Reactions of an Arylrhodium Complex with Aldehydes, Imines, Ketones, and Alkynones. New Classes of Insertion Reactions

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Organorhodium complexes of the general formula (DPPE)Rh(pyridine)(R) (R = *p*-tol (**2a**) and CH_2SiMe_3 (**2b**), DPPE = 1,2-bis(diphenylphosphino)ethane) were prepared from [(DPPE)Rh(μ-Cl)]$_2$, pyridine, and *p*-tolyllithium or Me_3SiCH_2MgCl. Complex **2a** inserted the electron-poor aldimines (*p*-tol)CH=N(C_6H_4-*p*-CO_2Me) (**3a-Tol**) and (Ph)CH=N(C_6H_4-*p*-CO_2Me) (**3a-Ph**) to give amide complexes that were isolated directly or trapped with PEt_3. In contrast, the reaction of aryl complex **2a** with the electron-neutral and electron-rich imines PhCH=NPh (**3b**) and (*p*-tol)CH=N(C_6H_4-*p*-OMe) (**3c**) did not form stable amide products. Instead, the amide from insertion of imines **3b** or **3c** underwent β-hydrogen elimination, followed by metalation of the resulting ketimine. The reaction of **2a** with **3a-Ph** was first order in arylrhodium complex and inverse first order in the concentration of pyridine. Aldehydes that cannot enolize, such as PhCHO and Me_3CCHO, inserted into the Rh−aryl bond of **2a** to form ketones and esters. The esters were formed from insertion of a second aldehyde into the Rh−O bond of an intermediate alkoxide, followed by β-hydride elimination. Complex **2a** underwent proton transfer with acetophenone to give π-oxaallyl complex **24** and with water to generate toluene and the dimeric hydroxide [(DPPE)Rh(μ-OH)]$_2$ (**36**). It also reacted with the *tert*-butyl-substituted ynone **25** to form a product that contained a metalated isobutyl group. Quenching the reaction between aryl complexes **2a** and **3a-Ph** with H_2O instead of PEt_3 also formed hydroxide **36** and the diarylmethylamine (Ph)(*p*-tol)CH−NH(C_6H_4-*p*-CO_2Me) (**35**).

Introduction

Insertions of alkenes into the metal−carbon bonds of late transition metal complexes are common,[1−23] and this elementary reaction is part of many catalytic processes.[24] Insertions of imines, aldehydes, and ketones into the metal−carbon or −hydrogen linkages of analogous complexes to form metal amides or alkoxides are less common, and direct observation of this elementary reaction is particularly rare.[25−29]

Nevertheless, late transition metal-catalyzed reactions of aldehydes and imines that are likely to occur by insertion of aldehydes or imines have emerged recently. For example, additions of aryl and vinyl groups to α,β-unsaturated carbonyl compounds, aldehydes, and imines catalyzed by rhodium[30,31] and other late metals[32−76] have become a versatile method for the construction of

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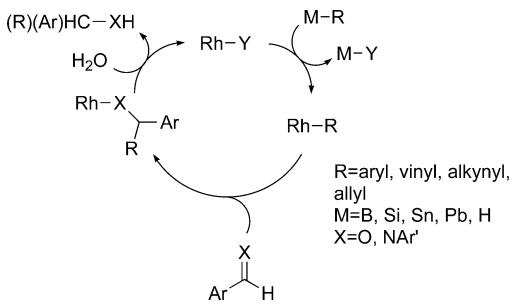
new carbon−carbon bonds. Few studies have been conducted to reveal the mechanism of the additions to aldehydes and imines, but insertions of aldehydes, ketones, and imines into late metal carbon bonds have been proposed to account for the formation of diarylmethanol or diarylmethylamine products (Scheme 1).

Scheme 1



These insertions would be analogous to classic insertions of alkenes into metal−carbon bonds.

The insertion of benzaldehyde into late transition metal−carbon bonds has been observed directly with discrete organometallic compounds in a few cases, but these insertions were likely to be driven by release of ring strain. One example involved insertion of benzaldehyde into the late metal−carbon bond of a ruthenium benzyne,[27] and the other involved insertion of formaldehyde into the metal−alkyl bond of a Ni metallacycle.[28] Prior to our work on the reactivity of the CO-ligated complexes $[(PPh_3)_2Rh(CO)R]$ (R = *p*-tol, *o*-tol, Me), insertion of aldehydes into acyclic late metal−carbon bonds was unknown.[25]

1,2-Insertions of imines into late metal−carbon bonds have not been reported. Arndtsen and Sen have described insertions of imines into Ni− and Pd−acyl linkages, but these reactions occur with 2,1-insertion regiochemistry and generate a metal−carbon bond.[77−80] Piers and Fryzuk described the only 1,2-insertion of an imine into a late metal−hydrogen bond to form a transition metal amide complex as product.[29]

The discrepancy between the large number of insertions of alkenes into discrete late metal hydride and alkyl complexes and the small number of insertions of aldehydes and imines with analogous complexes may result from unfavorable thermodynamic and kinetic factors. The insertion of an aldehyde or imine cleaves a stronger C−X π-bond than does the insertion of an olefin[81] and forms a product with an alkoxo or 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. Recent theoretical work by Cavallo support these claims, and an activation barrier for 2,1-insertion of an imine into a Pd−methyl bond was found to be greater than 40 kcal/mol.[82] The computed barrier for 1,2-insertion was not reported.

As we described previously,[25] organorhodium(I) complexes of the general formula $Rh(PPh_3)_2(CO)R$ (R =

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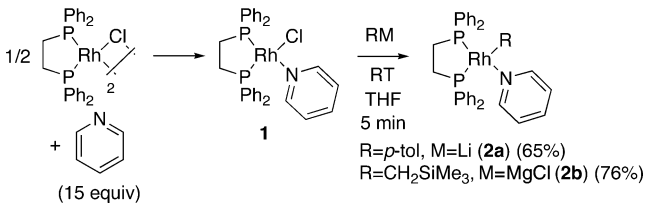
Scheme 2



p-tol, *o*-tol, Me) inserted aromatic aldehydes to form alkoxide intermediates. However, these complexes were unreactive toward imines. To promote insertions of imines, we sought to study complexes that contained an aryl group located *cis* to a ligand that is 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. Herein we describe the preparation of arylrhodium(I) complex (DPPE)Rh(py)(*p*-tol) (**2a**, DPPE = 1,2-bis(diphenylphosphino)ethane, py = pyridine) and its unusual reactivity with imines, aldehydes, ketones, and alkynones. Portions of this work have been reported in communication form.[26]

Results and Discussion

Preparation of Organorhodium(I) Complexes. To enhance the reactivity of arylrhodium complexes[83−94] toward insertion of aldehydes and imines, we sought complexes with dative ligands bound less tightly than those in the rhodium Vaska-type complexes we studied previously.[25] More specifically, we pursued rhodium complexes that contained a diphosphine backbone and a labile monodentate ligand. We envisioned the latter would be displaced by the aldehyde or imine to generate an intermediate that would undergo insertion.

Isolation of a stable arylrhodium complex with a pyridine ligand was accomplished with the diphosphine ligand DPPE (DPPE = 1,2-bis(diphenylphosphino)ethane). Reaction of the isolated chloride dimer [(DPPE)Rh(μ-Cl)]$_2$ with pyridine (15 equiv) gave a yellow solution containing the monomeric (DPPE)Rh(Cl)(py) (**1**), as determined by ^{1}H and ^{31}P NMR spectroscopy. Addition of solid *p*-tolyllithium to the bright yellow solution gave the desired arylrhodium complex (DPPE)Rh(py)(*p*-tol) (**2a**) in 65% isolated yield (Scheme 2). An analogous sequence was also conducted with DPPB (DPPB = 1,4-bis(diphenylphosphino)butane) as supporting ligand because this ligand generated active catalysts for the rhodium-catalyzed addition of arylboron and aryltin reagents to imines.[95] However, the final arylrhodium complex was unstable at room temperature. Reaction of $(CH_3)_3SiCH_2MgCl$ with the pyridine adduct **1** formed the alkylrhodium(I) complex (DPPE)Rh(py)(CH_2SiMe_3) (**2b**) in 76% isolated yield (Scheme 2).

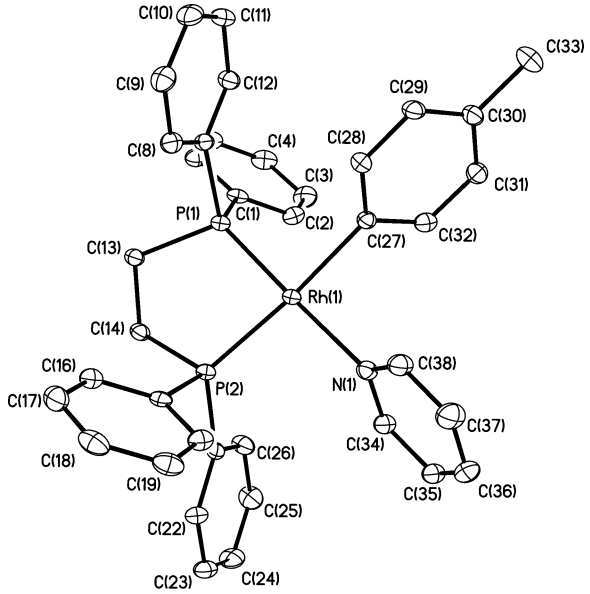


Figure 1. ORTEP diagram of (DPPE)Rh(py)(*p*-tol) **2a**.

Table 1. Selected Intramolecular Bond Distances and Angles for (DPPE)Rh(pyridine)(*p*-tolyl) (2a)

Bond Distances (Å)			
Rh(1)−C(27)	2.097(3)	Rh(1)−P(1)	2.1797(8)
Rh(1)−N(1)	2.132(3)	Rh(1)−P(2)	2.2481(8)
Bond Angles (deg)			
C(27)−Rh(1)−N(1)	87.50(10)	C(27)−Rh(1)−P(2)	174.94(8)
C(27)−Rh(1)−P(1)	90.96(8)	N(1)−Rh(1)−P(2)	96.16(7)
N(1)−Rh(1)−P(1)	177.77(7)	P(1)−Rh(1)−P(2)	85.47(3)

DPPE-ligated aryl and trimethylsilylmethyl complexes **2a** and **2b** were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis. Complex **2a** was also characterized by single-crystal X-ray diffraction. An ORTEP diagram of complex **2a** is provided in Figure 1, and selected bond distances and bond angles are given in Table 1. In the solid state, the ligands of **2a** are arranged in a typical square planar geometry. The Rh−N bond length is similar to other distances between rhodium(I) and a pyridine ligand.[96−99] The Rh−C bond length of **2a** (2.097 Å) is slightly longer than that in other rhodium aryl complexes that do not contain a CO ligand.[85,89,94]

Revealing spectroscopic characteristics of the organorhodium(I) complexes **2a** and **2b** included a pair of doublets of doublets in the ^{31}P NMR spectra. In addition, the *ipso*-aryl carbon atom directly bound to the Rh

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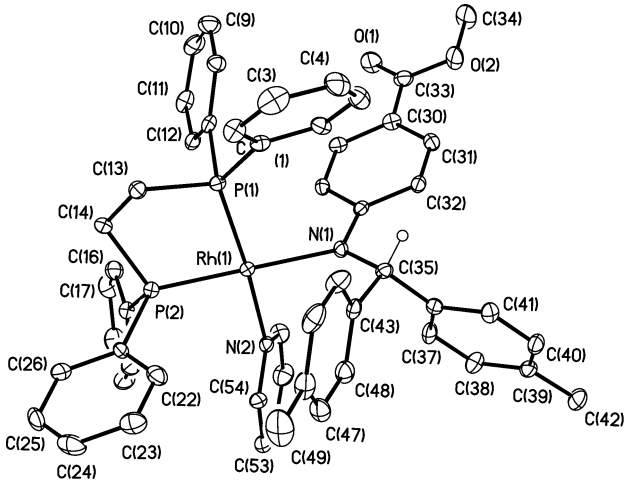


Figure 2. ORTEP diagram of (DPPE)Rh(pyridine)(NArCH(*p*-tolyl)$_2$) (**4**) (Ar = C_6H_4-*p*-CO_2Me).

