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Direct Observation of Aldehyde Insertion into Rhodium−Aryl and −Alkoxide Complexes

Christopher Krug and John F. Hartwig*

Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

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Abstract: Several organorhodium(I) complexes of the general formula $(PPh_3)_2(CO)RhR$ (R = *p*-tolyl, *o*-tolyl, Me) were isolated and were shown to insert aryl aldehydes into the aryl−rhodium(I) bond. Under nonaqueous conditions, these reactions provided ketones in good yield. The stability of the arylrhodium(I) complexes allowed these reactions to be run also in mixtures of THF and water. In this solvent system, diarylmethanols were generated exclusively. Mechanistic studies support the formation of ketone and diarylmethanol by insertion of aldehyde into the rhodium−aryl bond and subsequent β-hydride elimination or hydrolysis to form diaryl ketone or diarylmethanol products. Kinetic isotope effects and the formation of diarylmethanols in THF/water mixtures are inconsistent with oxidative addition of the acyl carbon−hydrogen bond and reductive elimination to form ketone. Moreover, the intermediate rhodium diarylmethoxide formed from insertion of aldehyde was observed directly during the reaction. Its structure was confirmed by independent synthesis. This complex undergoes β-hydrogen elimination to form a ketone. This alkoxide also reacts with a second aldehyde to form esters by insertion and subsequent β-hydrogen elimination. Thus, reactions of arylrhodium complexes with an excess of aldehyde formed esters by a double insertion and β-hydrogen elimination sequence.

Introduction

Insertion of alkenes into late transition metal−carbon bonds[1] is a common organometallic reaction in catalytic processes that form small molecules as well as macromolecules. Insertions of electrophilic heterocumulenes, such as CO_2 and isocyanates, are also known, but fewer catalytic processes involving these insertions have been developed.[2] In contrast, directly observed insertions of aldehydes into late metal−carbon bonds are rare and have been limited to reactions of metallacycles.[3] Indeed, insertion of aldehydes into a late metal−carbon bond should be less favorable than insertion of olefins. The carbon−oxygen π-bond is stronger than the carbon−carbon π-bond,[4] and the resulting alkoxides are often less stable kinetically than the starting alkyl. These trends make detection of aldehyde insertion products difficult. Insertion of CO_2 and isocyanates generates more stable carboxylate and carbamate products.

Nevertheless, catalytic cycles that may occur by aldehyde or related imine insertions have been emerging. Miyaura,[5] Oi,[6] Hayashi,[7] Batey,[8] Li,[9] and Fürstner[10] have developed rhodium(I)-catalyzed reactions that form alcohols and amines by addition of aryl main group reagents to aldehydes and imines. We recently reported a rhodium-catalyzed Heck-type coupling of imines with arenes that appeared to involve imine insertion,[11] and Yamamoto[12,13] has developed palladium- and platinum-catalyzed reactions that form amines and carbinols, perhaps by insertion of aldehydes or imines. Recently, Tamaru and Mori have independently developed nickel-catalyzed intra- and intermolecular additions of π-allyl donors to aldehydes, and these reactions may involve insertion of aldehyde into a metal−allyl linkage.[14] With an interest in observing new insertion

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, 1987.
(2) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747.
(3) (a) Carmona, E.; Gutiérrez-Puebla, E.; Marín, J. M.; Monge, A.; Paneque, M.; Poveda, M. L.; Ruiz, C. *J. Am. Chem. Soc.* **1989**, *111*, 2883. (b) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717.
(4) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987; p 162.
(5) (a) Sakai, M.; Ueda, M.; Miyaura, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 3279. (b) Ueda, M.; Miyaura, N. *J. Org. Chem.* **2000**, *65*, 4450. (c) Ueda, M.; Miyaura, N. *J. Organomet. Chem.* **2000**, *595*, 31.
(6) (a) Oi, S.; Moro, M.; Inoue, Y. *Chem. Commun.* **1997**, 1621. (b) Oi, S.; Moro, M.; Inoue, Y. *Organometallics* **2001**, *20*, 1036. (c) Oi, S.; Moro, M.; Fukuhara, H.; Kawanishi, T.; Inoue, Y. *Tetrahedron Lett.* **1999**, *40*, 9259.
(7) Hayashi, T.; Ishigedani, M. *J. Am. Chem. Soc.* **2000**, *122*, 976.
(8) Batey, R. A.; Thadani, A. N.; Smil, D. V. *Org. Lett.* **1999**, *1*, 1683.
(9) (a) Li, C. J.; Meng, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9538. (b) Huang, T.; Meng, Y.; Venkatraman, S.; Wang, D.; Li, C. J. *J. Am. Chem. Soc.* **2001**, *123*, 7451.
(10) Fürstner, A.; Krause, H. *Adv. Synth. Catal.* **2001**, *343*, 343.
(11) Ishiyama, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 12043.
(12) (a) Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6641. (b) Nakamura, H.; Nakamura, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4242. (c) Gevorgyan, V.; Quan, L. G.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 4089.
(13) For late metal-catalyzed reactions between vinyl or aryl groups and ketones, see: (a) Quan, L. G.; Lamrani, M.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 4827. (b) Quan, L. G.; Gevorgyan, V.; Yamamoto, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3545.
(14) For other late metal-catalyzed reactions between aryl or allyl groups and aldehydes, see: (a) Cheng, C. H.; Majumdar, K. K. *Org. Lett.* **2000**, *2*, 2295. (b) Shibata, K.; Kimura, M.; Shimizu, M.; Tamaru, Y. *Org. Lett.* **2001**, *3*, 2181. (c) Sato, Y.; Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2000**, *122*, 1624. (d) Sato, Y.; Takimoto, M.; Hayashi, K.; Katsuhara, T.; Takagi, K.; Mori, M. *J. Am. Chem. Soc.* **1994**, *116*, 9771. (e) Larock, R. C.; Doty, M. J.; Cacchi, S. *J. Org. Chem.* **1993**, *58*, 4579.

