Decarbonylation Dehydration of Fatty Acids to Alkenes in the Presence of Transition Metal Complexes[1]

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ABSTRACT

The catalytic decarbonylation of stearic acid into a mixture of heptadecenes has been accomplished by use of a catalyst system comprised of rhodium trichloride ($RhCl_3$) and triphenylphosphine. The isomeric composition of the heptadecenes formed was found, by spectroscopic and chemical methods, to be dependent upon the type of rhodium catalyst employed. Anhydrous $RhCl_3$ produced about the same amount of 2-heptadecene, twice the amount of 3-heptadecene, and about half the amount of 1-heptadecene as hydrated $RhCl_3$. The active catalytic species formed in situ has been identified as the rhodium I complex $[(C_6H_5)_3P]_2Rh(CO)Cl$. A mechanistic pathway to account for the observed decarbonylation products employing the above catalyst is presented.

INTRODUCTION

The transition metal-catalyzed abstraction of carbon monoxide from carbonyl compounds has been the topic of considerable interest in recent years (1,2). Of all the classes of carbonyl compounds studied, aldehydes and acyl halides have received the most attention, since they readily undergo decarbonylation to alkanes, alkenes, or alkyl halides (3,4). A variety of group VIII transition metals, as reduced metals, salts, or metals complexed with various ligands (e.g., phosphines) have been successfully utilized for the decarbonylation reaction, with most of the attention centered on the use of either rhodium or palladium metal catalyst systems. The application of transition metal catalysts to the decarbonylation of saturated carboxylic acids (e.g., stearic acid) has received little attention. Only two reports have been cited in the literature that describe attempts to decarbonylate such acids (5,6). In one of these (5) it is stated that when either propionic or hexanoic acid is heated at reflux in the presence of tris-(diethylphenylphosphine)-rhodium(III) chloride, ethylene or pentene-2, respectively, is produced. Up to three molecules of alkene are reportedly formed per each atom of rhodium used. However, yields of alkene were not specified and are assumed to be low from the given data.

In a later patent claim (6) it was stated that both esters and carboxylic acids may be decarbonylated via a reaction that is considered the reverse of carbonylation. Noble metals, in general, were claimed as effective catalysts, but all examples cited utilized some form of a palladium metal catalyst. The results obtained with the palladium catalysts were similar to those obtained in the previous report, namely, the conversions of acids to alkenes were poor.

We believe, as do others, that the metal catalyzed decarbonylation of carbonyl compounds occurs via a mechanistic pathway that is the reverse process of the carbonylation of alkenes. Accordingly, those metal catalysts which effect carbonylation should also promote decarbonylation. Since group VIII metal complexes, in general, have been found to be the most effective catalytic reagents for carbonylation reactions, particularly hydroformylations, we initiated studies described herein to find a transition metal complex that would effect the decarbonylation of saturated carboxylic acids to alkenes efficiently.

EXPERIMENTAL PROCEDURES

Materials and Equipment

$PdCl_2$, $RhCl_3$, $RhCl_3 \cdot 3H_2O$ and triphenylphosphines were used as received from commercial suppliers. The metal complexes $[(C_2H_5)_2C_6H_5P]_3RhCl_3$ (7), $[(C_6H_5)_3P]_2PdCl_2$ (8), $[(C_6H_5)_3P]_3RhCl$ (9), and $[(C_6H_5)_3P]_2RhCOCl$ (10) were prepared by procedures described in the literature. Stearic acid (98%) was purified by crystallization from acetone. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 237-B grating spectrometer using sodium chloride disks. Gas liquid chromatography (GLC) was conducted on stainless steel columns (6 ft x 1/8 in.) packed with 20% UCW-98 on 60-80 mesh Chromsorb W using a Hewlett-Packard Model 7620-A gas chromatograph equipped with dual flame ionization detectors. Product distributions were obtained by using an Infotronics digital electronic integrator.

