Communication

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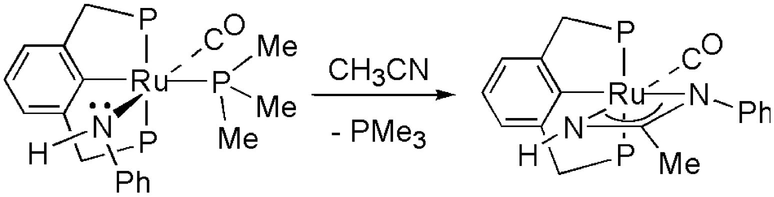

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Ruthenium(II) Anilido Complex Containing a Bisphosphine Pincer Ligand: Reversible Formation of Amidinate Ligands via Intramolecular C−N Bond Formation

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Summary: The reaction of the octahedral anilido complex (PCP)Ru(CO)(NHPh)(PMe$_3$) with acetonitrile produces the amidinate complex (PCP)Ru(CO){N(H)C(Me)N-(Ph)}. Mechanistic studies indicate that the reaction proceeds through coordination of the nitrile to the Ru(II) metal center, followed by intramolecular nucleophilic addition of the amido ligand.

Metathesis reactions of carbon−carbon multiple bonds using transition-metal catalysts have been applied to the synthesis of polymers as well as small organic molecules.[1−3] The extension of such methods to transformations involving carbon−nitrogen multiple bonds could allow the development of controlled routes for C−N bond formation, including the preparation of polymers that contain heteroatomic functionality.[4] Net metathesis reactions of acyclic imines catalyzed by transition-metal complexes have been observed; however, studies of such transformations reveal a high degree of mechanistic complexity. For example, catalytic metathesis reactions of acyclic imines using transition-metal nitrene complexes proceed by multiple pathways, including the formation of diazametallacycles, the production of HCl due to amine impurities, amido-mediated reactions, and reaction of amine impurities present in imines with metal imido ligands.[5−8] The reversible addition of acetonitrile to a Ti(IV) imido complex has been reported.[9] In addition, we have reported reactions of ruthenium benzylidene complexes with acyclic imines that occur via imine to enamine tautomerization.[10] This mechanistic complexity suggests that controlled transformations of unsaturated C−N bonds may require alternatives to transition-metal-catalyzed Chauvin-type mechanisms.[11] Recent reports of highly nucleophilic amido complexes that possess high d-electron counts suggest that such systems might be applied toward C−N bond-forming reactions.[12−14] In such a reaction, the metal complex would support a nucleophilic amido moiety as well as serving as a σ-Lewis acid to bind and activate the substrate toward intramolecular nucleophilic addition. In fact, such transformations may be central to polymerizations of carbodiimides and isocyanates.[15−17] The key step of many reactions mediated by late-transition-metal complexes with nondative ligands may involve intramolecular nucleophilic additions; however, only in a few cases are such transformations well characterized.[18,19]

The reaction of (PCP)Ru(CO)(Cl) (PCP = [2,6-(CH$_2$P-^{t}Bu$_2$)$_2$C$_6$H$_3$]) with TMSOTf yields (PCP)Ru(CO)(OTf) (**1**), and the addition of [Li][NHPh] to complex **1** allows the isolation of the anilido complex (PCP)Ru(CO)(NHPh) (**2**).[20] The direct reaction of (PCP)Ru(CO)(Cl) with [Li]-[NHPh] does not cleanly produce complex **2**. Complex **2** has been characterized by multinuclear NMR and IR spectroscopy. The IR spectrum of **2** reveals absorptions at 1901 (ν_{CO}) and 3420 cm^{-1} (ν_{NH}), and the ^{1}H NMR spectrum displays a broad resonance at 4.75 ppm due to the amido NH resonance. The octahedral complex (PCP)Ru(CO)(NHPh)(PMe$_3$) (**3**) can be prepared by reaction of **2** with trimethylphosphine (Scheme 1).[20] Complex **3** can also be prepared by metathesis of (PCP)-Ru(CO)(PMe$_3$)(Cl) with [Li][NHPh]. On the basis of phosphorus−carbon coupling constants, the geometry of **3** is tentatively assigned as having CO and PMe$_3$ ligands in a cis disposition. The synthesis and reactivity of a closely related (PCP)Ir^{III} anilido complex have been reported.[21]