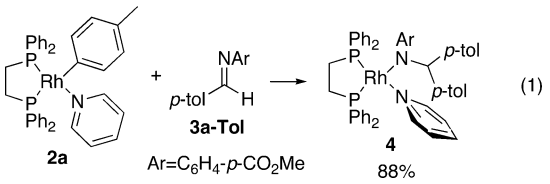
Table 2. Selected Intramolecular Bond Distances and Bond Angles for (DPPE)Rh(pyridine)-[NArCH(*p*-tol)$_2$] (Ar = *p*-C_6H_4-CO_2Me) (4)

Bond Distances (Å)			
Rh(1)−N(2)	2.145(3)	Rh(1)−P(2)	2.2055(9)
Rh(1)−N(1)	2.153(2)	Rh(1)−P(1)	2.2055(9)
N(1)−C(35)	1.465(3)		
Bond Angles (deg)			
N(2)−Rh(1)−N(1)	88.44(9)	N(2)−Rh(1)−P(1)	170.71(7)
N(2)−Rh(1)−P(2)	91.09(7)	N(1)−Rh(1)−P(1)	96.09(7)
N(1)−Rh(1)−P(2)	179.14(7)	P(2)−Rh(1)−P(1)	84.27(3)
C(27)−N(1)−C(35)	115.7(2)	C(36)−C(35)−C(43)	109.6(2)

center in aryl complex **2a** was observed by ^{13}C NMR spectroscopy as a doublet of doublets of doublets resonance at 175.0 (J_{CRh} = 94.1 Hz, J_{CP} = 31.5 Hz, J_{CP} = 15.0 Hz), and a similar signal was observed for the methylene carbon of the (trimethylsilyl)methyl fragment of **2b** (9.23 ppm, ddd, J_{CRh} = 69.1 Hz, J_{CP} = 22.4 Hz, J_{CP} = 10.7 Hz). The ^{1}H NMR spectrum of **2b** contained a doublet of doublets centered at 0.34 ppm for the methylene protons.

Reactions of Organorhodium(I) Complexes with Imines. Addition of 1 equiv of the *N*-aryl aldimine (*p*-tol)CH=N(C_6H_4-*p*-CO_2Me) (**3a-Tol**) to an arene solution of tolyl complex **2a** resulted in an immediate change of color from orange to red and formation of insertion product **4** (eq 1). The ^{1}H NMR spectrum of the reaction mixture obtained at room temperature contained broad signals, and the ^{31}P NMR spectra contained one broad doublet at 68.0 ppm (J = 178 Hz). Concentration of the reaction solution, followed by cooling to −35 °C, gave an orange crystalline material in 88% yield.

Single-crystal X-ray diffraction showed that the product was the pyridine-ligated amide complex **4**, resulting from insertion of the imine. An ORTEP diagram is provided in Figure 2, and selected bond distances and bond angles are given in Table 2. In the solid state, **4** adopts a square planar geometry with the bulky diarylmethyl and aryl substituents of the amide ligand positioned on either side of the plane of the molecule. The rhodium−nitrogen bond to the amido group is slightly longer than the rhodium−nitrogen bond to the pyridine ligand. This longer distance to the formally anionic amido group than to the dative pyridine is presumably due to the sterically demanding substituents on the amido nitrogen.



In contrast to NMR data obtained at room temperature, ^{1}H 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, four doublets corresponding to the aromatic protons of the *p*-tolyl groups, and a single methine resonance were observed. The *p*-tolyl groups are most likely diastereotopic because of slow rotation about the Rh−amide bond on the NMR time scale at −20 °C. ^{31}P NMR spectra acquired at −20 °C consisted of a single doublet, which was attributed to a small difference in chemical shifts of the phosphines and small P_A−P_B coupling. NMR simulations showed that the pair of doublets of doublets for an ABX pattern collapses to one doublet if the P_A−P_B coupling is small and the difference in chemical shift is small. Thus, to demonstrate the inequivalence of the phosphorus nuclei, a ^{31}P-decoupled ^{1}H NMR spectrum was acquired at −20 °C. Four inequivalent protons were observed for the methylene backbone of the DPPE ligand. Coalescence of the diastereotopic *p*-tolyl groups in the ^{1}H NMR spectrum of amide **4** at ambient temperature most likely results from an increased rate of rotation about the rhodium−nitrogen bond.

Bound pyridine in amide **4** exchanges with added pyridine at −20 °C, as determined by spin saturation experiments on samples of **4** containing 1 equiv of added pyridine. Selective irradiation of the *ortho* protons of bound pyridine resulted in complete saturation of the signals of both free and bound pyridine, suggesting that exchange between bound and free ligand is fast. This exchange with added pyridine is likely to be an associative process, considering the square planar, 16-electron configuration of **2a**.

Arylrhodium **2a** also underwent insertion of the aldimine (Ph)CH=N(C_6H_4-*p*-CO_2Me) (**3a-Ph**). In this case, the amide resulting from insertion (**5**) was treated with PEt_3 to replace the pyridine ligand and to form two diastereomers of PEt_3-ligated **6** (Scheme 3) that were isolated in 71% yield. Amides **6** were characterized by ^{1}H and ^{31}P NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. ^{1}H and ^{31}P NMR spectra of **6** obtained at room temperature contained sharp signals. The NMR spectral features, which included two *p*-tolyl resonances, two methyl ester resonances, and two methine resonances, were consistent with insertion to generate an amide with a stereocenter α to nitrogen and slow rotation about the Rh−N bond that creates a second stereochemical element. An ORTEP diagram of **6** is provided in Figure 3, and selected bond distances and bond angles are given in Table 3. The overall geometry of PEt_3-ligated **6** is similar to that of amido complex **4**, but the rhodium−nitrogen bond has been further lengthened by roughly 0.02 Å.

Complex **2a** also appeared to react with electron-neutral and electron-rich aldimines (Ph)CH=NPh (**3b**) and (*p*-tol)CH=N(C_6H_4-*p*-OMe) (**3c**) by insertion of the imine into the aryl−rhodium bond. However, the amido

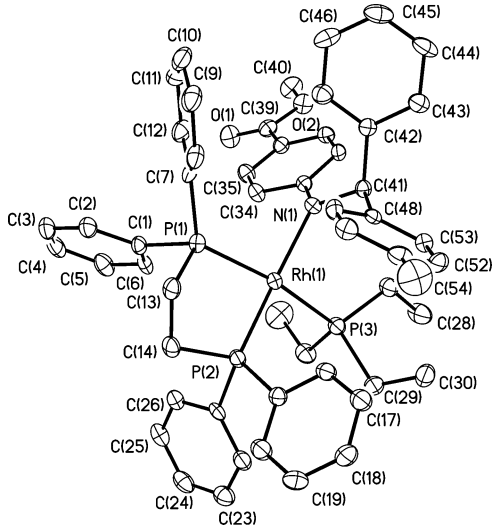


Figure 3. ORTEP diagram of (DPPE)Rh(PEt$_3$)[NArCH(Ph)(*p*-tolyl)] (Ar = C_6H_4-*p*-CO_2Me) (**6**).

Scheme 3

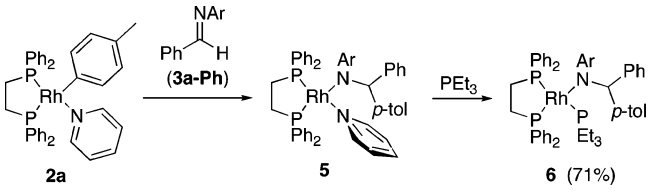


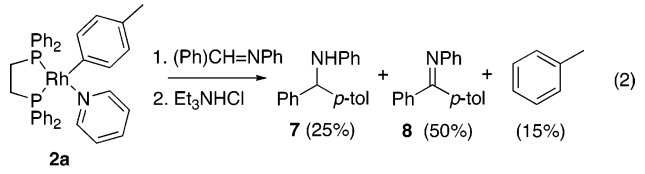
Table 3. Selected Bond Distances and Bond Angles for (DPPE)Rh(PEt$_3$)[NArCH(*p*-tol)(Ph)] (Ar = *p*-C_6H_4-CO_2Me) (6)

Bond Distances (Å)			
Rh(1)−N(1)	2.170(3)	Rh(1)−P(1)	2.2866(11)
Rh(1)−P(2)	2.2266(11)	Rh(1)−P(3)	2.3416(11)
N(1)−C(41)	1.467(4)		

Bond Angles (deg)			
N(1)−Rh(1)−P(2)	172.06(8)	N(1)−Rh(1)−P(3)	90.91
N(1)−Rh(1)−P(1)	95.43(8)	P(2)−Rh(1)−P(3)	92.33(4)
P(2)−Rh(1)−P(1)	82.88(4)	P(1)−Rh(1)−P(3)	166.97

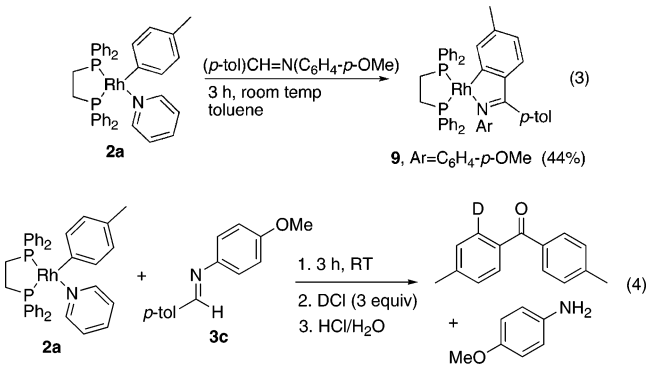
complexes formed from these insertions were less stable than those formed by insertion of the electron-poor imines **3a-Tol** and **3a-Ph**. This instability led to different final products.

Addition of **3b** (5 equiv) to a C_6D_6 solution of arylrhodium complex **2a** generated free diarylmethylamine (Ph)(*p*-tol)CH−NHPh (**7**) in 25% yield and toluene in 15% yield. Subsequent addition of Et_3NHCl (2−4 equiv) to the reaction solution generated the *E* and *Z* isomers of the ketimine (Ph)(*p*-tol)C=NPh (**8**) in 50% combined yield, as determined by ^{1}H NMR spectroscopy (eq 2). A ^{1}H NMR spectrum of the reaction mixture obtained prior to addition of Et_3NHCl showed that **2a** was fully consumed and that diarylmethylamine **7** and toluene were formed, along with complexes corresponding to two signals in the tolyl region (1:1 ratio) that comprised roughly 50% of the amount of **2a**. After addition of acid, these signals were absent, and two new signals corresponding to *E* and *Z* ketimine **8** were observed. We speculated that insertion of the imines with electron-neutral and electron-rich *N*-aryl groups occurred, but that these amides underwent β-hydrogen elimination and cyclometalation to form stable azametallacycles. Thus, we added ammonium salts to protonate the Rh−carbon bond and release the free imine.



