



This is to certify that the

thesis entitled

*The Utilization of a Cationic Ligand
for the Intercalation of Catalytically Active
metal complexes in Swelling, Layer-Lattice
presented by silicates*

William Harold Quayle

has been accepted towards fulfillment
of the requirements for

Ph. D. degree in Chemistry

J. J. Hinreiner
Major professor

Date Sept 11, 1978

THE UTILIZATION OF A CATIONIC LIGAND FOR
THE INTERCALATION OF CATALYTICALLY ACTIVE METAL
COMPLEXES IN SWELLING, LAYER-LATTICE SILICATES

By

William Harold Quayle

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1978

ABSTRACT

THE UTILIZATION OF A CATIONIC LIGAND FOR THE INTERCALATION OF CATALYTICALLY ACTIVE METAL COMPLEXES IN SWELLING, LAYER-LATTICE SILICATES

By

William Harold Quayle

The substitution of a positively charged phosphine ligand, $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{CH}_2\text{Ph})\text{BF}_4$, $(\text{P}-\text{P}^+\text{BF}_4)$, for PPh_3 in the preparation of a Wilkinson type complex, RhClL_x , has generated a cationic olefin hydrogenation catalyst. The catalyst employing a 1:1:1 ratio of $\text{P}-\text{P}^+\text{BF}_4:\text{PPh}_3:\text{Rh(I)}$ (A) is active for the hydrogenation of 1-hexene both in methanol solution and when exchanged within the intracrystal space of the mineral hectorite.



(Hectorite is a swelling, mica-like magnesio-silicate with cation exchange properties). Significantly, the activity of the mineral supported catalyst was about 1.9 times greater than the homogeneous catalyst.

^{31}P nmr studies have indicated that the 1:1:1 catalyst (A) is a mixture of two or more cationic, mixed phosphine, rhodium(I) chloride complexes that generate highly active intermediates for olefin hydrogenation. These intermediates are probably analogous to those proposed¹ for the uncharged RhClL_x system. Hectorite appears to increase the catalytic activity of the 1:1:1 system. This may be attributed to the solution-like environment within the support and the

ability of the large negatively charged silicate sheets to alter the stoichiometry and geometry of the complexes involved.

These results show that positively charged ligands may be employed to produce active cationic transition metal catalysts which are analogous to known, otherwise neutral, homogeneous catalysts and which are capable of electrostatic attachment to an anionic support. In particular, hectorite seems an ideal support for immobilization of such catalysts. Further implementation of this innovation should allow the simple, convenient preparation of a variety of cationic complexes and catalysts which would not be susceptible to desorption from anionic supports and which may also extend the range of solvent systems available to certain homogeneous catalysts.

It was found that 2:0:1 and 3:0:1 ratios of $P-P^+BF_4$, PPh_3 :Rh(I) generated complexes which were capable of oxidatively adding H_2 , but were inactive as olefin hydrogenation catalysts both in solution and when supported in the mineral environment. Similarly, Rh(I) and Rh(III) complexes bound to hectorite which had been exchanged with the cationic phosphine ligand ($P-P^+/Hect$) also added hydrogen but were catalytically inactive. The inactivity of these systems for olefin hydrogenation was attributed to steric crowding at the rhodium center by the bulky positively charged ligand, which interferes with the dissociative and associative processes that must occur within the metal's coordination sphere in order for catalysis to occur. The cationic ligand

does play an active role in the reactivity of the 1:1:1 catalyst, however since a 1:1 $\text{PPh}_3:\text{Rh}$ system is a very poor catalyst and loses activity very soon after initiation of the reaction. In addition, ^{31}P nmr studies have shown that all of the cationic ligand is bound to the rhodium in the 1:1:1 system. The coordination of $\text{P-P}^+\text{BF}_4$ with the less bulky ligand, PPh_3 , generates complexes which are not as sterically crowded, resulting in active catalytic species.

A rhodium(I) complex containing the cationic ligand was isolated and characterized by ir, ^1H nmr and ^{31}P nmr spectroscopy. It was found, as expected, that $[\text{RhCl}(\text{COD})-(\text{P-P}^+)]\text{BF}_4$ was spectroscopically similar to the analogous $\text{RhCl}(\text{COD})(\text{PPh}_3)$ complex.

Contact of $[\text{RhCl}(\text{COE})_2]_2$ with hectorite, $\text{P-P}^+/\text{Hect}$, kaolinite or silica gel, for 24 hours, resulted in the formation of supported Rh(0) materials. These materials were comparable in activity to commercial 5% Rh(0) on alumina for the hydrogenation of 1-hexene and benzene. The Rh(0) formation was attributed to a surface catalyzed disproportionation reaction of $[\text{RhCl}(\text{COE})_2]_2$ to Rh(0) and Rh(III) species. It was found that silylation of the surface hydroxyl groups of hectorite by a mixture of $(\text{Me}_3\text{Si})_2\text{NH}$ and Me_3SiCl inhibited the disproportionation reaction.

1. C. A. Tolman, P. Z. Meakin, D. L. Lindner, J. P. Jesson, J. Am. Chem. Soc., **96**, 2762 (1974).

**This work is dedicated to Laura with love,
a good day today and a better day tomorrow.**

ACKNOWLEDGMENTS

I wish to thank Dr. Thomas J. Pinnavaia for his patient assistance in making my graduate school experience one which was academically fulfilling, spiritually uplifting and for the most part, eminently enjoyable. I am also most grateful for the editorial assistance given by my second reader, Dr. Bruce A. Averill. Special acknowledgement is due for the excellent faculty, the research and support staff, and the facilities at Michigan State University.

The early encouragement and advice provided by Dr. Arnold L. Rheingold, Dr. Gerald Kokoszka, Dr. Robert Ellsworth and Mr. John R. Maloney has been a continuing motivational force in these and other endeavors.

The National Science Foundation and MSU furnished financial support for this study.

TABLE OF CONTENTS

	Page
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF SYMBOLS AND ABBREVIATIONS	x
I. INTRODUCTION.	1
A. Foundation, Homogeneous and Heterogeneous Catalysts	1
B. Background, Supported Metal Complex Catalysts	3
C. The Use of Hectorite as a Catalyst Support.	13
D. Rationale, the Use of Cationic Ligands in Metal Complex Catalysts.	17
II. EXPERIMENTAL.	21
A. Solvents and Reagents	21
B. Physical Methods.	22
1. Infrared Spectra.	22
2. Proton NMR Studies.	23
3. Phosphorus-31 NMR Studies	23
4. X-ray Diffraction Study	25
5. Elemental Analysis and Melting Points.	25

	Page
C. Syntheses	25
1. Known Rhodium Complexes	25
2. 1-Diphenylphosphino-2-benzyl- diphenylphosphoniummethane bromide .	27
3. Tetrafluoroborate Anion Exchange Resin	28
4. 1-Diphenylphosphino-2-benzyl- diphenylphosphoniummethane tetrafluoroborate	28
5. Chloro(1,5-cyclooctadiene) (1- diphenylphosphino-2-benzyl- phenylphosphoniummethane) rhodium(I) tetrafluoroborate. . . .	29
6. 1-Diphenylphosphino-2-benzyl- diphenylphosphoniummethane Exchanged Hectorite	29
7. Silylated Montmorillonite	30
D. Hydrogenation Studies and Catalyst Preparation	30
1. Hydrogenation Procedure and Apparatus	30
2. Homogeneous Catalysts	33
3. Heterogeneous Catalysts and Materials	34

	Page
III. RESULTS AND DISCUSSION.	40
A. Preparation and Characterization of P-P ⁺ BF ₄ and [RhCl(COD)(P-P ⁺)]BF ₄	40
B. Heterogeneous Systems I	52
1. RhCl(PPh ₃) ₃ /Hect, RhCl ₃ /Hect, P-P ⁺ /Hect, RhCl(PPh ₃) ₃ /P-P ⁺ /Hect, RhCl ₃ /P-P ⁺ /Hect and [RhCl(COE) ₂] ₂ /P-P ⁺ /Hect	52
2. Rh(0)/P-P ⁺ /Hect, Rh(0)/Hect, Rh(0)/Kaol and Rh(0)/SILG	54
3. R ₃ Si/Mont and [RhCl(COE) ₂] ₂ / R ₃ Si/Mont	56
C. Homogeneous Systems	58
1. Hydrogenations Employing O:X:1 P-P ⁺ BF ₄ :PPh ₃ :Rh Catalysts	59
2. Hydrogenations Employing Y:X:1 P-P ⁺ BF ₄ :PPh ₃ :Rh Catalysts	61
3. Characterization of Catalyst Precursors.	66
D. Heterogeneous Systems II. Hydrogenations Employing 1:1:1/Hect, 0:2:1/Hect, Rh(COD)(PPh ₃) ₂ ⁺ /Hect, 2:0:1/Hect and 3:0:1/Hect	91
IV. CONCLUSIONS AND RECOMMENDATIONS	97
BIBLIOGRAPHY.	104

LIST OF TABLES

Table	Page
1. Materials Used to Support Metal Complexes .	5
2. Methods for Binding Metal Complex Catalysts to Supports	7
3. Relevant 180 MHz Proton NMR Data for $P-P^+BF_4$ and $[RhCl(COD)(P-P^+)]BF_4$	44
4. Initial Hydrogenation TO#'s for Supported Rh(0) Catalysts	57
5. TO#'s for O:X:1 Hydrogenation Catalysts . .	60
6. TO#'s for Y:X:1 Hydrogenation Catalysts . .	62
7. TO#'s for 1:1:1/Hect, 1:1:1, 0:2:1 and Rh(COD)(PPh ₃) ₂ ⁺ Hydrogenation Catalysts. MINTO#'s for 0:2:1/Hect and Rh(COD)(PPh ₃) ₂ ⁺ / Hect Hydrogenation Catalysts.	92
8. Some Known Homogeneous Catalysts Potentially Suitable for Modification by Positively Charged Ligands	102

LIST OF FIGURES

Figure	Page
1. Schematic representation of hectorite structure	14
2. Hydrogenation apparatus (schematic)	32
3. Infrared spectra of $P-P^+BF_4$ (A) and $[RhCl(COD)(P-P^+)]BF_4$ (B) as nujol mulls between CsI salt plates. Insets were taken as fluorolube mulls.	42
4. 36.43 MHz ^{31}P nmr spectra of $P-P^+BF_4$ (A), $[RhCl(COD)(P-P^+)]BF_4$ (B) and $RhCl(COD)(PPh_3)$ (C) at 28° in CH_2Cl_2 . . .	46
5. Temperature dependent ^{31}P nmr spectra of $[RhCl(COD)(P-P^+)]BF_4$, 0.1 M in CH_2Cl_2 . The -80° spectrum was obtained at twice the instrument gain of the others.	51
6. Temperature dependent ^{31}P nmr spectra of $RhCl(COD)(PPh_3) + PPh_3$, 0.03 M in CH_2Cl_2 .	69
7. Temperature dependent ^{31}P nmr spectra of $RhCl(COD)(PPh_3) + PPh_3 + xH_2$, 0.03 M in CH_2Cl_2	74

8. Temperature dependent ^{31}P nmr spectra of $\text{RhCl}(\text{COD})(\text{PPh}_3) + \text{PPh}_3 + x\text{H}_2 + y(1\text{-hexene})$ 0.03 M in CH_2Cl_2 . The $+30^\circ$, -42° and -61° spectra were taken at twice the instrument gain of the $+1^\circ$ and -21° spectra. 77
9. Temperature dependent ^{31}P nmr spectra of $[\text{RhCl}(\text{COD})(\text{P-P}^+)]\text{BF}_4 + \text{PPh}_3$. 0.03 M in CH_2Cl_2 81
10. Temperature dependent ^{31}P nmr spectra of $[\text{RhCl}(\text{COD})(\text{P-P}^+)]\text{BF}_4 + \text{PPh}_3 + \text{H}_2$. 0.03 M in CH_2Cl_2 84
11. ^{31}P nmr spectra of CH_2Cl_2 solutions containing: A, $\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2 + \text{PPh}_3$; B, $\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2 + 2\text{PPh}_3$; and C, $\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2 + 3\text{PPh}_3$. A and B, $+28^\circ$; C, -34° 87
12. ^{31}P nmr spectrum of $[\text{RhCl}(\text{COE})(\text{P-P}^+)]_2(\text{BF}_4)_2$ at $+28^\circ$, 0.05 M in CH_2Cl_2 90

LIST OF SYMBOLS AND ABBREVIATIONS

acac	acetylacetonate
BBP	benzylbutylphthalate
$\text{BF}_4^-/\text{Resin}$	tetrafluoroborate anion exchange resin
Bu	butyl
COD	1,5-cyclooctadiene
COE	cyclooctene
Cp	cyclopentadienyl
CT	catalyst turnover
d	doublet
ddt	doublet of doublets of triplets
diphos	bis(1,2-diphenylphosphino)ethane
dipy	2,2'-dipyridyl
dt	doublet of triplets
esr	electron spin resonance
Et	ethyl
L	ligand (usually phosphine)
L^+	cationic ligand
m	multiplet
M	metal
Me	methyl
MINTO#	minimum turnover number

NBD	norbornadiene
nmr	nuclear magnetic resonance
P	phosphorus nucleus (usually in a phosphine)
P ⁺	phosphonium phosphorus nucleus
Ph	phenyl group
P-P ⁺	1-diphenylphosphino-2-benzyl-diphenylphosphoniummethane
P-P ⁺ BF ₄	P-P ⁺ tetrafluoroborate
P-P ⁺ Br	P-P ⁺ bromide
P-P ⁺ /Hect	P-P ⁺ exchanged form of hectorite
py	pyridine
P)-, P)-Br, P)-N(CH ₃) ₃ ⁺ , P)-SO ₃ ⁻ , P)-Y	polymer supported functional groups
R ₃ Si/Mont	silylated montmorillonite
s	singlet
S	usually solvent molecule
Si)-O ⁻ , Si)-O-	silica hydroxyl group functionality
TMS	tetramethylsilane
TO#	turnover number
X	usually halogen or - as below - unknown material
X/Hect, X/P-P ⁺ /Hect, X/Kaol, X/SILG, X/R ₃ Si/Mont, X/Y-Zeolite	designations for materials and/or catalysts supported on hectorite, P-P ⁺ /Hect, kaolinite, silica gel, R ₃ Si/Mont or Y-Zeolite - respectively

1:1:1, 0:2:1, etc.

designations for homogeneous catalysts generated in situ from $[\text{RhCl}(\text{COD})]_2$, $\text{P}-\text{P}^+\text{BF}_4^-$, $\text{PPh}_3:\text{Rh}$

)- PPh_2 ,)- PR_2

phosphine functional groups on supports, usually silica or polymer

INTRODUCTION

A. Foundation, Homogeneous and Heterogeneous Catalysts

During the past two decades transition metal catalysts in homogeneous solution have found more and more application in the promotion of industrially important chemical processes. Examples of the larger scale processes are the hydroformylation of propylene to butyraldehyde over cobalt carbonyl complexes (oxo process),¹ the aqueous oxidation of ethylene to acetaldehyde with palladium salts (Wacker process),^{2,3} the hydration of acetylene to acetaldehyde with mercury and iron salts,² the production of vinyl^{2,4} and substituted⁵ vinyl acetates from olefins and acetic acid over palladium salts, the production of phenol by the oxidation of toluene over cobalt and copper salts (Dow toluene-benzoic acid process),² and the production of acetic acid from methanol and carbon monoxide with rhodium complexes (Monsanto process).⁶ Concurrent advances in the field of transition metal organometallic chemistry have had a synergistic effect on the rapid development and mechanistic understanding of these systems.⁷

Theoretically, catalysis by discrete, soluble, transition metal complexes offers a number of distinct advantages over traditional heterogeneous transition metal catalysis, where

reactions occur at solid-gas or solid-liquid interfaces. Each metal complex is available for reaction in a homogeneous system, whereas metal centers below the active surface sites in heterogeneous catalysts are not accessible. This results in greater overall catalytic efficiency and allows easier interpretation of kinetics studies in homogeneous systems.

