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Imine Insertion into a Late Metal−Carbon Bond To Form a Stable Amido Complex

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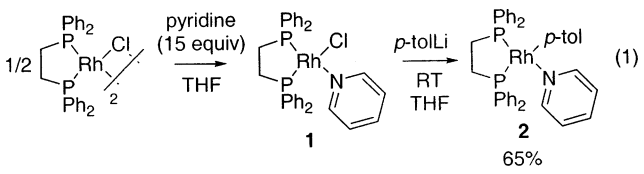
Late transition metal complexes that bind and insert alkenes into a metal−carbon bond are common and have been invoked as intermediates in many catalytic processes.[1] In contrast, late metal complexes that insert imines into metal−carbon or −hydrogen[2] bonds are limited. Arndtsen[3] and Sen[4] have described 2,1 insertions of imines into metal−acyl bonds of cationic Ni and Pd complexes to generate products with a new metal−carbon bond, but directly observed 1,2 insertions of imines into late metal−carbon bonds to form stable amido complexes are rare or unknown.

This difference may result from both thermodynamic and kinetic factors. The insertion of an imine cleaves a C−X π-bond that is stronger than the C=C bond in an olefin and forms a product with an amido group that is matched less favorably with a soft metal center than is an alkyl group from olefin insertion. In addition, stable aldimines bear substituents at N and C and are, therefore, more hindered than α-olefins. Finally, imines can bind to the metal through the nitrogen lone pair, and complexes with such σ-bound imines are less likely to undergo insertion than those with π-bound imines.

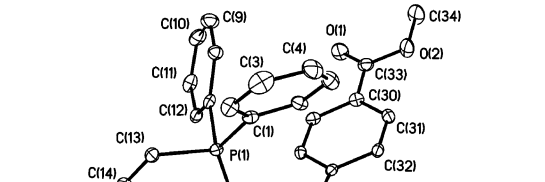
We recently began to identify late metal complexes that would insert aldehydes and imines to form metal alkoxo and amido complexes. Although organorhodium(I) complexes of the general formula $[Rh(PPh_3)_2(CO)R]$ (R = *p*-tol, *o*-tol, Me) inserted aromatic aldehydes to form alkoxide intermediates, they did not react with imines.[5] We now report an arylrhodium complex that does insert imines and gives rise to a stable amido complex from 1,2 insertion of an *N*-aryl benzaldimine.

To promote insertions of imines, we sought to study complexes that contain an aryl group located cis to a ligand more labile than PPh_3 or CO. To prepare complexes with such a coordination sphere, we targeted arylrhodium complexes with one chelating phosphine and one pyridine ligand. Such a complex, Rh(DPPE)(py)(*p*-tol) (**2**, DPPE = 1,2-bis(diphenylphosphino)ethane, py = pyridine), was prepared in two steps from the dimeric chloride $[(DPPE)Rh(\mu\text{-}Cl)]_2$ [6] (eq 1). Addition of pyridine (15 equiv) to a THF suspension of $[(DPPE)Rh(\mu\text{-}Cl)]_2$ generated a bright yellow solution of (DPPE)-Rh(Cl)(NC_5H_5) (**1**), as determined by ^{31}P and ^1H NMR spectroscopy, and reaction of the pyridine adduct with *p*-tolyllithium gave **2** in 65% isolated yield. The orange microcrystalline complex was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction (see Supporting Information for data).



(1)

Reaction of tolyl complex **2** with the *N*-aryl aldimine (*p*-tol)-CH=N(C_6H_4-*p*-CO_2Me) (**3a-Tol**) for less than 5 min led to dissipation of the orange color of the arylrhodium complex and generation of a red solution of amidorhodium complex **4** (eq 2). This complex was isolated in 88% yield upon recrystallization. X-ray diffraction of the orange microcrystalline material confirmed the structure of the pyridine-ligated amide **4** (Figure 1). In the solid state, **4** adopts a square planar geometry with the bulky diarylmethyl and aryl substituents of the amide ligand positioned above and below the plane of the molecule.



