Mechanism of Rhodium-Promoted Triphenylphosphine Reactions in Hydroformylation Processes

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Triphenylphosphine is converted into propyldiphenylphosphine rapidly during rhodium-catalyzed propylene hydrogenation and more slowly during low-pressure propylene hydroformylation. The pathway for this conversion involves the reversible oxidative addition of a phenyl–phosphorus bond of triphenylphosphine to rhodium, followed by the reductive elimination of propyldiphenylphosphine from a (diphenylphosphido)propylrhodium intermediate. The effects of reaction variables on this triphenylphosphine reaction have been studied, and a mechanism is proposed.

Introduction

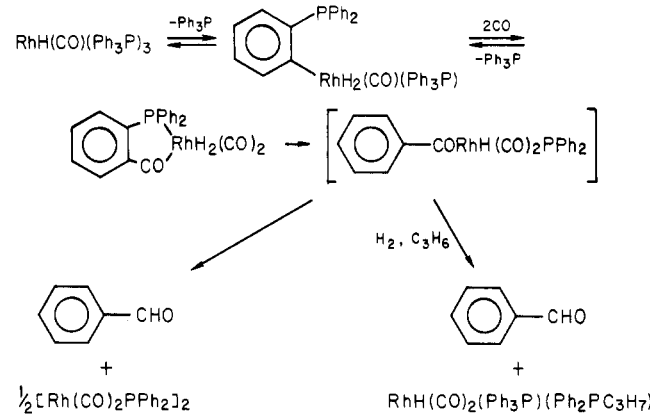
Rhodium–phosphine catalysts are widely used in olefin hydroformylation processes for the production of billion-pound quantities of oxo aldehydes and alcohols.[1] Phosphine side reactions occurring during rhodium hydroformylation lead to byproducts that mildly affect catalyst performance and to rhodium clusters that severely affect catalyst performance.[2]

During rhodium-catalyzed propylene hydroformylation triphenylphosphine (TPP) is slowly converted to propyldiphenylphosphine (PDPP).[3] This reaction has been postulated[4] to proceed via intramolecular C–H oxidative addition of the phenyl groups of coordinated triphenylphosphine (orthometalation). Triphenylphosphine, however, is known to react by direct oxidative addition of its P–C bonds to rhodium[5] as well as to other transition metals.[6] We wish to report on our studies that differentiate between the orthometalation and direct P–C oxidative addition pathways for the triphenylphosphine reactions under hydroformylation conditions and define the role of the metal complex in catalyzing these reactions.

Results and Discussion

Carbon–Phosphorus vs. Ortho Carbon–Hydrogen Bond Cleavage as the First Step in Rhodium-Catalyzed Phosphine Reactions. Gregorio et al. postulated[4] that the first step in the triphenylphospine reaction during hydroformylation is the oxidative addition of an ortho carbon–hydrogen bond of a coordinated triphenylphosphine to the rhodium, leading eventually to the cleavage of the phenyl–phosphorus bond (Scheme I). To test this hypothesis we used tris(*o*-dideuteriophenyl)-phosphine,[7] $(C_6H_3D_2)_3P$, as the ligand in a continuous rhodium-catalyzed propylene hydroformylation experiment. After 4 days of continuous operation (reaction conditions: 120 °C; 1000 ppm of Rh, 5 wt % phosphine; 60 psia of CO; 60 psia of H; 35 psia of C_3H_6) about 30% of the starting triphenyl-d_6-phosphine was converted to PDPP. Mass spectral analysis revealed that very little H–D exchange had occurred either in the starting TPP or in its reaction product PDPP (Table I).

Scheme I



Scheme II

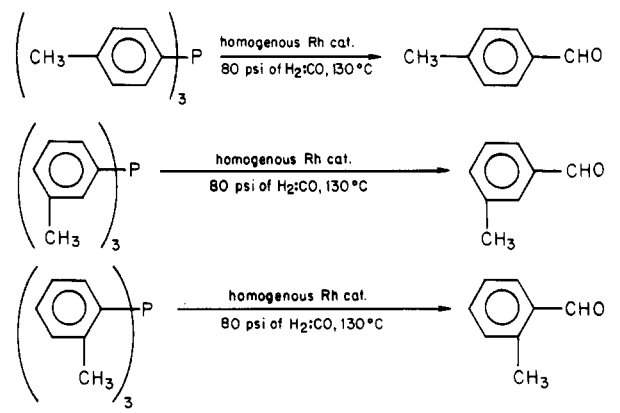


Table I. Rhodium-Catalyzed H-D Exchange in Triphenylphosphine and Its Reaction Product Propyldiphenylphosphine during Propylene Hydroformylation[a]

