

STRUCTURE AND REACTIVITY OF
RHODIUM COMPLEX HYDROFORMYLATION CATALYSTS

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INTRODUCTION

In the present work, the reactivity and selectivity of various *t*-phosphine rhodium complex hydroformylation catalysts are correlated with their structures. Such a study is of particular interest at this time because there has been a rapid commercial development in this area during the last 10 years and because the structure of the catalyst complexes can now be well characterized by nuclear magnetic resonance spectroscopy (NMR) under simulated hydroformylation conditions.

Known triphenylphosphine rhodium carbonyl hydride and novel, more stable alkylidiphenylphosphine rhodium carbonyl hydride complexes were particularly investigated in this study. The catalyst behavior of various alkylidiphenylphosphine rhodium carbonyl hydrides was studied as a function of substitution and branching of the alkyl groups. As a result of this work rhodium complexes of alkylidiphenylphosphine were recognized as potentially highly attractive catalyst candidates of increased stability for continuous hydroformylation.

It should be recalled that the triphenylphosphine rhodium carbonyl hydride (Ph_3P complex) catalyst system was discovered by Professor Wilkinson and coworkers in the late 1960's as a low pressure, low temperature catalyst for the selective hydroformylation of 1-olefins to produce *n*-aldehydes (1). Pruet and Smith at Union Carbide Corp., and the Wilkinson group at Imperial College found in the same period that the selectivity of Wilkinson's catalyst to *n*-aldehydes was greatly increased by the addition of excess Ph_3P ligand, especially at low CO partial pressures (2). The discovery of these effects resulted in the commercial development by Union Carbide and Davy McKee of a low pressure propylene hydroformylation process based on a catalyst system containing the tris-phosphine complex and excess triphenylphosphine ligand (3,4,5).

The commercial rhodium hydroformylation process operates at about 100°C. The gaseous propylene, H_2 and CO reactants are continuously introduced into a well stirred solution of the catalyst while a vapor mixture of unreacted reactants and products is being flashed off (Figure 1). The ratio of normal versus iso-butylaldehyde products in such an operation is high, in excess of ten. For an effective removal of high boiling aldehyde products in such a process, increased reaction temperatures are obviously advantageous.

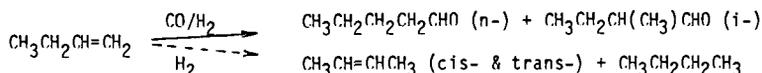
We have previously reported on our work relating to the mechanisms of triphenylphosphine rhodium complex catalyzed hydroformylations (6,7,8). We postulated that, in selective 1-*n*-olefin hydroformylation to *n*-aldehydes, the tris-(triphenylphosphine) rhodium carbonyl hydride complex is the stable precursor of the reactive trans-bis phosphine species. This postulate is based on correlating the data on equilibria among various Ph_3P -Rh complexes with hydroformylation rates and selectivities.

The structures of the various Ph_3P -Rh complexes and their equilibria were determined via NMR in the presence of varying amounts of excess Ph_3P and under different CO partial pressures. Studies of hydroformylation catalysis were carried out mainly using 1-butene as a reactant for the selective production of *n*-valeraldehyde at temperatures in excess of 100°C.

In the present work, the catalytic and structural studies were extended to various tris-(alkylidiphenylphosphine) rhodium carbonyl hydride complexes and related catalysts (Ph_2PR complexes). The previously described experimental methods were used

(6). Although the use of these catalysts was found to require higher temperatures than that of the Ph_3P complex catalysts, high selectivities toward valeraldehydes, particularly the n-isomer, could be maintained coupled with an increase in catalyst stability. Details of the work are described in Exxon patents (9). In this presentation, correlations of catalyst structure and activity are emphasized.

Using 1-butene instead of propylene in this laboratory allowed an additional insight into the reaction mechanism since isomerization side reactions producing 2-butenes could be also readily studied:



In contrast to the voluminous, prior patent literature, the present batch hydroformylation studies included not only the determination of the normal to iso (n/i) ratio of the aldehyde products but the paraffin hydrogenation and internal olefin isomerization by-products as well. A limited study of continuous hydroformylation, via a continuous product flash-off operation, was also made.

RESULTS AND DISCUSSION

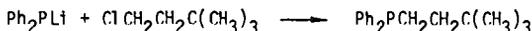
In contrast to Ph_3P complexes, Ph_2PR complexes were generally not considered for hydroformylation catalysis. For example, propyldiphenylphosphine, a Ph_3P degradation product during continuous propylene hydroformylation, was mainly regarded as a catalyst modifier rather than as a catalyst ligand on its own (10-12). In the present work, the structure and catalytic activity of Ph_2PR complexes was studied in detail and compared with those of the corresponding Ph_3P complexes.

Most of the Ph_2PR studies to be discussed were carried out with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ because they readily provided crystalline rhodium carbonyl hydride complexes. When an excess of these ligands was reacted with ethanolic solutions of rhodium dicarbonyl acetyl acetonate and then hydrogen at ambient temperature, the corresponding tris-phosphine complexes were formed as pure crystalline precipitates. The following overall reaction took place



The same reaction occurred when other alkylidiphenylphosphines were used. However, most of the products separated as oils.

Most of the alkylidiphenyl phosphine reactants used were prepared in our laboratory. The preferred displacement approach to these compounds involved the reaction of lithium diphenylphosphide with the appropriate alkyl chlorides in tetrahydrofuran, e.g.



The addition approach utilized the free radical chain addition of diphenyl phosphine to the corresponding olefins. The additions were initiated by irradiation with broad spectrum ultraviolet light and preferably employed activated olefinic reactants at a reaction temperature of about 15°, e.g.



On changing the structure of the alkyl group of the Ph_2PR ligands, major changes in catalyst activity were observed, primarily due to steric crowding. Steric crowding affected the structure and stability of the Ph_2PR complexes formed. The structure of the catalyst complexes, in turn, determined reactivity and selectivity.

All the findings including hydrocarbon by-product formation, could be corre-

lated with changing equilibria between the catalyst complexes present in hydroformylation systems and with the steric and electronic effects of ligands on such equilibria. These equilibria and the critical reaction steps are shown by the outline of an overall mechanistic scheme in Figure 2.

According to the figure, coordinatively saturated alkyldiarylphosphine rhodium complexes of varying carbonylation degrees are the main components of such hydroformylation catalyst systems. Upon reversible dissociation, these unreactive complexes generate coordinatively unsaturated species which react with the olefin and in turn, with CO and H₂ to provide the normal and iso aldehyde products, with the regeneration of the catalyst.

1. Studies of Catalyst Complex Structures and Equilibria by NMR

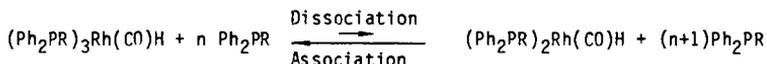
In comparative NMR studies, first the structure and stability of Ph₂PR and Ph₃P complexes were compared. Differences in the behavior of specific Ph₂PR ligands were also studied to ascertain electronic and steric influences of substituting the R alkyl groups.

