

Insertions of Ketones and Nitriles into Organorhodium(I) Complexes and β -Hydrocarbyl Eliminations from Rhodium(I) Alkoxo and Iminyl Complexes

Pinjing Zhao and John F. Hartwig*

Department of Chemistry, University of Illinois at Urbana–Champaign, 600 S. Mathews Avenue, Urbana, Illinois 61801, and Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

Received April 29, 2008

A series of tris(triethylphosphine)-ligated organorhodium(I) complexes were prepared, and their reactions with electron-poor aryl nitriles and diarylketones were studied. $[(\text{PEt}_3)_3\text{Rh}(\text{Ar})]$ (Ar = phenyl (**1a**) or *o*-anisyl (**1e**)) reacted with an excess of electron-poor aryl nitriles $\text{Ar}'\text{C}\equiv\text{N}$ (Ar' = *p*-CF₃C₆H₄ or 3,5-bis(CF₃)C₆H₃) to form Rh(I) iminyl complexes $\{(\text{PEt}_3)_3\text{Rh}[\text{N}=\text{C}(\text{Ar})(\text{Ar}')] \}$ (**2h–j**). In contrast, 3,5-bis(CF₃)C₆H₃CN did not insert into the M–C bond of the arylrhodium(I) complexes $[(\text{PEt}_3)_3\text{Rh}(\text{Ar})]$ (Ar = *p*-CF₃C₆H₄ (**1f**) or 3,5-bis(CF₃)C₆H₃ (**1g**)), containing more electron-poor aryl groups. The kinetic data for nitrile insertions were most consistent with a pathway involving initial ligand dissociation, followed by a classic migratory insertion. The iminyl complexes **2i–j** decomposed at higher temperatures via β -aryl eliminations with selective migration of the more electron-poor aryl group 3,5-bis(CF₃)C₆H₃ to form **1g** and the corresponding nitriles. Migratory aptitudes of various aryl groups were assessed by studying β -aryl eliminations from a variety of iminyl complexes. Kinetic data for these β -aryl eliminations were most consistent with initial phosphine dissociation and carbon–carbon bond cleavage of the resulting 14-electron intermediate. Insertions of diarylketones $\text{Ar}(\text{Ar}')\text{C}=\text{O}$ (Ar = 3,5-bis(CF₃)C₆H₃, Ar' = Ph or 3,5-bis(CF₃)C₆H₃) into **1a** also occurred, although the resulting Rh(I) alkoxides $\{(\text{PEt}_3)_2\text{Rh}[\text{OC}(\text{Ph})(\text{Ar})(\text{Ar}')] \}$ (**3f–g**) were not stable under the reaction conditions and could not be directly identified. Instead, a mixture of $\{(\text{PEt}_3)_3\text{Rh}[3,5\text{-bis}(\text{CF}_3)\text{C}_6\text{H}_3] \}$ (**1g**) and the ketone $\text{Ph}(\text{Ar}')\text{C}=\text{O}$ (Ar' = Ph or 3,5-bis(CF₃)C₆H₃) were detected as the major products, indicating that decomposition of alkoxides **3f–g** occurred by β -elimination of the more electron-poor aryl group. Independent preparation of **3f–g** and studies on their thermal decomposition with added PEt_3 confirmed that selective β -aryl elimination occurs to generate aryl complex **1g** and the corresponding ketones. Analogous β -aryl eliminations from bisphosphine rhodium(I) alkoxo complexes **3a–e** and trisphosphine rhodium(I) alkoxo complexes **4b–e** were also studied, and the kinetic results were most consistent with irreversible β -phenyl elimination from bis(phosphine) alkoxo complexes. Insertion of 3,5-bis(CF₃)C₆H₃CN into an alkylrhodium(I) complex $[(\text{PEt}_3)_3\text{Rh}(\text{Me})]$ (**1h**) did not occur; however, the electron-poor ketone $\text{Ar}_2\text{C}=\text{O}$ (Ar = 3,5-bis(CF₃)C₆H₃) inserted into **1h**, as judged by the detection of the corresponding alcohol $\text{HOC}(\text{Me})[3,5\text{-bis}(\text{CF}_3)\text{C}_6\text{H}_3]_2$ as the major organic product after quenching with $\text{Et}_3\text{N}\cdot\text{HCl}$. Vinylrhodium(I) complex $[(\text{PEt}_3)_3\text{Rh}(\text{CH}=\text{CH}_2)]$ (**1i**) also reacted with ketones of the type $\text{Ar}_2\text{C}=\text{O}$ (Ar = 3,5-bis(CF₃)C₆H₃) to form a Rh(I) alkoxo complex $(\text{PEt}_3)_2\text{Rh}\{\text{OC}(\text{CH}=\text{CH}_2)[3,5\text{-bis}(\text{CF}_3)\text{C}_6\text{H}_3]_2\}$ (**3h**), which was stabilized by the intramolecular coordination of the vinyl moiety to the rhodium center. The alkynylrhodium(I) complex $[(\text{PEt}_3)_3\text{Rh}(\text{C}\equiv\text{CPh})]$ (**1j**) did not react with ketones or nitriles. Instead, the propargylic alkoxides $\{(\text{PEt}_3)_2\text{Rh}[\text{OC}(\text{R})_2(\text{C}\equiv\text{CPh})] \}$ (R = Me or Ph) that would have resulted from insertion were shown to react rapidly in the presence of added PEt_3 to form the alkynyl complex **1j** and the corresponding ketones via β -alkynyl eliminations.

Introduction

Insertions of C–C multiple bonds into the metal–carbon bonds of late transition metal complexes and the reverse β -alkyl elimination reactions of metal alkyl complexes are classic elementary organometallic reactions. In recent years, new catalytic reactions have been developed that are likely to occur by insertions of aldehydes, aldimines, and nitriles,¹ and reactions that occur by β -elimination of aryl and allyl groups from

alkoxides have been reported.^{2–7} However, the direct observations of these insertions and eliminations remain rare.^{8,9} In particular, alkoxo and iminyl complexes that result from the insertions of ketones and nitriles into late-metal–carbon bonds (Scheme 1) have not been observed directly.

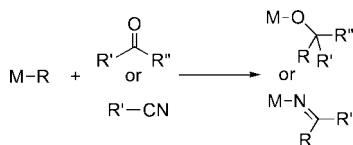
The challenge to observe nitrile and ketone insertions into late-metal–carbon bonds is created by both thermodynamic and kinetic factors that stem from the coordinating ability of the

* Corresponding author. E-mail: jhartwig@scs.uiuc.edu.

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Scheme 1



heteroatom and the steric environment about the C–X multiple bonds. First, C–X π -bonds tend to be stronger than C–C π -bonds. Second, the steric hindrance at the C–O π -bond of a ketone is greater than that of the C=C π -bond of terminal, monosubstituted, α -olefins. Third, coordination of a nitrile via the nitrogen lone pair (σ -complex) competes with coordination through the π -system, and coordination through the π -system is likely to precede migratory insertion.¹⁰

Indeed, relatively recent work from the authors' laboratory on the insertions of aldehydes and aldimines into arylrhodium(I) complexes to form isolable rhodium(I) alkoxo and amido complexes represented the first observation of such insertions into metal–carbon bonds of discrete, acyclic late-metal organometallic compounds.^{11–13} Moreover, recent work described in communication form showed that β -aryl eliminations occur

from rhodium alkoxo and iminyl compounds to generate arylrhodium products and free ketone or nitrile, respectively.^{14,15} These data underscore the thermodynamic hurdle toward observing insertions of ketones and nitriles into late-metal carbon bonds.