The results of several experiments support our proposal that an amide is formed by insertion and that it undergoes β-hydrogen elimination and cyclometalation. Most definitive, the major product from reaction of **2a** with the electron-rich aldimine (*p*-tol)CH=N(C_6H_4-*p*-OMe) (**3c**) was isolated, and this product **9** was shown to possess a cyclometalated ketimine, as shown in eq 3. This material was formed in a 3.5:1 ratio with a second material we have not yet identified. The ^{31}P NMR spectrum of **9** consisted of a pair of doublets of doublets at 55.0 (J_{PRh} = 123 Hz, J_{PP} = 19.5 Hz) and 76.3 (J_{PRh} = 203 Hz, J_{PP} = 19.5 Hz) ppm for the two inequivalent phosphorus atoms. The ^{1}H NMR spectrum contained two signals in the tolyl region and one signal for a methoxy group. Single-crystal X-ray diffraction confirmed its identity. An ORTEP diagram of **9** is provided in Figure 4, and selected bond distances and bond angles are given in Table 4. Complex **9** was formed by *ortho*-metalation of one of the C-aryl groups of the ketimine to form a five-membered metallacycle.

To obtain information on the connectivity of the minor product, DCl was added to a crude mixture generated from arylrhodium **2a** and aldimine **3c**, and the released ketimine was hydrolyzed with aqueous HCl. This hydrolysis generated monodeuterio 4,4′-dimethylbenzophenone and unlabeled *p*-anisidine, as determined by GC/MS (eq 4). These results indicated that the second product also results from metalation of a C-aryl group, but we have not been able to make a definitive assignment of the structure of this minor rhodium product.



Scheme 4 shows the individual steps in the reaction between **2a** and **3c** that would generate metallacycle **9**. Insertion of imine into the Rh−aryl bond of **2a** would give an amide intermediate **10**. β-Hydrogen elimination would generate the hydridorhodium complex **11**, which contains bound ketimine (*p*-tol)$_2$C=N(C_6H_4-*p*-OMe). Metalation of a C-aryl group of the ketimine would generate a Rh(III) metallacycle (**12**) containing two hydride ligands. Reductive elimination of H_2 would form **9**. Similar *ortho*-metalations involving imines and azobenzenes have been previously described by Bruce et al.[100]

(100) Bruce, M. I.; Goodall, B. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 687, and references therein.

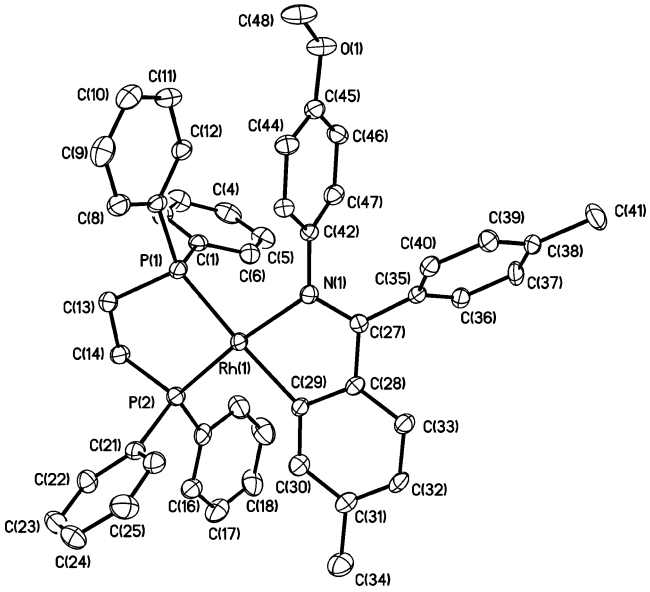
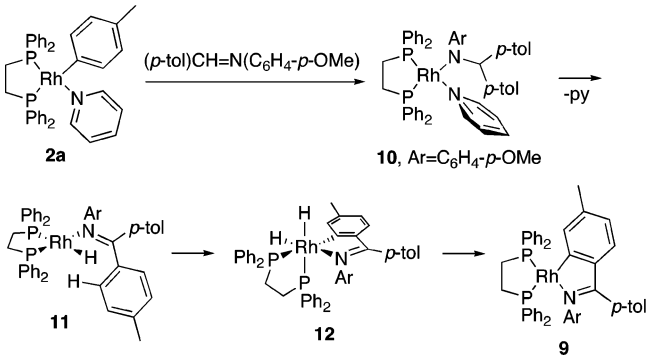


Figure 4. ORTEP diagram of (DPPE)Rh{C_6H_3-5-Me-2-C[(=N(Ar)(*p*-tol)]} (Ar = C_6H_4-*p*-OMe) (**9**).

Table 4. Selected Intramolecular Bond Distances and Bond Angles for Metallacycle 9

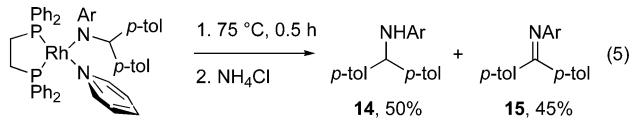
Bond Distances (Å)			
Rh(1)−C(29)	2.068(4)	Rh(1)−P(2)	2.1939(10)
Rh(1)−N(1)	2.108(3)	Rh(1)−P(1)	2.2766(11)
Bond Angles (deg)			
C(29)−Rh(1)−N(1)	79.57(12)	C(29)−Rh(1)−P(1)	170.98(10)
C(29)−Rh(1)−P(2)	94.36(10)	N(1)−Rh(1)−P(1)	101.13(8)
N(1)−Rh(1)−P(2)	173.84(8)	P(2)−Rh(1)−P(1)	84.70(4)
N(1)−C(27)−C(28)	116.3(3)	N(1)−C(27)−C(35)	123.3(3)

Scheme 4



The formation of H_2 by cyclometalation of the ketimine may explain the formation of diarylmethylamine **7** and toluene in the reaction between aryl complex **2a** and *N*-phenyl imine **3b**. This hydrogen may react with amide intermediate **10** and starting aryl complex **2a** to generate the amine and arene product. Alternatively, amine **7** could form from a combination of hydrogenolysis of the Rh−N bond in a metallacycle similar to **9** and hydrogenation of the C=N bond of the metalated unit. To distinguish between these two paths, aryl complex **2a** was allowed to react with aldimine **3b** in the presence of 1 equiv of ketimine (*p*-tol)(Ph)C=N(C_6H_4-*p*-CO_2Me) (**13**). Amine **7** was generated from reaction of **2a** with aldimine **3b**, but no amine from hydrogenation of added ketimine **13** was observed. Thus amine **7** is likely formed from hydrogenolysis of an amide intermediate that is analogous to the directly observed complex **4**, rather than by hydrogenation of the C=N bond in free or metalated ketimine.

The intermediacy of an amido complex from insertion of imines **3b** and **3c** into the Rh−aryl bond of **2a** was further supported by the reactivity of isolated amide **4**. As depicted in eq 5, heating of a C_6D_6 solution of **4** at 75 °C generated amine **14** and ketimine **15** in 50% and 45% yield. The products from this thermal chemistry are similar to those formed from the overall reaction of **2a** with aldimines **3b** and **3c**. We attribute the higher reactivity of the amide intermediates formed from reaction of aryl complex **2a** with imine **3b** or **3c**, in comparison to the reactivity of the amide generated from **2a** containing an electron-poor *N*-aryl group, to the electronic effect of the aryl group on the rate of β-hydrogen elimination of amides. β-Hydrogen eliminations from isolated complexes of the general formula $[(PPh_3)_2Ir(CO)(OCH(Me)(Ar)]$ have been shown to be slower when the aryl group contains a strong electron-withdrawing substituent in the *para*-position.[101]



4, Ar=C_6H_4-*p*-CO_2Me

An alternative mechanism for the formation of ketimine products could involve the oxidative addition of the iminoacyl C−H bonds of **3b** or **3c** to **2a**,[102−106] followed by reductive elimination of the iminoacyl and aryl ligands. However, two factors argue against formation of ketimines by this pathway. First, if formation of ketimine occurred by a C−H activation mechanism, then the mechanisms for the reaction of **2a** with two imines, one with an electron-neutral and one with an electron-poor *N*-aryl group, would be completely different. Amide complex **4** is clearly generated by insertion. Second, the products formed from thermolysis of amide **4** are similar to those formed from the overall reaction of aryl complex **2a** with imine **3b**.

Mechanistic Considerations. Effect of Added Pyridine. As noted above, free pyridine undergoes rapid exchange with the coordinated pyridine of **2a**. To determine if a similar exchange of imine for coordinated pyridine contributes to the higher reactivity of arylrhodium **2a** for insertion of imines, in comparison to the reactivity of $(PPh_3)_2$(CO)Rh(*p*-tol), kinetic experiments on the insertion reaction were conducted. Reactions of 0.026 M **2a** with 0.13 M imine (Ph)CH=N(C_6H_4-*p*-CO_2Me) (**3a-Ph**) were conducted at 2.0 °C with concentrations of added pyridine ranging from 0.089 to 0.46 M. The consumption of **2a** was monitored by ^{31}P NMR spectroscopy, and rate constants were obtained by fitting the curves to an exponential decay. The kinetic data showed a clear first-order decay in rhodium complex **2a**, first-order dependence on imine, and a clean inverse-first-order dependence on the concentra-

(101) Zhao, J.; Hesslink, H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 7220.
(102) Milstein, D. *Chem. Commun.* **1982**, 1357.
(103) Suggs, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 489.
(104) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 946.
(105) Barnhart, R. W.; Bosnich, B. *Organometallics* **1995**, *14*, 4343.
(106) Miller, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 1281.

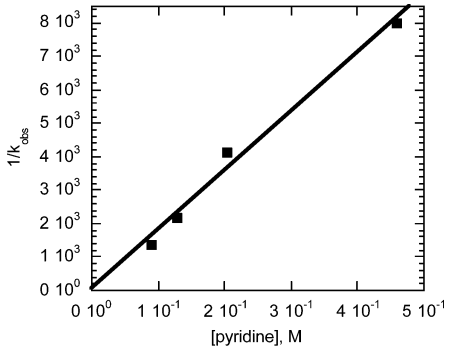
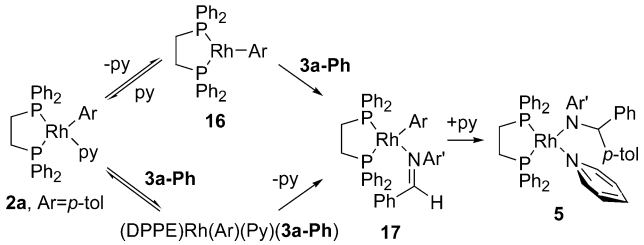
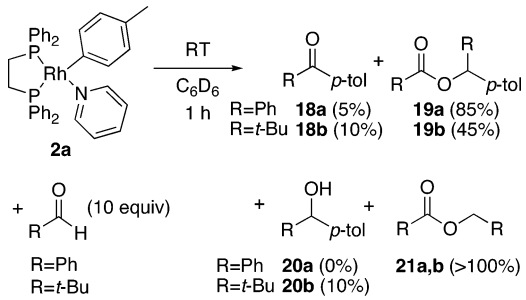


Figure 5. Plot of the inverse dependence of the observed rate constant on the concentration of pyridine.