Despite the progress which has been made in the area of surface analysis in recent years,⁸ detailed understanding of chemisorption-catalysis mechanisms is generally impracticable in heterogeneous systems because the surface structure is too easily altered by slight changes in catalyst preparation, pretreatment and reaction conditions. In contrast, homogeneous catalysts are readily characterized by powerful solution analysis and spectroscopic techniques. As a consequence, they are much easier to control with respect to specificity for substrates, product selection and reproducibility from batch to batch. Control of the electronic and steric requirements of a given metal center for a particular reaction can be modified through judicious choice of ligand and/or solvent system.

Homogeneous catalysts suffer from three major practical problems, however, which are sufficient to preclude their use in most industrially important processes. First, unlike heterogeneous systems, separation of the homogeneous catalyst from the products at the end of the reaction is a major difficulty. Distillation is often inefficient, resulting in

loss of catalyst and/or product contamination. It may also destroy thermally unstable catalysts and/or leave behind high-boiling reaction byproducts. Extraction of the catalyst or products with other solvents is beset with similar problems. Even if the separation can be made sufficiently efficient, the cost of the resulting process may often be prohibitive.

Second, homogeneous catalysts, particularly organometallic complexes, exhibit poor thermal stability compared to heterogeneous catalysts. Although reactions are often catalyzed efficiently under mild conditions, a desired increase in the reaction rate as a result of increased temperature is often limited in these systems.

Third, the term "soluble" catalyst is almost a misnomer for many complexes since they are often only slightly soluble, and most are soluble or active in only a limited range of solvents. This feature often limits the number of possible substrates for a given catalyst system. Heterogeneous catalysts are not so restricted by solvent considerations.

B. Background, Supported Metal Complex Catalysts

A number of review papers have highlighted the efforts of a growing authorship attempting to combine the attractive virtues of homogeneous catalysts with the practical engineering aspects of heterogeneous catalysts.⁹ The basic approach in this area has been to devise methods by which the more efficient, selective, homogeneous catalysts may be separated readily from the reactants/products. Efficient catalyst-product separation has been achieved in homogeneous systems

using: (i) complexes thermally stabilized in molten ligand solvents;¹⁰ (ii) separation of catalysts from products in biphasic solvent systems;¹¹ (iii) separation of products through selective, permeable membranes;^{12,13} or (iv) catalysts bound to soluble, high molecular weight polymers.¹³

However, the supereminent method in this approach has been the attachment of otherwise homogeneous transition metal catalysts to a variety of insoluble supports. In general, this method offers the ease of separation, thermal stability, reactant/product phase flexibility, and development of efficient flow and/or batch processes usually associated with heterogeneous catalysts. Moreover, these systems usually allow a greater degree of reaction control, specificity, reproducibility and efficiency associated with their homogeneous counterparts. In certain cases the support even enhances the activity and/or specificity of the catalyst by reducing the number of unwanted side reactions¹⁴ and/or preferentially selecting certain reagents over others based on molecular size restrictions¹⁵ or dipolar effects.¹⁶

Hartley's list of materials which have been used to support metal complex catalysts^{9h} is reproduced in Table 1. Of course, the choice of a particular support depends very much on the gross properties of the catalyst system and the desired effect of the supported catalyst on the specificity of the reaction. In general, inorganic materials have better mechanical and thermal stabilities under most reaction conditions than organic supports. However, organic polymers

Table 1. Materials Used to Support Metal Complexes*

<u>Inorganic</u>	<u>Organic</u>
Silica	Polystyrene
Zeolites	Polyamines
Glass	Polyvinyls
Clay	Polyallyls
Metal Oxides (alumina, etc.)	Polybutadiene
	Polyamino acids
	Urethanes
	Acrylic polymers
	Cellulose
	Cross-linked dextrans
	Agarose

*taken from F. R. Hartley, P. N. Vezey, Advan. Organometal. Chem., 17, 189 (1977).

offer a wider range of surface flexibility, pore size, surface area, and polar group functionalization than the usual inorganic supports (silica, glass, metal oxides).

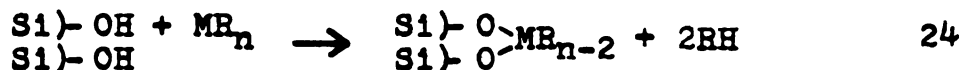
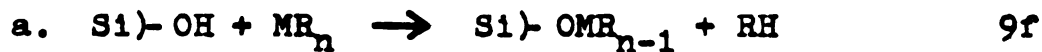
A partial list of the variety of methods which have been used to support catalysts is provided in Table 2. Many of these result in supported metal catalysts which have no counterparts in homogeneous solution. These are particularly interesting systems because each catalyst site has a molecularity identical to that of its neighbors. These catalysts therefore offer greater site specificity, uniformity and reproducibility than traditional heterogeneous catalysts. However, detailed elucidation of the chemical mechanisms governing their activity is difficult to achieve because analogies to well understood homogeneous systems are not easily made.

Immobilization of complexes whose catalytic activity in solution is reasonably well understood mechanistically generally allows the interpretation and subsequent control of the resulting heterogeneous systems' reactivity, based on principles of organometallic chemistry as well as knowledge of the properties of the support. This has been amply demonstrated by Grubbs, Kroll and Sweet for polymer attached Wilkinson's catalyst.^{31a,33e} The activity of the homogeneous catalyst (RhClL_2) was retained when it was attached by covalent linkage to phosphinated polystyrene. The selectivity differences observed between the supported and solution catalysts were rationalized in terms of effects

Table 2. Methods for Binding Metal Complex Catalysts to Supports

<u>Selected Methods, with Examples</u>	<u>References</u>
1. <u>Physisorption and ion-exchange</u>	
a. inorganic support + $\text{RhCl}(\text{CO})(\text{PPh}_3)/\text{BBP} \rightarrow$ supported liquid-phase catalysts	17
b. $2\text{P}-\text{SO}_3^- + [\text{Pd}(\text{NH}_3)_4]^{2+} \rightarrow$ $[\text{Pd}(\text{NH}_3)_4][\text{P}-\text{SO}_3]_2$	18
$\text{P}-\text{SO}_3^- + \text{Rh}_2(\text{OAc})_{4-x}^{x+} + \text{PPh}_3 \rightarrow$ $[\text{Rh}(\text{PPh}_3)_n][\text{P}-\text{SO}_3]$	19
c. $2\text{P}-\text{N}(\text{CH}_3)_3^+ + [\text{PdCl}_4]^{2-} \rightarrow$ $[\text{P}-\text{N}(\text{CH}_3)_3]_2[\text{PdCl}_4]$	20
d. $\text{Na}^+/\text{Hect} + \text{Rh}_2(\text{OAc})_{4-x}^{x+} + \text{PPh}_3 \rightarrow$ $\text{Rh}(\text{PPh}_3)_n^+/\text{Hect}$	21
e. $\text{Na}^+/\text{Y-Zeolite} + \text{Co}^{2+} + \text{NH}_3 + \text{NO} \rightarrow$ $[\text{Co}(\text{NH}_3)_n\text{NO}]^{2+}/\text{Y-Zeolite}$	22
$\text{Na}^+/\text{Y-Zeolite} + \text{Rh}(\text{NH}_3)_6^{3+} + \text{CO} + \text{H}_2 \rightarrow$ $\text{Rh}_x(\text{CO})_y/\text{Y-Zeolite}$	23

Table 2. (cont'd).

2. Supported functional group reactions(excluding phosphines)

(R = alkyl, allyl or aryl)

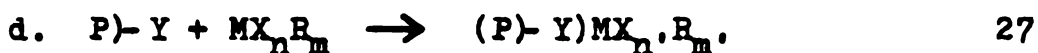
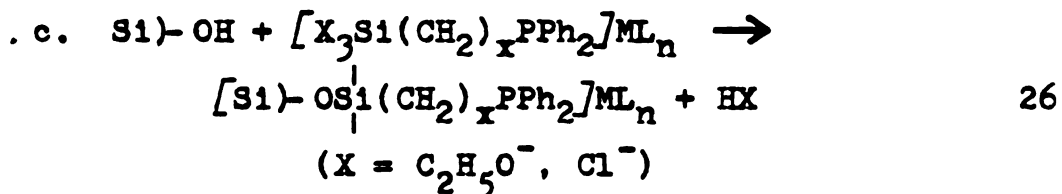
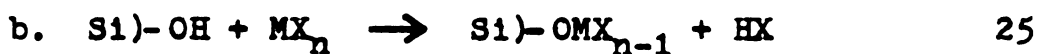
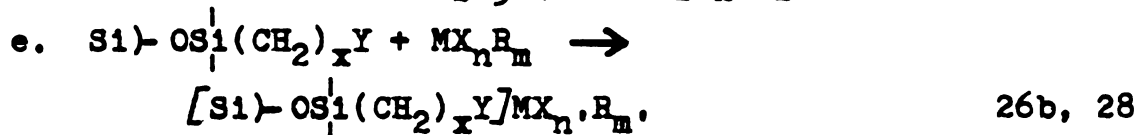
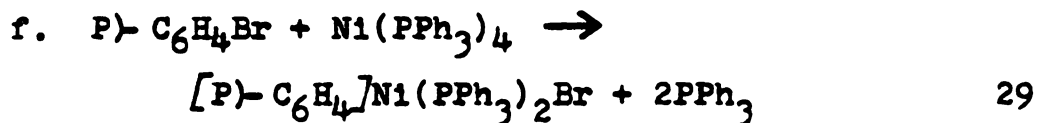
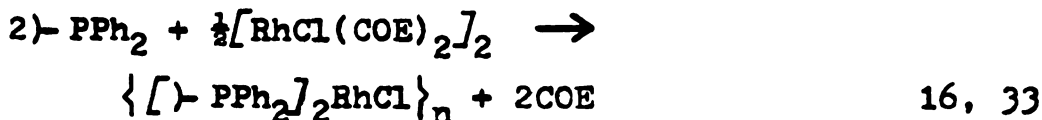
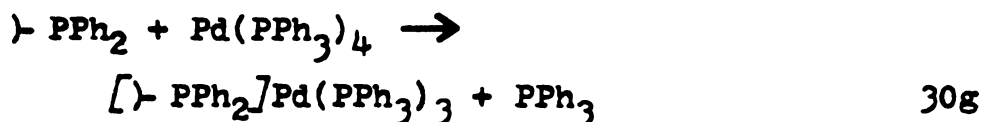
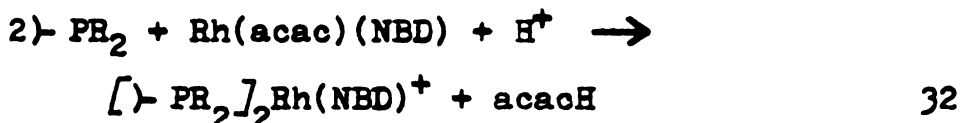
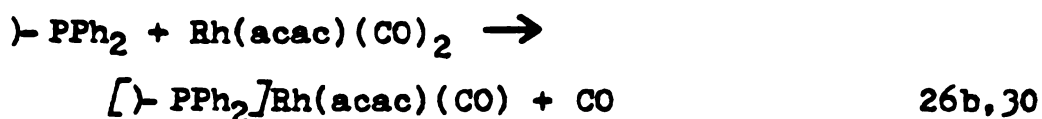
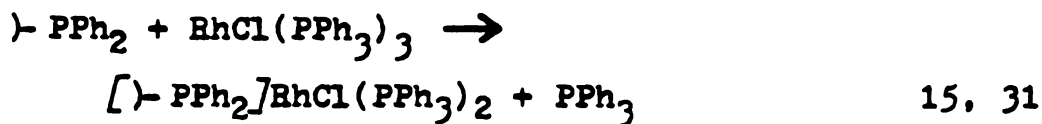
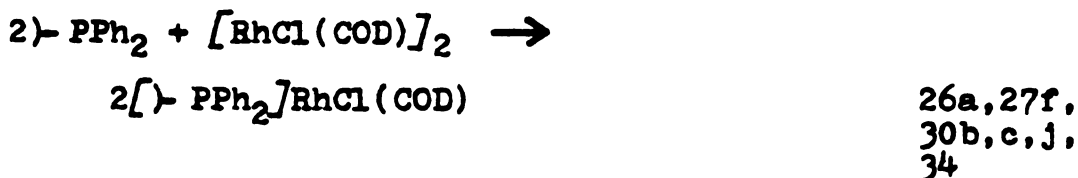
(Y = -CO₂H, -OH, -C₅H₄N,-CH₂CN, -NR₂, -SH,-CH₂C₅H₄, -(CH₂)_xNR₂)(Y = -CN, -NR₂, -C₅H₄N, -C₅H₄,-CH(COCH₃)₂, -SH)

Table 2. (cont'd).

3. Reactions with phosphinated supportsa. Direct reaction of metal halides
with supportb. Displacement of a ligand from the
metal complexc. Cleavage of μ -chloro dirhodium complexes

imposed by the polymer/solvent system.

The method most studied for complex attachment has been the covalent binding of transition metal complexes to supports via functional group ligands, although physisorption and ion-exchange methods were among the first to be studied in this area.^{9h} Physisorption is a particularly easy means of immobilization, but catalysts immobilized in this fashion suffer from the relative ease with which complexes desorb under most reaction conditions. Covalently and electrostatically bound complexes desorb much less readily, although the former may be leached from the support in the presence of excess free ligand or under conditions where the surface link is chemically degraded. Electrostatically bound complexes may desorb if electrolytes that compete for surface exchange sites are generated during the reaction, or if changes in oxidation state result in neutral or oppositely charged species.

Surface bound complexes often lose the number of vibrational, rotational and translational degrees of freedom associated with their solution chemistry. This generally results in loss of activity in the bound versus solution environment, especially for covalently bound complexes with short chain length linkages where surface steric effects are very strong. Optimum conditions for maximum catalytic activity would be those under which the translational motion of the complex is restricted, to prevent catalyst dimerization/polymerization and help maintain coordinative unsaturation at the metal center, while the vibrational and rotational

degrees of freedom of the complex are maintained. A covalent surface-complex link will always impose restrictions on the latter two types of molecular motion, whereas electrostatically bound ions may exist in very solution-like environments (in appropriate solvents) even when closely associated with the support. Ion-exchange then appears to be an attractive method for catalyst support; unfortunately, the vast majority of soluble catalysts are neutral species, incapable of electrostatic binding to suitable materials.

Pinnavaia, and coworkers, have demonstrated recently that cationic metal complex catalysts can be intercalated between the negatively charged sheets of swelling, mica-like layered silicates.²¹ For example, the complex $\text{Rh}(\text{PPh}_3)_x^+$ was shown to be an active catalyst for the hydrogenation of alkenes and alkynes in the intracrystal space of the clay mineral hectorite, under mild conditions. The supported catalyst exhibited much larger specificity for hydrogenation of terminal olefins versus internal olefins in methanol than did the solution catalyst.¹⁹ The activity of $\text{Rh}(\text{PPh}_3)_x^+/\text{Hect}$ was about ten times less than the homogeneous catalyst for the hydrogenation of 1-hexene, while the activity of this catalyst supported on a cation exchange resin was approximately forty times less.^{19b} In contrast, the activity of $\text{Rh}(\text{PPh}_3)_x^+/\text{Hect}$ for reduction of 1-hexyne was comparable to that of the solution catalyst. One might infer from these results that although the catalyst behaves as it would in solution for reduction of 1-hexyne,

selective steric and adsorptive effects imposed by the support alter the reactivity for 1-hexene hydrogenation. In addition, although direct comparison may not be legitimate due to differences in reaction conditions, the greater catalytic activity in the crystalline mineral relative to the amorphous polymer might be attributed to the complexes' greater uniform distribution and availability in the intracrystal environment.

