All three structures are distorted octahedra, with a hydride ligand occupying the vacant site of molecules 1 and

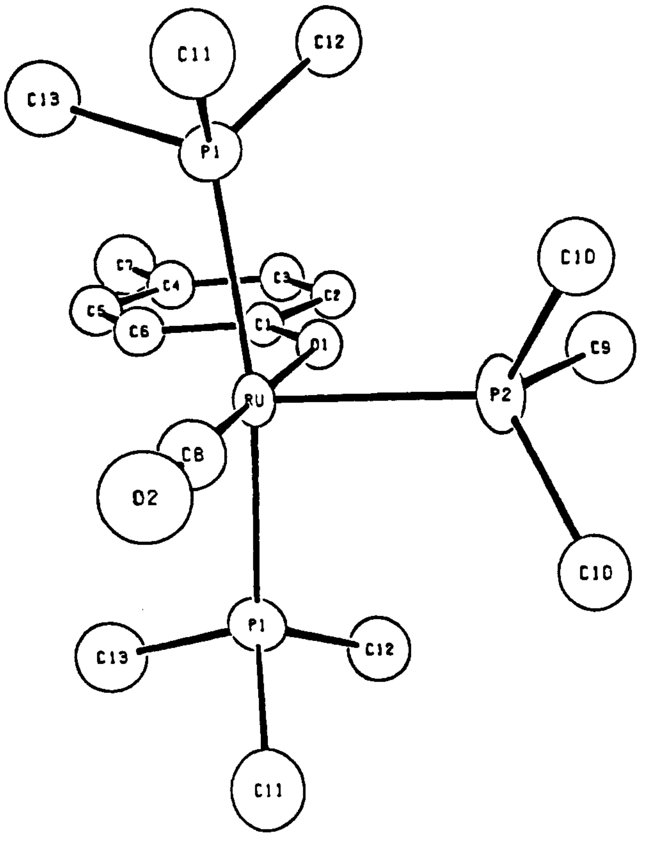

Figure 3. ORTEP drawing of 5. The ruthenium-bound hydrogen was not located.

Table VII. Selected Intramolecular Bond Angles for 5

P1–Ru–P1	163.60 (9)	C3–C4–C5	118.5 (9)
P1–Ru–P2	96.43 (5)	C3–C4–C7	119.1 (9)
P1–Ru–O1	85.60 (5)	C5–C4–C7	122.4 (9)
P1–Ru–C8	94.52 (6)	C4–C5–C6	121.7 (9)
P2–Ru–O1	84.21 (17)	C1–C6–C5	121.4 (9)
P2–Ru–C8	94.8 (3)	Ru–P1–C11	117.9 (3)
O1–Ru–C8	179.0 (4)	Ru–P1–C12	115.3 (3)
Ru–C8–O2	177.9 (9)	Ru–P1–C13	114.1 (3)
Ru–O1–C1	132.9 (5)	C11–P1–C12	104.0 (3)
O1–C1–C2	117.1 (7)	C11–P1–C13	101.3 (3)
O1–C1–C6	125.5 (8)	C12–P1–C13	102.0 (3)
C2–C1–C6	117.4 (8)	Ru–P2–C9	114.1 (4)
C1–C2–C3	119.3 (8)	Ru–P2–C10	117.70 (24)
C2–C3–C4	121.8 (9)	C9–P2–C10	102.1 (3)
		C10–P2–C10	100.6 (5)

5; the hydrides were not located on the Patterson map for these two compounds. To simplify the discussion, the distances and angles for one of the two independent molecules of 1 and 2 will be used; the two molecules are chemically equivalent in both cases. The Ru–N bond length in 1 is 2.160 (6) Å, and the aryl ring is located in the plane of the ruthenium, hydride, and nitrogen atoms, consistent with the inequivalence of the two sides of the aryl ring in the ^{1}H and ^{13}C{^{1}H} NMR spectra. The Ru–O bond length in 2 is 2.152 (3) Å. Although a slightly shorter M–O distance may be expected, simply on the basis of the smaller ionic radius of oxygen versus nitrogen, the difference in these two bond lengths is not statistically significant. Similarly, the O–C bond length in the aryloxide substituent of 2 (1.308 (7)) is slightly shorter than the N–C bond length (1.340 (9)) in 1. As observed for 1, the aryl ring is located in the plane of the hydride, ruthenium, and oxygen atoms. As noted in the previous section, the ring must be freely rotating on the NMR time scale if this structure also corresponds to the lowest energy configuration in solution.

The Ru–P distances of both structures reflect the weaker trans influence properties of the aryloxide and arylamide ligands relative to those of the hydride or phosphine ligands.[20] The Ru–P distance for the phosphine located trans to the aryloxide in 2 is 2.229 (2) Å, and the distance for the phosphine located trans to the arylamide in 1 is 2.268 (2) Å. The Ru–P distances for the mutually trans phosphine ligands range from 2.327 (2) to 2.343 (2) Å for the two structures, and the two Ru–P distances trans to the hydride substituents are 2.364 (2) Å for 2 and 2.363 (2) Å for 1. The shorter distances for the phosphines located trans to the *p*-cresolate and trans to the anilide are consistent with the weaker trans influence of heteroatom-containing substituents as compared to phosphine and hydride ligands.[15] The Ru–O–C angle in 2 is 133.3 (3)° and the Ru–N–C angle is 134.1 (5)° for 1, indicating that this angle is not particularly sensitive to the difference in π-donating abilities of the aryloxide and arylamide ligands.

In contrast to the similarity of 1 and 2, CO-substituted compound 5 has a Ru–O bond length of 2.108 (6), which is significantly shorter than that in 2. The O–C(aryl) bond distance in the aryloxide ligand of 5 (1.333 (10) Å) is not significantly longer than that of 2, 1.308 (7), and the Ru–O–C bond angle of 132.9 (5)° is also similar to that in 2, 133.3 (3)°. The difference in Ru–O bond distances in 1 and 5 may be attributed to the propensity of the aryloxide ligand in 5 to donate π-electron density into the π-accepting CO ligand trans to it.

A similar trend in bond lengths was observed for the Pt(II)–chloride distances in a series of square-planar complexes. X-ray structural analyses have been performed for compounds with the general formula LL′PtCl$_2$, where L is a phosphine and L′ is a π-accepting ligand such as CO or an isocyanide. When L is triethylphosphine and L′ is CO, the Pt–Cl bond distance trans to PEt$_3$ is longer (2.368 (3) Å) than that trans to CO (2.296 (4) Å).[18] When L is PEt$_2$Ph and L′ is ethyl isocyanide, the Pt–Cl bond distance trans to the phosphine is longer (2.390 (8) Å) than that trans to the isocyanide (2.314 (10) Å).[19] The Pt–Cl distance trans to the phosphine in (PEt$_3$)(PhNC)PtCl$_2$ is 2.333 (12) Å.[20] Therefore, whether the difference in bond lengths among these platinum and ruthenium compounds is largely caused by changes in the π-accepting or σ-donating properties of the dative ligands, the bonding of the aryloxide ligands in the ruthenium complexes in this study mimics the bonding in simple Pt(II) complexes.

Variable-Temperature NMR Spectra. The room-temperature NMR spectra of 1 and 2 indicate that the donating properties of the heteroatom can have a significant effect on the barrier to rotation of the aryl ring, and variable-temperature NMR experiments indicate that the ancillary ligands have a measurable effect on the double-bond character of the aryloxide O–C linkage. The O–C(aryl) linkage in the all-phosphine complex 2 appears to contain slightly more double-bond character than the CO-substituted product 5, as determined from the lower barrier to rotation in 5. A stacked plot of the aryl region of the ^{1}H NMR spectrum of 2 in the temperature range −9 to −88 °C is shown in Figure 4. At −88 °C, four inequivalent resonances are observed, indicating that rotation of the ring is slow on the NMR time scale. The same region in the ^{1}H NMR spectra of the CO substitution product 5 between −79 and −105 °C is shown in Figure 5. Even at −105 °C, only one of the aryl resonances of 5 has broadened, and it has not begun to separate into two in-

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[20] Badley, E. M.; Chatt, J.; Richards, R. L.; Sim, G. A. *J. Chem. Soc., Chem. Commun.* **1969**, 1322. Badley, E. M. Ph.D. Thesis, University of Sussex, 1969.