General Procedure

Stearic acid (100 mmole), rhodium trichloride hydrate (1 mmole), and triphenylphosphine (10 mmole) were placed into a round bottom glass flask equipped with magnetic stirrer, thermometer well, nitrogen inlet tube, and a spray trap at the top of which was connected an efficient water condenser. The stirred mixture was heated over a period of 0.5 hr to an internal temperature of 280 C under a nitrogen sweep adjusted to 120 ml/min. At the stearic acid melting point (70 C) a clear solution of stearic acid and triphenylphosphine containing dispersed metal salt was observed. At a temperature of 240 C, a homogeneous yellow solution was obtained. During the course of the reaction, yellow crystals formed on the sides of the reaction flask and were subsequently isolated. Progress of the reaction was monitored by IR analysis of the acid carbonyl band at 1700 cm^{-1}. In a typical experiment a 2 g sample of stearic acid was quantitatively decarbonylated in 1 hr; however, larger samples, run in the same molar proportions, required longer reaction time (80 g stearic acid, 5.5 hr). The latter runs were found to contain dimerized products, namely, a C_{34} monoene ($\simeq$6%) and a stearone (3%).

When the reaction was complete, the mixture was cooled and the black precipitate removed by filtration through Celite and washed with hexane. Removal of the hexane from the combined filtrate and wash left the crude monoenes as a yellow oil from which yellow crystals precipitated. These were collected by filtration. Benzene extraction of the black precipitate afforded yellow crystals after removal of solvent. The combined yellow crystals were recrystallized from benzene to obtain yellow prisms with mp 197 C (decomposes). Analysis found: C, 64.5%; H, 4.65%; P, 8.82%; Cl, 4.95%, calculated for $[(C_6H_5)_3P]_2Rh(CO)Cl$: C, 64.3%; H, 4.38%; P, 8.96%; mol wt by osmometry 715, theory 691. The monoenes were purified by distillation, bp 135-140 C (0.3 torr), leaving the dimerized products, if present, as a residue. The monoenes produced were identified as heptadecenes by mass spectrometry, and the double bond positions were determined by a reductive ozonolysis procedure previously described

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TABLE I

Decarbonylation of Stearic Acid[a]

	Catalyst	Mole ratio acid:catalyst	Mole added $(C_6H_5)_3P$	Time (hr)	% $C_{17}H_{34}$
1	$[(C_2H_5)_2C_6H_5P]_3RhCl_3$	150:1	–	3	14.4
2	"	50:1	–	3	15.2
3	$PdCl_2$	50:1	5	3	9.6
4	"	10:1	5	3	80.0
5	$[(C_6H_5)_3P]_2PdCl_2$	50:1	–	3	26.0
6	$[(C_6H_3)_3P]_3RhCl$	50:1	–	3	tr
7	$RhCl_3$ · anhydrous	50:1	–	3	tr
8	"	50:1	5	3	25.4[b]
9	$RhCl_3$ · anhydrous (N_2)	50:1	5	3	93.0
10	" "	100:1	10	3	100.0[c]
11	" "	100:1	10	1	23.0
12	$RhCl_3 \cdot 3H_2O$ (N_2)	100:1	10	1	90.0
13	" "	100:1	10	5.5	100.0[d]

[a] Rxn run on 2 g of acid at 280 C.

[b] Sample size 5 g of acid.

[c] Sample size 10 g of acid.

[d] Sample size 80 g of acid.

(11). The dimerized products were purified by thin layer chromatography and identified by mass spectrometry. For those reactions which did not go to completion, the unreacted stearic acid was esterified with BF_3/methanol and the product distribution ascertained by GLC.

RESULTS AND DISCUSSION

Reaction Variables

Our initial studies on the decarbonylation of fatty acids to alkenes utilized the transition metal systems previously reported in the literature (5,6). For example, attempts to decarbonylate stearic acid with the complex tris-(diethylphenylphosphine)rhodium(III) chloride, $[(C_2H_5)_2C_6H_5P]_3RhCl_3$, resulted in a poor (15%) conversion of acid to heptadecene (Table I, Exp. 1 and 2). This observed conversion represents a catalyst turnover of 7.5 molecules of alkene per atom of rhodium used and is comparable to the previously reported results obtained for propionic and hexanoic acids (5). During the course of the above reaction, it was noted that rhodium, initially in the +3 oxidation state, was reduced to the nascent metal, and it was at this point that the decarbonylation reaction ceased. This catalyst deterioration was evidenced by the formation of a mirror on the surface of the reaction flask and a color change of the reaction mixture, typically from yellow to black. With Wilkinson's catalyst, tris-(triphenylphosphine)-rhodium(I) chloride, $[(C_6H_5)_3P]_3RhCl$, and with rhodium trichloride, $RhCl_3$, both of which are very efficient catalysts for the decarbonylation of aldehydes and acyl halides, only a trace amount of alkene was formed (Table I, Exp. 6 and 7). Use of the palladium catalyst bis-(triphenylphosphine)-palladium chloride, $[(C_6H_5)_3P]_2PdCl_2$, for the decarbonylation of stearic acid under the same conditions resulted in alkene conversion of 26% (moles product per atom of palladium = 13:1) (Table I, Exp. 5).