Although the insertions of ketones into late-metal–carbon bonds have not been observed directly, a few stoichiometric organometallic processes are likely to occur by insertions of nitriles. Cheng and co-workers have observed that thermal decomposition of a Pd(II) aryl complex in neat acetonitrile at 160 °C gave a small amount of an imine product that presumably formed by nitrile insertion into the Pd–C linkage.¹⁶ Vicente and co-workers have reported insertions of nitriles into an *ortho*-hydroxyphenylpalladium(II) complex to form a Pd-imine complex that was likely promoted by proton transfer from the *ortho*-hydroxyl group to the cyano group rather than direct migratory insertion.¹⁷ More recently, Ceder and co-workers reported the reaction of acetonitrile with a cationic Ni(II) mesityl complex to form an imine complex that may result from nitrile insertions, although alternative pathways including nitrile protonation could not be excluded.¹⁸

The insertions of ketones and nitriles into late-metal–carbon bonds are likely involved in several recently developed catalytic transformations. Arylation and alkenylation of activated ketone substrates, such as β -ketoesters,^{19–22} cyclobutanones,^{2a,6,23,24} α,α,α -trifluoroacetophenone,²⁵ and isatins^{26,27} have been catalyzed by palladium and rhodium complexes. A rhodium-catalyzed reaction of cyanoformates with arylboronic acids has been reported in which the cyano group was selectively arylated over the ester group.²⁸ Palladium- and rhodium-catalyzed processes that likely occur by intramolecular insertions of nitriles^{29–36} and ketones^{34,37–39} into late-metal–aryl or –alkenyl linkages have also been reported, including processes that occur with good enantioselectivities.^{40,41} More recently, catalytic intermolecular additions of aryl nucleophiles to nitriles to form ketimines have been reported,^{42–48} including examples of C–H activation of the arenes to form the aryl nucleophiles.^{42,46}

Here we report a series of studies to evaluate the factors that control the insertions of ketones and nitriles into rhodium–aryl bonds and the opposite β -carbon eliminations from rhodium alkoxo and iminyl complexes. These studies demonstrate that

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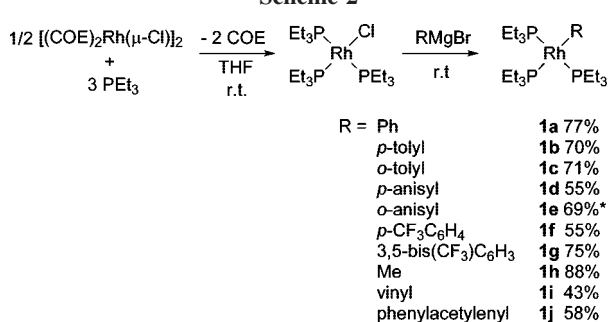
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Scheme 2



*(*o*-anisyl)Li was used in place of (*o*-anisyl)MgBr

the reactions are reversible and that the direction of the equilibrium can be controlled by the electronic properties of the aryl group on the metal and the electronic properties of the ketone or nitrile. Portions of this work have been reported in communication form.^{14,15}

Results and Discussion

Preparation of Organorhodium(I) Complexes. Organorhodium(I) complexes of the general formula [(PEt₃)₃Rh(R)] were prepared using a general procedure previously published,¹⁴ as shown in Scheme 2. Reaction of the common rhodium(I) precursor {[COE]₂Rh(μ-Cl)₂} (COE = *cis*-cyclooctene) with PEt₃ (6 equiv) generated [(PEt₃)₃RhCl] as an orange solution in THF, as judged by ³¹P NMR spectroscopy. Addition of the corresponding Grignard reagent to this intermediate generated the desired organorhodium(I) complexes [(PEt₃)₃Rh(R)] (**1a–j**) in 43–88% isolated yields after removal of the metal salt byproduct by filtration, evaporation, and recrystallization. The alkynyl complex **1j** was also prepared by addition of the alkyne to the silylamido complex {(PEt₃)₂Rh[N(SiMe₃)₂]} and added phosphine. This method led to higher yields of the alkynyl complex than did the addition of alkynyl Grignard reagents. All the organorhodium(I) complexes were formed in nearly quantitative yields; the isolated yields reflect the high solubility of the products rather than the chemical yields of the reaction sequence.

Complexes **1a–j** were characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy and elemental analysis. In general, resonances of two types of ethyl groups in two inequivalent phosphines were detected by ¹H NMR spectroscopy in a 2:1

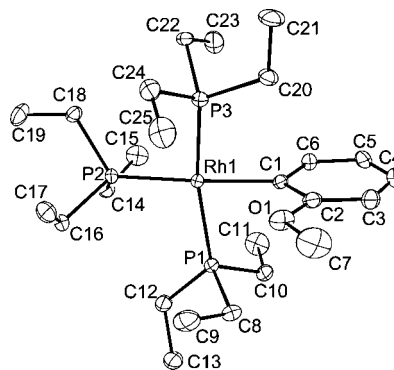


Figure 1. ORTEP diagram of {Rh(PEt₃)₃[(*o*-MeO)C₆H₄]} (**1e**) with 30% ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh–C(1) = 2.087(3), Rh–P(1) = 2.315(1), Rh–P(2) = 2.290(1), Rh–P(3) = 2.299(1), P(1)–Rh–C(1) = 82.69(8), P(1)–Rh–P(2) = 96.47(3), P(2)–Rh–P(3) = 97.18(3), P(3)–Rh–C(1) = 85.33(7), Rh–O = 3.23 Å.

ratio. Similarly, the ³¹P NMR spectra consisted of a doublet of doublets (phosphines *cis* to the organyl group) and a doublet of triplets (phosphine *trans* to the organyl group). The ¹³C NMR resonance of the *ipso*-carbon bonded to the Rh center was a doublet of doublets of triplets in each case (see Supporting Information).

