Inorg. Chem. **2005**, *44*, 2895–2907

Reactions of (PCP)Ru(CO)(NHPh)(PMe_3) (PCP = 2,6-($CH_2P^tBu_2$)$_2C_6H_3$) with Substrates That Possess Polar Bonds

Jubo Zhang,[†] T. Brent Gunnoe,*[,†] and Jeffrey L. Petersen[‡]

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, and C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

Received November 19, 2004

The Ru(II) amido complex (PCP)Ru(CO)(PMe_3)(NHPh) (**1**) (PCP = 2,6-($CH_2P^tBu_2$)$_2C_6H_3$) reacts with compounds that possess polar C═N, C≡N, or C═O bonds (e.g., nitriles, carbodiimides, or isocyanates) to produce four-membered heterometallacycles that result from nucleophilic addition of the amido nitrogen to an unsaturated carbon of the organic substrate. Based on studies of the reaction of complex **1** with acetonitrile, the transformations are suggested to proceed by dissociation of trimethylphosphine, followed by coordination of the organic substrate and then intramolecular N–C bond formation. In the presence of ROH (R = H or Me), the fluorinated amidinate complex (PCP)Ru(CO)(N(Ph)C(C_6F_5)NH) (**6**) reacts with excess pentafluorobenzonitrile to produce (PCP)Ru(CO)(F)(N(H)C(C_6F_5)NHPh) (**7**). The reaction with MeOH also produces *o*-$MeOC_6F_4CN$ (>90%) and *p*-$MeOC_6F_4CN$ (<10%). Details of the solid-state structures of (PCP)Ru(CO)(F)(N(H)C(C_6F_5)NHPh) (**7**), (PCP)Ru(CO)[PhNC{NH(hx)}N(hx)] (**8**), (PCP)Ru(CO){N(Ph)C(NHPh)O} (**9**), and (PCP)Ru(CO){OC(Ph)N(Ph)} (**10**) are reported.

Introduction

Late transition metal complexes that possess amido, alkoxide, or aryloxide ligands have been implicated in several processes including the preparation of small molecules, polymer synthesis, and biological transformations.[1−10] For example, Pd-catalyzed syntheses of arylamines and aryl ethers proceed through Pd(II) arylamide or aryloxide intermediates, respectively, and Pd(II) amido complexes can be used for the preparation of polyanilines.[5−7,11,12] Amido complexes are possible intermediates in the hydroamination of unsaturated C−C bonds as well as styrene oxidative amination,[13,14] rhodium amido systems are potential intermediates in anti-Markovnikov hydroamination of vinylarenes,[15] and Co(III) hydroxide intermediates have been reported to be important in catalytic hydrolysis of nitriles.[16] Copper amido complexes have been used for the polymerization of β-lactams, and copper alkoxides have been reported to initiate the polymerization of carbodiimides.[17,18]

The study of late transition metal complexes that possess amido ligands has increased in the past decade with interest in such systems derived, in part, from the opportunity to access reactive fragments due to filled−filled interactions

* To whom correspondence should be addressed. E-mail: brent_gunnoe@ncsu.edu.
[†] North Carolina State University.
[‡] West Virginia University.

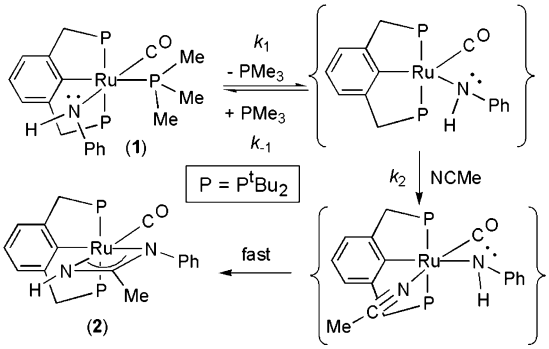
(1) Bergman, R. G. *Polyhedron* **1995**, *14*, 3227−3237.
(2) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44−56.
(3) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163−1188.
(4) Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1−27.
(5) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805−818.
(6) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046−2067.
(7) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125−146.
(8) Goldsmith, C. R.; Jonas, R. T.; Stack, T. D. P. *J. Am. Chem. Soc.* **2001**, *124*, 83−96.
(9) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1−40.
(10) Volbeda, A.; Garcin, E.; Piras, C.; de Lacey, A. L.; Fernandez, V. M.; Hatchikian, E. C.; Frey, M.; Fontecilla-Camps, J. C. *J. Am. Chem. Soc.* **1996**, *118*, 12989−12996.
(11) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852−860.
(12) Zhang, X.-X.; Sadighi, J. P.; Mackewitz, T. W.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 7606−7607.
(13) Timokhin, V. I.; Anastasi, N. R.; Stahl, S. S. *J. Am. Chem. Soc.* **2003**, *125*, 12996−12997.
(14) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675−703.
(15) Utsunomiya, M.; Kuwano, R.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 5608−5609.
(16) Kian, J. H.; Britten, J.; Chin, J. *J. Am. Chem. Soc.* **1993**, *115*, 3618−3622.
(17) Cheng, J.; Deming, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 9457−9458.
(18) Shibayama, K.; Seidel, S. W.; Novak, B. M. *Macromolecules* **1997**, *30*, 3159−3163.

10.1021/ic0483592 CCC: $30.25 © 2005 American Chemical Society
Published on Web 03/19/2005

that result from occupied dπ-manifolds.[2,19,20] That is, for metal systems that possess filled dπ orbitals, both π and π* orbitals that result from overlap of the amido-based p-orbital with a metal orbital of π-symmetry will be occupied and reactive amido ligands are anticipated. Highly basic parent amido ligands coordinated to tetraphosphine Ru(II) hydride fragments have been reported,[21−24] and this chemistry has recently been extended to a parent amido complex of Fe(II) that displays reactivity consistent with a basic and nucleophilic amido ligand as well as an 18-electron Ir(III) parent amido complex.[25−27] Holland et al. have recently reported the synthesis and reactivity of three-coordinate Fe(II) amido systems.[28] In addition, amido complexes coordinated to Ru(II) systems that possess cyclopentadienyl or η^6-arene ligands have been reported.[29−33]

Our group has been interested in exploitation of late transition metal amido complexes using the combination of metal-based Lewis acidity and ligand-centered basicity/nucleophilicity. We have prepared and studied a series of Ru(II) and Cu(I) complexes that possess reactive amido ligands,[34−38] and recently we have reported that the five-coordinate Ru(II) amido complex (PCP)Ru(CO)(NH_2) (PCP = 2,6-($CH_2P^tBu_2$)$_2C_6H_3$) activates dihydrogen as well as initiating intramolecular C−H activation of a *t*-Bu moiety of the PCP ligand.[39] Herein, the details of extension of our studies with (PCP)Ru(II) amido systems to reactions of the anilido complex (PCP)Ru(CO)(PMe_3)(NHPh) (**1**) with compounds that possess C═O, C═N, or C≡N bonds are reported. In addition, the reactivity of a PCP−Ru amidinate complex with aromatic C−F bonds is disclosed.

Scheme 1. Proposed Mechanism for the Formation of (PCP)Ru(CO)(N(H)C(Me)NPh) (**2**) from the Reaction of (PCP)Ru(CO)(PMe_3)(NHPh) (**1**) with Acetonitrile (P = $^tBu_2$P)



Results and Discussion

Reaction of (PCP)Ru(CO)(PMe_3)(NHPh) (1) with Acetonitrile. As previously communicated,[40] the Ru(II) anilido complex (PCP)Ru(CO)(PMe_3)(NHPh) (**1**) reacts with acetonitrile to form the amidinate complex (PCP)Ru(CO)(N(Ph)C(Me)NH) (**2**) and free PMe_3 (Scheme 1).[40] Kinetic studies at room temperature reveal that a likely reaction pathway for amidinate formation involves initial dissociation of PMe_3, coordination of acetonitrile, and intramolecular C−N bond formation (see below). The proposed mechanism includes C−N bond formation that is initiated by the combined Lewis acidity of Ru(II) and nucleophilicity of the anilido ligand. In closely related reactions, Bercaw et al. have reported the conversion of a scandium amido complex and acetonitrile to yield a five-membered heterometallacycle,[41] and a polyhedral borane has been reported to react with ammonia in the presence of base and acetonitrile to yield an amidinate moiety.[42] Similar intramolecular nucleophilic bond formations have been proposed in catalytic nitrile hydration,[16,43] and addition reactions of coordinated nitriles have been reviewed.[44,45]

The rate of conversion of **1** and acetonitrile to complex **2** has been determined under various conditions, and the kinetic studies are consistent with the proposed mechanism. The anticipated rate law for the mechanism depicted in Scheme 1 is shown in eq 1. For reactions with 10 equiv of acetonitrile

$$\text{rate} = \frac{k_1 k_2[\text{Ru}][\text{NCMe}]}{k_{-1}[\text{PMe}_3] + k_2[\text{NCMe}]} \qquad (1)$$

and 10−25 equiv of PMe_3, the rate of conversion of complex

(19) Holland, P. L.; Andersen, R. A.; Bergman, R. G. *Comments Inorg. Chem.* **1999**, *21*, 115−129.
(20) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25−41.
(21) Kaplan, A. W.; Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6828−6829.
(22) Fulton, J. R.; Bouwkamp, M. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 8799−8800.
(23) Fulton, J. R.; Sklenak, S.; Bouwkamp, M. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 4722−4737.
(24) Holland, A. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 14684−14695.
(25) Fox, D. J.; Bergman, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 8984−8985.
(26) Fox, D. J.; Bergman, R. G. *Organometallics* **2004**, *23*, 1656−1670.
(27) Rais, D.; Bergman, R. G. *Chem.−Eur. J.* **2004**, *10*, 3970−3978.
(28) Eckert, N. A.; Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Inorg. Chem.* **2004**, *43*, 3306−3321.
(29) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781−2794.
(30) Boncella, J. M.; Eve, T. M.; Rickman, B.; Abboud, K. A. *Polyhedron* **1998**, *17*, 725−736.
(31) Takemoto, S.; Kobayashi, T.; Matsuzaka, H. *J. Am. Chem. Soc.* **2004**, *126*, 10802−10803.
(32) Blake, R. E., Jr.; Heyn, R. H.; Tilley, T. D. *Polyhedron* **1992**, *11*, 709−710.
(33) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *34*, 488−499.
(34) Blue, E. D.; Davis, A.; Conner, D.; Gunnoe, T. B.; Boyle, P. D.; White, P. S. *J. Am. Chem. Soc.* **2003**, *125*, 9435−9441.
(35) Conner, D.; Jayaprakash, K. N.; Wells, M. B.; Manzer, S.; Gunnoe, T. B.; Boyle, P. D. *Inorg. Chem.* **2003**, *42*, 4759−4772.
(36) Conner, D.; Jayaprakash, K. N.; Gunnoe, T. B.; Boyle, P. D. *Inorg. Chem.* **2002**, *41*, 3042−3049.
(37) Jayaprakash, K. N.; Conner, D.; Gunnoe, T. B. *Organometallics* **2001**, *20*, 5254−5256.
(38) Jayaprakash, K. N.; Gunnoe, T. B.; Boyle, P. D. *Inorg. Chem.* **2001**, *40*, 6481−6486.
(39) Conner, D.; Jayaprakash, K. N.; Cundari, T. R.; Gunnoe, T. B. *Organometallics* **2004**, *23*, 2724−2733.
(40) Zhang, J.; Gunnoe, T. B.; Boyle, P. D. *Organometallics* **2004**, *23*, 3094−3097.
(41) Shapiro, P. J.; Henling, L. M.; Marsh, R. E.; Bercaw, J. E. *Inorg. Chem.* **1990**, *29*, 4560−4565.
(42) Li, F.; Shelly, K.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 1865−1868.
(43) Breno, K. L.; Pluth, M. D.; Tyler, D. R. *Organometallics* **2003**, *22*, 1203−1211.
(44) Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771−1802.
(45) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299−338.