Essentially no reaction was obtained with uncomplexed palladium chloride, $PdCl_2$. However, addition of the co-catalyst triphenylphosphine gave a 10% conversion of acid to alkene (Table I, Exp. 3). Increasing the catalyst concentration five fold resulted in an 80% conversion to alkene (Table I, Exp. 4).

Addition of the co-catalyst triphenylphosphine to the $RhCl_3$-stearic acid system greatly improved the conversion to alkene, as it did for the $PdCl_2$-stearic acid system (Table I, Exp. 7 and 8). Olefin formation was dramatically increased when the above reaction was carried out with the aid of a nitrogen purge (Table I, Exp. 9 and 10). Undoubtedly, the purge serves to remove the coproducts, carbon monoxide, and water from the reaction vessel and thus helps drive the reaction to completion.

From the above experiments it was concluded that $RhCl_3$, used with excess phosphine ligand and an efficient nitrogen purge, was the best catalyst for decarbonylating stearic acid. To determine the optimum reaction conditions we studied the effect on this reaction of temperature, of catalyst concentration and structure, of various flow rates of nitrogen purge, and of a number of different phosphine ligands.

The nature of the $RhCl_3$ catalyst used was found to be an important factor affecting catalyst reactivity. In a comparative study made between anhydrous and hydrated $RhCl_3$, both in the presence of excess triphenylphosphine, the latter was significantly more efficient (Table I, Exp. 11 and 12). This difference in metal reactivity can be attributed to the structural differences of the two metal salts. Although the exact structure of hydrated $RhCl_3$ remains unknown, evidence suggests that it is a six coordinate monomeric species. Anhydrous $RhCl_3$ is thought to have a polymeric structure similar to $PdCl_2$. This type of structure would account for the lower activity of anhydrous $RhCl_3$, since it would make the metal less accessible for formation of the active catalyst.

Temperature played an important role in affecting the rate of the decarbonylation reaction. At 70 C a clear solution of stearic acid and triphenylphosphine was observed; however, the black $RhCl_3$ salt remained insoluble. When the reaction temperature was raised to 240 C, the $RhCl_3$ dissolved and a yellow homogeneous solution was obtained that subsequently deposited yellow crystals on the sides of the reaction vessel. No decarbonylation reaction was observed below 240 C or prior to the formation of the yellow solution and/or crystal formation. The temperature that yielded the maximum rate of alkene formation was in the range of 280-285 C. Above the latter temperature, dimerization and polymerization adversely affected the yields of alkene.

The optimum yields of heptadecene were obtained when the reactant ratios for stearic acid:$RhCl_3$:$(C_6H_5)_3P$ were maintained at 100:1:10. This ratio of reactants gave the best conversions in the shortest time period. Whereas it was possible to increase the molar ratio of reactants to 200:1:10, these ratios required considerably longer reaction times to attain good conversions. In addition, these latter reactions yielded larger amounts of dimerized products. An alternate procedure for increasing catalyst turnover was to run the reactions at the optimum reactant ratio and, when the initial decarbonylation reaction was complete, to add additional stearic acid and triphenylphosphine and continue with the reaction. Thus, a catalyst turnover of up to 250 moles of alkene per mole of $RhCl_3$ could be attained.

The flow rate of the nitrogen purge through the reaction vessel affected the conversion of stearic acid to olefin. As can be seen in Table II, the faster the nitrogen flow the better are the conversions during the same time period. The optimum practical flow rate of nitrogen was 120 ml/min. Faster rates made it difficult to keep the reaction products from volatilizing, while slower rates gave poorer conversions. Without the nitrogen purge the percent conversion to alkene dropped to $<$10%.

The decarbonylation reaction was also studied with a variety of different organo-phosphines, all used in excess (Table III). Of all the phosphines investigated, none worked as well as triphenylphosphine; substituting triphenylphosphite in place of the phosphine gave no reaction. Higher conversions of stearic acid to heptadecene were obtained with other phosphine derivatives, but they required longer reaction times (Table III).