The solid-state structure of *ortho*-anisyl complex **1e** was determined by X-ray diffraction (Figure 1). In the solid state, **1e** adopts a square-planar geometry with the angles around the Rh center totaling 362°. The Rh–C(*ipso*) distance (2.09 Å) and Rh–P distances (2.29–2.31 Å) are very similar to those of the related square-planar complex [(PMe₃)₃Rh(Ph)].⁴⁹ One might imagine that the oxygen of the *ortho*-methoxy substituent could interact with the open coordination site in the axial position of the rhodium. An additional metal–oxygen interaction would render the *o*-*o*-anisyl complex more stable than the parent *o*-phenyl complex, as suggested in an early study on [(PMe₃)₃Rh(*o*-anisyl)],⁵⁰ and could affect the thermodynamics for insertion and elimination (*vide infra*). However, the long distance between the Rh center and the methoxy oxygen (3.23 Å) indicates the absence of significant Rh–O coordination, and none of the spectral data support such an interaction. Structures of a series of square-planar Pd(II)-(*o*-anisyl) complexes also lack a significant Pd–O interaction.^{51,52}

Preparation of Rhodium(I) Iminyl Complexes. Rhodium(I) iminyl complexes of the general formula [(PEt₃)₃Rh(N=CArAr')] were prepared using a previously published general procedure,¹⁴ as shown in Scheme 3. {[COE]₂Rh(μ-Cl)₂} was treated with 6 equiv of PEt₃, followed by 2 equiv of LiN(SiMe₃)₂ and 2 equiv of the corresponding diarylimines. This procedure formed HN(SiMe₃)₂ and the rhodium iminyl complex in nearly quantitative chemical yields. Iminyl complexes **2a–j** were isolated as crystalline solids in 48–78% yields and were characterized by spectroscopic methods and elemental analysis. The phosphines located *cis* and *trans* to the iminyl group were clearly identified in a 2:1 ratio in both the ¹H and ³¹P NMR

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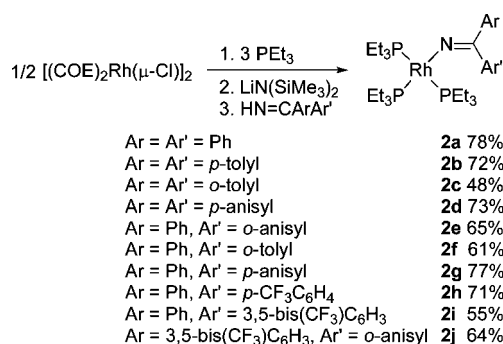
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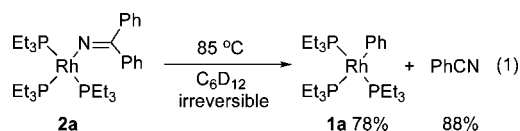
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Scheme 3



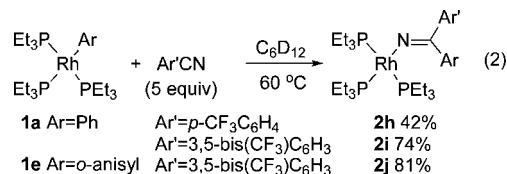
spectra, with patterns analogous to those of organorhodium(I) complexes **1a–j**. The square-planar geometry of complex **2a** was revealed previously by X-ray diffraction.¹⁴ The plane of the iminyl group was found to be roughly orthogonal to the square plane at rhodium. The Rh–N–C angle was found to be 130.6(2)°. However, a single set of resonances for the phenyl groups of diphenyliminyl complex **2a** and a single set of resonances for the unsymmetrical diaryliminyl complexes **2b–d** were observed by ¹H and ¹³C NMR spectroscopy. Thus, inversion at nitrogen of the iminyl complexes was fast on the NMR time scale.

Sequential Insertions and Eliminations Involving Organorhodium(I) Complexes and Arylnitriles. To probe the potential to observe iminyl complexes by addition of nitriles to rhodium aryl complexes, [(PEt₃)₃Rh(Ph)] (**1a**) was allowed to react with 5–20 equiv of PhCN at 60–90 °C in THF or cyclohexane solvent. These reactions did not generate the corresponding insertion product {(PEt₃)₃Rh[N=C(Ph)₂]} (**2a**). This lack of reactivity is consistent with the observation of β-aryl eliminations from diaryliminyl complexes we have reported previously.¹⁴ We showed in prior work that complex **2a** undergoes irreversible β-phenyl elimination to form **1a** and benzonitrile in good yields (eq 1). Thus the equilibrium for insertion and elimination in this case favors elimination, and the reaction between the aryl complex **1a** and the benzonitrile should not generate observable quantities of iminyl complex **2a**. Other electron-rich nitriles containing aryl groups different from that on the starting rhodium complex, such as 2-methoxybenzonitrile, *o*-tolunitrile, and 4-methoxybenzonitrile, also did not react with **1a**.

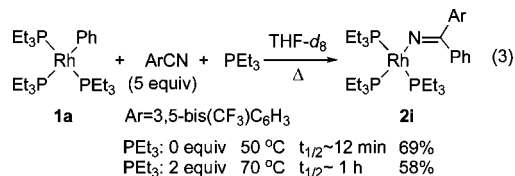


In contrast to the lack of reactivity with aromatic nitriles containing electron-rich aryl groups, insertions of electron-poor nitriles into the Rh–C bond of **1a** were observed. Reaction of **1a** with 5 equiv of the electron-poor aryl nitrile *p*-CF₃C₆H₄CN at 60 °C formed the insertion product {(PEt₃)₃Rh[N=C(Ph)(*p*-CF₃C₆H₄)]} (**2h**) in 42% yield, along with a mixture of unidentified rhodium complexes, as determined by ¹H NMR spectroscopy (eq 2). A higher-yielding reaction was observed between **1a** and 5 equiv of 3,5-bis(CF₃)C₆H₃CN. This reaction formed the insertion product {(PEt₃)₃Rh[N=C(Ph)[3,5-bis(CF₃)C₆H₃]]} (**2i**) in 74% yield (eq 2). Likewise, 3,5-bis(CF₃)C₆H₃CN inserted into the Rh–C bond of [(PEt₃)₃Rh(*o*-anisyl)] (**1e**) to form {(PEt₃)₃Rh[N=C(*o*-anisyl)[3,5-bis(CF₃)C₆H₃]]} (**2j**) in 81% yield. In contrast to this reactivity of electron-poor nitriles with complexes **1a** and **1e** containing

electron-neutral to electron-rich aryl groups, 3,5-bis(CF₃)C₆H₃CN (5 equiv) did not react with the arylrhodium complexes containing more electron-poor aryl groups [(PEt₃)₃Rh(*p*-CF₃C₆H₄)] (**1f**) and {(PEt₃)₃Rh[3,5-bis(CF₃)C₆H₃]} (**1g**), even after 2–6 h at 60–85 °C. We suggest that the strength of the metal–carbon bond to an electron-poor aryl group leads to a high kinetic barrier that prevents insertion of the nitrile from occurring.



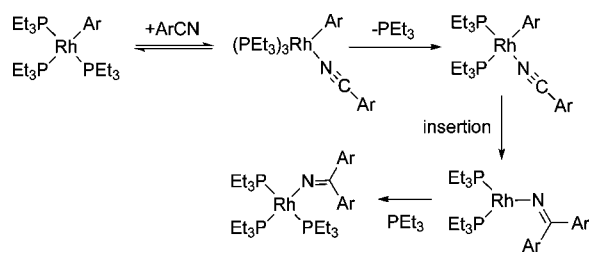
In contrast to the insertions of nitriles into the M–C bond of arylrhodium(I) complexes, reactions of aryl nitriles with other organorhodium(I) complexes did not give clean products. For example, the reaction between [(PEt₃)₃Rh(Me)] (**1h**) and 3,5-bis(CF₃)C₆H₃CN (5 equiv) went to completion after 30 min at 60 °C, but formed several intractable rhodium species by ³¹P NMR spectroscopy. Likewise, [(PEt₃)₃Rh(CH=CH₂)] (**1i**) was fully consumed by reaction with 3,5-bis(CF₃)C₆H₃CN (5 equiv) at room temperature for 30 min, but a mixture of several unidentified rhodium complexes was formed. [(PEt₃)₃Rh(C≡CPh)] (**1j**) did not react with 3,5-bis(CF₃)C₆H₃CN (5–10 equiv) after heating at 85 °C for 2–4 h.