Variable-temperature NMR spectroscopy of (PCP)Ru-(CO)(NHPh)(PMe$_3$) (**3**) reveals three fluxional processes (Chart 1). At low temperature, the ^{31}P NMR spectrum

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Scheme 1. Preparation of (PCP)Ru(CO)(NHPh)(PMe_3) (3; P = $^tBu_2P$)

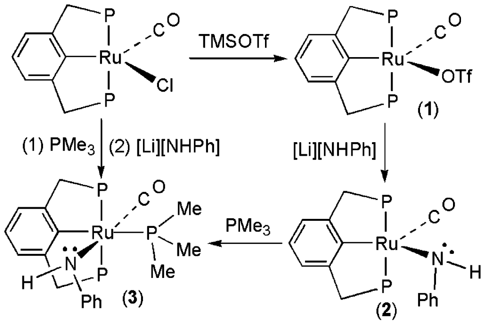
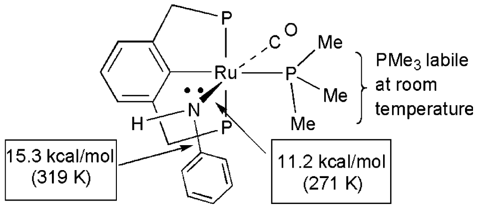
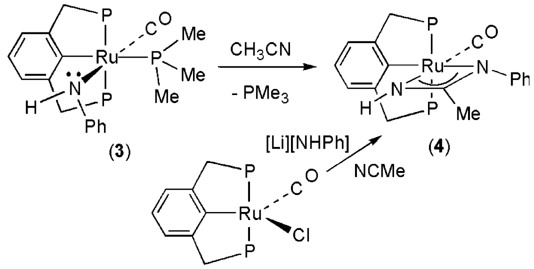


Chart 1. Dynamic Behavior of (PCP)Ru(CO)(NHPh)(PMe_3) (3) Observed by Variable-Temperature NMR Spectroscopy (P = $^tBu_2P$)



displays three unique resonances (two doublet of doublets due to the PCP ligand and a triplet due to PMe_3), indicating that the anilido ligand has a preferred orientation in which the $^tBu_2P$ moieties are chemically inequivalent. As the temperature is increased, the resonances due to the PCP ligand broaden and coalesce (271 K) into a single time-averaged resonance, and the symmetry equivalence of the $^tBu_2P$ fragments at elevated temperatures is likely due to rapid rotation about the Ru−N_{amido} bond and inversion at N ($\Delta G^\ddagger = 11.2(2)$ kcal/mol at 271 K). In addition, hindered rotation of the phenyl ring is indicated by five distinct resonances due to the anilido phenyl at room temperature. As the temperature is increased, the resonances due to ortho and meta protons broaden and coalesce. The coalescence point (319 K) of the resonances due to the ortho protons was used to calculate $\Delta G^\ddagger = 15.3(2)$ kcal/mol (319 K) for N_{amido}−C_{ipso} bond rotation. We have previously reported that rotational barriers for N_{amido}−C_{ipso} of $TpRuL_2(NHPh)$ (L = $P(OMe)_3$, PMe_3) complexes are between approximately 9.8 and 12.8 kcal/mol.[22] Finally, dissociation of the PMe_3 ligand has been observed. The addition of excess PMe_3 to a solution of **3** results in a single coalesced resonance for free and bound phosphine.

Scheme 2. Two Routes for the Formation of (PCP)Ru(CO)(N(H)C(Me)NPh) (4; *P* = $^tBu_2P$)



