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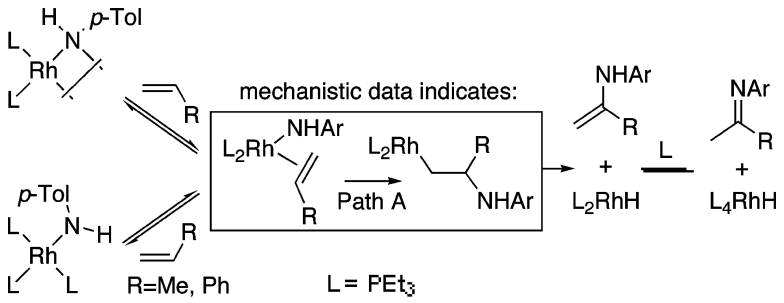

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Transfer of Amido Groups from Isolated Rhodium(I) Amides to Alkenes and Vinylarenes

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Abstract: The reaction of monomeric and dimeric rhodium(I) amido complexes with unactivated olefins to generate imines is reported. Transamination of $\{(PEt_3)_2RhN(SiMePh_2)_2\}$ (**1a**) or its $-N(SiMe_3)_2$ analogue **1b** with *p*-toluidine gave the dimeric $[(PEt_3)_2Rh(\mu\text{-NHAr})]_2$ (Ar = *p*-tolyl) (**2a**) in 80% isolated yield. Reaction of **2a** with PEt_3 generated the monomeric $(PEt_3)_3Rh(NHAr)$ (Ar = *p*-tolyl) (**3a**). PEt_3-ligated arylamides **2a** and **3a** reacted with styrene to transfer the amido group to the olefin and to form the ketimine Ph(Me)C=N(*p*-tol) (**4a**) in 48−95% yields. The dinuclear amido hydride $(PEt_3)_4Rh_2(\mu\text{-NHAr})(\mu\text{-H})$ (Ar = *p*-tolyl) (**5a**) was formed from reaction of **2a** in 95% yield, and a mixture of this dimeric species and the $(PEt_3)_nRhH$ complexes with $n = 3$ and 4 was formed from reaction of **3a** in a combined 75% yield. Propene reacted with **2a** to give Me_2C=N(*p*-tol) (**4b**) and **5a** in 90 and 57% yields. Propene also reacted with **3a** to give **4b** and **5a** in 65 and 94% yields. Analogues of **2a** and **3a** with varied electronic properties also reacted with styrene to form the corresponding imines, and moderately faster rates were observed for reactions of electron-rich arylamides. Kinetic studies of the reaction of **3a** with styrene were most consistent with formation of the imine by migratory insertion of olefin into the rhodium-amide bond to generate an aminoalkyl intermediate that undergoes β-hydrogen elimination to generate a rhodium hydride and an enamine that tautomerizes to the imine.

Introduction

Transfer of an alkyl group from a transition-metal complex to an olefin to form a new C−C bond, typically by migratory insertion, is a common organometallic reaction. Related transfers of an amido group from an isolated amido complex to an olefin to form a new C−N bond are rare. A few catalytic reactions have been reported in which insertion of an olefin into a metal amide is a likely step.[1−4] Although strong evidence for insertion has been presented in some cases, the precursors to the insertion process and the immediate products from this step were not observed directly in these processes. More common are the reactions of late-transition-metal olefin complexes with free amines to generate aminoalkyl products.[5−8]

Intramolecular insertion of an olefin into a lanthanide amide has been observed directly as part of the mechanism of cyclizations by hydroamination,[9] but only activated olefins, such as norbornene and acrylonitrile, have displayed any reactivity at the M−N bond of isolated late-transition-metal amides. Casalnuovo reported that an iridium(III) arylamido complex inserts norborene, but reactions with olefins that lack the strain of norbornene did not occur.[10] Trogler reported the reaction of a platinum arylamide with acrylonitrile, but reactions with olefins that lack the polarity of acrylonitrile were not reported.[11] Two examples of the insertion of unactivated alkynes into late transition-metal amides have been reported recently, one into a molybdenum amide[12] and one into a ruthenium amide.[13] The reaction of a palladium amide with the activated dimethylacetylene dicarboxylate has also been described.[14] However, reactions with alkenes have not. We report the transfer of an amido group of a series of isolated rhodium(I) amido complexes to alkenes and vinylarenes. These reactions generate imines in a new carbon−nitrogen bond-forming process.

Results and Discussion

1. Preparation of Rhodium Amido Complexes. A. Synthesis of Dinuclear Amido Complexes. Isolable dimeric rhodium arylamido complexes ligated by PEt_3 were prepared by the route in Scheme 1. The three-coordinate complex $\{Rh(PEt_3)_2[N(SiMePh_2)_2]\}$ (**1a**) served as an isolable precursor to

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(14) Villanueva, L. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1992**, *11*, 2963.

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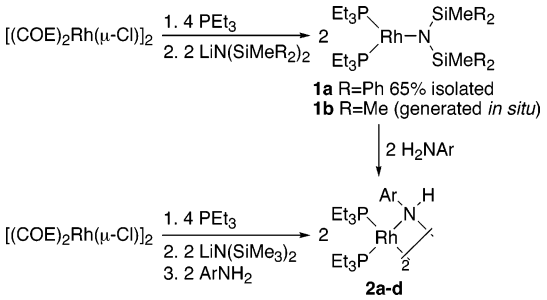
Scheme 1



the desired arylamido complexes. The related $\{Rh(PEt_3)_2[N(SiMe_3)_2]\}$ (**1b**) generated in situ was also a convenient precursor to the dinuclear arylamido complexes. These complexes are both related to $\{Rh(PPh_3)_2[N(SiMe_3)_2]\}$, which was reported many years ago by Lappert.[15] Because complex **1a** is more crystalline than **1b**, purification is simpler, and this complex was isolated in 65% yield in pure form. The mononuclearity of these silylamides was demonstrated by X-ray diffraction of **1a**.