Mechanism of the Insertion of Nitriles into Arylrhodium(I) Complexes. The mechanistic data in our previous study on β-aryl eliminations from Rh(I) iminyl complexes to generate arylrhodium(I) complexes and aryl nitriles¹⁴ were most consistent with reversible ligand dissociation to generate a 14-electron Rh(I) intermediate, followed by rate-limiting β-aryl elimination. One would, therefore, expect that insertions of the electron-poor nitriles into arylrhodium(I) complexes to form Rh(I) iminyl complexes should occur through a similar, but reverse, pathway involving a coordinatively unsaturated Rh(I) intermediate. To test this assertion, we compared insertions of 3,5-bis(CF₃)C₆H₃CN into **1a** without added PEt₃ and with 2 equiv of added PEt₃ (eq 3). Both reactions were conducted in THF-*d*₈, with an initial 0.014 M concentration of **1a** and 0.070 M concentration of the nitrile. Conversions were measured by ¹H NMR spectroscopy at multiple times. The reaction without added phosphine gave 69% of the insertion product **2i**, and the half-life was estimated to be around 12 min at 50 °C. The reaction with 2 equiv of added phosphine was much slower, with a half-life around 60 min at 70 °C, and it gave a slightly lower yield of **2i** (58%). This inverse dependence of the rate on the added ligand, albeit qualitative, is consistent with a pathway shown in Scheme 4 occurring by reversible associative replacement of PEt₃ with nitrile,⁵³ insertion of the nitrile into the 14-electron intermediate [(PEt₃)₂Rh(Ph)], and coordination of phosphine to

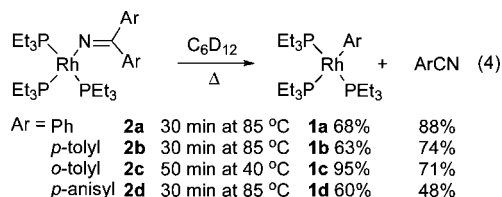
(53) Both associative and dissociative pathways are possible for this exchange. However, the pathway for insertion conducted with a high concentration of nitrile, most likely, occurs by associative displacement of the phosphine in the square-planar starting complex by the nitrile.

Scheme 4



form the final four-coordinate product. Such a mechanism is consistent with the classic migratory insertion pathways for olefin insertions into late transition metal aryl complexes.

Decomposition of Rh(I) Iminyl Complexes via β -Aryl Eliminations. Symmetrical iminyl complexes **2a–d** underwent β -aryl eliminations to afford the corresponding rhodium aryl complexes **1a–d** in 60–95% yields and the corresponding aryl nitriles in 48–88% yields (eq 4).¹⁴ The reactions of compounds **2b–d** were conducted to assess the electronic and steric effects on the reaction. The more electron-rich *p*-tolyl and *p*-anisyl derivatives **2b** and **2d** reacted with rates and yields that were similar to those of reactions of the parent iminyl complex **2a**. In contrast, the *o*-tolyl complex **2c** underwent β -aryl elimination at much lower temperatures and in higher yields than the phenyl, *p*-tolyl, or *p*-anisyl derivatives. This increase in reactivity could result from a starting iminyl complex that is less stable with *o*-tolyl groups because of the steric hindrance in the imine conformation that creates overlap of the aryl π -system with the C=N bond. The steric hindrance is less severe in the rhodium product that contains an aryl group that lies perpendicular to the square coordination plane.



Trends in the migratory aptitudes of electron-rich and electron-neutral aryl groups were determined by conducting the reactions with the unsymmetrically substituted iminyl complexes **2e–g** and determining the ratios of the rhodium aryl complexes and nitrile products by a combination of NMR and GC methods with internal standards. These results are summarized in Scheme 5. Most striking, *o*-anisyl phenyl iminyl complex **2e** underwent exclusive migration of the *o*-anisyl group at 60 °C, with a half-life of roughly 200 s in C₆D₁₂ to afford 77% yield of [(PEt₃)₃Rh(*o*-anisyl)] (**1e**) and 82% yield of benzonitrile. At the

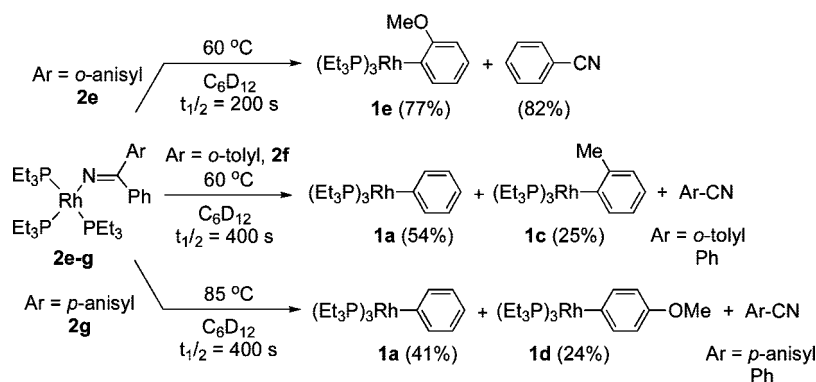
same temperature, *o*-tolyl phenyl iminyl complex **2f** underwent competitive migration of the two aryl groups. This reaction occurred with a half-life of roughly 400 s in C₆D₁₂ to afford [(PEt₃)₃RhPh] (**1a**) and [(PEt₃)₃Rh(*o*-tolyl)] (**1c**) in a roughly 2:1 ratio (79% overall yield), slightly favoring migration of the phenyl group. In contrast to the phenyl *o*-anisyl iminyl complex **2e**, phenyl *p*-anisyl iminyl complex **2g** underwent competitive migration of the two aryl groups to form a roughly 2:1 ratio of rhodium aryl products **1a** and **1d** (65% overall yield) in favor of complex **1a**, which results from migration of the less electron-donating phenyl group. Thus, the reactions of unsymmetrical iminyl complexes **2e–g** reveal the unexpected relative migratory aptitudes: *o*-anisyl $\gg$ phenyl $>$ *p*-anisyl $\sim$ *o*-tolyl.

One might consider that the faster rate of migration of the *o*-anisyl could result from the steric properties of this group, the electron density on the anisyl group, or coordination of the *o*-methoxy group. The competitive migration of phenyl and *o*-tolyl groups shows that steric effects alone do not control the relative rates for migration of the aryl groups. Likewise, the similar migratory aptitudes of the *p*-anisyl and phenyl groups show that a simple electronic effect cannot account for the faster migration of the *o*-anisyl complex. Finally, one could envision that coordination of the *o*-anisyl group could trigger migration. However, binding of the *o*-methoxy group to the metal would consume the open coordination site needed for migration of the aryl group. Thus, we do not have a clear explanation for the faster migration of the *o*-methoxy group at this time, and computational work is currently being conducted. Preliminary results of DFT calculations reproduce the relative migration barriers without evidence for binding of the *o*-methoxy group to the metal in the species that undergoes migratory deinsertion.