Scheme 5



Scheme 6

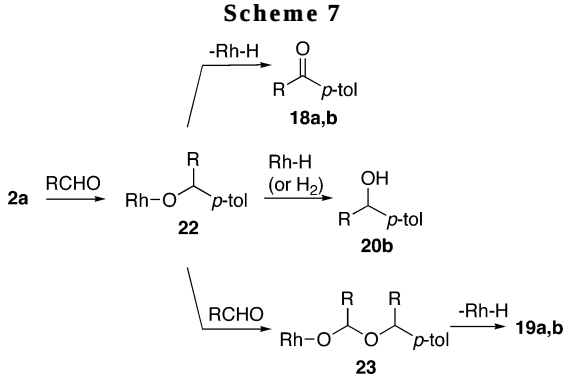


tion of added pyridine (Figure 5). Although these data do not reveal the coordination mode of the imine prior to insertion, they do imply that coordination of imine to the site occupied by pyridine in **2a** precedes the insertion process.

Scheme 5 shows two pathways for formation of amide intermediate **5**. The top path is initiated by reversible dissociation of pyridine to form a three-coordinate intermediate (**16**) followed by coordination of imine to form imine-bound aryl complex **17** and insertion to form amide **5**. The bottom path involves an associative displacement of pyridine to form **17** prior to insertion. Both paths would predict a first-order dependence on the concentration of aryl complex **2a** and imine **3a-Ph** and an inverse dependence on the concentration of pyridine. Although our data are consistent with both mechanisms, we favor generation of the imine complex **17** by the associative path because **2a** is a square planar, d^8 species.

Reaction of Organorhodium(I) Complexes with Aldehydes. Reactions of arylrhodium complex **2a** with aryl and *tert*-butyl aldehydes are summarized in Scheme 6. Addition of 1.1−2 equiv of benzaldehyde to **2a** in C_6D_6 resulted in a dark colored solution after a few minutes, but ^{31}P NMR spectroscopy showed that most of **2a** remained. In contrast, reaction of **2a** with 10 equiv of benzaldehyde fully consumed the starting rhodium

Scheme 7



complex and formed ester **19a** in 85% yield, as measured by ^1H NMR spectroscopy with an internal standard. The ketone 4-methylbenzophenone (**18a**), which would result from insertion of benzaldehyde followed by β-hydride elimination, was formed in only 5% yield. In addition, the ester **21a**, which contains two benzaldehyde units and no aryl group from rhodium, was formed. These three products were identified by comparison of NMR and GC/MS of crude reactions with those of material prepared independently or purchased commercially. Several rhodium products were formed after the complete consumption of rhodium complex **2a**.

The ester **19a** would form by insertion of PhCHO into the Rh−aryl bond and insertion of a second aldehyde into the resulting rhodium alkoxide **22** to form alkoxide **23** (Scheme 7, bottom path). β-Hydrogen elimination would then generate the final ester **19a**. The second ester **21a** would form by a rhodium-catalyzed Tischenko reaction, presumably initiated by the rhodium hydride generated from β-hydrogen elimination of alkoxides **22** and **23**. Insertion of 2 equiv of PhCHO into the rhodium hydride, followed by β-hydride elimination, would form ester **21a** and regenerate the starting hydride.

As shown in Scheme 6, reaction of the aliphatic aldehyde Me_3CCHO with aryl complex **2a** formed ketone and ester products that were analogous to those formed from reaction of benzaldehyde. In addition, the alcohol **20b** and some toluene were formed. The organic products were identified by independent synthesis of ketone **18b**, alcohol **20b**, and esters **19b** and **21b**. The toluene and alcohol **20b** may form from reaction of intermediate **22** with a rhodium hydride or H_2 (Scheme 7, middle path), as was proposed to account for formation of the small amount of amine from the reaction of aryl complex **2a** with imine **3b**.

In contrast to arylrhodium complex **2a**, alkylrhodium complex **2b** did not insert imines or aldehydes to form products that we were able to characterize. Complex **2b** was consumed upon reaction with imine **3a-Tol**, but several rhodium products were formed, as determined by ^{31}P NMR spectroscopy. Similarly, the reaction of benzaldehyde with **2b** did not form ketone or ester products similar to **18a**, and **19a** formed from **2a**, although the ester **21a** from a Tischenko process was observed by GC/MS. The distinct reactivity of aryl complex **2a** and alkyl complex **2b** is not currently understood.

Reaction of Arylrhodium(I) Complex 2a with Acetophenone and Aldehydes with Enolizable Hydrogens. The facile insertion of aldehydes and imines into the Rh−aryl bond of **2a** led us to investigate

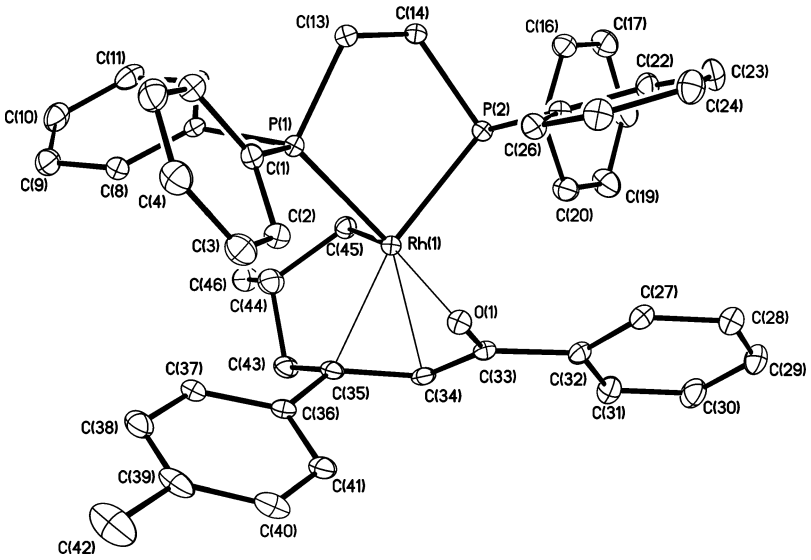
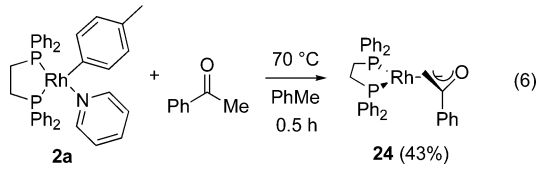


Figure 6. ORTEP diagram of (DPPE)Rh[$CH_2CHMeCH_2C$(*p*-tol)=CHC(O)Ph] (**26**).

the reactions of **2a** with ketones. Heating of a solution of **2a** and PhC(O)Me (1.1 equiv) at 70 °C consumed **2a** and formed in 43% isolated yield the π-oxaallyl complex **24** (eq 6). Similar complexes containing PPh_3 ligands were prepared by Slough from $[(PPh_3)_2Rh(\mu\text{-Cl})]_2$ and a potassium enolate.[107] The ^{1}H NMR spectrum of **24** contained broad signals at 3.54 and 4.37 ppm for the *syn*- and *anti*-protons of the methylene group, and the ^{13}C NMR spectrum contained signals at 51.6 and 157.6 ppm for the methylene and carbonyl carbons of the π-oxaallyl ligand. Such fast proton transfer of a low-valent, late metal hydrocarbyl complex is unusual.[108,109]



In contrast to the reactions of aryl complex **2a** with benzaldehyde and pivalaldehyde, reactions of aliphatic aldehydes containing enolizable hydrogens did not cleanly form products from insertion. The reaction of aryl complex **2a** with 1-hexanal formed several products, as judged by NMR spectroscopy.

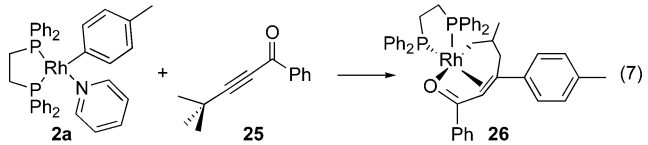
C−C Bond Cleavage from Reaction of Arylrhodium Complex 2a with an Ynone. The proton transfer between **2a** and acetophenone suggested that insertion of a ketone C=O bond into the rhodium−aryl bond of **2a** would require a more electrophilic ketone. Thus, we conducted the reaction of **2a** with ynone **25**. Reaction of **25** with **2a** in C_6D_6 immediately consumed the arylrhodium complex and formed the unexpected complex **26** shown in eq 7. The ^{1}H NMR spectrum of the product did not contain a singlet corresponding to a *tert*-butyl group. Instead, it contained a doublet at 0.60 ppm (J = 9.6 Hz). The ^{31}P NMR spectrum of the product contained a broad singlet at 47.1 ppm and a multiplet of equal intensity centered at 48.3 ppm.

Table 5. Selected Bond Distances and Bond Angles for 26

Bond Distances (Å)			
Rh(1)−C(45)	2.079(3)	Rh(1)−O(1)	2.276(2)
Rh(1)−C(34)	2.167(3)	Rh(1)−P(1)	2.2880(10)
Rh(1)−C(35)	2.181(3)	Rh(1)−P(2)	2.3035(9)
Rh(1)−C(33)	2.232(3)	O(1)−C(33)	1.300(3)
C(33)−C(34)	1.411(4)	C(34)−C(35)	1.453(4)

Bond Angles (deg)			
C(45)−Rh(1)−C(34)	92.88(12)	C(35)−Rh(1)−C(33)	69.59(11)
C(45)−Rh(1)−C(35)	82.98(12)	C(45)−Rh(1)−O(1)	156.50(10)
C(34)−Rh(1)−C(35)	39.06(11)	C(34)−Rh(1)−O(1)	63.70(10)
C(45)−Rh(1)−C(33)	124.55(12)	C(35)−Rh(1)−O(1)	79.55(10)
C(34)−Rh(1)−C(33)	37.40(11)	C(33)−Rh(1)−O(1)	33.49(9)
C(45)−Rh(1)−P(1)	91.28(9)	C(35)−Rh(1)−P(1)	111.10(8)
C(34)−Rh(1)−P(1)	148.69(8)	C(33)−Rh(1)−P(1)	143.03(8)
P(1)−Rh(1)−P(2)	85.16(3)		

The identity of the isolated product was established by single-crystal X-ray diffraction. An ORTEP diagram of **26** is provided in Figure 6, and selected bond distances and angles are given in Table 5. Apparently, reaction of **2a** with **25** resulted in exclusive addition of the *p*-tolyl group of **2a** to the β-position of the ynone, but subsequent rearrangement of the *tert*-butyl group to form the stable polyhapto ligand of **26** generates the final product.



Three potential mechanisms that account for the formation of **26** are shown in Scheme 8. Each path is initiated by addition of the *p*-tolyl group of **2a** to the β-position of **25** to generate the rhodium allenoate **27**. C−H activation of a methyl group would give metallacyclic intermediate **28**, and reductive elimination to form an O−H bond and tautomerization of the resulting allenol would give **29**. Path A consists of an intramolecular Michael addition of rhodium alkyl **29** to the enone to give the cyclopropylmethyl enolate complex **30**.