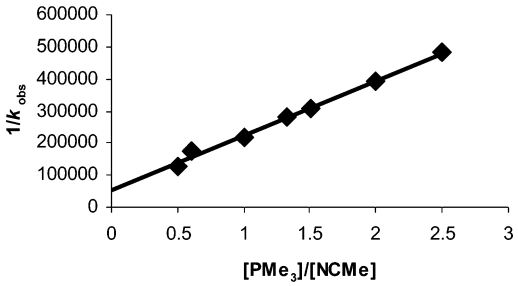


Figure 1. Plot of $1/k_{obs}$ versus [PMe_3]/[NCMe] for the conversion of complex **1** and NCMe to complex **2** ($R^2 = 0.99$).

1 and acetonitrile to the amidinate complex **2** is inverse first-order in concentration of PMe_3 (see the Supporting Information). Under these reaction conditions, no evidence of PCP−Ru species other than complex **1** and complex **2** was observed during the kinetic experiments. These results are consistent with the term in the denominator k_{-1}[PMe_3] dominating the term k_2[NCMe] *under the specific conditions of these experiments* with k_{obs} under pseudo-first-order conditions being equal to k_1k_2[NCMe]/k_{-1}[PMe_3].

A plot of k_{obs} versus the concentration of NCMe for reactions with 10 equiv of PMe_3 and between 10 and 50 equiv of NCMe reveals a first-order dependence on the concentration of NCMe at low concentrations of NCMe while saturation kinetics are apparent at higher concentrations (see the Supporting Information). Thus, in agreement with the observation of an inverse dependence of reaction rate on concentration of PMe_3 at lower concentrations of NCMe, the term k_{-1}[PMe_3] is greater than k_2[NCMe] with the pseudo-first-order rate constant equal to k_1k_2[NCMe]/k_{-1}[PMe_3]. At elevated concentrations of NCMe, the term k_2[NCMe] becomes greater than k_{-1}[PMe_3] with k_{obs} independent of the concentration of NCMe.

These results suggest that at higher concentrations of NCMe, the rate of formation of complex **2** should be independent of the concentration of PMe_3. Monitoring the rate of disappearance of complex **1** in the presence of 100 equiv of acetonitrile with 10, 15, or 20 equiv of PMe_3 reveals that k_{obs} is independent of PMe_3 concentration and is equal to $1.29(7) \times 10^{-5}$ s^{-1}. In addition, the magnitude of k_{obs} is similar to that for the reaction with 10 equiv of PMe_3 and 50 equiv of NCMe ($k_{obs} = 9.6 \times 10^{-6}$). For reactions in the presence of a large excess of NCMe, some decomposition was observed (∼10%) toward the latter portions of the reaction. Dissolution of the amidinate complex **2** in CD_3CN reveals that **2** undergoes relatively slow decomposition in the presence of excess nitrile.

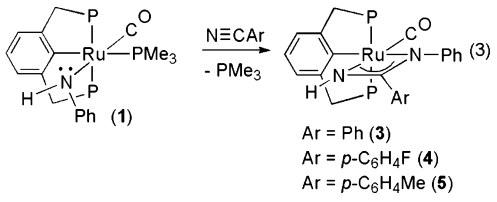
For reactions that are pseudo-first-order in concentration of **1**, rearrangement of the rate law shown in eq 1 indicates that a plot of $1/k_{obs}$ versus [PMe_3]/[NCMe] should be linear with the slope equal to k_{-1}/k_1k_2 and the *y*-intercept equal to $1/k_1$ (eq 2). From the plot shown in Figure 1, k_1 was estimated

$$1/k_{obs} = \frac{k_{-1}[PMe_3]}{k_1k_2[NCMe]} + \frac{1}{k_1} \qquad (2)$$

to be 1.8×10^{-5} s^{-1}, and using the value of k_1 and the slope from the plot in Figure 1, the ratio of k_{-1}/k_2 was calculated to be 3; however, small deviations in the slope can result in substantial deviations for the *y*-intercept. Since k_1 indicates the rate of dissociation of PMe_3 from complex **1**, independent studies of the rate of exchange of the coordinated PMe_3 of **1** with free PMe_3 provide an independent method for determining k_1. We have previously reported that the addition of free PMe_3 to a C_6D_6 solution of **1** results in line broadening of phosphine resonances at elevated temperatures, and the line broadening was attributed to phosphine exchange.[40] The addition of PMe_3-d_9 to a C_6D_6 solution of **1** at room temperature results in the exchange of coordinated and free PMe_3 with an approximate half-life of 7 min. This corresponds to a rate constant for dissociation of PMe_3 of approximately 1.7×10^{-3} s^{-1}, which is 94 times greater than the value of k_1 calculated from the plot in Figure 1 and is a reasonable value in consideration of the potentially substantial error for the *y*-intercept.

Thus, the kinetic data provide evidence for the coordination of acetonitrile through exchange with PMe_3 followed by intramolecular N−C bond formation. A pathway involving intermolecular nucleophilic attack of the amido ligand on uncoordinated acetonitrile is anticipated to exhibit a reaction rate that is independent of PMe_3 concentration without evidence for saturation kinetics at higher concentrations of acetonitrile. Indirect evidence for the proposed reaction pathway comes from the complex (PCP)Ru(CO)(CN^{t}Bu)(NHPh) (see below). It was anticipated that the isonitrile ligand would be less labile than PMe_3, and consistent with this notion and the proposal that the five-coordinate complex (PCP)Ru(CO)(NHPh) is directly involved in amidinate formation, a C_6D_6 solution of (PCP)Ru(CO)(CN^{t}Bu)(NHPh) and 20 equiv of NCMe shows no evidence of reaction after 48 h. In contrast, under identical conditions, complex **1** and NCMe are substantially converted to the amidinate complex **2**. At lower temperatures, an intermolecular pathway for N−C bond formation may become viable similar to a previously reported intermolecular addition of a Ru(II) anilido ligand to CO_2.[46]

Reactions of 1 with Nitriles. The formation of amidinate complex **2** upon combination of **1** with acetonitrile can be extended to other nitriles. For example, the reactions of complex **1** and benzonitrile, *p*-fluorobenzonitrile, or *p*-tolunitrile at room temperature produce the corresponding amidinate complexes **3**, **4**, and **5** in 48%, 49%, and 52% isolated yield, respectively (eq 3). IR spectroscopy of all three

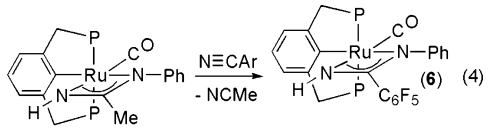


amidinate complexes reveals $\nu_{CO} = 1898$ cm^{-1} with ν_{NH} ranging from 3342 to 3348 cm^{-1}. Although NMR spectroscopy indicates the selective formation of a single isomer for

(46) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 6499−6508.

each product, the stereochemistry of **3**−**5** has not been determined; however, we presume that the NH of the amidinate ligand is trans to the Ru−CO bond as is observed for the methyl amidinate complex (PCP)Ru(CO)(N(Ph)C(Me)NH) (**2**).[40] Attempted reactions of **1** with pentafluorobenzonitrile or *p*-nitrobenzonitrile result in decomposition to multiple products. Although we were unable to isolate and characterize the decomposition products, the change in reactivity could be due to initial nucleophilic addition of the amido group to the electron-deficient aromatic system rather than reaction at the nitrile moiety.

The reaction of **2** with C_6F_5CN at room temperature produces the amidinate complex (PCP)Ru(CO)(N(Ph)C(C_6F_5)NH) (**6**) in 70% isolated yield (eq 4). The production



of **6** is irreversible between room temperature and 90 °C as indicated by the failure of **6** to react with NCMe to produce **2** and C_6F_5CN. The failure of **1** and C_6F_5CN to produce **6** suggests that the conversion of complex **2** and C_6F_5CN to produce (PCP)Ru(CO)(N(Ph)C(C_6F_5)NH) (**6**) does not likely occur through the formation of (PCP)Ru(CO)(NHPh) and free acetonitrile as previously suggested.[40] In addition, the reversibility of formation of amidinate complex **2** indicated by the conversion of **2** and C_6F_5CN to **6** is not general. The combination of complex **2** with excess benzonitrile, *p*-fluorobenzonitrile, or *p*-tolunitrile in C_6D_6 at 90 °C results in a minor amount of decomposition after 24 h without observation of complex **3**, **4**, or **5**, respectively (eq 4). In addition, the reaction of *p*-tolunitrile with complex **3** in a C_6D_6 solution does not yield observable quantities of complex **5** after 24 h at 90 °C. The electronic similarity of complexes **3** and **5** suggests that the failure of complex **3** and *p*-tolunitrile to convert to complex **5** and benzonitrile is likely due to kinetic factors.

Reaction of 6 with Fluorinated Aromatic Compounds. In the absence of other reactive substrates, complex **6** is stable at room temperature under inert atmosphere in C_6D_6. In the presence of excess C_6F_5CN at room temperature, the perfluorophenyl amidinate complex **6** reacts to form (PCP)Ru(CO)(F)(N(H)C(C_6F_5)NHPh) (**7**) in 80% isolated yield. ^{1}H NMR features of **7** include a doublet at 12.7 ppm due to the amino hydrogen with J_{HF} = 62 Hz, and ^{19}F NMR spectroscopy reveals a doublet of triplets at −11.3 ppm with J_{HF} = 62 and J_{PF} = 17 Hz. The observation of H−F coupling indicates the presence of hydrogen bonding between the fluoride ligand and the hydrogen atom of the NHPh moiety (Chart 1). Reports of intramolecular H···F hydrogen bonding are relatively uncommon for transition metal complexes;[47−51] however, closely related Ir−F···H−N hydrogen bonds have been reported with $^1J_{HF}$ = 52, 84 Hz as well as an intramolecular Ru−F···H−O hydrogen bond with $^1J_{HF}$ = 66 Hz.[47,48,51]

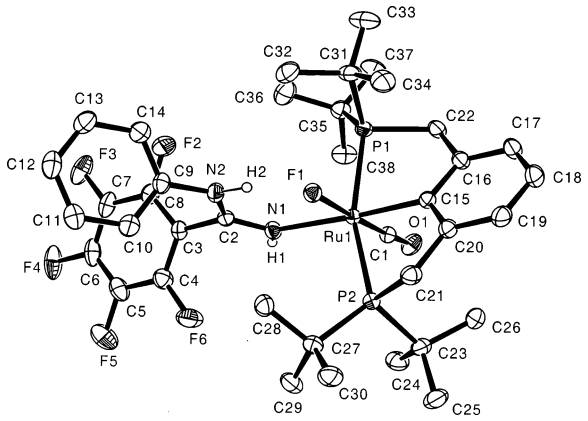
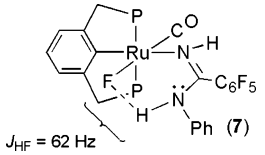


Figure 2. ORTEP of (PCP)Ru(CO)(F)(N(H)C(C_6F_5)NHPh) (**7**) (30% probability). Selected bond lengths (Å) and angles (deg): Ru−F1, 2.106(2); N1−C2, 1.286(3); N2−C2, 1.342(4); C2−N1−Ru1, 131.1(2); N1−C2−N2, 121.0(3).

Chart 1. Observed H−F Coupling Is Consistent with Intramolecular Hydrogen Bonding



A single crystal of **7** was obtained, and the solid-state structure was solved by X-ray crystallography (Figure 2). Table 1 presents selected crystallographic data and collection parameters. The X-ray structure reveals that the fluoride ligand is trans to CO. The N1−C2 and N2−C2 bond distances of 1.286(3) and 1.342(4) Å are consistent with a carbon−nitrogen double bond and a bond order that is intermediate between a single and double bond, respectively. Consistent with solution NMR spectroscopy, the N2−H2 bond is oriented to form an intramolecular hydrogen bond with the fluoride ligand.