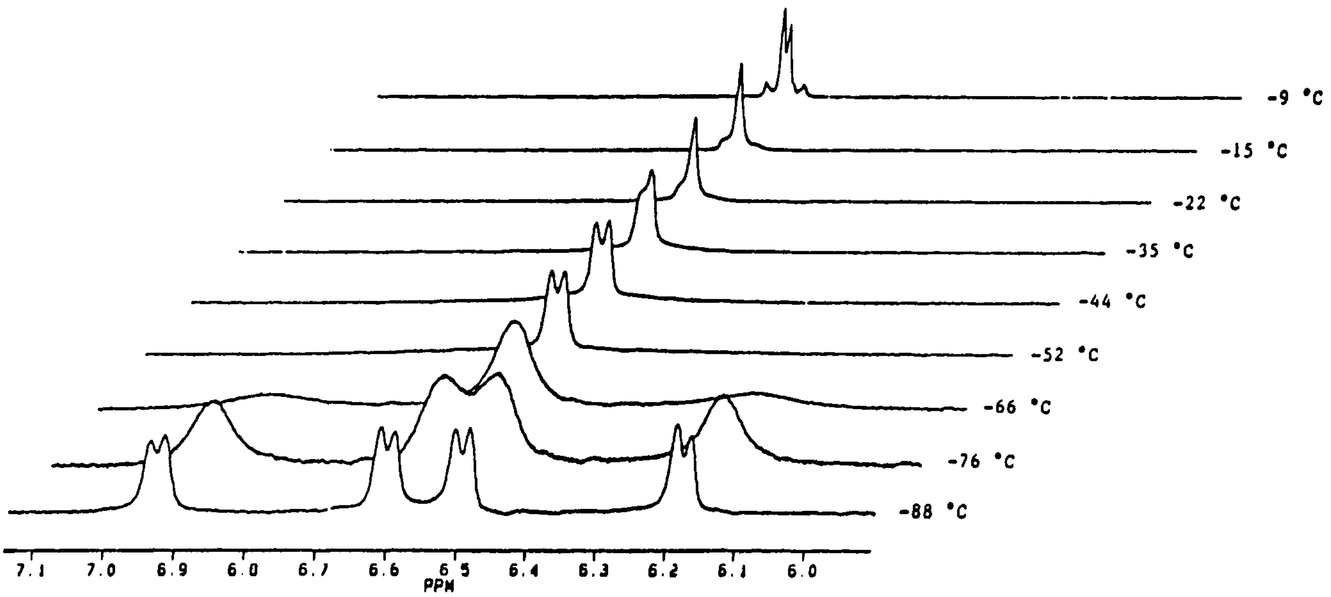

Figure 4. Variable-temperature ^1H NMR spectra of the aryl region of 2.

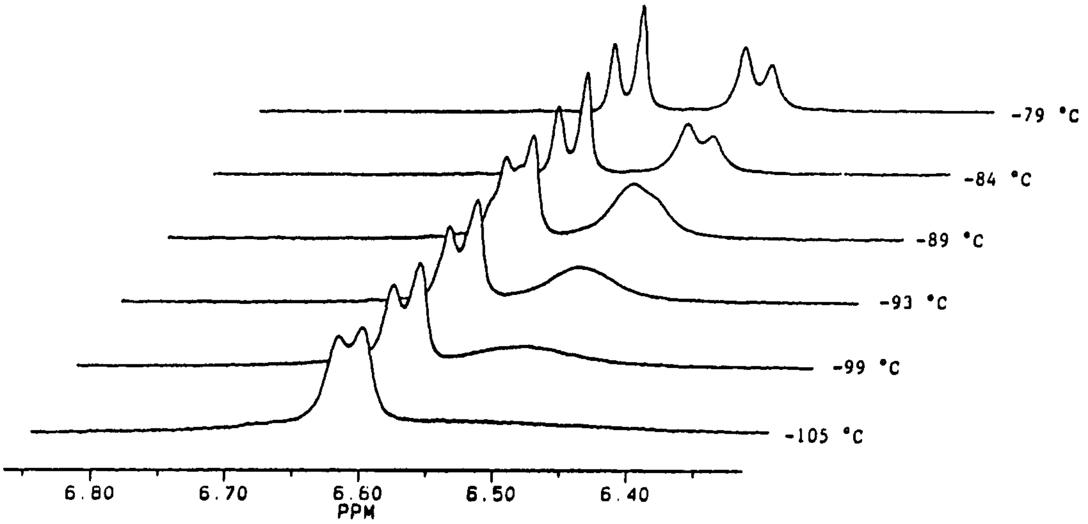

Figure 5. Variable-temperature ^1H NMR spectra of the aryl region of 8.

equivalent resonances, indicating a barrier to rotation that is lower than that observed for 2. ^1H NMR spectroscopy of the sterically similar benzyl hydride complex[15] showed no change in the aryl region, even at −105 °C, indicating that the slow rotation of the ring in complex 1 at room temperature and complex 2 at −88 °C is a result of electronic rather than steric factors. We did not expect the substitution of CO to cause a significant perturbation in the steric interactions of the cresolate substituent, since the substitution occurs trans to it. Indeed, the X-ray diffraction study shows that the M–O–C angles for 2 and 5 are almost identical. Although differences in σ-donating properties appears to have a larger effect on the M–O bond lengths in 2 and 5, the difference in π-accepting ability of the ligand trans to the cresolate does have a measurable effect on the rotational barriers of these two compounds, presumably due to differences in π-donation of the oxygen lone pair.

H/D-Exchange Reactions with $(PMe_3)_4Ru(H)_2$ (6). Addition of 20 equiv of aniline-*N,N*-d_2 to the dihydride $(PMe_3)_4Ru(H)_2$[21] (6) at 25 °C for 1 h led to H/D exchange, forming the dideuteride $(PMe_3)_4Ru(D)_2$. this assignment was based on the absence of hydride signals in the ^1H NMR spectrum, the presence of the corresponding resonances in the ^2H NMR spectrum, and the additional coupling in the $^{31}P\{^1H\}$ NMR spectrum. To ensure that the exchange occurred only between the hydride substituents and the NH protons of aniline, the dideuteride $(PMe_3)_4Ru(D)_2$ was treated with 20 equiv of protiated aniline, leading to formation of the dihydride and incorporation of deuterium into the N–H bonds of the aniline, as determined by the presence of only an N–D signal in the ^2H NMR spectrum of this mixture. Similarly, addition of aniline-*N,N*-d_2 to the cyclometalated hydride complex 4 at room temperature led to incorporation of deuterium into the hydride position.

When qualitative determination of the basicity of the metal center was attempted, the importance of trace amounts of water became evident (Scheme II). When dideuteride 6-d_2 was treated with 20 equiv of cyclopentadiene ($pK_a \sim 16$),[22] ^2H NMR spectroscopy showed no detectable resonance for the diene after 4 h; only a

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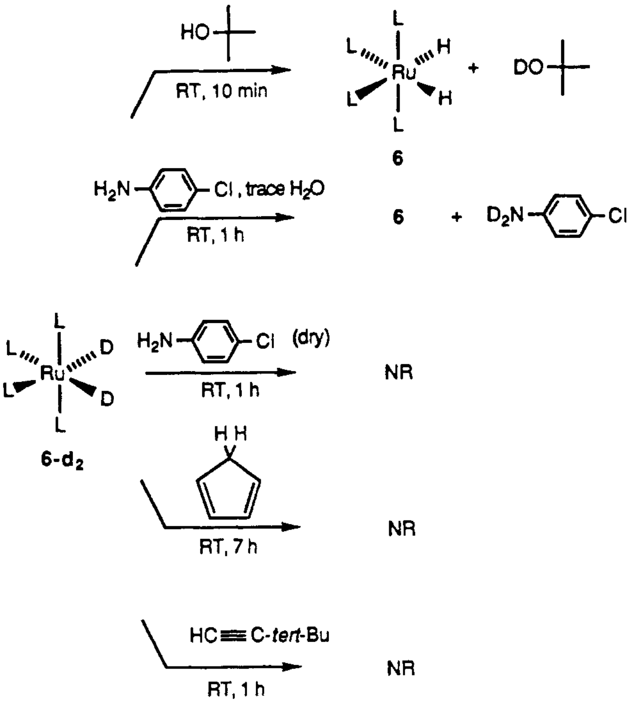
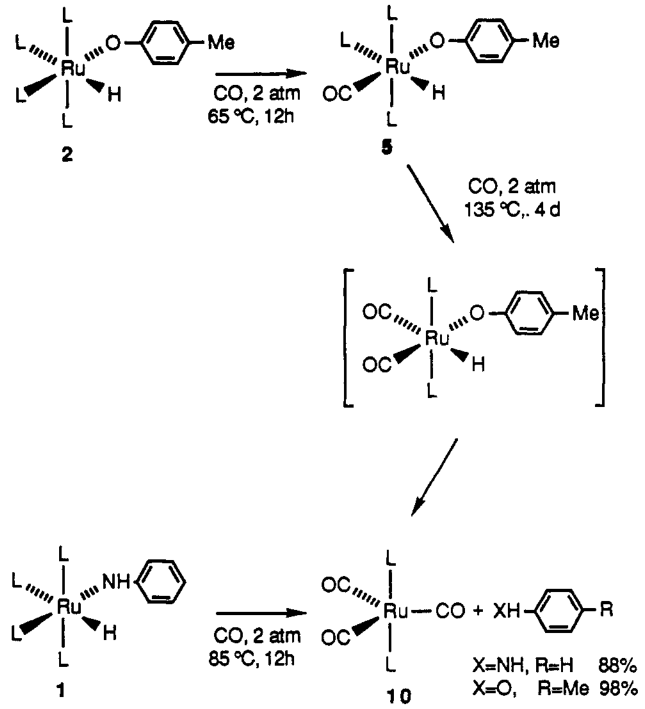
[21] Statler, J. A.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 1731.

