(η^3-Oxaallyl)rhodium(I) Complexes as Catalyst Precursors for the Disproportionation of Aldehydes

Greg A. Slough,* John R. Ashbaugh, and Luke A. Zannoni

The Department of Chemistry, The College of Wooster, Wooster, Ohio 44691

Received March 21, 1994[⊗]

Addition of 50 equiv of benzaldehyde to a benzene solution of $(Ph_3P)_2Rh(\eta^3\text{-}CH_2C(Ph)O)$ (**1**) resulted in rapid disproportionation of the aldehyde, yielding benzyl benzoate in near quantitative yield. Similar disproportionation reactions occurred with isobutyraldehyde, *n*-heptanal, and furfural; however, the yields in these reactions were lower. The catalytic efficiency of the (η^3-oxaallyl)rhodium(I) complex depended on the α-substitution pattern of the aldehyde, the concentration of the aldehyde, and the polarity of the aldehyde. The labeled complex $(Ph_3P)_2Rh(\eta^3\text{-}CH_2{}^{13}C(Ph)O)$ (**^{13}C-1**) transformed during catalysis into two carbon-labeled products, demonstrating that the η^3-oxaallyl complex served as a precursor to the actual catalyst. The (η^3-allyl)rhodium(I) complex $(Ph_3P)_2Rh(\eta^3\text{-}CH_2CHCH_2)$ (**5**) failed to react with benzaldehyde, but upon addition of 4 equiv of hydrogen gas, catalysis ensued with near quantitative disproportionation of the aldehyde. Rapid disproportionation of benzaldehyde also occurred when $(DIPHOS)Rh(C_6H_6)^+ClO_4^-$ and 18-crown-6-solubilized $PhCH_2O^-K^+$ were mixed, establishing the intermediacy of a rhodium alkoxide. A complete mechanistic scheme for oxaallyl modification and disproportionation catalysis is presented.

Introduction

Recently, we reported the direct synthesis of (η^3-oxaallyl)rhodium(I) complexes from μ-dichloro–rhodium dimers and potassium enolates. These materials showed physical and chemical properties fundamentally different from those of the isoelectronic (η^3-allyl)rhodium(I) complexes.[1] For example, $(Ph_3P)_2Rh(\eta^3\text{-}CH_2C(Ph)O)$ (**1**) displayed a dynamic NMR spectrum at room temperature, indicating fluctional bonding modes for the oxaallyl ligand. The same complex also added carbon monoxide, forming the oxygen-bound enolate complex *trans*-$(Ph_3P)_2(CO)Rh(OC(Ph)CH_2)$. Rhodium allyl complexes, on the other hand, undergo either addition or substitution reactions with CO, but the η^3-allyl ligand is maintained.[2]

We have continued our study of (η^3-oxaallyl)rhodium(I) complexes by investigating their reactivity with aldehydes. To our surprise, addition of 50 equiv of benzaldehyde to a variety of rhodium oxaallyl complexes gave nearly quantitative conversion of the aldehyde to benzyl benzoate. This result was puzzling since disproportionation of aldehydes (Tishchenko reaction) has typically been promoted by either transition metal hydrides, such as $(Ph_3P)_3RuH_2$,[3] or by aluminum alkoxides[4] or transition metal alkoxides.[5] Other assorted catalysts such as boric acid,[6] lithium tungsten dioxide,[7] disodium tetracarbonylferrate,[8] and ethyllanthanide complexes[9] have also been reported for similar dimerization reactions. To our knowledge, no transition metal enolate complex has been implicated as a catalyst for aldehyde disproportionation. We report our results on the rhodium oxaallyl catalyzed disproportionation of aldehydes and provide evidence for the mechanism of this unique catalytic mixture.

Results

Addition of 1 equiv of benzaldehyde to a C_6D_6 solution of oxaallyl complex **1, 2,** or **3** resulted in a distinct color change and complete consumption of the aldehyde after 5 min at 25 °C. Proton NMR analysis of the mixture showed a 10% decrease in the oxaallyl resonance, δ 3.48, and formation of a new singlet at δ 5.26. A 5% yield of acetophenone was also observed.[10] Addition of a second portion of benzaldehyde (3 equiv) further decreased the oxaallyl resonance (40% remained), and the signal at δ 5.26 increased in intensity. Benzyl benzoate was the reaction product on the basis of proton and carbon NMR data and of capillary gas chromatographic analysis.

The catalytic nature of the reaction was examined by mixing a 50:1 mol ratio of benzaldehyde and complex **1** in C_6D_6. After 25 min at 25 °C, no aldehyde remained. Separation of the mixture gave a 92% yield of benzyl benzoate. Oxaallyl complexes **2** and **3** gave uniformly high yields of benzyl benzoate when exposed to 50 equiv

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1994.

(1) Slough, G. A.; Hayashi, R.; Ashbaugh, J. R.; Shamblin, S. L.; Aukamp, A. M. *Organometallics* **1994,** *13,* 890.

(2) Clement, D. A.; Nixon, J. F.; Poland, J. S. *J. Organomet. Chem.* **1974,** *76,* 117.

(3) Ito, T.; Horino, H.; Koshitaka, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1982,** *55,* 504. Hayashi, Y.; Yamamoto, T.; Yamamoto, A.; Komiya, S.; Kushi, Y. *J. Am. Chem. Soc.* **1986,** *108,* 385.

(4) Tischenko, V. E. *Zh. Russ. Fiz.-Khim. Ova.* **1906,** *38,* 482. Villani, T. J.; Nord, F. F. *J. Am. Chem. Soc.* **1947,** *69,* 2605. Lin, I.; Day, A. R. *J. Am. Chem. Soc.* **1952,** *74,* 5133. Ogata, Y.; Kawasaki, A.; Kishi, I. *Tetrahedron* **1967,** *23,* 825. Saegusa, T.; Kitagawa, S.; Ueshima, T. *Bull. Chem. Soc. Jpn.* **1967,** *40,* 1960. Ogata, Y.; Kawasaki, A. *Tetrahedron* **1969,** *25,* 929.

(5) Bernard, K. A.; Atwood, J. D. *Organometallics* **1988,** *7,* 235. Bernard, K. A.; Atwood, J. D. *Organometallics* **1989,** *8,* 795.