TABLE II

Decarbonylation of Stearic Acid[a]
Effect of N_2 Flow Rate

Flow rate (ml/min)	Conversion to $C_{17}H_{34}$ (%)
0	10
60	60
120	77
200	83

[a]Mole ratio stearic acid:$RhCl_3 \cdot nH_2O$:$(C_6H_5)_3P$ was 100:1:10, 280 C, 1 hr.

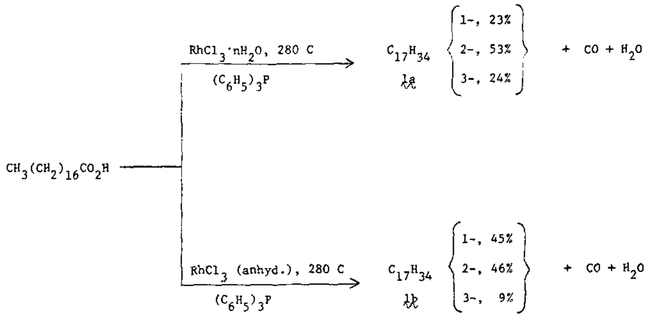
TABLE III

Decarbonylation of Stearic Acid
as Function of Phosphine Ligand[a]

Phosphine	Time (hr)	Conversion to $C_{17}H_{34}$ (%)
$(C_6H_5)_3P$	1	90
$(4\text{-}CH_3C_6H_4)_3P$	1	46
"	3	100
$(2\text{-}CH_3C_6H_4)_3P$	1	19
$(4\text{-}CH_3OC_6H_4)_3P$	1	36
$(C_2H_5)_2(C_6H_5)P$	4	19
"	6	51
$(C_4H_{13})_3P$	3	12[b]
$(C_6H_5O)_3P$	3	N.R.

[a]Mole ratio of stearic acid:$RhCl_3 \cdot nH_2O$:phosphine of 100:1:10, 280 C.

[b]Metal reduction.



Scheme I

Products of Decarbonylation

The rhodium trichloride triphenylphosphine catalyzed decarbonylation of stearic acid results in the formation of carbon monoxide, water, and the monounsaturated hydrocarbon heptadecene (Scheme I). To confirm the identity of the volatile products of decarbonylation, the following experiments were performed. The decarbonylation reaction was carried out in such a fashion that the exit gases from the reaction vessel were continuously passed through an infrared gas cell. Periodic monitoring of the exit gases by IR showed the continuous presence of carbon monoxide as evidenced by strong absorption bands at 4.6 and 4.7 $m\mu$. In a second experiment, a Dean-Stark trap equipped with an efficient condenser was utilized, and water was readily collected (70% theoretical). These experiments together proved that the volatile products of the decarbonylation reaction were carbon monoxide and water and thus demonstrated that the reaction is a decarbonylation-dehydration process as opposed to a decarboxylation process.

The structure of the heptadecene produced from the decarbonylation of stearic acid depended upon the type of rhodium catalyst employed. The alkene mixtures 1a and 1b (Scheme I), obtained with $RhCl_3 \cdot nH_2O$ and anhydrous $RhCl_3$, respectively, were analyzed by spectroscopic and chemical methods. The molecular weights of 1a and 1b were found by mass spectrometry to be 238, agreeing with the empirical formula for a C_{17} monoene. The IR spectra of 1a and 1b, aside from the expected carbon-hydrogen absorptions, were characterized by strong absorptions at 990, 960, and 910 cm^{-1}, all indicative of an unsaturated hydrocarbon. Comparison of monenes 1a and 1b with model alkenes by argentation TLC indicated a major difference in their geometrical isomer composition. Aside from the presence of terminal alkene in both mixtures 1a and 1b, the internal double bonds of mixture 1a were found to be composed of a 50/50 mixture of *cis* and *trans* isomers, whereas most of the internal double bonds of mixture 1b were in the *cis* geometry.

Information as to the positions of unsaturation in monoenes 1a and 1b was obtained by a reductive ozonolysis-oxidation procedure (11). This study showed that the double bonds of both 1a and 1b were located exclusively at positions near the end of the hydrocarbon chain (1, 2, and 3 positions) with the following structural differences being noted. For monoene 1a, 53% of the double bond was located at the 2 position, 23% at the 1 position, and the remainder located at the 3 position. Monoene 1b had >90% of its double bond equally distributed between the 1 and 2 positions with the remainder at the 3 position.