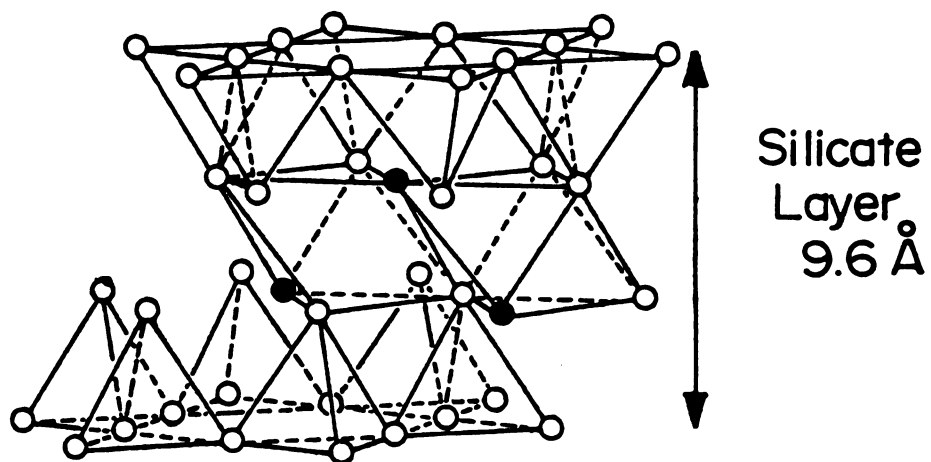
These preliminary studies on catalysts electrostatically bound in the solvent swollen intracrystal space of layer-lattice silicates have illustrated the attractiveness of the approach. The method of support is relatively easy compared with other systems. The catalysts exhibit solution-like behavior and desirable, potentially controllable, selectivity effects when exchanged on these cheap, ubiquitous minerals. (Other properties of these supports are described in Section I. C.) It has been found, however, that certain of these systems possess undesirable properties. Desorption of catalytically active, presumably uncharged species occurs during reactions when $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]^+$, a known homogeneous hydrogenation catalyst,³⁵ exchanged onto these minerals is employed as a hydrogenation³⁶ or hydroformylation catalyst.³⁷ In addition, the lack of numerous, well studied, cationic homogeneous catalysts limits the range and type of complexes which could be supported.

The intent of this dissertation was to investigate the possibility that positively charged ligands might be employed

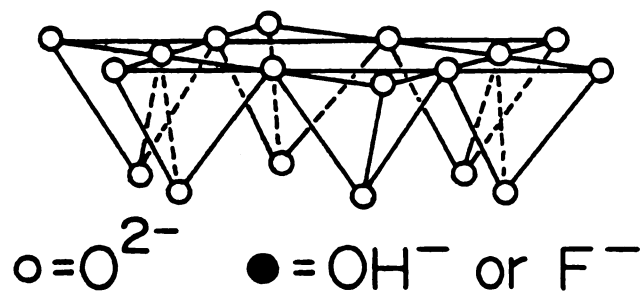
to produce active cationic transition metal catalysts analogous to well known, otherwise neutral, homogeneous catalysts and capable of electrostatic attachment to anionic supports. This innovation should allow simple, convenient preparation of a variety of new cationic catalysts which would not be susceptible to desorption from anionic supports as a result of changes in metal oxidation state.

C. The Use of Hectorite as a Catalyst Support

Hectorite is a member of the class of naturally occurring clay minerals known as smectites. This mineral's attractiveness as a catalyst support is directly related to the unique properties of the crystalline, two dimensional structure characteristic of smectites.³⁸ As illustrated schematically in Figure 1, it is composed of alternating arrays of exchangeable cations and negatively charged silicate layers. The silicate layer of hectorite consists of an octahedral magnesia (brucite) sheet which shares oxygen atoms with two parallel tetrahedral silica sheets on either side of it. The thickness of this layer is about $9.6 \text{ \AA}$. In the tetrahedral sheets, three of the four oxygen atoms of each tetrahedron are shared by three neighboring tetrahedra. The fourth oxygen atom is shared with the brucite sheet. This results in roughly hexagonal holes in the tetrahedral sheets formed by rings of six oxygen atoms. Hydroxyl groups replace oxygen atoms located within these holes in the brucite sheet where intersheet sharing does not occur.



$\text{Na}^+ \cdot x\text{H}_2\text{O}$ — Exchange Cations



Si^{4+} fills tetrahedral sites

Mg^{2+} and Li^+ fill octahedral sites

(Adapted from reference 38a)

Figure 1. Schematic representation of hectorite structure

Isomorphous substitution of lithium cations for magnesium cations in the brucite sheet results in negatively charged silicate layers. This charge is compensated for by an array of hydrated sodium ions located between these layers. This interlayer space can be swelled considerably by a large number of solvents, particularly polar solvents such as water, alcohols and ketones. As a consequence, the sodium ions may be readily replaced by a variety of other cations and cationic complexes by simple ion-exchange methods.

In sufficiently swollen smectite systems the interlayer cations exist in solution-like environments. Hydrated Cu^{2+} and Mn^{2+} ions exhibit rapid, solution-like molecular tumbling on the esr time scale,³⁹ as do protonated amine functionalized nitroxide spin probes.⁴⁰ Of the low molecular weight alcohol and water systems studied, these latter cations were most mobile in methanol swollen interlayers of hectorite. Cationic organometallic catalysts exhibiting solution-like mobility in hectorite interlayers should not lose appreciable activity compared to their homogeneous counterparts as a result of increased catalyst-substrate collision lifetimes. In addition, these solvated interlayer ions should be readily susceptible to attack by reagent molecules from bulk solution.

The $755 \text{ m}^2/\text{g}$ surface area of the hectorite used in this study compares favorably with those of other support materials. (The surface area is computed from the unit cell weight and dimensions, 769 g/mol and $5.25 \times 9.18 \text{ \AA}$ respectively, without inclusion of the additional area that

may be attributed to crystal edges, 2-3%). For example, the surface area of a commonly used organic polymer, Amberlite XAD-2, is $120 \text{ m}^2/\text{g}$.^{30j} The various types of silica used have varied from 200 ⁴¹ or 340 ^{17b} to $500 \text{ m}^2/\text{g}$.^{26b} Hectorite's large surface area, combined with its relatively low cation exchange capacity (CEC), $73 \text{ meq}/100 \text{ g}$, provides monovalent interlayer cations with a large interlayer area of $86 \text{ \AA}^2/\text{ion}$. Commercially available cation exchange resins offer no more than $16 \text{ \AA}^2/\text{ion}$. Zeolites are restricted to cationic complexes of small size. Complexes containing triphenylphosphine ligands would be much too large to exchange into Y-type zeolites.^{22c}

Smectites have been known for many years as effective heterogeneous catalysts for a number of reactions. Theng has reviewed their use in the petroleum industry as cracking and polymerization catalysts.^{38c} The active sites are of the Brönsted and Lewis acid type. Synthetic smectites incorporating Ni(II) in the brucite sheet may be used as light petroleum hydrogenation catalysts, as well as Fisher-Tropsch process catalysts.⁴² The nickel increases the surface acidity and hence, activity of these catalysts, which are also active for hydroisomerization and oligomerization of light hydrocarbon fractions.⁴³

The interlayer regions of smectites often alter the reactivities and stabilities of transition metal complexes. For example, Cu^{2+} -arene complexes, not found in homogeneous solution, are found and stabilized in smectites.⁴⁴ The

thermodynamic stability constants of Ni^{2+} , Zn^{2+} and Cd^{2+} ethylenediamine complexes in smectite interlayers are at least 100 times greater than those of the solution complexes.⁴⁵ As mentioned in Section I. B, the intracrystal environment enhances the selectivity of certain catalytic reactions as well.²¹ In this regard it is interesting to note that brucite interlayers play an important role in the reduction of N_2 to N_2H_4 over $\text{V}(\text{OH})_2$ doped $\text{Mg}(\text{OH})_2$.⁴⁶ The intracrystal environment allows relatively unstable N_2H_2 , the initial reduction product, to accumulate in sufficient local concentration to effect disproportionation to N_2 and N_2H_4 , without appreciable decomposition to the elements. The ability of interlayer environments to play active, often constructive roles in transition metal complex chemistry and catalysis is one of the many reasons why clay minerals such as hectorite are being investigated as attractive homogeneous catalyst supports.

D. Rationale, the Use of Cationic Ligands in Metal Complex Catalysts

A catalyst system was chosen for this study to test the utilization of cationic ligands in otherwise neutral homogeneous catalysts. Wilkinson's olefin hydrogenation catalyst, $\text{RhCl}(\text{PPh}_3)_3$, has been studied relatively well, both in homogeneous solution⁴⁷ and in supported environments (Table 2). The complex does not dissociate chloride to any observable extent in most solvent systems. It was felt that substitution of a cationic ligand for PPh_3 in this catalyst would afford a cationic complex with the neutral compound's characteristics,

which would be capable of electrostatic attachment to anionic supports like hectorite.

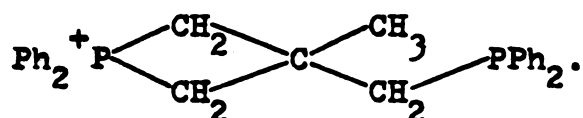
The homogeneous catalyst may be generated in situ by the addition of an appropriate number of moles of PPh_3 to $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$,^{47c} $[\text{RhCl}(\text{COE})_2]_2$ ^{47f} or $[\text{RhCl}(\text{COD})]_2$,⁴⁸ followed by addition of H_2 to generate the catalytically active dihydride. Alternatively, the desired amount of the solid compound, $\text{RhCl}(\text{PPh}_3)_3$, may be added directly to the solution,^{47g} followed by addition of hydrogen. The supported catalyst has been prepared by methods 1a, 2c, 3b and 3c of Table 2. Method 3c has received the most attention in the literature.

It was felt that an appropriate cationic phosphine ligand could be substituted for PPh_3 in the in situ generation of the catalyst system. The cationic ligand should have a noncoordinating counter-ion such as BF_4^- or PF_6^- so that it will not interfere with the activity of the metal center. The supported catalyst might be generated by a number of methods. The hectorite could be exchanged with the cationic ligand to produce a phosphinated material which could react with either $\text{RhCl}(\text{PPh}_3)_3$, $[\text{RhCl}(\text{COE})_2]_2$ or $[\text{RhCl}(\text{COD})]_2$, analogous to methods 3b or 3c (Table 2). Alternatively, the cationic catalyst might be generated in situ, as above, and exchanged with the hectorite, similar to method 2c (Table 2). This last method may be the most attractive, since it would allow the formation of a homogeneous catalyst of known composition, which should

retain its form when exchanged onto the support.

There are a few examples of cationic phosphine ligands in the literature. Quagliano, and coworkers,⁴⁹ have prepared a series of high-spin, uncharged, four-coordinate species of the general formula, $[MX_3(L^+)]$, where $M = Co(II)$, $Ni(II)$; $X = Cl, Br, I$ and $L^+ = [Ph_2PCH_2CH_2PPh_2CH_2Ph]^+$ or $[Ph_2PCH_2PPh_2CH_2Ph]^+$. Analogous complexes of these two ligands show d-d electronic spectra which are nearly identical and, surprisingly, the spectra of $[CoBr_3(L^+)]$ and $[CoBr_3(PPh_3)]^-$ are almost superposable. For related studies see reference 50.

Berglund and Meek⁵¹ obtained similar results with $Co(II)$ and $Ni(II)$ complexes incorporating the ligand



This ligand was also used to prepare cationic, square planar, d^8 complexes of $Au(III)$ and $Pd(II)$; $[Au(L^+)Cl_3]Cl$ and $[Pd(L^+)_2Cl_2](ClO_4)_2$.^{51b} These diamagnetic complexes are electrolytes in solution.

Other groups have shown that positively charged phosphine ligands give cationic species if substituted in Cr , Mo and W carbonyl compounds. The complexes $\{(CO)_5W[P(OCH_2)_3PCH_3]\}BF_4$,⁵² $[(CO)_5W(Ph_2PCH_2CH_2PPh_2CH_2Ph)]X$,⁵³ $[(CO)_5W(\underline{cis}\text{-}Ph_2PCHCHPPh_2-CH_3)]I$,⁵⁴ $[(CO)_5W(\underline{trans}\text{-}Ph_2PCHCHPPh_2CH_3)]I$,⁵⁴ $[(CO)_5W(Ph_2PCCPPh_2CH_3)]I$,⁵⁴ and $[(CH_3L^+)M(CO)_5]BF_4$ ⁵⁵ (where $CH_3L^+ = [(CH_3)_2PCH_2CH_2P(CH_3)_3]^+$, $[Ph_2PCH_2PPh_2CH_3]^+$, $[Ph_2PCH_2CH_2PPh_2CH_3]^+$, etc, and $M = Cr, Mo$ and W) are some

examples. Both infrared and ^{31}P nmr spectroscopic studies of these systems indicate that the ligand-metal electronic interaction is not affected by the presence of the positive charge on the ligand...except for those ligands containing alkene or alkyne linkages, where a small effect is observed.

Of the cationic ligands mentioned above,

$[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{CH}_2\text{Ph}]^+$ appears to mimic the behavior of PPh_3 in these systems and is relatively easy to synthesize. In this dissertation, Wilkinson type catalysts and catalyst precursors employing this ligand in solution and in hectorite supported environments were tested for behavior in comparison with analogous neutral species. The hydrogenation of 1-hexene was used to test the catalytic activity of the resulting systems. The solution compositions of the catalyst precursors were elucidated by ^1H and ^{31}P nmr techniques.

II. EXPERIMENTAL

A. Solvents and Reagents

All solvents were reagent grade except the spectrograde solvents used in nmr studies. The solvents were degassed prior to use by standard pump-flush or freeze-pump-thaw techniques. Benzene, toluene and hexane were dried over lithium aluminum hydride for at least 24 hours and freshly distilled before use. Methylene chloride was dried over Linde 4A molecular sieves for at least 24 hours and also freshly distilled before use. The methanol used in hydro-genations reportedly contained 0.2% water and was purchased from Matheson, Coleman and Bell.

Sodium hectorite (B1-26) was obtained from the Baroid Division of National Lead, Co., pre-centrifuged and spray-dried. The unit cell formula is $\text{Na}_{0.42}[\text{Mg}_{5.42}\text{Li}_{0.68}\text{Al}_{0.02}]^{44d}(\text{Si}_{8.00})\text{O}_{20}(\text{OH},\text{F})_4$ and the experimentally determined cation exchange capacity is 73 meq/100 g.^{39b} The small amount of CaCO_3 impurity found with this mineral was not removed prior to use. Sodium montmorillonite, Upton, Wyoming, was obtained from the Source Clay Minerals Depository. Kaolinite (A. P. I. No. H-5) was from Wards Natural Science Establishment and silica gel, 60-200 mesh, grade 950 was purchased from Matheson, Coleman and Bell.

The trichlororhodium(III) hydrate used in this study was either obtained as a gift from Monsanto, Co., or purchased from Engelhard Industries, Inc. Most of the di- μ -chloro bis(1,5-cyclooctadiene)dirhodium(I) was obtained from Strem Chemicals, Inc. Aldrich Chemical Company was the source of triphenylphosphine, benzyl bromide, cyclooctene and 1,5-cyclooctadiene, while sodium tetrafluoroborate and potassium hexafluorophosphate were purchased from Alfa Products-Ventron. 1,1,1,3,3,3-Hexamethyldisilazane and chlorotrimethylsilane were gifts of Dow Corning Corporation. Dowex (AG2-X8) anion (Cl^-) exchange resin, 50-100 mesh, was a gift from Dow Chemical Company. Bis(1,2-diphenylphosphino)ethane was obtained from PCR, Incorporated.

1-Hexene was purchased from Pfaltz and Bauer, Incorporated. It was purified before use by the following procedure. The olefin was shaken and extracted three times with an equal volume of acidified ($\text{pH} = 1$), aqueous ferrous sulfate (Matheson, Coleman and Bell), dried over anhydrous, 12 mesh calcium chloride (Matheson, Coleman and Bell), under nitrogen atmosphere for at least two hours, and finally distilled immediately before use under argon over fresh sodium borohydride (Fisher Scientific Company).

B. Physical Methods

1. Infrared Spectra

A Perkin-Elmer model 237B grating spectrophotometer was employed to record infrared spectra of Fluorolube (Hooker Chemical Company) or paraffin oil (J. T. Baker Chemical Co.)

mulls of samples placed between CsI plates. A wire mesh screen served as an attenuator in the reference beam of the spectrometer. Mulls of oxygen sensitive samples were prepared in a nitrogen filled glove box immediately before measurement.