The formation of complex **7** occurs through the net addition of HF to the amidinate complex (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) (**6**). The activation of C−F bonds has attracted considerable attention due to potential synthetic utility as well as importance for waste remediation;[52−54] however, the inherent strength of C−F bonds presents a substantial challenge to the development of such methodologies. The use of transition metal complexes is a promising strategy with metal-mediated C−F activations reported to proceed by oxidative addition, σ-bond metathesis, electron

(47) Peris, E.; Lee, J. C., Jr.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3485−3491.
(48) Patel, B. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 13105−13106.
(49) Murphy, V. J.; Hascall, T.; Chen, Y. J.; Parkin, G. *J. Am. Chem. Soc.* **1996**, *118*, 7428−7429.
(50) Esteruelas, M. A.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, *18*, 2953−2960.
(51) den Reijer, C. J.; Wörle, M.; Pregosin, P. S. *Organometallics* **2000**, *19*, 309−316.
(52) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373−431.
(53) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425−2468.
(54) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber.* **1997**, *130*, 145−154.

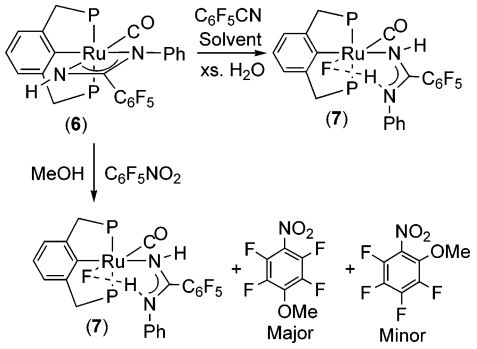
Table 1. Selected Crystallographic Data and Collection Parameters for Complexes **7**−**10**

	complex			
	(PCP)Ru(CO)(F)(N(H)C(C_6F_5)-NHPh) (**7**)	(PCP)Ru(CO)[PhNC{NH(hx)}-N(hx)] (**8**)	(PCP)Ru(CO){N(Ph)C-(NHPh)O} (**9**)	(PCP)Ru(CO){OC(Ph)-N(Ph)} (**10**)
empirical formula	$C_{38}H_{50}F_6N_2OP_2Ru$	$C_{44}H_{75}N_3OP_2Ru$	$C_{38}H_{54}N_2O_2P_2Ru$	$C_{38}H_{53}NO_2P_2Ru$
formula wt	827.81	825.08	733.84	718.82
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$P\bar{1}$	$P2_1/c$
a, Å	9.0368(5)	44.327(10)	13.2370(8)	16.4184(9)
b, Å	20.0690(10)	10.868(2)	14.0281(8)	11.5064(6)
c, Å	21.0286(10)	21.270(5)	21.1699(16)	20.7716(11)
α, deg	90	90	79.378(2)	90
β, deg	98.292(1)	116.770(3)	74.244(1)	109.963(1)
γ, deg	90	90	89.938(1)	90
V (Å^3)	3773.9(3)	9149(4)	3713.5(4)	3688.3(3)
Z	4	8	4	4
D_{calcd}, g cm^{-3}	1.457	1.198	1.313	1.295
R1, wR2 ($I > 2\sigma(I)$)	0.0431, 0.1042	0.0761, 0.1363	0.0587, 0.1112	0.0502, 0.1184
GOF	1.027	0.931	0.967	0.986

transfer, radical chain pathways, α- and *β*-fluoride eliminations, and reductive defluorination.[55−62] Although the fluoride ligand of **7** was clearly derived from C_6F_5CN, the source of H^+ was uncertain. Monitoring the rate of the formation of complex **7** in various solvents (benzene, methylene chloride, tetrahydrofuran, and pentane) produced inconsistent kinetics and percent yield even when solvent identity was held constant. For example, multiple reactions of complex **6** with C_6F_5CN in C_6D_6 revealed that the half-life for the formation of complex **7** varied between 5 and 24 h. These results suggested the possibility of an impurity catalyzing the reaction or serving as a reactant. The role of adventitious water was tested by comparing the reactions of (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) with C_6F_5CN in rigorously dried C_6D_6 (twice distilled from CaH_2 under dinitrogen and stored over molecular sieves) versus C_6D_6 with 10 equiv (based on the concentration of complex **6**) of H_2O added. In the absence of H_2O, only minimal formation of **7** (<5%) was observed after 12 h at room temperature. In contrast, the addition of 10 equiv of H_2O resulted in quantitative production of **7** after 12 h at room temperature (Scheme 2). The dependence of the reaction on the presence of H_2O is consistent in all four solvents listed above and indicates that the source of proton for the formation of **7** is likely H_2O. Unfortunately, the identification of organic products that accompany the formation of complex **7** upon reaction of **6** with C_6F_5CN and H_2O is complicated by the formation of multiple compounds in low concentrations.

The addition of 10 equiv of MeOH to a dry C_6D_6 solution of (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) (**6**) with 10 equiv of C_6F_5CN quantitatively produces complex **7** during a period of 5 h at room temperature. In contrast to the reaction

Scheme 2. Reactions of Complex **6** that Produce (PCP)Ru(CO)(F)(N(H)C(C_6F_5)NHPh) (**7**)

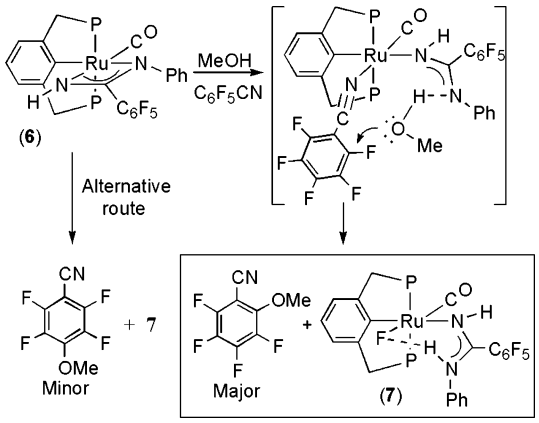


with H_2O, the formation of *o*-$MeOC_6F_4CN$ (>90%) and *p*-$MeOC_6F_4CN$ (<10%) is readily identified from the reaction with MeOH. Unfortunately, a previously reported competitive nucleophilic addition of methoxide to the nitrile carbon of C_6F_5CN complicates a detailed kinetic analysis of this reaction.[63] In control experiments, C_6F_5CN does not react with MeOH at 70 °C for at least 1 day, and C_6D_6 solutions of MeOH with (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) at room temperature show no reaction for at least 48 h.

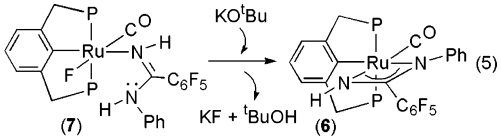
We propose that (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) mediates nucleophilic displacement of fluoride by methoxide with the Ru complex serving as a reservoir for proton (basic amidinate ligand) and fluoride (Lewis acidic metal). The Ru(II) complex could bind and activate C_6F_5CN toward nucleophilic attack by *free* MeOH or deprotonate methanol to promote methoxide addition to *free* C_6F_5CN. However, we suggest that a more likely reaction pathway is simultaneous activation of MeOH and C_6F_5CN by the metal center similar to the depiction in Scheme 3. The failure of complex **6** to react with MeOH at room temperature indicates that deprotonation of MeOH to form discrete methoxide ion is an unlikely reaction pathway (the formation of small quantities of thermally disfavored methoxide is still possible). Most importantly, the selective substitution at the ortho position suggests that the metal center interacts with C_6F_5CN during the substitution since simple nucleophilic displacement of

(55) Jones, W. D. *J. Chem. Soc., Dalton Trans.* **2003**, 3991−3995.
(56) Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359−361.
(57) Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 8674−8675.
(58) Braun, T.; Perutz, R. N. *Chem. Commun.* **2002**, 2749−2757.
(59) Hughes, R. P.; Smith, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 6084−6085.
(60) Watson, L. A.; Yandulov, D. V.; Caulton, K. G. *J. Am. Chem. Soc.* **2001**, *123*, 603−611.
(61) Albietz, P. J., Jr.; Houlis, J. F.; Eisenberg, R. *Inorg. Chem.* **2002**, *41*, 2001−2003.
(62) Harrison, R. G.; Richmond, T. G. *J. Am. Chem. Soc.* **1993**, *115*, 5303−5304.
(63) Bolton, R.; Sandall, J. P. B. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1288−1292.

Scheme 3. Proposed Pathway for Regioselective Substitution of the Aromatic C−F Bond of C_6F_5CN by Methoxide



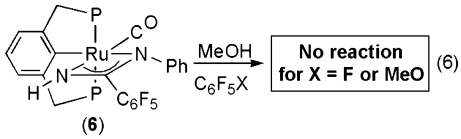
fluoride from C_6F_5CN by alkoxide nucleophiles is highly regioselective for substitution at the position para to the cyano group.[63,64] In addition, attack of *free* methoxide on coordinated C_6F_5CN would be expected to enhance the para selectivity. The small amount of *p*-$MeOC_6F_4CN$ likely forms from the addition of free methoxide to coordinated perfluorobenzonitrile or addition of activated methanol to free perfluorobenzonitrile (Scheme 3, "alternative route"). Analogous ortho selectivity has been reported for the reaction of a fluorinated phosphine bound to Pt(II) with hydroxide, Rh-catalyzed silylation of 2,3,4,5,6-pentafluoroacetophenone, and Rh-mediated C−F activation of pentafluoroanisole under photolytic conditions.[65−67] The addition of base to complex **7** at room temperature results in the net removal of HF and regeneration of (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) (eq 5). This



reaction is quantitative by ^1H, ^{31}P, and ^{19}F NMR spectroscopy.

Although the A values for fluoride and cyanide groups are almost identical,[68] a potential alternative explanation for the observed regioselectivity of methoxide/fluoride substitution is steric control over ortho versus para selectivity. The activation of MeOH by the Ru(II) complex could result in a bulky nucleophile, and steric differentiation between para- and ortho-selective fluoride displacement could guide attack to the ortho position. In this scenario, the interaction of the basic amidinate ligand of complex **6** with MeOH would generate a sterically hindered nucleophile, and the C−F substitution reaction would occur at the position ortho to the cyano group due to reduced steric profile of cyano versus fluoride. Analysis of the reaction of KO^{t}Bu with C_6F_5CN by ^{19}F NMR spectroscopy indicates that the para-substituted compound (*p*-^{t}BuOC_6F_4CN) is produced in about 70% yield while the ortho-substituted compound (*o*-^{t}BuOC_6F_4CN) is produced in about 20% yield. Given that the bulky nucleophile *t*-butoxide exhibits a preference for para attack over ortho selectivity, it is likely that the pathway shown in Scheme 3 better explains the Ru-mediated selectivity.