(6) Stapp, P. R. *J. Org. Chem.* **1973,** *38,* 1433.

(7) Villacorta, G. M.; San Filippo, J., Jr. *J. Org. Chem.* **1983,** *48,* 1151.

(8) Yamashita, M.; Watanabe, Y.; Mitsudo, T-a.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1976,** *49,* 3597.

(9) Yokoo, K.; Mine, N.; Taniguchi, H.; Fujiwara, Y. *J. Organomet. Chem.* **1985,** *279,* C19.

(10) The relative yields of components in the mixture were measured against the internal standard hexamethylbenzene.

(11) The catalytic turnover rate was half the rate of aldehyde consumption since two aldehydes are required for each turnover of catalyst. The molarity of the catalyst itself was half the molarity of oxaallyl due to chemical modification (see text).

0276-7333/94/2313-3587$04.50/0

Scheme 1

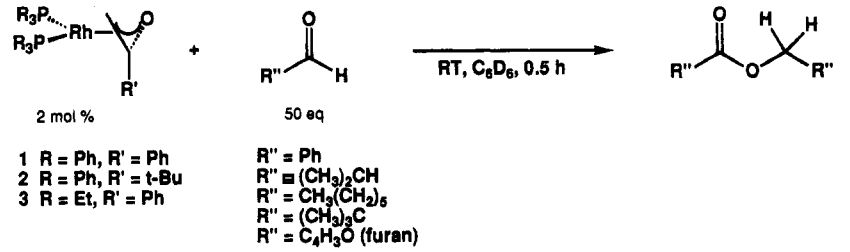


Table 1. Disproportionation Catalysis of Aldehydes with Complex 1 (0.011 mmol)

entry	aldehyde	no. of equiv	ester	ester NMR yield, %[a,b]	ester GC yield, %[c]
1	C_6H_6CHO	50	$PhCOOCH_2Ph$	94	95
2		100		17	14
3		500		<2	2
4	$(CH_3)_2CHCHO$	50	$C_3H_7COOC_4H_9$	11	13
5	$(CH_3)_3CCHO$	50	$(CH_3)_3CCOOC(CH_3)_3$	0	0
6	$CH_3(CH_2)_5CHO$	50	$C_6H_{13}COOC_7H_{15}$	87	87
7	$(C_4H_3O)CHO$	50	$(C_4H_3O)CO-OCH_2(C_4H_3O)$	45	41
8		100		13	14

[a] All measurements made in C_6D_6. [b] Percents based on the ratio of aldehyde and carbinol hydrogen, and on the ratio with the internal standard hexamethylbenzene. [c] Area counts compared to the standard curve of the ester.

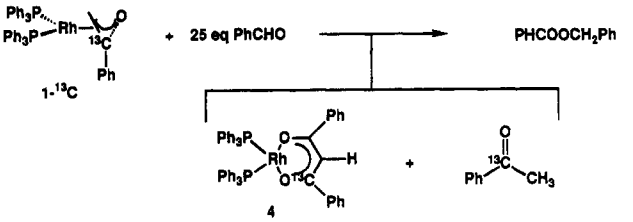
of benzaldehyde. All three oxaallyl complexes gave a turnover efficiency of $\approx 120 M_{aldehyde}/M_{complex} h$.[11]

Isobutyraldehyde, *n*-heptanal, and furfural also participated in the disproportionation with complex **1**, but all showed much lower efficiencies (see Table 1). *n*-Heptanal (50 equiv) and furfural (50 equiv) reacted smoothly over 1.0 h at 25 °C, giving 87% and 45% yields of esters, respectively. Aldehydes with α-substitution significantly affected the disproportionation reaction. Isobutyraldehyde and trimethylacetaldehyde showed either low catalytic conversion (12% in the case of isobutyraldehyde) or no reactivity with the catalyst. The result with *n*-heptanal is particularly important since it shows that enolizable hydrogens have little influence on the reactivity of the oxaallyl complex.

Aldehyde concentration and aldehyde polarity both showed inhibitory effects on this reaction. Benzaldehyde (entries 1–3) reacted smoothly at concentrations below 1.4 M; however, at higher concentrations, considerably lower yields of ester resulted. For example, a 100:1 mol ratio of benzaldehyde (2.7 M) and complex **1** gave only a 16% yield of benzyl benzoate. This represents 16 turnovers of the catalyst as opposed to 50 turnovers of the catalyst at a lower aldehyde concentration. Furfural displayed a similar inhibitory effect. Overall, furfural was less effective than benzaldehyde for the disproportionation, and as the concentration of furfural increased, the yield of ester decreased (see entries 7 and 8).

We conducted two control experiments which excluded hydroxylic base as the catalyst for this reaction.[12] An azeotropic mixture of C_6D_6 and deuterium oxide was prepared, and the NMR solvent was transferred into two NMR tubes. In one tube was added 0.30 mL, the amount needed for the NMR experiment, while in the second tube only 0.07 mL was added. Anhydrous C_6D_6 was added to the second tube to bring the total volume

Scheme 2



to 0.30 mL. Benzaldehyde (50:1 mol ratio with respect to the catalyst) and complex **1** were added sequentially to each tube. After 0.5 h at 25 °C each mixture was examined. The mixture containing only azeotropic C_6D_6 consumed only 6% of the benzaldehyde, while the mixture containing a lower concentration of azeotropic C_6D_6 consumed 21% of the benzaldehyde. These results suggested that hydrolysis of complex **1** led to inactive hydroxylic species.

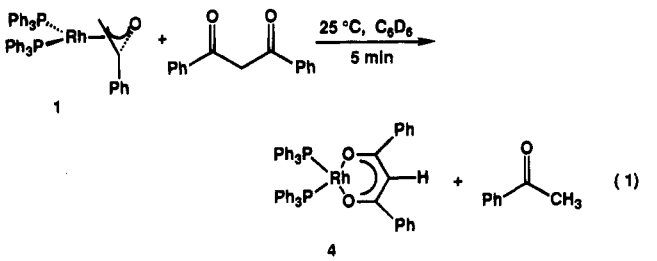
Oxaallyl Catalyst or Catalyst Precursor? The surprising reactivity of (η^3-oxaallyl)rhodium(I) complexes with aldehydes posed the question as to the role of the original rhodium complex in the catalysis. Stoichiometric reactions between complex **1** and benzaldehyde, described earlier, showed decay in the concentration of **1**, indicating that the aldehyde modified the oxaallyl ligand system. To establish the fate of the η^3-ligand, carbon-13 enriched oxaallyl complex $(Ph_3P)_2Rh(\eta^3\text{-}CH_2{}^{13}C(Ph)O)$ (**^{13}C-1**) was prepared from $Ph^{13}COCH_3$.[1] Addition of benzaldehyde (25 equiv) to a solution of **^{13}C-1** resulted in the characteristic orange to red-orange color change and quantitative formation of benzyl benzoate. The ^{1}H NMR spectrum showed no ^{13}C-labeled oxaallyl or benzaldehyde after catalysis. One distinct carbon–proton coupled resonance appeared at δ 2.09 (J_{H-C} = 5 Hz), and this signal was assigned to [^{13}CO]acetophenone.