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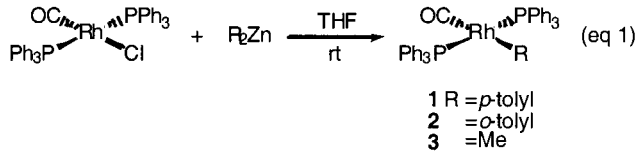
processes, we sought to prepare discrete organometallic complexes that would insert aldehydes and imines. Thus, we targeted potential intermediates in these new catalytic processes. Here, we describe the preparation of stable, phosphine-ligated aryl−, alkyl−, and alkoxo−rhodium(I) complexes that allow for the direct observation of aldehyde insertions to form alkoxide intermediates. These alkoxide intermediates generate ketone or diarylmethanol products, depending on reaction conditions.

Results and Discussion

Preparation of Rhodium−Aryl Complexes. Many of the reported systems for addition of arylmetalloids to aldehydes and imines involve cationic and often "ligandless" rhodium complexes generated in situ. Discrete arylrhodium complexes would be difficult to isolate in these systems. In addition to these catalysts, we found that the rhodium analogue of Vaska's complex provided 5 to 10 turnovers for the addition of potassium phenyltrifluoroborate to benzaldehyde in THF/water mixtures. Although this catalyst is less reactive than the most active species generated in situ, the Vaska-type system would be more amenable to isolation of potential intermediates, while remaining relevant to catalytic chemistry.

Triphenylphosphine−ligated arylrhodium(I) complexes can be difficult to isolate in pure form,[15−18] but rhodium−aryl compounds with a mixed phosphine and CO ligation sphere are stable. Complexes of the general formula $(PPh_3)_2Rh(CO)$-Ar have been reported. Although we found that literature procedures generate product mixtures,[17] as determined by ^{31}P NMR spectroscopy of crude reaction solutions, reaction of 1 equiv of bis(*p*-tolyl)zinc with $(PPh_3)_2Rh(CO)Cl$ in THF at room temperature did give the desired *p*-tolyl rhodium complex **1** as a yellow crystalline material in 77% yield (Figure 1). Single crystals suitable for X-ray analysis were grown from a THF/pentane solution at −35 °C.[18] This method allowed for the preparation of the *o*-tolyl and methyl analogues **2** and **3** in 70% and 59% yields, respectively (eq 1).



Reactions of Aldehydes To Form Ketones. We investigated the reactivity of these isolated organorhodium(I) complexes with various unsaturated substrates. Reaction of *p*-tolyl **1** with aryl aldehydes in C_6D_6 gave diaryl ketones in good yields in most cases after 80 min at 85 °C (Table 1). Reactions of *o*-tolyl **2** and methyl **3** with benzaldehyde were less selective or gave lower yields of the desired ketone. Heating of **2** and benzaldehyde in benzene-d_6 gave 2-methylbenzophenone (57% yield by ^1H NMR spectroscopy), along with several unidentified products. Heating of **3** at 85 °C for 8 h with benzaldehyde formed acetophenone, but in less than 10% yield (Table 1, entry 8). Aldehyde insertions were limited to aryl aldehydes; heating of **1** in C_6D_6 in the presence of 1-hexanal did not form the corresponding ketone, as determined by GC-MS or ^1H NMR spectroscopy.

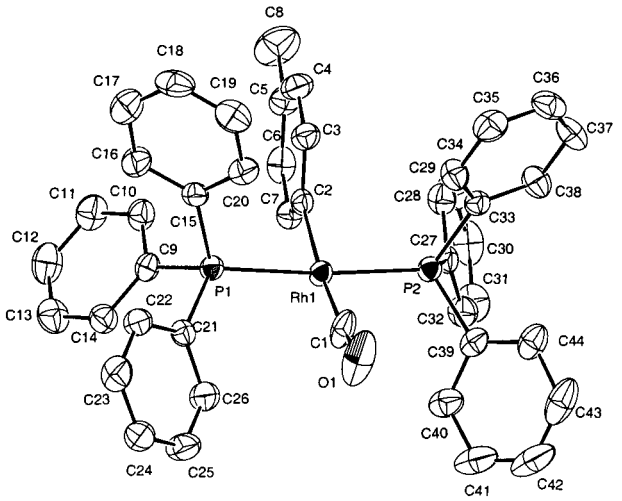
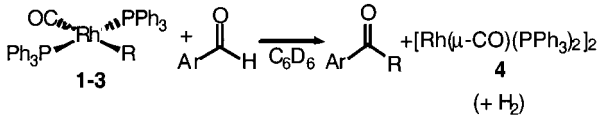


Figure 1. Ortep diagram of **1**. Representative bond lengths (Å) and bond angles (deg): Rh(1)−P(1) 2.3141; Rh(1)−P(2) 2.3016; Rh(1)−C(1) 1.862; Rh(1)−C(2) 2.090; C(1)−O(1) 1.131; P(1)−Rh(1)−P(2) 174.7; C(1)−Rh-(1)−C(2) 172.7; P(1)−Rh(1)-C(2) 88.33; P(2)−Rh(1)−C(1) 90.70.