For the reaction of **6** with MeOH, replacement of the cyano group with a nitro group results in nucleophilic substitution with opposite regioselectivity (Scheme 2). The combination of $C_6F_5NO_2$, MeOH, and (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) at room temperature yields complex **7** (quantitative by NMR spectroscopy), *p*-$MeOC_6F_4NO_2$ (>90%), and *o*-$MeOC_6F_4NO_2$ (<10%). The change in regioselectivity is possibly explained by the poor coordinating ability of the nitro group in comparison with the nitrile group of C_6F_5CN. Coordination of the nitro group of $C_6F_5NO_2$ might not occur during the nucleophilic substitution since the reaction of free methoxide with $C_6F_5NO_2$ also yields *p*-$MeOC_6F_4NO_2$;[64] however, the metal center is clearly involved in the overall transformation since MeOH does not react with $C_6F_5NO_2$ in the absence of (PCP)Ru(CO)(N(H)C(C_6F_5)NPh). Nucleophilic substitution is not observed when either C_6F_5OMe or C_6F_6 is added to (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) (**6**) and MeOH (eq 6), and the qualitative reactivity pattern is

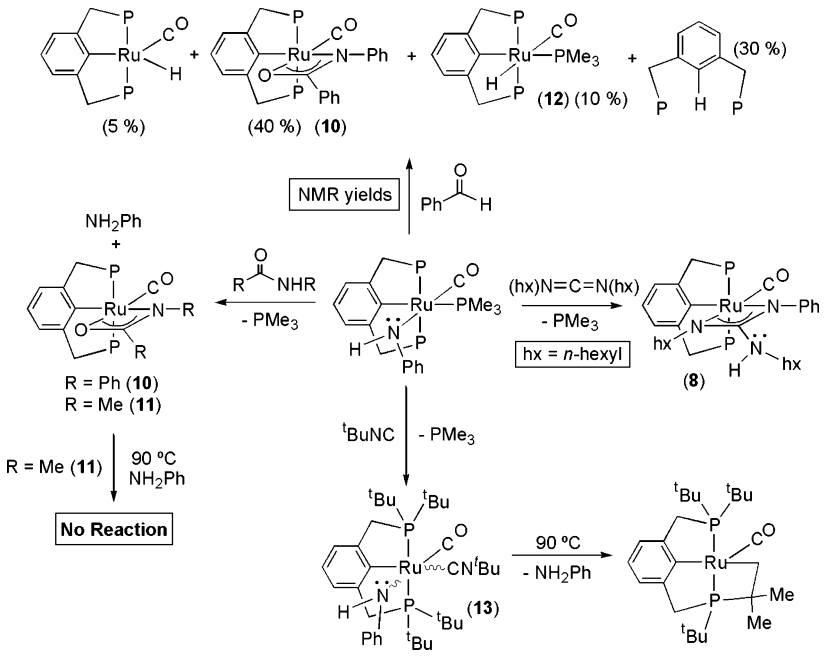


consistent with Hammett values for the different substituents indicating that an electron-withdrawing group on the perfluorophenyl ring is necessary to observe the nucleophilic displacement (e.g., σ_p/σ_o: NO_2, 0.78/0.71; CN, 0.66/0.56; F, 0.06/0.34; OCH_3, −0.27/0.12).[69] The reactivity trend is also consistent with an electron-transfer pathway; however, the regioselectivity of methoxide substitution of fluoride to produce *o*-$MeOC_6F_4CN$ is inconsistent with an initial redox event.[70]

Reactions of 1 with Carbodiimide, Isocyanate, Carboxamides, Benzaldehyde, and *t*-Butylisonitrile. Having observed metal-mediated N−C bond formation with nitriles, we became interested in extending N−C bond formation to other polar multiple bonds. Transition metal amido complexes have been reported to initiate the polymerization of carbodiimides, and it has been proposed that the mechanism for polymer formation involves coordination of the carbodiimide followed by intramolecular nucleophilic attack of a nitrogen-based ligand on the carbodiimide carbon.[18,71] The reaction of complex **1** and di-*n*-hexylcarbodiimide produces free trimethylphosphine and (PCP)Ru(CO)[PhNC{NH(hx)}-

(64) Banks, R. E. *Fluorocarbons and their Derivatives*; MacDonald and Company, 1970.
(65) Park, S.; Pontier-Johnson, M.; Roundhill, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 3101−3103.
(66) Ishii, Y.; Chatani, N.; Yorimitsu, S.; Murai, S. *Chem. Lett.* **1998**, 157−158.
(67) Ballhorn, M.; Partridge, M. G.; Perutz, R. N.; Whittlesey, M. K. *Chem. Commun.* **1996**, 961−962.
(68) Hirsch, J. A. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Interscience Publishers: New York, 1967; Vol. 1, pp 199−222.
(69) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.
(70) Hintermann, S.; Pregosin, P. S.; Ruegger, H.; Clark, H. C. *J. Organomet. Chem.* **1992**, *435*, 225−234.
(71) Goodwin, A.; Novak, B. M. *Macromolecules* **1994**, *27*, 5520−5522.

Scheme 4. Reactions of Complex **1** with Substrates that Possess Polar C−X (X = O or N) Multiple Bonds[a]



[a] Unless otherwise noted, reactions were performed at room temperature.

N(hx)] (**8**) (hx = hexyl) (Scheme 4). Complex **8** is produced at room temperature within 30 min and is isolated in 41% yield. A closely related series of reactions has been reported for *cis*-(PMe$_3$)$_4$Ru(H)(NH$_2$);[24] however, the final products for the tetraphosphine system are η^1-guanidinate complexes. Similarly, reaction of Cp*Ir(PMe$_3$)(Ph)(NH$_2$) with diisopropylcarbodiimide yields an η^1-guanidinate complex,[27] and the combination of (bpy)Re(CO)$_3$(NH*p*-tol) with (*p*-tol)-N═C═S yields the analogous sulfur-coordinated product (Cp* = pentamethylcyclopentadienyl, *p*-tol = *para*-tolyl, and bpy = 2,2′-bipyridine).[72] For the {(PCP)Ru(CO)} fragment, the lability of PMe$_3$ allows the formation of a κ^2-guanidinate ligand. The resonance due to the amino hydrogen was not located in the ^{1}H NMR spectrum of complex **8** likely due to overlap with other resonances.

A single-crystal X-ray diffraction study of complex **8** has confirmed its identity (Figure 3). Table 1 presents crystallographic data and collection parameters. The coordination geometry is pseudo-octahedral with the P1−Ru−P2 angle of 157.05(7)°. The Ru−N1 bond distance (2.197(6) Å) is slightly shorter than the Ru−N2 distance (2.212(6) Å). The two amidinate N−C bond distances are similar (1.346(9) vs 1.300(9) Å), and the C26−N3−C39 bond angle of 122.6(7)° is also consistent with N3−C26 double bond character. The N3−C26 bond distance of 1.383(10) Å reveals some multiple bonding between the amino group and the guanidinate carbon.

The amido complex can also initiate C−N bond formation with substrates that possess C−O multiple bonds. For example, the reaction of (PCP)Ru(CO)(PMe$_3$)(NHPh) with phenylisocyanate produces (PCP)Ru(CO){N(Ph)C(NHPh)O} (**9**) in 44% isolated yield at room temperature. Complex **9**

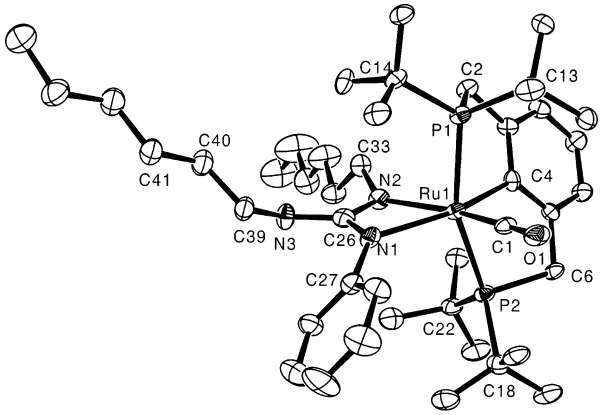


Figure 3. ORTEP of (PCP)Ru(CO)[PhNC{NH(hx)}N(hx)] (**8**) (30% probability). Selected bond lengths (Å) and angles (deg): Ru1−C1, 1.784(8); Ru1−N1, 2.197(6); Ru1−N2, 2.212(6); N2−C26, 1.300(9); N1−C26, 1.346(9); N3−C26, 1.383(10); N3−C39, 1.459(10); N1−Ru1−N2, 59.8(2); Ru1−N2−C33, 139.1(5); Ru1−N1−C27, 132.2(5); N2−C26−N3, 124.7(7); N2−C26−N1, 112.4(7); N1−C26−N3, 122.9(7).

likely forms upon coordination of the isocyanate (through ligand exchange with PMe$_3$) followed by N−C bond formation. Subsequent proton transfer and possible rearrangement would yield complex **9** (Scheme 5).

The solid-state structure of **9** reveals two independent molecules in the unit cell. In both structures the N−H bond of the NHPh amino group is anti with respect to the C−O bond of the amidate ligand. In one structure, the phenyl group is oriented toward the NPh moiety of the amidate ligand, while the phenyl group of the NHPh is oriented toward the amidate oxygen in the second structure. One of the two independent structures is shown in Figure 4, and Table 1 lists crystallographic data and collection parameters. The coordination sphere is pseudo-octahedral with the amidate oxygen trans to the Ru−CO bond. Both N−C bond distances (1.317(5) and 1.383(5) Å) are shorter than N−C single bonds, indicating a competition for π-interaction. The

(72) Hevia, E.; Pérez, J.; Riera, V.; Miguel, D. *Organometallics* **2003**, *22*, 257−263.

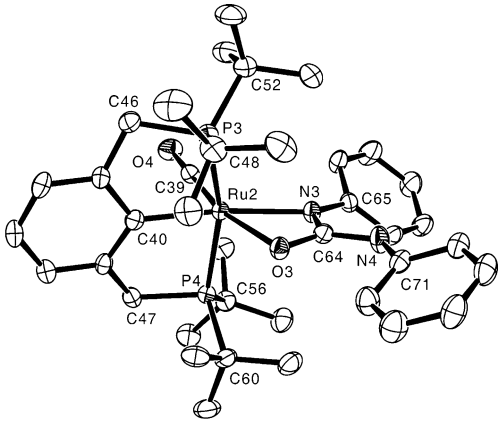
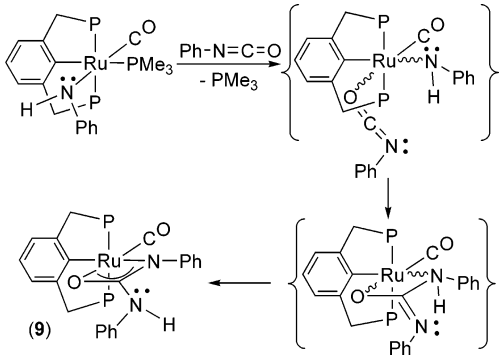


Figure 4. ORTEP of (PCP)Ru(CO){N(Ph)C(NHPh)O} (**9**) (30% probability). Selected bond lengths (Å) and angles (deg): Ru2−O3, 2.261(3); Ru2−N3, 2.208(3); N3−C64, 1.317(5); O3−C64, 1.274(5);, Ru2−C39, 1.787(5); Ru2−N3−C65, 139.7(3); Ru2−N3−C64, 92.6(3); Ru2−O3−C64, 91.4(3); N3−C64−O3, 116.6(4); N3−C64−N4, 123.1(4); O3−C64−N4, 120.3(4); C64−N4−C71, 128.5(4).

Scheme 5. Possible Pathway for the Conversion of (PCP)Ru(CO)(NHPh)(PMe_3) (**1**) and Phenylisocyanate to (PCP)Ru(CO){N(Ph)C(NHPh)O} (**9**)



C64−N4−C71 bond angle of 128.5(4)° is consistent with N−C double bond character. Details of the second structure can be found in the Supporting Information.