The reaction of (PCP)Ru(CO)(NHPh)(PMe_3) (**3**) with acetonitrile produces the Ru^{II} amidinate complex (PCP)-Ru(CO){N(H)C(Me)N(Ph)} (**4**) (Scheme 2).[23] Although isolated yields are low (~35%), NMR tube reactions reveal nearly quantitative transformation. Complex **4** can also be prepared by the reaction of (PCP)Ru(CO)(Cl) and [Li][NHPh] in acetonitrile. Although group 1 amides are known to react with some nitriles,[24] a ^{13}C NMR spectrum of a mixture of acetonitrile and [Li][NHPh] does not yield resonances consistent with the formation of amidinate. Complex **4** is characterized by ν_{CO} 1898 cm^{-1} and ν_{NH} 3360 cm^{-1} in its IR spectrum. The ^1H NMR spectrum of **4** displays resonances at 3.84 ppm (broad singlet) and 1.58 ppm due to the N−H and amidinate methyl groups, respectively. A solid-state X-ray diffraction study of **4** confirms its identity with one of the *t*Bu groups exhibiting an orientational disorder (Figure 1). The reactions of amido complexes of titanium, zirconium, and tantalum with acetonitrile have been reported to yield amidinate products; however, the metal products were only characterized by IR spectroscopy and elemental analysis.[25] Although mechanistic studies were not reported, reactions of titanium and tungsten amido ligands with nitriles have been disclosed.[26,27]

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(20) Complex **2**: to a 20 mL THF solution of **1** (0.2400 g, 0.357 mmol) was added 2 equiv of [Li][NHPh], and the mixture was stirred for approximately 30. The volatiles were removed, and the residue was extracted with 10 mL of benzene. After filtration, the volatiles were removed from the filtrate. The resulting dark green solid was washed with 10 mL of pentane and dried in vacuo (0.1100 g, 50%). IR (THF solution): ν_{CO} 1901 cm^{-1}, ν_{NH} 3420 cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 7.09 (2H, phenyl, d, $^3J_{HH} = 7$ Hz), 6.93 (2H, phenyl, t, $J_{HH} = 7$ Hz), 6.86 (1H, phenyl, t, $J_{HH} = 7$ Hz), 6.70 (2H, phenyl, d, $J_{HH} = 7$ Hz), 6.36 (1H, phenyl, t, $J_{HH} = 7$ Hz), 4.75 (1H, N*H*, br s), 3.41 (4H, PCP CH_2, m), 1.42 (18H, PCP CH_3, vt, $N = 12$ Hz), 1.14 (18H, PCP CH_3, vt, $N = 12$ Hz). Additional data are presented in the Supporting Information. Complex **3**: (PCP)Ru(CO)(Cl) (0.3540 g, 0.56 mmol) in 40 mL of benzene was added to approximately 0.3 mL of PMe_3. Two equivalents of [Li][NHPh] (~0.110 g) was added, and the mixture was stirred for ~12 h. The solution was filtered, and the filtrate was dried under reduced pressure. The resulting residue was washed with 3 × 10 mL of pentane to yield a yellow solid that was dried under vacuum (0.1500 g, 40%). IR (benzene solution): ν_{CO} 1904 cm^{-1}, ν_{NH} 3342 cm^{-1}. ^1H NMR (toluene-d_8, δ): 7.20 (4H, phenyl, overlapping multiplets), 7.01 (1H, amido phenyl, br t, $^3J_{HH} = 7$ Hz), 6.36 (1H, amido phenyl, br t, $^3J_{HH} = 7$ Hz), 6.19 (1H, amido phenyl ortho, br d, $^3J_{HH} = 7$ Hz), 5.95 (1H, amido phenyl ortho, br d, $^3J_{HH} = 7$ Hz), 3.53 (2H, PCP CH_2, m), 3.30 (2H, PCP CH_2, m), 1.71 (9H, PMe_3, br s, at 283 K resonates as a doublet with $^2J_{PC} = 5$ Hz), 1.21 (18H, PCP CH_3, br vt), 1.10 (18H, PCP CH_3, br vt). Additional data are presented in the Supporting Information.