Carbon NMR analysis of the same mixture revealed two ^{13}C-enriched signals both of nearly equal intensity. The signals at δ 196 and 167 matched resonances for authentic samples of acetophenone and $(Ph_3P)_2Rh(\eta^2\text{-}PhC(O)CHC(O)Ph)$ (**4**).[1] The $^{31}P\{^1H\}$ NMR spectrum provided information about the rhodium center after catalysis. Three phosphorus signals at δ 55.9 (d, J = 195.6 Hz), 40.3 (d, J = 121.0 Hz), and 31.6 (d, J = 137.8 Hz) completely replaced the ABX phosphorus signal for oxaallyl **^{13}C-1**. The resonance at δ 55.9 matched the

(12) Hydroxylic bases and nonenolizable aldehydes participate in the Cannizarro reaction with overall redox of the aldehyde. For a review and leading reference for the main-group Cannizarro reaction see: Geissman, T. A. *Org. React.* **1944**, *2*, 94. Swain, C. G.; Powell, A. L.; Sheppard, W. A.; Morgan, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 3576. For examples of transition metal complexes which promote the Cannizarro reaction see: Cook, J.; Hamlin, J. E.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2342. Bianchi, M.; Matteoli, U.; Menchi, G.; Frediani, P.; Piacenti, F. *J. Organomet. Chem.* **1982**, *240*, 65.

phosphorus NMR data reported for complex **4**. The relative intensities of the three signals were 50%, 27%, and 23%, respectively. After all rhodium oxaallyl initiated catalyses, varying ratios of the two high field phosphorus doublets were found. The less successful catalysis of 100 equiv of benzaldehyde showed only the resonances at δ 55.9 and 31.6. Despite the variation in the upfield signals, the total integration of the two upfield signals always matched the integration of complex **4**, suggesting that oxaallyl **1** was transformed into equal portions of **4** and a catalyst. After aldehyde disproportionation the catalyst then partitioned between two species.

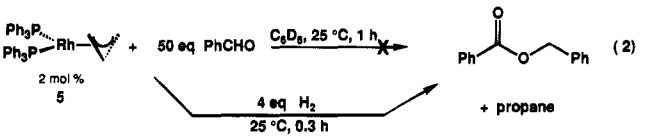
Formation of complex **4** clearly demonstrated that dibenzoylmethane must be produced in the catalytic mixture. Previous studies with oxaallyl **1** showed that dibenzoylmethane reacted rapidly with **1** ($T_{1/2}$ <1 min at 25 °C) to produce acetophenone and **4**.[1,13] We



reasoned that a straightforward route to dibenzoylmethane involved condensation of the oxaallyl ligand with benzaldehyde, followed by β-hydrogen elimination of the secondary alkoxide. This sequence would produce both dibenzoylmethane and a three-coordinate rhodium(I) hydride which would be a reasonable catalyst for the disproportionation. To test this hypothesis, we developed two alternate routes to three-coordinate rhodium(I) catalytic species.

Alternate Routes to Catalytic Species. Sivak and Muetterties[14] studied the hydrogenation of $(Ph_3P)_2Rh(\eta^3\text{-}CH_2CHCH_2)$ (**5**) and found that exhaustive hydrogenation of the allyl group gave an unstable three-coordinate rhodium hydride. The unstable hydride was formulated as $[(Ph_3P)_2RhH]_n$ by analogy with the more stable phosphite-containing rhodium hydrides. Little is known about the chemistry of bis(phosphine)rhodium hydride complexes. Fryzuk has prepared and investigated the reactivity of the binuclear bis[(diisopropylphosphino)propane]rhodium hydride complex.[15] This material reacts with butadiene and phenol, forming stable addition products with each reagent.[16,17]

Addition of excess benzaldehyde (50 equiv) to a solution of rhodium allyl **5** in C_6D_6 resulted in no reaction. After 1.0 h at room temperature, >99% of the



aldehyde remained unreacted. Exposure of the mixture to 0.73 atm (4 equiv) of hydrogen gas in a resealable NMR tube led to a distinct color change from yellow to red-orange. Less than 2% of the aldehyde remained after 21 min at 25 °C, and a 95% yield of benzyl benzoate was isolated. A small multiplet at δ 1.44 and a triplet at δ 1.01 also appeared in the catalytic mixture, indicating the production of propane. The $^{31}P\{^1H\}$ NMR of the mixture showed one major signal centered at δ 40.3 (doublet, J = 121.0 Hz). This phosphorus signal matched the unassigned phosphorus signal found in the oxaallyl **1** initiated catalysis, suggesting that a common rhodium product formed in both catalytic reactions. The mild reaction conditions for this catalysis precluded decarbonylation of the aldehyde substrate.[18]

Hydrogenation of rhodium allyl **5** in the presence of a variety of aldehydes also proceeded smoothly with efficient ester formation. Table 2 summarizes the results of these disproportionation experiments. Compared with the results in Table 1, the chemical yields of each dimeric ester were comparable for both catalytic methodologies. However, the hydrogenolysis method of complex **5** showed substantially higher catalytic efficiency with furfural. These data also suggested that the transformation of (η^3-oxaallyl)rhodium(I) **1** into the catalytically active three-coordinate rhodium hydride occurred smoothly with benzaldehyde, isobutyraldehyde, heptanal, and furfural, producing suitable concentrations of the active catalyst. The higher molar ratios found in the hydrogenolysis reactions reflect the increased concentration of the catalytic species, since all of the allyl complex can be converted to catalyst.