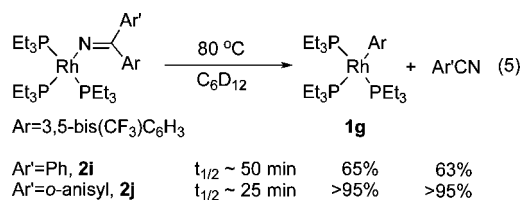
The more electron-poor iminyl complex {(PEt₃)₃Rh[N=C(Ph)-(p-CF₃C₆H₄)]} (**2h**) was more thermally stable than the iminyl complexes containing electron-rich aryl groups. Complex **2h** slowly decomposed after heating at 80 °C for 16 h to give the free imine HN=C(Ph)(p-CF₃C₆H₄). In contrast, {(PEt₃)₃Rh[N=C(Ph)[3,5-bis(CF₃)C₆H₃]]} (**2i**), which contains an even more electron-poor aryl group, underwent β -aryl eliminations to give {(PEt₃)₃Rh[3,5-bis(CF₃)C₆H₃]} (**1g**, 65%) and PhCN (63%). No competing formation of **1a** or 3,5-bis(CF₃)C₆H₃CN was observed by ¹H NMR spectroscopy (eq 5). Likewise, {(PEt₃)₃Rh[N=C(*o*-anisyl)[3,5-bis(CF₃)C₆H₃]]} (**2j**) selectively underwent β -elimination of the 3,5-bis(trifluoromethyl)phenyl group to form **1g** and 2-methoxybenzonitrile in nearly quantitative yields.

A comparison of the rates of β -aryl elimination illustrates the importance of the overall electronic properties of the iminyl group and of the individual aryl groups. β -Aryl elimination of

Scheme 5



the 3,5-bis(CF₃)C₆H₃ group from **2i** to form the rhodium aryl complex **1g** and benzonitrile (eq 5) was much slower than β -aryl elimination of the *o*-anisyl group of [(PEt₃)₃Rh{N=C(*o*-anisyl)(Ph)}] (**2e**) to form **1e** and benzonitrile (Scheme 5).¹⁴ Thus, the complex with the overall more electron-rich iminyl group reacts faster. However, a comparison of the migratory aptitudes of the individual aryl groups shows that the most electron-poor 3,5-bis(CF₃)C₆H₃ group migrates preferentially over a phenyl group. In fact, migration of the 3,5-bis(CF₃)C₆H₃ group is even preferred over migration of the *ortho*-anisyl group (eq 5), which migrates much faster than a phenyl group. Thus, the β -aryl elimination in this system is fastest when the iminyl group is sterically hindered and electron rich, but the migratory aptitude of an individual aryl group is greatest for the most electron-poor 3,5-bis(trifluoromethyl)phenyl groups.

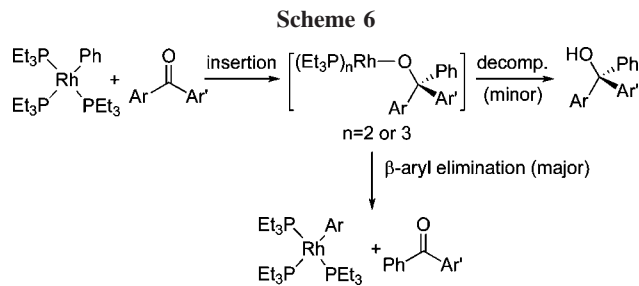


Trends in rates for insertions of aryl nitriles are complementary. Electron-poor aryl nitriles insert into rhodium aryl complexes to form iminyl complexes. Although the formation of an iminyl complex from insertion of a more electron-rich aryl nitrile is not thermodynamically favored, one might expect that this insertion would occur reversibly. However, no reaction was observed between [(PEt₃)₃RhPh] and aryl nitriles containing electron-donating substituents. If insertion occurred reversibly, one would expect an equilibrium to be established between the combination of [(PEt₃)₃Rh(Ph)] and Ar'CN and the combination of [(PEt₃)₃RhAr'] and PhCN. Because this equilibrium was not established, one can conclude that the insertion of an electron-rich nitrile has a higher barrier than insertion of an electron-poor aryl nitrile. Because deinsertions of the more electron-rich aryl nitriles are faster than deinsertions of the more electron-poor nitriles, one can conclude that the higher barrier for insertion is largely due to the unfavorable thermodynamics for insertion with this class of nitrile.

Reactions of Arylrhodium(I) Complexes with Ketones. Studies on the insertions of diaryl ketones into rhodium–aryl linkages were conducted in parallel with studies on the insertions of aryl nitriles. We had previously observed β -aryl eliminations from arylmethoxide complexes¹⁵ and sought to determine the thermodynamic and kinetic factors that control the addition and elimination of ketones.

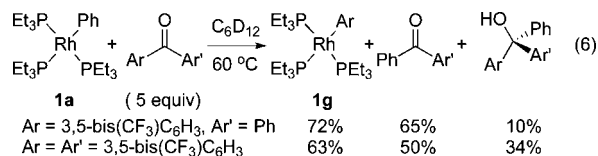
To determine if the products from insertions of ketones into arylrhodium linkages could be observed in the presence of an excess of ketone, we heated [(PEt₃)₃Rh(Ph)] (**1a**) with an excess (5–20 equiv) of benzophenone. This reaction did not generate the corresponding insertion product [(PEt₃)₂Rh(OCPh₂)] (**3a**). Other ketones, including acetone, acetophenone, and the electron-rich diarylketone (*p*-tolyl)₂C=O, also did not form products from insertion into the M–C bond of **1a**.

However, studies of the reactions of arylrhodium complexes with electron-poor aryl ketones showed that this class of ketone inserts into rhodium–aryl bonds, such as those in **1a–g**. This insertion was typically followed by a β -aryl elimination process. For example, the reaction of phenylrhodium complex **1a** with 5 equiv of the electron-poor diarylketone (Ph)[3,5-bis(CF₃)-



C₆H₃]C=O fully consumed **1a** after 2 h at 60 °C. However, no Rh(I) alkoxo complexes were detected by ¹H or ³¹P NMR spectroscopy. Instead, the arylrhodium(I) complex {(PEt₃)₃Rh[3,5-bis(CF₃)C₆H₃]} (**1g**) and benzophenone were observed as the major products, together with a small amount of the alcohol HOC(Ph)₂[3,5-bis(CF₃)C₆H₃] (eq 6). Complex **1a** also reacted with an excess of [3,5-bis(CF₃)C₆H₃]₂C=O under analogous conditions to give a mixture of bis-trifluoromethylphenyl rhodium complex **1g**, (Ph)[3,5-bis(CF₃)C₆H₃]C=O, and HOC(Ph)-[3,5-bis(CF₃)C₆H₃]₂. These reactions likely occur by insertion of the ketone into the arylrhodium bond to form a rhodium triarylmethoxide ligand, followed by parallel β -aryl elimination of the electron-poor aryl group of the triarylmethoxide ligand and protonolysis of the Rh–O bond in this complex, perhaps by adventitious water (Scheme 6). In comparison, the arylrhodium complex **1g**, containing the electron-poor 3,5-bis-trifluoromethylphenyl group, did not react with benzophenone, (Ph)[3,5-bis(CF₃)C₆H₃]C=O, or [3,5-bis(CF₃)C₆H₃]₂C=O (5–20 equiv, 60–85 °C) to form insertion products.