[22] Streitweiser, A., Jr.; Nebenzahl, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 2188.

Scheme II



Scheme III



resonance for the hydride of starting material 5-d_2 was observed. Similarly, no exchange with the sterically more accessible but less acidic C–H bond of *tert*-butylacetylene (pK_a = ~22)[23] was observed after 5 h; dideuteride 6-d_2 was treated with 20 equiv of *tert*-butylacetylene at room temperature, and ^{2}H NMR spectroscopy showed no propargyl C–D resonance. In contrast, the O–H proton of *tert*-butyl alcohol (pK_a ~ 16) exchanged with 6-d_2. After 10 min at room temperature, solutions of 6-d_2 and 20 equiv of *tert*-butyl alcohol showed only signals in the ^{2}H NMR spectrum corresponding to the O–D substituent of the organic reagent.

Exchange with diphenylamine (pK_a ~ 22) was slower than exchange with *N*-methylaniline or aniline and led to roughly 50% exchange after 20–30 min at room temperature. However, when 6-d_2 was treated with 20 equiv of diphenylamine, which had been dried by benzene azeotropic distillation using a Dean-Stark trap and isolated by sublimation, no exchange was observed after 2 h at room temperature. We attempted to stop the H/D exchange with the parent aniline by exhaustive drying with vacuum distillation from sodium or CaH_2 or by azeotropic distillation with benzene. However, exchange of the aniline N–H with the ruthenium deuteride still occurred over the course of 10 min. To ensure that exchange in the case of aniline was a result of the difficulty in obtaining dry arylamine, which is a liquid, and not due to a steric difference between aniline and diphenylamine, *p*-chloroaniline, which is a solid, was dried by using the same method employed for diphenylamine. Indeed, *no* exchange was observed by ^{2}H NMR spectroscopy after 0.5 h at room temperature, and addition of 0.1 μL of water to this sample led to complete exchange after 15 min. These results demonstrate that this metal center is capable of rapid uncatalyzed exchange with alcohol O–H bonds, but exchange with less acidic N–H bonds at room temperature requires catalysis by trace amounts of water.

A qualitative comparison of the H/D-exchange rate and the phosphine dissociation rate was performed to determine whether exchange also requires the formation of an intermediate resulting from phosphine dissociation. Dihydride 6 was treated with 4 equiv of PMe_3-d_9 at 25 °C. $^{31}P\{^1H\}$ NMR spectra were obtained after 1 and 24 h at room temperature, and in both cases only resonances for 6-d_2 and free PMe_3-d_9 were observed. No free PMe_3-d_0 was formed, indicating that phosphine dissociation was significantly slower than H/D exchange.

Another possible intermediate in both the formation of 1 from 3 and in the H/D-exchange reactions is $(PMe_3)_4Ru$ (7). If the exchange occurs by way of this intermediate, D_2 must be incorporated into 6 at the same or faster rate than the acidic substrates. However, exchange with D_2 was much slower than it was with the amines or alcohols. Addition of 19 atm (>2000 equiv) of D_2 to the dihydride complex was conducted at 25 °C for 24 h. After this time, only partial incorporation of deuterium into the hydride position had occurred. A deuteride signal was observed in the ^{2}H NMR spectrum, but a hydride signal was also observed in the ^{1}H NMR spectrum.

To probe the intermediacy of 7 in the formation of 1, benzyl hydride compound $(PMe_3)_4Ru(CH_2Ph)(H)$ (8) was heated to 75 °C for 2 h in the presence of 1 equiv of aniline at the concentrations used to synthesize 1. We have reported previously that intermediate 7 is generated by thermally induced reductive elimination of $(PMe_3)_4Ru(CH_2Ph)(H)$ (8) and forms 4 by addition of a ligand C–H bond.[22] These thermolysis conditions provided roughly 45% conversion of 8 to cyclometalated hydride 4. Only small amounts (ca. 5%) of anilide hydride were observed. Heating for an additional 16 h led to complete disappearance of 7 and formation of a 3:1 ratio of 4 and hydrido anilide 1, undoubtedly formed from 4.

CO-Induced Reductive Elimination. Addition of carbon monoxide to 1, followed by heating to 85 °C for 8 h, led to reductive elimination of aniline in 94% yield by ^{1}H NMR spectroscopy, as shown in Scheme III. Addition of CO to 2, followed by heating to 135 °C for 5 days, led to formation of *p*-cresol in 98% yield by ^{1}H NMR spectroscopy (Scheme III). The organometallic product was $(PMe_3)_2Ru(CO)_3$ (10) in both cases and was formed in 79%

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[23] Streitweiser, A., Jr.; Reuben, D. M. E. *J. Am. Chem. Soc.* **1971**, *93*, 1794.

Table VIII. ^{1}H NMR Spectroscopic Data

	δ, ppm	multiplicity[a]	*J*, Hz	integration	assgn[b]
$(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me) (1)[c]	7.18	d	8.6	2	aromatic
	7.14		8.5	2	
	2.37	s		3	*p*-Me
	1.18	t	2.8	18	*trans*-PMe_3
	1.14	d	5.5	9	*cis*-PMe_3
	0.98	d	7.5	9	
	−7.65	dq	102.8, 27.5	1	Ru–H
$(PMe_3)_4Ru(H)(NHC_6H_5)$ (2)[c]	6.43	t	6.8	1	aromatic
	6.59	d	8.0	1	
	7.20	t	7.5	1	
	7.35	m		2	
	1.71	d	7.3	1	NH
	1.81	t	2.6	18	*trans*-PMe_3
	1.03	d	6.8	9	*cis*-PMe_3
	0.96	d	4.9	9	
	−7.69	dq	99.0, 26.4	1	Ru–H
$(PMe_3)_3(CO)Ru(H)(OC_6H_4$-*p*-Me) (5)[c]	7.16	d	8.3	2	aromatic
	7.03	d	8.3	2	
	2.36	s		3	*p*-Me
	1.16	t	2.6	18	*trans*-PMe_3
	1.08	d	6.4	9	*cis*-PMe_3
	−5.92	dt	117.8, 26.5	1	Ru–H
$(CO)_3Ru(PMe_3)_2$ (10)[c]	1.20	t	3.7		PMe_3

[a] The multiplicities reported for the PMe_3 resonances are aparent splittings and do not necessarily reflect true coupling constants. [b] The assignments, *cis*-PMe_3 and *trans*-PMe_3 refer to mutually cis and mutually trans PMe_3 ligands. [c] C_6D_6, 20 °C.