	% deuterium content			
phosphine	d_6	d_5	d_4	d_3
starting TPP-d_6	80	19	1	
TPP after reaction	77	22	1	
PDPP product			82	18

[a] Continuous hydroformylation reaction conditions: 1000 ppm of Rh as $Rh(acac)(CO)_2$; 5 wt % $(C_6H_3D_2)_3P$, in *n*-valeraldehyde trimer; 50 psia of H_2; 50 psia of CO; 35 psia of C_3H_6.

(1) Cornils, B. In "New Syntheses with Carbon Monoxide"; Falbe, J., Ed.; Springer-Verlag: Berlin, 1980.
(2) Bryant, D. R.; Billig, E. U.S. Patent 4 277 627, 1981.
(3) Bryant, D. R.; Galley, R. A. U.S. Patent 4 283 304, 1981.
(4) Gregorio, G.; Montrasi, G.; Tampieri, M.; Cavalieri d'Oro, P.; Pagani, G.; Andreetta, A. *Chim. Ind. (Milan)* **1980**, *62*, 389.
(5) (a) Kaneda, K.; Sano, K.; Teranishi, S. *Chem. Lett.* **1979**, 821. (b) Lewin, M.; Aizenshtat, Z.; Blum, J. *J. Organomet. Chem.* **1980**, *184*, 255.
(6) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed. Wiley: New York, 1980, p 1247.
(7) Parshall, P. W.; Knoth, W. H.; Schum, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 4990.

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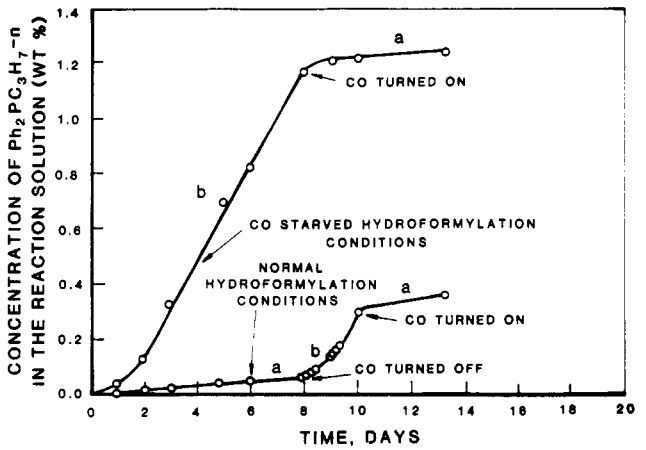


Figure 1. Propyldiphenylphosphine accumulation vs. time under propylene hydroformylation (curves a) and hydrogenation (curves b). Conditions: 105 °C; 150 ppm of Rh as $RhH(CO)(Ph_3P)_3$; 9 wt % $(C_6H_5)_3P$; 30 psia of C_3H_6, 100 psi of H_2, and nil or 10 psi of CO.

This result is in agreement with previous studies[8] which indicate that orthometalation deuterium exchange reactions of rhodium triphenylphosphine complexes are sluggish. The relatively small H–D exchange relative to the conversion of TPP to PDPP suggests a direct phosphorus–phenyl bond cleavage as the likely pathway of triphenylphosphine reaction. To test this hypothesis we studied the rhodium-catalyzed reaction of different substituted triarylphosphines under an atmosphere of hydrogen and carbon monoxide.

It is known[4] that TPP reacts upon heating in the presence of rhodium, H_2, and CO to, among other products, benzene and benzaldehyde. Using rhodium-containing solutions of tri-*o*-, tri-*m*-, and tri-*p*-tolylphosphines and individually treating them with CO:H_2, we found that only one isomeric tolualdehdye is formed from each phosphine (Scheme II). The tolualdehydes produced are those resulting from intermediates formed by direct carbon–phosphorus bond cleavage and are not those expected to form by the earlier proposed orthometalation mechanism.