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(23) Complex **4**: a benzene solution (50 mL) of (PCP)Ru(CO)(Cl) (0.5600 g, 1.0 mmol) was added to excess PMe_3 (0.45 mL, 5.0 mmol). To the resulting yellow solution was added 1.5 equiv of [Li][NHPh] (~0.1500 g). After the mixture was stirred for 1 h, 10 equiv of CH_3CN (0.52 mL) was added, and the mixture was stirred for 24 h. The solution was filtered, and the volatiles were removed from the filtrate. Extraction using 50 mL of hexanes was followed by filtration. The hexanes filtrate was dried under reduced pressure, and the resulting solid was washed with 10 mL of CH_3CN to yield a light green powder (0.2300 g, 35%). IR (THF solution): ν_{CO} 1898 cm^{-1}, ν_{NH} 3360 cm^{-1}. ^1H NMR (C_6D_6, δ): 7.27 (2H, amidinate phenyl, t, $^3J_{HH} = 8$ Hz), 7.17 (2H, amidinate phenyl, d, $^3J_{HH} = 8$ Hz), 7.01 (3H, PCP phenyl, br m), 6.84 (1H, amidinate phenyl, t, $^3J_{HH} = 8$ Hz), 3.84 (1H, N*H*, br s), 3.20 (4H, PCP CH_2, m), 1.58 (3H, CH_3CN, s), 1.18 (18H, PCP CH_3, vt, $N = 12$ Hz), 1.04 (18H, PCP CH_3, vt, $N = 12$ Hz). Additional data are presented in the Supporting Information.

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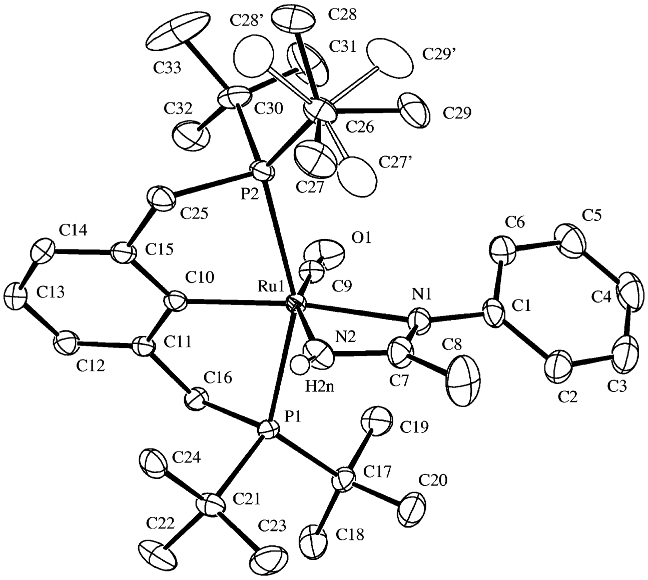
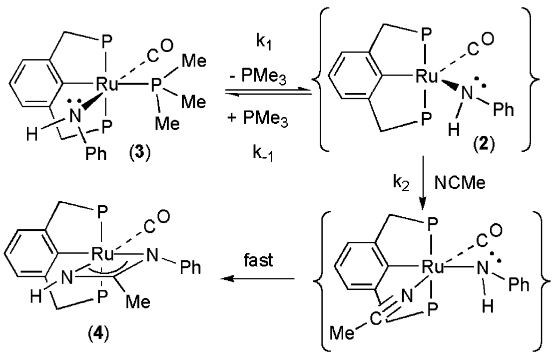


Figure 1. ORTEP (50% probability) of (PCP)Ru(CO){N(H)C(Me)N(Ph)} (**4**). Bond lengths and angles can be found in the Supporting Information.

Scheme 3. Proposed Mechanism for the Formation of (PCP)Ru(CO)(N(H)C(Me)NPh) (4) from the Reaction of (PCP)Ru(CO)(PMe_3)(NHPh) (3) with Acetonitrile (P = $^tBu_2P$)



A viable pathway for the formation of **4** from the reaction of complex **3** and acetonitrile includes initial formation of (PCP)Ru(CO)(NCMe)(NHPh) via PMe_3/NCMe ligand exchange followed by intramolecular nucleophilic attack of the amido nitrogen on the bound nitrile and proton transfer (Scheme 3). The anticipated rate law for this mechanism is shown in eq 1. Kinetic

$$\text{rate} = \frac{k_1k_2[\mathbf{3}][\text{NCMe}]}{k_{-1}[\text{PMe}_3] + k_2[\text{NCMe}]} \qquad (1)$$

experiments for the conversion of **3** and acetonitrile to the amidinate complex **4** under pseudo-first-order conditions indicate an inverse first-order dependence on the concentration of PMe_3 (Figure 2). In addition, a plot of k_{obs} versus the concentration of NCMe exhibits a first-order dependence on the concentration of NCMe at low concentrations, while saturation kinetics are apparent at higher concentrations (Figure 3). These results are consistent with the rate law depicted in eq 1. Thus, the kinetic data provide evidence for the coordination of acetonitrile and intramolecular C−N formation, since 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. At lower temperatures an intermolecular pathway may become viable, similar to a previously reported intermolecular addition of a Ru(II) anilido ligand to CO_2.[28] Although evidence has been obtained that the N−C bond formation step is intramolecular, the nature of the proton-transfer step that is required to complete the reaction has not been discerned.