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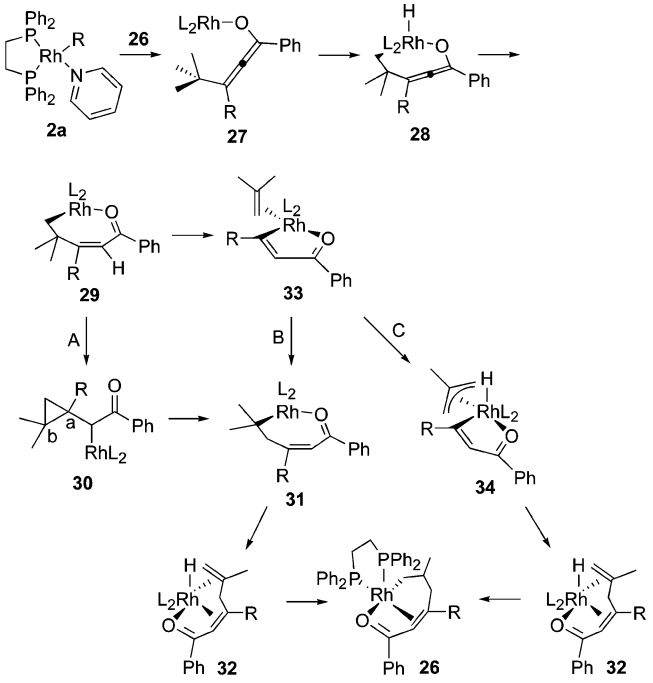
Scheme 8

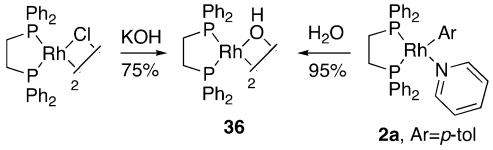


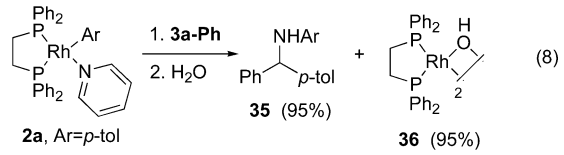
Cleavage of the cyclopropane at the C_a-C_b bond would give the tertiary alkyl complex **31**.[110] β-Hydrogen elimination and reinsertion would produce **26**. Alternatively, path B consists of β-vinyl elimination of **29** to generate coordinated isobutylene and vinylrhodium **33**. Olefin rotation and reinsertion would give **31**. Path C involves C−H activation of a methyl group of the coordinated isobutylene of **33** to give π-allyl **34**. C−C reductive elimination would generate the alkene hydride **32**, and **26** would form from insertion of the alkene into the rhodium hydride.

Although we do not have mechanistic data on the formation of **26**, bond-breaking steps similar to those shown in paths A−C have been reported previously with other late metal complexes. β-Carbon elimination of strained cycloalkyl ligands, analogous to the ring-opening of cyclopropylmethyl intermediate **30** in path A of Scheme 8, has been reported by Murakami and Bergman.[111−113] 1,2-Insertion of propylene into a Pd−Me bond followed by β-hydride elimination, rotation of the resulting olefin, and reinsertion to generate an agostic, tertiary alkyl has been demonstrated.[17] Also, the activation of sp^3 C−H bonds of α-olefins has been observed directly[114] and is likely an important step in the Ni-catalyzed isomerization of olefins. By any mechanism, the mild conditions for this structural rearrangement are remarkable.

Hydrolysis of Rhodium Amide and Aryl Compounds. Hydrolysis of amide and alkoxide complexes has been proposed to be the step of the Rh-catalyzed additions of organoboron or organotin reagents to aldehydes and imines that releases the final amine or alcohol product. Thus, we conducted reactions of arylrhodium complex **2a** with imine **3a-Ph**, and instead of trapping the amide with PEt_3, the product was quenched with water. This reaction sequence generated amine **35** and the dimeric Rh-hydroxide complex **36** in essentially quantitative yields (eq 8). The identity of the hydroxide complex was confirmed by independent synthesis (Scheme 9).

Scheme 9





We previously reported[25] that the arylrhodium complexes $(PPh_3)_2Rh(CO)(Ar)$, which contain a carbonyl ligand, did not react with water, and reactions of these complexes with aldehydes in mixtures of THF and water gave diarylcarbinol products instead of the diaryl ketones formed in dry arene solvents. In contrast, arylrhodium complex **2a** reacted rapidly with H_2O (1.5 equiv) to form toluene and the hydroxide complex **36** in quantitative yields (Scheme 9) at room temperature. Thus, the stability of the Rh−carbon bond to hydrolysis is highly dependent on the set of ligands and is apparently much faster with a full set of σ-donors as ancillary ligands and a phosphine *trans* to the aryl group. Hydrolyses of late metal−carbon bonds to form arenes or alkanes and metal hydroxides are uncommon,[27,114−116] and the rate of hydrolysis is likely to be an important factor in determining which Rh complexes catalyze the additions of main group aryl reagents discussed in the Introduction. Rapid hydrolysis of the rhodium aryl intermediate would prevent catalytic reactions that occur by insertion of aldehyde or imine into the rhodium−aryl bond, followed by hydrolysis of the amide or alkoxide.

Comparison of the Reactivity of 2a with Imines and Aldehydes to Other Late Metal Organometallic Complexes. The directly observed insertion of **3a-Tol** into the Rh−aryl bond of **2a** is the first example of a 1,2-insertion of an imine into a late metal−carbon bond to form a stable amide. Piers and Fryzuk have observed directly the insertion of imines into the Rh−H bond of a dimeric rhodium hydride complex to give amido hydride products. The reactions were proposed to occur through an imine that was bound through two metals, one at the C=N π-bond and the second at the nitrogen lone pair.[29] Arendtsen and Sen both have reported 2,1-insertions of imines into Pd- or Ni-acyl complexes.[77−80] These insertions may occur by direct nucleophilic attack of the imine nitrogen at the electrophilic acyl carbon. Indeed, Yamamoto has studied the

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mechanism of Pd-catalyzed aminocarbonylation of aryl halides and concluded that direct attack of amine on a Pd-acyl intermediate may account for the observed products.[117] Further, Arndtsen prepared a cationic Pd-Me complex containing a σ-bound imine ligand and showed that it did not insert imine.[78] Thus, the insertions of imines and aldehydes into the rhodium−aryl bond of **2a** reported here are likely to occur by a mechanism that is distinct from that of the previously reported 2,1-insertions. The pathway for 1,2-insertion is most likely akin to the migratory insertion pathway that is common for the insertion of olefins into late metal carbon bonds.

Few examples of 1,2-insertions of aldehydes into late metal−carbon bonds to form stable alkoxides have been reported. These examples were limited to insertions of aldehydes into strained metal−carbon bonds of metallacycles. Insertions of aldehydes into metal−carbon bonds of discrete complexes to form alkoxides that undergo β-hydrogen elimination have been reported in a few cases. Consistent with the instability of late metal alkoxides with β-hydrogens, the reactions of $(PPh_3)_2$Rh(CO)R with aldehydes we reported previously generated an alkoxide intermediate that eliminated ketone and formed a rhodium hydride product.

The alkoxides resulting from insertion of aldehyde are not just reactive toward β-hydrogen elimination. The formation of ester products **19a** and **19b** from reaction of aryl complex **2a** with aromatic aldehydes suggests that the alkoxide intermediates formed from insertion of aldehyde into the Rh−aryl bond are also highly reactive toward insertion of a second aldehyde.

Such insertion of aldehydes into late metal−oxygen bonds has also been reported only a few times previously.[25,118] We showed that an ester analogous to **19a** and **19b** formed if an excess of aldehyde was added to $(PPh_3)_2$Rh(CO)Ar or if aldehyde was added to the isolated alkoxide $(PPh_3)_2$Rh(CO)OR resulting from insertion of aldehyde.[25] Further, a rhodium-catalyzed Tischenko reaction that presumably occurs by a mechanism similar to that shown in Scheme 7 has been reported by Slough,[119] and Tischenko reactions catalyzed by isolated metal hydrides of other metals have been reported.[120−122] In addition, Kaplan and Bergman reported the reaction of a ruthenium hydroxide with aldehydes to form carboxylate complexes by a mechanism involving attack of a dissociated hydroxide on a Ru-bound aldehyde.[123]

Conclusions

The reactions of **2a** with imines, aldehydes, ketones, and water provide insight into the factors that promote insertion of C−N and C−O multiple bonds into late metal−carbon bonds. Insertion of *N*-aryl benzaldimines **3a-Ph**, **3a-Tol**, **3b**, and **3c** into the Rh−aryl bond of **2a** formed isolable amide products, or metallacycles resulting from a sequence of imine insertion, β-hydride elimination from the amide intermediate, and *ortho*-metalation of the resulting ketimine. Aryl aldehydes and aliphatic aldehydes that did not contain acidic protons reacted with **2a** to form organic products that are consistent with insertion of aldehyde. In contrast, aryl complex **2a** reacted with acetophenone or H_2O to form toluene and an enolate or hydroxide complex.

We propose that two factors lead to the unusually high reactivity of **2a** with aldehydes and imines. First, the presence of a weakly bound pyridine ligand allows coordination of aldehydes and imines in the square plane of the rhodium and reaction by migratory insertion. Second, proton transfer between weak acids and **2a** suggests that the rhodium−carbon bond of **2a** or the intermediate generated from exchange of water for pyridine is more polar than the metal−carbon bond in a typical late metal organometallic complex. This polarization may make the aryl group of **2a** or the species resulting from dissociation of pyridine more nucleophilic toward insertion of aldehydes and imines. At the same time, this basicity limits the chemistry between **2a** and aldehydes such as *n*-hexanal and ketones such as acetophenone, which possess enolizable hydrogens. Further studies to delineate the factors that control the reactivity of late metal−aryl bonds with aldehydes and imines and that promote reactions with late metal alkyl complexes should lead to new transformations of these common organic reagents.