Accelerated Propyldiphenylphosphine Formation under RhTPP-Catalyzed Propylene Hydrogenation. We found that the conversion of triphenylphosphine to propyldiphenylphosphine, which is very slow during the low-pressure rhodium hydroformylation of propylene, is greatly accelerated under propylene hydrogenation conditions (eq 1).

$$\underset{\text{TPP}}{(C_6H_5)_3P} + H_2 + C_3H_6 \xrightarrow[130\ ^\circ C]{RhH(CO)(Ph_3P)_3} \underset{\text{PDPP}}{(C_6H_5)_2PC_3H_7} \quad (1)$$

Benzene is the other major TPP decomposition product, and it is initially formed in equimolar ratio with the PDPP. As the concentation of PDPP increases, however, it is in turn slowly converted into dipropylphenylphosphine and benzene, and the mole ratio of benzene to PDPP becomes greater than 1. Trace amounts of biphenyl have been detected by GC–MS analysis of the reaction mixture.

The difference in the rates of TPP reaction under propylene hydroformylation and propylene hydrogenation conditions is shown in Figure 1. Interestingly under hydrogenation conditions there is an induction period and

(8) (a) Ito, T.; Kitazume, S.; Yamamoto, A.; Ikeda, A. *J. Am. Chem. Soc.* **1970**, 92(10), 3011. (b) Osborne, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1964**, 1711. (c) Jardine, F. M.; Osborne, J. A.; Wilkinson, G. *Ibid.* **1967**, 1574.

Table II. Rhodium-Catalyzed H–D Exchange in Triphenylphosphine under Different Reaction Conditions[a]

	reactant gas pressure, psia			% deuterium content in TPP after reactn[b]			
entry	CO	D_2	C_3H_6	d_0	d_1	d_2	d_3
1	0	40	40	73.2	23.0	3.4	0.4
2	0	120	0	99.0	1.0		
3	40	40	0	100			

[a] Reaction condition: 1000 ppm of Rh as Rh(acac)-$(CO)_2$; 5 wt % Ph_3P in toluene as solvent. The catalyst is heated at 130 °C in a pressure reactor for 3 h under the gas pressures shown above. [b] Determined by chemical ionization mass spectroscopy.

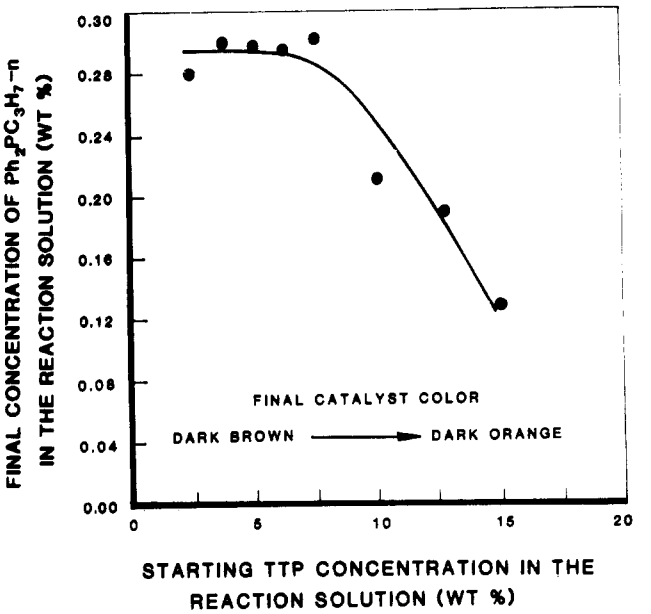


Figure 2. Propyldiphenylphosphine concentration in catalysts containing 1000 ppm of rhodium as $RhH(CO)(Ph_3P)_3$ and varying concentrations of triphenylphosphine after exposure to 50 psi of H_2 and 50 psi of C_3H_6 at 130 °C for 1 h.

a catalyst color change (yellow to orange) during which the rate of production of PDPP increases. When the hydrogenation conditions are changed to hydroformylation by the addition of carbon monoxide, the color of the catalyst returns to yellow and the rate of PDPP production drops.