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

	δ, ppm	multiplicity[a]	*J*, Hz	assgnt[b]
$(PMe_3)_4Ru(H)$-$(OC_6H_4$-*p*-Me) (1)[c]	20.55	d	15.4	*cis*-PMe_3
	27.22	d	23.4	
	22.89	td	12.8, 3.8	*trans*-PMe_3
	20.93	s		*p*-Me
	118.26	s		aromatic
	120.34	s		
	129.77	s		
	169.13	d	4.5	
$(PMe_3)_4Ru(H)$-(NHC_6H_5) (2)[c]	21.52	dm	14.2	*cis*-PMe_3
	27.44	dm	24.1	
	23.27	td	12.9, 4.0	*trans*-PMe_3
	107.39	s		aromatic
	114.64	s		
	117.78	d	4.1	
	128.91	s		
	129.45	s		
	161.83	t	3.2	
$(PMe_3)_3(CO)Ru(H)$-$(OC_6H_4$-*p*-Me) (5)[c]	17.84	d	18	*cis*-PMe_3
	20.45	td	14.6, 3.0	*trans*-PMe_3
	20.83	s		*p*-Me
	119.30	s	10.3	aromatic
	119.40	s		
	129.79	s		
	168.40	d	4.9	
	204.78	td	14.2, 8.8	CO
$(CO)_3Ru(PMe_3)$ (10)[c]	22.69	t	16.3	PMe_3
	210.93	t	16.5	CO

[a] The multiplicities reported for the PMe_3 resonances are aparent splittings and do not necessarily reflect true coupling constants. [b] The assignments, *cis*-PMe_3 and *trans*-PMe_3 refer to mutually cis and mutually trans PMe_3 ligands. [c] C_6D_6, 20 °C.

yield for elimination of aniline and 89% yield for elimination of *p*-cresol. Compound **10** was independently prepared by successive photolysis and thermolysis of $Ru_3(CO)_{12}$ and PMe_3 during the course of a separate study,[24] and was characterized by ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and IR spectroscopy. The NMR data are provided in Tables VIII–X. The stoichiometry was confirmed by observing a quartet in the $^{31}P\{^1H\}$ NMR spectrum of the

Table X. $^{31}P\{^1H\}$ NMR Spectroscopic Data (C_6D_6, 20 °C)

	spin syst	δ, ppm	*J*, Hz
$(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me) (1)	A_2BC	$\delta_A = 1.54$	$J_{AB} = 32.5$
		$\delta_B = 14.92$	$J_{AC} = 27.1$
		$\delta_C = -12.62$	$J_{BC} = 15.9$
$(PMe_3)_4Ru(H)(NHC_6H_5)$ (2)	A_2BC	$\delta_A = -0.98$	$J_{AB} = 26.4$
		$\delta_B = -14.55$	$J_{AC} = 30.8$
		$\delta_C = 5.14$	$J_{BC} = 19.0$
$(PMe_3)_3(CO)Ru(H)(OC_6H_4$-*p*-Me) (5)	A_2B	$\delta_A = 0.23$	$J_{AB} = 25.1$
		$\delta_B = -15.77$	
$(CO)_3Ru(PMe_3)$ (10)	A_3	2.20	

Scheme IV

complex containing ^{13}CO. Monitoring the reductive elimination reaction of **2** showed that the reaction first formed CO-substituted product **5**, but a bis(CO)-substituted complex $(PMe_3)_2(CO)_2Ru(H)(OC_6H_4$-*p*-Me) (**9**) was not observed.

Anilide and Cresolate Exchange Reactions. Addition of 3 equiv of *p*-cresol to the anilide hydride complex **1** at 25 °C led to complete reaction of this compound in less than 20 min to form the cresolate hydride **2**. A 1–2 equiv amount of free aniline was observed, along with 2 equiv of free *p*-cresol (Scheme IV).

Discussion

Aniline Addition Reactions. H/D Exchanges. Several possible mechanisms for the H/D-exchange reactions are shown in Scheme V. One mechanism, pathway a, involves reversible addition of a proton to the metal center, leading to a cationic metal complex. The structure of the cation is written as Ru(IV), though it may exist as a Ru(II)–(η^2-H_2) compound since several related ruthenium hydrogen complexes are known.[25] Pathway b postulates

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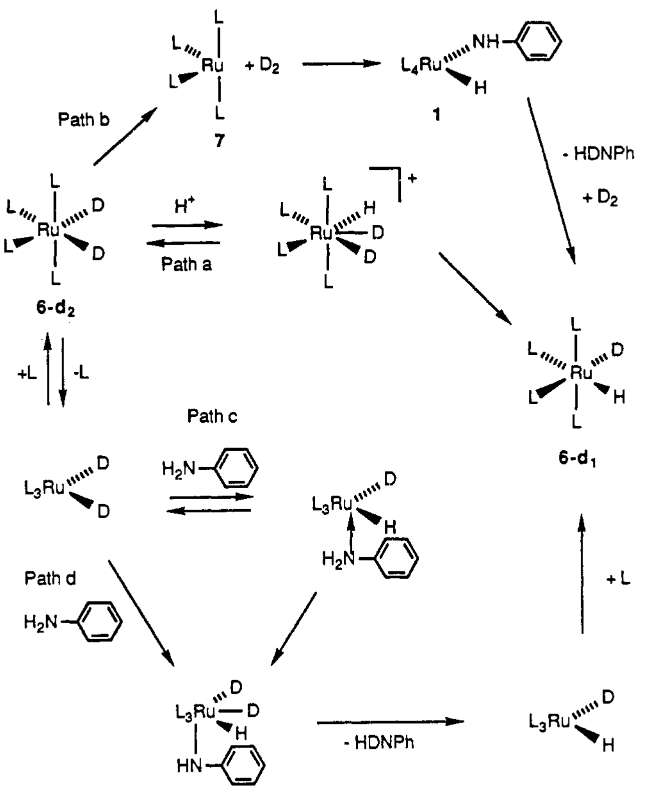
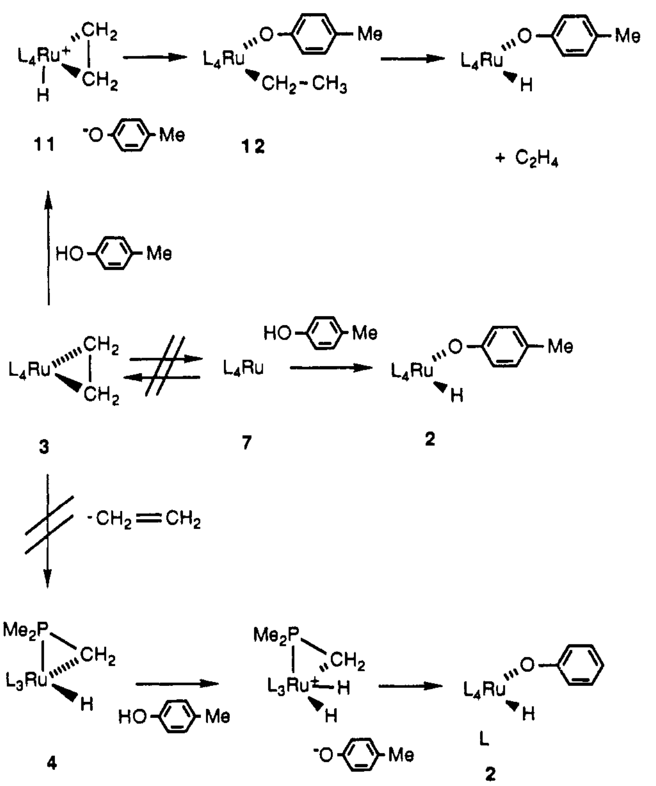
(24) Burn, M. J.; Andersen, R. A.; Bergman, R. A. Unpublished results.

Scheme V



Scheme VI



H_2 reductive elimination to form the L_4Ru intermediate, which oxidatively adds aniline-N,N-d_2 to form the anilide deuteride 1-d_2; this complex then reacts with the extruded hydrogen to re-form the H/D-scrambled product. Two other mechanisms involve initial dissociation of phosphine. In pathway c, the anilide nitrogen atom coordinates to the resulting vacant coordination site, enhancing the acidity of the aniline N–H bond (analogous to the enhanced acidity of coordinated water in aqua ions[26]). In pathway d, the unsaturated intermediate undergoes N–H oxidative addition to form a trihydride intermediate.

Our results are consistent only with the proton-transfer pathway a. The rate of H/D exchange is significantly faster than the rate of phosphine dissociation from dihydride 6, ruling out the possibility of reaction by pathways c and d. Pathway b is ruled out by the failure of D_2 to incorporate into the dihydride 6 on the time scale of the H/D exchange with aniline. Our results with a range of weak acids demonstrate that the metal center is not basic enough to exchange with weak carbon acids such as *tert*-butylacetylene and cyclopentadiene but is basic enough to exchange rapidly with *tert*-butanol. Moreover, our ability to significantly slow the H/D-exchange process of arylamines by obtaining rigorously dry samples of solid amines indicates that exchange with these substrates occurs by a water-catalyzed process. Based on our observations with *tert*-butanol we propose that the catalysis operates by reversible protonation of the metal center with water and H/D exchange between water and aniline to incorporate deuterium into the anilide N–H position.