Because of the ease of removing the volatile hexamethyldisilazine from the reaction mixture, most of the dinuclear rhodium amido complexes in this work were prepared by the reaction of arylamines with crude hexamethyldisilazide **1b**. In some cases, we generated **1b** in situ from $[(PEt_3)_2Rh(\mu\text{-}Cl)]_2$ and $LiN(SiMe_3)_2$, and to the solution of this complex we added the arylamine. In other cases, we isolated **1b**, partially purified it by drying in vacuo to a thick, dark-purple gel, and to a solution of this material added the arylamine to generate the rhodium amide. For example, addition of *p*-toluidine to **1a** generated the dinuclear toluidide complex **2a** in 77% isolated yield.

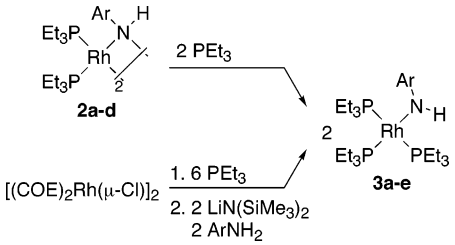
Alternatively, the arylamido complexes were prepared in one pot from $[(COE)_2Rh(\mu\text{-}Cl)]_2$. For example, reaction of the rhodium olefin complex with PEt_3, followed by $LiN(SiMe_3)_2$ and then *p*-toluidine, generated the dimeric amido complex **2a** in 80% yield. The *p*-anisidide (**2b**), *o*-anisidide (**2c**), and *p*-trifluoromethylanilide (**2d**) analogues of toluidide **2a** were generated cleanly by analogous one-pot procedures and isolated in 55−72% yields. The dinuclear arylamido complexes **2a**−**d** were mixtures of anti and syn isomers in a ratio of 5:1 to 20:1.

Complexes **2a**−**d** were characterized by spectroscopic methods and elemental analysis. ^1H and ^{31}P NMR spectra of isolated **2a** contained resonances from the anti and syn isomers in a 6:1 ratio. The ^1H NMR spectrum consisted of two sets of methyl and methylene groups of equivalent phosphines, along with two sets of tolyl methyl groups. The ^{31}P NMR spectrum consisted of two sets of doublets with 176 and 171 Hz couplings to rhodium. X-ray diffraction data on the $PPhEt_2$ analogue of **2a**, $[(PPhEt_2)_2Rh(\mu\text{-}NHAr)]_2$ (Ar = *p*-tolyl) (**2e**), revealed a single anti isomer. Dissolution of the crystalline material in C_6D_6 at room temperature afforded a mixture of anti and syn isomers in a 1.4:1 ratio. Therefore, the identity of the major isomer of the isomeric mixture of **2a**−**d** in solution is not definitive.

B. Synthesis of Mononuclear Amido Complexes. Monomeric arylamides were prepared by the synthetic route in Scheme 2. Reaction of dimeric amido complex **2a** with PEt_3 formed the corresponding monomeric **3a** containing three phosphine ligands.[16] The ^1H NMR spectrum of this product

(15) Cetinkaya, B.; Lappert, M. F.; Torroni, S. *Chem. Commun.* **1979**, 843.

Scheme 2



consisted of resonances corresponding to a 2:1 ratio of ethyl groups of the two types of inequivalent phosphines. A single signal for an N−H proton was also observed, along with a single methyl group and a single set of aromatic resonances for a tolyl group. The ^{31}P NMR spectrum of this product consisted of a 2:1 ratio of a doublet of doublets and a triplet of doublets with 141 and 153 Hz couplings to rhodium.

This complex and the analogous monomeric *p*-anisidide, *o*-anisidide, *p*-trifluoroemthylanilide, and 2,6-diisopropylanilide complexes **3b**−**e** were most conveniently prepared by a one-pot sequence. This sequence involved the addition of 6 equiv of PEt_3 to $[(COE)_2Rh(\mu\text{-}Cl)]_2$, which generated 2 equiv of $[Rh(PEt_3)_3Cl]$. To this complex was added $LiN(SiMe_3)_2$ and then the arylamine. Reaction of the phosphine-ligated rhodium chloride occurred only after addition of the arylamine; no reaction was observed between $[Rh(PEt_3)_3Cl]$ and $LiN(SiMe_3)_2$ at room temperature. This procedure afforded the corresponding rhodium arylamido complexes in 44−68% isolated yields.

We also generated secondary arylamido complexes by this route. Reactions of $[(COE)_2Rh(\mu\text{-}Cl)]_2$ with 6 equiv of PEt_3 and 2 equiv of $LiN(SiMe_3)_2$ per dimer, followed by 2 equiv of di-4-anisylamine, generated the trisphosphine complex **3f** in 78% yield. The same procedure with *N*-methylaniline afforded *N*-methylanilide **3g** in 42% yield. The product from addition of *N*-methylaniline to **1b** without added PEt_3 was unstable.

C. Solid-State Structures of the Silylamido and Dimeric Arylamido Complexes. The ORTEP diagrams of rhodium amides **1a** and **2e** are provided in Figure 1. In the solid state, **1a** adopted a Y-shaped geometry at rhodium that contrasts with the T-shaped geometry of most monomeric, three-coordinate d^8 transition-metal complexes,[17,18] including that of a recently isolated three-coordinate Pd(II) diarylamido complex.[19] The difference in geometry may be attributed to both steric and electronic factors. The steric bulk of the silylamido substituents favor a Y-shaped geometry, and the preference for Y-shape geometry of Ni(I) amido complexes was similarly attributed to the steric bulk of the amido group.[20,21] In addition, a Y-shaped geometry allows for overlap of the nitrogen electron lone pair with a d orbital in the trigonal plane.[22]

Dimeric arylamide **2e** exists as a single isomer in the solid state. The Rh_2N_2 core is planar, as defined by crystallographic