The concentration of the aldehyde component in these reactions again surfaced as an important consideration. Entries 2 and 3 in Table 2 show a threshold concentration effect; that is, benzaldehyde (100 equiv, 2.7 M) reacted in near quantitative yield in the presence of

Table 2. Disproportionation Catalysis of Aldehydes with Rhodium Allyl Complex 6 (0.011 mmol) and Hydrogen Gas

entry	aldehyde	no. of equiv	ester	isolated yield, %	ester NMR yield, %[a,b] (GC yield, %)[c]
1	C_6H_6CHO	50	$PhCOOCH_2Ph$	95	97 (97)
2		100		94	97 (96)
3		500			1 (2)
4	$(CH_3)_2CHCHO$	100	$C_3H_7COOC_4H_9$	8	15 (16)
5	$(CH_3)_3CCHO$	50	$(CH_3)_3CCOOC(CH_3)_3$		0 (0)
6	$CH_3(CH_2)_5CHO$	100	$C_6H_{13}COOC_7H_{15}$	86	91 (93)
7	$(C_4H_3O)CHO$	100	$(C_4H_3O)CO\text{—}OCH_2(C_4H_3O)$	97	98 (98)

[a] All measurements made in C_6D_6. [b] Percents based on the ratio of aldehyde and carbinol hydrogen, and on the ratio with the internal standard hexamethylbenzene. [c] Area counts compared to the standard curve of the ester.

(13) The putative complex $[(Ph_3P)_2RhH]$ reacted slowly with dibenzoylmethane in benzene. Equal molar quantities of complex **5** and dibenzoylmethane failed to react; however, addition of 4 equiv of H_2 to the same mixture gave an 18% yield of **4**. The dominant ^{31}P NMR signal, 59%, was centered at δ 40.3 (J = 122.1 Hz).

(14) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

(15) (a) Fryzuk, M. D. *Inorg. Chem.* **1982**, *21*, 2134. (b) Fryzuk, M. D. *Organometallics* **1982**, *1*, 408. (c) Fryzuk, M. D. *Can. J. Chem.* **1983**, *61*, 1347. (d) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185. (e) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *J. Chem. Soc., Chem. Commun.* **1984**, 1556.

(16) Fryzuk, M. D.; Piers, W. E.; Rettig, S. J.; Einstein, F. W. B.; Jones, T.; Albright, T. A. *J. Am. Chem. Soc.* **1989**, *111*, 5709.

(17) Fryzuk, M. D.; Jang, M.-L.; Jones, T.; Einstein, F. W. B. *Can. J. Chem.* **1986**, *64*, 174. Fryzuk, M. D. *Inorg. Chem.* **1982**, *21*, 2134.

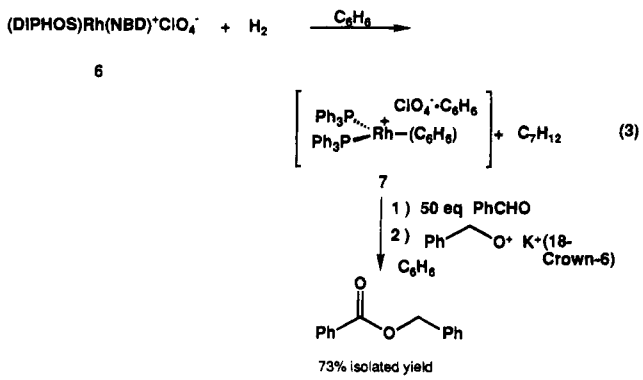
(18) Tris(triphenylphosphine)rhodium chloride and cationic rhodium complexes are the most reactive for catalytic decarbonylation. Significant catalytic turnover of these complexes requires temperatures about 150 °C. Doughty, D. H.; Anderson, M. P.; Casalnuovo, A. L.; McGuiggen, M. F.; Tso, C. C.; Wang, H. H.; Pignolet, L. H. *Adv. Chem. Ser.* **1982**, 196. Doughty, D. H.; Pignolet, L. H. *J. Am. Chem. Soc.* **1978**, *100*, 7083.

rhodium allyl and hydrogen, while higher concentrations (500 equiv, 6.7 M) gave nearly complete inhibition. This phenomenon coupled with the concentration effect noted with the oxaallyl promoted catalysis suggested that one of the disproportionation intermediates was sensitive to aldehyde concentration and not the oxaallyl complex itself. The hydrogenolysis methodology presumably has a higher threshold because it forms the rhodium hydride in a higher concentration.

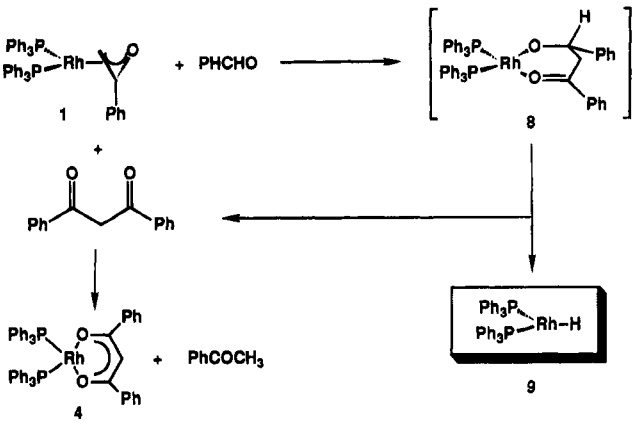
A useful indicator of the efficiency of the (η^3-allyl)-rhodium(I)–hydrogen catalysis was the relative intensity of the phosphorus doublet centered at δ 40.3 after the reaction. The putative hydride complex **9** showed high catalytic efficiency with both benzaldehyde and furfural, and in each reaction mixture a single resonance at δ 40.3 appeared after disproportionation. The reaction with heptanal was somewhat less efficient and showed two resonances of equal intensites centered at δ 40.3 and 31.6 (J = 127.8 Hz). The isobutyraldehyde reaction showed the same two resonances, but the signal at δ 31.6 dominated by a factor of 3. Neither rhodium product was catalytically active toward aldehyde disproportionation. We tried to characterize both rhodium products from the catalysis; however we have been unsuccessful. In an attempt to increase the signal-to-noise of the rhodium products, an isobutyraldehyde reaction mixture was concentrated *in vacuo* and redissolved in fresh benzene-d_6. This solution revealed that neither of the original rhodium products remained and that three new phosphorus containing products formed.