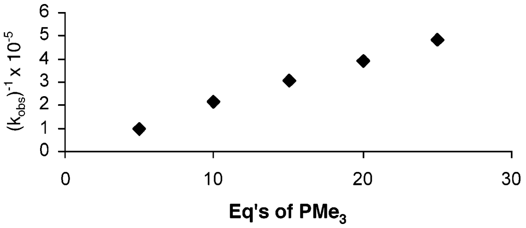


Figure 2. Plot of $(k_{obs})^{-1}$ versus equivalents of PMe_3 (based on complex **3**) for the conversion of **3** to **4**.

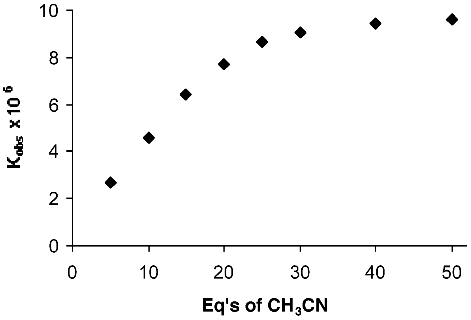
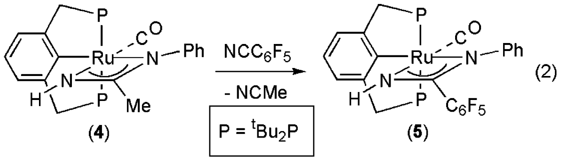


Figure 3. Plot of k_{obs} versus concentration of CH_3CN for the conversion of (PCP)Ru(CO)(PMe_3)(NHPh) (**3**) to (PCP)Ru(CO){N(H)C(Me)N(Ph)} (**4**).

The C−N bond formation between the anilido ligand and NCMe that produces complex **4** is reversible. For example, the reaction of a pentane solution of complex **4** with excess pentafluorobenzonitrile results in the release of acetonitrile and the formation of (PCP)Ru(CO){N(H)C(C_6F_5)N(Ph)} (**5**) (eq 2). Complex **5** has been



characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy as well as IR spectroscopy. Salient features in the ^1H NMR spectrum of **5** include a downfield chemical shift for the NH resonance (4.82 ppm) compared with **4**. In analogy to observations for the formation of **4**, the production of complex **5** likely proceeds through the formation of (PCP)Ru(CO)(NHPh)(NCMe) followed by NCMe/NCC_6F_5 exchange and intramolecular C−N bond formation.

A series of recent reports has revealed that octahedral Ru^{II} amido complexes exhibit reactivity consistent with highly basic amido ligands.[12−14] The reaction of (PCP)-

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Ru(CO)(NHPh) with nitriles demonstrates that the nucleophilic nature of such amido ligands can be combined with the activating ability of a Lewis acidic site on the metal center to achieve controlled C−N bond-forming reactions. The “double activation” ability (i.e., Lewis acidic metal in tandem with nucleophilic nondative ligand) of other complexes has been suggested to be central to related reactions. For example, the collective effect of Lewis acidic activation of cobalt-coordinated nitrile and intramolecular nucleophilic attack by hydroxide ligand has been shown to increase the rate of nitrile hydration by approximately 4 orders of magnitude relative to the metal center serving only as a Lewis acid,[29] and Tyler et al. have suggested a similar mechanism for a molybdenum catalyst.[30] Furthermore, a recent report of catalytic transamidation using metal amido systems may implicate a dual role of the metal amido intermediates.[31] Work reported herein provides direct evidence that C−N bond formation can be promoted by “doubly activating” metal centers.

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Supporting Information Available: Experimental details and complete tables of crystal data, collection and refinement data, atomic coordinates, bond distances and angles, and anisotropic displacement coefficients for (PCP)-Ru(CO){N(H)C(Me)N(Ph)} (**4**). This material is available free of charge via the Internet at http://pubs.acs.org.

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