(16) The anilide complex has been generated in solution, but never isolated, Brunet, J. J.; Commenges, G.; Neibecker, D.; Philippot, K.; Rosenberg, L. *Inorg. Chem.* **1994**, *33*, 6373.
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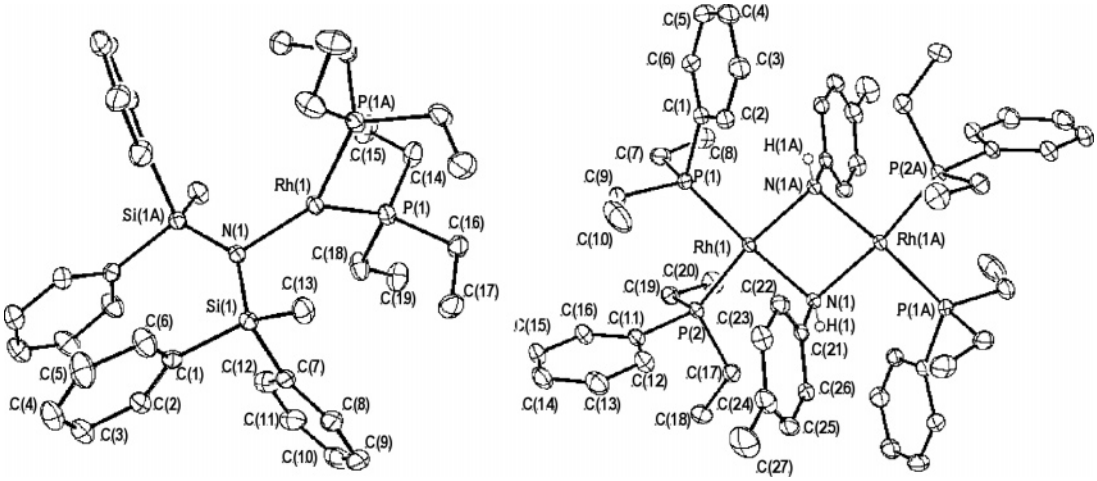
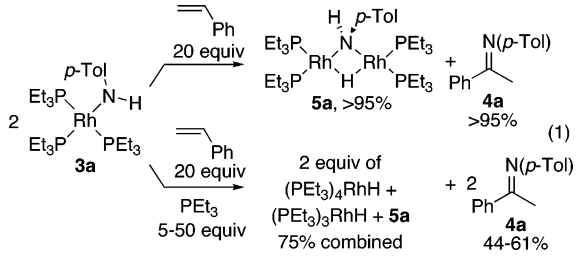


Figure 1. ORTEP diagram of **1a** (left) and **2e** (right). Only hydrogens bonded to the amido hydrogens are shown for clarity.

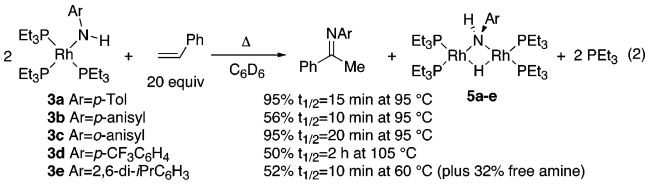
symmetry. The rhodium centers adopt slightly distorted square planar geometries; the sum of the angles at each rhodium center totaled 363°. The two *p*-tolyl substituents on the amido moieties are anti to each other. This anti planar geometry contrasts with recently reported folded structures of dinuclear Rh(I) arylamido complexes containing diolefin or nitrile ligands.[23] It is difficult to predict whether the core of a dinuclear d^8 amido complex will be planar or puckered because of a complicated combination of different structural factors. Nevertheless, it has been suggested that bulky substituents on the terminal ligands as well as on the bridging amido groups could promote planar geometries by minimizing steric repulsion.[24,25]

2. Reactions of Amido Complexes with Olefins. A. Reactions of Monomeric Arylamido Complexes with Vinylarenes. Both the monomeric and dimeric primary amido complexes reacted with olefins to generate products from a combination of C−N bond formation and elimination of imine. Monomeric toluidide complex **3a** reacted with an excess of styrene in the absence of added PEt_3 to produce the ketimine Ph(Me)C═N(*p*-tol) (**4a**) and the dimeric hydride $(PEt_3)_4Rh_2(\mu\text{-NHAr})(\mu\text{-H})$ (**5a**) in greater than 95% yields after 7 h at 85 °C (eq 1). Reaction of **3a** with styrene in the presence of added PEt_3 at 105 °C also generated ketimine **4a**, although more slowly and in yields (44−61%) that depended on the concentration of added PEt_3. In the presence of added PEt_3, a mixture of the dinuclear hydride **5a** and the known monomeric hydrides[26] $(PEt_3)_4RhH$ and $(PEt_3)_3$-RhH was generated in a total yield of roughly 75%.



The yields of the rhodium and imine products were determined by a combination of NMR and gas chromatography (GC) methods with internal standards. The imine was identified by comparison of the NMR and GC mass spectra to those of material prepared independently and fully characterized. The amido hydride complex **5a** was isolated from the reactions and was fully characterized, including a confirmation of connectivity by X-ray diffraction.

We investigated the steric and electronic effects on the process by conducting the reaction with varied arylamido and vinylarene reagents (eq 2). The monomeric *p*-anisidide (**3b**), *o*-anisidide (**3c**), and 4-trifluoromethylanilide (**3d**) complexes reacted with styrene to form the analogous imines in 56, >95, and 50% yields, respectively. The rates of the reactions of anilides **3b** and **3c** with styrene were comparable to the rates of the reactions of the toluidide complex **3a** with styrene. The *p*-toluidide **3a** reacted with 20 equiv of styrene at 95 °C with a half life of roughly 15 min, while the *p*-anisidide **3b** and *o*-anisidide **3c** reacted under the same conditions with half-lives of roughly 10 and 20 min, respectively. Thus, the more electron-rich amide reacted slightly faster, and the mono ortho-substituted amide reacted slightly slower, but the differences in rates were small.