The use of transition metal complexes as catalysts for the amine/carboxamide transamidation has recently been reported.[73] Although detailed mechanistic studies have not been reported, it was suggested that activation of the carboxamide by the Lewis acidic metal in combination with a nucleophilic amide ligand might be important for catalytic activity. Thus, we explored the reaction of complex **1** with carboxamides. The combination of (PCP)Ru(CO)(PMe_3)(NHPh) and 1 equiv of benzanilide or *N*-methylacetamide at room temperature converts quantitatively to free aniline and the amidate complexes (PCP)Ru(CO){OC(Ph)N(Ph)} (**10**) and (PCP)-Ru(CO){OC(Me)N(Me)} (**11**) (Scheme 4). Complexes **10** and **11** are isolated in 55% and 50% yield, respectively. In a similar set of transformations, Shafer et al. have recently reported the conversion of Ti and Zr amido complexes to amidate complexes upon reaction with carboxamides.[74] The structure of the amidate complex **10** has been determined by a single-crystal X-ray diffraction study (Figure 5 and

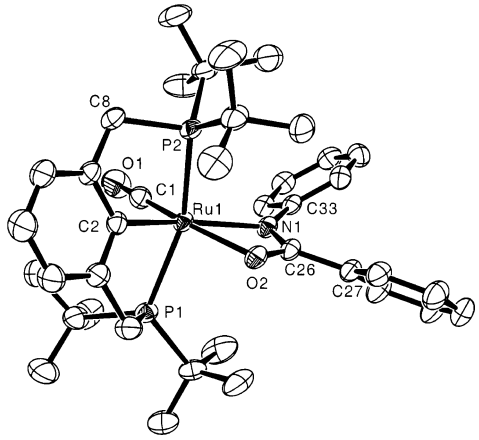
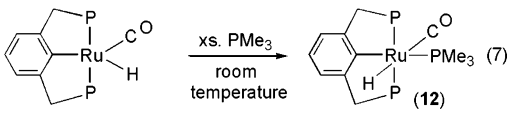


Figure 5. ORTEP of (PCP)Ru(CO){OC(Ph)N(Ph)} (**10**) (30% probability). Selected bond lengths (Å) and angles (deg): Ru1−C1, 1.787(5); Ru1−N1, 2.186(3); Ru1−O2, 2.206(2); N1−C26, 1.311(5); O2−C26, 1.283(4); C26−C27, 1.500(5); Ru1−N1−C33, 135.4(2); Ru1−N1−C26, 92.8(2); Ru1−O2−C26, 92.7(2); O2−C26−N1, 114.8(3); N1−C26−C27, 126.5-(4); O2−C26−C27, 118.6(3).

Table 1). Similar to complex **9**, the amidate oxygen is trans to the Ru−CO bond. The amidate N1−C26 bond distance of complex **10** (1.311(5) Å) is statistically identical to the analogous bond of complex **9** (1.317(5) Å), and the C26−C27 bond distance of 1.500(5) Å is close to the value for a C−C single bond.

The amidate complexes **10** and **11** do not react with free amine NH_2R to initiate "NR" metathesis reactions. For example, a solution of excess aniline and (PCP)Ru(CO){OC(Me)-N(Me)} (**11**) showed no observed reaction after 2 days at room temperature, and only minor decomposition was observed after heating to 90 °C for 24 h without formation of (PCP)Ru(CO){OC(Me)N(Ph)} or methylamine (Scheme 4).

Complex **1** also initiates N−C bond formation with carbonyl groups of aldehydes. For example, the reaction of (PCP)Ru(CO)(PMe_3)(NHPh) with benzaldehyde produces the amidate complex (PCP)Ru(CO){OC(Ph)N(Ph)} (**10**) (Scheme 4). The transformation results in the *net* removal of dihydrogen from the amido complex (PCP)Ru(CO)(PMe_3)-(NHPh) and benzaldehyde. In addition to the formation of complex **10** (40%), free PCPH is produced in approximately 30% yield along with the Ru(II) hydride complexes (PCP)-Ru(CO)(PMe_3)H (**12**) (10%) and (PCP)Ru(CO)H (5%) as well as a small amount of an uncharacterized species (observed by ^{31}P NMR spectroscopy). The hydride complex (PCP)Ru(CO)H has been previously reported,[75] and the identity of complex **12** was confirmed by independent preparation and characterization (eq 7). The phosphorus−



(7)

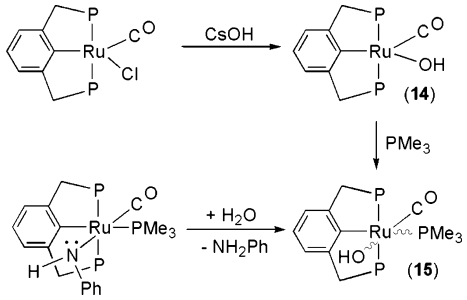
hydrogen coupling constants of **12** suggest that the PMe_3 and hydride ligands are in a cis orientation (see Experimental Section).

(73) Eldred, S. E.; Stone, D. A.; Gellman, S. H.; Stahl, S. S. *J. Am. Chem. Soc.* **2003**, *125*, 3422−3423.

(74) Li, C.; Thomson, R. K.; Gillon, B.; Patrick, B. O.; Schafer, L. L. *Chem. Commun.* **2003**, 2462−2463.

(75) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Y. *Organometallics* **2000**, *19*, 3429−3434.

Scheme 6. Preparation of Ru(II) Hydroxide Complexes

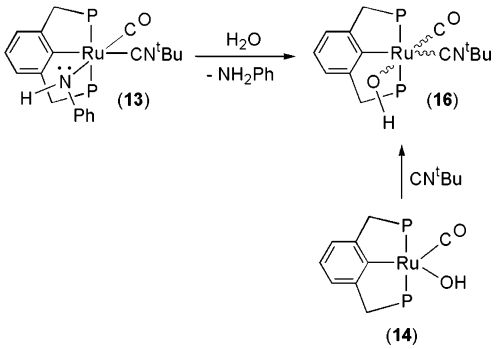


Although the detailed mechanism of the transformation of complex **1** and benzaldehyde has not been determined, the reaction bears some similarity to the organic reaction of aromatic aldehydes with strong bases (e.g., NaOH) to produce an alcohol and carboxylate (i.e., the Cannizzaro reaction).[76]

The combination of complex **1** and *t*-BuNC at room temperature results initially in a ligand exchange to produce (PCP)Ru(CO)(CN^{t}Bu)(NHPh) (**13**) and free PMe_3 (Scheme 4). Complex **13** has been isolated in 41% yield. The stereochemistry of complex **13** has not been determined. As discussed above, NMR spectroscopy reveals no evidence of reaction between complex **13** and excess NCMe after 48 h at room temperature. Heating complex **13** in C_6D_6 to 90 °C does not result in observable reactivity between the amido and isonitrile ligands; rather, the formation of a previously reported cyclometalated species and free aniline is observed (Scheme 4).[39] The cyclometalated complex is in equilibrium with a second complex that likely results from coordination of *t*-BuNC.

Ru(II) Hydroxide Complex. If reaction conditions are not carefully controlled, several of the complexes discussed herein are observed to undergo transformation to a new complex. Anticipating the possible involvement of water leading to the formation of a Ru(II) hydroxide complex, we prepared (PCP)Ru(CO)(OH) (**14**) (92% isolated yield) upon reaction of (PCP)Ru(CO)Cl with CsOH at room temperature (Scheme 6). The reaction of **14** with PMe_3 at room temperature cleanly generates the octahedral complex (PCP)-Ru(CO)(PMe_3)(OH) (**15**) (97% isolated yield; Scheme 6). The conversion of **14** to **15** results in an upfield shift for the resonance of the hydroxyl proton from 3.85 to −4.42 ppm. The upfield chemical shift of **15** relative to **14** is consistent with the disruption of hydroxide to Ru π-donation upon conversion from a five-coordinate Ru(II) complex to an octahedral 18-electron system since the inability of the hydroxide ligand to π-donate to Ru(II) for complex **15** likely increases electron-density at the hydroxide moiety. Examples of transformations that produce (PCP)Ru(II) hydroxide complexes include reaction of the anilido complex (PCP)-Ru(CO)(PMe_3)(NHPh) (**1**) with water to produce complex **15** and the addition of water to (PCP)Ru(CO)(CN^{t}Bu)(NHPh) (**13**) to yield (PCP)Ru(CO)(CN^{t}Bu)(OH) (**16**) (Schemes 6 and 7). Complex **16** has been independently prepared and isolated in 95% yield upon reaction of (PCP)Ru(CO)(OH) (**14**) with CN^{t}Bu at room temperature. The stereochemistry of **16** has not been determined.

Scheme 7. Reactions that Produce (PCP)Ru(CO)(CN^{t}Bu)(OH) (**16**)



Summary and Conclusions

The octahedral Ru(II) complex (PCP)Ru(CO)(PMe_3)-(NHPh) (**1**) reacts with a range of substrates to initiate N−C bond formations that produce aza-metallacycles. Although the kinetic details of each reaction have not been probed, we suggest that the reaction pathways are likely to be analogous to the reaction of the anilido complex and acetonitrile with trimethylphosphine dissociation, substrate coordination, and intramolecular nucleophilic attack of the amido nitrogen at the β-carbon of the coordinated substrate.[40] These transformations demonstrate the feasibility of using metal-centered Lewis acidity in combination with the nucleophilicity at the amido ligand to mediate control of N−C bond-forming reactions. Consistent with the suggested reactivity patterns, the coordination of *tert*-butyl isonitrile to the fragment (PCP)Ru(CO)(NHPh) does not produce subsequent reactivity since intramolecular nucleophilic attack would result in N_{amido} addition to an electron-rich nitrogen of the isonitrile ligand. Such reactions could ultimately provide methodologies for controlled N−C bond forming transformations.

Experimental Section

General Methods. All procedures were performed under an atmosphere of dinitrogen in a glovebox or using standard Schlenk techniques. Oxygen levels were <15 ppm for glovebox manipulations. Benzene and tetrahydrofuran were distilled from sodium/benzophenone. Pentane and methanol were distilled from P_2O_5. Acetonitrile was distilled from P_2O_5 followed by distillation from CaH_2. Methylene chloride was purchased as an OptiDry solvent (<50 ppm H_2O) and passed through two columns of activated alumina prior to use. All solvent manipulations were performed under an atmosphere of dinitrogen. C_6D_6, CD_2Cl_2, and $CDCl_3$ were degassed via three freeze−pump−thaw cycles and stored over 4 Å molecular sieves. ^{1}H and ^{13}C NMR measurements were performed on either a Varian Mercury 300 or 400 MHz spectrometer and referenced to TMS using resonances due to residual protons in the deuterated solvents or the ^{13}C resonances of the deuterated solvents. All ^{31}P NMR spectra were recorded on a Varian Mercury instrument operating at a frequency of 161 MHz with 85% phosphoric acid (0 ppm) as external standard. All ^{19}F spectra were recorded on a Varian Mercury instrument operating at a frequency of 376.5 MHz with CF_3CO_2H (−78.5 ppm) as external standard.

(76) March, J. *Advanced Organic Chemistry*: *Reactions, Mechanisms, and Structure*, 4th ed.; John Wiley and Sons: New York, 1992.

GC−MS was performed using a HP GCD system with a 30 m × 0.25 mm HP-5 column with 0.25 μm film thickness. IR spectra were acquired using a Mattson Genesis II FT-IR as solutions in a KBr solvent cell. Elemental analyses were conducted by Atlantic Microlab, Inc. (PCP)Ru(CO)Cl, (PCP)Ru(CO)OTf, (PCP)Ru(CO)(NHPh), (PCP)Ru(CO)(PMe_3)(NHPh) (**1**), (PCP)Ru(CO)(N(Ph)C(Me)NH) (**2**), (PCP)Ru(CO)(N(Ph)C(C_6F_5)NH) (**6**), (PCP)Ru(CO)(H), and *N*,*N*′-dihexylcarbodiimide were synthesized as previously reported.[39,40,75,77] Benzonitrile, *p*-tolunitrile, 4-fluorobenzonitrile, *tert*-butyl isocyanide, hexafluorobenzene, pentafluorobenzonitrile, pentafluoronitrobenzene, pentafluoroanisole, benzanilide, *N*-methylacetamide, and cesium hydroxide monohydrate were purchased from commercial sources and used without further purification. Phenylisocyanate and benzaldehyde were vacuum distilled prior to use.