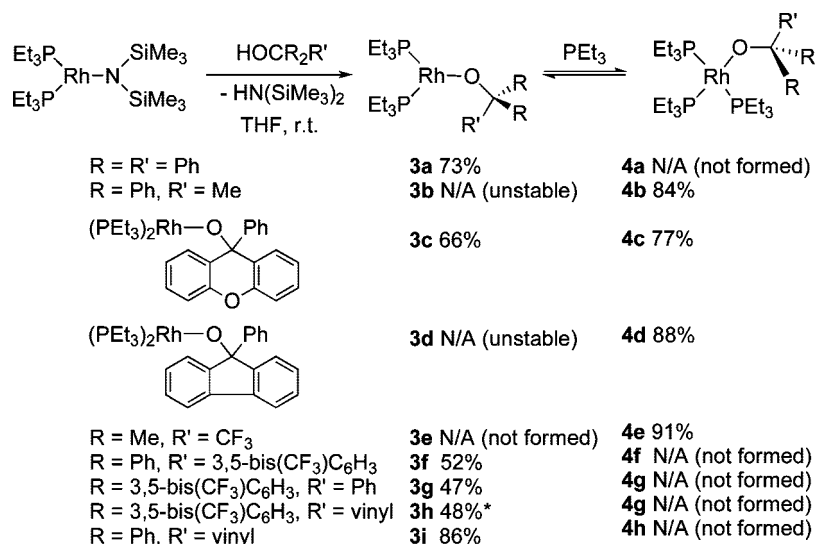
These data, along with the observed β -aryl eliminations from alkoxo complexes **3a**, **3f**, and **3g** (vide infra), imply that the insertions of electron-poor arylketones into rhodium(I) aryls are largely controlled by thermodynamic factors. However, the lack of reaction of phenylrhodium complex **1a** with more electron-rich diaryl ketones, such as (*p*-tolyl)₂C=O, implies that the barriers for insertion can be sufficiently high when the thermodynamics are less favorable to prevent reversible insertion from occurring. This trend is essentially identical to that for the electronic effects on the rate of insertions and eliminations involving aryl nitriles.



Reactions of Vinyl-, Methyl-, and Alkynylrhodium(I) Complexes with Ketones. In contrast to the products of insertions of diarylketones into phenylrhodium complex **1a**, the product from insertion of a diarylketone into the analogous vinylrhodium complex was stable. Reaction of [(PEt₃)₃Rh-(CH=CH₂)] (**1i**) with [3,5-bis(CF₃)C₆H₃]₂C=O (5 equiv) occurred to completion after 30 min at 60 °C to form the Rh(I) alkoxide (PEt₃)₂Rh{OC(CH=CH₂)[3,5-bis(CF₃)C₆H₃]} (**3h**) in nearly quantitative yield (eq 7). Complex **3h** was prepared independently by a procedure similar to that used previously to prepare analogous Rh(I) alkoxo complexes (see Supporting Information).⁵⁴ This complex is stabilized by coordination of the vinyl group. This coordination was deduced from the observation of two inequivalent phosphines by ¹H and ³¹P

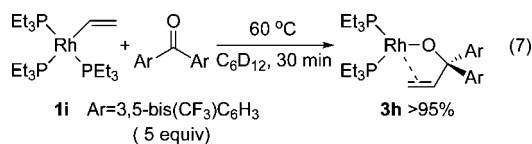
(54) Zhao, P.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 9642.

Scheme 7

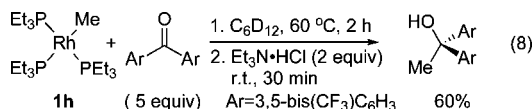


*Isolated as crude product with ~85% purity (see supporting information).

NMR spectroscopy and upfield resonances for the olefinic protons at 3.8–4.5 ppm. More electron-rich ketones, such as acetophenone and benzophenone, did not react with vinylrhodium complex **1i**.



Reactions of the methylrhodium complex $[(\text{PEt}_3)_3\text{Rh}(\text{Me})]$ (**1h**) were less defined than reactions of the aryl and vinyl complexes, but this complex did appear to insert electron-poor diaryl ketones. Reaction of **1h** with 5 equiv of $[3,5\text{-bis}(\text{CF}_3)\text{C}_6\text{H}_3]_2\text{C}=\text{O}$ fully consumed the methyl complex **1h** after 2 h at 60 °C to form a mixture of several unidentified rhodium complexes. However, hydrolysis of the reaction mixture indicated that these products likely form by insertion of the ketone into the $\text{Rh}-\text{Me}$ bond. Quenching of the reaction mixture by stirring with $\text{Et}_3\text{N}\cdot\text{HCl}$ (2 equiv) for 30 min generated the tertiary alcohol $\text{HOC}(\text{Me})[3,5\text{-bis}(\text{CF}_3)\text{C}_6\text{H}_3]_2$ in 60% yield, as determined by ^1H NMR and GC analysis (eq 8). Less electron-poor ketones, such as acetophenone and benzophenone, did not react with methylrhodium complex **1h**.



In contrast to the alkyl, vinyl, and aryl complexes, the alkynylrhodium complex $[(\text{PEt}_3)_3\text{Rh}(\text{C}\equiv\text{CPh})]$ (**1j**) was stable in the presence diaryl ketones. Reaction with benzophenone or $[3,5\text{-bis}(\text{CF}_3)\text{C}_6\text{H}_3]_2\text{C}=\text{O}$ (5 equiv) did not consume the alkynyl complex, even after heating at 85 °C for 6 h. This lack of reactivity appears to result from the strong thermodynamic preference for the alkynyl complex and free ketone, not from a high kinetic barrier (vide infra).

β -Aryl Eliminations from Rh(I) Alkoxo Complexes. **Synthesis of Rh(I) Arylalkoxide Complexes.** The hypothesis that phenylrhodium complex **1a** reacts with an electron-poor diaryl ketone to form the new arylrhodium complex **1g** by

insertion, followed by β -aryl elimination, was evaluated by studying rhodium(I) arylmethoxide complexes that were prepared independently. A series of Rh(I) alkoxo complexes **3a–d** and **3f–i** were prepared by addition of the corresponding tertiary alcohol to $[(\text{PEt}_3)_2\text{Rh}[\text{N}(\text{SiMe}_3)_2]]$ (Scheme 7).¹⁵ As described previously,¹⁵ bis(phosphine)triarylmethoxide complexes **3a**, **3c**, and **3f–g** contain an interaction between the metal and a portion of the π -system of one of the aryl groups of the arylmethoxide ligand. These alkoxo complexes were also converted to the more stable tris(phosphine) complexes (**4b–e**) by addition of excess PEt_3 .