Formation of 1. Mechanisms similar to those for the H/D exchange can be invoked for the formation of anilide hydride 1 from cyclometalated hydride 4. The lack of phosphine inhibition (despite rapid reversible phosphine dissociation at these temperatures) indicates that reaction does not occur by pathways involving phosphine dissociation. Our results do not rule out reaction by way of intermediate $(PMe_3)_4Ru$ (7), which could form 1 by direct oxidative addition of the aniline N–H bond.[27] Although the independent generation of 7 from benzyl hydride 8 demonstrated that intramolecular C–H oxidative addition with this intermediate is faster than reaction with aniline, the possibility remains that intermediate 7 is formed reversibly from cyclometalated hydride 4 and oxidatively adds the N–H bond of aniline to form the thermodynamic product 1 in a subsequent slower step.

Our results are also consistent with an overall N–H addition reaction that proceeds by a mechanism involving proton transfer, similar to the proton-catalyzed H/D-exchange reactions with amines. The results of the H/D-exchange study suggest that trace amounts of water are likely to be important in such a mechanism, but the lack of a dramatic rate increase for reaction of rigorously dried *p*-chloroaniline with 4 in the presence of added water suggests that water-catalyzed proton transfer is not as important in the reaction of 1 as it is in the H/D exchange with dihydride 6. This may reflect a rate-determining step that does not involve proton transfer; i.e., the rate of reductive elimination from $[(PMe_3)_3Ru(CH_2PMe_2)(H)_2]^+$ (formed by protonation of 4) to open the metallacycle and form $[(PMe_3)_4Ru(H)]^+$ is slower than protonation of the ruthenium hydrido anilide. Consistent with this hypothesis, H/D exchange of the hydride substituent of 4 with aniline-d_2 occurs rapidly at 25 °C, a much lower temperature than required for formation of 1. We hope that future studies with this compound and others will help us

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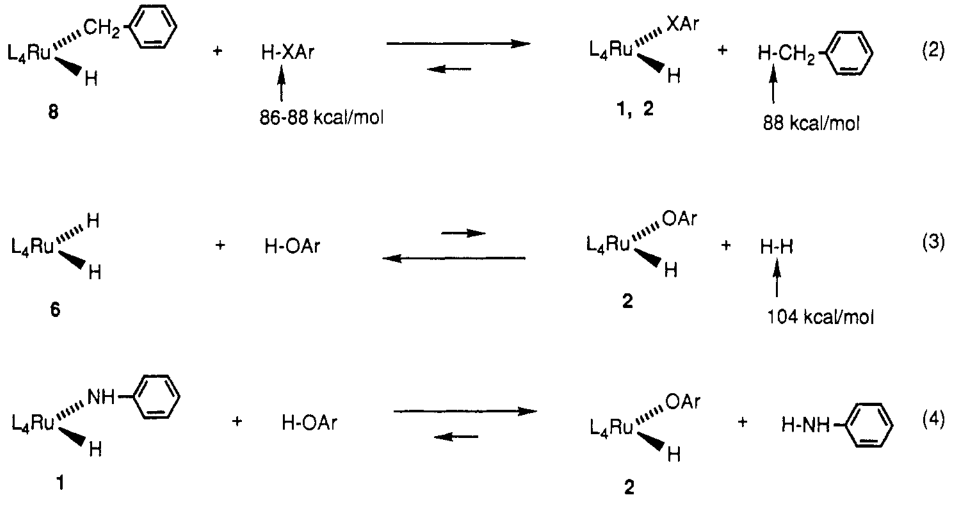
[25] See for example: (a) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (b) Bautista, M.; Kelly, A. E.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (c) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124.

[26] Burgess, J. *Metal Ions in Solution*; Horwood-Wiley: New York, 1978.

[27] In a recent study, heating the compound $(DMPE)_2Ru$(naphthyl)(H) in the presence of aniline was reported to yield no reaction (ref 10i), although previous studies with this ruthenium compound implied addition of the aniline aromatic C–H bonds occurs.

Scheme VII



Relative Bond Strengths: $L_4Ru\text{-}H > L_4Ru\text{-}OAr > L_4Ru\text{-}NHPh > L_4Ru\text{-}CH_2Ph$

to distinguish the oxidative addition process from proton-transfer processes.

Addition of *p*-Cresol. We have reported that addition of *p*-cresol to the benzyne complex $(PMe_3)_4Ru(\eta^2\text{-}C_6H_4)$ occurs faster than phosphine dissociation, implying direct protonation of the electron-rich metal center by this acidic substrate, followed by C–H reductive elimination to form the observed phenyl aryloxide intermediate $(PMe_3)_4Ru(Ph)(OC_6H_4\text{-}p\text{-}Me)$.[28] Addition of *p*-cresol to either **3** or **4** also occurs rapidly at room temperature (<5 min), suggesting that protonation by the cresol occurs to form cationic intermediate **11** (Scheme VI), followed by reductive elimination to form the ethyl cresolate $(PMe_3)_4Ru(Et)(OC_6H_4\text{-}p\text{-}Me)$ (**12**) and β-hydrogen elimination to form the product **2**. Protonation of **4** followed by C–H reductive elimination and ion-pair collapse would form **2** directly. Moreover, the reaction of $(PMe_3)_4Ru(C_2H_4)$ with *p*-cresol cannot occur via the Ru^0 intermediate **7** because ethylene dissociation is much slower than the cresol addition. The addition of 1 equiv of ethylene-d_4 to **3** was monitored over the course of 12 h at 25 °C. After this time no resonance for free ethylene was observed in the ^1H NMR spectrum, and the chemical shift of bound ethylene did not change, indicating that dissociation of ethylene from **3** does not occur on this time scale.[29] Field has reported the addition of alcohols to the iron dihydride $(DMPE)_2Fe(H)_2$ to form a cationic complex containing three metal-bound hydrogen atoms,[30] an intermediate analogous to the one involved in the protonation of **3**.

CO-Induced Reductive Elimination. Reductive elimination of aniline from **1** is markedly faster than elimination of *p*-cresol from **2**. However, we were not able to observe or isolate the bis(CO) adduct $(PMe_3)_2(CO)_2Ru(H)(OC_6H_4\text{-}p\text{-}Me)$, the precursor to the O–H elimination reaction, and so the marked difference in rates for the reductive elimination of aniline from **1** and *p*-cresol from **2** may reflect conditions necessary for a second CO substitution reaction rather than a difference in rates of the two reductive elimination processes.

It is evident that substitution of the poor σ-donor and strong π-acceptor CO for the strong σ-donor PMe_3 favors reductive elimination over the all-PMe_3-substituted compound, at least kinetically. In addition, the organometallic product $(PMe_3)_2Ru(CO)_3$ is formed irreversibly, suggesting that an electron-rich metal center is crucial to the thermodynamic stability of anilide and cresolate hydride compounds **1** and **2**.

Qualitative Thermodynamic Results. This ruthenium system constitutes a rare example of a series of compounds which undergo C–H, N–H, and O–H reductive elimination reactions. No evidence for direct reductive elimination from **1** or **2** was obtained; only upon addition of CO or H_2 was elimination of aniline or *p*-cresol observed. As reported earlier, thermolysis of the benzyl hydride complex $(PMe_3)_4Ru(H)(CH_2Ph)$ (**8**) at 85 °C for 4 h leads directly to reductive elimination of toluene and formation of the $(PMe_3)_4Ru^0$ intermediate **7**, which undergoes activation of ligand C–H bonds and forms cyclometalated hydride **4**. As illustrated in Scheme VII, these results demonstrate a dramatic contrast between the thermodynamic stabilities of benzyl hydride **8** and heteroatom-substituted compounds **1** and **2**. Compounds **1** and **2** are formed by the addition of cresol and aniline to **4**, the product of reactive elimination from **8**. The strength of the benzyl C–H bond of toluene (88.0 ± 1 kcal/mol) is comparable to that of the O–H bond of cresol (86.5 ± 2 kcal/mol for phenol) and the N–H bond of aniline (88.0 ± 2 kcal/mol). In light of these similar bond strengths, the observation that the equilibrium in eq 2 of Scheme VII lies to the right requires that the Ru–O and Ru–N linkages in **1** and **2** must be stronger than the Ru–C linkage in **8**.[31,32] Moreover, because dihydrogen has been shown to react with **1** and **2** to form the dihydride **6** and either aniline or *p*-cresol (eq 3),[33] the Ru–H bond must be at least 16 kcal stronger (the difference between the corresponding H–H and N–H bonds) than either the Ru–N or Ru–O bond.