(PCP)Ru(CO)(N(Ph)C(Ph)NH) (3). A 100 mL round-bottom flask was charged with (PCP)Ru(CO)Cl (0.460 g, 0.82 mmol), 40 mL of benzene, and excess PMe_3 (0.2 mL, 1.9 mmol). To this solution was added 1.5 equiv of LiNHPh (0.130 g, 1.3 mmol). After stirring for 30 min, excess benzonitrile (1.0 mL, 9.8 mmol) was added, and the reaction mixture was stirred for 24 h. The volatiles were evaporated under reduced pressure, and the residue was washed with acetonitrile to give a yellow-green powder that was collected by vacuum filtration and dried in vacuo (0.280 g, 48%). IR (THF solution): $\nu_{CO} = 1898\ cm^{-1}$, $\nu_{NH} = 3342\ cm^{-1}$. ^1H NMR ($CDCl_3$, δ): 7.24 (5H, m, phenyl), 7.03 (2H, t, J_{HH} = 12 Hz, phenyl), 6.90 (2H, d, J_{HH} = 7 Hz, phenyl), 6.70 (4H, m, phenyl), 4.88 (1H, *br* s, NH), 3.36 (4H, m, PCP CH_2), 1.23 (18H, vt, N = 12 Hz, PCP CH_3), 1.19 (18H, vt, N = 12 Hz, PCP CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 77.9. $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 212.1 (CO, t, J_{PC} = 13 Hz), 169.2, 167.2, 150.6, 147.9, 137.4, 131.9, 131.8, 128.8, 128.4, 128.3, 127.7, 123.7, 123.2, 121.4 (phenyl and N*C*N), 37.2−37.8 (overlapping multiplets, PCP *C*H_2 and *C*Me_3), 31.4, 31.1 (vt, N = 4 Hz, PCP *C*H_3). Anal. Calcd for $C_{38}H_{54}N_2OP_2Ru$: C, 63.49; H, 7.58; N, 3.90. Found: C, 63.65; H, 7.72; N, 3.82.

(PCP)Ru(CO)(N(Ph)C(*p*-FC_6H_4)NH) (4). The reaction procedure is analogous to that reported for complex **3**; however, *p*-FC_6F_4CN was used in place of benzonitrile and the final isolation was performed by dissolving the residue in 2 mL of benzene and adding 10 mL of acetonitrile to precipitate the product. Vacuum filtration through a fine porosity frit allowed collection of the green solid that was dried under vacuum (49% isolated yield). IR (THF solution): $\nu_{CO} = 1898\ cm^{-1}$, $\nu_{NH} = 3344\ cm^{-1}$. ^1H NMR (C_6D_6, δ): 7.00−7.12 (9H, overlapping m's, phenyl), 6.74 (1H, t, J_{HH} = 7 Hz, phenyl), 6.60 (2H, t, J_{HH} = 8 Hz, phenyl), 4.59 (1H, *br* s, N*H*), 3.20 (4H, m, PCP CH_2), 1.17 (18H, vt, N = 12 Hz, PCP CH_3), 1.06 (18H, vt, N = 12 Hz, PCP CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 78.6. $^{19}F\{^1H\}$ NMR (C_6D_6, δ): −111.8. $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 212.0 (t, J_{PC} = 13 Hz, *C*O), 169.0, 165.8, 164.6, 161.3, 150.4, 147.8, 133.4, 129.7, 129.6, 128.5, 128.4, 123.7, 123.2, 121.4, 120.0, 115.4, 115.1 (phenyl and N*C*N), 37.1−37.7 (PCP *C*H_2 and *C*Me_3, overlapping multiplets), 31.3, 31.0 (each a vt, N = 4 Hz, PCP *C*H_3). Anal. Calcd for $C_{38}H_{53}FN_2OP_2Ru$: C, 62.02; H, 7.26; N, 3.81. Found: C, 62.52; H, 7.13; N, 3.82.

(PCP)Ru(CO)(N(Ph)C(*p*-MeC_6H_4)NH) (5). The reaction procedure is analogous to that reported for complex **3**; however, *p*-MeC_6H_4CN was used in place of benzonitrile and the final isolation was performed by dissolving the residue in 2 mL of benzene and adding 10 mL of acetonitrile to precipitate the product. Vacuum filtration through a fine porosity frit allowed collection of the green solid that was dried under vacuum (52% isolated yield). IR (THF solution): $\nu_{CO} = 1898\ cm^{-1}$, $\nu_{NH} = 3348\ cm^{-1}$. ^1H NMR (C_6D_6, δ): 7.24 (2H, d, J_{HH} = 8 Hz, phenyl), 7.13 (4H, m, phenyl), 7.02 (3H, m, phenyl), 6.82 (2H, d, J_{HH} = 7 Hz, phenyl), 6.74 (1H, d, J_{HH} = 7 Hz, phenyl), 4.73 (1H, *br* s, N*H*), 3.21 (4H, m, PCP CH_2), 1.95 (3H, s, *p*-CH_3), 1.19 (18H, vt, N = 12 Hz, PCP CH_3), 1.10 (18H, vt, N = 12 Hz, PCP CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 78.6. $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 212.1 (*C*O, t, J_{PC} = 13 Hz), 169.3, 167.4, 150.8, 147.9, 138.6, 134.7, 129.0, 128.4, 127.7, 123.7, 123.1, 121.4, 119.7 (phenyl and N*C*N), 37.1−37.7 (PCP *C*H_2 and *C*Me_3, overlapping multiplets), 31.4, 31.0 (each a vt, N = 4 Hz, PCP *C*H_3), 21.5 (phenyl *C*H_3). Anal. Calcd for $C_{39}H_{56}N_2OP_2Ru$: C, 64.00; H, 7.71; N, 3.81. Found: C, 64.15; H, 7.43; N, 3.61.

(PCP)Ru(CO)(F)(N(H)C(C_6F_5)NHPh) (7). A round-bottom flask was charged with benzene (∼10 mL), (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) (0.200 g, 0.25 mmol), C_6F_5CN (0.480 g, 2.5 mmol), and H_2O (45 μL, 2.5 mmol). The resulting solution was stirred for 12 h. The volatiles were evaporated under reduced pressure, the residue washed with 2 × 10 mL of pentane and then collected by vacuum filtration. The brown microcrystalline solid was dried in vacuo (0.165 g, 80%). IR (CH_2Cl_2 solution): $\nu_{CO} = 1896\ cm^{-1}$, $\nu_{NH} = 3364\ cm^{-1}$. ^1H NMR (CD_2Cl_2, δ): 12.7 (1H, FLHN(Ph), d, J_{HF} = 62 Hz), 7.14 (2H, phenyl, d, J_{HH} = 7 Hz), 7.01 (1H, phenyl, t, J_{HH} = 7 Hz), 6.94 (2H, phenyl, d, J_{HH} = 7 Hz), 6.81 (1H, *br* s, Ru−N*H*), 6.78 (1H, t, J_{HH} = 7 Hz, phenyl), 6.70 (2H, d, J_{HH} = 7 Hz, phenyl), 3.50 (2H, m, PCP CH_2), 3.27 (2H, m, PCP CH_2), 1.32 (18H, vt, N = 12 Hz, PCP CH_3), 1.23 (18H, vt, N = 12 Hz, PCP CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 80.5 (d, J_{PF} = 17 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 169.2, 156.1, 149.0, 139.1, 129.3, 124.8, 123.1, 122.4, 121.5 (phenyl and N*C*N), 36.1 (overlapping m's, PCP *C*H_2 and *C*Me_3), 30.9, 30.7 (each a vt, N = 4 Hz, PCP *C*H_3), CO and C_6F_5 ring carbons were not observed due to C−F coupling. ^{19}F NMR (CD_2Cl_2, δ): −11.3 (dt, J_{HF} = 62 Hz, J_{PF} = 17 Hz), −139.3, −151.7, −160.9 (each multiplet, C_6F_5 ring). Repeated attempts to obtain elemental analysis failed to produce satisfactory results. NMR spectra of complex **6** are provided in the Supporting Information.

(PCP)Ru(CO)[PhNC{NH(hx)}N(hx)] (8). (PCP)Ru(CO)OTf (0.2100 g, 0.31 mmol) was dissolved in 10 mL of THF, and approximately 2 equiv of LiNHPh (0.060 g, 0.61 mmol) was added. After stirring for approximately 30 min, the volatiles were evaporated under reduced pressure. The residue was extracted with 10 mL of benzene and filtered through a fine porosity frit. The dark green filtrate was combined with excess PMe_3 (0.1 mL, 1 mmol), and the color changed to yellow. Two equivalents of *N*,*N*-dihexylcarbodiimide (0.1300 mg, 0.62 mmol) was added to the solution, and the reaction mixture was stirred for 2 h. The solution was concentrated to approximately 3 mL, and 10 mL of CH_3CN was added to precipitate the product. Filtration through a fine porosity frit and drying in vacuo provided a green powder (0.105 g, 41%). Crystals suitable for an X-ray diffraction study were obtained by cooling a toluene/acetonitrile (1:5) solution to −20 °C for a several days. IR (THF solution): $\nu_{CO} = 1894\ cm^{-1}$. ^1H NMR (C_6D_6, δ): 7.40 (2H, d, J_{HH} = 8 Hz, phenyl), 7.30 (2H, t, J_{HH} = 8 Hz, phenyl), 7.02 (3H, s, PCP phenyl), 6.80 (1H, t, J_{HH} = 8 Hz, phenyl), 3.30 (2H, m, PCP CH_2), 3.16 (2H, m, PCP CH_2), 3.00 (4H, m, NCH_2), 1.60 (2H, m, CH_2), 1.0−1.3 (50H, overlapping m's, PCP CH_3 and hexyl), 0.80 (6H, overlapping m's, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 75.3. $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 212.5 (t, J_{PC} = 16 Hz, *C*O), 170.5, 159.1, 153.2, 148.2, 129.4, 128.2, 123.8, 122.8, 121.7, 121.1, 117.0 (phenyl and N*C*N), 48.1, 44.3, 42.3, 37.6, 37.3, 36.7, 32.2, 32.0, 31.7, 30.9, 30.5, 30.1, 28.6, 27.0,

(77) Gusev, D. G.; Madott, M.; Dolgushin, F. M.; Lyssenko, K. A.; Antipin, M. Y. *Organometallics* **2000**, *19*, 1734−1739.

23.0, 14.4 (PCP *C*H$_3$ and hexyl). Anal. Calcd for $C_{44}H_{75}N_3OP_2Ru$: C, 64.05; H, 9.16; N, 5.09. Found: C, 64.00; H, 9.15; N, 5.01.

(PCP)Ru(CO){N(Ph)C(NHPh)O} (9). (PCP)Ru(CO)OTf (0.430 g, 0.64 mmol) was dissolved in 20 mL of THF, and 2 equiv of LiNHPh (0.120 g, 1.2 mmol) was added. After stirring for approximately 30 min, the volatiles were evaporated under reduced pressure. The residue was extracted with 10 mL of benzene and filtered through a fine porosity frit. The dark green benzene filtrate was combined with excess PMe_3 (0.2 mL, 2 mmol), and the color changed to yellow. Excess phenyl isocyanate (0.10 mL, 0.92 mmol) was added to the reaction solution followed by stirring for 1 h. The reaction solution was reduced to dryness under reduced pressure, and the residual material was washed with MeOH. Vacuum filtration through a fine porosity frit followed by drying in vacuo yielded a green powder (0.200 g, 44%). Crystals suitable for an X-ray diffraction study were obtained by cooling a toluene/pentane (1:5) solution of **9** to −20 °C for 1 day. IR (THF solution): ν_{CO} = 1902 cm^{-1}. ^{1}H NMR (C_6D_6, δ): 7.36 (2H, d, J_{HH} = 7 Hz, phenyl), 7.27 (2H, t, J_{HH} = 7 Hz, phenyl), 7.15 (2H, d, J_{HH} = 7 Hz, phenyl), 7.04 (5H, overlapping m's, phenyl), 6.87 (1H, t, J_{HH} = 7 Hz, phenyl), 6.76 (1H, t, J_{HH} = 7 Hz, phenyl), 3.25 (4H, m, PCP C*H*$_2$), 1.18 (18H, vt, N = 12 Hz, PCP C*H*$_3$), 1.11 (18H, vt, N = 12 Hz, PCP C*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 75.6. ^{13}C{^{1}H} NMR (C_6D_6, δ): 211.3 (t, J_{PC} = 13 Hz, *C*O), 167.6, 155.4, 149.0, 148.1, 139.4, 129.8, 128.8, 123.5, 123.3, 121.8, 121.1, 117.9 (phenyl and N*C*N), 37.3, 36.8 (each a t, J_{PC} = 5 Hz, PCP *C*Me$_3$), 36.5 (t, J_{PC} = 10 Hz, PCP *C*H$_2$), 30.8, 30.7 (each a t, J_{PC} = 2 Hz, PCP *C*H$_2$). Anal. Calcd for $C_{38}H_{54}N_2O_2P_2Ru$: C, 62.19; H, 7.42; N, 3.82. Found: C, 62.13; H, 7.08; N, 3.74.