The facile conversion of TPP to PDPP under propylene hydrogenation conditions has enabled us to study the scope and mechanism of this reaction in short duration laboratory experiments. The conclusions reached from the study of this reaction may be applicable for the TPP reactions under hydroformylation conditions. The two reactions cannot however be identical, since we surprisingly found that whereas the H–D exchange reaction of coordinated triphenylphosphine under hydroformylation conditions is sluggish (see above), the H–D exchange under propylene hydrogenation conditions proceeds to a significant extent under otherwise comparable reaction conditions (Table II).

Effect of Reaction Conditions on the Rates of Triphenylphosphine Conversion to Propyldiphenylphosphine during Rhodium-Catalyzed Propylene Hydrogenation. Effect of Triphenylphosphine Concentration. We found that increasing triphenylphosphine concentration inhibits the reaction of triphenylphosphine to form PDPP during the rhodium-catalyzed propylene hydrogenation (Figure 2). This suggests that rhodium-phosphine equilibria play a role in the reaction of TPP to give PDPP. High phosphine concentrations maintain the rhodium in a more coordinatively saturated form, which may be less reactive to oxidative P–C bond addition.

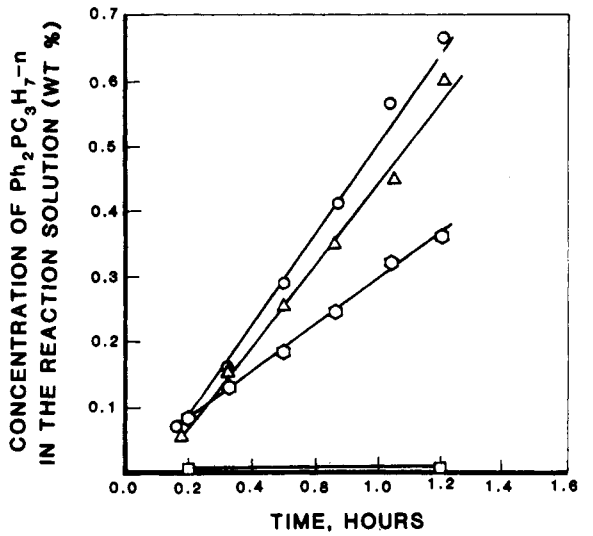


Figure 3. Propyldiphenylphosphine accumulation vs. time under propylene hydrogenation using different rhodium compounds as catalysts (conditions: 130 °C, 5 wt % $(C_6H_5)_3P$; 1000 ppm of Rh, 50 psi of H_2, 50 psi of C_3H_6): ○, $RhH(CO)(PPh_3)_3$; △, $Rh(acac)(CO)_2$; ○, $Rh_3(\mu\text{-}PPh_2)_3(Ph_3P)_2(CO)_3$; □, $RhCl(CO)(Ph_3P)_2$ and $RhCl(Ph_3P)_3$.

Effect of the Rhodium Complex Type. The rate of conversion of triphenylphosphine, with propylene and hydrogen, to propyldiphenylphosphine varies with the rhodium complex used (Figure 3). The monomeric rhodium complexes $RhH(CO)(Ph_3P)_3$ and $Rh(acac)(CO)_2$ are more active than the trinuclear phosphido-bridged cluster[9] $Rh_3(\mu\text{-}Ph_2P)_3(Ph_3P)_2(CO)_3$, which could presumably convert its phosphido bridges to PDPP and act as a template for cluster catalysis.[5]

It is noteworthy that with $RhH(CO)(Ph_3P)_3$ as the catalyst, within 3–4-h reaction time the catalyst color changes from yellow to dark brown and the catalytic activity for both propylene hydrogenation and propylidiphenylphosphine formation diminishes. We believe that this lower catalyst activity is due to the formation of phosphido-bridged rhodium clusters, which by being more coordinatively and structurally stable than their mononuclear counterparts, are also less reactive toward the P–C bond cleavage reaction.

$RhCl(Ph_3P)_3$ is a significantly better propylene hydrogenation catalyst than $RhCl(CO)(Ph_3P)_2$. Neither of these chloride-containing square-planar complexes promotes the reaction of triphenylphosphine to propyldiphenylphosphine, under either hydrogenation or hydroformylation conditions. Thus hydrogenation ability in a catalyst is not sufficient to promote the carbon–phosphorus bond cleavage reaction; apparently the electronic and/or steric effects of the chloride substituent alter the activity of the rhodium catalyst. Alternatively, it is likely that the rhodium(III) dihydride $H_2RhCl(PPh_3)_2(S)$, formed from $RhCl(PPh_3)_3$ and thought to be an active form of the olefin hydrogenation catalyst, is not effective in promoting the TPP to PDPP transformation.