The solid-state structure of trityl alkoxo complex **3a** was determined by X-ray diffraction (Figure 2). This structure consists of a pseudo-square-planar rhodium center with two *cis*-oriented triethylphosphine ligands and one triphenylmethoxy ligand that is bound through oxygen and the C(14)–C(15) carbons of an η^2 -phenyl unit. The $\text{Rh}-\text{O}$ distance is similar to those in previously isolated Rh(I) alkoxides,^{54,55} and the $\text{Rh}-\text{C}(14)$ and $\text{Rh}-\text{C}(15)$ distances are longer than the $\text{Rh}-\text{C}_{\text{olefin}}$ distances of an analogous $[(\text{Et}_3\text{P})_2\text{Rh}(\eta^1:\eta^2\text{-OCMe}_2\text{CH}_2\text{CH}=\text{CH}_2)]$ complex (2.14 and 2.20 Å).⁵⁴ Most relevant to the reaction mechanism of β -aryl elimination, the C–C bond between the alkyl carbon and the aryl group bound to rhodium is longer than the other C–C bonds between the sp^3 and *ipso* carbons. This structural feature suggests that this complex with an η^2 -arene interaction lies on the β -elimination pathway.

Reactions of Rh(I) Arylalkoxide Complexes. The bis-(phosphine)arylalkoxide complexes **3a**, **3f**, and **3g** underwent β -aryl elimination in the presence of added PEt_3 to form stable arylrhodium(I) products and the corresponding ketones (eq 9). Tris(phosphine)arylalkoxide complexes **4b–d** underwent β -aryl elimination to form the stable phenyl complex **1a** and ketones in the absence of added ligand (eq 10). The yields of β -elimination product ranged from 61% to 95% for the arylrhodium product and 57–95% for the ketone. No methylrhodium complex was observed from heating of **4e**. Instead, the alcohol $\text{HOCMe}_2\text{CF}_3$ was the dominant organic product, along with intractable rhodium species.

(55) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563.

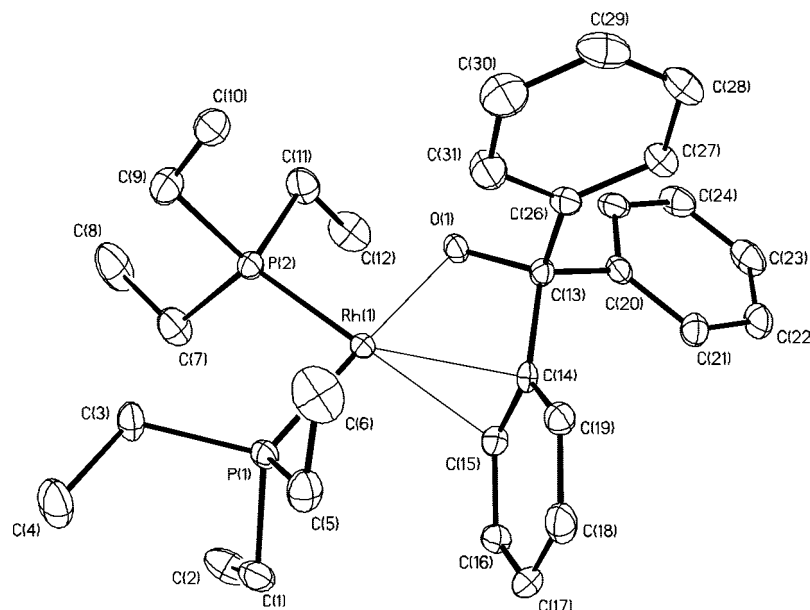
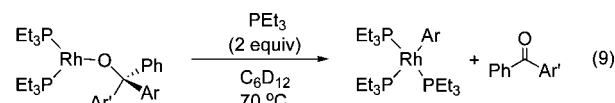


Figure 2. ORTEP diagram of $[\text{Rh}(\text{PEt}_3)_2(\text{OCPh}_3)]$ (**3a**). Hydrogen atoms are omitted for clarity. Selected bond distances ($\text{\AA}$) and bond angles (deg): $\text{Rh}-\text{O} = 2.069(3)$, $\text{Rh}-\text{C}(14) = 2.350(4)$, $\text{Rh}-\text{C}(15) = 2.398(4)$, $\text{Rh}-\text{P}(1) = 2.228(1)$, $\text{Rh}-\text{P}(2) = 2.222(1)$, $\text{O}-\text{C}(13) = 1.407(5)$, $\text{P}(1)-\text{Rh}-\text{P}(2) = 97.21(5)$, $\text{O}-\text{Rh}-\text{P}(2) = 88.05(9)$, $\text{Rh}-\text{O}-\text{C}(13) = 101.4(2)$, $\text{O}-\text{C}(13)-\text{C}(14) = 104.7(3)$.



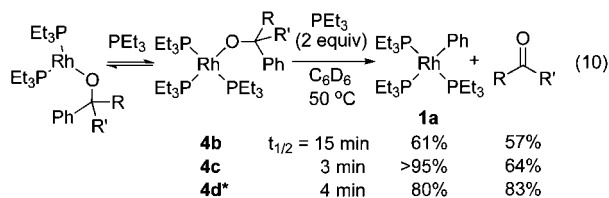
$\text{Ar} = \text{Ar}' = \text{Ph}$ **3a'** $t_{1/2} \sim 10$ min **1a** 68% 62%

$\text{Ar} = 3,5\text{-bis}(\text{CF}_3)\text{C}_6\text{H}_3$ **3f** $t_{1/2} \sim 5$ min **1g** 66% 59%

$\text{Ar}' = \text{Ph}$

$\text{Ar} = \text{Ar}' = 3,5\text{-bis}(\text{CF}_3)\text{C}_6\text{H}_3$ **3g** $t_{1/2} \sim 7$ min **1g** >88% >95%

[†]reaction run in C_6D_6 at 50 °C



4b $t_{1/2} = 15$ min 61% 57%

4c 3 min >95% 64%

4d* 4 min 80% 83%

*reaction run in C_6D_{12} at 80 °C.

Quantitative kinetic studies showed that β -phenyl elimination from the bis(phosphine) complex **3a** was unaffected by added PEt_3 . Rate constants were measured by ^1H NMR spectroscopy at 50 °C with an initial 0.014 M concentration of **3a**. Reactions were conducted while varying the concentration of PEt_3 from 0.028 to 0.14 M. A clear exponential decay of **3a** indicated that the reaction was first-order in rhodium. The rate constants were indistinguishable in the presence and absence of added PEt_3 and in the presence or absence of added benzophenone product. These results support a mechanism involving irreversible β -aryl elimination from a 14-electron intermediate, which parallels the mechanism for β -aryl elimination from rhodium iminyl complexes.