(2)

Figure 1. ORTEP diagram of **4**. Selected bond lengths (Å) and bond angles (deg): Rh(1)−N(1) 2.153; Rh(1)−N(2) 2.145; Rh(1)−P(1) 2.207; Rh(1)−P(2) 2.205; N(2)−Rh(1)−N(1) 88.44; N(2)−Rh(1)−P(2) 91.09; N(1)−Rh-(1)−P(2) 179.14; N(2)−Rh(1)−P(1) 170.71.

^{31}P NMR spectra of **4** at room temperature consisted of a broad doublet at 68.0 ppm (J_{PRh} = 178 Hz), and ^1H NMR spectra contained broad resonances. Amide **4** undergoes reversible dissociation of pyridine on the NMR time scale in solution. Spin saturation transfer experiments on **4** at −20 °C with 1 equiv of added pyridine showed saturation transfer between the ortho protons of the bound pyridine and those of the free pyridine. We have not yet distinguished between an associative and dissociative mechanism for this exchange.

In contrast to NMR data obtained at room temperature, ^1H NMR spectra of **4** obtained at −20 °C were sharp and confirmed the identity of this complex in solution. Two signals for the *p*-tolyl methyl groups and four doublets corresponding to the aromatic protons of the *p*-tolyl groups were observed. These data indicate that the *p*-tolyl groups are diastereotopic because rotation about the Rh−amide nitrogen bond is slow on the NMR time scale at −20 °C. ^{31}P NMR spectra of amide **4** acquired at −20 °C consisted of a single doublet due to similar chemical shifts of the phosphines and small P_A-P_B coupling.

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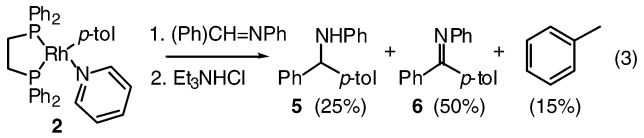
To determine if the high lability of the pyridine, which would allow coordination of imine in the square plane, contributes to the enhanced reactivity of arylrhodium **2**, kinetic experiments on the insertion reaction were conducted. Reactions of 0.026 M **2** with 0.13 M imine (Ph)CH═N(C_6H_4-*p*-CO_2Me) (**3a-Ph**) were conducted with concentrations of added pyridine ranging from 0.089 to 0.46 M. These kinetic data showed a clear first-order decay in rhodium complex **2**, first-order dependence on imine, and a clean inverse first-order dependence on the concentration of added pyridine (see Supporting Information). Although these data do not reveal the coordination mode of the imine prior to insertion, they do imply that coordination of imine to the site occupied by pyridine in **2** precedes the insertion process.

The electron-neutral and electron-rich aldimines (Ph)CH═NPh (**3b**) and (*p*-tol)CH═N(C_6H_4-*p*-OMe) (**3c**) also appeared to insert into the aryl−rhodium bond of **2**. However, the amido complexes formed from these insertions were less stable than those formed by insertion of the electron-poor imines **3a-Tol** and **3a-Ph**, and this instability led to different final products. Addition of **3b** (5 equiv) to a C_6D_6 solution of arylrhodium complex **2** generated diarylmethylamine (Ph)(*p*-tol)CH−NHPh, **5** (25%), and toluene (15%), and subsequent addition of Et_3NHCl (2−4 equiv) to the reaction solution generated the *E* and *Z* isomers of ketimine (Ph)-(*p*-tol)C═NPh, **6**, in 50% total yield, as determined by ^{1}H NMR spectroscopy (eq 3).