Reactions of the monomeric 4-trifluoromethylanilide **3d** were much slower than those of the toluidide or anisidide complexes. The half life for reaction of **3d** was about 2 h at 105 °C. This slower rate is consistent with the trend of faster rates for reactions of the more electron-rich amides. However, the difference in rate between reaction of *p*-toluidide **3a** and 4-trifluoromethylanilide **3d** is much larger than the difference in rates between reaction of **3a** and *p*-anisidide **3b**. We have not been able to obtain structural data on **3d** or fully purify this complex as a solid because attempts to crystallize this complex **3d** simply led to dissociation of phosphine and formation of crystalline samples of the dinuclear complex **2d**. The structure of **3d** may be important to understand the large difference in

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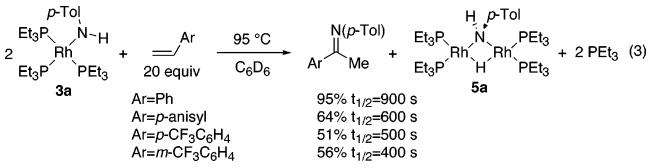
(24) Ruiz, J.; Martinez, M. T.; Vicente, C.; Garcia, G.; Lopez, G.; Chaloner, A.; Hitchcock, P. B. *Organometallics* **1993**, *12*, 4321 and the references therein.
(25) Aullon, G.; Lledos, A.; Alvarez, S. *Inorg. Chem.* **2000**, *39*, 906.
(26) Yoshida, T.; Thorn, D. L.; Okano, T.; Otsuka, S.; Ibers, J. A. *J. Am. Ceram. Soc.* **1980**, *102*, 6451.

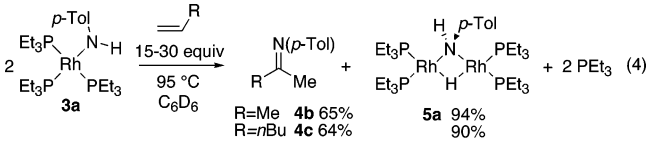
reactivity because the NMR spectra of this complex contained some unexpected features. Four distinct aryl resonances were observed in the ^{1}H NMR spectrum, six distinct aryl resonances were observed in the ^{13}C NMR spectrum, and one aromatic hydrogen resonated upfield (6.3 ppm in C_6D_6) of the typical aromatic region. Although the C−H coupling constant for this upfield hydrogen was similar in value to those of the other aromatic hydrogens, we suggest, albeit tentatively, that the large difference in activity is due to stabilization of the ground-state structure of **3d** by a weak agostic C−H or η^2 arene interaction.[17]

The more hindered 2,6-diisopropylanilide complex **3e** also reacted with styrene, and this complex was much more reactive than the other amido complexes. At 60 °C, this complex generated the corresponding imine product in 52% yield, along with free amine in 32% yield. Heating of **3e** in the absence of olefin at 60 °C generated the amine in 26% yield. Thus, the lower yield from reaction of this amido complex results from faster competitive decomposition to form free amine by a pathway that has not yet been identified. Although the yield of the reaction of this complex with styrene was lower than the yields of reactions of the less hindered amides, the reaction was the fastest. The half life of the reaction of this complex with styrene was about 10 min at 60 °C vs 10−30 min at 95 °C for reactions of the other arylamido complexes.

The effect of the electronic properties of the vinylarenes on the amido transfer process was evaluated by conducting reactions with 4-vinylanisole and both 4- and 3-trifluoromethylstyrene (eq 3). The monomeric toluidide **3a** reacted with 20 equiv of 4-vinylanisole, 4-trifluoromethylstyrene, and 3-trifluoromethylstyrene to afford the corresponding imines in 64, 51, and 56% yields. The reaction with 4-trifluoromethylstyrene was faster than the reaction with 4-vinylanisole but by a factor of only about 2. Moreover the reaction of **3a** with a 1:1 mixture of 4-trifluoromethylstyrene and 4-vinylanisole favored formation of the product from reaction of trifluoromethylstyrene by a factor of about 2. Thus, the reaction is slightly faster with the more electron-poor vinylarenes, but the electronic effects are not large.

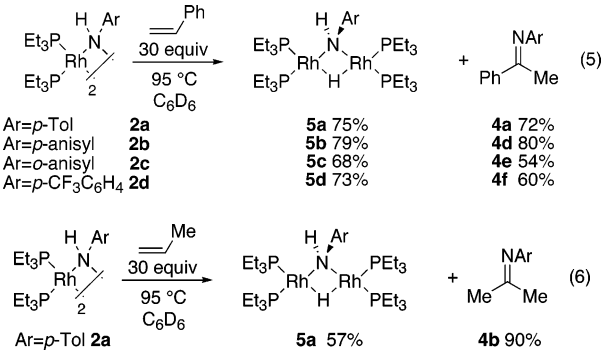


B. Reactions of Monomeric Arylamido Complexes with Alkenes. Monomeric toluidide complex **3a** also reacted with alkenes (eq 4). The reaction of **3a** with 15 equiv of 1-hexene generated a mixture of syn and anti imines (Me)(*n*-Bu)C═N-(*p*-tol) (**4c**) in a total yield of 64%, along with rhodium hydride **5a** in 90% yield. Reaction with 30 equiv of propene generated the imine $(Me)_2C$═N(*p*-tol) (**4b**) in 65% yield and **5a** in 94% yield. Complex **3a** did not react with internal alkenes, such as cyclohexene, and did not react with unstrained 1,1-disubstituted alkenes, such as isobutylene.

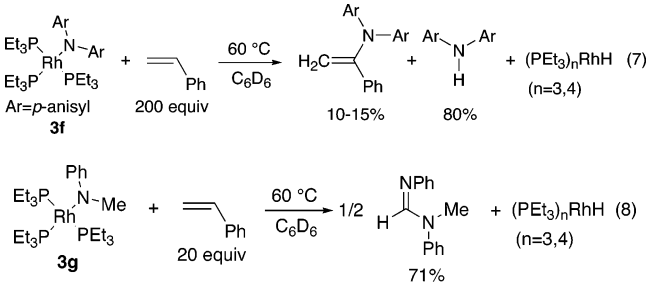


C. Reactions of Dinuclear Arylamido Complexes with Vinylarenes and Alkenes. Dimeric *p*-toluidide complex **2a** underwent similar reactions with olefins, as shown in eqs 5 and 6. Complex **2a** reacted with styrene (30 equiv) in C_6D_6 at 95 °C to form the ketimine **4a** in 72% yield and the amido hydride dimer **5a** in 75% yield after 1.5 h. The *p*-anisidide and *o*-anisidide analogues **2b** and **2c** also reacted with styrene under these conditions to form the corresponding ketimines in 80 and 62% yields, respectively. Dimeric trifluoromethylanilide **2d** was less reactive than the more electron-rich arylamides, and required 10 h at 95 °C to consume the amido complex and form the ketimine (60% yield).