The simplicity of the phosphorus NMR in each experiment was surprising. First, the hydrogenolysis of **5** by itself or the presence of the less reactive styrene oxide gave brown heterogeneous reaction mixtures.[14] Presumably, the aldehyde stabilizes the three-coordinate rhodium hydride, allowing it to catalyze the disproportionation, and then smoothly transforms the active catalyst into two rhodium products. Second, the similarity of the rhodium products in each aldehyde reaction indicated that no aldehyde residue remained associated with the rhodium. Infrared analysis of an active catalytic mixture, benzaldehyde as substrate, showed that no metal carbonyl resulted. Therefore, decarbonylation of the aldehyde is not a likely termination step for the catalyst.

Our second route to a catalytically active complex involved the *in situ* generation of a rhodium alkoxide complex. Hydrogenation of (DIPHOS)Rh(norbornadiene)$^+ClO_4^-$ (**6**) in benzene followed by concentration at high vacuum yielded the air-sensitive solvated rhodium



Scheme 3



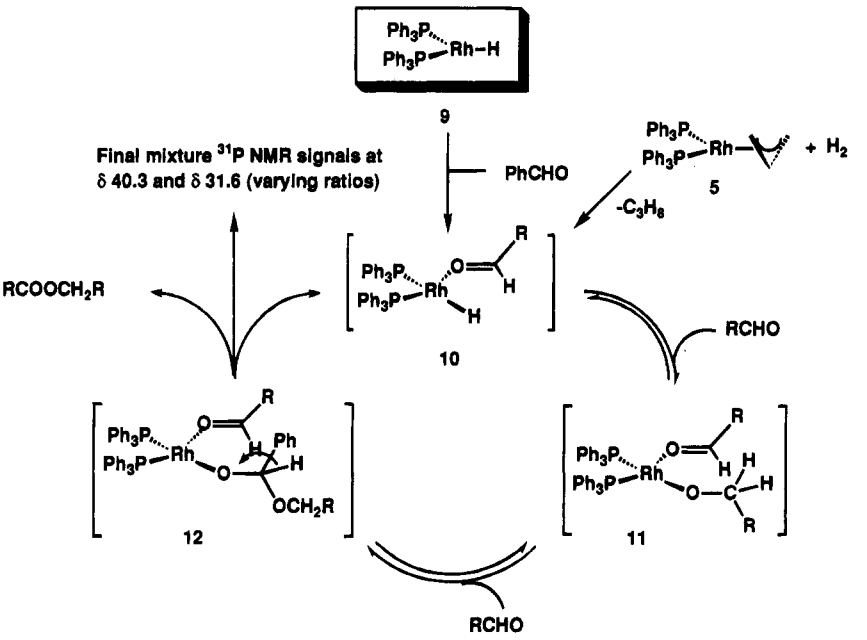
cation (DIPHOS)Rh(C_6H_6)$^+ClO_4^-$·C_6H_6 (**7**).[19] (DIPHOS)-Rh(norbornadiene)$^+ClO_4^-$ was selected for our experiments instead of $(Ph_3P)_2$Rh(norbornadiene)$^+ClO_4^-$ because this complex reacts with exactly 2.0 mol equiv of hydrogen to give the solvated rhodium(I) cation.[20] Suspension of the metal cation in C_6H_6 followed by addition of benzaldehyde (50 equiv, 0.23 M) gave no disproportionation, but addition of 18-crown-6-solvated potassium benzyloxide (1 equiv of alkoxide relative to the rhodium cation) led to a homogeneous orange-red solution from which a 73% yield of benzyl benzoate was isolated after 0.7 h at 27 °C. Approximately 20% of the benzaldehyde remained unreacted. A control experiment utilizing only 18-crown-6-solubilized potassium benzyloxide and benzaldehyde (50 equiv) provided only a 1% yield of benzyl benzoate after 0.7 h at 27 °C. After 24 h, this same solution showed a 4% yield of benzyl benzoate. These data demonstate that the rhodium alkoxide is about 80 times more reactive as a catalyst than the "naked" main-group alkoxide.

Proposed Catalytic Mechanism. Modification of the oxaallyl ligand in **1** during catalysis, and development of alternative methods for the preparation of catalytic disproportionation species, strongly suggested that the oxaallyl rhodium complex is not the active catalyst. Rather, the oxaallyl ligand must be removed from **1** with formation of a three-coordinate rhodium hydride catalyst. A unified catalytic mechanism for the generation of a rhodium hydride and the disproportionation of aldehydes is presented in Schemes 3 and 4. Nucleophilic addition of the oxaallyl ligand to an aldehyde substrate initiates ligand modification by formation of an unstable β-alkoxy–ketone complex. Rapid β-hydrogen elimination produces dibenzoylmethane and a three-coordinate rhodium hydride, **9**. Dibenzoylmethane, in turn, reacts with excess oxaallyl **1**, forming complex **4** and acetophenone. This mechanistic sequence implies that β-hydrogen elimination must be fast, relative to condensation, since dibenzoylmethane must have access to complex **1**. Otherwise, complex **1** would be comsumed prior to reaction with dibenzoylmethane.

(19) Halpern, J. A.; Riley, D. P.; Chan, A. S.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055.

(20) $(Ph_3P)_2$Rh–(norbornadiene)$^+ClO_4^-$ has been shown to react with 3.0 mol equiv of hydrogen, giving a Rh(III)–hydride complex. (a) Shapley, J. R.; Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2816. (b) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397. (c) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2135.

Scheme 4



Aldehyde disproportionation initiates through complexation of an aldehyde to the three-coordination rhodium hydride **9**. This preequilibrium step stabilizes the rhodium hydride since decomposition products are not observed.[14] Hydrometalation of the aldehyde C=O bond results in a rhodium alkoxide complex which coordinates a second aldehyde molecule. Intramolecular transfer of the alkoxide ligand to the aldehyde gives a rhodium acetal, which after β-hydrogen elimination, produces the disproportionationated ester and complex **9**.