Effect of Propylene and Hydrogen Concentration. Although higher TPP concentration reduces the rate of PDPP formation, higher propylene concentrations promote PDPP formation (Figure 4). It is also noteworthy that at higher propylene concentrations darkening of the catalyst color, which has been associated with the formation of phosphido-bridged rhodium clusters,[2] is diminished. Diminished color formation suggests that at higher propylene concentrations, phosphido-bridged rhodium clusters either are not formed or are effectively broken down to mononuclear rhodium (yellow) complexes.

(9) Billig, E.; Jamerson, J. D.; Pruett, R. L. *J. Organomet. Chem.* **1980**, *192*, C49.

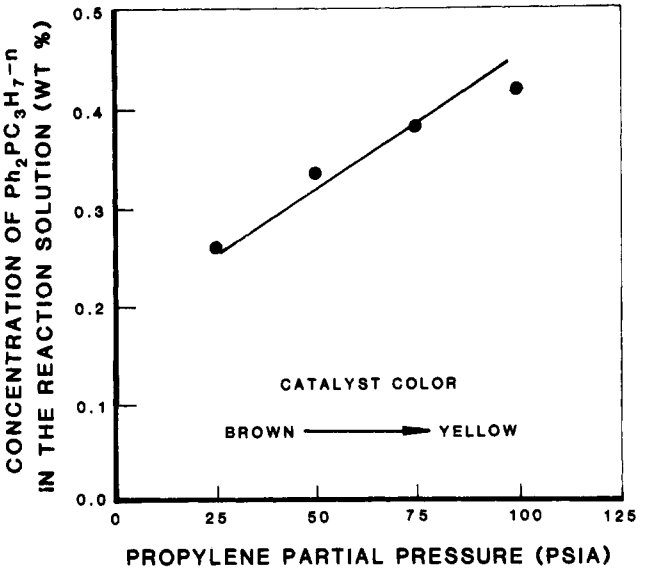
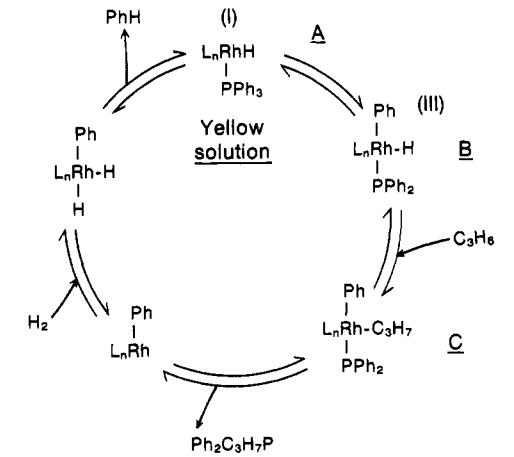
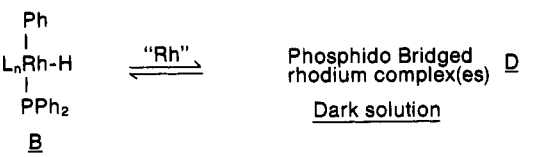


Figure 4. Propyldiphenylphosphine concentrations in catalysts containing 1000 ppm of Rh as $RhH(CO)(Ph_3P)_3$ and, 5 wt % triphenylphosphine and exposed to 50 psi of H_2 and varying pressures of C_3H_6 for 1 h.

Scheme III





L_n = other ligands such as Ph_3P, C_3H_6, CO, H

Hydrogen between 25 and 100 psi has no effect on the rate of formation of PDPP. However, in the absence of hydrogen virtually no reaction of triphenylphosphine is observed, and the catalyst solution remains yellow. Apparently only a low level of hydrogen is required to trigger the reaction of TPP to PDPP and possibly the rhodium clustering process as well.