Ligand exchange studies of the tris-Ph₃P complex using sterically non-crowded Ph₂PR reactants generally showed substantial reaction:



The more basic Ph₂PR ligand formed a more stable complex than Ph₃P. In the above reaction, the ratio of complexed Ph₂PCH₂CH₂C(CH₃)₃ to complexed Ph₃P in the -60 to + 35° temperature range was about 3.

Ligand exchange between complexed and free phosphine ligands also occurred, in a reversible manner, when there was only one phosphine present. Such an exchange took place via coordinatively unsaturated trans-bis-phosphine rhodium carbonyl hydride intermediates:



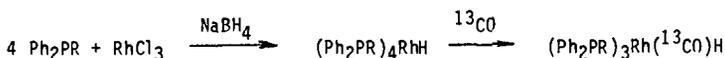
Since the equilibria strongly favor the coordinatively saturated tris-phosphine complexes, only the NMR spectra of these species could be detected. However, the rate of ligand dissociation could be determined by line shape analyses of the signals.

The qualitative aspects of the comparative ³¹P NMR ligand exchange studies of the Ph₂PCH₂CH₂C(CH₃)₃, Ph₃P and Ph₂PCH₂CH₂Si(CH₃)₃ complex systems are indicated by the ³¹P spectra in Figures 3a and b. At -60°C, the typical doublet signal of the tris-phosphine complexes plus singlet signals of the free phosphines were observed for all three systems. However, the doublet signal of the Ph₂PR type complexes remained sharp at 35° while the Ph₃P complex exhibited a broad doublet. Similarly, the Ph₂PR complex still showed a very broad doublet at 60° where the doublet of the Ph₃P complex had already collapsed. Further increases in the ligand exchange rates, resulted in a single composite signals for the Ph₃P and Ph₂PR systems at 90° and 120°, respectively.

Clearly higher temperatures in the Ph₂PR complex systems were necessary to reach ligand exchange rates comparable to that of the Ph₃P complex. Since the increase in ligand exchange rate parallels that of complex dissociation to yield coordinatively unsaturated species, these data indicate that in the Ph₂PR complex systems a comparable generation of such reactive species occurs at higher temperatures. This suggests that to achieve comparable hydroformylation rates, higher temperatures are needed when complexes of Ph₂PR are used in place of Ph₃P. On the other hand, at the higher temperatures, the Ph₂PR complexes are more stable than the Ph₃P complex.

In view of recent suggestions, of a potential CO dissociation from the tris-Ph₃P complex to generate hydride species leading to n-aldehyde products (13, 14), ligand exchange was also studied by ¹³C NMR. For these studies, ¹³CO enriched tris-

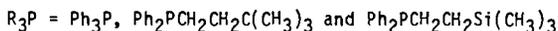
phosphine complexes were used. Such complexes could be readily derived by reacting the corresponding tetrakis-phosphine rhodium hydride complexes with ^{13}C O at atmospheric pressure. For example, the following sequence of reactions was carried out with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$:



The first reaction to form the tetrakis-phosphine rhodium hydride was carried out in 10 minutes in refluxing ethanol solution in a manner reported for the Ph_3P derivative (15). The resulting crystalline hydride could be reacted with ^{13}C O at room temperature either in toluene solution or ethanol suspension.

Variable temperature ^{13}C NMR studies of tris-phosphine monocarbonyl hydride complexes are illustrated by Figure 4. The spectra indicate that at -30° , the Ph_3P complex has the expected structure. The double quartet signals of the complexed ^{13}C O show coupling to one rhodium and three phosphine ligands. At increased temperatures up to 110°C , this signal of the Ph_3P complex collapsed into doublets. That was the consequence of the exchange of the phosphine ligands. Rhodium coupling remained since no ^{13}C O dissociation occurred. However, free ^{13}C O could be detected in this system at 140°C when free triphenyl phosphine ligand was used as the solvent ($\text{P}/\text{Rh} = 260$).

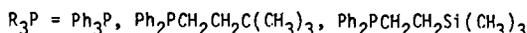
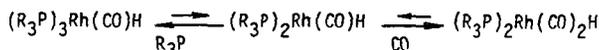
The ^{13}C O NMR studies show that the CO ligand of these tris-phosphine monocarbonyl hydride complexes is very strongly bound. During hydroformylation, carbonyl free phosphine rhodium hydride complexes are not present, except under non-equilibrium CO starvation conditions. The main reaction in these systems is always phosphine rather than CO dissociation. Proton NMR studies of the hydride region of tetrakis-phosphine rhodium hydrides were known (15). The dissociation in *d*-toluene solutions of three tetrakis-phosphine rhodium hydrides was studied by ^{31}P NMR ligand exchange methods in the presence of excess phosphine ligands in the present work.



In general, it was found that significant ligand exchange of these hydrides occurred at much lower temperatures than those observed for the corresponding carbonyl hydrides. The doublet signal of the tetrakis-triphenylphosphine rhodium hydride collapsed at -30° while the corresponding Ph_2PR complexes gave broad singlet signals for complexed ^{31}P at about $+20^\circ$. Thus it was found Ph_2PR ligands are more strongly complexed than Ph_3P in carbonyl free rhodium hydrides as well.

The increase in hydrogenation and isomerization side reactions during 1-butene hydroformylation under CO starvation conditions can be explained by the formation of carbonyl free rhodium hydride complexes. Tetrakis-triphenylphosphine rhodium hydride is a known hydrogenation catalyst (16). In the present work, it was found to be an effective 1-butene isomerization catalyst even at 0° . Its low temperature catalytic activity is attributed to its facile dissociation to provide the corresponding highly reactive tris-phosphine rhodium hydride.

At increased CO partial pressure, tris-phosphine rhodium carbonyl hydrides are converted to the corresponding trans-bis-phosphine dicarbonyl hydrides via the following equilibrium reactions:



Complexes of Ph_3P and Ph_2PR type ligands showed similar equilibria between mono- and dicarbonyl hydride complexes.

Increased concentrations of excess phosphine ligand effectively reduced the amount of dicarbonyl hydride formed. This is illustrated by Figure 5. The figure shows that, in the absence of a significant excess of the Ph_2PR type ligand, conversion to the dicarbonyl hydride is essentially complete under about 200 kPa pressure of 1 to 1 H_2/CO . However, at a five-fold excess of Ph_2PR (P/Rh ratio of 15/1) the ratio of dicarbonyl to monocarbonyl complex is only about 1 to 3.

In the case of bis-phosphine dicarbonyl hydride complexes, the relative dissociation rates of phosphine and carbonyl ligands were also studied by NMR:



A 1% solution of the bis- Ph_3P complex plus excess Ph_3P to provide a P/Rh ratio of 9 were used for the study. This solution was prepared under 400kpa $\text{H}_2/^{13}\text{CO}$ pressure, from the tetrakis- Ph_3P complex which was largely converted to the desired bis-phosphine rhodium dicarbonyl hydride. Variable temperature NMR studies indicated reversible CO and phosphine ligand dissociation.