(PCP)Ru(CO){OC(Ph)N(Ph)} (10). (PCP)Ru(CO)OTf (0.190 g, 0.28 mmol) was dissolved in 10 mL of THF, and 2 equiv of LiNHPh (0.050 g, 0.51 mmol) was added. The mixture was stirred for 30 min, and then the volatiles were removed under reduced pressure. The residue was extracted with 10 mL of benzene and filtered through a fine porosity frit. The dark green benzene filtrate was combined with PMe_3 (0.1 mL, 1 mmol) with a color change to yellow observed. One equivalent of benzanilide (0.055 g, 0.28 mmol) was added, and the reaction mixture was stirred for 2 h. The solution was concentrated to 3 mL under reduced pressure, and 10 mL of CH_3CN was added to precipitate the product. Filtration through a fine porosity frit and drying in vacuo yielded a green powder (0.110 g, 55%). Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a pentane solution of **10**. IR (THF solution): ν_{CO} = 1902 cm^{-1}. ^{1}H NMR (C_6D_6, δ): 7.67 (2H, m, phenyl), 7.28 (2H, d, J_{HH} = 8 Hz, phenyl), 7.10 (2H, t, J_{HH} = 6 Hz, phenyl), 7.06 (3H, s, PCP phenyl), 6.98 (3H, m, phenyl), 6.82 (1H, t, J_{HH} = 6 Hz, phenyl), 3.34 (2H, m, PCP C*H*$_2$), 3.22 (2H, m, PCP C*H*$_2$), 1.15 (36H, overlapping m's, PCP C*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 75.9. ^{13}C{^{1}H} NMR (C_6D_6, δ): 211.4 (t, J_{PC} = 12 Hz, *C*O), 170.7, 167.9, 149.0, 148.6, 135.7, 126.6, 129.4, 128.6, 124.5, 123.5, 122.2, 121.7 (phenyl and N*C*N), 37.6, 36.9 (t, J_{PC} = 6 Hz, PCP *C*Me$_3$), 36.7 (t, J_{PC} = 10 Hz, PCP *C*H$_2$), 31.0, 30.8 (vt, N = 4 Hz, PCP *C*H$_3$). Anal. Calcd for $C_{38}H_{53}NO_2P_2Ru$: C, 63.49; H, 7.43; N, 1.95. Found: C, 63.49; H, 7.47; N, 2.02.

(PCP)Ru(CO){OC(Me)N(Me)} (11). The procedure used is analogous to that for complex **10** with **11** isolated in 50% yield. IR (THF solution): ν_{CO} = 1902 cm^{-1}. ^{1}H NMR (C_6D_6, δ): 7.06 (3H, m, phenyl), 3.30 (2H, m, PCP C*H*$_2$), 3.15 (2H, m, PCP C*H*$_2$), 2.96 (3H, s, C*H*$_3$), 1.49 (3H, s, C*H*$_3$), 1.24 (18H, vt, N = 12 Hz, PCP C*H*$_3$), 1.18 (18H, vt, N = 12 Hz, PCP C*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 75.0. ^{13}C{^{1}H} NMR (C_6D_6, δ): 210.7 (t, J_{PC} = 12 Hz, *C*O), 173.6, 169.4, 149.5, 122.9, 121.3 (phenyl and N*C*N), 36.2−37.8 (overlapping multiplets, PCP C*H*$_3$), 30.9, 30.8 (vt, N = 4 Hz, PCP *C*H$_3$), 19.2 (s, *C*H$_3$). Anal. Calcd for $C_{28}H_{49}NO_2P_2Ru$: C, 56.55; H, 8.30; N, 2.36. Found: C, 56.53; H, 8.06; N, 2.34.

(PCP)Ru(CO)(PMe$_3$)(H) (12). (PCP)Ru(CO)H (0.100 g, 0.19 mmol) was dissolved in 10 mL of benzene. Excess PMe_3 (0.1 mL, 1.1 mmol) was added via syringe with an immediate color change from red to yellow. After stirring for 10 min, the volatiles were removed under reduced pressure to give a yellow powder (0.110 g, 96%). IR (THF solution): ν_{CO} = 1900 cm^{-1}. ^{1}H NMR (C_6D_6, δ): 7.00 (3H, m, phenyl), 3.16 (4H, overlapping m's, PCP C*H*$_2$), 1.28 (18H, vt, N = 12 Hz, PCP C*H*$_3$), 1.22 (18H, vt, N = 12 Hz, PCP C*H*$_3$), 0.92 (9H, d, J_{PH} = 5 Hz, P(C*H*$_3$)$_3$), −9.60 (1H, m, Ru-*H*). ^{31}P{^{1}H} NMR (C_6D_6, δ): 104.5 (*br* s, PCP), −22.3 (*br* s, PMe_3). ^{13}C{^{1}H} NMR (C_6D_6, δ): 207.5 (m, CO), 150.4, 138.5, 122.9, 120.5 (phenyl), 40.4, 38.4, 35.2 (PCP *C*H$_2$ and *C*Me$_3$), 31.4, 29.7 (vt, N = 4 Hz, PCP *C*H$_3$), 21.1 (d, $^1J_{PC}$ = 16 Hz, PMe_3). Anal. Calcd For $C_{28}H_{53}OP_3Ru$: C, 56.08; H, 8.91. Found: C, 55.67; H, 8.89.

(PCP)Ru(CO)(CN^{t}Bu)(NHPh) (13). (PCP)Ru(CO)OTf (0.2100 g, 0.31 mmol) was dissolved in 10 mL of THF, and 2 equiv of LiNHPh (0.060 g, 0.61 mmol) was added. After stirring for 30 min, the volatiles were evaporated under reduced pressure. The residue was extracted with 10 mL of benzene and filtered through a fine porosity frit. The dark green benzene filtrate was combined with PMe_3 (0.1 mL, 1 mmol) with an immediate color change to yellow. Two equivalents of *tert*-butyl isonitrile (0.07 mL, 0.6 mmol) was added, and the reaction mixture was stirred for 30 min. The solution was concentrated to 1 mL under reduced pressure, and 10 mL of CH_3CN was added to precipitate the product. Filtration through a fine porosity frit and drying in vacuo provided a green powder (0.090 g, 42%). IR (THF solution): ν_{CO} = 1923 cm^{-1}, ν_{NH} = 3346 cm^{-1}, ν_{CN} = 2124 cm^{-1}. ^{1}H NMR (C_6D_6, δ): 7.20 (1H, t, J_{HH} = 7 Hz, phenyl), 7.13 (3H, overlapping m's, phenyl), 7.02 (1H, t, J_{HH} = 7 Hz, phenyl), 6.68 (1H, d, J_{HH} = 7 Hz, phenyl), 6.39 (1H, t, J_{HH} = 7 Hz, phenyl), 6.14 (1H, d, J_{HH} = 7 Hz, phenyl), 3.47 (2H, m, PCP C*H*$_2$), 3.23 (2H, m, PCP C*H*$_2$), 1.21 (18H, vt, N = 12 Hz, PCP C*H*$_3$), 1.17 (9H, s, CN^{t}Bu C*H*$_3$), 1.10 (18H, vt, N = 12 Hz, PCP C*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 83.2. ^{13}C{^{1}H} NMR (C_6D_6, δ): 206.7 (*C*O, t, $^2J_{PC}$ = 12 Hz), 175.0, 163.1, 156.0, 148.6, 124.2, 122.3, 118.8, 114.5, 108.0 (phenyl and *C*N^{t}Bu), 56.2 (s, N*C*Me$_3$), 38.0 (PCP *C*H$_2$, t, J_{PC} = 10 Hz), 37.1, 36.7 (PCP *C*Me$_3$, each t, J_{PC} = 6 Hz), 31.6, 31.1 (PCP *C*H$_3$, each vt, N = 4 Hz), 30.4 (isonitrile *C*H$_3$). Anal. Calcd For $C_{36}H_{58}N_2OP_2Ru$: C, 61.96; H, 8.38; N, 4.01. Found: C, 62.02; H, 8.39; N, 3.96.

(PCP)Ru(CO)(OH) (14). To a solution of (PCP)Ru(CO)Cl (0.200 g, 0.36 mmol) in 15 mL of THF was added an excess of CsOH·H$_2$O. The mixture was stirred overnight (∼12 h), and the CO absorption (IR spectroscopy) was observed to change from 1919 to 1896 cm^{-1}. The solution was filtered through a fine porosity frit, and the volatiles were removed from the filtrate under reduced pressure to give a brown powder (0.180 g, 92%). NMR and IR spectroscopy revealed a clean product, and no further purification steps were taken. IR (THF solution): ν_{CO} = 1896 cm^{-1}. ^{1}H NMR (C_6D_6, δ): 6.98 (3H, m, phenyl), 3.85 (1H, *br* s, OH), 3.03 (4H, overlapping m's, PCP C*H*$_2$), 1.22 (36H, overlapping m's, PCP C*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 67.3. ^{13}C{^{1}H} NMR (C_6D_6, δ): 212.2 (*C*O, t, $^2J_{PC}$ = 12 Hz), 162.9 (t, J_{PC} = 2 Hz, phenyl), 149.4 (t, J_{PC} = 7 Hz, phenyl), 128.0 (s, phenyl), 122.4 (t, J_{PC} = 7 Hz, phenyl), 36.8, 35.7 (each a vt, N = 14 Hz, PCP *C*Me$_3$), 34.2 (vt, N = 20 Hz, PCP *C*H$_2$), 30.0 (overlapping m's, PCP *C*H$_3$). Anal. Calcd For $C_{25}H_{44}O_2P_2Ru$: C, 55.64; H, 8.22. Found: C, 55.40; H, 8.10.

(PCP)Ru(CO)(PMe$_3$)(OH) (15). To a solution of (PCP)Ru(CO)-(OH) (0.100 g, 0.2 mmol) in 10 mL of benzene was added excess

PMe_3 (0.1 mL). Upon addition of PMe_3, the color of the solution changed from brown to yellow. After stirring at room temperature for 5 min, the volatiles were evaporated under reduced pressure to give a yellow powder. After drying in vacuo, 0.110 g of the yellow powder was isolated (97%). IR (THF solution): $\nu_{CO} = 1892\ cm^{-1}$. ^1H NMR (C_6D_6, δ): 7.11 (3H, m, phenyl), 3.50 (2H, m, PCP CH_2), 3.23 (2H, m, PCP CH_2), 1.45 (9H, d, $^2J_{PH} = 6$ Hz, PMe_3), 1.24 (18H, vt, $N = 12$ Hz, PCP CH_3), 1.17 (18H, vt, $N = 12$ Hz, PCP CH_3), −4.42 (1H, d, $J_{PH} = 8$ Hz, OH). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 74.9 (d, $^2J_{PP} = 20$ Hz, PCP phosphine), −23.2 (t, $^2J_{PP} = 20$ Hz, *P*Me_3). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 206.2 (*C*O, m), 148.5 (t, $J_{PC} = 7$ Hz, phenyl), 128.9 (s, phenyl), 124.3 (s, phenyl), 122.0 (m, phenyl), 39.8 (m, PCP *C*H_2), 38.7, 37.3 (each a vt, $N = 4$ Hz, PCP *C*Me_3), 31.7, 31.3 (each a vt, $N = 4$ Hz, PCP *C*H_3), 23.0 (d, $^1J_{PC} = 18$ Hz, P(*C*H_3)$_3$). Anal. Calcd For $C_{28}H_{53}O_2P_3Ru$: C, 54.62; H, 8.68. Found: C, 54.71; H, 8.48.