The origin of the aldehyde concentration effect is not known; however two explanations seem reasonable. First, trace amounts of carboxylic acid contaminants remain in the aldehyde sample even after repeated distillation. As a consequence, when larger amounts of aldehydes are used in a reaction, the amount of reactive carboxylic acid also increases. Protonolysis of the rhodium hydride, rhodium alkoxide, or rhodium acetal would presumably terminate redox catalysis. Second, the aldehyde concentration effect may be an ionization phenomenon. Increasing the concentration of polar components in a reaction mixture may facilitate formation of ion pairs which dramatically reduce the catalytic activity. This possibility is supported by data from the benzyloxide control experiment, in that removal of the benzyloxide ligand from the rhodium center reduces the efficiency of the disproportionation by a factor of 80.

Discussion

Rhodium oxaallyl complexes offer many attractive features, making them a valuable class of homogeneous catalysts. η^3-Oxaallyl complexes are formally coordinately unsaturated; thereby, access to a coordination site occurs readily. The oxaallyl complex also offers an electron-rich rhodium center suitable for oxidative addition reactions. Finally, the oxaallyl ligand can be easily substituted through sequential coordination, nucleophilic addition, and β-elimination reactions, forming organic carbonyl compounds. The present study clearly demonstrates that the oxaallyl ligand is sufficiently nucleophilic to condense with a variety of aliphatic and aromatic aldehydes. This observation has important implications for other catalytic reactions involving nucleophilic addition to aldehydes, such as the aldol condensation.[21]

This work is also important in the development of rhodium hydride chemistry since few useful reactions involving three-coordinate rhodium hydride complexes are known. The paucity of reactions with these hydride complexes presumably results from their reported instability. Results from this work suggest that electrophilic aldehydes stabilize the unsaturated rhodium hydride either by coordination of the aldehyde or rapid conversion of the hydride into an alkoxide ligand. Either possibility is consistent with our results with the less reactive styrene oxide. Reaction mixtures utilizing rhodium allyl **5**, hydrogen, and styrene oxide gave only insoluble rhodium products with no evidence of catalytic isomerization.[22]

Finally, several comments are needed about an alternative mechanism for the modification of the oxaallyl ligand. Inspection of the reaction mixture of **1** and benzaldehyde suggests that reversible oxidative addition of the aldehyde C—H bond could also promote formation of a rhodium hydride.[23] C—H activation of benzaldehyde with oxaallyl **1** would generate trigonal-bipyramidal complexes **13** or **14** depending upon the stereochemistry of the addition (see Scheme 5). Complex **13** would certainly eliminate acetophenone with concomitant production of *trans*-$(Ph_3P)_2(CO)RhPh$ (**15**). However no evidence for this decomposition was found.[24] Alterna-

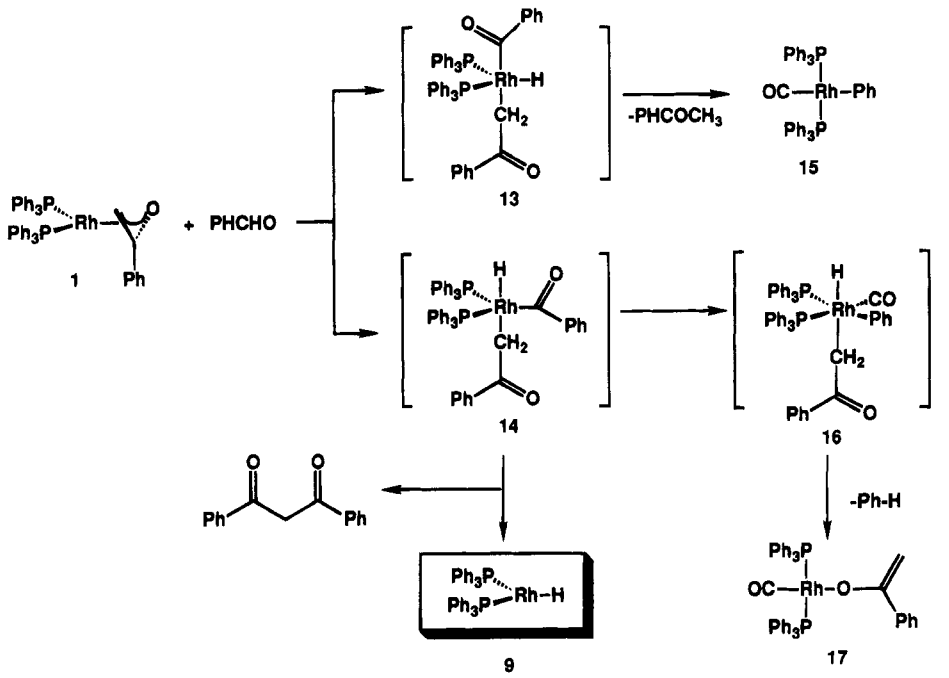
(21) (a) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022. (b) Slough, G. A.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 938.

(22) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227. For a review of *cis*-alkylrhodium hydrides and their isomerization chemistry see: Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221.

(23) Ireland, R. E.; Thompson, W. J. *Tetrahedron Lett.* **1979**, 4507. Suggs, J. *J. Am. Chem. Soc.* **1978**, *100*, 640. Stille, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 5664. Egglestone, D. L.; Baird, M. C.; Lock, C. J. L.; Turner, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1576.

(24) No ^{31}P NMR data were collected indicating the formation of *trans*-$(Ph_3P)_2(CO)RhPh$. Dahlenburg, L.; Mirzaei, F.; Yardimcioglu, A. *Z. Naturforsch., B* **1982**, *37*, 310.

Scheme 5



tively, intramolecular condensation of the acyl and enolate ligands in complex **14** would produce dibenzoylmethane and the putative three-coordinate rhodium hydride $[(Ph_3P)_2RhH]$ (**9**). Complex **14** could also decompose by deinsertion of the acyl ligand followed by elimination of benzene (PhH). *trans*-Rhodium enolate **17** would result from this pathway. Diagnostic evidence for this decomposition, namely a broad ^{31}P NMR signal at δ 25.8, was absent, suggesting that this pathway is not competitive.[25] Although our data cannot unequivocally rule out a C—H oxidative addition mechanism, we must conclude, however, that the C—H activation must proceed stereospecifically with formation of only complex **14** and that **14** must transform exclusively into complex **9** and dibenzoylmethane. Since both conditions are not likely, we believe that this mechanism is not operative.