As it is shown by Figure 6, the ^{13}C NMR spectrum of the resulting solution showed the expected double triplet for the complexed ^{13}C CO ligand as well as the singlet signal of free ^{13}C CO. At + 35°, the fine structure of the complexed CO disappeared. Also, the signals of complexed and free ^{13}C CO considerably broadened as a consequence of CO exchange. At 90°C, only one, broad ^{13}C CO signal was obtained due to further increased ligand exchange rates.

Similar variable temperature ^{31}P NMR studies showed reversible phosphine ligand dissociation. However, a free versus bound Ph_3P ratio much below the expected value was found at low temperature. This suggests the presence of unidentified rhodium complex species undergoing rapid ligand exchange.

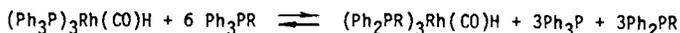
When 1-olefins are hydroformylated under conditions where the dicarbonyl hydride predominates in the above type of system, the n/i ratio of aldehyde products is greatly decreased but still remains above two. It is believed that most of the remaining preference of such catalyst systems for producing n-aldehydes is due to ^{13}C dissociation to provide the trans-bis-phosphine monocarbonyl hydride intermediate of linear hydroformylation.

The electronic effects on the properties of tris- Ph_2PR rhodium carbonyl hydride catalyst complexes were studied by substituting groups of varying electrophilicity on the β -carbons of the alkyl groups of their ligands. The basicities of some of these ligands of general formula $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{R}'$ and their ^{31}P NMR parameters of their complexes are shown by Table I.

The data of the table indicate that by appropriate electronegative β -substituents the proton basicity of aqueous alkyldiphenylphosphines was reduced to the level of triphenylphosphine. However, no apparent correlation could be observed between the inverse basicity values, $\Delta\text{HNP}'\text{s}$, and the NMR parameters. Most of the $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{R}'$ complexes showed little change of their chemical shift and coupling constant values. Also, all the $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{R}$ ligands displaced Ph_3P from its complex. Thus the observed basicity was not a major factor in the NMR data.

In view of the above study, the difference between the sterically non-hindered alkyldiarylphosphine and triphenylphosphine complexes is apparently attributed to minor differences in their π -backbonding ability and steric hindrance.

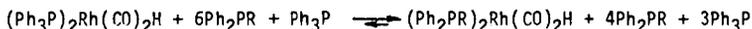
Steric hindrance was found to have a major effect on the structure of the complexes formed when α - and β - branched alkyldiphenylphosphine ligands were used. These effects were first studied by determining the degree of Ph_3P ligand displacement with such Ph_2PR ligands as indicated by the following simplified scheme



In the case of the monomethyl branched ligands, such as isobutyl-, secondary butyl- and cyclohexyl- diphenylphosphines, partial displacement occurred. The ratio of bound Ph_2PR to Ph_3P was about 3 to 2. However, β , β - and α,α -dimethyl branched ligands such

as neopentyl- and t-butyl-diphenyl phosphines were not able to displace any of the Ph_3P .

Displacement of Ph_3P by the above sterically hindered phosphine ligands could be enhanced under about 400 kpa H_2/CO pressure. This pressure results in the formation of major amounts of the bis-triphenylphosphine rhodium dicarbonyl hydride complex. The latter, in turn, was found to be more subject to displacement by the sterically demanding phosphine ligands:



Thus, at equilibrium the mixtures containing monosubstituted ligands showed the displacement of about 80% of the Ph_3P from the dicarbonyl complex. However, there was still no noticeable displacement by the neopentyl and t-butyl derivatives.

The above inhibition of ligand displacement is clearly due to steric effects. Electronic effects would result in increased ligand displacement since these branched alkylidiphenylphosphine ligands have higher basicities than their straight chain isomers.

Another effect of steric crowding is on the dissociation rate of the complexes formed. This is illustrated by the example of triphenylphosphine plus isobutylidiphenylphosphine rhodium complex catalyst system in Figure 7. The -30°C spectrum of this system shows that both ligands participate in the complex formation to form four different tris-phosphine complexes. However, no distinct phosphorus signals of these complexes can be observed at ambient temperature. Only a broad phosphorus signal is observed in the complex region. This indicates a high ligand exchange rate at a relatively low temperature. This is clearly the consequence of increased phosphine dissociation due to steric decompression:



The increased dissociation rate to provide reactive coordinatively unsaturated complex species results in increased catalytic activity. However, steric crowding also results in a reduced ratio of monocarbonyl hydride versus dicarbonyl hydride complexes, i.e. reduced n/i ratio of products.

2. Hydroformylation Process Studies

The main aim of the present 1-butene hydroformylation studies was to determine the effect of the structure of phosphine-rhodium complex catalysts on activity, selectivity and stability. The well known Ph_3P complex catalyst system which we studied previously(6) was a catalyst primarily used for comparison in this work. As a $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{R}'$ type alkylidarylphosphine ligand, 2-trimethylsilyl ethyldiphenylphosphine (SEP), was studied in detail.

In the following at first, the Ph_3P and SEP based rhodium complex hydroformylation catalyst systems will be compared at different temperatures and excess phosphine concentrations. Thereafter, the detailed structural effects of various Ph_2PR ligands will be discussed with emphasis on steric crowding. The catalytic results will be correlated with the structural findings of the NMR studies.

The effect of temperature on the Ph_3P and SEP complex catalyst systems is shown in Table II. Most of the batch experiments were carried out at a one molal phosphine ligand concentration to maintain the selectivity and stability of the catalyst at increased temperatures. The results show that, at comparable temperatures, the triarylphosphine complex is always more active than the alkylidarylphosphine complex. However, the activity and selectivity of the latter is better maintained particularly at higher temperatures.

At the relatively low temperature of 110° , a lower n/i aldehyde product ratio is obtained with the SEP complex. However, there is no significant difference between

the higher n/i values of the two systems at 145°. In the 135 to 160° range, the use of the SEP complex leads to a higher total (n+i) aldehyde selectivity. This is mainly due to the reduced butene-1 to butene-2 isomerization side reactions in the presence of the more basic SEP ligand. The top temperature of 160° has generally less adverse effect on the selectivity of the SEP complex system.

The effect of increasing concentrations of the SEP and Ph₃P ligands at 145° is shown in Table III. This increase in both systems resulted in a decreased activity but increased n/i aldehyde selectivity. At high ligand concentrations, the n/i values depended on the phosphine concentration rather than on the P/Rh ratio. When these phosphines were used as the only solvents, the n/i ratios reached maximum values but the selectivities to total aldehyde products decreased.

The SEP and Ph₃P rhodium complex catalyst systems were also compared in continuous 1-butene hydroformylation, operating via product flash-off (PFO) from the reaction mixture (Figure 1). The reaction conditions and data obtained are shown by Table IV.