2. Proton NMR Studies

A Varian Associates A56/60D analytical spectrometer was used to obtain 60 MHz proton nmr spectra as one check of the identity and purity of solvents and compounds. Chemical shifts were usually measured relative to tetramethylsilane.

Fourier transform proton nmr spectra at 180 MHz were obtained with the assistance of Ms. Elene Bouhoutsos-Brown and Mr. Kevin Ott on a Brüker WH-180 spectrometer interfaced to a Nicolet 1180 computer with 32K of memory. Samples were prepared by mixing solutions of the desired compounds in 10 mm diameter nmr tubes in a nitrogen filled glove box, capping the tubes and sealing them with a few turn of black electrical tape. A small amount of tetramethylsilane was included in each sample as an internal reference. Degassed deuterio-chloroform, or in some cases dideuterodichloromethane, was employed as solvent and served as an internal deuterium lock for the instrument.

3. Phosphorus-31 NMR Studies

Fourier transform, proton decoupled phosphorus-31 nmr spectra were recorded on a Brüker HFX-10 spectrometer modified for multinuclear measurements as described by Traficante, et al,⁵⁶ and interfaced to a Nicolet 1083

computer with 12K of memory, a Diablo disc memory unit and a Nicolet 293 I/O controller. In the external lock mode employed during these measurements, the spectrometer maintained a constant fluorine-19 lock on a sample of hexafluorobenzene contained in a microprobe assembly externally adjacent to the Dewar assembly of the main sample probe. Spectra were obtained at approximately 36.44 MHz. Chemical shifts, relative to an 85% phosphoric acid external reference solution, were calculated by taking the irradiation frequency to be 36.43 MHz. Corrections for magnetic susceptibility differences were not made.

Most samples were prepared by mixing solutions of the desired compounds in 10 mm diameter nmr tubes in a nitrogen filled glove box, capping the tubes and sealing them with a few turns of black electrical tape. Degassed, spectrograde solvents were utilized. In experiments where one atmosphere of hydrogen pressure was required, the samples were prepared in the glove box, as above, in 10 mm nmr tubes equipped with a female 14/35 pyrex joint stopper and one or two side arms. The tubes were attached to a hydrogenation line and the pressure was monitored as a function of time, hydrogen added as necessary, prior to conducting the nmr experiment. These latter tubes were not spun in the probe. Comparisons of the half-height linewidths of a sample of $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]\text{PF}_6$ under spinning and non-spinning conditions showed no appreciable increase in linewidth as a result of not spinning the sample.

4. X-ray Diffraction Study

A Phillips x-ray diffractometer with Ni-filtered Cu K(α) radiation was utilized to determine the 001 basal spacing of a sample of P-P⁺/Hect. The powdered mineral was deposited on a microscope slide and the diffraction pattern was scanned from 2° through 22° of 2 θ . The peak positions were converted to d-spacings with a standard chart. The 001 spacing of a sample wet with methanol was obtained by adding methanol to the slide, allowing 10 min for equilibration, and then scanning the diffraction pattern.

5. Elemental Analyses and Melting Points

All chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Despite good agreement between calculated and observed analyses for most elements of known compounds, rhodium analyses from this company were occasionally ten to twenty percent lower, reproducibly, than the theoretical values for certain complexes. The cause of this error is unknown, but consideration of this fact in interpreting analyses of unknown compounds should not be overlooked.

Melting points were determined on a Thomas-Hoover model 6406-H Capillary Melting Point Apparatus.

C. Syntheses

1. Known Rhodium Complexes

RhCl(PPh₃)₃: Chlorotris(triphenylphosphine)rhodium(I) was synthesized by the method of Osborn, et al.,^{47g} without modification, by the interaction of excess triphenylphosphine

with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in ethanol. Anal. Calc. for $\text{C}_{54}\text{H}_{45}\text{ClP}_3\text{Rh}$: C, 70.10; H, 4.90; Rh, 11.12. Found: C, 70.09; H, 5.00; Rh, 10.94.

$[\text{RhCl}(\text{COE})_2]_2$: Di- μ -chlorotetrakis(cyclooctene)dirhodium(I) was prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and COE by the method of van der Ent and Onderdelinden.⁵⁷ The compound was stored under nitrogen at about $+2^\circ$. Solid samples could be handled briefly in air for weighing and transfer without noticeable effect; even when stored under nitrogen, however, this material was observed to discolor markedly over a long period of time (six months). Samples older than six months were not used. Anal. Calc. for $\text{C}_{16}\text{H}_{28}\text{ClRh}$: C, 53.57; H, 7.87; Rh, 28.68. Found: C, 53.59; H, 7.86; Rh, 25.56.

$[\text{RhCl}(\text{COD})]_2$: The di- μ -chlorobis(1,5-cyclooctadiene)dirhodium(I) utilized in a few of the nmr experiments and preparations was obtained from the reaction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and COD in refluxing ethanol, under nitrogen, after the method of Chatt and Venanzi.⁵⁸ The compound was not recrystallized but its nmr and ir spectra were identical to those obtained for the commercially available material (Strem), which was used in the hydrogenation reactions and most nmr experiments.

$\text{RhCl}(\text{COD})(\text{PPh}_3)$: Chloro(1,5-cyclooctadiene)triphenylphosphinerhodium(I) was prepared from $[\text{RhCl}(\text{COD})]_2$ and PPh_3 without modification of the Chatt and Venanzi preparation.⁵⁸

$[\text{Rh}(\text{COD})(\text{PPh}_3)_2]\text{BF}_4$, $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]\text{PF}_6$: The tetrafluoroborate and hexafluorophosphate salts of the (1,5-cyclooctadiene)bis(triphenylphosphine)rhodium(I) cation were

prepared from $[\text{RhCl}(\text{COD})]_2$, either NaBF_4 or KPF_6 respectively, and PPh_3 without modification of the Schrock and Osborn preparation.⁵⁹

All of these known compounds were checked for identity and purity by comparison of their ^1H and ^{31}P nmr spectra, ir spectra and melting points with those reported in the literature.

2. 1-Diphenylphosphino-2-benzoyldiphenylphosphonium-ethane bromide

$(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{CH}_2\text{Ph})\text{Br}$: $\text{P-P}^+\text{Br}$ was synthesized from diphos and benzyl bromide by a modification of Quagliano's method.⁴⁹ In a nitrogen filled glove box, 6.1 ml (.025 mol) benzyl bromide was added, drop-wise, over a period of ten minutes, to a stirred solution of 10.0 g. (.025 mol) diphos in about 250 ml dry, degassed benzene or toluene. The reaction flask was stoppered and allowed to stand overnight. The resulting microcrystalline powder was filtered from the solution, slurried and washed twice with 60 ml benzene or toluene. The soluble portion was taken up in 250 ml degassed methanol and the insoluble dicationic salt was filtered on a fine frit. The methanol solution was reduced to one eighth the original volume and the resulting white crystals were collected and dried on a fritted filter. The compound was not recrystallized. ~70% yield. (mp $244-247^\circ$, lit.⁴⁹ $240-245^\circ$.) Anal. Calc. for $\text{C}_{33}\text{H}_{31}\text{BrP}_2$: C, 69.60; H, 5.49; P, 10.88. Found: C, 69.43; H, 5.48; P, 11.08.

3. Tetrafluoroborate Anion Exchange Resin

BF_4^- /Resin: Approximately 171 g (1500 meq) NaBF_4 , dissolved in 300 ml H_2O and filtered free of an insoluble impurity, was added to about 162 g (518 meq Cl^-) AG2-X8 Dowex anion exchange resin (50-100 mesh). The mixture was stirred for one day, filtered and a fresh solution containing 100 g (1000 meq) NaBF_4 was stirred with the resin overnight. The resin was then filtered and washed seven times with 200 ml quantities of H_2O and twice with methanol, filtered, dried on an aspirator and degassed under high vacuum at room temperature for four days.

4. 1-Diphenylphosphino-2-benzylidiphenylphosphonium-ethane tetrafluoroborate

$(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{CH}_2\text{Ph})\text{BF}_4$: In a nitrogen filled glove box, 31 g (100 meq BF_4^-) BF_4^- /Resin was added to the filtered methanol solution obtained from a preparation of $\text{P-P}^+\text{Br}$ (Section II. C. 2). This was stirred four hours, filtered, and then fresh BF_4^- /Resin (31 g) was added to the solution. It was necessary to add additional methanol at this point. After an additional four hours the procedure was repeated a third time. The solvent was reduced under vacuum to one eighth the original volume. In the glove box, the resulting white, needle-like crystals were collected on a frit and washed with benzene or toluene. ~70% yield. (mp 188-189°.)
Anal. Calc. for $\text{C}_{33}\text{H}_{31}\text{BF}_4\text{P}_2$: C, 68.77; H, 5.42; P, 10.75; Br, 0.00. Found: C, 68.95; H, 5.57; P, 10.66; Br, less than 0.1.

5. Chloro(1,5-cyclooctadiene)(1-diphenylphosphino-2-benzyldiphenylphosphoniumethane)rhodium(I) tetrafluoroborate

$[\text{RhCl}(\text{COD})(\text{P}-\text{P}^+)]\text{BF}_4$: In a nitrogen filled glove box, 1.636 g (2.84 mmol) $\text{P}-\text{P}^+\text{BF}_4$ in 20 ml dichloromethane was added to a stirred dichloromethane solution (20 ml) of 0.700 g (1.42 mmol) $[\text{RhCl}(\text{COD})]_2$, analogous to the Chatt and Venanzi preparation of $\text{RhCl}(\text{COD})(\text{PPh}_3)$.⁵⁸ After the solution had been allowed to age 1 hr, the solvent was removed under vacuum, and the complex was washed with two 20 ml portions of toluene, filtered and washed quickly with 10 ml methanol. The light-yellow, microcrystalline complex was not recrystallized (mp 195-200° decomp.). Anal. Calc. for $\text{C}_{41}\text{H}_{43}\text{BClF}_4\text{P}_2\text{Rh}$: C, 59.84; H, 5.27; P, 7.53. Found: C, 60.20; H, 5.34; P, 6.88.

6. 1-Diphenylphosphino-2-benzyldiphenylphosphonium-ethane Exchanged Hectorite

$\text{P}-\text{P}^+/\text{Hect}$: In a nitrogen filled glove box, 1.12 g (1.97 mmol) $\text{P}-\text{P}^+\text{Br}$ in 200 ml methanol was added to a stirred suspension of 1.00 g (0.73 meq Na^+) hectorite in 40 ml methanol. After 24 hours the mineral was filtered and washed with methanol until the filtrate gave a negative bromide test with silver nitrate. The mineral was allowed to dry under N_2 on the frit. (001 basal spacings: dry, 18.8 Å; wet (CH_3OH), 19.6 Å). Anal. Found: P, 3.08%. This corresponds to 49.7 meq $\text{P}-\text{P}^+$ per 100 g hectorite, approximately 68% of the cation exchange capacity.

7. Silylated Montmorillonite

$R_3Si/Mont$: Mr. Alan M. Alanko donated this material, prepared by the following method. Sodium montmorillonite (1.0 g) was added to a neat mixture of 20.0 g (124.0 mmol) $[(CH_3)_3Si]_2NH$ plus 4.48 g (62.2 mmol) $SiCl(CH_3)_3$. The mixture was stirred 18 hours under N_2 , centrifuged, decanted and washed twice with 30 ml hexane, once with 30 ml 1 N $NaCl(aq)$ and sufficient H_2O to eliminate Cl^- from the washings. The mineral was resuspended in water and freeze-dried. The ir spectrum of the mineral contained bands at 2910, 2850 and 845 cm^{-1} attributable to $(CH_3)_3Si$ group vibrations, but the band(s) expected between 1250-1270 cm^{-1} due to Si-C stretching were not observable.

D. Hydrogenation Studies and Catalyst Preparation

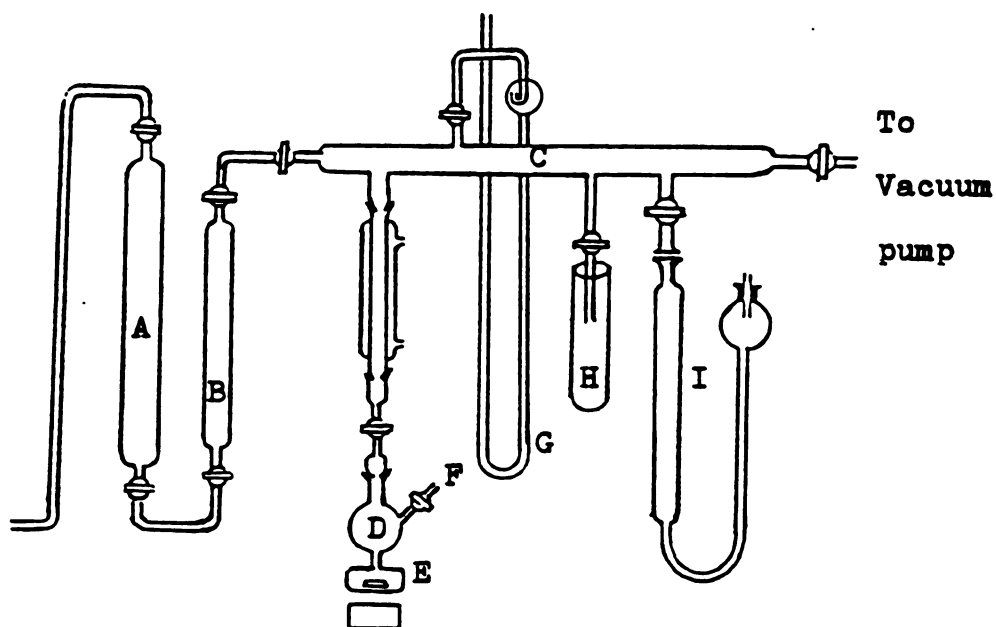
1. Hydrogenation Procedure and Apparatus

The substrate, 1-hexene, was hydrogenated on a standard hydrogenation apparatus (vide infra). The rate of hydrogen uptake was measured at atmospheric pressure and ambient temperature. No corrections for variable pressure or temperature between or during experiments were made on the rates or turnover numbers. Turnover numbers (TO#) are defined as the rate per millimole of rhodium in units of ml $H_2/min/mmol$ Rh. Minimum turnover numbers (MINTO#) are reported for heterogeneous catalyst systems in which a maximum rhodium content is assumed based on the amount initially used in the catalysts' preparation.

The extent of reaction is expressed as catalyst

turnover (CT), based on the known substrate to rhodium ratio, substrate and rhodium mole quantities and approximate total hydrogen uptake at particular intervals. For example, for a substrate to rhodium ratio of 1500:1, at 50% hydrogenation the CT would be 750. The hydrogen pressure in the system was approximated by subtracting the vapor pressure of methanol (114 mmHg at 25°)⁶⁰ from 740 mmHg.

A drawing of the hydrogenation apparatus is presented in Figure 2. In a typical experiment the hydrogenation flask would be attached to the apparatus and the stirrer set at the routine rate. A vacuum was carefully applied to the manifold, manometer and measuring buret, followed by pressurization with hydrogen. This process was repeated two times. The reaction flask (including septum) was then exposed to vacuum (sufficient to induce solvent bubbles) and then hydrogen was added. After one hour equilibration time, freshly distilled 1-hexene (see Section II. A) was added to the reaction flask by inert atmosphere syringe techniques via the rubber septum. The Hg manometer was quickly adjusted to atmospheric pressure through judicious use of the Hg leveling bulb and manifold vent. The timer was started and the initial buret reading was noted. The hydrogen pressure was monitored regularly, utilizing the Hg leveling bulb to maintain atmospheric pressure above the reaction solution, and the buret reading was noted each time. Fresh hydrogen was added and the buret and manometer were reset each time approximately 50 ml H₂ was consumed.