Catalyst Structure

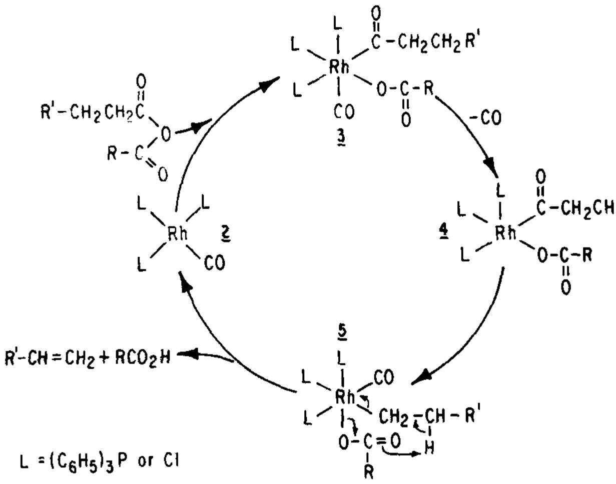
The yellow crystalline precipitate (complex A) that is formed in situ by the reaction of $RhCl_3$, triphenylphosphine and stearic acid at 240 C, was identified as the rhodium complex, chlorocarbonylbis-triphenylphosphine rhodium(I), $[(C_6H_5)_3P]_2Rh(CO)Cl$, on the basis of the following analytical and spectroscopic data. Complex A crystallized from benzene as yellow prisms, mp 197 C (de-

TABLE IV

Decarbonylation of Stearic Acid by Rhodium Complexes[a]

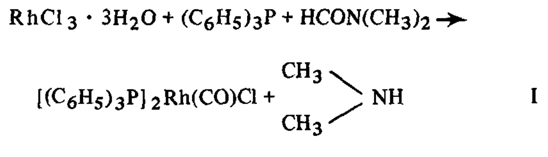
Complex	Moles added $(C_6H_5)_3P$	$C_{17}H_{34}$ (%)
$[(C_6H_5)_3P]_2Rh(CO)Cl$[b]	–	28
"	10	81
$[(C_6H_5)_3P]_2Rh(CO)Cl$[c]	10	86
$[(C_6H_5)_3P]_3RhCl$	10	100
$Rh_2(CO)_4Cl_2$	10	95

[a] Mole ratio stearic acid:catalyst, 100:1, 280 C, 1 hr.
[b] Recovered catalyst.
[c] Synthesized catalyst.



Scheme II

composes). The IR spectrum (KBr) of complex A has strong absorption bands at 1421, 1435, 744, and 690 cm^{-1} which are characteristic of triphenylphosphine. The strongest absorption band in the spectrum, however, appeared at 1975 cm^{-1}. This is indicative of a carbon monoxide stretching mode. Since this band fell below 2000 cm^{-1}, it strongly indicated that complex A was a mononuclear rhodium (I) phosphine complex (12). Further evidence for the structure of complex A was obtained from elemental analysis and molecular weight determinations. Confirmation of the structure of complex A was obtained by comparison of its physical and chemical properties with an authentic sample of $[(C_6H_5)_3P]_2Rh(CO)Cl$ obtained by the procedure of Rusina and Vlick (10).



$$RhCl_3 \cdot 3H_2O + (C_6H_5)_3P + HCON(CH_3)_2 \rightarrow [(C_6H_5)_3P]_2Rh(CO)Cl + (CH_3)_2NH \qquad \text{I}$$

To establish that complex A was indeed the active decarbonylation catalyst, the following experiments were performed (Table IV). Heating stearic acid with recovered complex A alone, under the optimum reaction conditions described earlier, resulted in a 28% conversion to heptadecene with concommitant catalyst decomposition. When the reaction was carried out with added triphenylphosphine ligand, an 81% conversion to alkene was obtained. Moreover, this latter reaction did not result in metal reduction, and the complex A was recovered. Similar results were obtained when the synthesized rhodium complex was used for the decarbonylation of stearic acid (Table IV). The stabilization of the rhodium catalyst, $[(C_6H_5)_3P]_2Rh(CO)Cl$, by excess triphenylphosphine has also been noted by Cradock et al. (12). They found that the high selectivity of their hydroformylation procedure was due to the stabilization of complex by excess triphenylphosphine which inhibited the catalysts decomposition to other inactive rhodium species.