Dimeric **2a** also reacted with propene. Reaction with an excess of propene formed the ketimine Me_2C═N(*p*-tol) (**4b**) (90%) and amido hydride **5a** (57%) after 16 h at 95 °C (Scheme 3). The rhodium allyl complex $[(PEt_3)_2Rh(\eta^3\text{-}C_3H_5)]$ was also formed from the reaction with propene in roughly 30% yield. The identity of the allyl complex was confirmed by independent synthesis from $[(PEt_3)_2Rh(\mu\text{-Cl})]_2$ and allyl Grignard.



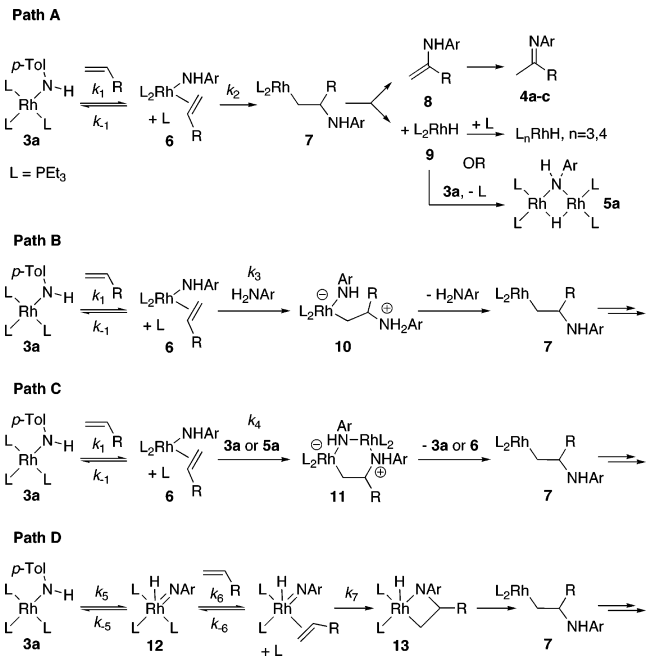
D. Reactions of Monomeric Diarylamido and *N*-Alkylarylamido Complexes with Vinylarenes. The amido complexes generated from secondary amines were less reactive toward olefins. Nevertheless, the diarylamide $(PEt_3)_3Rh(NAr_2)$ (Ar = *p*-anisyl, **3f**) did react with styrene to transfer the amido group and form enamine (eq 7). Free diarylamine $HN(p\text{-anisyl})_2$ was the major product (ca 80% yield), but reaction with 200 equiv of styrene led to the formation of enamine $(Ph)[N(p\text{-anisyl})_2]C$═$CH_2$ in 10−15% yield. In contrast, heating of the *N*-methylanilide **3g** with vinylarenes only led to β-hydrogen elimination without participation of the olefin. This reaction generated the amidine PhN═C(H)N(Me)Ph as the organic product (eq 8).[27]



3. Studies of the Mechanism of the Amido Transfer to Olefins. A. Potential Formation of the Imine by a Rhodium-Catalyzed Process. Small amounts of free amine are generated

(27) Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7010.

Scheme 3



from the reactions of the arylamido complexes with olefins. This observation and the report by Brunet of slow catalytic formation of imines from olefins and amines catalyzed by related rhodium complexes[28,29] led us to consider that free *p*-toluidine generated during the reactions of **2a** or **3a** could undergo a reaction with the olefin catalyzed by the rhodium product. However, reaction of *p*-toluidine with styrene in the presence of 5 mol % **5a** generated less than 5% ketimine **4a** after 18 h at 95 °C. Thus, further discussion of the mechanism focuses on stoichiometric reactions that transfer the amido group to the olefin.

B. Potential Pathways for the Transfer of the Amido Group. Several potential pathways for the reaction of monomeric amide **3a** with olefins that involve dissociation of phosphine are shown in Scheme 3. Pathways involving dissociation of phosphine to form an intermediate olefin complex **6** are considered because the reaction is inhibited by added phosphine (vide infra). The rate equations that correspond to Paths A−D are shown in eqs 9−14.

Path A involves insertion of the coordinated olefin on **6** into the amide group to form aminoalkyl intermediate **7**, followed by β-hydrogen elimination. Tautomerization of the resulting enamine **8** to the imine and reaction of the rhodium hydride **9** with the starting rhodium amide would generate the final products. Path B involves external attack of the amine on a coordinated olefin to form an aminoalkyl intermediate **10** that would undergo proton transfer and dissociation of the resulting coordinated amine to generate the same three-coordinate aminoalkyl intermediate **7** as is formed by Path A. Path C involves external attack of the rhodium amide on the coordinated olefin to generate a dinuclear intermediate **11** that could dissociate to generate the same three-coordinate aminoalkyl intermediate **7**.[30] Path D involves α-elimination to form a rhodium imido hydride intermediate **12** that could undergo a [2 + 2] reaction with the olefin[31,32] and subsequent reductive elimination from metallacycle **13** to form the aminoalkyl intermediate.

$$-\mathrm{d}[\mathbf{3a}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathbf{3a}] \quad (9)$$

For Path A

$$k_{\mathrm{obsd}} = k_1k_2[\mathrm{olefin}]/(k_{-1}[\mathrm{PEt_3}] + k_2) \quad (10)$$

For Path B

$$k_{\mathrm{obsd}} = k_1k_3[\mathrm{olefin}][\mathrm{H_2NAr}]/(k_3[\mathrm{H_2NAr}] + k_{-1}[\mathrm{PEt_3}]) \quad (11)$$

For Path C

$$-\mathrm{d}[\mathbf{3a}]/\mathrm{d}t = k_1k_4[\mathbf{3a}]^2[\mathrm{olefin}]/(k_{-1}[\mathrm{PEt_3}] + k_4[\mathbf{3a}]) \quad (12)$$

