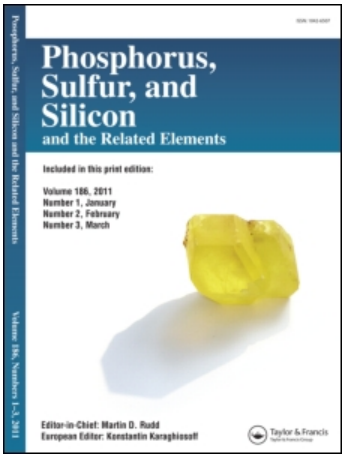


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# Regulation of Catalytic Activity by Phosphine Ligand Design

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# REGULATION OF CATALYTIC ACTIVITY BY PHOSPHINE LIGAND DESIGN

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Abstract Starting with the catalytic complex $[Rh(PPh_3)_3Cl]$, the influence of variation of phosphine ligand properties on the activity of rhodium phosphine complexes as catalysts for the hydrogenation of olefins was systematically studied. The following catalyst modifications were examined (a) varying the basicity of the triarylphosphine ligands, (b) replacing $Cl^-$ by a non-coordinating anion ($BF_4^-$) to make the catalyst cationic, (c) substituting a chelating diphosphine for the monophosphine ligands to ensure cis-coordination, and (d) varying the chain length of the diphosphine ligand to vary the chelate ring size and flexibility. By systematic manipulation of these parameters, enhancements of catalytic activity by factors in excess of $10^4$ were achieved.



## INTRODUCTION

The range and variety of tertiary phosphines that are utilized as ligands in transition metal complex catalysts, and the widespread importance of phosphine ligands in this context, are unparalleled by any other class of ligands.[1] A variety of factors contribute to this distinctive and versatile role of phosphine ligands, notably their ability to accommodate a wide range of metal oxidation states and the scope for varying the electronic and, particularly, the steric properties of such ligands.

Notwithstanding the widespread recognition of this important role, the choice of phosphine ligands for catalytic applications has generally been either "casual" (for example, the widespread use of the convenient and readily available triphenylphosphine ligand) or based on empirical considerations. This paper addresses the scientific basis for the selection and design of phosphine ligands for catalytic complexes and for the regulation

of catalytic activity.

The ability to relate ligand properties to catalytic activity clearly rests upon an understanding of the catalytic mechanism. Catalytic reactions such as hydrogenation and hydroformylation typically proceed through multistep mechanisms involving sequences of steps such as oxidative addition, migratory insertion and reductive elimination.[2] We have previously identified and elaborated, in some detail, such mechanistic sequences for the hydrogenation of olefins catalyzed by $[Rh(PPh_3)_3Cl]$ (Wilkinson's catalyst)[2] and $[Rh(PPh_2CH_2CH_2PPh_2)(MeOH)_2]^+$.[3,4] For optimal catalytic activity the rates of all the steps in such a sequence should be high and, preferably, comparable. Enhancement of catalytic activity requires the simultaneous enhancment of the rates of several chemically diverse steps. One approach to achieving this is through the appropriate choice of the ligands of the catalytic complex. Phosphine ligands, which lend themselves so effectively to systematic variation of electronic and structural parameters, have played a particularly important role in this context. The potential for even greater accomplishment along these lines is enhanced with our increasing mechanistic understanding of catalytic reactions and with the accessibility of a wider range of phosphine ligands (for example, chiral phosphine ligands for asymmetric catalysis).[5]



## RESULTS AND DISCUSSION

Starting with $[Rh(PPh_3)_3Cl]$, we have systematically examined, in the most extensive such study to date, the influence of ligand variation on the activity of rhodium phosphine complexes as hydrogenation catalysts. The following are among the more significant results of this study.

1. The catalytic activity of complexes of the type $[Rh\{P(p\text{-}C_6H_4X)_3\}_3Cl]$ is enhanced, from a limiting turnover frequency of ca 0.05 $sec^{-1}$ to 0.5 $sec^{-1}$ at 25°C, by increasing the

basicity of the phosphine (i.e., by electron donating substituents, X = $CH_3$, $OCH_3$, etc.). This is attributed to increasing the driving force of the migratory insertion step, $[RhH_2(\text{-}C{=}C\text{-})(PR_3)_2Cl] \longrightarrow [RhH(\text{-}C\text{-}\overset{|}{C}H)(PR_3)_2Cl]$, by stabilizing the coordinately unsaturated (electron-deficient) product.

2. Substantial enhancement of catalytic activity (along with some modification of the catalytic mechanisms) is observed for cationic complexes, i.e., $[Rh(PR_3)_2S_2]^+$, generated by replacement of $Cl^-$ with a non-coordinating ion such as $BF_4^-$ in a weakly coordinating solvent (S) such as methanol. This is attributed to enhanced susceptibility of the coordinated olefin to nucleophilic attack (i.e., by a migrating "$H^-$" ligand) in the migratory insertion step.

3. Substantial further enhancement of the catalytic activiity, resulting in a limiting turnover frequency of ca 20 $sec^{-1}$ at 25°C is obtained by replacing the monodentate phosphine ligands with a chelating diphosphine such as 1,2-bis(diphenylphosphino)ethane, i.e., using the complex $[Rh(PPh_2CH_2CH_2PPh_2)S_2]^+$ as catalyst. This is attributed to the higher activity of the catalytic pathway involving a cis-diphosphine complex, relative to the trans-diphosphine complex which is the predominant species with monodentate phosphine ligands.

4. Increasing the chain length of the diphosphine chelate ring along sequence of catalytic complexes $[Rh\{PPh_2(CH_2)_nPPh_2\}S_2]^+$, with n = 2, 3 or 4, results in further substantial enhancement of the catalytic activity, reflected in higher rates of all the component steps of the catalytic sequence and in limiting turnover frequencies approaching $10^4$ $sec^{-1}$ at 25°C.[6] This is attributed to the increasing flexibility associated with increasing chelate ring size, facilitating the attainment of the favored transition state geometries of the various reaction steps. Further increase in the chelate ring size

(n = 5) resulted in the formation of the metallated complex, $[Rh\{PPh_2CH_2CH_2\overset{\frown}{C}HCH_2CH_2PPh_2\}H(MeOH)_2]^+$, involving intramolecular oxidative addition of an unactivated C-H bond to the Rh atom; this further attests to the remarkably high reactivity of the $[Rh\{PPh_2(CH_2)_5PPh_2\}(MeOH)_2]^+$ complex.[6]

## CONCLUDING REMARKS

By such systematic and rational variation of the phosphine ligands, it proved possible to increase the catalytic activity of rhodium phosphine complexes, from a limiting turnover frequency of ca $10^{-1}$ $sec^{-1}$ for $[Rh(PPh_3)_3Cl]$ by factors in excess of $10^4$ to unprecedentedly high levels. Furthermore, such highly active catalysts also were found to be effective for the hydrogenation of characteristically unreactive substrates, for example, of naphthalene to 1,2,3,4-tetrahydronaphthalene and (with unusual regioselectivity) of anthracene to 1,2,3,4-tetrahydroanthracene.[7]

The understanding yielded by these studies of the relation between phosphine ligand properties and catalytic activity has important implications for further advances in the design of catalytic complexes and the regulation of catalytic activity and selectivity.



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