In addition to the procedure of Rusina and Vlick (10), the rhodium complex $[(C_6H_5)_3P]_2Rh(CO)Cl$ can be prepared by alternate procedures (13,14), and these are shown in equations II and III.

$$\underset{\underline{B}}{[(C_6H_5)_3P]_3RhCl} + CO \rightarrow \underset{\underline{A}}{[(C_6H_5)_3P]_2Rh(CO)Cl} \qquad \text{II}$$

$$\underset{\underline{C}}{[Rh(CO)_2Cl]_2} + (C_6H_5)_3P \rightarrow \underset{\underline{A}}{[(C_6H_5)_3P]_2Rh(CO)Cl} \qquad \text{III}$$

Accordingly, the decarbonylation of stearic acid should also occur with either catalyst complex B or C when the reactions are performed in the presence of excess triphenylphosphine, More importantly, successful decarbonylations with complexes B or C would confirm that complex A is the true active catalytic species formed in situ during our decarbonylation process. The above conclusions were confirmed as shown in Table IV.

Mechanism of Decarbonylation

A mechanistic rationale which readily accounts for the observed products in the rhodium metal catalyzed decarbonylation of stearic acid is shown in Scheme II. In formulating this reaction pathway the following two assumptions were made: (a) the initial step of the reaction involves the formation of stearic anhydride from stearic acid, and (b) the organometallic reactions shown proceed by the 16 and 18 electron rules as proposed by Tolman (15). The initial step of the catalytic mechanism requires the oxidative-addition of stearic anhydride to the four coordinated rhodium metal complex A, chlorocarbonyl[bis-triphenylphosphine]rhodium(I), complex 2, Scheme II, to give the six coordinate acyl-metal complex 3, Scheme II. The latter complex then undergoes loss of a ligand, either triphenylphosphine or carbon monoxide, to the five coordinate acyl complex 4, which can then rearrange to the six coordinate alkyl rhodium metal complex 5. Complex 5 undergoes reductive elimination of 1-heptadecene and free stearic acid with regeneration of the four coordinate rhodium complex 2 for recycle. Prior to the reductive elimination step, the σ-bonded alkyl metal complex 5 can undergo rearrangement via a hydride transfer mechanism (16) to an internal σ-bonded carbon metal complex analogous to 5. Reductive elimination of heptadecene from this latter complex accounts for the formation of 2- and 3-heptadecene found in the reaction mixture. Alternatively, the latter heptadecene isomers may arise from the isomerization of the initially formed 1-heptadecene by the active catalyst, $[(C_6H_5)_3P]_2Rh(CO)Cl$, with the isomer distribution being dependent upon the extent of isomerization.

Confirmation that the decarbonylation of stearic acid proceeds via the intermediate formation of the anhydride was obtained in the following manner. Heating stearic anhydride with complex A, chlorocarbonyl[bis-triphenylphosphine]rhodium(I), at a molar ratio of 100:1 (anhydride:catalyst) for 1 hr at 280 C resulted in a 45% yield of heptadecene which represents a 90% conversion of the anhydride. In a similar experiment carried out with added triphenylphosphine (10:1, phosphine:catalyst) and a nitrogen sweep (120 ml/min) the yield of heptadecene was increased to >80%. This latter yield represents a conversion of >160% from anhydride and thus confirms that anhydride formation from acid does occur in situ. Results similar to the above were also obtained when Wilkinson's catalyst, tris-triphenylphosphine rhodium(I) chloride, complex B, was used in place of complex A.

As noted previously, the addition of excess triphenylphosphine ligand to the decarbonylation reactions of stearic acid enhances the catalytic activity of both rhodium (I) complexes A and B. As shown in Scheme II, in going from complex 3 to 4, a neutral ligand must dissociate from complex 3 with the choice being between triphenylphosphine and carbon monoxide. In addition to its strong ligand properties, the excess triphenylphosphine causes the preferential loss of carbon monoxide from complex 3 and accordingly preserves catalyst activity. In the absence of added triphenylphosphine, a buildup of carbon monoxide ligands about the rhodium catalyst occurs during the course of the reaction. This results in the formation of polynuclear rhodium carbonyl complexes, such as $Rh_4(CO)_{10}[(C_6H_5)_3P]_2$, which precipitate from the reaction mixture and have been shown not to have catalytic activity (17). The above conclusions are supported by the recovery of complex A from the reaction mixture in those reactions performed with excess triphenylphosphine ligand, whereas in the absence of excess triphenylphosphine a black granular rhodium-carbonyl precipitate is obtained.

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