For Path D,
if α-elimination is rate-limiting, then

$$k_{\mathrm{obsd}} = k_5 \quad (13)$$

if α-elimination is fully reversible, then

$$k_{\mathrm{obsd}} = K_5k_6k_7[\mathrm{olefin}]/(k_{-6}[\mathrm{PEt_3}] + k_7) \quad (14)$$

The rate equation for Path A is first-order in **3a** and olefin, inverse first-order in added PEt_3, and zero-order in added *p*-toluidine. The rate equation for Path B involving rate-limiting attack of aniline on the coordinated olefin is first-order in **3a** and olefin, inverse first-order in added PEt_3, and first-order in *p*-toluidine. The same reaction orders would be predicted for Path B with reversible attack of aniline, followed by rate-limiting proton transfer, or reversible attack of aniline, followed by reversible proton transfer and rate-limiting dissociation of amine. The rate equation for Path C predicts that the reaction would be second-order in **3a** because the transition state of the irreversible step involves two rhodium centers. This rate equation also predicts that the reaction would be first-order in olefin, inverse first-order in added phosphine, and zero-order in added amine. The rate equation for Path D is zero-order in all reagents if α-elimination to generate the imido species is rate limiting, but the rate equation is first-order in olefin, inverse order in added phosphine, and zero-order in amine if the generation of the imido complex is fully reversible prior to reaction with the olefin.

The rate equations for all paths are similar if the aminoalkyl intermediate is generated reversibly and β-hydrogen elimination is rate-limiting. For this reason, we tested whether the β-hydrogen elimination step was rate-limiting by measuring the isotope effect for reactions of styrene and styrene-d_8. The reactions of styrene and styrene-d_8 at 105 °C with 10 equiv of added PEt_3 in C_7D_8 solvent occurred with rate constants that were within 10% of each other. Although isotope effects on β-hydrogen elimination are often small,[33−37] the absence of any detectable isotope effect from these reactions argues strongly against β-hydrogen elimination as the final irreversible step.

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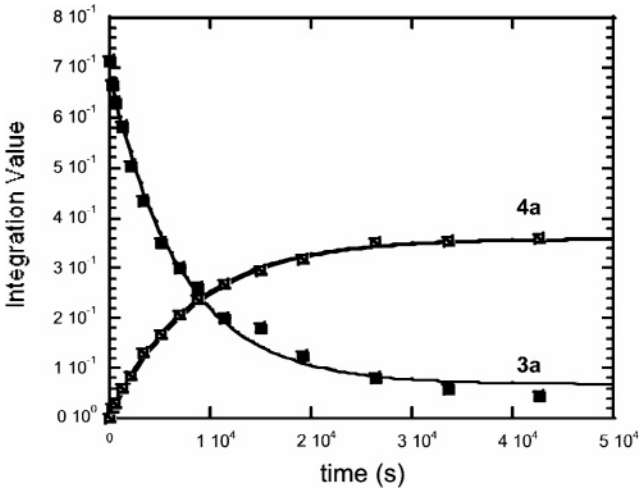

Figure 2. Representative plot of the decay of rhodium complex **3a** (0.058 M) with styrene (5.2 M) in the presence of PEt_3 (0.29 M) and *p*-toluidine (0.006 M) in C_7D_8 at 105 °C. The curve for the consumption of **3a** depicts the results of an unweighted least-squares fit to $y = a\exp(-bx) + c$ ($a = 0.61 \pm 0.01$, $b = 0.00014 \pm 0.00001$, $c = 0.06 \pm 0.01$). The curve for the accumulation of **4a** depicts the results of an unweighted least-squares fit to $y = -a\exp(-bx) + c$ ($a = 0.354 \pm 0.003$, $b = 0.000120 \pm 0.000003$, $c = 0.360 \pm 0.003$).

Thus, versions of pathways A−D with rate-limiting β-hydrogen elimination were not considered further.

C. Conditions of the Kinetic Experiments. To begin to distinguish between the possible mechanisms for the transfer of the amido group, we determined the order of the reaction in rhodium, olefin, added ligand, and added amine. Because the kinetic expressions are more complex starting from the dimeric species, because dimeric **2a** could undergo first-order decay or half-order decay, and because first and half-order rate behaviors are difficult to distinguish, our kinetic studies focused on reactions of monomeric **3a**. Reactions of **3a** were conducted with a 0.029 M concentration of **3a**, 0.4−2.6 M concentrations of styrene, and 0.14−1.43 M concentrations of added PEt_3. Because *p*-toluidine is generated in 3−8% yield as a side product, and this byproduct could affect the rate of the reaction, we also conducted kinetic studies with 3.0 or 29 mM added *p*-toluidine. Under all conditions, rhodium reactant **3a** decayed exponentially (Figure 2). These data show that the reactions are first-order in **3a**.

D. A Side Note Concerning the Curve of the Appearance of Imine Product. The curve of the appearance of imine and rhodium products from reaction of dimeric arylamides **2a**−**d** depended on the concentration of free amine and added phosphine. In the absence of amine and phosphine, the appearance of imine from **2a** and styrene was sigmoidal (Figure 3). Moreover, monitoring of the reaction by ^1H and ^{31}P NMR spectroscopy revealed the accumulation of a rhodium complex in small quantities that formed and decayed in concert with the initial lag in the formation of the imine. This intermediate did not accumulate during reactions of dimeric **2a**−**d** conducted with added phosphine or with any reaction of mononuclear complexes **3a**−**d**. Thus, this observation does not affect our kinetic data with monomer **3a**, but one could imagine that this complex could be an intermediate in the conversion of **3a** and olefins to the rhodium product **5a** and the imine.

However, we showed by independent synthesis that this intermediate was the bis PEt_3-ligated rhodium enamido complex of the anion of the product imine, $(PEt_3)_2Rh[(p\text{-tol})NC(Ph){=}CH_2]$. This material was prepared independently by the reaction of the potassium enamide of the *N*-tolylketimine with $[(PEt_3)_2Rh(\mu\text{-Cl})]_2$ generated in situ and displayed the same ^1H and ^{31}P NMR signals of the intermediate that accumulated in small amounts at the beginning of the reaction. The enamido complex was fully characterized by NMR spectroscopic methods, and a more comprehensive study of the synthesis, structure, and reactivity of this complex will be reported separately.