In the first three experiments, the SEP system was operated at 120° while the Ph₃P system was running at 100°. Most importantly the results indicate that the increased temperature of the SEP-Rh system is highly advantageous for achieving higher butene conversions without increasing the stripping gas rate. At the lower temperature of the Ph₃P-Rh system, a higher conversion operation was not feasible under these conditions because of the limited product flash-off capability due to vapor liquid equilibria. It is noted that the selectivities of the two systems are similar.

In the other three experiments, the stability of the SEP and Ph₃P based rhodium catalyst systems was compared in a six day continuous PFO operation at 145°C. The butene conversion achieved with the SEP system showed less than 10% change. The conversion in the case of the Ph₃P system dropped from 82 to 65% during the test period. About 1/2% per day of the Ph₃P ligand was converted to butyldiphenylphosphine via ortho-metalation(10). No similar degradation of the SEP ligand was observed. In addition, as shown by the table, the selectivity of the SEP complex system was somewhat higher and did not change significantly when a mixture of 1- and 2-butenes was used in place of the pure 1-butene feed. (The 2-butene is apparently of very low reactivity under these conditions).

In more detailed PFO process studies of the SEP-Rh catalyst system at 120°, complete maintenance for 30 days of both hydroformylation activity and selectivity was established. In these studies, the n/i ratios of the valeraldehyde products were correlated with the excess phosphine ligand concentration and CO partial pressure. As was expected on the basis of the NMR studies of catalyst structures, the n/i ratio was directly dependent on the [SEP] and inversely dependent on the pCO.

The catalytic properties of a high number of alkylidiphenylphosphine rhodium complexes were studied in batch experiments. Comparative results obtained with complexes of ligands of the formula Ph₂PCH₂CH₂R' and Ph₃P are shown by Table V.

The results show that, at the 1M phosphine concentrations, all the Ph₂PCH₂CH₂R' complexes are highly selective catalysts for hydroformylation at 145°. They provide aldehyde products having n/i ratios in the 8.9-18.9 range. In general, their product linearity is similar to that of the Ph₃P system (n/i = 11.2). The total aldehyde selectivity of the Ph₂PR complex catalyst is higher. Their n + i aldehyde selectivity is in the 86.9 to 91.8% range while the corresponding n + i value of the Ph₃P system is 81.2. However, as expected on the basis of the NMR ligand dissociation rates, the Ph₃P system is more than twice as active.

The activity and selectivity of all these catalysts is highly dependent on the excess phosphine ligand concentration. When the phosphine ligand concentration was dropped to 0.14 M, the reaction rate usually increased about fourfold and the n/i ratio of the aldehyde products decreased to about a half of the previous value. Of course, these effects are expected on the basis of the catalytic mechanisms suggested by the NMR studies.

No definite correlation could be found between the basicity of the Ph₂PCH₂CH₂R' ligands and the catalytic properties of their rhodium complexes. Overall

the differences among these complexes were smaller than the difference between them as a group and the Ph_3P complex. The Ph_3P ligand stands out by virtue of its increased π -backbonding ability which weakens the CO coordination to the rhodium. Also, Ph_3P is a sterically more demanding ligand than $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{R}'$ ligands. Both properties increase the reactivity of the Ph_3P -Rh complex catalyst system.

The effect on catalysis of the steric crowding of alkyldiphenyl phosphine ligands by methyl substitution on the α - or β -carbon atoms of their alkyl group was also studied. The comparative experiments were carried out using two different ligand concentrations at 145° . The results are shown by Table VI.

Compared to straight chain and γ -methyl substituted alkyldiphenylphosphines, the α - and β -methyl substituted derivatives led to increased hydroformylation rates but reduced selectivities. The rate increasing effect was observed at the higher phosphine ligand concentration of 1M. The selectivities were decreased in terms of lower n/i ratios of aldehyde products and increased isomerization side-reactions to 2-butenes. The isomerization was particularly increased at the low ligand concentration of 0.14 M. At an extreme, this resulted in a reduced reaction rate since 2-butenes are much less reactive than 1-butene. The effect of steric crowding was further increased when the α , α - and β , β -dimethyl substituted alkyldiphenylphosphines were used in place of the monomethyl substituted ligands.

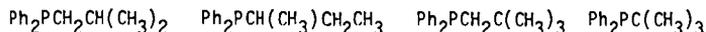
The increased reactivity of branched alkyldiphenylphosphine rhodium complexes is attributed to the accelerated dissociation via steric decompression of tris-phosphine rhodium carbonyl hydride complexes to provide reactive species. The reduced n/i ratio of the products is due to the increase of rhodium dicarbonyl hydride catalyst complexes. The increased isomerization to 2-butenes is apparently a consequence of the reversibility of reactions forming the secondary butyl rhodium complex intermediate.

CONCLUSIONS

The present correlation of the structure of *t*-phosphine rhodium carbonyl hydride complexes with high temperature hydroformylation catalysis data leads to the extension of our previously proposed rhodium hydroformylation mechanisms to alkyldiphenylphosphine ligand based catalysts. In view of their increased stability, alkyldiphenylphosphines are now recognized as rhodium complex catalyst ligands potentially superior to the commercially widely used triphenylphosphine.

Alkyldiphenylphosphines form remarkably stable tris-phosphine rhodium carbonyl hydride complexes of the formula $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{R}')_3\text{Rh}(\text{CO})\text{H}$. These act as a preferred reversible reservoir for the generation of the highly reactive, coordinatively unsaturated trans-bis-phosphine carbonyl hydride intermediates of 1-olefin hydroformylation to provide mostly n-aldehyde products. In accord with the complex equilibria found among variously carbonylated rhodium complex catalyst precursors, the stability and selectivity of such catalyst systems directly depends on the excess phosphine ligand concentration. It is inversely related to the partial pressure of the CO reactant. Changes in the R' group of such ligands did not result in any profound change of the catalytic properties of their rhodium complexes although they caused wide variations in their proton basicities.

In contrast branched alkyldiphenylphosphines having β - or α - alkyl substituents e.g.



form rhodium carbonyl hydride complexes of widely differing stabilities. These complexes in turn exhibit a broad range of catalyst behavior. Tris-phosphine rhodium carbonyl hydride complexes of these ligands are thermally unstable due to steric crowding. This facilitates the generation of reactive species. Under CO pressure, complexes of these ligands are largely converted to bis-phosphine rhodium dicarbonyl hydride, $(\text{Ph}_2\text{PR})_2\text{Rh}(\text{CO})_2\text{H}$, intermediates of nonselective hydroformylation.

Thus profound electronic differences between sterically noncrowded alkylidiphenylphosphine and triphenylphosphine rhodium carbonyl hydride complexes resulted in two types of catalyst systems having distinct properties. In contrast, small changes in the electronic character of alkylidiphenylphosphine complexes did not cause significant changes in catalysis. However, small changes in the steric requirements of α - and β - branched alkylidarylphosphines produced tremendous changes in the catalytic behavior of their rhodium complexes. Moderate steric crowding of such complexes may result in highly desired catalyst properties. However, such steric effects on catalysis are difficult to predict.