Experimental Section

General Procedures. Unless noted otherwise, all manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. All glassware was oven-dried for approximately 1 h prior to use. THF, toluene, diethyl ether, and pentane were distilled from sodium benzophenone ketyl under nitrogen or were collected after passing through Q-5 and alumina in a solvent purification system. C_6D_6 and THF-d_8 were dried over sodium benzophenone ketyl and vacuum transferred prior to use. $CDCl_3$ was used as received. ^{1}H NMR spectra were obtained on 300, 400, or 500 MHz spectrometers. ^{1}H NMR spectra were recorded relative to residual protiated solvent. ^{13}C NMR spectra were obtained at 100.6 or 125.0 MHz, and chemical shifts were recorded relative to the solvent resonance. Both ^{1}H NMR and ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ^{31}P NMR spectra were obtained at 121.6, 162.0, or 202.4 MHz, and chemical shifts are reported relative to 85% H_3PO_4. The temperature of the NMR probe was calibrated for kinetic experiments using a digital thermometer. The aldimines (*p*-tol)CH=N(C_6H_4-*p*-CO_2Me) (**3a-Tol**), (Ph)CH=N(C_6H_4-*p*-CO_2Me) (**3a-Ph**), (Ph)CH=NPh (**3b**), and (*p*-tol)CH=N(C_6H_4-*p*-OMe) (**3c**) were prepared using procedures reported for the preparation of similar compounds.[124] [(DPPE)Rh(μ-Cl)]$_2$,[125] 4-methylbenzophenone imine,[126] 4,4′-dimethylbenzophenone imine,[126] solid *p*-tolyllithium,[127] **20b**,[128] **21b**,[121] and **25**[129] were prepared according to literature procedures. Compound **18b**[130] was synthesized

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by PCC oxidation of **20b** in CH_2Cl_2. PhBr, NaO-*t*-Bu, Cs_2CO_3, C_6H_4Br-*p*-CO_2Me, dodecahydrotriphenylene, 1,3,5-trimethoxybenzene, Et_3NHCl, DCl (1.0 M solution in Et_2O), Me_3SiCH_2MgCl (1.0 M solution in Et_2O), **18a**, **20a**, **21a**, acetophenone, anhydrous EtOH and MeOH, Me_3CCHO, PhC(O)Cl, Na metal, $Me_3CC(O)Cl$, $NaBH_4$, triethylamine, and PEt_3 were used as received. PhCHO was distilled and stored in a glovebox. $Pd_2(dba)_3$, $Pd(OAc)_2$, and (±)-BINAP were used as received. Pyridine and distilled H_2O were degassed by sparging with nitrogen prior to use. KOH pellets were crushed into a powder using a mortar and pestle.

Preparation of (DPPE)Rh(pyridine)(*p*-tolyl) (DPPE = 1,2-bis(diphenylphosphino)ethane) (2a). Into a 50 mL round-bottom flask equipped with a magnetic stir bar was placed [(DPPE)Rh(μ-Cl)$_2$] (185 mg, 0.172 mmol). THF (10 mL) and pyridine (209 μL, 2.58 mmol) were added to generate a cloudy yellow solution after ca. 10 min. *p*-Tolyllithium (34.6 mg, 0.353 mmol) was added as a solid, and an orange solution was generated. After 5 min of stirring at room temperature, all volatile materials were removed under reduced pressure. The product was extracted into Et_2O, and the resulting solution filtered through Celite. The clear orange solution was slowly concentrated and cooled to −35 °C to give 150.0 mg of orange crystalline **2a** (65% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 1.87−2.05 (m, 4H), 2.20 (s, 3H), 6.08 (t, J = 6.8 Hz, 2H), 6.46 (t, J = 8.0 Hz, 1H), 6.91 (d, J = 6.8 Hz, 2H), 7.05−7.16 (m, 12H), 7.64−7.73 (m, 6H), 7.83−7.88 (m, 4H), 8.53−8.55 (m, 2H). ^{13}C NMR (125.8 MHz, THF-d_8): δ 21.3, 28.5−28.8 (m), 31.0−31.5 (m), 124.2, 126.6 (d, J = 5.7 Hz), 127.9 (d, J = 9.3 Hz), 128.5, 128.6 (d, J = 8.4 Hz), 129.0, 129.7, 133.8 (d, J = 12.3 Hz), 134.4 (d, J = 11.6 Hz), 135.7, 138.7 (d, J = 38.2 Hz), 139.3 (d, J = 21.1 Hz), 139.4, 153.2, 175.0 (ddd, J_{RhC} = 94.1 Hz, $^2J_{CP}$ = 31.5 Hz, $^2J_{CP}$ = 15.0 Hz). ^{31}P NMR (202 MHz, C_6D_6): δ 57.6 (dd, J_{RhP} = 122 Hz, J_{PP} = 19.6 Hz), 74.3 (dd, J_{RhP} = 200 Hz, J_{PP} = 19.6 Hz). Anal. Calcd for $C_{38}H_{36}NP_2Rh$: C, 67.96; H, 5.40; N, 2.09. Found: C, 67.69; H, 5.30; N, 1.94.

Preparation of (DPPE)Rh(pyridine)(CH_2SiMe_3) (2b). Into a 50 mL round-bottom flask equipped with a magnetic stir bar was placed [(DPPE)Rh(μ-Cl)$_2$] (170 mg, 0.158 mmol). THF (10 mL) and pyridine (192 μL, 2.38 mmol) were added, and a cloudy yellow solution was generated after ca. 10 min. Me_3SiCH_2MgCl (325 μL, 0.325 mol) was added by syringe, and an orange solution was generated. After 5 min of stirring at room temperature, all volatile materials were removed under reduced pressure. The product was extracted into Et_2O, and the resulting solution filtered through Celite. The clear orange solution was slowly concentrated and cooled at −35 °C to give 161 mg of bright orange **2b** (76% yield). **2b** was stored at −35 °C. ^{1}H NMR (400 MHz, C_6D_6): δ −0.03 (s, 9H), 0.34 (dd, J = 5.6 Hz, J = 5.6 Hz, 2H), 1.76−2.02 (m, 4H), 6.23 (t, J = 6.8 Hz, 2H), 6.60 (t, J = 7.6 Hz, 1H), 7.02−7.07 (m, 6H), 7.12−7.14 (m, 2H), 7.20−7.25 (m, 4H), 7.60−7.64 (m, 4H), 7.98−8.03 (m, 4H), 8.68 (d, J = 4.8 Hz, 2H). ^{13}C NMR (125.8 MHz, THF-d_8): δ 4.24, 9.23 (ddd, J_{CRh} = 69.1 Hz, J_{CP} = 22.4 Hz, J_{CP} = 10.7 Hz), 29.7−30.1 (m), 31.3−31.8 (m), 124.4, 128.2 (d, J_{CP} = 7.8 Hz), 128.4 (d, J_{CP} = 8.6 Hz), 129.0, 129.2, 133.6 (d, J = 12.7 Hz), 134.5 (d, J = 10.8 Hz), 135.7, 139.4 (d, J_{CP} = 38.5 Hz), 139.5 (d, J_{CP} = 21.3 Hz), 153.5. ^{31}P NMR (202 MHz, C_6D_6): δ 55.9 (dd, J_{PRh} = 137 Hz, J_{PP} = 23.6 Hz), 80.0 (dd, J_{PRh} = 195 Hz, J_{PP} = 23.2 Hz). Anal. Calcd for $C_{35}H_{40}NP_2RhSi$: C, 62.96; H, 6.04; N, 2.10. Found: C, 62.76; H, 5.87; N, 2.02.

Preparation of Amide 4. Into a 20 mL scintillation vial equipped with a stir bar were placed **2a** (112 mg, 0.167 mmol) and **3a-Tol** (46.4 mg, 0.184 mmol, 1.1 equiv). Toluene (6−8 mL) was added, and the solution stirred for 10−15 min at room temperature. The solution was concentrated under reduced pressure to 1 mL and cooled at −35 °C for 12 h. An orange solid precipitated, which was isolated from the supernatant, washed with cold toluene, and dried to give 150 mg of **4** (88%). Complex **4** was stored at −35 °C. ^{1}H NMR (400 MHz, THF-d_8, −20 °C): δ 1.54−2.25 (m, 4H), 2.10 (s, 3H), 2.31 (s, 3H), 2.37 (s, 3H), 3.57 (s, 3H), 4.84 (s, 1H), 5.49 (dd, J = 9.4 Hz, J = 2.2 Hz, 1H), 6.32 (d, J = 7.6 Hz, 2H), 6.46 (d, J = 7.6 Hz, 2H), 6.59 (d, J = 4 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 7.10−7.50 (m, 26 H), 7.69 (m, 4H), 8.45 (d, J = 5.2 Hz, 2H), 8.51 (dd, J = 9.0 Hz, J = 2.2 Hz, 1H). ^{31}P NMR (162 MHz, THF-d_8, −20 °C): δ 67.5 (d, J = 177 Hz). Anal. Calcd for $C_{61}H_{59}N_2O_2P_2Rh$: C, 72.04; H, 5.85; N, 2.75. Found: C, 72.04; H, 5.90; N, 2.52.

Preparation of (DPPE)Rh(PEt_3)[NArCH(Ph)(*p*-tol)] (Ar = C_6H_4-*p*-CO_2Me) (6). Into a 20 mL scintillation vial equipped with magnetic stir bar were placed **2a** (142 mg, 0.211 mmol) and **3a-Ph** (56.1 mg, 0.222 mmol, 1.05 equiv). Toluene (8 mL) was added, and the solution was stirred for 5 min at room temperature. PEt_3 (32.4 μL, 0.222 mmol, 1.05 equiv) was added by microliter syringe. The solution was concentrated in vacuo to about 2 mL and diluted with Et_2O (approximately 4 mL total volume). The solution was layered with pentane and allowed to stand overnight at room temperature, giving a yellow precipitate. The supernatant was removed using a pipet, and the solid was washed with pentane and dried under reduced pressure to give 142 mg (71%) of a 1:1.25 mixture of diastereomers. Complex **6** was stored at −35 °C. ^{1}H{^{31}P} NMR (400 MHz, C_6D_6, integrations are approximated to a 1:1 ratio of diastereomers): δ 0.71−0.76 (m, 18 H), 0.97−1.04 (m, 6H), 1.30−1.37 (m, 8H), 1.41−1.53 (m, 2H), 1.63−1.68 (m, 2H), 1.76−1.84 (m, 2H), 2.07 (s, 3H), 2.17 (s, 3H), 3.62 (s, 3H), 3.64 (s, 3H), 5.42 (s, 1H), 5.44 (s, 1H), 6.81 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 6.96−7.14 (m, 32H), 7.17−7.46 (m, 24H), 8.02−8.10 (m, 6H). ^{31}P NMR (202.4 MHz, C_6D_6): δ 6.80 (ddd, J_{PRh} = 346 Hz, J_{PP} = 142 Hz, J_{PP} = 43.9 Hz), 48.3−51.1 (m), 64.2−65.6 (m). All signals for both diastereomers were not observed due to overlap of signals. Anal. Calcd for $C_{54}H_{59}NO_2P_3Rh$: C, 68.28; H, 6.26; N, 1.47. Found: C, 67.94; H, 6.53; N, 1.33.

Reaction of 2a with PhCH=NPh (3b). To a small vial were placed **2a** (10.0 mg, 0.0149 mmol) and dodecahydrotriphenylene (1 mg) as internal standard. These compounds were dissolved in C_6D_6 (0.7 mL), and an ^{1}H NMR spectrum was acquired. The solution was then added to a separate vial containing **3b** (13.6 mg, 0.0744 mmol, 5 equiv), and the resulting solution stirred at room temperature for 1 h. Et_3NHCl (6.20 mg, 0.0447 mmol, 3 equiv) was added, and the solution stirred for 2 h or until the solution had changed from a dark color to an orange color. An ^{1}H NMR spectrum was acquired, and yields of ketimine **8** and diarylmethylamine **7** were calculated to be 50% and 25%.