We presume this complex was formed by proton transfer between the ketimine product, or initial enamine product, and the starting rhodium amide. Indeed, reaction of dimeric toluidide **2a** and the ketimine generated some of the enamido complex. However, this proton transfer occurred to only partial conversion, and the equilibrium between the combination of *p*-toluidide **2a** and free imine and the combination of *p*-toluidine and this enamido complex lies toward the combination of *p*-toluidide **2a** and free imine. Addition of *p*-toluidine to the isolated enamido complex generated about 75% free **4a** and 80% of **2a**. Because of the thermodynamics of this protonolysis, the enamido complex is not present during reactions conducted with added arylamine or after some of the amine has been generated from hydrolysis by traces of water in the system. The monomeric arylamido complexes with three PEt_3 ligands are resistant to formation of the enamido complex because the stability of the enamido complex is largely derived from a polydentate coordination mode. The trisphosphine amide **3a** failed to react with ketimine **4a** even at 85 °C in C_6D_6.

E. Kinetic Orders of the Reagents and Additive. Data revealing the order of the reaction in olefin and added phosphine are shown in Figures 4 and 5. In the presence or absence of added toluidine, the decay of **3a** was first-order in olefin and inverse first-order in the concentration of added PEt_3. These data suggest that reversible dissociation of PEt_3 occurs prior to the rate-determining step and that reaction with olefin occurs prior to or as part of the rate-determining step. The rate constants for the decay of the reactant or the appearance of the rhodium product were unaffected by added amine. Thus, any involvement of the amine would likely occur after the rate-determining step.

These data are inconsistent with reaction by Paths B and C. The lack of an order in amine is inconsistent with reaction by the Path B involving attack of free amine on the coordinated olefin. The first-order rate behavior in **3a** is inconsistent with reaction by path C involving external attack of the rhodium amide on a coordinated olefin. Instead, our kinetic data are consistent with reaction by Paths A and D, which involve insertion of olefin or the combination of reversible α-elimination and rate-limiting [2 + 2] addition.

Prior literature and additional data argue against reaction by Path D. The spontaneous generation of a low-valent, late-metal imido complex from an amide group has little precedent, although examples of the generation of late-metal carbene intermediates from alkyl groups have been reported.[38−42]

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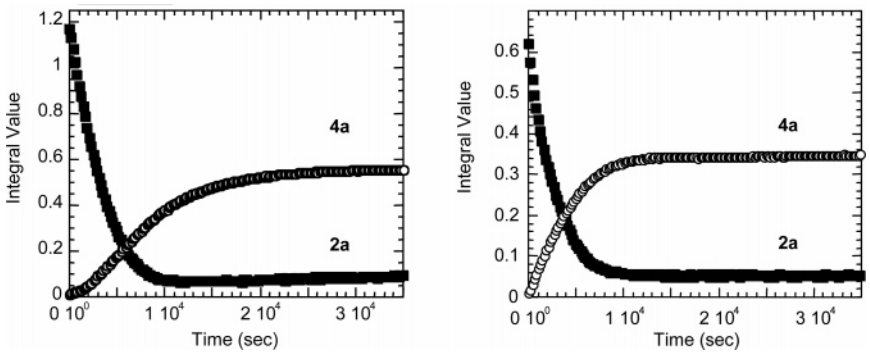

Figure 3. (Left) Plot of the consumption of amide **2a** and the formation of ketimine **4a** over time. (Right) Plot of the consumption of amide complex **2a** and the formation of ketimine **4a** over time in the presence of added *p*-toluidine (5 equiv). Reactions were carried out using 0.029 M **2a** and 0.87 M styrene in C_6D_6 at 85 °C and monitored by ^{1}H NMR.

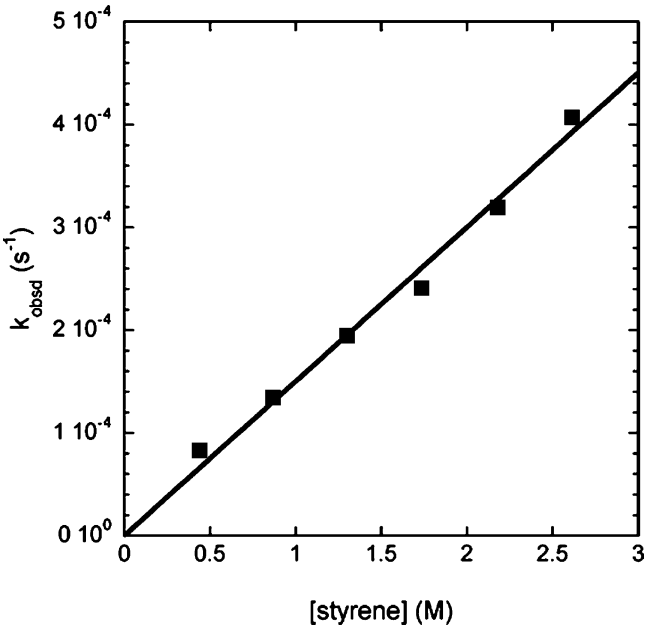

Figure 4. Plot of k_{obsd} vs [styrene] for the reaction of rhodium complex **3a** (0.029 M) with styrene in the presence of added PEt_3 (0.29 M) and *p*-toluidine (0.003 M) in C_7D_8 at 105 °C. The curve depicts the results of an unweighted least-squares fit to $y = ax$ ($a = 1.50 \pm 0.03 \times 10^{-2}$).