Table 1. Yields of Diaryl Ketone Product in the Reaction of Organorhodium Complexes and Aryl Aldehydes[a]



entry	Rh complex	Ar	yield (%)
1	1	Ph	68
2	1	2-naphthyl	75
3	1	2-naphthyl	53[b]
4	1	*o*-tolyl	78
5	1	*p*-$F_3CC_6H_4$	38[c]
6	1	*p*-$OMeC_6H_4$	74
7	2	Ph	57[d]
8	3	Ph	<10[e]

[a] Reaction conditions: 1.5 equiv of aldehyde in C_6D_6, [Rh] = 0.013 M. 80 min at 85 °C. [b] 10 equiv of aldehyde was used. [c] 4 h reaction time. [d] 16 h reaction time. [e] 8 h reaction time.

A ^{31}P NMR signal at 37.3 ppm (J_{PRh} = 195 Hz) corresponding to the known dimer $[Rh(\mu\text{-}CO)(PPh_3)_2]_2$ (**4**) was generated by the reaction with aldehyde.[19] As the reaction progressed, complex **4** underwent decomposition, as determined by obtaining at various time intervals ^{31}P NMR spectra of reaction solutions containing tris(2,4,6-trimethoxyphenyl)phosphine as internal standard. Yet, we were able to isolate complex **4** from the reaction between **1** and *p*-$F_3CC_6H_4CHO$ at room temperature in THF. Its structure was confirmed by X-ray diffraction.

Toluene was produced in 19−25% yield as a side product of the reactions between *p*-tolyl **1** and aryl aldehydes. We considered that hydrolysis by traces of adventitious water or simple thermal decomposition of **1** could form the toluene side product. Thus, a solution of **1** was heated at the temperature of the reaction in the absence of aldehyde. Although about 10%

(15) (a) Takesada, M.; Yamazaki, H.; Hagihara, N. *Nippon Kagaku Zasshi* **1968**, *89*, 1121. (b) Kulzick, M. A.; Price, R. T.; Andersen, R. A.; Muetterties, E. L. *J. Organomet. Chem.* **1987**, *333*, 105. (c) Yamamoto, M.; Onitsuka, K.; Takahashi, S. *Organometallics* **2000**, *19*, 4669. (d) Zecchin, S.; Schiavon, G.; Pilloni, G.; Martelli, M. *J. Organomet. Chem.* **1976**, *110*, C45.

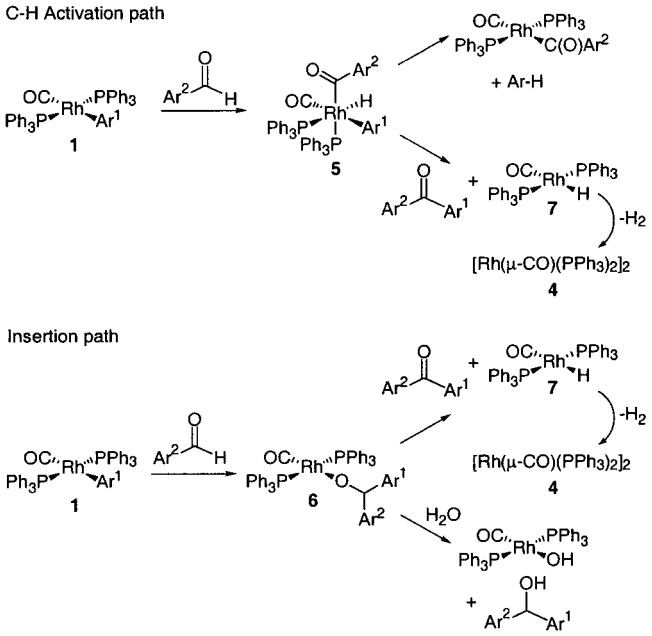
(16) Keim, W. *J. Organomet. Chem*. **1968**, *14*, 179.

(17) Dahlenburg, L.; Mirzaei, F.; Yardimcioglu, A. *Z. Naturforsch.* **1982**, *37B*, 310.

(18) For the only other aryl−rhodium(I) complex that has been structurally characterized, see: Boyd, S. E.; Field, L. D.; Hambley, T. W.; Partridge, M. G. *Organometallics* **1993**, *12*, 1720.

(19) Evans, D.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660.

Scheme 1



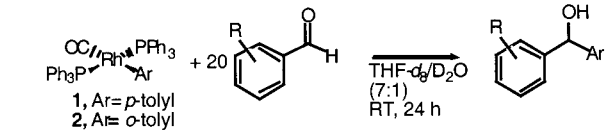
of **1** had undergone decomposition, an ^{1}H NMR spectrum acquired after 80 min at 85 °C showed that no toluene had formed.

Mechanistic Studies on the Formation of Ketones. Tsuji[20] and more recently Pignolet,[21] Goldman,[22] O'Connor,[23] and Crabtree[24] reported on the rhodium(I)-catalyzed decarbonylation of aldehydes. In addition, catalytic hydroacylation of olefins has been reported.[25,26] These processes have been shown to occur by initial C−H bond cleavage of the aldehyde. Thus, we investigated whether the formation of ketone from a reaction between **1** and aryl aldehydes occurred by initial cleavage of the aldehyde C−H bond as shown at the top of Scheme 1. Ketone and toluene would then form from competing C−C and C−H reductive elimination from the phenacyl hydride **5**.