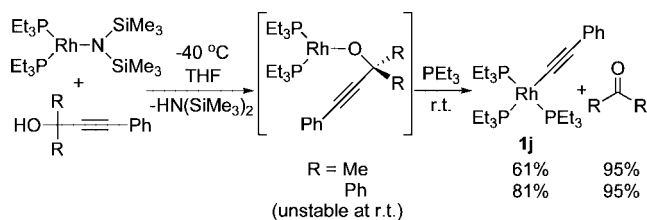
Qualitative kinetic studies were conducted on the β -phenyl eliminations from trisphosphine alkoxide complexes **4b–d**. As expected from the direct reaction from the two-coordinate arylmethoxide complex **3a**, reactions of the three-coordinate complexes **4b–d** were inhibited by added PEt_3 . The reactions in eq 10 were conducted with 2 and 10 equiv of added PEt_3 . The yields of these reactions were lower (27–50%) in the

presence of added PEt_3 than in the absence of added PEt_3 . Thus, only qualitative measurements of the rates in the presence of added phosphine were conducted. The reactions conducted in the presence of 10 equiv of added ligand were 2–3 times slower than those conducted in the presence of 2 equiv of added ligand. Although qualitative and complicated by chemistry leading to side products, this inhibition of the reaction by added PEt_3 is consistent with reaction of the trisphosphine arylmethoxides by dissociation of PEt_3 and rate-limiting β -phenyl elimination from the resulting bisphosphine rhodium complex.

The complexes containing two different types of aryl groups allowed an assessment of the relative migratory aptitudes of the aryl groups. Compounds containing electron-poor and electron-neutral aryl groups underwent elimination of the electron-poor aryl group. For example, complex **3f** underwent selective migration of the 3,5-bis(trifluoromethyl)phenyl to form **1g** and benzophenone (eq 9). These products are consistent with the proposed pathway for reaction of phenylrhodium complex **1a** with ketone $(\text{Ph})[3,5\text{-bis}(\text{CF}_3)\text{C}_6\text{H}_3]\text{C}=\text{O}$ to form 3,5-bis(trifluoromethyl)phenylrhodium **1g** and benzophenone. The compounds containing cyclic structures underwent elimination of the aryl group external to the ring structure. Thus, tris(phosphine)arylmethoxide complexes **4c** and **4d** generated phenylrhodium complex **1a**, along with the cyclic ketones xanthone and fluorenone, respectively (eq 10).

In contrast, the allylic alkoxide **3h** in eq 7 and the structurally related $\{(\text{PEt}_3)_2\text{Rh}[\text{OC}(\text{CH}=\text{CH}_2)\text{Ph}_2]\}$ (**3i**) were both stable toward β -eliminations. Both compounds remained unchanged after heating at 80–120 °C in C_6D_{12} or THF for 8 h. Such high stability of **3h** and **3i** can be rationalized by the stable structure of the allylic alkoxide generated by coordination of the vinyl moiety to the rhodium center. Since insertion of $[3,5\text{-bis}(\text{CF}_3)\text{C}_6\text{H}_3]_2\text{C}=\text{O}$ into the vinyl complex **1i** occurred (eq 7), but insertion of benzophenone did not, the thermal stability of **3h** can be attributed to thermodynamic factors, but the stability of the diphenylallyloxide **3i** must be attributed to a high barrier for β -aryl elimination from the allyloxide complexes containing a coordinated alkene.

Scheme 8



Experiments to form a 1,1-diarylpropargylic alkoxorhodium complex revealed that the lack of insertion of ketone into the alkynylrhodium species results from thermodynamic factors. Attempts were made to generate the Rh(I) propargylic alkoxides $\{(\text{PEt}_3)_2\text{Rh}[\text{OC}(\text{R})_2(\text{C}\equiv\text{CPh})]\}$ ($\text{R} = \text{Me}$ or Ph) by reaction of the corresponding propargylic alcohol with $\{(\text{PEt}_3)_2\text{Rh}[\text{N}(\text{SiMe}_3)_2]\}$. The resulting bis(phosphine) alkoxo species were unstable in solution at the temperature required to form them (ca. -20°C), and we were unable to acquire clean ^1H or ^{13}P NMR spectra (see Supporting Information). In the presence of added PEt_3 (1 equiv), the presumed propargylic alkoxide complexes quickly decomposed to form alkynylrhodium complex **1j**, along with acetone or benzophenone, respectively. Apparently β -alkynyl eliminations from propargylic alkoxides occur below room temperature (Scheme 8).^{56–59} Thus, the combination of the alkynylrhodium complex and free ketones is more stable than the rhodium propargylic alkoxide compounds. This observation is consistent with the favorable match between the d^8 Rh(I) center and an alkynyl ligand.^{60–62} These data, together with those presented earlier in this paper, show that the migratory aptitudes for the deinsertion processes follow the trend alkynyl > aryl > alkyl. In contrast, the vinyl complex rapidly forms products from insertion of ketones (eq 7).

Conclusions

We report the direct observation of insertions of electron-poor aryl nitriles and diarylketones into the Rh–C bonds of arylrhodium(I) complexes to form isolable rhodium(I) iminyl and alkoxo complexes, respectively. The resulting iminyl and alkoxo complexes also underwent the reverse of this insertion

process, β -aryl eliminations. A series of general conclusions can be made from our data.

1. In some cases the insertions of aryl ketones and nitriles into rhodium–carbon bonds are reversible and are controlled by thermodynamics, but in other cases, the insertion has sufficiently high barriers to prevent insertion from occurring. The cases in which the barriers are high include the insertions of nitriles and ketones into rhodium complexes containing electron-poor aryl groups and insertions of electron-rich aryl nitriles and ketones.
2. The iminyl complexes possessing the overall more electron-rich iminyl group reacted faster, but the most electron-poor 3,5-bis(CF_3) C_6H_3 group migrated preferentially over a phenyl group. Thus the overall rates of deinsertion of nitriles from different complexes follow a different trend from that of migratory aptitudes of the aryl groups contained in the iminyl ligand. The β -aryl elimination from the iminyl complexes is fastest when the iminyl group is sterically hindered and electron rich, but the migratory aptitude of an individual aryl group is greatest for the most electron-poor 3,5-bis(trifluoromethyl)phenyl groups, followed by the *o*-anisyl group and then the electron-neutral aryl groups.
3. The relative migratory aptitudes of different hydrocarbyl groups during the elimination processes follow the trend alkynyl > aryl > alkyl.
4. The rhodium vinyl complexes underwent insertion to form stable allylic alkoxide complexes in which the oxygen and olefin of the allylic alcohol unit chelate the metal center. Thus, the presence of pendant olefins can significantly affect the thermodynamics for insertion versus elimination. Previous studies on the reactions of an analogous rhodium homoallylic alkoxo complex showed that migration of an allyl group can occur to form a stable allylrhodium species.⁵⁴
5. The mechanism of the insertions and deinsertions follows a migratory insertion and elimination pathway that is typical for insertions of olefins and β -eliminations from alkyl ligands. This evaluation of the relative thermodynamics for these insertion and elimination reactions and the relative kinetic barriers for these processes should allow a better interpretation of current catalytic chemistry and should assist in the design of new processes.

Acknowledgment. Financial support for this work was provided by the Department of Energy, Office of Basic Energy Sciences.

Supporting Information Available: Experimental and computational details and structural and analytical data of new compounds. This material is available free charge via the Internet at <http://pubs.acs.org>.

OM800378V

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