- A. BASF O₂ Scrubber
- B. Linde 4A Molecular Sieve
- C. Manifold
- D. Reaction Flask
- E. Magnetic Stirrer
- F. Rubber Septum
- G. Open Hg Manometer with Meter Stick Scale
- H. Manifold Vent
- I. 50 ml Measuring Buret and Hg Leveling Bulb

Figure 2. Hydrogenation apparatus (schematic)

2. Homogeneous Catalysts

Homogeneous catalysts were prepared in situ in a nitrogen filled glove box immediately prior to use. Stock solutions of the desired catalysts' components were added to the hydrogenation flask with stirring, followed by sufficient methanol to make 26.25 ml total solution volume. (30 ml total volume on addition of 1-hexene). The flask was sealed and attached to the hydrogenation apparatus, whereupon hydrogen was added and allowed to equilibrate with the catalyst solution one hour prior to addition of 3.75 ml (0.03 mol) 1-hexene. All homogeneous catalysts contained 0.02 mmol rhodium(I), which results in a substrate to rhodium ratio of 1500:1.

The following convention characterizes catalysts generated from $[\text{RhCl}(\text{COD})]_2$ in situ. A 1:1:1 ratio indicates 0.02 mmol P-P^+ , 0.02 mmol PPh_3 and 0.02 mmol Rh(I) . A 0:2:1 label indicates 0.04 mmol PPh_3 and 0.02 mmol Rh(I) while 2:0:1 is 0.04 mmol P-P^+ and 0.02 mmol Rh(I) .

The preparation of the 1:1:1 catalyst serves to illustrate the method. One ml of 0.02 M Rh(I) stock solution (0.01 M $[\text{RhCl}(\text{COD})]_2$ in dichloromethane) was placed in the hydrogenation flask followed by addition of 2 ml (0.01 M) $\text{P-P}^+ \text{BF}_4^-$ methanol stock solution and 21.25 ml methanol. After 30 min of stirring, 2 ml (0.01 M) PPh_3 methanol stock solution was added and stirring continued an additional 30 min. The flask was kept closed during stirring in the dry box and remained so until attached to the hydrogenation

apparatus.

Stock solutions older than two weeks were not used. One ml of 0.02 M $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]\text{BF}_4$ in dichloromethane was used as stock solution for that catalyst.

A test was made for the presence of dissociated chloride ion before and after use of 0:2:1 and 1:1:1 catalysts. Addition of four drops 0.01 M $\text{AgNO}_3(\text{aq})$ to the catalyst solutions did not produce turbidity until 30 to 60 minutes had passed, whereas immediate precipitation should have been observed if chloride ion was present prior to addition. Ag^+ does not precipitate BF_4^- under these conditions.

3. Heterogeneous Catalysts and Materials

All preparations were conducted in a nitrogen filled glove box. $\text{RhCl}(\text{PPh}_3)_3/\text{Hect}$: 0.200 g hectorite was added to 0.048 g (0.05 mmol) $\text{RhCl}(\text{PPh}_3)_3$ in 40 ml benzene. The suspension was stirred for six days, filtered, and washed with five 10 ml portions of benzene. The filtrate resulting from each wash was colored yellow; the mineral remained orange-yellow. The catalyst was added to the hydrogenation flask with 26.25 ml methanol and stirred for ten minutes prior to the hydrogenation of 3.75 ml (0.03 mol) 1-hexene. During the reaction the catalyst solution developed an orange-yellow color which turned to brown-yellow near the end. Upon filtration following the reaction, the mineral was light tan, and the solution was brown-yellow.

$\text{RhCl}(\text{PPh}_3)_3/\text{P-P}^+/\text{Hect}$: 0.200 g (0.10 meq P-P^+) $\text{P-P}^+/\text{Hect}$ was added to 0.048 g (0.05 mmol) $\text{RhCl}(\text{PPh}_3)_3$ in

40 ml benzene. The suspension was stirred 18 hours and filtered. The mineral's color was unchanged from that of P-P⁺/Hect. The mineral was not tested as a catalyst.

RhCl₃/Hect: 0.014 g (0.05 mmol) RhCl₃·3H₂O in 20 ml ethanol was added to 0.014 g (0.01 meq Na⁺) hectorite. The suspension was stirred one day and filtered. Ethanol washes removed most of the red color due to RhCl₃ from the mineral. RhCl₃/Hect was not tested as a catalyst.

RhCl₃/P-P⁺/Hect: 0.071 g (0.27 mmol) RhCl₃·3H₂O in 25 ml ethanol was added to 0.071 g (0.035 meq P-P⁺) P-P⁺/Hect. The suspension was stirred one day and filtered. Ethanol washes did not remove the orange-pink color from the mineral. This material proved inactive for the hydrogenation of 1-hexene in methanol, but addition of hydrogen did cause the color to change from orange-pink to very light yellow and no desorption of complex was observed (color).

[RhCl(COE)₂]₂/P-P⁺/Hect: Contact of 0.026 g (0.072 mmol Rh) [RhCl(COE)₂]₂ in 25 ml benzene with 0.200 g (0.10 meq P-P⁺) P-P⁺/Hect for three minutes, with stirring, resulted in a yellow mineral which was washed with two 10 ml portions of benzene. This material was inactive for the hydrogenation of 1-hexene in methanol, but it did lighten in color on addition of hydrogen.

Rh(0)/P-P⁺/Hect: 0.018 g (0.05 mmol Rh) [RhCl(COE)₂]₂ in 30 ml benzene was stirred with 0.200 g (0.10 meq P-P⁺) P-P⁺/Hect for 24 hours. During that time the suspension changed color from yellow to dark gray. On filtration the

mineral was dark gray, and the solution light yellow. The mineral was washed once with 10 ml methanol and found active for hydrogenation of 3.75 ml (0.03 mol) 1-hexene in 26.25 ml methanol. No catalyst desorption was observed during the reactions. Analysis of the mineral after catalysis gave 1.59% Rh, (0.03 mmol Rh/0.200 g).

Rh(0)/Hect: This material is prepared by replacing P-P⁺/Hect with hectorite in the preparation of Rh(0)/P-P⁺/Hect (vs.). The resulting mineral exhibits catalytic behavior that is similar to the latter catalyst. Anal. 1.49% Rh, (0.03 mmol Rh/0.200 g).

Rh(0)/Kaol: This material is prepared by replacing P-P⁺/Hect with kaolinite in the preparation of Rh(0)/P-P⁺/Hect (vs.). On filtration the mineral was dark gray, but the solution was colorless. The mineral was washed once with 10 ml methanol and found active for the hydrogenation of 3.75 ml (0.03 mol) 1-hexene in 26.25 methanol. Anal. 2.93% Rh, (0.05 mmol Rh/0.200 g).

Rh(0)/SILG: This material is prepared by replacing P-P⁺/Hect with silica gel in the preparation of Rh(0)/P-P⁺/Hect (vs.). The resulting material is dark gray and is extremely active for the hydrogenation of both 3.75 ml (0.03 mol) 1-hexene in methanol and 2.67 ml (0.03 mol) benzene in methanol. Anal. 1.19% Rh, (0.02 mmol Rh/0.200 g).

$[\text{RhCl}(\text{COE})_2]_2/\text{R}_3\text{Si}/\text{Mont}$: 0.009 g (0.025 mmol Rh)
 $[\text{RhCl}(\text{COE})_2]_2$ in 30 ml benzene was stirred for 24 hours with 0.09 g $\text{R}_3\text{Si}/\text{Mont}$. After filtration, the mineral was

an orange-yellow color; the filtrate was nearly colorless. The mineral was not tested for catalytic activity. Anal. 2.67% Rh, (0.023 mmol Rh/0.09 g).

0:2:1/Hect: 2 ml (0.01 M) PPh_3 methanol stock solution was added with 20 ml methanol to 1 ml (0.02 M Rh(I)) $[\text{RhCl}(\text{COD})]_2$ dichloromethane stock solution with stirring. An additional 2 ml (0.01 M) PPh_3 methanol stock solution was added after 10 min and stirred for 30 min in a small hydrogenation flask. The flask was attached to the hydrogenation apparatus and hydrogen was added, with stirring, for 2.5 hours. In the glove box this solution was added, with swirling, to 0.200 g (0.146 meq Na^+) hectorite (previously equilibrated with 10 ml methanol for 30 min). After five minutes contact time the mixture was filtered and the mineral was washed four times with 15 ml aliquots methanol. The filtrates were light yellow, as was the mineral, which was placed in the hydrogenation flask with 25.25 ml methanol and 1 ml dichloromethane. The initial exposure time to hydrogen was reduced to 30 min prior to the hydrogenation of 3.75 ml (0.03 mol) 1-hexene. During the reaction the solution acquired a yellow color, confirmed upon filtration from the mineral at completion. This filtrate was catalytically active.

$\text{Rh}(\text{COD})(\text{PPh}_3)_2^+/\text{Hect}$: 20 ml methanol was added to one ml (0.02 M) $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]\text{BF}_4$ dichloromethane stock solution with stirring in a small hydrogenation flask. The flask was attached to the hydrogenation line following the procedure

for preequilibration with hydrogen, contact with hectorite and methanol washing given for 0:2:1/Hect. The first filtrate was light yellow, indicative of incomplete cation exchange. The procedure for hydrogenation of 1-hexene with this catalyst was the same as given for 0:2:1/Hect. The mineral darkened from light yellow to brown-yellow and near CT 975 complex desorption was noticed (solution color yellow). Upon filtration following the reaction the filtrate was yellow and catalytically active.

2:0:1/Hect and 3:0:1/Hect: These materials were prepared following the procedure for 0:2:1/Hect, except that 4 ml (0.01 M) $P-P^+BF_4$ methanol stock solution was used instead of PPh_3 for 2:0:1/Hect and 6 ml of that solution for 3:0:1/Hect. These minerals proved inactive for hydrogenation of 1-hexene in methanol.

1:1:1/Hect: 2 ml (0.01 M) $P-P^+BF_4$ methanol stock solution was added with 20 ml methanol to 1 ml (0.02 M $Rh(I)$) $[RhCl(COD)]_2$ dichloromethane stock solution with stirring. After 10 min, 2 ml (0.01 M) PPh_3 methanol stock solution was added and stirred 30 min in a small hydrogenation flask. The flask was attached to the hydrogenation apparatus and hydrogen was added, with stirring, for 2.5 hours. In the glove box, this solution was added, with swirling, to 0.200 g (0.146 meq Na^+) hectorite (previously equilibrated with 10 ml methanol for 30 min). After five minutes contact time, the mixture was filtered and the mineral was washed four times with 15 ml aliquots methanol. The mineral was

yellow, and the filtrates nearly colorless. The mineral was placed in the hydrogenation flask with 25.25 ml methanol and 1 ml dichloromethane. The initial hydrogen exposure time was 30 min prior to hydrogenation of 3.75 ml (0.03 mol) 1-hexene. No catalyst desorption was observed during or after reaction. Filtrates from two different reactions taken CT 750 and CT 1300 were inactive for hydrogenation of 1-hexene. Analysis of the material prior to olefin hydrogenation yielded: Rh, 0.88%; P, 0.84%; Cl, 0.23%. This corresponds to 0.0171 meq Rh(I)/0.2 g, 0.0542 meq P/0.2 g and 0.0130 meq Cl⁻/0.2 g; or a Rh:P:Cl ratio of 1.00:3.17:0.76. The expected ratio was 1.00:3.00:1.00.

III. RESULTS AND DISCUSSION

A. Preparation and Characterization of $P-P^+BF_4$ and $[RhCl(COD)(P-P^+)]BF_4$

The cationic phosphine ligand, $(Ph_2PCH_2CH_2PPh_2CH_2Ph)BF_4$, was prepared from the reaction of the known bromide salt, $P-P^+Br$, with tetrafluoroborate anion exchange resin under oxygen free conditions. The preparation of $P-P^+Br$ from the stoichiometric addition of benzyl bromide to diphos was conducted in benzene rather than acetone⁴⁹ solution, under oxygen free conditions, to facilitate the precipitation of the cation, and inhibit the formation of phosphine oxide impurity. $P-P^+BF_4$ is soluble in methylene chloride, chloroform, dimethylsulfoxide and N,N-dimethylformamide; partially soluble in methanol, ethanol, acetonitrile and pyridine and insoluble in water, acetone, ethers and nonpolar solvents such as benzene, hexane and carbon tetrachloride.

The infrared spectrum of $P-P^+BF_4$ (Figure 3) can be analyzed in the following way.⁶¹ The three bands at 1600 cm^{-1} are most likely due to phenyl group skeletal vibrations, as are the weaker bands in the region between 1525 and 1400 cm^{-1} . The strong band at 1440 cm^{-1} can be assigned to methylene group scissoring vibrations and the bands on either side of it may also merit this assignment, although they could also

Figure 3. Infrared spectra of $P-P^+BF_4$ (A) and $[RhCl(COD)(P-P^+)]BF_4$ (B) as nujol mulls between CsI salt plates. Insets were taken as fluorolube mulls.

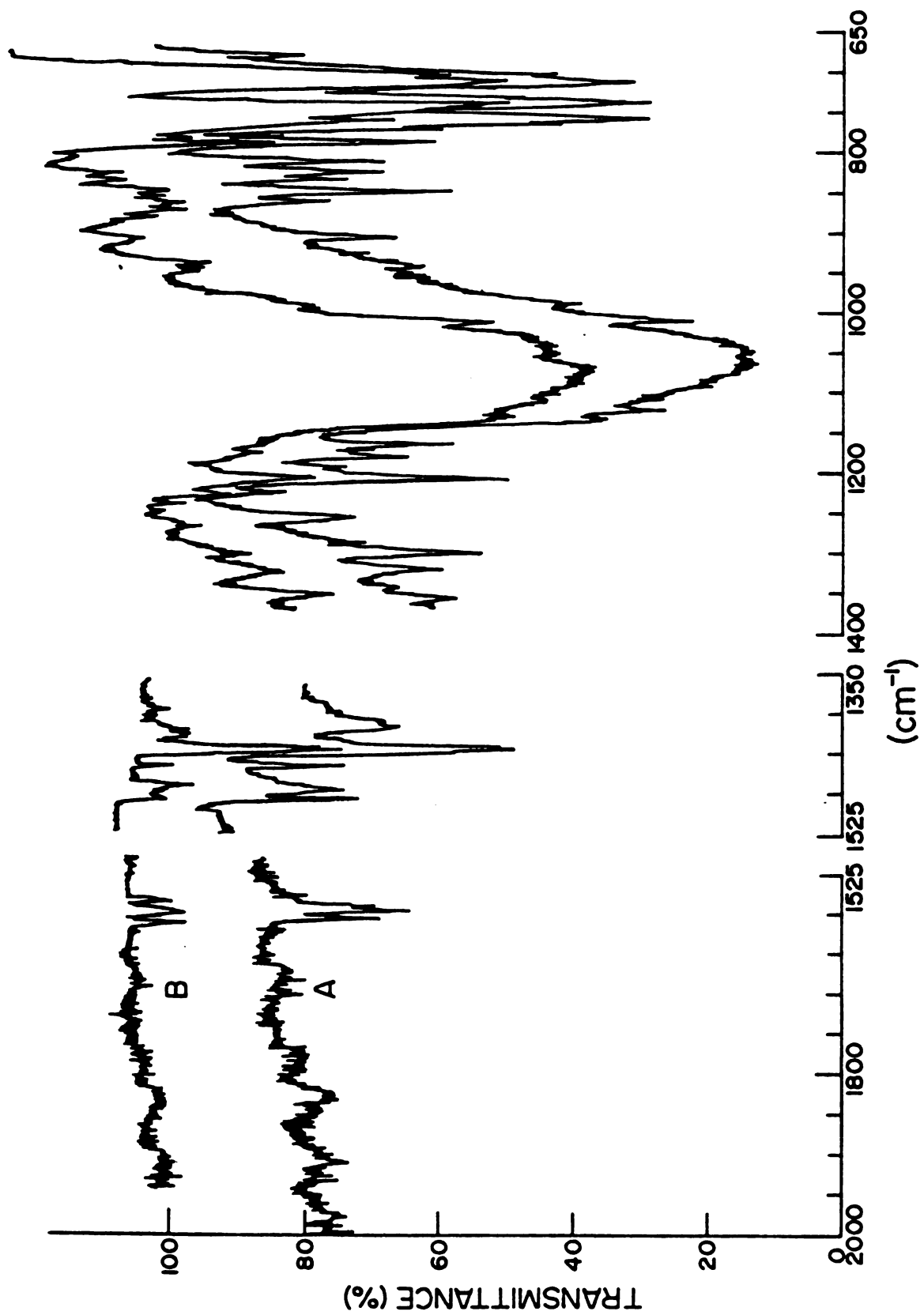


Figure 3

be due to aryl skeletal vibrations. Although specific band assignments have not been made, the bands in the region 1350-1100 cm^{-1} are probably due to phenyl group in plane C-H bond bending and/or methylene group twisting and wagging vibrations. The broad, strong band at 1060 cm^{-1} is characteristic of the tetrafluoroborate anion.⁶² The region from 900 to 675 cm^{-1} , particularly the three sharper bands, can be assigned to phenyl ring out of plane C-H bond bending vibrations.