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[28] (a) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717. (b) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics*, in press.

[29] Burn, M. J.; Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. Unpublished results.

[30] Baker, M. V.; Field, L. D.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 546.

[31] Bond dissociation energies are taken from: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[32] For an analysis of relative bond energies in (pentamethylcyclopentadienyl)ruthenium systems, see: (a) Bryndza, H. E.; Fong, L. K.; Raciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444-56. (b) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379.

[33] Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.*, in press.

Similarly, the reaction of *p*-cresol with the anilide hydride 1 to form free aniline and the cresolate hydride 2 (eq 4) shows that the Ru–O linkage is stronger than the Ru–N bond for these two compounds. The following trend in bond strengths then results: $L_4(H)Ru–H > L_4(H)Ru–OAr > L_4(H)Ru–NHPh > L_4(H)Ru–CH_2Ph$.(34)

Experimental Section

General Considerations. 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 by using 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 interfaced 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. ^2H NMR spectra were recorded at 76.4 MHz on the 500-MHz instrument, and chemical shifts were recorded relative to the solvent resonance. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane, and all coupling constants are reported in Hz.

IR spectra were obtained on a Nicolet 510 spectrometer equipped with a Nicolet 620 processor using potassium bromide ground pellets, Nujol mull, or solution cells as stated. 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.

To prepare sealed NMR tubes, the sample tube was attached via Cajon adapters directly to Kontes vacuum stopcocks.(35) 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. CO was purchased from Matheson. *p*-Cresol was dried by azeotroping with benzene using a Dean-Stark trap, followed by vacuum distillation. Dry diphenylamine and *p*-chloroaniline were obtained by refluxing a benzene solution using a Dean-Stark trap and subliming at 60 °C. Aniline was either vacuum-distilled from sodium or calcium hydride or refluxed in benzene with a Dean-Stark trap and then vacuum-distilled. Dry cyclopentadiene was obtained by heating cyclopentadiene dimer to 170 °C over CaH_2, and the monomer was collected by distillation. *tert*-Butylacetylene was stored under vacuum over P_2O_5 and was used by vacuum transfer. $(PMe_3)_3Ru(H)(CH_2PMe_2)$ (4) was prepared by the method of Werner,[15] $(PMe_3)_4Ru(C_2H_4)$ was prepared by the addition of EtMgBr to $(PMe_3)_4Ru(Cl)_2$,[14] and $(PMe_3)_4Ru(OAc)(Cl)$ was prepared by the method of Andersen and Mainz.(36)

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. Ether and tetrahydrofuran were distilled from purple solutions of sodium/benzophenone ketyl. Deuterated solvents for use in NMR experiments were dried as their protiated analogues but were vacuum-transferred from the drying agent.

$(PMe_3)_4Ru(H)(NHC_6H_5)$ (1). (a) Addition of Aniline to $(PMe_3)_4Ru(C_2H_4)$. The ruthenium complex $(PMe_3)_4Ru(C_2H_4)$ (3) (350 mg, 0.804 mmol) was dissolved in a minimum amount of hexane (10 mL). It was important to run this reaction in alkane solvent; thermolysis of 3 in benzene led to formation of predominantly $(PMe_3)_4Ru(H)(Ph)$. To this solution was added 1.5 equiv (116 mg) of aniline. The solution was transferred to a glass reaction vessel fused to a Kontes vacuum adaptor and partially degassed by exposing to vacuum for 2–3 s. The vessel was heated to 135 °C for 24 h, over which time the clear solution turned yellow. Upon cooling to room temperature, 266 mg (66.3%) of product, which was judged to be pure by ^1H NMR spectroscopy, crystallized from the reaction mixture as pale yellow blocks. A portion of the material was recrystallized for microanalysis and an X-ray diffraction study by allowing a refluxing solution of 1 in hexane to cool slowly to room temperature. IR (KBr): 3370 (w), 2967 (s), 2906 (s), 1845 (s), 1588 (s), 1484 (s), 1463 (m), 1426 (m), 1338 (s), 1297 (m), 1276 (m), 942 cm^{-1} (s). Anal. Calcd for $C_{18}H_{43}NP_4Ru$: C, 43.37; H, 8.69; N, 2.81. Found: C, 43.18; H, 8.73; N, 2.65.

(b) Addition of Aniline to $(PMe_3)_3Ru(CH_2PMe_2)(H)$ (4). The ruthenium complex $(PMe_3)_3Ru(H)(CH_2PMe_2)$ (12.6 mg, 0.0311 mmol) was dissolved in 0.7 mL of C_6D_6, and 2 μL of mesitylene as an internal standard was added. A ^1H NMR spectrum was obtained on the sample. To the solution was then added 2.9 μL (1.0 equiv) of aniline. The NMR tube was attached to a Kontes vacuum adaptor, degassed by two freeze, pump, thaw cycles, and sealed. The sample was heated to 110 °C for 24 h, after which time ^1H NMR spectroscopy showed formation of 1 in 93% yield, as determined by comparison to the spectrum before heating.

Addition of Aniline to 4 in the Presence of PMe_3. Ruthenium complex $(PMe_3)_3Ru(H)(CH_2PMe_2)$ (4) (14.6 mg, 0.0359 mmol) was dissolved in 1.2 mL of C_6D_6, and 2 μL of mesitylene as an internal standard was added. To the solution was then added 16.8 μL (5.0 equiv) of aniline. The sample was divided into two NMR tubes. One NMR tube was attached to a Kontes vacuum adaptor, degassed by two freeze, pump, thaw cycles, and sealed. To the other tube was added 4.0 equiv (0.24 M) of PMe_3 before sealing by the same method. The reaction was monitored at 1-h intervals at 110 °C for 4 h and showed that the rate for the sample containing PMe_3 was ca. 10–20% faster than that for the sample containing no PMe_3. Integration versus the mesitylene internal standard showed yields for the two samples which were within 10%.

Addition of *p*-Chloroaniline to 4 in the Presence of H_2O. Ruthenium complex $(PMe_3)_3Ru(H)(CH_2PMe_2)$ (4) (11.9 mg, 0.0294 mmol) was dissolved in 1.2 mL of C_6D_6. To the solution was then added 38 mg (10 equiv) of *p*-chloroaniline. The sample was divided into two NMR tubes. One NMR tube was attached to a Kontes vacuum adaptor, degassed by two freeze, pump, thaw

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(34) A reviewer has expressed concern about our use of bond dissociation energies in this thermodynamic analysis and has requested additional justification for it. Taking eq 2 as an example, a simple thermochemical cycle can be constructed that leads to the bond energy changes that can be summed to give the total energy change for this process. We first assume that because there are two molecules on each side of eq 2 and the largest contribution to ΔS° normally comes from translational entropy, the entropy change for this transformation will be small, and so to a reasonable approximation $\Delta G^\circ \cong \Delta H^\circ$. One then can write down four bond-cleavage and -formation reactions whose enthalpies add up to the enthalpy change for eq 2. These are $L_4Ru(H)(CH_2Ph) = L_4RuH + PhCH_2$ (i), $ArXH = ArX + H$ (ii), $ArX + L_4RuH = L_4Ru(H)(XAr)$ (iii), and $PhCH_2 + H = PhCH_3$ (iv). These are the *experimental definitions* of four bond energies: eqs i and ii define the Ru–C bond energy in 8 and the X–H bond energy in cresol (or aniline), respectively, and eqs iii and iv define the reverse or negative values ($-\Delta H$) of the Ru–X bond energies in 1 (2) and the benzyl C–H bond energy in toluene, respectively. The enthalpy change for eq 2 is rigorously equal to the sum of the enthalpy changes represented by eqs i–iv. We suspect that what may be troubling the reviewer is the suspicion that other bond energies (e.g., those associated with the metal–phosphine linkages) change when the reactions represented by eqs i through iv occur and that (for example) the metal–phosphorus bond energies in $L_4Ru(H)(CH_2Ph)$ are not equal to those in L_4RuH. This may well be the case, but it does not change the fact that eq 2 is the sum of the four reactions noted above, and therefore its thermodynamics can be analyzed in terms of the enthalpies of these transformations. Not only is this aspect of bond energy definitions true for the organometallic complexes in the equations but is also applied to the organic compounds. For example, because their bonding is closer to sp^2, the methylene C–H bonds in the benzyl radical are undoubtedly stronger than the methyl C–H bonds in toluene. In spite of this, the enthalpy of the reverse of eq iv is universally regarded as a legitimate definition of the C–H bond energy in toluene.