Suggested Mechanism of Triphenylphosphine Reactions in the Presence of Rhodium, Propylene, and Hydrogen. The experimental results detailed above can be rationalized on the basis of the reaction mechanism shown in Scheme III. It is proposed that a coordinatively

unsaturated rhodium(I) complex, A, oxidatively adds a carbon–phosphorus bond of coordinated triphenylphosphine to form a rhodium(III) intermediate B. Higher propylene concentrations favor reaction of this intermediate to C and ultimately to propyldiphenylphosphine whereas lower propylene concentrations favor the formation of phosphido-bridged rhodium complex(es) D. The phosphine concentration determines the concentration of the coordinatively unsaturated rhodium complex A, which initiates the phosphine breakdown sequence.

Chelating phosphines that enhance the degree of phosphine substitution and consequently the degree of coordinative saturation in rhodium complexes have been used as stabilizers with (triphenylphosphine)rhodium catalysts in the low-pressure hydroformylation.[10]

The reversibility of the reaction steps in the mechanism in Scheme III is supported by the observation that rhodium catalyzes aryl group scrambling between triarylphosphines (eq 2). This reaction must occur through a

$$(C_6H_5)_3P + (CH_3C_6H_4)_3P \underset{130\ °C}{\overset{Rh}{\rightleftharpoons}} (C_6H_5)_2(CH_3C_6H_4)P + (C_6H_5)(CH_3C_6H_4)_2P \quad (2)$$

series of oxidative additions/reductive eliminations of carbon–phosphorus bonds to rhodium. A more detailed account of this novel reaction is given in the accompanying communication.[11]

Diphenylphosphine is a possible intermediate during triphenylphosphine reaction. We studied its activity and fate under rhodium triphenylphosphine catalyzed propylene hydrogenation conditions. Surprisingly, diphenylphosphine reacts rapidly and forms predominantly triphenylphosphine along with lower molecular weight phosphorus containing byproducts. Propyldiphenylphosphine is a minor product. This observation and the fact that no low molecular weight phosphorus products are observed in the triphenylphosphine reactions support the proposed mechanism in Scheme III and suggest that the alternative pathway for PDPP formation involving free or coordinated diphenylphosphine is less likely.

Experimental Section

All phosphines were purchased and used without purification. Gas chromatographic analyses were made by using a Varian 3700 series gas chromatograph equipped with a phosphorus selective Flame Photometric Detector (FPD) and a CDS-111 electronic integrator. The concentrations of TPP and PDPP were determined by using the phosphine oxide $(p\text{-}FC_6H_4)_3PO$ as an internal standard. Positive identification of phosphine reaction products was by gas chromatography–Fourier transform infrared (GC–IR) spectroscopy using a Digilab FTS-15 spectrometer equipped with a liquid-nitrogen-cooled detector at 8 cm^{-1} resolution and by gas chromatography–mass spectroscopy (GC–MS) using an AEI Model MS-50 mass spectrometer.

Rhodium-Catalyzed Triphenylphosphine Reaction to Propyldiphenylphosphine during Propylene Hydrogenation. The TPP reaction studies were done in a 100-mL stainless-steel autoclave equipped with magnetic stirring. The autoclave was heated by a 200-W band heater equipped with a proportional temperature controller. Internal temperature was monitored with a platinum resistance thermometer of ±0.1 °C accuracy. The autoclave was connected to a gas manifold for pressurization with reactant gases.

In a typical experiment a solution containing 1.25 g (4.77 mmol) of triphenylphosphine, 0.0627 g (0.243 mmol) of $Rh(acac)(CO)_2$,[12] and 23.7 g of peroxide-free tetraglyme was charged to the autoclave and heated under 5 psi of nitrogen pressure to the desired temperature, and then hydrogen and propylene (100 psi of a 1:1 mixture) were added. Propylene was slowly hydrogenated to propane. The reaction pressure was maintained by feeding 1:1 hydrogen and propylene.[13] Liquid samples were withdrawn periodically by using a Pressure Lok (Precision Sampling Corp., Baton Rouge, LA) gas tight syringe and analyzed by gas chromatography using the following chromatographic conditions: Column, 6 ft × $^1/_8$ in. packed with 20 wt % OV-101 on Chromosorb W; injector temperature, 270 °C; column temperature, 235 °C; helium flow rate, 40 mL/min.