The relevant 180 MHz proton nmr spectral data for $\text{P-P}^+\text{BF}_4$ are presented in Table 3. No attempt was made to analyze the compound's complex phenyl proton resonance pattern. The assignment of the three methylene proton resonances is based in part on Keiter's assignments for analogous bromide salt systems,^{53a} as well as the observed downfield shift of the 2.65 ppm resonance attributable to deshielding of the methylene protons adjacent to trivalent phosphorus on ligand coordination to rhodium.

The proton decoupled ^{31}P nmr spectrum of $\text{P-P}^+\text{BF}_4$ consists of two doublets (Figure 4). The doublet at +12.1 ppm upfield from 85% H_3PO_4 is assigned to trivalent phosphorus (compare this with +12.5 ppm for diphos^{61a}). The doublet at -27.1 ppm is assigned to the quaternized phosphorus ($J_{\text{PP}^+} = 46 \text{ Hz}$).

$[\text{RhCl}(\text{COD})(\text{P-P}^+)]\text{BF}_4$ was prepared as a test of the viability of utilizing $\text{P-P}^+\text{BF}_4$ in place of PPh_3 in the preparation of cationic analogs of otherwise neutral Rh(I) phosphine complexes. The interaction of two equivalents of PPh_3

Table 3. Relevant 180 MHz Proton NMR Data for $P-P^+BF_4$
and $[RhCl(COD)(P-P^+)]BF_4$



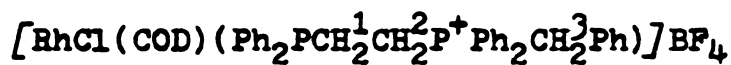
$$\delta(H^1) = 2.65 \quad ddt$$

$$\delta(H^2) = 2.09 \quad dt$$

$$\delta(H^3) = 4.37 \quad d$$

$$J_{H^1H^2} = 10.6, J_{H^1P} = \sim 6, J_{H^1P^+} = \sim 3,$$

$$J_{H^2P^+} = 6.4, J_{H^3P^+} = 14.5$$



$$\delta(H^1) = 3.72 \quad m$$

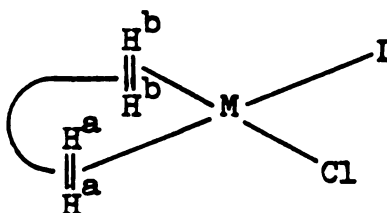
$$\delta(H^2) = \sim 2.1 \quad m$$

$$\delta(H^3) = 4.48 \quad d$$

$$\delta(H^a) = 5.47 \quad s$$

$$\delta(H^b) = 3.12 \quad s$$

$$J_{H^3P^+} = 14.0$$



Compare $RhCl(COD)(PPh_3)$, $\delta(H^a) = 5.52$, $\delta(H^b) = 3.10$

Chemical shifts are in ppm relative to TMS in $CDCl_3$ at 25° .

Coupling constants are expressed in Hz.

Figure 4. 36.43 MHz ^{31}P nmr spectra of $\text{P-P}^+\text{BF}_4$ (A), $[\text{RhCl}(\text{COD})(\text{P-P}^+)]\text{BF}_4$ (B) and $\text{RhCl}(\text{COD})(\text{PPh}_3)$ (C) at 28° in CH_2Cl_2 .

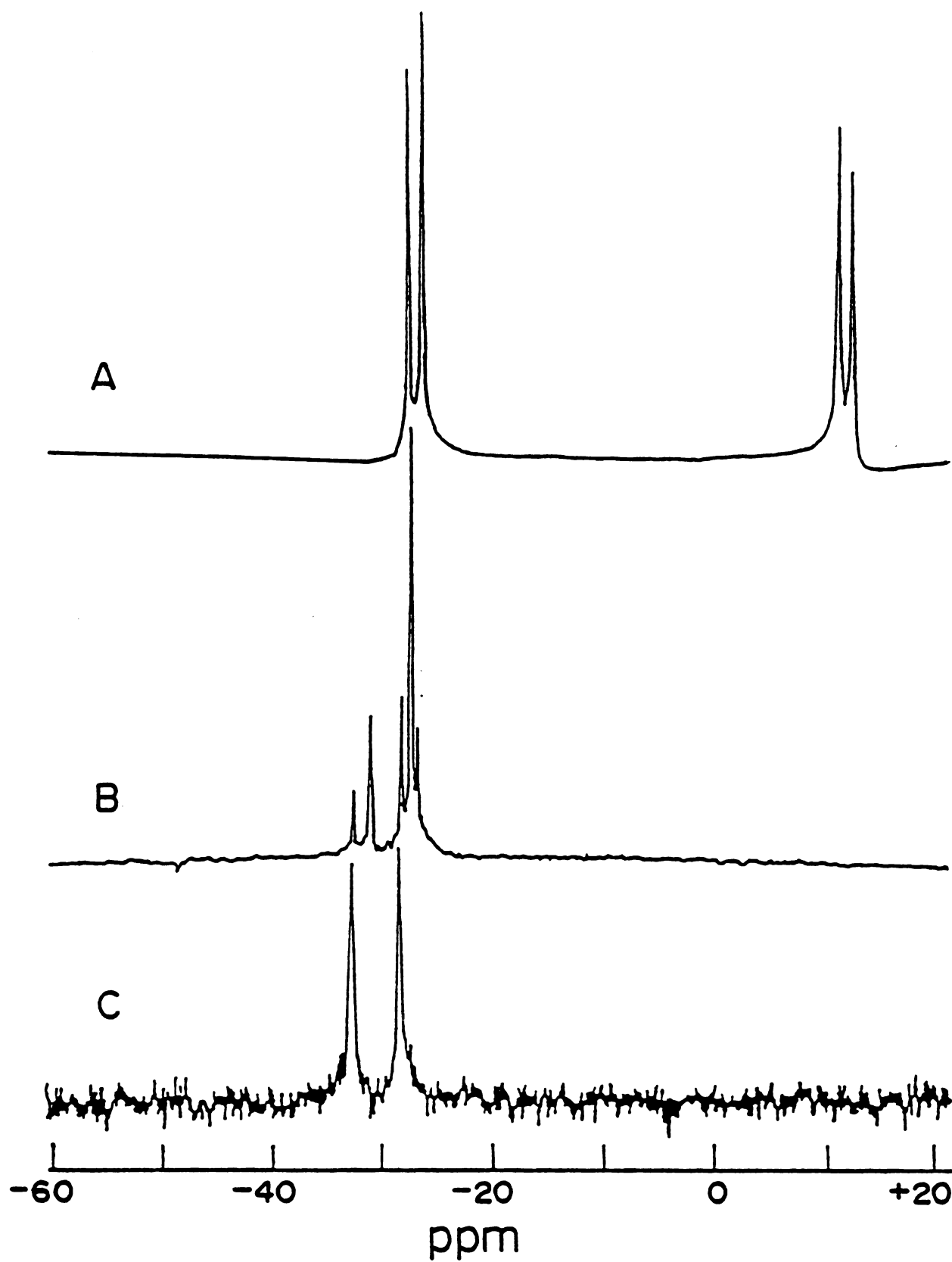


FIGURE 4

with $[\text{RhCl}(\text{COD})]_2$ results in chloride bridge cleavage and the formation of two equivalents of $\text{RhCl}(\text{COD})(\text{PPh}_3)$.⁵⁸ Under the same reaction conditions the substitution of $\text{P-P}^+\text{BF}_4$ for PPh_3 produces the analogous cationic complex, $[\text{RhCl}(\text{COD})(\text{P-P}^+)]\text{BF}_4$.

The infrared spectrum of this complex, (Figure 3), contains most of the bands characteristic of the cationic ligand and BF_4^- . Bands due to Rh-COD and Rh-Cl stretching vibrations would be expected between $600\text{-}300\text{ cm}^{-1}$ and $300\text{-}200\text{ cm}^{-1}$ respectively.⁶³

The proton nmr spectrum of $[\text{RhCl}(\text{COD})(\text{P-P}^+)]\text{BF}_4$ exhibits two sharp COD vinyl proton resonances which compare favorably in position with those observed for $\text{RhCl}(\text{COD})(\text{PPh}_3)$ (Table 3).^{36b,64} In addition, three resonances attributable to cationic ligand methylene protons are observed, although the one at ~ 2.1 ppm is not well resolved due to overlapping COD methylene proton resonances in the range $2.4 - 1.9$ ppm.

The phosphorus-31 nmr spectra of $[\text{RhCl}(\text{COD})(\text{P-P}^+)]\text{BF}_4$ and $\text{RhCl}(\text{COD})(\text{PPh}_3)$ at $+28^\circ$ are shown in Figure 4. The phosphorus chemical shift for the latter compound is -30.6 ppm and $J_{\text{PRh}} = 151$ Hz.

At $+28^\circ$, $[\text{RhCl}(\text{COD})(\text{P-P}^+)]\text{BF}_4$ exhibits a five line pattern. It was expected that a first order spectrum would contain six lines consisting of a doublet of doublets near -31 ppm (where $J_{\text{PRh}} = \sim 150$ Hz and $J_{\text{pp}^+} = \sim 46$ Hz) for the phosphorus bound to rhodium (P) and a doublet near -27.1 ppm ($J_{\text{pp}^+} = \sim 46$ Hz) for the quaternized phosphorus (P^+). The

absence of a doublet at +12.1 ppm indicates that there is no free cationic ligand in the solution. Comparison of Figure 4(A) with 4(B) shows that the three upfield peaks in the latter spectrum lie in the region expected for the P^+ doublet. The three upfield resonances cannot be considered a triplet since the two smaller peaks are not symmetrically disposed about the larger peak. First order analysis of any bonding scheme in which the cationic ligand retains its integrity and is bound to rhodium all predict spectra consisting of at least six lines. Moreover, the observed five line pattern cannot be rationalized in terms of any bonding configuration which might result if the integrity of the cationic ligand was destroyed on reaction with $[RhCl(COD)]_2$ and/or solvent - either by oxidative addition of the phosphonium group to rhodium or by cleavage of the ligand's ethylene bridge or by quaternization of the trivalent phosphorus.

Comparison of the ^{31}P nmr spectra of $RhCl(COD)(PPh_3)$ and $P-P^+BF_4$ indicates that the difference in the expected chemical shift between P and P^+ for $[RhCl(COD)(P-P^+)]BF_4$ (~130 Hz) is smaller than the expected P-Rh coupling constant (~150 Hz). Complex nmr spectra are often observed for spin systems where coupling constants are larger than, or approximate the difference in chemical shifts between nuclei. In addition, complex spectra often appear deceptively simple, particularly in multispin systems where the coupling between two of the nuclei is weak.⁶⁵ The ^{31}P nmr spectrum of $[RhCl(COD)(P-P^+)]-BF_4$ is readily interpreted as an ABX splitting pattern in

which the coupling between Rh and P^+ is relatively small compared with J_{PRh} and J_{PP^+} .

As shown in Figure 5, the ^{31}P nmr spectrum of $[RhCl(COD)(P-P^+)]BF_4$ is also temperature dependent. Spectra below -80° were not recorded, so it is not known whether that is the limiting temperature. Since the -80° spectrum is not susceptible to first order analysis both the $+28^\circ$ and -80° spectra were submitted to the ABX spectral analysis technique outlined by Becker,⁶⁵ with the following results: at $+28^\circ$, $\delta P = -29.5$ ppm, $\delta P^+ = -27.3$ ppm, $J_{PRh} = +149$ Hz, $J_{PP^+} = +54$ Hz and $J_{P^+Rh} = +7$ Hz. At -80° , $\delta P = -31.8$ ppm, $\delta P^+ = -27.3$ ppm, $J_{PRh} = +153$ Hz, $J_{PP^+} = +62$ Hz and $J_{P^+Rh} = -6$ Hz.

Despite the anomalous temperature dependent behavior of the cationic complex, the chemical shift of P is very close to that of PPh_3 for the analogous uncharged complex, which does not exhibit a temperature dependent nmr spectrum, the J_{PRh} values for the respective complexes are nearly identical. Although $P-P^+BF_4$ is expected to be more basic and possess greater steric bulk than PPh_3 , it may be inferred from the 1H and ^{31}P nmr data that, at least for $RhCl(COD)L$ complexes, the cationic ligand interacts with the rhodium center to much the same degree.

The ABX analyses were based on the following considerations in line with Becker's treatment.⁶⁵ A, B and X correspond to the P, P^+ and Rh nuclei respectively. The $(ab)_+$ and $(ab)_-$ quartets were identified as peaks 1, 2, 3, 5 and 3, (4, 4), 5 respectively for the $+28^\circ$ spectrum and the

Figure 5. Temperature dependent ^{31}P nmr spectra of $[\text{RhCl}(\text{COD})(\text{P-P}^+)]\text{BF}_4$, 0.1 M in CH_2Cl_2 . The -80° spectrum was obtained at twice the instrument gain of the others.

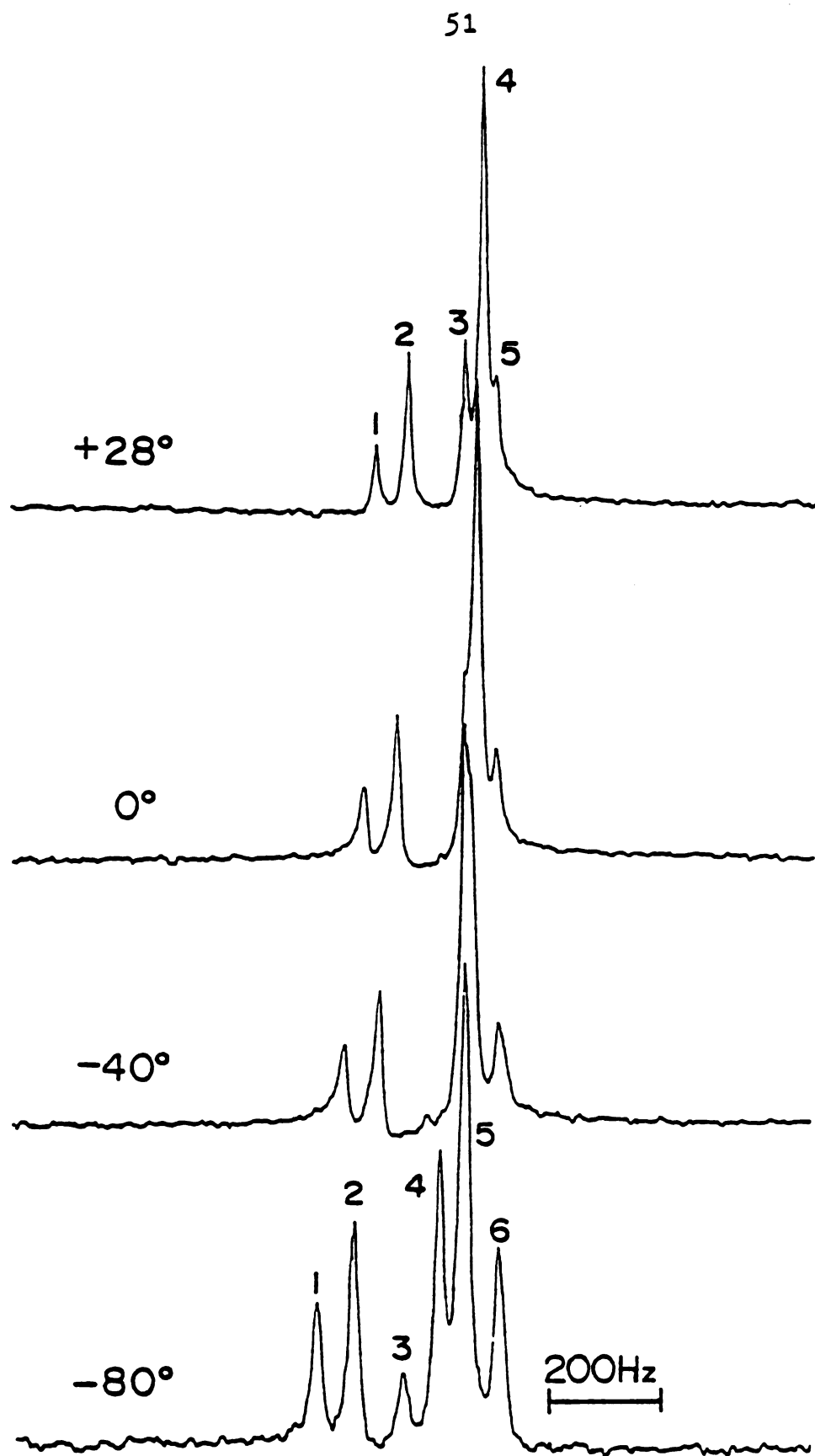


FIGURE 5

difference between peaks 1 and 2 was taken as J_{AB} (54 Hz). From the $+28^\circ$ spectral data; $\frac{1}{2}|J_{AX} + J_{BX}| = 78$ Hz, $2D_+ = 151$ Hz and $2D_- = 54$ Hz. These values allow only one possible solution for the set of values for $(\nu_A - \nu_B)$ and $\frac{1}{2}(J_{AX} - J_{BX})$ in the $+28^\circ$ spectral analysis. The $(ab)_+$ and $(ab)_-$ quartets in the -80° spectrum were identified as peaks 1, 2, 5, 6 and 3, 4, 5, 6 respectively and the difference between peaks 1 and 2 was taken as J_{AB} (62 Hz). From the -80° spectral data; $\frac{1}{2}|J_{AX} + J_{BX}| = 73$ Hz, $2D_+ = 250$ Hz and $2D_- = 104$ Hz. Of the two solutions for the -80° ABX spectral analysis the one in which $J_{PRh} = +236$ Hz and $J_{P^+Rh} = -89$ Hz was rejected since these values are much too large to consider as reasonable for the complex and ligand.