Independent Preparation of *N*-[(4-Methylphenyl)-(phenyl)methyl]-*N*-phenylamine (7).[131] The following reaction was not conducted in an inert atmosphere. Into a 250 mL round-bottom flask equipped with a magnetic stir bar was placed ketimine **8** (200 mg, 0.738 mmol). The ketimine was dissolved in EtOH (30 mL), and $NaBH_4$ (2.21 g, 59.0 mmol, 80 equiv) was added in four portions. The yellow color eventually dissipated to give a colorless solution after 2−3 h. When the reaction was complete, as determined by TLC, the volatile materials were removed by rotary evaporation. The remaining solid was quenched with water, and the product was extracted into Et_2O. The organic layer was separated and dried over $MgSO_4$ and filtered. The Et_2O was removed by rotary evaporation, and the residue was purified by silica gel chromatography eluting with 30% ethyl acetate in hexane to give 173 mg (86%) of the diarylmethylamine. ^{1}H NMR (300 MHz, C_6D_6): δ 2.08 (s, 3H), 3.91 (d, J = 3.6 Hz, 1H), 5.41 (d,

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J = 4.2 Hz, 1H), 6.44 (d, J = 7.8 Hz, 2H), 6.70 (m, 1H), 6.93 (d, J = 7.8 Hz, 2H), 7.01−7.25 (m, 9H).

Independent Preparation of *N*-[(*E,Z*)-(4-Methylphenyl)(phenyl)methylene]-*N*-phenylamine (8).[132] Into a 20 mL scintillation vial were placed 4-methylbenzophenone imine (500 mg, 2.56 mmol), bromobenzene (402 mg, 2.56 mmol), $Pd_2(dba)_3$ (6.60 mg, 0.00641 mmol, 0.25 mol %), (±)-BINAP (12.0 mg, 0.0192 mmol, 0.75 mol %), and NaO*t*-Bu (345 mg, 3.59 mmol, 1.4 equiv). Toluene (10 mL) was added, and the vial capped. The mixture was heated at 80 °C for 12 h. The yellow solution was allowed to cool to room temperature and was filtered through Celite. The volatile materials were removed under reduced pressure, and the imine was purified by silica gel chromatography, eluting with 10% ethyl acetate in hexane. Compound **8** (636 mg, 92%) was obtained as a 1:1 mixture of *E* and *Z* isomers. ^{1}H NMR (300 MHz, C_6D_6): δ 1.91 (s, 3H), 2.05 (s, 3H), 6.72 (d, J = 7.8 Hz, 2H), 6.74−7.06 (m, 22H), 7.94 (d, J = 8.1 Hz, 2H), 7.98−8.01 (m, 2H).

Preparation of Cyclometalated Complex 9. To a 20 mL scintillation vial equipped with a magnetic stir bar were added **2a** (114 mg, 0.170 mmol) and imine **3c** (57.3 mg, 0.255 mmol, 1.50 equiv). Toluene (4−6 mL) was added, and the resulting solution was stirred at room temperature for 3 h. The dark solution was concentrated in vacuo, was layered with pentane, and cooled overnight at −35 °C. An olive green solid precipitated. The dark supernatant was removed with a pipet, and the solid was washed with pentane and dried in vacuo to give 62.0 mg of **9** (44%). Crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into a concentrated toluene solution of **9**. ^{1}H NMR (400 MHz, C_6D_6): δ 1.77 (s, 3H), 1.85 (m, 4H), 1.95 (s, 3H), 2.94 (s, 3H), 5.93 (d, J = 7.6 Hz, 2H), 6.60−6.62 (m, 4H), 6.68 (d, J = 7.6 Hz, 1H), 6.84 (d, J = 8.0 Hz, 2H), 6.98−7.16 (m, 13H), 7.51 (br s, 1H), 7.73−7.77 (m, 4H), 8.32−8.36 (m, 4H). ^{31}P NMR (121.6 MHz, C_6D_6): δ 55.0 (dd, J_{PRh}=123 Hz, J_{PP} = 19.5 Hz), 76.3 (dd, J_{PRh} = 203 Hz, J_{PP} = 19.5 Hz).

Reaction of 2a with PhCH=NPh (3b) in the Presence of Added Ketimine 13. To a small vial were added **2a** (10.0 mg, 0.0149 mmol), **3b** (3.00 mg, 0.0164 mmol, 1.1 equiv), and **13** (4.90 mg, 0.0149 mmol). These compounds were dissolved in C_6D_6 (0.7 mL), and the resulting solution was stirred for 2 h. GC/MS analysis of the solution showed the formation of amine **7** and ketimine **8** and no formation of the diarylmethylamine from **13**.

Preparation of Methyl 4-{[(*E,Z*)-(4-Methylphenyl)(phenyl)methylene]amino}benzoate (13). To a 20 mL scintillation vial equipped with a magnetic stir bar were added 4-methylbenzophenone imine (0.500 g, 2.56 mmol), C_6H_4Br-*p*-CO_2Me (543 mg, 2.56 mmol), $Pd(OAc)_2$ (11.5 mg, 0.0513 mmol, 2 mol %), (±)-BINAP (47.9 mg, 0.0769 mmol, 3 mol %), and Cs_2CO_3 (1.17 g, 3.59 mmol, 1.4 equiv). Toluene (∼8 mL) was added, and the mixture heated at 100 °C for 5 h. The yellow solution was allowed to cool to room temperature and filtered. The volatile materials were removed under reduced pressure, and the ketimine was purified by silica gel chromatography using 10% ethyl acetate in hexane as eluent. The ketimine (689 mg, 82%) was obtained as a 1:1 mixture of *E* and *Z* isomers. ^{1}H NMR (400 MHz, C_6D_6): δ 1.90 (s, 3H), 2.05 (s, 3H), 3.42 (s, 3H), 3.43 (s, 3H), 6.70−6.74 (m, 6H), 6.83 (d, J = 7.6 Hz, 2H), 6.86−6.91 (m, 6H), 6.98 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.93−7.95 (m, 2H), 7.99−8.01 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 21.4, 51.8, 120.5, 120.6, 124.5, 127.9, 128.2, 128.7, 128.8, 129.0, 129.3, 129.4, 129.5, 130.2, 130.3, 131.0, 132.5, 135.7, 136.2, 139.2, 141.6, 155.7, 155.8, 166.9, 168.7, 169.0. Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 79.98; H, 5.90; N, 4.02.

Deuterium Labeling Study of the Reaction of 2a with (*p*-tol)CH=N(C_6H_4-*p*-OMe) (3c). Into a small vial were placed **2a** (10.0 mg, 0.0149 mmol) and **3c** (3.70 mg, 0.0164 mmol, 1.10 equiv). These compounds were dissolved in C_6D_6 (0.7 mL), and the resulting solution was stirred for 3 h. DCl (48.0 μL of a 1.0 M Et_2O solution, 0.045 mmol, 3.0 equiv) was added by syringe. After 15 min, 10 drops of a 1 N aqueous HCl solution were added, and the contents were stirred overnight at room temperature. A 6 M aqueous solution of NaOH was added dropwise until the solution was basic. GC/MS analysis of the C_6D_6 layer showed the products of ketimine hydrolysis (4,4′-dimethylbenzophenone and *p*-anisidine). (M + 1)/(M+) ratios (authentic material in parentheses): *p*-anisidine, 0.083 (0.073); 4,4′-dimethylbenzophenone, 2.39 (0.14).

Thermolysis of 4. Into a small vial were placed **2a** (10.0 mg, 0.0149 mmol) and 1,3,5-trimethoxybenzene (1 mg) as internal standard. These compounds were dissolved in C_6D_6 (0.7 mL), and a ^{1}H NMR spectrum was acquired. The solution was then added to a separate vial containing **3a-Tol** (3.56 mg, 0.0156 mmol, 1.05 equiv), and the resulting solution was stirred at room temperature for 10 min. The red-orange solution was transferred to an NMR tube and heated at 75 °C for about 0.5 h. Et_3NHCl (6.20 mg, 0.0447 mmol, 3 equiv) was added, and the solution was stirred for 2 h or until it had changed from a dark color to a red-orange color. A ^{1}H NMR spectrum was acquired, and the yields of diarylmethylamine **14** and ketimine **15** were calculated to be 50% and 45%.

Independent Preparation of Methyl 4-{[Bis(4-methylphenyl)methyl]amino}benzoate (14). This reaction was not conducted under an inert atmosphere. Into a 250 mL round-bottom flask equipped with a magnetic stir bar was placed ketimine **15** (95.0 mg, 0.277 mmol). The ketimine was suspended in MeOH (30 mL), and $NaBH_4$ (0.842 g, 22.2 mmol, 80 equiv) was added in four portions. The yellow color of the ketimine faded after 2−3 h of heating at reflux. However, the ketimine was not completely consumed, as determined by TLC, after additional heating at reflux or upon addition of excess $NaBH_4$. The volatile materials were removed by rotary evaporation, and the remaining solid was quenched with water. The product was extracted into Et_2O. The organic layer was separated and dried over $MgSO_4$ and filtered. The Et_2O was removed by rotary evaporation, and the residue was purified by silica gel chromatography eluting with 10% ethyl acetate in hexane to give 51.1 mg (54%) of **14**. ^{1}H NMR (500 MHz, C_6D_6): δ 2.08 (s, 6H), 3.52 (s, 3H), 4.28 (d, J = 5.0 Hz, 1H), 5.37 (d, J = 5.0 Hz, 1H), 6.28 (d, J = 7.3 Hz, 2 H), 6.94 (d, J = 8.0 Hz, 4H), 7.06 (d, J = 8.5 Hz, 4H), 8.07 (d, J = 7.0 Hz, 2H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 21.0, 51.1, 61.9, 112.9, 119.7, 127.9, 129.6, 131.7, 137.2, 139.7, 151.2, 166.9. Anal. Calcd for $C_{23}C_{23}NO_2$: C, 79.97; H, 6.71; N, 4.05. Found: C, 79.75; H, 6.95; N, 3.91.

Independent Preparation of Methyl 4-{[Bis(4-methylphenyl)methylene]amino}benzoate (15). To a 20 mL scintillation vial equipped with a magnetic stir bar were added 4,4′-dimethylbenzophenone imine (0.500 g, 2.39 mmol), C_6H_4Br-*p*-CO_2Me (540 mg, 2.63 mmol, 1.10 equiv), $Pd(OAc)_2$ (10.7 mg, 0.0478 mmol, 2 mol %), (±)-BINAP (44.7 mg, 0.0718 mmol, 3 mol %), and Cs_2CO_3 (1.09 g, 3.35 mmol, 1.4 equiv). Toluene (∼8 mL) was added, and the mixture was heated at 100 °C for 5 h. The yellow solution was allowed to cool to room temperature and filtered. The volatile materials were removed under reduced pressure, and the ketimine was purified by silica gel chromatography using 10% ethyl acetate in hexane as eluent. Recrystallization from EtOH gave 410 mg (50%) of **15**. ^{1}H NMR (400 MHz, C_6D_6): δ 1.91 (s, 3H), 2.07 (s, 3H), 3.42 (s, 3H), 6.74 (m, 4H), 6.88 (d, J = 7.6 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 21.1, 21.3, 51.2, 120.9, 125.2, 128.9, 129.2, 129.6, 130.0, 130.8, 133.4, 137.2, 138.7, 141.4, 156.7, 166.4, 168.3. Anal. Calcd for $C_{23}C_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.46; H, 5.71; N, 3.67.