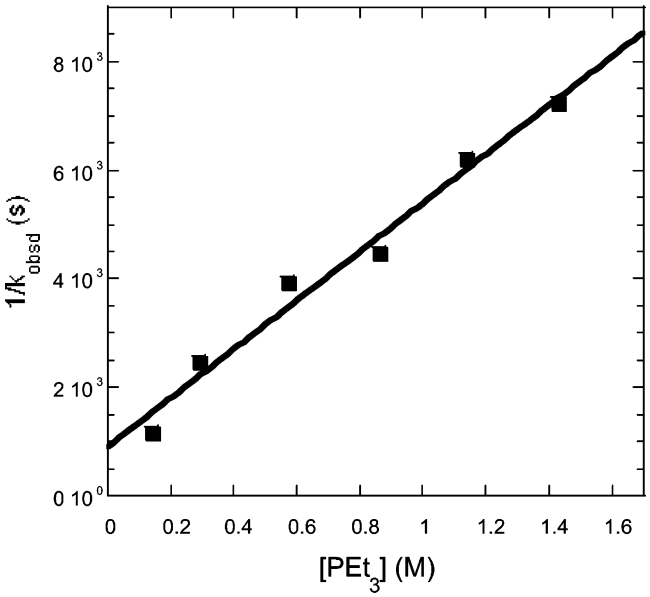

Figure 5. Plot of $1/k_{obsd}$ vs [PEt_3] for the reaction of rhodium complex **3a** (0.029 M) with styrene (2.57 M) in the presence of added PEt_3 and *p*-toluidine (0.003 M) in C_7D_8 at 105 °C. The curve depicts the results of an unweighted least-squares fit to $y = ax + b$ ($a = 4.5 \pm 0.3 \times 10^3$, $b = 9 \pm 3 \times 10^2$).

Further, few late-metal imido complexes react with alkenes, and products from cycloadditions of imido complexes have been limited to those formed from olefins containing activated C−C multiple bonds in α,β-unsaturated carbonyl compounds.[32] Most of the reactions of olefins with imido complexes generate aziridine,[43,44] and it is not clear if the imido group is transferred by an outer-sphere process of if a concerted [2 + 2] reaction to form an azametallacyclobutane occurs. Thus, the first and the second steps of pathway D, which are akin to the Green mechanism for formal insertion of olefins into metal alkyl groups,[45,46] have little precedent for the reaction of a low-valent, late-metal amido complex.

Nevertheless, we sought experimental data that could distinguish between Paths A and D. One could imagine that deuterium labeling could distinguish between these pathways because the two mechanisms would place the starting N−H hydrogen in a different position in the initially formed enamine product.[47] However, tautomerization of the enamine in this case scrambles the position of the label and prevents gaining information from this experiment.

Instead, measurements of isotope effects and reactivity of secondary amido complexes could distinguish between these mechanisms. The order in olefin requires that the α-elimination be reversible. If this step occurred, then one would expect to observe an equilibrium isotope effect when the reaction is conducted with toluidide complex **3a**−d_1 with deuterium in the N−H position. If reductive elimination of the resulting metallacycle were rate-limiting, then one would also expect to observe an isotope effect, although this isotope effect could be normal or inverse.[48−50] In contrast to these predictions, the rate constants

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for reaction of the N−D complex with added D_2N−*p*-Tol were indistinguishable from the rate constants for the reaction of the N−H complex with added toluidine (3.4±0.2 for **3a**−d_1 vs 3.0±0.2 × 10^{-4} s^{-1} for **3a**).

Formation of the analogous products from reactions of secondary amido complexes, which lack an N−H proton, more clearly distinguishes between Paths A and D. Path D cannot occur with a secondary amido complex. Although the *N*-methylanilido complex **3g**, which possesses the least steric and electronic perturbation from the arylamido complexes, undergoes β-hydrogen elimination without any reaction with the olefin, the dianisylamido complex **3f** did transfer the amido group to olefins. The transfer of this diarylamido group from rhodium to stryene was much slower and occurred in lower yield than the transfer of the arylamido groups, presumably because the diarylamido complexes are much more hindered and are less electron-donating than the monoarylamido complexes. Nevertheless, we did observe reaction of the dianisylamido complex **3f** with an excess of styrene to form measurable amounts of enamine. The formation of enamine from this reaction provides strong experimental evidence against Path D.

Thus, our kinetic data rules out Paths B and C, and several factors argue against reaction by Path D. Both the observation of some C−N bond formation with the secondary amide and the lack of an isotope effect of the N−H proton from reactions of the primary arylamides argue against reaction by Path D. Thus, Path A, which occurs by olefin insertion into the amide, remains the only path in Scheme 4 that is consistent with all of our experimental data.

4. Conclusions

The catalytic amination of olefins has been a long-term goal, and several mechanisms for hydroamination reactions have been deduced recently. Although oxidative addition of amine[51] and transfer of the resulting amido group to an olefin can be envisioned to be part of a catalytic cycle for hydroamination, the intermolecular transfer of the amido group from an isolated amido complex to an unactivated olefin had not been observed previously. The closest examples involve insertion of the strained norbornene into an iridium amido complex and the cyclization of lanthanide amido complexes generated in situ from aminoalkenes. The paucity of clear examples of insertions of olefins into amido complexes stands in contrast to the many examples of the transfer of alkyl and aryl groups to olefins, usually by insertion mechanisms.

Our current study demonstrates that amido groups can be transferred from simple late-transition-metal amido complexes to vinylarenes and alkenes to form imines. Although we have not directly observed the immediate product from an insertion process, detailed mechanistic data are consistent with a pathway involving insertion of the olefin into the rhodium-amido linkage, followed by β-hydrogen elimination and tautomerization of the resulting enamine to the ketimine. The mechanistic data are inconsistent with several plausible alternative reaction pathways.

At the current time, we do not have a firm explanation for the origin of the regioselectivity of the C−N bond formation. The regioselectivity of the reaction of the rhodium amides with propene and 1-hexene is the same as the typical regioselectivity of insertion of alkenes into metal−alkyl bonds,[52,53] but the regioselectivity of the reaction of the rhodium amides with vinylarenes contrasts with the typical regioselectivity of insertion of vinylarenes into late-transition metal−alkyl[54] and −aryl bonds. The reactions of late metal aryl complexes typically form stilbenes, rather than 1,1-disubstituted olefins, after β-hydrogen elimination.[55,56] Thus, studies to understand the origins of this selectivity by Path A, or another path that could be revealed by further data, and efforts to observe directly the initial products from reaction of the amido complex with olefins will be the focus of future studies.

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Supporting Information Available: Experimental details, kinetic plots, and full structural characterization of **1a** and **2e** (CIF and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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