Alternatively, the ketone could form as shown at the bottom of Scheme 1. Insertion of aldehyde would form diarylmethoxide **6**, and subsequent β-hydrogen elimination would form ketone. β-Hydrogen elimination from alkoxo complexes is a common route to hydride complexes[27] and has been observed directly in related iridium alkoxo complexes.[28] In either the C−H activation or insertion mechanism, the rhodium dimer **4** would form from decomposition of the resulting unstable rhodium hydride **7** (Scheme 1).

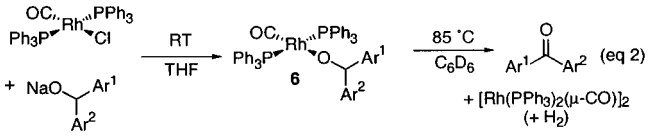
Several experiments strongly favor insertion of aldehyde and subsequent β-H elimination. First, reactions of **1** with 2-naphthaldehyde and 2-naphthaldehyde-d_1 occurred with rate constants of 9.8 and 9.9 × 10^{-4} s^{-1}, indicating the absence of a deuterium isotope effect in the rate determining step. Second, reaction of **1** with 2-naphthaldehyde at room temperature for 24 h generated the proposed alkoxide intermediate **6**. This intermediate **6** was observed directly by ^{1}H and ^{31}P NMR spectroscopy. It accumulated as roughly 25% of the reaction mixture after 20 h at room temperature.

Scheme 2



Rh:	R	yield (%)	Rh:	R	yield (%)
1	H	83	**1**	*o*-Me	73
1	*p*-OMe	84 (40 h)	**2**	*p*-Cl	87 (72 h)
1	2-napthyl	85	**2**	H	95 (19h at 55 °C)
1	*p*-Cl	74			

Independent synthesis was used to demonstrate that the ^{1}H and ^{31}P NMR signals of the intermediate corresponded to insertion product **6**. Reaction of $(PPh_3)_2Rh(CO)Cl$ and sodium 2-naphthyl-*p*-tolylmethoxide led to formation of the same species, which was isolated from a cold toluene/Et_2O solution in 56% yield. As required by the insertion mechanism, heating of this isolated complex in C_6D_6 gave diaryl ketone in 80% yield by ^{1}H NMR spectroscopy (eq 2).

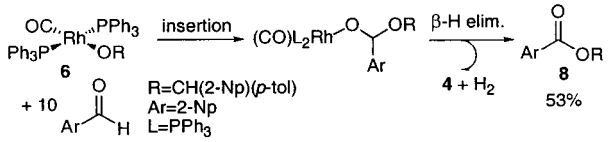


Because the insertion mechanism does not directly account for the formation of toluene, we further evaluated the origin of this side product. We reasoned that $RhH(CO)(PPh_3)_3$ would generate hydride **7** by phosphine dissociation and, therefore, could serve as a model for the reactivity of the initial hydride product $RhH(CO)(PPh_3)_2$. Reaction of $RhH(CO)(PPh_3)_3$ with *p*-tolyl complex **1** consumed the hydride and formed toluene in 27% yield (^{1}H NMR spectroscopy) and dimeric **4**, after 2 h at 85 °C. Thus, an independent side reaction of the hydride product with *p*-tolyl **1** most likely accounts for the formation of the small amounts of toluene in the reaction of **1** with aryl aldehydes.

Reactions of Aldehydes To Form Diarylmethanols. The intermediacy of diarylmethoxide **6** in the formation of ketone suggested that aldehydes would react with **1** to form alcohols in the presence of water by hydrolysis of **6**. This reaction sequence would account for the formation of arylmethanols in some of the catalytic chemistry described in the Introduction. Thus, arylrhodium complexes **1** and **2** were treated with aldehydes at room temperature and at 55 °C in a mixture of THF and water. These reactions gave diarylmethanols and $(PPh_3)_2Rh(CO)OH$[29] after 24−72 h (Scheme 2). Reactions of *o*-tolyl **2** were slower than were those of *p*-tolyl **1**, presumably because the greater steric hindrance of **2** prevents association of aldehyde. Reactions that formed alcohol in aqueous THF were faster than those that formed ketone in the less polar benzene.

(20) Tsuji, J.; Ohno, K. *Tetrahedron Lett*. **1967**, 2173.
(21) Doughty, D. H.; Pignolet, L. H. *J. Am. Chem. Soc*. **1978**, *100*, 7083.
(22) Abu-Hasanayn, F.; Goldman, M. E.; Goldman, A. S. *J. Am. Chem. Soc*. **1992**, *114*, 2520.
(23) O'Conner, J. M.; Ma, J. *J. Org. Chem*. **1992**, *57*, 5075.
(24) Beck, C. M.; Rathmill, S. E.; Park, Y. J.; Chen, J.; Crabtree, R. H.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5311.
(25) (a) Barnhart, R. W.; Wang, X.; Noheda, P.; Bergens, S. H.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc*. **1994**, *116*, 1821. (b) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936. (c) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 946.
(26) (a) Lenges, C. P.; Brookhart, M. *J. Am. Chem. Soc*. **1997**, *119*, 3165. (b) Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc*. **1998**, *120*, 6965.
(27) (a) Blum, O.; Milstein, D. *J. Am. Chem. Soc*. **1995**, *117*, 4582. (b) Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc*. **1998**, *120*, 6826. (c) Blum, O.; Milstein, D. *J. Organomet. Chem*. **2000**, 593−594, 479.
(28) Zhao, J.; Hesslink, H.; Hartwig, J. F. *J. Am. Chem. Soc*. **2001**, *123*, 7220.
(29) Li, P. C. H.; Thompson, M. *Analyst* **1994**, *119*, 1947.