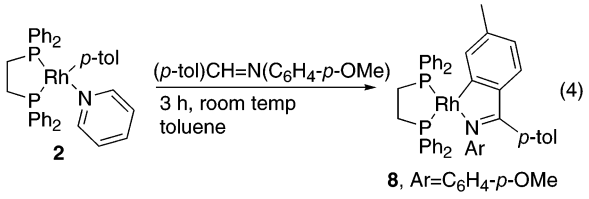


(3)

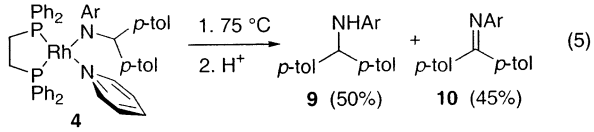
Our data indicate that these products are formed from insertion of imine, β-hydrogen elimination of the resulting amidorhodium complex, and cyclometalation of the coordinated imine to form a rhodium complex that releases ketimine upon protonation with Et_3NHCl. The diarylmethylamine and toluene formed prior to addition of Et_3NHCl is most likely generated from protonolysis of the amidorhodium and arylrhodium complexes with residual water or by reaction with a rhodium hydride. Consistent with the formation of amine from the amido complex and not from free ketimine, reaction of arylrhodium **2** with aldimine **3b** in the presence of the ketimine (Ph)(*p*-tol)CH═N(C_6H_4-*p*-CO_2Me) (**7**) generated amine **5** from arylation of the *N*-phenyl aldimine and no amine from added ketimine **7**.

Evidence for the formation of ketimines from arylrhodium complex **2** and aldimines **3b** and **3c** was obtained from several experiments. First, reaction of **2** with *p*-methoxy-substituted aldimine **3c** for 3 h consumed **2** and formed a major rhodium product **8** (eq 4) containing a cyclometalated ketimine and a minor complex in a 3.5:1 ratio. Major product **8** was identified by X-ray diffraction. Further, addition of DCl in ether to the crude mixture generated from arylrhodium **2** and aldimine **3c**, followed by hydrolysis, generated monodeuterio 4,4′-dimethylbenzophenone and unlabeled *p*-anisidine, as determined by GC/MS analysis. We have not yet definitively assigned the structure of the minor rhodium product.

Formation of ketimine from decomposition of a diarylmethylamido complex was supported by the reactivity of amide **4**. Heating of **4** generated amine **9** and ketimine **10** in 50% and 45% yield (eq 5), as was observed from reaction of **2** with aldimines **3b** and **3c**. Thus, the isolation of amido complex **4** from insertion of **3a-Tol** was possible because of the greater stability of the amido group containing an electron-poor *N*-aryl substituent.



(4)



(5)

C−H bond cleavage to generate an iminoacyl complex and reductive elimination of the *p*-tolyl and iminoacyl groups could also account for the formation of ketimine. However, this mechanism is inconsistent with isolation of diarylmethylamido complex **4**. It is also inconsistent with the formation of **5** as the only amine product when the reaction of arylrhodium **2** with aldimine **3b** was conducted in the presence of added ketimine **7**.

The regiochemistry of the insertion in the current study is distinct from that of previous 2,1 insertions of imines into metal carbon bonds of metal−acyl complexes.[3,4] The electrophilicity of the acyl group makes possible direct nucleophilic attack by the imine nitrogen at the acyl carbon,[7] while insertion into the rhodium aryl bond is likely to occur by a path more akin to the migratory insertion of olefins into late metal carbon bonds. Thus, the two types of insertions are likely to occur by distinct mechanisms.

The insertion of imine into a rhodium aryl linkage can be an important step in catalytic transformations of imines. Several groups have recently reported the rhodium-catalyzed reactions of imines[8] with organotin, boron, and zirconium[9] reagents to form diarylmethylamines. These reactions could occur by well-precedented nucleophilic attack on a coordinated imine[10−14] or the previously unknown insertion of imine into a rhodium aryl complex. Our results suggest that the insertion of imine is a viable step in this catalytic process and may allow the development of a series of new catalytic transformations of imines.

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Supporting Information Available: Experimental procedures and full structural characterization of **2**, **4**, and **8** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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