Experimental Section

General Considerations. All manipulations of air-sensitive materials were performed under nitrogen by vacuum-line techniques or in a Vacuum Atmosphere drybox equipped with an inert gas purifier. Air-sensitive compounds were exposed to benzene or benzene-d_6 (C_6D_6) which were dried over sodium and benzophenone immediately before use. Dibenzoylmethane (Aldrich) was recrystallized prior to use, while benzaldehyde (Aldrich), isobutyraldehyde (Aldrich), *n*-heptanal (Aldrich), and furfural (Eastman Kodak) were each doubly distilled and degassed by freeze–pump–thaw cycles prior to use in a drybox. Carbon-13 labeled benzoic acid was prepared from PhLi and $^{13}CO_2$, and from this acid $Ph^{13}COCH_3$ was prepared by the method of Tegner.[26] Oxaallyl complexes $(Ph_3P)_2Rh(\eta^3\text{-}CH_2C(Ph)O)$ (**1**), $(Et_3P)_2Rh(\eta^3\text{-}CH_2C(Ph)O)$ (**2**), and $(Ph_3P)_2Rh(\eta^3\text{-}CH_2C(t\text{-}Bu)O)$ were prepared by a previously reported method.[1] Rhodium allyl complex $(Ph_3P)_2Rh(\eta^3\text{-}CH_2CHCH_2)$ (**5**) was prepared by the method of Sivak and Muetterties.[14] $(DIPHOS)Rh(NBD)^+ClO_4^-$ was prepared by literature methods.[27]

^1H NMR spectra were acquired on either a Bruker WP200 (200 MHz) or JEOL FX-90Q (90 MHz) spectrometer. Broadband decoupled and gated ^{13}C NMR spectra were obtained on a Bruker WP270 (69.9 MHz) or a JEOL FX-90Q (22.5 MHz) spectrometer, while proton decoupled $^{31}P\{^1H\}$ NMR spectra were obtained on a JEOL FX-90Q (36.3 MHz) spectrometer. Chemical shifts were recorded relative to the residual benzene signal in benzene-d_6 (δ 7.16) in the ^1H NMR spectra and relative to the central carbon resonance of benzene (δ 128.0) in the carbon spectra. All $^{31}P\{^1H\}$ NMR resonances were measured relative to an external standard of 85% H_3PO_4. An NMR tube containing a capillary tube of 85% H_3PO_4 standing in C_6D_6 was measured just prior to and just after $^{31}P\{^1H\}$ NMR accumulations. Infrared spectra were measured on a Perkin-Elmer 16 (FT) spectrometer. Gas chromatographic analysis was conducted on a Hewlett Packard 5890 IIA gas chromatograph equipped with a flame ionization detector. All analyses were done with a 25-m OV-1 capillary column.

General Procedure: Disproportionation of Benzaldehyde under (η^3-Oxaallyl)rhodium (1) Catalysis. In a drybox, an oven-dried, thick-walled NMR tube, equipped with a rotary valve, was charged with solid (η^3-oxaallyl)rhodium (**1**) (8.0 mg, 0.0107 mmol) and C_6D_6 (0.30 mL). Benzaldehyde (56.8 mg, 54.4 μL, 0.536 mmol) was added to the orange solution by syringe. The tube was sealed and the mixture agitated at 25 °C for 0.3 h. ^1H NMR analysis of the reaction mixture showed no aldehyde (no resonance at δ 9.31) remaining. In a fume hood, the reaction mixture was poured into pentane (10 mL) and extracted with saturated aqueous NaCl (5 mL). The aqueous layer was rinsed twice with pentane (8 mL). The combined organics were dried over Na_2SO_4 (0.5 g), filtered, and concentrated on a rotary evaporator to yield a yellow oil. Benzyl benzoate (52.3 mg, 92% yield) was isolated by flash chromatography using CH_2Cl_2 as eluant. ^1H NMR (200 MHz, $CDCl_3$): δ 5.31 (s, 2H), 7.30–7.49 (m, 8H), 8.03 (m, 2H). IR (CCl_4): 1734 (vs), 1281 (vs) cm^{-1}. The isolated ester coeluted with an authentic sample on a capillary GC. The ester eluted at 10.29 min using an oven temperature program

(25) Initally, we mistakenly assigned the signal at δ 31.6 to complex **17**. Preparation of an authentic sample of **17** by the method in ref 16b showed this is not the case.

(26) [^{13}C]benzoic acid was prepared from PhLi and $^{13}CO_2$, and then the method of Tegner was followed for the preparation of [^{13}CO]-acetophenone. Tegner, C. *Acta Chem. Scand.* **1952**, *6*, 782.

(27) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397. Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3178.

of 100 °C for 2.0 min, ramp of 10 °C min^{-1} to a maximum of 180 °C, and then at 180 °C for 2.0 min.

Catalyses using different aldehydes and different amounts of aldehyde were the same except the volume and type of aldehyde were changed. Catalyses using rhodium oxaallyl complexes **2** and **3** were the same as those for **1** except 4.9 mg of **2** and 7.8 mg of **3** were used.

General Procedure for the *in Situ* Hydrogenation of (η^3-Allyl) bis(triphenylphosphine)rhodium(I): Catalyst for the Disproportionation of Benzaldehyde. In a drybox, a thick-walled NMR tube equipped with a rotary valve was charged successively with $(Ph_3P)_2Rh(\eta^3\text{-}C_3H_5)$ (**5**) (7.1 mg, 0.0107 mmol), hexamethylbenzene (2 mg, 0.0123 mmol, internal standard), C_6D_6 (0.30 mL), and benzaldehyde (113.6 mg, 108.8 μL, 1.07 mmol). The mixture was agitated at 25 °C for 1.0 h, and the ^1H NMR spectrum showed a singlet at δ 9.31 corresponding to benzaldehyde and weak signals at δ 5.23 (m, 1H), 3.07 (d, J = 6.8 Hz, 2H), and 2.51 (broad d, 2H) corresponding to the allyl residue. No signal at δ 5.31, corresponding to benzyl benzoate, was observed. The solution was degassed twice by freeze–pump–thaw cycles under vacuum. After the final thaw approximately 4 equiv of hydrogen (580 mmHg) was added. The solution was mixed thoroughly at 25 °C, and the solution changed to a deep orange color. After 21 min, 98% of the aldehyde was consumed, giving benzyl benzoate (97% NMR yield). The $^{31}P\{^1H\}$ NMR spectrum of the mixture showed a doublet at δ 40.3 (J = 121 Hz). In a fume hood, the reaction mixture was concentrated *in vacuo* to give a yellow-orange oil. The oil was diluted with 3:1 hexane/ethyl acetate (2 mL) and the rhodium catalyst was filtered on a 1-in. plug of silica gel. The ester eluted with 3:1 hexane/ethyl acetate, and the combined eluant was concentrated on a rotory evaporator to yield a yellow oil. Benzyl benzoate (107 mg, 95% yield) was isolated by flash chromatography using CH_2Cl_2 as eluant.