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LITERATURE CITED

- Osborn, J. A., Jardine, F. H., Young, J. F. and Wilkinson, G., J. Chem. Soc. A, 1966, 171.
- Pruett, R. L. and Smith, J. A., Org. Chem. 1969, 34, 327; U. S. Patent 3,527,809; Evans, D., Osborn, J. A. and Wilkinson G., J. Chem. Soc. A, 1968, 3133.
- Brewster, E. A. V. and Pruett, R. L., U. S. Patent 4,247,486; Bryant, D. R. and Billig, E., U.S. Patent 4,277,627 (both assigned to Union Carbide Corp.).
- Chem. Eng. Dec. 5, 1977, 110.
- New Syntheses with Carbon Monoxide, Editor: Falbe, J., Springer Verlag, Berlin-Heidelberg-New York, 1980, Chapter 1 on "Hydroformylation, Oxo Synthesis Roelen Reaction" by Cornils, B.
- Oswald, A. A., Hendriksen, D. E., Kastrup, R. V. and Merola, J. S., Preprints, Div. Pet. Chem., Inc., Am. Chem. Soc. Natl. Meeting, Las Vegas, Nev., Spring 1982, 27 (2) 292. Advances in Synthesis Gas Chemistry Symposium, Presentation on "Rhodium Hydroformylation Mechanisms."
- Advances in Chemistry, Editors: Alyea, E. C.; Meek, D. W., American Chemical Society, 1982, 196, 78, Chapter on ³¹P NMR Studies of Equilibria and Ligand Exchange in Triphenylphosphine Rhodium Complex and Related Chelated Bis-Phosphine Rhodium Complex Hydroformylation Catalysts" by Kastrup, R. V., Merola, J. S., Oswald, A. A.
- ACS Symposium Series Editors: Quin, L. D., Verkade, J. G., 1981, 171, 503, Chapter on ³¹P NMR Studies of Catalytic Intermediates in Triphenylphosphine Rhodium Complex Catalyzed Hydroformylations," Oswald, A. A., Kastrup, R. V., Merola, J. S., Mozeleski, E. J.
- Oswald, A. A., Jermansen, T. G., Westner, A. A., Huang, I-D., Patent Cooperation Treaty (PCT) International Patent Publication No. WO/80/01690, August 21, 1980, British Patent Application 8,223,961, February 21, 1983, and U. S. Patent 4,298,541 (assigned to Exxon Research and Engineering Co.)
- Gregorio, G., Montrasi, G., Tampieri, M., Cavalieri d'Oro, P., Pagani, G., Andreetta, A., Chim. Ind. (Milan) 1980, 62 (5), 389.
- Paul, J. L., Pieper, L. W. and Wade, E. L., U.S. Patent 4,151,209 (to Celanese Corp.).
- Morrell, D. G. and Sherman, P. D., U.S. Patent 4,260,828 (to Union Carbide Corp.).
- Hughes, O. R. and Young, D. A., J. Am. Chem. Soc. 1981, 103, 6636.
- Unruh, J. D. and Christenson, J. R., J. Mol. Cat. 1982, 14, 19.
- Lewison, J. J., and Robinson, S. D., J. Chem. Soc. A, 1970, 2947.
- Dewhurst, K. C., Keim, W. and Reilly, C. A., Inorg. Chem. 1968, 1, 546; Dewhurst, K. C., U. S. Patent 3,480,659 (assigned to Shell Oil Co.).
- Streuli, C. A., Anal. Chem. 1960, 32, 985.