(PCP)Ru(CO)(CN^{t}Bu)(OH) (16). Excess CN^{t}Bu (0.1 mL) was added to a solution of (PCP)Ru(CO)(OH) (**14**) (0.100 g, 0.19 mmol) in 10 mL of benzene. The addition of the isonitrile resulted in an immediate color change from brown to yellow. After stirring for 5 min, the volatiles were removed under reduced pressure to give a pale yellow powder. After drying in vacuo, 0.105 g of yellow powder was isolated (95%). IR (THF solution): $\nu_{CN} = 2123\ cm^{-1}$, $\nu_{CO} = 1906\ cm^{-1}$. ^1H NMR (C_6D_6, δ): 7.16 (3H, m, phenyl), 3.64 (2H, m, PCP CH_2), 3.24 (2H, m, PCP CH_2), 1.37 (18H, vt, $N = 12$ Hz, PCP CH_3), 1.28 (18H, vt, $N = 12$ Hz, PCP CH_3), 1.04 (9H, s, isonitrile CH_3), −4.53 (*br* s, OH). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 86.8. $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 206.0 (*C*O, t, $^2J_{PC} = 12$ Hz), 176.8, 149.0, 128.4, 123.7, 121.6 (PCP phenyl and *C*N), 55.6 (*C*NCMe_3), 37.7 and 36.5 (overlapping, PCP *C*H_2 and *C*Me_3), 31.1 and 30.9 (each a vt, $N = 4$ Hz, PCP *C*H_3), 30.6 (CN*C*Me_3). Anal. Calcd for $C_{30}H_{53}NO_2P_2Ru$: C, 57.86; H, 8.58; N, 2.25. Found: C, 57.79; H, 8.43; N, 2.29.

Reaction of (PCP)Ru(CO)(NHPh)(PMe_3) (1) with Benzaldehyde. A screw-cap NMR tube was charged with 20 mg of (PCP)-Ru(CO)(NHPh)(PMe_3) (**1**) in 0.6 mL of C_6D_6. Approximately 2 equiv of benzaldehyde (~5 μL) was added via microsyringe. After 12 h at room temperature, the color of the reaction solution changed from green to yellow. The ^1H NMR spectrum revealed a complex mixture of products. ^{31}P NMR spectroscopy showed two major products consistent with formation of the amidate complex (PCP)-Ru(CO){OC(Ph)N(Ph)} (**10**) (75.6 ppm) (~40%) and the free organic substrate PCPH (34.0 ppm) (~30%). The assignments of these resonances were confirmed upon addition of authentic samples. The existence of free PCPH was also consistent with ^{31}P NMR spectroscopy as well as a resonance at 2.9 ppm in the ^1H NMR spectrum. From the reaction mixture, complex **10** was isolated in approximately 20−30% yield depending on the scale of the reaction. The ruthenium hydride complexes (PCP)Ru(CO)(PMe_3)H (**12**) (~10%) and (PCP)Ru(CO)H (~5%) were also observed by ^1H and ^{31}P NMR spectroscopy and confirmed upon addition of authentic samples. Other uncharacterized compounds were observed by ^{31}P NMR spectroscopy with total yield of <15% as estimated by ^{31}P NMR resonances.

***p*- and *o*-MeOC$_6$F$_4$CN.** The previously reported procedure was used to prepare *p*- and *o*-$MeOC_6F_4CN$.[78] The product mixture was analyzed by ^{19}F NMR in C_6D_6. Three compounds were observed using ^{19}F NMR spectroscopy (δ): starting material C_6F_5CN: −133.2 (m), −144.6 (tt, $J_{FF} = 21.7$, 5.6 Hz), and −159.5 (m); *p*-$MeOC_6F_5CN$ (>90% product): −135.5 (d, $J_{FF} = 13$ Hz) and −157.1 (d, $J_{FF} = 13$ Hz); *o*-$MeOC_6F_4CN$ (<10% product): −133.9 (ddd, $J_{FF} = 21$, 7, 4 Hz), −147.0 (td, $J_{FF} = 21$, 4 Hz), −156.8 (ddd, $J_{FF} = 21$, 7, 4 Hz), and −162.9 (t, $J_{FF} = 21$ Hz). Some fluorine resonances exhibit evidence of coupling that is not resolved.

Reaction of (PCP)Ru(CO)(N(H)C(C$_6$F$_5$)NPh) (6), C$_6$F$_5$CN, and H$_2$O. An NMR tube was charged with complex **6** (0.0200 g, 0.025 mmol) and C_6D_6 (0.5 mL). Ten equivalents each of C_6F_5CN (0.050 g, 0.25 mmol) and H_2O (5 μL, 0.25 mmol) were added, and the solution was monitored by NMR spectroscopy. After 12 h, all of the (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) was quantitatively transformed to (PCP)Ru(CO)(F)(N(H)C(C_6F_5)NHPh) (**7**) according to ^1H, ^{31}P, and ^{19}F NMR spectroscopy. ^{19}F NMR spectroscopy also revealed multiple new resonances accompanied by excess C_6F_5CN and complex **7**. These new organic species were not assigned due to the formation of multiple species in low yields.

Reaction of (PCP)Ru(CO)(N(H)C(C$_6$F$_5$)NPh) (6), C$_6$F$_5$CN, and MeOH. An NMR tube was charged with complex **6** (0.0200 g, 0.025 mmol) and C_6D_6 (0.5 mL). Ten equivalents each of C_6F_5CN (0.050 g, 0.25 mmol) and MeOH (8 μL, 0.25 mmol) were added, and the solution was monitored by NMR spectroscopy. After 6 h, all of the complex (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) was quantitatively transformed to (PCP)Ru(CO)(F)(N(H)C(C_6F_5)-NHPh) (**7**) as determined by ^1H, ^{31}P, and ^{19}F NMR spectroscopy. ^{19}F NMR spectroscopy also revealed the new organic species *o*-$MeOC_6F_4CN$ and *p*-$MeOC_6F_4CN$ (~10:1 ratio). The identity of the organic products was confirmed by comparison with independently made compounds (see above). In addition, another organic species {−142.2 (d, $J_{FF} = 8$ Hz), −153.2 (t, $J_{FF} = 22$ Hz), −162.0 (m) by ^{19}F NMR spectroscopy} was formed by reaction of MeOH with C_6F_5CN catalyzed by the base.[63] The product mixture was also analyzed using GC−MS. The organic products *o*-$MeOC_6F_4CN$ and *p*-$MeOC_6F_4CN$ were identified as resolved GC traces with identical parent ions in the corresponding mass spectra (Mw = 205). In addition, a GC trace corresponding to the starting material C_6F_5CN was identified with Mw = 193. The third organic product was identified by GC−MS with Mw = 225 and is likely the result of addition of MeOH to the CN triple bond of C_6F_5CN to produce $C_6F_5C(=NH)OMe$ (as previously reported).[63]

Reaction of (PCP)Ru(CO)(N(H)C(C$_6$F$_5$)NPh) (6), C$_6$F$_5$NO$_2$, and MeOH. An NMR tube was charged with complex **6** (0.0200 g, 0.025 mmol) and C_6D_6 (0.5 mL). Ten equivalents each of $C_6F_5NO_2$ (0.055 g, 0.25 mmol) and MeOH (8 μL, 0.25 mmol) were added, and the solution was monitored by NMR spectroscopy. After 5 h, all of the complex (PCP)Ru(CO)(N(H)C(C_6F_5)NPh) was quantitatively transformed to (PCP)Ru(CO)(F)(N(H)C(C_6F_5)NHPh) (**7**) as determined by ^1H, ^{31}P, and ^{19}F NMR spectroscopy. ^{19}F NMR spectroscopy also revealed two new organic species. The major organic product {−148.6 (d, $J_{FF} = 20$ Hz) and −157.4 (d, $J_{FF} = 20$ Hz)} was assigned as *p*-$MeOC_6F_4NO_2$ (>90%), and the minor product {−143.2 (ddd, $J_{FF} = 23$, 7, 3 Hz), −149.8 (d, $J_{FF} = 23$ Hz) −155.2 (m), and −161.6 (t, $J_{FF} = 23$ Hz)} was assigned as *o*-$MeOC_6F_4NO_2$ (<10%). The product mixture was also analyzed by GC−MS. The organic products *p*-$MeOC_6F_4NO_2$ and *o*-$MeOC_6F_4NO_2$ were identified as resolved peaks in the GC with identical parent ion peaks (Mw = 225). The starting material $C_6F_5NO_2$ (Mw = 213) was also observed by GC−MS.

Reaction of (PCP)Ru(CO)(F)(N(H)C(C$_6$F$_5$)NHPh) (7) with KO^{t}Bu. An NMR tube was charged with (PCP)Ru(CO)(F)(N(H)C-(C_6F_5)NHPh) (**7**) (0.0200 g, 0.24 mmol) and C_6D_6 (0.5 mL). Excess KO^{t}Bu powder (~0.0200 g) was added to the benzene solution, and the heterogeneous reaction was monitored by NMR spectroscopy. The concentration of complex **7** decreased and was ac-

(78) Birchall, J. M.; Haszeldine, R. N.; Jones, M. E. *J. Chem. Soc.* (*C*) **1971**, 1343−1347.

companied by the formation of the Ru(II) amidinate complex (PCP)Ru(CO)(NHC(C_6F_5)NPh) (**6**) as determined by ^{1}H, ^{31}P, and ^{19}F NMR spectroscopy. After approximately 20 min, complex **7** was quantitatively transformed to (PCP)Ru(CO)(NHC(C_6F_5)NPh) (**6**). After several hours of reaction, the color changed from yellow to dark brown, and NMR spectroscopy revealed decomposition of (PCP)Ru(CO)(NHC(C_6F_5)NPh) into multiple products.

Reaction of C_6F_5CN with KO^{t}Bu. To a solution of C_6F_5CN (0.100 g, 0.52 mmol) in 5 mL of THF was added a solution of KO^{t}Bu (0.050 g, 0.45 mmol) in 5 mL of THF. Upon combination of the two solutions, an immediate change from colorless to yellow was observed. After stirring for 1 h, the volatiles were evaporated, and the resulting residue was extracted with 5 mL of benzene. The benzene filtrate was dried to a yellow oil under reduced pressure, and a ^{19}F NMR spectrum of the oil was acquired. While a small amount of starting material (C_6F_5CN) was observed, the major product (>70%) exhibited resonances at −135.5 and −149.8 ppm (each a doublet) and was assigned as *p*-^{t}BuO−C_6F_4CN. Resonances attributed to the ortho-substituted compound were also observed (∼20%) at −133.7, −147.4, −150.8, and −160.0 ppm. Other minor products were observed in low yields and were not assigned.

Rate of Phosphine Exchange between (PCP)Ru(CO)(PMe_3)(NHPh) (1) and PMe_3-d_9. In a screw-cap NMR tube, approximately 0.020 g of complex **1** was dissolved in 0.6 mL of C_6D_6. The NMR tube was charged with an excess of PMe_3-d_9 (∼15 equiv) and immediately monitored by NMR spectroscopy. By monitoring the appearance of free PMe_3 and disappearance of the resonance due to the coordinated PMe_3, the half-life for phosphine ligand exchange was determined to be approximately 7 min. There was no change in the appearance of other resonances in the ^{1}H NMR spectra.

Acknowledgment. The National Science Foundation (CAREER Award; CHE 0238167) and the Alfred P. Sloan Foundation (Research Fellowship) are acknowledged for financial support of this research. Mass spectra were obtained at the Mass Spectrometry Facility for Biotechnology (NCSU). Partial funding for the facility was obtained from the North Carolina Biotechnology Center and the National Science Foundation. We acknowledge useful discussions with Professor SonBinh Nguyen.

Supporting Information Available: Details of X-ray data acquisition, crystal data, collection and refinement data, atomic coordinates, bond distances and angles, and anisotropic displacement coefficients for complexes **7**−**10**, NMR spectra of complex **7**, and details of kinetic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0483592