Purification Procedures and Analytical Data for Aldehyde Disproportionation Reactions. Isobutyraldehydes. The reaction mixture was concentrated *in vacuo* to give a yellow-orange oil. The oil was diluted with 2:1 pentane/ether (2 mL), and the rhodium catalyst was removed by filtration on a 1-in. plug of silica gel. The ester eluted with a 2:1 pentane/ether solvent mixture. The combined eluant was concentrated, the oil was dissolved in acetone (4 mL), and 4 drops of 1.4 M Jones' reagent was added and stirred for 0.2 h. The mixture was diluted with ether (15 mL) and extracted successively with water (10 mL), twice with 5% NaOH (10 mL each wash), and with water (10 mL). The organic layer was dried over $MgSO_4$ and filtered. A colorless oil was isolated after rotary evaporation. The oil was dissolved in 2:1 pentane/ether (2 mL) and passed through a 1-in. plug of silica gel. 2-Methylpropyl 2-methylpropanoate (6 mg, 8% yield) was isolated. ^1H NMR (C_6D_6): δ 0.76 (d, J = 6.6 Hz, 3 H), 0.93 (m, 1H), 1.07 (d, J = 8.3 Hz, 3H), 1.71 (m, 1H), 2.28 (m, 1H), 3.81 (d, J = 6.3 Hz). The ester coeluted with an authetic sample of 2-methylpropyl 2-methylpropanoate at 1.21 min using an oven temperature program of 80 °C for 3.0 min, ramp of 15 °C min^{-1} to a maximum of 180 °C, and then at 180 °C for 2.0 min.

***n*-Heptanal.** The same procedure for the isolation of 2-methylpropyl 2-methylpropanoate was followed except 3:1 hexane/ethyl acetate was used to elute the ester from the silica gel plug. Heptyl heptanoate (107 mg, 88% yield) was isolated. ^1H NMR (C_6D_6): δ 0.86 (t, 6H), 1.22 (m, 14 H), 1.52 (m, 4 H), 1.79 (m, 4H), 4.78 (t, J = 4.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 14.2, 23.0, 23.9, 29.5, 32.1, 35.0, 71.0, 158.5. IR (CCl_4): 1737 (m) cm^{-1}. The ester eluted in 11.5 min using an oven temperature program of 80 °C for 2.0 min, ramp of 15 °C min^{-1} to a maximum of 180 °C, and then at 180 °C for 2.0 min.

Furfural. The procedure for the isolation of benzyl benzoate was used to purify the ester. 2-Furanylmethyl 2-furancarboxylate (102 mg, 97% yield) was isolated. ^1H NMR (C_6D_6): δ 5.09 (s, 2H), 5.92 (dd, J = 1.8, 3.5 Hz, 1H), 4.42 (dd, J = 1.8, 3.1 Hz, 1H), 6.22 (dd, J = 0.6, 3.5 Hz, 1H), 6.92 (dd, J = 0.8, 3.5 Hz, 1H), 7.07 (m, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 58.0, 86.3, 110.8, 111.2, 111.8, 118.2, 143.4, 144.9, 146.4, 149.8, 158.0. IR (CCl_4): 1741 (vs) cm^{-1}. The ester eluted in 6.94 min using an oven temperature program of 80 °C for 2.0 min, ramp of 15 °C min^{-1} to a maximum of 180 °C, and then at 180 °C for 2.0 min.

***In Situ* Rhodium Alkoxide as Catalyst for the Disproportionation of Benzaldehyde.** Into an oven-dried, 10-mL two-neck pear flask was added $[(DIPHOS)Rh(NBD)]^+ClO_4^-$ (20 mg, 0.029 mmol). The flask was evacuated under vacuum, and C_6H_6 (~1 mL) was layered onto the orange solid. The suspension was exposed to 1 atm of hydrogen for 1.0 h at 27 °C. Excess hydrogen and C_6H_6 were evacuated under vacuum, yielding a brown-red solid residue. Fresh C_6H_6 (~2 mL) was layered onto the solid and the suspension stirred under a N_2 atmosphere. Freshly distilled benzaldehyde (63 μL, 0.59 mmol) was added by syringe and the mixture stirred at 25 °C. After 0.5 h, capillary GC analysis showed no benzyl benzoate. A 0.056 M stock solution of 18-crown-6-solubilized potassium benzyloxide[28] (0.52 mL, 0.029 mmol) was added dropwise and an orange-red solution formed within 2 min. Stirring the mixture at 27 °C for 0.7 h consumed 80% of the benzaldehyde by GC analysis. In a fume hood, the reaction mixture was poured into pentane (10 mL) and extracted with saturated aqueous NaCl (5 mL). The aqueous layer was rinsed twice with pentane (8 mL). The combined organics were dried over Na_2SO_4 (0.5 g), filtered, and concentrated on a rotary evaporator to yield a yellow oil. Benzyl benzoate (45 mg, 73% yield) was isolated by flash chromatography using CH_2Cl_2 as eluant.

Acknowledgment. We gratefully acknowledge the generous support of the National Science Foundation (Grant No. CHE-9200699) for this work. J.R.A. thanks the Howard Hughes Medical Foundation for a summer research assistantship. We also acknowledge Johnson Matthey for a generous loan of $RhCl_3$·(hydrate).

OM940215F

(28) Potassium benzyloxide was prepared from benzyl alcohol and potassium hydride, and the solid was collected on a frit under vacuum. In a drybox, solid potassium benzyloxide (40.9 mg) was added to a 5.00-mL volumetric flask and suspended in C_6H_6. Enough 18-crown-6 was added to dissolve the solid and the solution was diluted to 5.00 mL.