Figure 1
SCHEME OF CONTINUOUS HYDROFORMYLATION UNIT WITH
CONTINUOUS PRODUCT FLASH-OFF

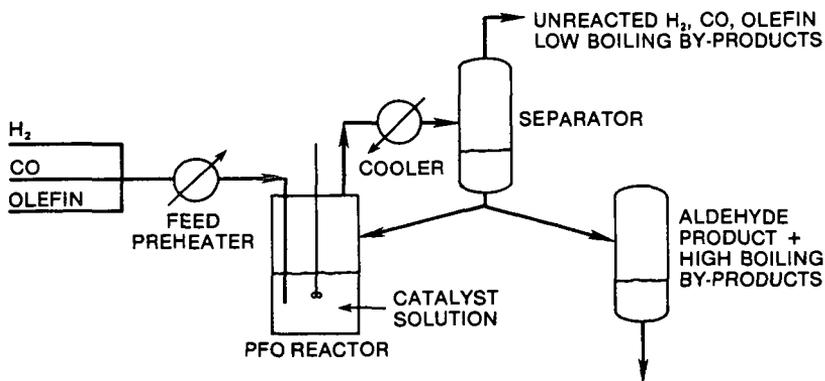


Figure 2
CATALYTIC INTERMEDIATES IN PHOSPHINE RHODIUM
COMPLEX CATALYZED HYDROFORMYLATION OF 1-BUTENE

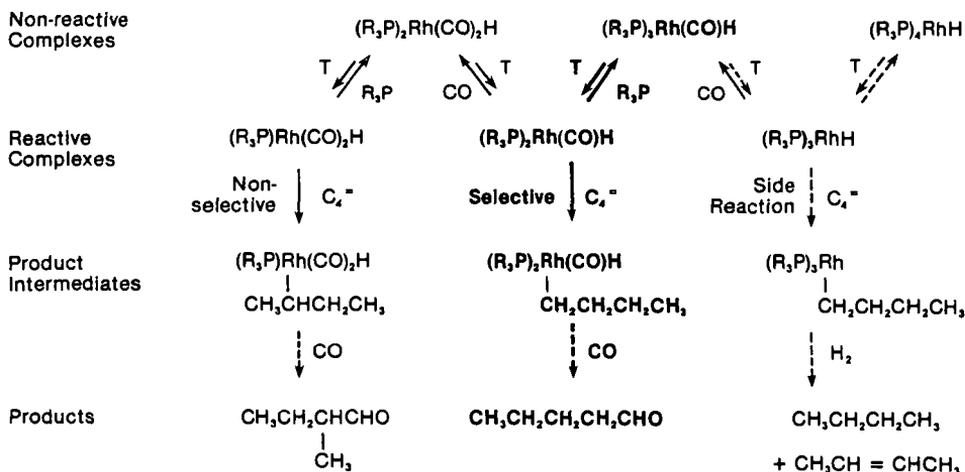


FIGURE 3
³¹P NMR STUDY OF LIGAND EXCHANGE AT VARIOUS TEMPERATURES
 (Ph₃P)₃RhClO₄ + 6 Ph₃PR ⇌ (Ph₃PR)₃RhClO₄ + 7 Ph₃PR

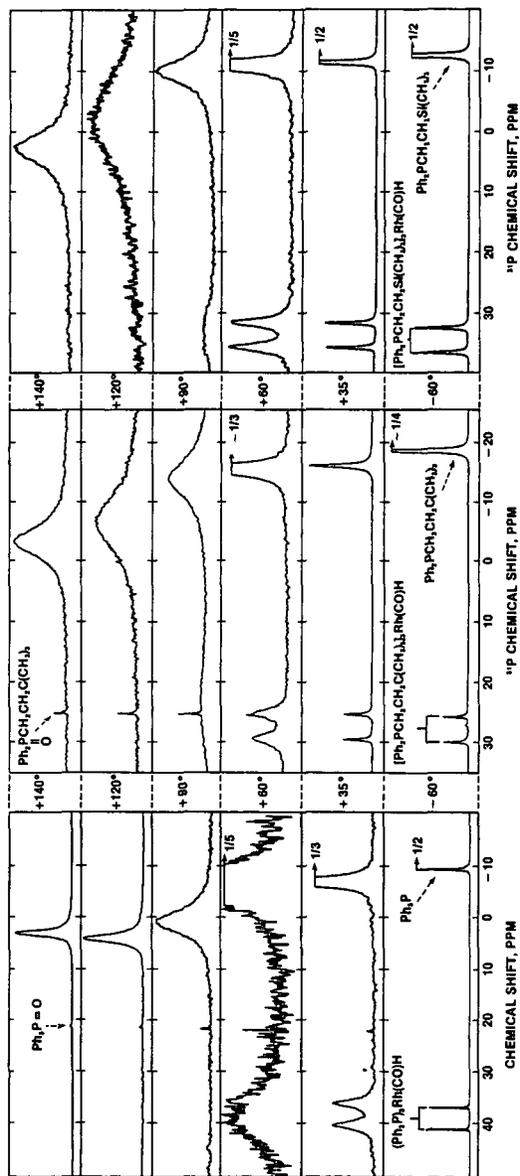


Figure 4

EFFECT OF TEMPERATURE ON ^{13}C NMR SPECTRUM: P/Rh = 9
 $\text{CO} + (\text{Ph}_3\text{P})_3\text{RhH} \rightleftharpoons [(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{H}] \rightleftharpoons (\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{H} + \text{Ph}_3\text{P}$

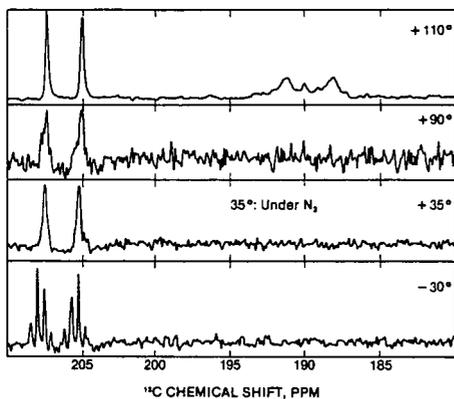


Figure 5

EFFECT OF EXCESS PHOSPHINE UNDER 200 kPa H_2/CO AT 0°
 $(\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})_2\text{H} + n\text{Ph}_3\text{P} \rightleftharpoons (\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})\text{H} + (n-1)\text{Ph}_3\text{P} + \text{CO}$

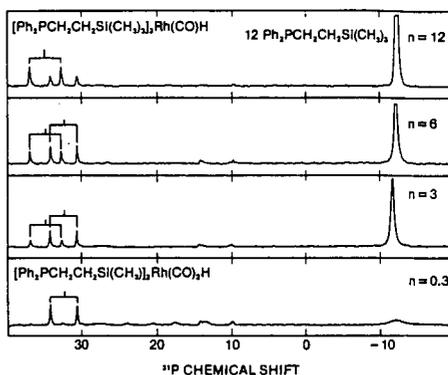


Figure 6

EFFECT OF TEMPERATURE ON ^{13}C NMR SPECTRUM: P/Rh = 9
 $\text{CO} + (\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})\text{H} \rightleftharpoons [(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})_2\text{H}] \rightleftharpoons \text{Ph}_3\text{P} + \text{Rh}(\text{CO})_2\text{H} + \text{Ph}_3\text{P}$

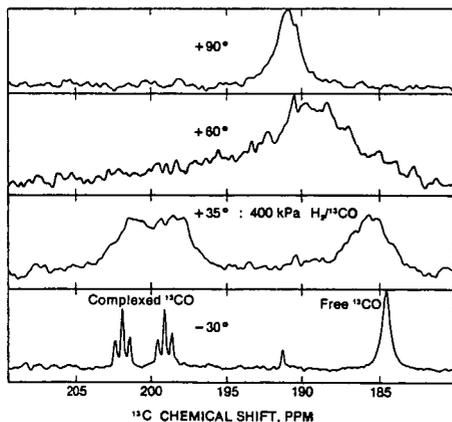


Figure 7

EFFECT OF MODERATE STERIC HINDRANCE
 ON LIGAND DISPLACEMENT AND EXCHANGE

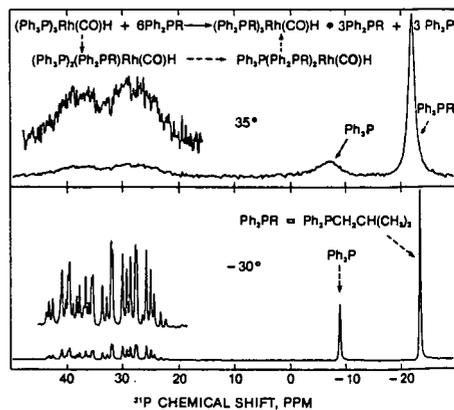


Table I

Δ HNP'S of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{R}$ LIGANDS AND ^{31}P NMR PARAMETERS^{a)}
OF THEIR $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{R}')_3\text{Rh}(\text{CO})\text{H}$ COMPLEXES

Phosphine Ligand		Phosphine Complex		
Structure	Inverse Basicity, b) ΔHNP	Chem. Shift ppm	Chem. Shift α , ppm	Coupling Constant $J_{\text{P-Rh}}$, cps
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$	385	-12.2	34.6	150
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$	412	-16.8	27.5	152
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	392	-16.8	27.5	151
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Ph}$	416	-16.6	27.6	153
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{-N} \begin{array}{c} \square \\ \diagdown \\ \text{O} \end{array}$	450	-23.0	21.6	151
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CO}_2\text{CH}_3$	455	-17.7	27.9	151
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SO}_2\text{CH}_3$	543	-18.6	27.3	151
Ph_3P	510	-7.5	38.3	155

- a) At 35° in toluene solvent, relative to 1M phosphoric acid.
 b) Basicity determinations were carried out according to the modified method of Streuli(17) using perchloric acid as a titrant and pure nitromethane as a solvent. Half neutralization potentials (HNP's) were determined relative to the value of diphenyl guanidine.