B. Heterogeneous Systems I

1. $RhCl(PPh_3)_3/Hect$, $RhCl_3/Hect$, $P-P^+/Hect$,
 $RhCl(PPh_3)_3/P-P^+/Hect$, $RhCl_3/P-P^+/Hect$ and
 $[RhCl(COE)_2]_2/P-P^+/Hect$

Although hectorite physisorbs the uncharged species $RhCl(PPh_3)_3$ and $RhCl_3$, both desorb from the support upon washing with an appropriate solvent. The $RhCl(PPh_3)_3/Hect$ system is an active catalyst for the hydrogenation of 1-hexene in methanol, but much of the activity can be attributed to desorbed catalyst in solution, the quantity of which increases as the reaction progresses. Filtrates taken from $RhCl(PPh_3)_3/Hect$ hydrogenation systems are yellow in color and exhibit a reactivity for 1-hexene hydrogenation only one fourth less than the original activity.

In an effort to eliminate the desorption problem associated with these systems, phosphinated hectorite, $P-P^+/Hect$, was prepared by the exchange reaction between $P-P^+Br$ and $Na^+/Hect$. It was felt that this material could be employed in the same way that phosphinated polymers and silica gels are used to prepare supported catalysts, as outlined in the reactions listed in part 3 of Table 2. $P-P^+$ would serve not only as a phosphine ligand but also as the electrostatic binding agent for the otherwise neutral catalysts generated by this method.

Aside from the prominent bands attributable to the mineral, the infrared spectra of mull samples of $P-P^+/Hect$ exhibit bands at 1440 cm^{-1} and in the region $800 - 600\text{ cm}^{-1}$ characteristic of the ligand, albeit of lesser intensity. Although the concentration of $P-P^+$ is high within the mineral, about 68% of the cation exchange capacity, X-ray diffraction analysis of $P-P^+/Hect$ powder indicated that at least a monolayer of additional solvent may be incorporated within the mineral interlayers under wet conditions (see Section III. C. 6). This should allow easier penetration by metal complex precursors to intercalated ligand sites.

No detectable (color) amount of $RhCl(PPh_3)_3$ was supported on $P-P^+/Hect$ after 18 hours contact. It has been found that efficient displacement of PPh_3 from this complex by polymer supported phosphines requires two weeks equilibration time.^{15,31} No attempt was made to determine whether longer contact times would allow support of $RhCl(PPh_3)_3$ on

the phosphinated mineral since the other reactions listed in part 3 of Table 2 produce similar catalysts in much less time.

The addition of RhCl_3 to $\text{P-P}^+/\text{Hect}$ produces an orange-pink colored mineral which presumably contains either Rh(III) or Rh(I) phosphine complexes. These species do not appear to desorb (color) from the phosphinated hectorite. Addition of hydrogen produces a very light yellow material. This color change is characteristic of the formation of Rh(III) dihydride phosphine complexes, but even though phosphinated polymer supported RhCl_3 is an active hydrogenation catalyst,^{27c,30a,c,j} $\text{RhCl}_3/\text{P-P}^+/\text{Hect}$ proved to be inactive for the hydrogenation of 1-hexene. A rationale for this inactivity is provided in Section III. C. 2.

Exposure of $[\text{RhCl}(\text{COE})_2]_2$ to phosphinated hectorite over short periods of time (minutes) produces a yellow material which presumably contains rhodium(I) phosphine complexes (see the last reaction listed in part 3b of Table 2). The yellow color cannot be washed from the mineral. However, $[\text{RhCl}(\text{COE})_2]_2/\text{P-P}^+/\text{Hect}$ was also inactive for the hydrogenation of 1-hexene in methanol, although it lightened in color on addition of hydrogen. A rationale for the inactivity of $[\text{RhCl}(\text{COE})_2]_2/\text{P-P}^+/\text{Hect}$ is provided in Section III. C. 2.

2. $\text{Rh(0)}/\text{P-P}^+/\text{Hect}$, $\text{Rh(0)}/\text{Hect}$, $\text{Rh(0)}/\text{Kaol}$,
and $\text{Rh(0)}/\text{SILG}$

During the course of the work on the $[\text{RhCl}(\text{COE})_2]_2/\text{P-P}^+/\text{Hect}$ systems it was found that prolonged contact (hours) of $[\text{RhCl}(\text{COE})_2]_2$ with $\text{P-P}^+/\text{Hect}$ resulted in the formation of

a dark gray material. The cause of the dark gray color was deduced to be supported rhodium metal since this material is not only an efficient catalyst for the hydrogenation of 1-hexene but, like other supported Rh(0) catalysts,⁶⁶ it hydrogenates benzene as well. The zero valent rhodium cannot be washed from the mineral.

Although the mechanism remains uncertain at this point, the formation of Rh(0) appears to result from surface catalyzed disproportionation of $[\text{RhCl}(\text{COE})_2]_2$, which produces Rh(0) and Rh(III) species. Rhodium metal is precipitated after a period of months from methanol, methylene chloride or benzene stock solutions of $[\text{RhCl}(\text{COE})_2]_2$ stored under N_2 in pyrex flasks. The originally light yellow solutions change to a deep yellow or orange-red color during this process depending upon the initial concentration, a color change characteristic of the formation of non-phosphinated Rh(II) species, especially RhCl_3 . Rh(0) formation occurs within hours, however, when $[\text{RhCl}(\text{COE})_2]_2$ is brought into contact with natural hectorite, kaolinite or silica gel. (Kaolinite is an alumino-silicate mineral composed of alternating layers of aluminum and silica.) The resulting Rh(0) materials, Rh(0)/Hect, Rh(0)/Kaol and Rh(0)/SILG, are all excellent catalysts for the hydrogenation of 1-hexene and hydrogenate benzene as well. The rhodium metal does not wash free of the support, either prior to or during the course of hydrogenation experiments.

The activities of these metal supported catalysts

compare favorably with the commercial catalyst, 5% Rh/Al₂O₃ (see Table 4). The rate behavior of the catalysts for 1-hexene hydrogenation is typical of supported metal catalysts.⁶⁶ During the course of the reaction the initial rate is the fastest and is maintained until at least 75% hydrogenation, when the rate decreases as a result of decreased substrate concentration. One possible rationalization of the lower activity of the smectite catalysts may be that each specific support allows only a certain degree of rhodium metal aggregation - isolated atoms vs. clusters - resulting in differences in the nature of the active sites between the catalysts.

3. R₃Si/Mont and [RhCl(COE)₂]₂/R₃Si/Mont

Silylation of surface hydroxyls appears to inhibit the [RhCl(COE)₂]₂ disproportionation reaction. The edges of the silicate sheets in smectites contain surface silanols which can be silylated with a 2:1 mixture of (Me₂Si)₂NH and Me₃SiCl. [RhCl(COE)₂]₂ may be exposed to silylated montmorillonite for days before any observable disproportionation occurs. Montmorillonite is structurally related to hectorite but contains Al³⁺ ions instead of Mg²⁺ ions in the octahedral sheets.

No attempt was made to prepare a phosphinated derivative of silylated montmorillonite or hectorite because of the lack of success in producing catalytically active materials with phosphinated hectorite as a support for rhodium-phosphine complexes. However, silylation offers an attractive

Table 4. Initial Hydrogenation TO#'s for Supported Rh(0)
Catalysts

<u>Catalyst</u>	<u>Substrates</u>		<u>Loading</u>
	<u>1-Hexene</u>	<u>Benzene</u>	<u>mmol Rh/0.2 g</u>
Rh(0)/P-P ⁺ /Hect	391	1	0.03
Rh(0)/Hect	393	1	0.03
Rh(0)/Kaol	413	NA	0.05
Rh(0)/SILG	1301	5	0.01
5% Rh/Al ₂ O ₃	1010	NA	

TO#'s reported as ml H₂/min/mmol Rh at 10% hydrogenation.

Conditions: Substrates 1 M in methanol, 0.2 g catalyst in 30 ml total volume at 25° and atmospheric pressure. The 5% Rh/Al₂O₃ result is taken from reference 67.

method for protecting catalysts and substrates from surface silanol interference. Naturally, there may be situations when the presence of surface hydroxyls is a desired feature, but if reactions of known homogeneous catalysts are to occur exclusively in interlayer space, the disruptive silanol interaction may be minimized through silylation. This is particularly important for systems which would utilize moisture sensitive organometallics, which are known to bind hydroxyls of silica gel and alumina.^{9f,h,24,68}

C. Homogeneous Systems

Unlike $[\text{RhCl}(\text{COE})_2]_2$, $[\text{RhCl}(\text{COD})]_2$ is stable toward disproportionation and may be stored in solution under oxygen free conditions for long periods of time. Tsuji has prepared $\text{RhCl}(\text{PPh}_3)_3$ from $[\text{RhCl}(\text{COD})]_2$ and excess PPh_3 ,⁴⁸ and a number of workers have utilized $[\text{RhCl}(\text{COD})]_2$ as a precursor in the preparation of polymer and/or silica bound rhodium-phosphine complex catalysts.^{26a,c,27f,30b,c,j,34}

Although the initial studies with phosphinated hectorite were unsuccessful in generating mineral bound cationic catalysts, it was felt that if a cationic rhodium phosphine catalyst employing the positively charged ligand could be generated in situ, it might be possible to bind this active species by direct exchange with the mineral.

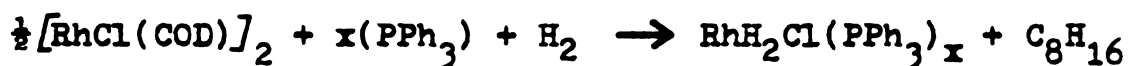
Methanol was chosen as the solvent system for these studies. Benzene is generally the solvent of choice for Wilkinson type catalysts but methanol was chosen because the cationic ligand is not soluble in nonpolar solvents.

Methanol is also capable of swelling hectorite interlayers, thus providing a more solution-like environment for mineral bound complexes.

Wilkinson's catalyst has not been employed for the hydrogenation of olefins in methanol previously, due to its low solubility in this solvent. As a result it was necessary to investigate the general catalytic behavior for 1-hexene hydrogenation of Wilkinson's catalyst generated from $[\text{RhCl}(\text{COD})]_2$ and an appropriate number of moles of PPh_3 in order that legitimate comparison of this catalyst might be made with those incorporating $\text{P-P}^+\text{BF}_4^-$.

1. Hydrogenations Employing 0:X:1 $\text{P-P}^+\text{BF}_4^-:\text{PPh}_3:\text{Rh}$ Catalysts

The variation in catalytic activity as a function of the $\text{PPh}_3:\text{Rh}$ ratio was studied for the $[\text{RhCl}(\text{COD})]_2 - \text{PPh}_3$ system in methanol. It was assumed, based on previous work with analogous systems,⁴⁷ that the combination of stock solutions of $[\text{RhCl}(\text{COD})]_2$ and PPh_3 , followed by addition of hydrogen, would reduce COD to cyclooctane via rhodium hydride intermediates prior to formation of the desired catalyst, according to the following reaction.



The results for the 1-hexene hydrogenation activity of the systems employing $\text{PPh}_3:\text{Rh}$ ratios from 6:1 to 0:1 are presented in Table 5. These results complement the findings of other workers in this area.⁴⁷ A 2:1 $\text{PPh}_3:\text{Rh}$ ratio produces the most active catalyst, favoring

Table 5. TO#'s for 0:X:1 Hydrogenation Catalysts

Catalyst	<u>Catalyst Turnover (CT)</u>									
	100	200	300	400	500	600	700	800	900	
P-P ⁺ , PPh ₃ , Rh										
0:6:1	55	58	60	58	53	53	NA			
0:5:1	76	66	62	56	52	49	NA			
0:4:1	133	118	124	106	100	93	87	83	86	
0:3:1	242	206	232	224	216	204	195	147	131	
0:2:1	536	528	463	374	284	216	147	99	52	
0:1.5:1	316	251	236	155	56	13	0			
0:1:1	30	23	(Either Rh(0) Forms or Reaction Stops)							
0:0:1	(No Reaction - Rh(0) Forms Within 1-2 Hrs)									

TO# (ml H₂/min/mmol Rh). Substrate = 1-Hexene, 1 M (CH₃OH), 30 ml total volume, 25°, 740 torr. 0.02 mmol Rh(I) ([RhCl(COD)]₂), 1-Hexene:Rh = 1500:1.

coordinatively unsaturated intermediates such as $\text{RhCl}(\text{PPh}_3)_2$ and $\text{RhH}_2\text{Cl}(\text{PPh}_3)_3$. Increasing the $\text{PPh}_3:\text{Rh}$ ratio results in a loss of activity due to the competition of excess PPh_3 with substrate for coordination sites at the metal center. The loss of activity at $\text{PPh}_3:\text{Rh}$ ratios lower than 2:1 was at one time attributed to the formation of a catalytically inactive dimeric species,^{47a} $[\text{RhCl}(\text{PPh}_3)_2]_2$, but Tolman has recently shown that the dimer is a good catalyst for olefin hydrogenation.^{47c} Rhodium complexes containing less than two phosphines may either be unable to activate molecular hydrogen, or they may form tightly bound olefin complexes which are incapable of reductive elimination under hydrogenation conditions. $[\text{RhCl}(\text{COD})]_2$, in the absence of PPh_3 , is not a catalyst, but it is slowly reduced under hydrogenation conditions to rhodium(0), an excellent olefin hydrogenation catalyst.