Scheme 3



Insertions of Aldehydes into Rhodium Diarylmethoxide Complexes. Reactions with **6** with an excess of aldehyde formed ester in competition with ketone, and this competitive formation of ester accounts for the lower yield of ketone noted in entry 3 of Table 1. This ester could form by insertion of aldehyde into the rhodium alkoxo complex and subsequent β-hydrogen elimination from the resulting alkoxo complex. Thus, we tested whether ester would form from addition of aldehyde to isolated alkoxide **6**. Indeed, reaction of diarylmethoxide **6** with an excess of 2-naphthaldehyde gave the diarylmethyl-2-naphthoate **8** in 53% yield (Scheme 3). Although metal-catalyzed Tishchenko reactions are known,[26b,30] direct observation of aldehyde insertions into alkoxo complexes are rare. Recently, Han and Hillhouse reported the only previously observed insertion of aldehydes into late metal alkoxo complexes.[31]

Conclusions. This work represents a rare example of directly observed insertion of aldehydes into a late transition metal−carbon and −oxygen bonds, particularly in unstrained systems. These data support the mechanism proposed by several groups for the rhodium-catalyzed formation of aryl methanols and aryl methylamines, as well as our proposed insertion of a tethered imine into a rhodium(III) aryl group.[11] Further studies on new insertions and on the detailed mechanism of the insertion chemistry reported here are in progress.

Experimental Section

General. 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, diethyl ether, toluene, and pentane were distilled from sodium benzophenone ketyl under nitrogen. CH_2Cl_2 was dried over CaH_2 and distilled under nitrogen. Ethyl alcohol, deuterium oxide, and H_2O were degassed prior to use by nitrogen sparging for 1 h. C_6D_6, and THF-d_8 were purchased from Cambridge Isotope Laboratories, Inc., dried over sodium benzophenone ketyl, and vacuum transferred prior to use. Column chromatography was performed using Merck silica gel 60 (230−400 mesh). Preparatory thin-layer chromatography plates were purchased from Analtech.

^{1}H NMR spectra were obtained on either a General Electric QE Plus 300-MHz spectrometer or Bruker DPX 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 MHz on a Bruker DPX 400-MHz instrument, 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 or 202.4 MHz on a General Electric Omega 300-MHz or 500-MHz instrument and chemical shifts are reported relative to 85% H_3PO_4. Elemental analysis was performed by Robertson Microlit Laboratories, Inc., Madison, NJ. High-resolution mass spectrometry was performed by the University of Illinois at Urbana−Champaign on a Micromass 70-VSE instrument.

p-Chlorobenzaldehyde, *p*-trifluoromethylbenzaldehyde, *o*-tolualdehyde, 2-naphthaldehyde, and 2-naphthoyl chloride were purchased from Aldrich and used as received. Benzaldehyde and *p*-anisaldehyde were purchased from Aldrich and were distilled prior to use. Both were degassed via three freeze−pump−thaw cycles. All aldehyde substrates were stored in a glovebox to slow oxidation to the corresponding carboxylic acid. Me_2Zn (2.0 M in toluene), *p*-tolylmagnesium bromide (1.0 M in Et_2O), and *o*-tolylmagnesium chloride (1.0 M in THF) were purchased from Aldrich and used as received. KF_3BPh,[8] $(PPh_3)_2Rh(CO)Cl$,[32] bis(*p*-tolyl)zinc,[33] and bis(*o*-tolyl)zinc[33] were prepared according to literature procedures. 2-Naphthaldehyde-d_1 was prepared by an analogous procedure to that reported for PhCDO.[34] $RhD(CO)(PPh_3)_3$ was prepared in an analogous manner to $RhH(CO)(PPh_3)_3$ using $NaBD_4$ and EtOD.[19]

Kinetic experiments were performed on a General Electric Omega 300- or 500-MHz instrument. All yields determined by ^{1}H NMR were calculated using 1,3,5-trimethoxybenzene or Cp_2Fe as an internal standard. A pulse delay of 80 s ($5 \times T_1$) was used to compensate for the slow relaxation time of Cp_2Fe.

Preparation of *trans*-Carbonyl(*p*-tolyl)bis(triphenylphosphine)-rhodium(I) (1).[17] In a 20 mL scintillation vial equipped with a magnetic stir bar were placed 0.250 g (0.360 mmol) of $(PPh_3)_2Rh(CO)Cl$ and 0.0900 g (0.360 mmol) of bis(*p*-tolyl)zinc. Dry THF (8 mL) was added via syringe, and the resulting solution was stirred for 0.5 h at room temperature. The solution was filtered through Celite and concentrated under reduced pressure. Degassed ethyl alcohol was added to the concentrated solution via cannula, giving a yellow precipitate. The supernatant was removed via cannula, and the product was washed with pentane and dried in vacuo, yielding **1** in 77% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 2.09 (s, 3H), 6.45 (d, J = 7.8 Hz, 2H), 6.87 (d, J = 7.8 Hz, 2H), 6.99−7.04 (m, 18H), 7.64−7.71 (m, 12H). ^{31}P NMR (121.6 MHz, C_6D_6): 35.2 (J_{PRh} = 159 Hz).