(35) 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., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; Americal Chemical Society: Washington, DC, 1987; p 227.

(36) Mainz, V. V.; Andersen, R. A. *Organometallics* 1984, *3*, 675.

cycles, and sealed. To the other tube was added 0.1 μL of H_2O (0.006 mmol, 0.4 equiv, 0.009 M) before sealing by the same method. Monitoring the reaction at 1-h intervals at 85 °C for 4 h showed that the rate for the sample containing H_2O was only about twice that for the sample containing no added water.

$(PMe_3)_4Ru(D)(NDC_6H_5)$ (1-d_2). To a stirred solution of $(PMe_3)_4Ru(OAc)(Cl)$ (202 mg, 0.404 mmol) in 8 mL of THF was added $^1/_4$ equiv (4.2 mg) of lithium aluminum deuteride as a slurry in THF. The resulting pale yellow, cloudy solution was filtered, and to the resulting clear yellow solution was added 1.5 equiv of LiNDPh, generated by addition of *n*-BuLi (379 μL, 1.6 M in hexanes) to an ether (2 mL) solution of D_2NPh (57.6 mg). The pale yellow color became darker upon addition of the lithium anilide. After stirring for 2 h, the solution was filtered and the solvent removed from the filtrate under reduced pressure. The resulting yellow solid was extracted with toluene. The toluene solution was reduced in volume to 1–2 mL, layered with hexanes, and cooled to −40 °C to provide 76.2 mg (38%) of 1-d_2, which was pure by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and showed no hydride or N–H resonance in the ^1H NMR spectrum and only a hydride and N–H resonance in the ^2H NMR spectrum. ^2H NMR: δ 1.66 (br s), −7.67 (m). IR (KBr): 2967 (s), 2906 (s), 2497 (w, N–D), 1588 (s), 1484 (s), 1463 (m), 1426 (m), 1340 (s), 1326 (shoulder, Ru–D), 1298 (m), 1276 (m), 949 cm^{-1} (s).

$(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me) (2). (a) Addition of Cresol to $(PMe_3)_4Ru(C_2H_4)$. The ruthenium complex $(PMe_3)_4Ru(C_2H_4)$ (702 mg, 1.61 mmol) was dissolved in a minimum amount of pentane (15 mL). To this solution was added at room temperature 1 equiv (174 mg) of *p*-cresol in 3 mL of pentane. The clear solution turned yellow, and gas evolution (presumably ethylene) was observed. Over the course of 12 h, 527 mg (63.7%) of product, which was pure by ^1H NMR spectroscopy, crystallized from the reaction mixture as pale yellow blocks. A portion of this material was recrystallized for microanalysis by vapor-diffusing pentane into a solution of 2 in toluene. IR (KBr): 2968 (s), 2908 (s), 1836 (s), 1600 (s), 1501 (s), 1498 (s), 1425 (m), 1323 (s), 1310 (s), 1301 (s), 1290 (s), 1281 (s), 1156 (m), 943 cm^{-1} (s). Anal. Calcd for $C_{19}H_{44}OP_4Ru$: C, 44.44; H, 8.63. Found: C, 44.56; H, 8.53.

(b) Addition of *p*-Cresol to $(PMe_3)_3Ru(CH_2PMe_2)(H)$ (4). Ruthenium complex $(PMe_3)_3Ru(CH_2PMe_2)(H)$ (98.8 mg, 0.244 mmol) was dissolved in 5 mL of toluene. A 1-equiv (26.3 mg) sample of *p*-cresol in 0.5 mL of toluene was added at room temperature. The clear solution turned yellow. Removal of toluene under vacuum, followed by crystallization from pentane at −40 °C, provided 77.6 mg (62.0%) of 2, which was judged pure by ^1H NMR spectroscopy.

$(PMe_3)_3(CO)Ru(H)(OC_6H_4$-*p*-Me) (5). To a 125-mL glass reaction vessel fused to a Kontes vacuum adapter was added 15 mL of a C_6H_6 solution of 252 mg (0.491 mmol) of $(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me) (2). The entire reaction vessel was cooled in liquid nitrogen and 430 Torr of CO (calculated to be 2 atm at 20 °C) was added. The vacuum adaptor was closed, and the vessel was warmed to room temperature. The reaction was then heated to 85 °C for 12 h, after which time the volatile materials were removed under vacuum, leaving a pale yellow residue. This residue was crystallized from pentane/toluene (100:1) at −40 °C to yield 77.2 mg (33.8%) of analytically pure white product containing crystals suitable for an X-ray diffraction study. IR (KBr): 2981 (m), 2971 (m), 2911 (m), 2901 (m), 1906 (s), 1852 (m), 1600 (m), 1501 (s), 1429 (m), 1423 (m), 1312 (s), 1301 (s), 943 cm^{-1} (s). Anal. Calcd for $C_{17}H_{35}O_2P_3Ru$: C, 43.87; H, 7.58. Found: C, 43.59; H, 7.56.

$(PMe_3)_4Ru(D)_2$ (6-d_2). To a solution of $(PMe_3)_4Ru(OAc)(Cl)$ (302 mg, 0.605 mmol) in 10 mL of ether was added at room temperature 16 mg of $LiAlD_4$ (0.60 equiv) as a solid. The suspension was stirred for 1 h, after which time the initial pale yellow solution became clear; a white solid precipitate was also observed. The solvent was removed under reduced pressure, and the resulting white solid was extracted three times with a total of 25 mL of pentane. The pentane solution was concentrated to 1–2 mL and cooled to −40 °C to provide 79.1 mg (32%) of 6-d_2, which was pure by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. ^2H NMR: δ −9.75 (m). $^{31}P\{^1H\}$ NMR: δ −0.19 (tm, *J* = 26.2 Hz, 2 P), −8.07 (tt, 26.2, 5.8, 2 P). IR (KBr): 1309 cm^{-1} (Ru–D).

H/D Exchange Reactions. Addition of Aniline-*N,N*-d_2 to $(PMe_3)_3Ru(CH_2PMe_2)(H)$ (4). To a solution of 4 (15.6 mg) in 0.7 mL of C_6H_6 was added 68 μL (20 equiv) of aniline-*N,N*-d_2. After 1 h, the solution was transferred to an NMR tube. ^2H NMR spectroscopy showed that complete exchange had occurred. A ratio of the deuteride resonance of 4 to the N–D resonance of aniline was roughly 1:40.

Addition of Aniline-*N,N*-d_2 to $(PMe_3)_4Ru(H)_2$ (6). A solution of 21 mg of $(PMe_3)_4Ru(H)_2$ (6) in 0.6 mL of C_6H_6 was added to 96 mg (20 equiv) of aniline-*N,N*-d_2. The resulting solution was placed in an NMR tube, and ^2H NMR spectroscopy showed a resonance for the dideuteride (6-d_2) and for the N–D of aniline in a ratio of roughly 1:20. A similar procedure, except using C_6D_6 solvent, was used for monitoring the reaction by ^1H NMR spectroscopy. After 1 h at room temperature, no hydride resonance was observed for starting material 6.

Addition of Aniline to $(PMe_3)_4Ru(D)_2$ (6-d_2). A solution of 16.8 mg of $(PMe_3)_4Ru(D)_2$ (6-d_2) in 0.6 mL of C_6H_6 was added to 76 mg (20 equiv) of aniline. The resulting solution was placed in an NMR tube, and ^2H NMR spectroscopy after 6 h showed only a resonance for the N–D of aniline.

Addition of *p*-Chloroaniline to $(PMe_3)_4Ru(D)_2$ (6-d_2). A solution of 15.2 mg of $(PMe_3)_4Ru(D)_2$ (6-d_2) in 0.6 mL of C_6H_6 was added to 95 mg (20 equiv) of *p*-chloroaniline. The resulting solution was placed into an NMR tube equipped with a rubber septum, and ^2H NMR spectroscopy after 30 min showed only a hydride resonance. After this time, 0.10 μL (0.15 equiv) of H_2O was added by syringe. The reaction was monitored at 5-min intervals by ^2H NMR spectroscopy and showed only an N–H resonance after 15 min.