Rhodium-Catalyzed Triphenylphosphine Reaction to Propyldiphenylphosphine during Propylene Hydroformylation. Because of the low rate of TPP decomposition to PDPP during propylene hydroformylation, the rate data in Figure 1 were obtained by using a continuous hydroformylation reactor. The continuous reactor consisted of a 3-oz Fischer-Porter pressure bottle (Fischer & Porter Co., Warminster, PA) submersed in a thermostated oil bath. A 20-mL aliquot of a catalyst containing 0.0631 g (0.136 mmol) of $Rh(CO)(acac)(Ph_3P)$, 8.1 g (30.92 mmol) of Ph_3P, and 81.9 g of *n*-valeraldehyde trimer (ester diol monovalerate) as the high boiling solvent was introduced into the reactor with a syringe through a septum and valve assembly. The reactant gases (CO, H_2, C_3H_6) and nitrogen were sparged through the solution by using a fine porosity metallic sparger. The flow rate of gases (adjusted individually with Brooks mass flow meters, Brooks Instrument Div. Hatfield, PA) was such that the rate of aldehyde stripping is equal to the rate of aldehyde production. Small liquid samples were withdrawn from the reactor and analyzed by GC for PDPP concentration. Turning off the carbon monoxide feed changed the reaction from propylene hydroformylation to propylene hydrogenation.

Tri-*p*-tolylphosphine Decomposition to *p*-Tolualdehyde. A solution containing 0.0627 g (0.243 mmol) of $Rh(acac)(CO)_2$, 1.25 g (4.107 mmol) of $(p\text{-}CH_3C_6H_4)_3P$, and 23.7 g of benzene was charged in the autoclave described above, purged with nitrogen, pressured with 60 psig of H_2:CO, and heated to 130 °C. After temperature equilibration the H_2:CO pressure was raised to 120 psig, and the mixture was allowed to react for 16 h. The detection and identification of the product aldehyde were made by GC–IR spectroscopy using the following chromatographic conditions. Column, 10 ft × $^1/_8$ in. packed with 9 wt % Carbowax 20M TPA on 40/60 mesh Chromosorb W;[14] injector temperature, 240 °C; column temperature, 120 °C for 18 min and then heated to 200 °C at 10 °C/min; IR-light pipe temperature, 220 °C; helium flow rate, 30 mL/min. One aldehyde peak was seen in the GC scan, which shows an IR spectrum identical with that of the reference gas-phase spectrum of *p*-tolualdehyde (Sadler Research Laboratories, Inc., Philadelphia, PA) In identical experiments using tri-*o*-tolylphosphine or tri-*m*-tolylphosphine, *o*-tolualdehyde and *m*-tolualdehyde are formed exclusively from the respective phosphines.

Registry No. TPP, 603-35-0; PDPP, 7650-84-2; $Rh(acac)(CO)_2$, 14874-82-9; $Rh(CO)(acac)(Ph_3P)$, 25470-96-6; $RhH(CO)(PPh_3)_3$, 17185-29-4; $Rh_3(\mu\text{-}PPh_2)_3(Ph_3P)_2(CO)_3$, 75047-27-7; $RhCl(CO)(Ph_3P)_2$, 13938-94-8; $RhCl(Ph_3P)_3$, 14694-95-2; C_3H_6, 115-07-1; $(p\text{-}CH_3C_6H_4)_3P$, 1038-95-5; $(m\text{-}CH_3C_6H_4)_3P$, 6224-63-1; $(o\text{-}CH_3C_6H_4)_3P$, 6163-58-2.

(10) Matsumoto, M.; Tamura, M. U.S. Patent 4 215 077, 1980.
(11) Abatjoglou, A. G.; Bryant, D. R. *Organometallics*, second paper of two in this issue.
(12) $Rh(acac)(CO)_2$ is a convenient rhodium catalyst precursor. In the presence of excess triphenylphosphine and hydrogen, it is readily converted to $RhH(CO)(Ph_3P)_3$ and acetylacetone.
(13) The accumulation of propane can reduce the partial pressures of propylene and hydrogen and cause a slowdown of the reaction. If high conversions of TPP to PDPP are desired, the accumulated propane should be vented periodically.
(14) Under these chromatographic conditions, the *m*- and *p*-tolualdehydes coelute. The characterization of the produced isomers is based on their gas-phase IR spectra. With a 50-m glass capillary Carbowax 20M column, the tolualdehyde isomers were separated and the conclusions reached on the basis of the IR spectra were fully supported by their GC retention times.