Preparation of *trans*-Carbonyl(*o*-tolyl)bis(triphenylphosphine)-rhodium(I) (2).[17] The title compound was prepared in 70% yield in an analogous manner to that of **1**, but using bis(*o*-tolyl)zinc. ^{1}H NMR (300 MHz, C_6D_6): δ 1.95 (s, 3H), 6.49 (t, J = 7.2 Hz, 1H), 6.56 (d, J = 7.5 Hz, 1H), 6.78 (t, J = 7.5 Hz, 1H), 6.99−7.03 (m, 18H), 7.07 (d, J = 7.2 Hz, 1H), 7.60−7.71 (m, 12H). ^{31}P NMR (121.6 MHz, C_6D_6): 35.6 (J_{PRh} = 160 Hz).

Preparation of *trans*-Carbonyl(methyl)bis(triphenylphosphine)-rhodium(I) (3).[17] The title compound was prepared in 59% yield in an analogous manner to that of **1**, but using dimethylzinc. ^{1}H NMR (300 MHz, C_6D_6): δ −0.08 (dt, J = 7.8 Hz, 3H), 7.01−7.06 (m, 18H), 7.86−7.88 (m, 12H). ^{31}P NMR (202.4 MHz, C_6D_6): 43.2 (J_{PRh} = 159 Hz).

Preparation of *trans*-Carbonyl[(2-naphthyl)(*p*-tolyl)methoxy]bis-(triphenylphosphine)rhodium(I) (6). Into a 20 mL scintillation vial equipped with magnetic stir bar were placed 0.100 g (0.145 mmol) of $(PPh_3)_2Rh(CO)Cl$ and 0.117 g (0.434 mmol) of (2-naphthyl)(*p*-tolyl)-sodium methoxide.[35] The components were dissolved in 5 mL of dry THF, and the resulting solution was stirred at room temperature for 1 h. The volatile materials were removed under reduced pressure, and the product was extracted into toluene. The solution was filtered through Celite and concentrated under reduced pressure. Slow addition of Et_2O and cooling to −35 °C gave the title compound in 56% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 2.19 (s, 3H), 5.72 (s, 1H), 6.78−6.84 (m, 5H), 6.97−7.05 (m, 18H), 7.28−7.37 (m, 4H), 7.61−7.64 (m, 2H), 7.89−7.94 (m, 12H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 21.3, 85.9, 123.9, 124.2, 124.8, 126.5, 126.9, 126.9 (overlap of signals observed by ^{1}H/^{13}C correlation spectroscopy), 127.5, 127.7, 127.9, 128.3 (vt, J = 3.9 Hz), 130.0, 132.1, 133.3, 133.5 (vt, J = 20.5 Hz), 133.9, 135.0 (vt, J = 6.5 Hz), 148.1, 149.2, 190.4 (dt, J_{CRh} = 62.5 Hz, J_{CP} = 19.3 Hz).

(30) (a) Murahashi, S.; Naota, T.; Ito, K.; Maeda, Y.; Taki, H. *J. Org. Chem.* **1987**, *52*, 4319. (b) Ito, T.; Horino, H.; Koshiro, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 504.
(31) Han, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1997**, *119*, 8135.
(32) Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *11*, 99.
(33) De Graaf, P. W. J.; Boersma, J.; Van der Kerk, G. J. M. *J. Organomet. Chem.* **1977**, *127*, 391.
(34) Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, *22*, 3815.
(35) Prepared by deprotonation of the corresponding (2-naphthyl)(*p*-tolyl)-methanol with excess NaH in THF, giving a viscous oil upon filtration and removal of all volatile materials.

^{31}P NMR (202.4 MHz, C_6D_6): 28.4 (J_{PRh} = 149 Hz). Anal. Calcd for $C_{55}H_{45}O_2P_2Rh$: C, 73.17; H, 5.02. Found: C, 72.94; H, 5.25.

Representative Procedure for the Reactions of Complexes 1−3 with Aldehydes in C_6D_6. To a small vial were weighed 9.0 mg (0.011 mmol) of **1** and about 1 mg of Cp_2Fe. C_6D_6 (0.7 mL) was added via syringe, and the yellow suspension was transferred to an NMR tube, which was subsequently warmed in a 55 °C oil bath for 5 min to ensure complete dissolution of **1**. An ^{1}H NMR spectrum was acquired, and the solution was transferred to a small vial equipped with a magnetic stir bar. Aldehyde (1.5 equiv) was added via syringe (or as a solid) to the solution, and the vial was capped and placed in an 85 °C oil bath for a specified period of time (Table 1). An ^{1}H NMR spectrum was acquired following completion of the reaction, and a yield was calculated on the basis of the amount of ketone formed relative to the amount of **1** used in the reaction.

Synthesis of Benzhydrol from KF_3BPh and Benzaldehyde Using Rhodium Catalysis. To a small vial equipped with stir bar were placed 80 mg (0.75 mmol) of benzaldehyde, 287 mg (1.55 mmol) of KF_3-BPh, and 52 mg (0.075 mmol) of $(PPh_3)_2Rh(CO)Cl$. THF (1.5 mL) was added, and the vial was capped with a piercable septum. Degassed H_2O (1.0 mL) was added via syringe, and the mixture was stirred at 80 °C for 15 h. The mixture was removed from the oil bath, diluted with H_2O (15 mL), and extracted with EtOAc (1 × 20 mL). The organic extract was washed with brine, dried over anhydrous $MgSO_4$, and filtered. All volatile materials were removed using rotary evaporation. The solid residue that remained was purified by chromatography on silica gel using 10% EtOAc in hexane to give a 43% yield of pure benzhydrol. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (d, J = 3.2 Hz, 1H), 5.87 (d, J = 3.6 Hz, 1H), 7.28−7.41 (m, 10 H).