Table II

EFFECT OF TEMPERATURE ON THE HYDROFORMYLATION OF 1-RUTENE WITH
 TRIS-PHOSPHINE RHODIUM CARBONYL HYDRIDE CATALYSTS USING TRIPHENYLPHOSPHINE
 (TPP) AND 2-TRIMETHYLSILYL-ETHYLDIPHENYLPHOSPHINE (SEP) AS LIGANDS

Reactions at 2500 kPa of $5/1\text{H}_2/\text{CO}$ with 20g 1-Butene Plus 80g Mixture of 1 M Phosphine
 Ligand Plus 2-Ethylhexyl Acetate Using $\text{AcacRh}(\text{CO})_2$ as Catalyst Precursor

Seq. No.	Li-gand	Temp. °C	Rh Conc. mM	H ₂ /CO Feed	H ₂ /CO Ratio Final	H ₂ /CO Consumption Dependent Factors (at 50% Conversion)			Rate Constant			Re-action Time min	Aldehyde Linearity			Product Parameters			Ry-Products Selectivity %
						Normal-ized at 1 M Rh	k min ⁻¹	Found	n/1	100n			Total	Aldehyde Selectivity %	2-Ru-tenes	Ru-tane			
										Ratio	n + i						n	i	
1	SEP	110	4.00	52/48	4.9	8	0.032	22	7.6	88.4	93.9	83.0	10.9	4.3	1.8				
2		125	1.00	52/48	4.6	26	0.026	27	8.2	89.1	94.1	83.8	10.3	4.0	1.9				
3		135	1.00	53/47	5.1	46	0.046	15	9.8	90.8	90.2	81.9	8.3	5.9	3.9				
4		145	1.00	54/46	6.9	73	0.073	10	11.4	91.9	89.2	82.1	7.2	6.8	3.9				
5		160	0.50	56/44	6.9	130	0.065	11	11.3	91.9	82.8	76.1	6.7	10.8	6.4				
6		170	0.25	56/44	5.2	160	0.040	17	8.9	89.9	78.7	70.8	7.9	13.8	7.5				
7	TPP	90	3.00	52/48	5.0	11	0.033	22	12.3	92.5	89.6	82.8	6.8	7.7	2.7				
8		110	0.50	52/48	5.1	34	0.017	40	12.9	92.8	91.3	84.8	6.5	5.7	3.0				
9		125	0.50	52/48	4.7	116	0.058	12	11.9	92.3	89.1	82.2	6.9	7.9	3.1				
10		135	0.50	54/46	6.4	156	0.078	9	12.8	92.7	84.2	78.1	6.1	10.7	5.1				
11		145	0.25	54/46	5.7	200	0.050	14	11.2	91.8	81.2	74.6	6.6	13.3	5.5				
12		160	0.25	56/44	5.6	256	0.064	11	7.6	88.4	78.9	69.7	9.2	15.8	5.3				

Table III
EFFECT OF TRIPHENYLPHOSPHINE AND 2-TRIMETHYLSILYL-ETHYLDIIPHENYLPHOSPHINE LIGAND CONCENTRATION ON THE RHOIUM HYDROFORMULATION OF 1-RUTENE

Reactions at 145° at 2500 kPa of 5/1 H₂/CO Initial Reactant (53/47 or 54/46 H₂/CO Feed) and 20g 1-hutene Plus 80g Mixture of Phosphine Ligand Plus 2-Ethylhexyl Acetate, Using Acacrh(CO)₂ as Catalyst Precursor [SEP Ligand: Ph₂PCH₂CH₂Si(CH₃)₃]

Seq. No.	Catalyst System Parameters				H ₂ /M Consumption Dependent Factors (50% Conversion)				Product Parameters				By-Product Selectivity, %			
	Li-gand, L	M in Mixture at Start	Wt. % in Solvent	Rh Conc. mM	H ₂ /CO Ratio Final	Normal-ized at 1 M Rh	k min ⁻¹	Re-action Time min	Aldehyde Linearity 100n	Total n + 1	Aldehyde Selectivity, %	n		1	2-Bu-tenes	Ru-tane
1	TPP	0.14	4.7	0.05	2822	5.8	800	0.040	18	4.0	80.2	83.0	66.6	16.4	13.4	3.6
2				0.50	280	5.3	640	0.340	2	4.4	81.5	81.8	66.7	15.1	13.0	5.2
3		0.56	18.5	0.25	2240	5.1	320	0.080	9	7.6	88.4	82.3	73.6	9.7	11.7	5.1
4				2.00	200	4.9	285	0.570	1.5	7.2	87.0	80.0	70.3	9.7	14.0	5.9
5		1.00	32.9	0.25	4000	5.7	200	0.050	14	11.2	91.8	81.2	74.6	6.6	13.3	5.5
6				2.00	500	5.2	220	0.440	2	11.1	91.7	82.1	75.3	6.8	12.7	5.3
7		2.20	72.1	0.25	4400	5.9	92	0.023	32	21.7	95.6	80.0	76.5	3.5	14.3	5.7
8				2.00	1100	5.2	90	0.180	4	21.5	95.0	81.0	77.4	3.6	13.5	5.5
9		3.00	100.0	2.00	1500	3.6	48	0.096	9	31.0	96.9	73.3	71.0	2.3	19.6	7.1
10	SEP	0.14	5.0	0.10	1400	5.0	180	0.036	19	4.6	82.2	90.7	74.6	16.1	6.5	2.8
11				0.50	280	5.4	200	0.100	4	5.1	83.5	86.2	72.0	14.2	7.6	6.2
12		0.56	20.0	0.25	2240	5.5	132	0.033	21	8.0	88.8	89.6	79.6	10.0	7.0	3.4
13				2.00	200	6.0	105	0.210	3.5	9.9	90.9	86.1	78.2	7.9	8.2	5.7
14		1.00	35.9	0.50	2000	6.9	68	0.034	20	12.2	92.4	87.5	80.9	6.6	8.3	4.2
15				2.00	500	5.9	70	0.140	5	11.7	92.1	86.4	79.6	6.8	7.4	6.2
16		2.20	78.7	1.00	2200	5.1	38	0.038	18	14.6	93.6	86.9	81.3	5.6	8.7	4.4
17				2.00	1100	5.6	35	0.070	9	15.1	93.8	84.0	78.8	5.2	9.1	6.9
18		2.80	100.0	2.00	1400	5.6	25	0.050	15	20.1	95.2	82.8	78.9	3.9	9.1	8.0

Table IV

CONTINUOUS HYDROFORMYLATION OF 1-BUTENE IN THE PRODUCT FLASH-OFF MODE
WITH SEP-Rh AND $\text{Ph}_3\text{P-Rh}$ COMPLEX CATALYST SYSTEMS