Addition of Wet Diphenylamine to $(PMe_3)_4Ru(D)_2$ (6-d_2). A solution of 14.8 mg of $(PMe_3)_4Ru(D)_2$ (6-d_2) in 0.6 mL of C_6D_6 was added to 122 mg (20 equiv) of diphenylamine. The resulting solution was placed into an NMR tube, and ^1H NMR spectroscopy after 5 min showed that little exchange had occurred. After 20–30 min, ^1H NMR spectroscopy showed roughly 50% exchange, as determined by integration of the hydride resonance in the ^1H NMR spectrum relative to the phosphine resonances. After 24 h at room temperature, the C_6D_6 solvent was removed under reduced pressure and replaced with C_6H_6. The benzene solution was then placed into an NMR tube, and ^2H NMR spectroscopy showed only a resonance for the N–H proton of the amine.

Addition of Dry Diphenylamine to $(PMe_3)_4Ru(D)_2$ (6-d_2). To a solution of 10.2 mg of 6-d_2 in C_6H_6 was added 84.3 mg (20 equiv) of dry diphenylamine. The reaction was monitored by ^2H NMR spectroscopy, and after 2 h at room temperature, no NH resonance was observed, indicating that exchange did not occur.

Addition of Cyclopentadiene to $(PMe_3)_4Ru(D)_2$ (6-d_2). A solution of 15.2 mg of $(PMe_3)_4Ru(D)_2$ (6-d_2) in 0.6 mL of C_6H_6 was added to 49 mg (20 equiv) of cyclopentadiene monomer. The resulting solution was placed in an NMR tube, and ^2H NMR spectroscopy after 6 h showed only the deuteride resonance of 6-d_2; no resonances were observed for the cyclopentadiene. A similar procedure, except using C_6D_6 solvent, was used for monitoring the reaction by ^1H NMR spectroscopy. After 6 h at room temperature, no hydride resonance was observed for starting material 6-d_2.

Addition of *tert*-Butylacetylene to $(PMe_3)_4Ru(D)_2$ (6-d_2). A solution of 15.2 mg of $(PMe_3)_4Ru(D)_2$ (6-d_2) in 0.6 mL of C_6H_6 was placed into an NMR tube. The sample was degassed by two freeze, pump, thaw cycles. To it was added 20 equiv of *tert*-butylacetylene by vacuum transfer. The resulting solution was placed into an NMR tube, and ^2H NMR spectroscopy after 6 h showed only the deuteride resonance of 6-d_2; no propargyl C–D resonance was observed.

Addition of D_2 to $(PMe_3)_4Ru(H)_2$ (6). Into a Fischer-Porter bottle was placed a solution of 8.2 mg of 6 in 4 mL of C_6H_6. The solution was exposed to 19 atm of H_2 (ca. 2000 equiv) for 24 h. After this time the solution was concentrated to 0.6 mL and placed into an NMR tube for analysis by ^2H NMR spectroscopy. Only a resonance for the deuteride position of 6 was observed. The solvent was then removed under reduced pressure and replaced with C_6D_6 for ^1H NMR spectroscopic analysis. A hydride resonance for 6 was observed in addition to the two phosphine signals.

Addition of PMe_3-d_9 to 6-d_2. A solution of 8.8 mg of 6-d_2 in C_6D_6 was placed into an NMR tube equipped with a Kontes vacuum adaptor. The sample was degassed by two freeze, pump, thaw cycles, and to the sample was added 4 equiv of PMe_3-d_9.

The $^{31}P\{^1H\}$ NMR spectra obtained after 1 and 24 h showed only resonances for **6**-d_2 and PMe_3-d_9. No free PMe_3-d_0 was observed.

Addition of *p*-Cresol to 1. To a solution of 6.4 mg (0.013 mmol) of anilide hydride **1** in 0.6 mL of C_6D_6 was added 4 mg (0.04 mmol) of *p*-cresol. The solution was placed into an NMR tube, and ^1H NMR spectroscopy showed the presence of 1 equiv of free aniline, 2 equiv of *p*-cresol, and 1 equiv of cresolate hydride **2**.

CO-Induced Reductive Elimination of Aniline from $(PMe_3)_4Ru(H)(NHC_6H_5)$ (1). To a 9-in. NMR tube was added a solution of 10.2 mg (0.205 mmol) of **1** and 2 μL of mesitylene as an internal standard in 0.7 mL of C_6D_6. A ^1H NMR spectrum of the initial solution was obtained. The NMR tube was then attached to a Kontes vacuum adaptor, and the sample was degassed by two freeze, pump, thaw cycles. The tube was cooled in liquid nitrogen and exposed to 440 Torr of CO. The tube was sealed at the level of liquid nitrogen to provide a tube of 8.5-in. length. The sample was heated to 85 °C for 24 h, and ^1H NMR spectroscopy showed a 94% yield of aniline (identified by comparison to an authentic sample) and 79% yield of $(CO)_3Ru(PMe_3)_2$ (**10**) (identified by comparison to an independently prepared sample[27]), as determined by comparison to the initial solution.

CO-Induced Reductive Elimination of *p*-Cresol from $(PMe_3)_4Ru(H)(OC_6H_4$-*p*-Me) (2). To a 9-in. NMR tube was added a solution of 10.2 mg (0.205 mmol) of **2** and 2 μL of mesitylene as an internal standard in 0.7 mL of C_6D_6. A ^1H NMR spectrum was obtained on the initial solution. The NMR tube was then attached to a Kontes vacuum adaptor, and the sample was degassed by two freeze, pump, thaw cycles. The tube was cooled in liquid nitrogen and was exposed to 440 Torr of CO. The tube was sealed at the level of the liquid nitrogen to provide a tube of 8.5-in. length. The sample was heated to 85 °C for 24 h, and ^1H NMR spectroscopy showed 98% yield of *p*-cresol (identified by comparison to an authentic sample) and 89% yield of $(CO)_3Ru(PMe_3)_2$ (**10**) (identified by comparison to an independently prepared sample[27]), as determined by comparison to the initial solution.

X-ray Crystal Structure Determination of Complexes 1, 2, and 5. (a) Mounting Procedure. Pale yellow, air-sensitive crystals of **1** were obtained by allowing a refluxing solution of **1** in hexanes to cool to room temperature. Clear, air-sensitive crystals of **2** were obtained by slowly cooling a pentane solution of **2** to −40 °C. Clear, air-sensitive crystals of **5** were obtained by cooling a toluene/pentane (1:100) solution to −40 °C. End fragments cleaved from some of these crystals were mounted in a viscous oil, and then placed in the X-ray beam. The final cell parameters and specific data collection parameters for the data set for **1**, **2**, and **5** are given in Table I.

(b) Structure Determination. For **1**, 6540 raw intensity data were collected; for **2**, 7384 were collected, and for **5**, 1732 were collected. These data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the azimuthal scan data showed a variation $I_{min}/I_{max} = \pm 1\%$ for the average curve. No correction for absorption was applied for compounds **1** and **5** but was applied for **2**. Inspection of the systematic absences indicated space group $P\bar{1}$ for **1**, $P2_1/n$ for **2**, and *Cmca* for **5**. Removal of systematically absent and redundant data left 6540 unique data in the final data set for **1**, 6686 for **2**, and 1608 for **5**.

Each structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. The final refinement for **1** and **5** 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 refinement for **2** included isotropic refinement of all non-hydrogen atoms.

The final residues for the 243 variables for **1** were refined against the 4632 accepted data for which $F^2 > 3\sigma(F^2)$ and were $R = 8.0\%$, $R_w = 10.8\%$, and GOF = 4.19. The R value for all 6540 accepted data was 10.6%. The final residuals for the 451 variables for **2** were refined against the 4589 accepted data for **2** for which $F^2 > 3\sigma(F^2)$ and were $R = 4.1\%$, $R_w = 6.3\%$, and GOF = 2.76. The R value for all 6686 accepted data was 10.7%. The final residuals for the 71 variables for **5** were refined against the 1094 accepted data for **5** for which $F^2 > 3\sigma(F^2)$ and were $R = 5.1\%$, $R_w = 6.7\%$, and GOF = 2.47. The R value for all 1608 accepted data was 10.7%.

The positional parameters, thermal parameters of the non-hydrogen atoms, and anisotropic thermal parameters for compounds **1**, **2**, and **5** are available as supplementary material.

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Supplementary Material Available: Tables of general temperature factor expressions (B's), positional parameters and their estimated standard deviations, and root-mean-square amplitudes of anisotropic displacements for **1**, **2**, and **5** (7 pages); listings of structure factors (87 pages). Ordering information is given on any current masthead page.