Representative Procedure for the Kinetic Experiments of the Reaction between 2a and 3a-Ph. Into a small

(132) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871.

vial was placed **2a** (12.0 mg, 0.0179 mmol), toluene (0.40 mL), and pyridine (5.1 μL, 0.0625 mmol, 3.5 equiv). This solution was transferred to an NMR tube equipped with a screw-capped top containing a Teflon septum. The solution was cooled with dry ice. In a separate vial was placed imine **3a-Ph** (21.5 mg, 0.0893 mmol, 5 equiv), which was then dissolved in toluene (0.30 mL). This solution was drawn into a 1 mL syringe and added to the cold solution contained in the NMR tube. The contents of the NMR tube were mixed briefly, and the tube was placed into the NMR probe cooled to 2.0 °C. The consumption of **2a** was monitored by ^{31}P NMR spectroscopy, and the rate constants were determined by fitting the data to an exponential decay using KaleidaGraph software. This procedure was repeated using 5, 8, and 18 equiv of pyridine.

Representative Procedure for the Reaction of 2a with PhCHO or Me_3CCHO. Into a small vial were placed **2a** (10.0 mg, 0.0149 mmol) and 1 mg of 1,3,5-trimethoxybenzene. The contents were dissolved in C_6D_6 (0.7 mL), and an ^{1}H NMR spectrum was acquired. The sample was returned to a small vial equipped with a magnetic stir bar, and aldehyde (10 equiv) was added by microliter syringe. The solution was stirred at room temperature for 1 h. An ^{1}H NMR spectrum was acquired, and the yields of products shown in Scheme 6 were calculated.

Independent Preparation of (4-Methylphenyl)(phenyl)methyl Benzoate (19a). Into a 50 mL two-neck round-bottom flask equipped with magnetic stir bar was placed 4-methyl benzhydrol (150 mg, 0.758 mmol). The flask was flushed with nitrogen, and CH_2Cl_2 (8 mL) was added by syringe. Fresh PhC(O)Cl (260 μL, 2.27 mmol, 3 equiv) and Et_3N (15 equiv) were added by syringe. The resulting solution was stirred for 3 h at room temperature. The solution was diluted with CH_2Cl_2, and 10% aqueous HCl was added to quench the excess benzoyl chloride. The mixture was washed with aqueous $NaHCO_3$, and the organic layer was separated and dried over $MgSO_4$. The solution was decanted from $MgSO_4$, and the volatile materials were removed under rotary evaporation. The crude material was purified by silica gel chromatography using 10% ethyl acetate in hexane to give the title compound in 63% yield (145 mg). ^{1}H NMR (400 MHz, C_6D_6): δ 2.05 (s, 3H), 6.93 (d, J = 8.0 Hz, 2H), 7.00−7.13 (m, 6H), 7.30−7.34 (m, 3H), 7.40 (d, J = 8.0 Hz, 2H), 8.19−8.21 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 21.0, 77.5, 127.5, 127.7, 128.0, 128.6, 128.7, 129.4, 130.0, 130.9, 132.9, 137.6, 138.1, 141.1, 165.4. Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.15; H, 6.01.

Independent Preparation of 2,2-Dimethyl-1-(4-methylphenyl)propyl Pivalate (19b). Into a 20 mL scintillation vial were placed alcohol **20b** (212 mg, 1.07 mmol) and Na metal (82.0 mg, 3.57 mmol, 3 equiv). THF (6−8 mL) was added and the mixture stirred for 6 h at room temperature. The cloudy pale yellow solution was decanted into a separate vial containing $Me_3CC(O)Cl$ (214 mg, 1.79 mmol, 1.5 equiv). The solution became colorless upon addition of the sodium alkoxide. After 1 h of stirring, the volatile materials were removed by rotary evaporation, and the product was extracted into hexane. The solution was filtered through Celite and concentrated. Silica gel chromatography using 2.5% ethyl acetate in hexane gave 66.0 mg of **19b** (21%). ^{1}H NMR (500 MHz, C_6D_6): δ 0.91 (s, 9H), 1.17 (s, 9H), 2.10 (s, 3H), 5.67 (s, 1H), 6.96 (d, J = 7.5 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 21.1, 26.1, 27.2, 35.2, 38.9, 82.4, 127.5, 128.3, 135.7, 136.9, 177.1. Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.58; H, 10.17.

Preparation of 24. Into a 20 mL scintillation vial equipped with a magnetic stir bar was placed **2a** (109 mg, 0.162 mmol). The solid was dissolved in toluene (8 mL), and acetophenone (21.0 μL, 0.179 mmol, 1.1 equiv) was added by syringe. The solution was heated at 70 °C for 0.5 h. The solution was then allowed to cool to room temperature and was concentrated under reduced pressure to about 1 mL. Cooling of the concentrated solution gave an orange solid. The dark colored supernatant was removed by pipet, and the solid recrystallized a second time from toluene to give 43.0 mg of **24** (43%). ^{1}H NMR (400 MHz, C_6D_6): δ 1.80 (m, 4H), 3.54 (br s, 1H), 4.37 (br s, 1H), 6.87−7.17 (m, 15H), 7.36 (br m, 2H), 7.73 (br m, 2H), 8.00−8.17 (m, 6H). ^{31}P NMR (202.4 MHz, C_6D_6): δ 79.0 (dd, J_{PRh} = 215 Hz, J_{PP} = 34.2 Hz), 65.4 (dd, J_{PRh} = 198 Hz, J_{PP} = 34.2 Hz). Anal. Calcd for $C_{34}H_{31}OP_2Rh$: C, 65.82; H, 5.04. Found: C, 65.67; H, 5.00.

Preparation of 26. Into a 20 mL scintillation vial equipped with a magnetic stir bar was placed **2a** (196 mg, 0.292 mmol). The solid was dissolved in 8 mL of toluene. Addition of a toluene solution of ynone **25** (57.0 mg, 0.306 mmol, 1.05 equiv) by pipet generated a dark colored solution. The solution was filtered through Celite and concentrated under reduced pressure to about 1 mL. Cooling the solution to −35 °C gave a yellow-orange solid. The dark supernatant was removed by pipet, and the solid was washed with a minimal amount of cold Et_2O and pentane. The solid was then dissolved in THF and concentrated to about 2 mL. The solution was layered with pentane and cooled to −35 °C overnight. The mother liquor was decanted from the yellow-orange crystals, which were dried in vacuo to give 102 mg (41%) of **26**. ^{1}H NMR (400 MHz, C_6D_6): δ 0.60 (d, J = 9.6 Hz, 3H), 0.65−0.74 (m, 2H), 1.71−1.78 (m, 2H), 1.95−2.05 (m, 3H), 2.27 (s, 3H), 2.40−2.51 (m, 1H), 2.62 (m, 1H), 5.20 (s, 1H), 6.78−7.13 (m, 21H), 7.26−7.38 (m, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.61−7.64 (m, 2H), 7.80 (d, J = 8.0 Hz, 2H). ^{31}P NMR (121.6 MHz, C_6D_6): δ 47.1 (br s), 48.1−48.7 (m). Anal. Calcd for $C_{46}H_{45}OP_2Rh{\cdot}C_4H_8O$: C, 70.58; H, 6.28. Found: C, 70.88; H, 6.25.

Independent Preparation of Methyl 4-{[(4-Methylphenyl)(phenyl)methyl] amino}benzoate (35). The reaction was not conducted under an inert atmosphere. Into a 250 mL round-bottom flask equipped with a magnetic stir bar was placed **13** (170 mg, 0.517 mmol). The ketimine was suspended in EtOH (30 mL), and $NaBH_4$ (1.56 g, 41.3 mmol, 80 equiv) was added in four portions. The yellow color of the ketimine faded after 2−3 h of heating at reflux. Upon complete consumption of the starting material, as determined by TLC, the volatile materials were removed by rotary evaporation, and the remaining solid was quenched with water and the product was extracted into Et_2O. The organic layer was separated and dried over $MgSO_4$ and filtered. The Et_2O was removed by rotary evaporation, and the residue was purified by silica gel chromatography eluting with 10% ethyl acetate in hexane to give 118 mg (70%) of **35**. ^{1}H NMR (500 MHz, C_6D_6): δ 2.08 (s, 3H), 3.53 (s, 3H), 4.15 (d, J = 4.5 Hz, 1H), 5.35 (d, J = 4.5 Hz, 1H), 6.24 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 7.00−7.05 (m, 3H), 7.07−7.12 (m, 4H), 8.06 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 21.0, 51.1, 62.1, 112.8, 119.5, 127.6, 127.7, 127.8, 129.0, 129.6, 131.7, 137.2, 139.5, 142.6, 151.2, 167.0. Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.25. Found: C, 79.73; H, 6.55; N, 4.10.

Preparation of [(DPPE)Rh(μ-OH)]$_2$ (36). Into a 50 mL Schlenk flask equipped with a magnetic stir bar were placed [(DPPE)Rh(μ-Cl)]$_2$ (150 mg, 0.140 mmol) and KOH (783 mg, 14.0 mmol, 100 equiv). These were suspended in toluene (10 mL), and H_2O (6 mL) was added by cannula. The biphasic mixture was heated at 75 °C for 2 h. The orange-brown organic layer was removed by cannula to a separate flask, and $MgSO_4$ was added to remove water. The solution was filtered through Celite and concentrated under reduced pressure. Addition of pentane gave a yellow-orange precipitate. The solution was cooled briefly to complete the precipitation. The supernatant was removed by pipet and redissolved in THF. Concentration of the solution and layering with Et_2O gave an orange solid, which was isolated from the supernatant and dried to give 109 mg (75%) of **36**. ^{1}H NMR (400 MHz, C_6D_6): δ −0.55 (s, 2H), 1.72 (d, J = 17.2 Hz, 8H), 6.98 (m, 24H), 8.03 (m, 16H). ^{31}P NMR (202.4 MHz, C_6D_6): δ 74.4 (d, J = 190 Hz). Anal. Calcd for $C_{52}H_{50}O_2P_4Rh_2$: C, 60.25; H, 4.86. Found: C, 59.99; H, 5.07.

Reaction of 2a and PhCH=N(C_6H_4-*p*-CO_2Me (3a-Ph) with Aqueous Workup. Into a small vial equipped with a magnetic stir bar were placed **2a** (10 mg, 0.0149 mmol) and 1 mg of 1,3,5-trimethoxybenzene. C_6D_6 (0.7 mL) was added, and an ^{1}H NMR spectrum was acquired. The sample was added to a separate vial containing **3a-Ph** (3.7 mg, 0.0156 mmol, 1.05 equiv), and the solution stirred for 5 min at room temperature. H_2O (1.0 μL, 0.0521 mmol, 3.5 equiv) was added by microliter syringe, and the solution was stirred for 0.5 h. An ^{1}H NMR spectrum was acquired, and the yields of hydroxide **36** and amine **35** were calculated to be >95%.

Reaction of 2a with H_2O. Into a small vial equipped with a stir bar were placed **2a** (10 mg, 0.0149 mmol) and 1 mg of 1,3,5-trimethoxybenzene. Complex **2a** was dissolved in C_6D_6 (0.7 mL), and an ^{1}H NMR spectrum was acquired. H_2O (1.5 μL, 0.0833 mmol, 5.5 equiv) was added by microliter syringe. The solution was stirred for 2 h at room temperature. An ^{1}H NMR spectrum after this time showed the quantitative formation of toluene and hydroxide **36**.

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Supporting Information Available: Full crystallographic reports for compounds **2a**, **4**, **6**, **9**, and **26** and corresponding .cif files are available free of charge via the Internet at http://www.pubs.acs.org.

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