	<u>TPP</u>	<u>SEP</u>	<u>SEP</u>	<u>SEP</u>	<u>SEP</u>	<u>TPP</u>
• Temperature, °C	100	120	120	140	140	140
Pressure, kPa	800	1050	1050	1275	1275	1275
P_{H_2} , kPa	565	675	760	724	775	724
P_{CO} , kPa	69	90	83	138	149	138
• Rhodium Conc., mM	2.50	2.50	4.44	4.44	4.44	4.44
• Phosphine Conc., mM	310	600	360	1000	1000	1000
1-Butene Feed, mole/hr/L	4.0	4.0	4.0	2.8*	2.8	2.8
Aldehyde Product, mole/hr/L	1.0	1.0	1.5	1.6	1.6	2.3
• Conversion per Pass, %	26	26	38	56	60	82
				52**	55**	65**
• n/i Selectivity %	92	92	91	90	90	84
n/i ratio	21	22	21	35	32	29
Hydrocarbon Selectivity, %	7	7	7	8	9	14
• Stripping Gas, mole/hr/L	35	25	38	24	24	21

*Plus 3 mole/hr/L 2-butenes **After 6 days operation

Table V

HYDROFORMYLATION OF 1-BUTENE WITH VARIOUS TRIS-PHOSPHINE RHODIUM CARRONYL HYDRIDE CATALYSTS

Reactions at 145° at 2500 kPa of 5/1 H_2/CO (54/46) Feed and 20g 1-Butene Plus 80g Mixture of 1M Phosphine Plus 2-Ethylhexyl Acetate Using $AcacRh(CO)_2$ as a Catalyst Precursor

Ligand No.	Ligand Structure	Rh Conc. mM	Ligand Conc. M/Kg	Final H_2/CO Ratio	Rate Constant k_p , min ⁻¹ $\frac{d[CO]}{dt}$, 1MRh	Re-action Time min.	Linearity $n \times 100$		Selectivities, Mole %			By-Products 2-Ru-tenes	Ru-tene
							n/1 Ratio	n + 1 %	n+1	n	1		
1	$Ph_2PCH_2CH_2Si(CH_3)_3$	1.0 0.1	1 0.14	6.2 5.1	86 363	16 19	8.9 4.6	89.9 82.2	87.1 90.7	78.3 74.6	8.8 16.1	7.7 6.5	5.2 2.8
2	$Ph_2PCH_2CH_2C(CH_3)_3$	0.5 0.1	1 0.14	5.5 5.4	100 490	14 14	9.8 4.4	90.7 81.6	88.6 90.4	80.4 73.7	8.2 16.7	7.9 6.9	3.5 2.7
3	$Ph_2P(CH_2)_5CH_3$	0.5 0.5	1 0.14	5.3 5.9	96 282	14 5	8.8 4.3	89.8 81.0	89.7 88.9	80.6 72.0	9.2 16.9	6.7 6.9	3.6 4.2
4	$Ph_2PCH_2CH_2$ 	0.5 0.25	1 0.14	5.2 4.9	90 552	16 5	10.7 5.5	91.5 84.6	90.9 90.2	83.1 76.3	7.8 13.9	6.4 6.2	2.7 3.6
5	$Ph_2PCH_2CH_2$ 	0.5 0.5	1 0.14	4.5 4.9	92 288	15 5	9.3 5.4	90.3 84.3	91.8 90.6	82.9 76.3	8.9 11.3	5.6 4.6	2.6 4.8
6	$Ph_2PCH_2CH_2SO_2C_2H_5$	0.5 0.25	1 0.14	5.2 5.8	26 64	52 44	18.9 5.7	95.0 85.2	88.1 86.8	83.7 73.9	4.4 12.9	8.1 9.3	3.8 3.9
7	Ph_3P	0.25 0.05	1 0.14	5.7 5.8	200 800	14 18	11.2 4.0	91.8 80.2	81.2 83.0	74.6 66.6	6.6 16.4	13.3 13.4	5.5 3.6

Table VI

EFFECT OF THE BRANCHING OF ALKYL DIPHENYL PHOSPHINE LIGANDS ON THE RATE AND SELECTIVITY OF RHODIUM HYDROFORMYLATION

Reactions at 2500 kPa, with 5 to 1 H₂/CO and 20g 1-Butene Plus 80g Mixture of Alkyl Diphenyl Phosphine Ligand and 2-Ethylhexyl Acetate Solvent, Using AcacRh(m)₂ as Catalyst Precursor at 145°C

Seq. No.	Catalyst System Parameters Ph ₂ PR Ligand Conc. M	Rh Conc. mm	L/Rh Ratio	H ₂ /CO Feed Ratio	H ₂ /CO Final Ratio	Rate Constant		Re-action Time min	Aldehyde Linearity 100n	Selectivities, Mole %						
						Normalized at 1 M Rh	k min ⁻¹			n/1 Ratio	Aldehydes Total	By-Products 2-Ru-tenes				
1	-CH ₂ CH ₂ CH ₂ CH ₃	1.0	0.25	4000	53/47	5.2	120	0.030	23	9.6	90.5	88.7	80.3	8.4	7.8	3.5
2		0.14	0.010	1400	53/47	5.5	530	0.053	13	4.2	80.8	89.1	72.0	17.1	7.8	3.1
3	-CH ₂ CH ₂ C(CH ₃) ₃	1.0	0.50	2000	53/47	5.5	100	0.050*	14*	9.8	90.7	88.6	80.4	8.2	7.9	3.5
4		0.14	0.10	1400	53/47	5.3	490	0.049	14	4.4	81.6	90.4	73.7	16.7	6.9	2.7
5	-CH ₂ C(CH ₃) ₃	1.0	0.10	10000	54/46	4.9	250	0.025	27	2.6	72.5	62.9	45.6	17.3	34.7	2.4
6		0.14	0.25	560	54/46	5.0	284	0.071*	23*	1.7	63.4	52.7	33.4	19.3	44.5	2.8
7	-CH ₂ CH(CH ₃) ₂	1.0	0.25	4000	54/46	6.5	232	0.058	12	4.4	81.6	86.8	70.8	16.0	9.6	3.6
8		0.14	0.10	1400	54/46	6.0	580	0.058	12	3.3	76.9	76.5	58.8	17.7	21.0	2.5
9	-CH(CH ₃) ₂ CH ₃	1.0	0.20	2800	53/47	5.4	220	0.044	16	3.4	77.2	86.5	66.8	19.7	10.5	3.0
10		0.14	0.05	2800	53/47	5.3	460	0.023	30	3.2	76.2	69.3	52.8	16.5	28.1	2.6
11		1.00	0.20	5000	53/47	5.3	40	0.008*	92*	3.6	78.2	87.5	68.4	19.1	9.4	3.1
12		0.14	0.10	1400	53/47	5.5	370	0.037*	20*	3.2	76.2	75.4	57.5	17.9	22.0	2.6
13		1.0	0.20	5000	53/47	5.4	190	0.038	18	5.4	84.5	88.1	74.4	13.7	8.4	3.5
14		0.14	0.05	2800	53/47	5.5	500	0.025	27	3.4	77.1	8.2	63.4	18.8	15.0	2.8

*The rate of reaction was decreasing with time. The initial rate is listed.