Representative Procedure for the Reactions of Complexes 1 and 2 with Aldehydes in THF-d_8 and D_2O. To a small vial were weighed 9.0 mg (0.011 mmol) of **1** and about 1 mg of Cp_2Fe or 1,3,5-trimethoxybenzene. Addition of THF-d_8 (0.7 mL) via syringe generated a clear, yellow solution. An ^{1}H NMR spectrum was acquired, and the solution was transferred to a small vial equipped with a magnetic stir bar. Aldehyde (20 equiv) was added via syringe (or as a solid) to the solution, and the vial was capped with a piercable septum. Degassed D_2O (0.1 mL) was added via syringe, and the resulting solution was stirred at the specified temperature and period of time (Scheme 2). An ^{1}H NMR spectrum was acquired following completion of the reaction, and a yield was calculated on the basis of the amount of carbinol formed relative to the amount of **1** or **2** used in the reaction.

Reaction between $HRh(CO)(PPh_3)_3$ and 1. Into a small vial were placed 10 mg (0.012 mmol) of **1** and about 1 mg of 1,3,5-trimethoxybenzene. C_6D_6 (0.7 mL) was added, and the suspension was transferred to an NMR tube. The sample was warmed in a 70 °C oil bath for 5 min and occasionally shaken until **1** was completely dissolved. An ^{1}H NMR spectrum was acquired, and the sample was transferred to a vial containing 11 mg (0.012 mmol) of $HRh(CO)(PPh_3)_3$. The sample was heated at 85 °C for 2 h. An ^{1}H NMR spectrum was acquired, and the yield of toluene produced was calculated to be 27%.

Reaction between Rhodium Alkoxide 6 and 2-Naphthaldehyde. Into a small vial were placed 9.0 mg (0.010 mmol) of **6** and 16 mg (0.10 mmol, 10 equiv) of 2-naphthaldehyde. The reagents were dissolved in 0.7 mL of C_6D_6. 1,3,5-Trimethoxybenzene (1 mg) was added to the solution, and the solution was transferred to an NMR tube. An ^{1}H NMR spectrum was acquired. The sample was heated at 85 °C for 0.5 h, after which time alkoxide **6** was consumed. An ^{1}H NMR spectrum was acquired, from which a 57% yield of [(*p*-tolyl)(2-naphthyl)methyl] 2-naphthoate was calculated.

Independent Preparation of [(*p*-Tolyl)(2-naphthyl)methyl] 2-Naphthoate. Into a 25 mL round-bottom flask equipped with a magnetic stir bar were placed 80.0 mg (0.322 mmol) of (*p*-tolyl)(2-naphthyl)-methanol and 184 mg (0.967 mmol, 3 equiv) of 2-naphthoyl chloride. Dry CH_2Cl_2 (4 mL) was added via syringe. Et_3N (0.670 mL, 4.81 mmol, 15 equiv) was added, and the resulting solution was stirred at room temperature for 1.5 h. The volatile materials were removed using rotary evaporation, and the products were extracted into EtOAc (1 × 20 mL). The organic extract was washed with water, $NaHCO_3$, and brine and dried over anhydrous $MgSO_4$. The solution was filtered, and all volatile materials were removed in vacuo. The title compound was isolated in pure form following preparatory TLC (5% EtOAc/hexanes) as a clear oil in 66% yield. ^{1}H NMR (500 MHz, C_6D_6): δ 2.07 (s, 3H), 6.99 (d, J = 7.5 Hz, 2H), 7.13−7.23 (m, 4H), 7.43−7.61 (m, 10H), 7.97 (s, 1H), 8.35 (dd, J = 8.5 Hz, J = 1.5 Hz, 1H), 8.87 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 21.1, 77.6, 125.0, 125.3, 126.0, 126.1, 126.2, 126.6, 127.3, 127.4, 127.6, 127.7, 128.1, 128.2, 128.3, 128.4, 129.3, 129.4, 131.3, 132.4, 132.9, 133.1, 135.6, 137.2, 137.7, 137.8, 165.8. HRMS calcd for $C_{29}H_{22}O_2$: 402.1620; found 402.1624.

Representative Procedure for Kinetic Experiments of 1 with 2-Naphthaldehyde. To a small vial was weighed 9.0 mg (0.011 mmol) of **1**. C_6D_6 (0.7 mL) was added via syringe, and the suspension was transferred to an NMR tube. The contents were warmed to 50 °C for 2−3 min or until **1** was entirely dissolved. Ten equivalents of 2-naphthaldehyde or 2-naphthaldehyde-d_1 were added to the yellow solution, and the sample was placed in the NMR probe at 60 °C. The intensity of the doublet at δ = 6.37 in the ^{1}H NMR spectrum of **1** was monitored over 2 h by acquiring ^{1}H NMR spectra every 30 s. Rate constants were determined by fitting the data to an exponential decay using KaleidaGraph software.

Independent Preparation of Diarylmethanols and Diaryl Ketones. All products that are not commercially available have been reported previously[14a,37−42] and were synthesized according to the following procedure: Into a 50 mL two-neck round-bottom flask equipped with a magnetic stir bar was placed 1.00 g of aldehyde. Dry Et_2O (7−9 mL) was then added via syringe. The solution was cooled to 0 °C, and 1.5 equiv of *p*-tolylmagnesium bromide was added dropwise via syringe. The solution was allowed to warm to room temperature, and the solution was stirred for 1 h. Upon formation of a precipitate, 3−5 mL of dry THF was added, and the solution was stirred for an additional hour. Excess Grignard reagent was then quenched with aqueous ammonium chloride, and the organic products were extracted with Et_2O (1 × 40 mL). The extracts were washed with brine, dried over $MgSO_4$, and filtered, and the volatile materials were removed under reduced pressure. No further purification of the crude alcohol was performed.

The crude alcohol (500 mg) was placed into a 50 mL two-neck round-bottom flask equipped with a stir bar. Dry CH_2Cl_2 (8 mL) was added via syringe. While stirring, 1.5 equiv of pyridinium chlorochromate was added as a solid, giving a dark-colored solution. After 2 h, the solution was filtered through Celite, and the ketone product was purified using silica gel chromatography (CH_2Cl_2 eluent). 4-Methylbenzophenone:[36] ^{1}H NMR (300 MHz, C_6D_6) δ 2.00 (s, 3H), 6.87 (d, J = 8.1 Hz, 2H), 7.13−7.05 (m, 3H), 7.76−7.71 (m, 4H). 4-Methyl-4′-trifluoromethylbenzophenone:[37] ^{1}H NMR (300 MHz, C_6D_6) δ 2.00 (s, 3H), 6.88 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H). (4-Methylphenyl)naphthyl ketone:[38] ^{1}H NMR (300 MHz, C_6D_6) δ 2.03 (s, 3H), 6.92 (d, J = 7.8 Hz, 2H), 8.19 (s, 1H), 8.04 (dd, J = 8.7 Hz, J = 1.8 Hz, 1H), 7.26 (m, 2H), 7.47−7.58 (m, 3H), 7.79 (d, J = 8.1 Hz, 2H). 4-Methyl-2′-methylbenzophenone:[36] ^{1}H NMR (300 MHz, C_6D_6) δ 1.96 (s, 3H), 2.28 (s, 3H), 6.85 (d, J = 8.1 Hz, 2H), 6.86−7.18 (m, 4H), 7.80 (d, J = 8.1 Hz, 2H). 4-Methyl-4′-methoxybenzophenone:[36] ^{1}H NMR (300 MHz, C_6D_6) δ 2.03 (s, 3H), 3.19 (s, 3H), 6.65 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H). 2-Methylbenzophenone:[36] ^{1}H NMR (400 MHz, C_6D_6) δ 2.25 (s, 3H), 6.88−7.15 (m, 7H), 7.78−7.80 (m, 2H). (4-Methylphenyl)(phenyl)-methanol:[36] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 1H), 2.34 (s, 3H), 5.84 (s, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.29 (s, 1H), 7.33−7.41 (m,

(36) Commercially available.
(37) French, F. A.; DoAmaral, J. R.; Blanz, E. J.; French, D. A. *J. Med. Chem.* **1971**, *14*, 862.
(38) Myata, A.; Matsunaga, K.; Ishikawa, M. JP Patent 07089894 A2, 1995.

6H). (2-methylphenyl)(phenyl)methanol:[36] ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14 (s, 1H), 2.27 (s, 3H), 6.03 (s, 1H), 7.15−7.35 (m, 8H), 7.52−7.55 (m, 1H). (2-Methylphenyl)(4′-methylphenyl)methanol:[39] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 1H), 2.31 (s, 3H), 2.40 (s, 3H), 6.05 (s, 1H), 7.19−7.25 (m, 3H), 7.29−7.34 (m, 4H), 7.61 (d, J = 1.2 Hz, 1H). (2-Methylphenyl)(4′-chlorophenyl)methanol:[40] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.16 (s, 1H), 2.26 (s, 3H), 6.00 (s, 1H), 7.15−7.18 (m, 2H), 7.22−7.33 (m, 6H). (4-Methylphenyl)(4′-chlorophenyl)methanol:[41] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 (s, 1H), 2.31 (s, 3H), 5.73 (s, 1H), 7.11−7.29 (m, 8H). (4-Methylphenyl)(2-naphthyl)methanol:[42] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 1H), 2.35 (s, 3H), 6.00 (s, 1H), 7.17 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.42−7.51 (m, 3H), 7.79−7.86 (m, 3H), 7.92 (s, 1H). (4-Methylphenyl)(2′-methoxyphenyl)methanol:[14a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 1H), 2.34 (s, 3H), 3.80 (s, 3H), 5.79 (s, 1H), 6.87 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 9.0 Hz, 2H).

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Supporting Information Available: Full structural characterization of **1**. This information is available free of charge via the Internet at http://www.pubs.acs.org.

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(39) Okubo, M.; Hayashi, S.; Matsunaga, M.; Uematsu, Y. *Bull. Chem. Soc. Jpn*. **1981**, *54*, 2337.
(40) Barkow, A.; Gruetzmacher, H.-F. *Int. J. Mass Spectrom. Ion Processes* **1995**, *142*, 195.
(41) Pourbaix, C.; Carreaux, F.; Carboni, B. *Org. Lett.* **2001**, *3*, 803.
(42) Artico, M.; Stefancich, G.; Silvestri, R.; Massa, S.; Apuzzo, G.; Simonetti, G. *Eur. J. Med. Chem.* **1992**, *27*, 693.