2. Hydrogenations Employing Y:X:1 $\text{P-P}^+\text{BF}_4:\text{PPh}_3:\text{Rh}$ Catalysts

The combination of various quantities of $\text{P-P}^+\text{BF}_4$ and $[\text{RhCl}(\text{COD})]_2$, followed by exposure of the resulting solutions to hydrogen, does not produce species capable of acting as catalysts for the reduction of 1-hexene. As seen in Table 6, the systems derived from $\text{P-P}^+\text{BF}_4:\text{Rh}$ ratios of 1:1, 2:1 and 3:1 were all inactive. The cationic ligand might be expected to be more basic than PPh_3 . Wilkinson has found that ligands of much higher basicity than PPh_3 generally afford less active hydrogenation catalysts.^{47f} In fact, at a phosphine:Rh

Table 6. TO#s for Y:X:1 Hydrogenation Catalysts

Catalyst P-P ⁺ :PPh ₃ :Rh	Catalyst Turnover (CT)									
	100	200	300	400	500	600	700	800	900	
1:0:1	(NO RXN)									
2:0:1	(NO RXN)									
3:0:1	(NO RXN)									
1:1:1	95	90	97	93	84	79	71	64	58	
2:1:1	69	98	121	122	64	18	NA			
1:2:1	404	353	330	309	303	286	263	240	218	
2:2:1	209	238	254	268	274	286	269	264	248	

TO# (ml H₂/min/mmol Rh). Substrate = 1-Hexene, 1 M (CH₃OH), 30 ml total volume, 25°, 740 torr. 0.02 mmol Rh(I) ([RhCl(COD)]₂), 1-Hexene:Rh = 1500:1.

ratio of 2:1 the PEt_3 system shows very little activity, but PPh_2Et (which should have nearly the same electronic properties as the cationic ligand) is highly active. At a phosphine:Rh ratio of 2:1 the PPh_2Et system is only one tenth less active than the PPh_3 system. As a result, electronic effects alone cannot explain why $\text{P-P}^+\text{BF}_4$ is a poorer ligand for olefin hydrogenation than PPh_3 .

The primary difference between $\text{P-P}^+\text{BF}_4$ and PPh_3 is one of steric bulk. PPh_3 is generally considered to be quite bulky, but comparison of space-filling models of the two ligands indicates that, regardless of the conformation about the ethylene bridge, $\text{P-P}^+\text{BF}_4$ should be much more bulky than PPh_3 . Tolman has enumerated some of the effects on the activity and selectivity of homogeneous catalysts as the size of the substituents on phosphorus ligands increases.⁶⁹ In general, smaller ligands in competition for coordination sites with the bulky ligands are usually bound preferentially, and less crowded isomers are favored if the possibility of different isomers exists. Further, both increases in the rates of phosphorus ligand dissociative reactions and decreases in rates of associative ones are observed as the ligand size increases. If the phosphorus ligands are particularly bulky, they can often interfere with or prevent the coordination of other ligands which would normally be strongly bound, for example, CO , O_2 or C_2H_4 . This is especially true if there are two or more larger ligands in the coordination sphere of the metal. All of these effects,

in combination with the electronic requirements of the system, contribute to the reactivity patterns of homogeneous catalysts.

The yellow 2:0:1 and 3:0:1 systems do lighten in color on exposure to hydrogen, characteristic of the formation of Rh(III) dihydride complexes. However, the 2:0:1 and 3:0:1 catalysts must be so crowded at the metal center that coordination by olefin, followed by metal alkyl formation and reductive elimination of product, is sterically hindered. The inactivity of the 1:0:1 system is not surprising in view of the behavior of the 0:1:1 catalyst.

In view of the results with these homogeneous systems, it is not surprising that the heterogeneous systems employing phosphinated hectorite as a support were inactive as olefin hydrogenation catalysts (Section III. B. 1). The complexes formed within the interlayers of $P-P^+/Hect$ should be little different from the 1:0:1, 2:0:1 and 3:0:1 homogeneous species.

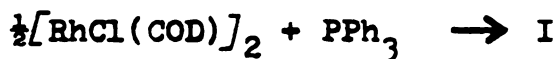
Combination of the cationic ligand with a less bulky phosphine ligand should and apparently does reduce the steric crowding at the metal center sufficiently to produce an active hydrogenation catalyst. A 1:1:1 ratio of $P-P^+BF_4$: PPh_3 :Rh affords a catalyst of good longevity but of much lower activity than the analogous 0:2:1 catalyst (Tables 6 and 5). The lower activity of this system can be attributed to the steric and electronic effects discussed earlier. The probable bonding configuration of this catalyst is discussed in the next section.

2:1:1, 1:2:1 and 2:2:1 ratios of $P-P^+BF_4:PPh_3:Rh$ also afford active homogeneous catalysts (Table 6). The 2:1:1 catalyst is interesting in that, as expected from comparison of the 0:2:1 and 0:3:1 catalysts (Table 5), addition of another mole of $P-P^+BF_4$ decreases the initial rate due to phosphine competition for olefin coordination sites at the metal center. However, the complexes must undergo ligand redistribution reactions because during the course of the reaction the rates increase. Formation of small amounts of " $RhCl(PPh_3)_2$ " species should increase the rate since this would be the most active catalyst in the solution.

Consideration of the results for the 1:2:1 system indicates that less bulky PPh_3 must be able to compete for coordination sites much more efficiently than $P-P^+BF_4$. The resulting catalyst system is nearly as active as the 0:2:1 catalyst and more active than the 0:3:1 system. The major species in solution no doubt resemble those of the 0:2:1 catalyst, the cationic ligand competing only moderately well compared to PPh_3 for olefin coordination sites on the metal. The 2:2:1 catalyst is simply an extension of the 1:2:1 system in which an additional mole of $P-P^+BF_4$ has been added. The 2:2:1 catalyst is much more active than the analogous 0:4:1 system, again indicating that $P-P^+BF_4$ is less able to compete for coordination sites than PPh_3 due to its large steric bulk.

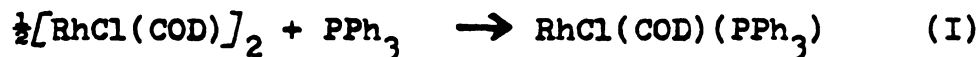
3. Characterization of Catalyst Precursors

A phosphorus-31 nmr study was undertaken in an effort to better understand the nature of the homogeneous catalysts. Of particular interest were those catalysts derived from 0:2:1 and 1:1:1 P-P⁺BF₄:PPh₃:Rh ratios. The 0:2:1 catalyst is generated by the sequential addition of PPh₃, H₂ and 1-hexene to [RhCl(COD)]₂ as represented below.



It was felt that ³¹P nmr analysis of these four steps would allow characterization of the catalyst precursors and the major components of the catalyst solution. CH₂Cl₂ was used as the solvent in these studies since good spectra could not be obtained with methanol due to the limited solubility of [RhCl(COD)]₂ and most other catalyst precursors in that solvent.

As described in Section III. A, and in the literature,^{58,64} PPh₃ cleaves the chloride bridge of [RhCl(COD)]₂ to produce RhCl(COD)(PPh₃) at a 1:1 PPh₃:Rh ratio.

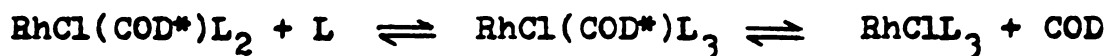
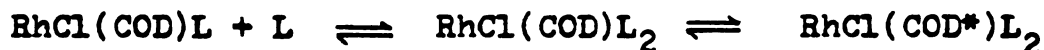


The phosphorus chemical shift for I in CH₂Cl₂ is -30.6 ppm and J_{PRh} = 151 Hz. These values may be obtained either from the generation of I in situ or from the dissolution of solid I.

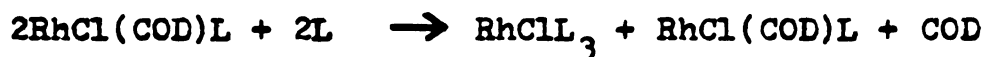
Addition of another equivalent of PPh₃ to I produces

solution II. The temperature dependent ^{31}P nmr spectra of II are reproduced in Figure 6. The doublet of triplets at $\delta\text{P}_c = -47.8$ ppm ($J_{\text{P}_c\text{Rh}} = 193$ Hz, $J_{\text{P}_c\text{P}_t} = 39$ Hz) and the doublet of doublets at $\delta\text{P}_t = -31.2$ ppm ($J_{\text{P}_t\text{Rh}} = 146$ Hz) are characteristic of $\text{RhCl}(\text{PPh}_3)_3$ (lit. ^{47}c $\delta\text{P}_c = -48.9$ ppm, $\delta\text{P}_t = -32.2$ ppm, $J_{\text{P}_c\text{Rh}} = 192$ Hz, $J_{\text{P}_c\text{P}_t} = 38$ Hz, $J_{\text{P}_t\text{Rh}} = 146$ Hz). P_c is the phosphorus cis to the two trans phosphines, P_t , in the roughly square planar complex. The resonance at $\delta\text{P} = +7.1$ ppm may be attributed to free PPh_3 (lit. ^{47}c $\delta\text{P} \sim +6$ ppm). The same spectral features were observed for II when toluene or CH_2Cl_2 were used as the solvents. Addition of two equivalents of PPh_3 directly to $\frac{1}{2}[\text{RhCl}(\text{COD})]_2$ also generates II.

The presence of $\text{RhCl}(\text{PPh}_3)_3$ in solution II was a surprising result. Proton nmr studies have shown that RhClL_3 complexes are produced on addition of L to $\text{RhCl}(\text{COD})\text{L}$, where L equals the more basic, less bulky ligands PPh_2Me , PPhMe_2 and PBu_3 ,⁷⁰ presumably according to the following scheme.



COD^* represents monodentate 1,5-cyclooctadiene. The overall reaction might be represented as follows.



However, proton nmr studies of the addition of one equivalent of PPh_3 to $\text{RhCl}(\text{COD})(\text{PPh}_3)$ in CHCl_3 have not provided any evidence for $\text{RhCl}(\text{PPh}_3)_3$ formation. The observed temperature dependence of the COD vinyl proton resonances

Figure 6. Temperature dependent ^{31}P nmr spectra of
 $\text{RhCl}(\text{COD})(\text{PPh}_3) + \text{PPh}_3$. 0.03 M in CH_2Cl_2 .

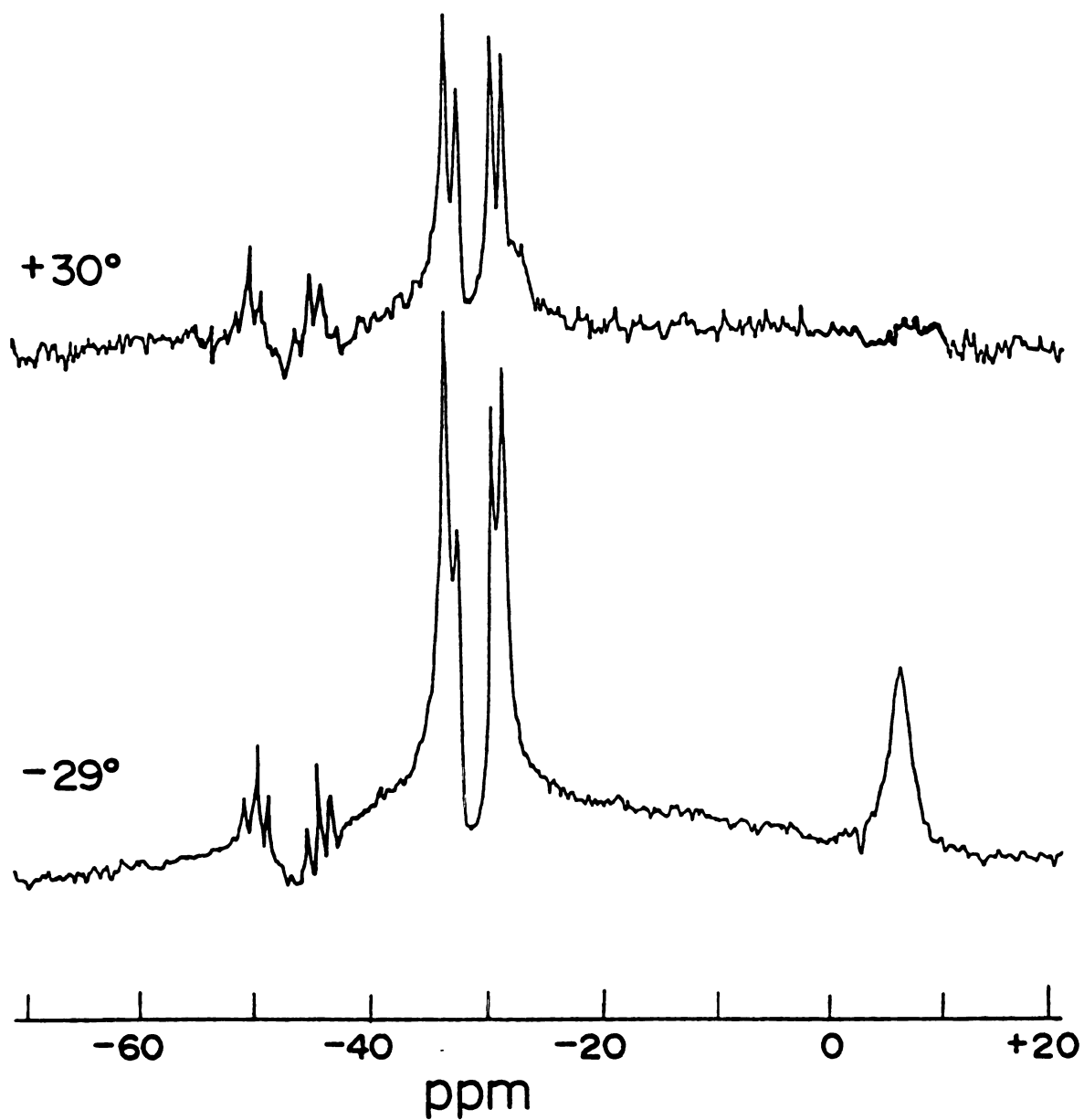


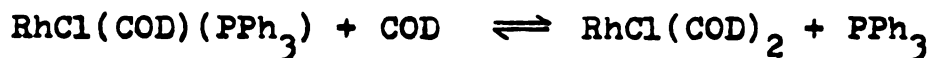
FIGURE 6

from -60° to 0° has been attributed to a phosphine exchange process involving a pentacoordinate intermediate.^{64,70}



The distinct vinyl proton resonances observed at low temperature for $\text{RhCl}(\text{COD})(\text{PPh}_3)$ broaden and coalesce as the temperature is raised. No free COD was observed in the proton nmr.

The ^{31}P nmr spectra show the presence of $\text{RhCl}(\text{PPh}_3)_3$ and free PPh_3 . $\text{RhCl}(\text{PPh}_3)_3$ appears to be a stable complex over the temperature range studied but the free PPh_3 appears to be in rapid thermal equilibrium with a second phosphine containing species. If $\text{RhCl}(\text{PPh}_3)_3$, $\text{RhCl}(\text{COD})(\text{PPh}_3)$ and COD are present in solution following reaction, an equilibrium might be set up between $\text{RhCl}(\text{COD})(\text{PPh}_3)$ and COD such that free PPh_3 and $\text{RhCl}(\text{COD})_2$ are favored at lower temperatures.



It was found however that addition of one equivalent of free COD to $\text{RhCl}(\text{COD})(\text{PPh}_3)$ produced no apparent change in the ^{31}P spectrum of the complex between $+30^{\circ}$ and -80° .

Similarly, Vrieze found that the proton nmr spectrum of $\text{RhCl}(\text{COD})(\text{PPh}_3)$ was unaffected by addition of excess COD, although only the temperatures between $+25^{\circ}$ and $+60^{\circ}$ were studied.⁶⁴ It is possible that $\text{RhCl}(\text{PPh}_3)_3$ may serve to

activate the exchange between COD and PPh_3 in some way.

Although $\text{RhCl}(\text{COD})_2$ has not been observed spectroscopically nor has it been isolated, the analogous norbornadiene complex, $\text{RhCl}(\text{NBD})_2$, has been observed in cold solutions of

$[\text{RhCl}(\text{NBD})]_2$ containing excess NBD,⁷¹ and the butadiene complex, $\text{RhCl}(\text{C}_4\text{H}_6)_2$, has been isolated.⁷² At higher temperatures, $\text{RhCl}(\text{COD})(\text{PPh}_3)$ may not be observed by ^{31}P nmr since the peaks attributable to it at -30.6 ppm may be overlapped by the doublet of doublets arising from $\text{RhCl}(\text{PPh}_3)_3$ at -31.2 ppm.

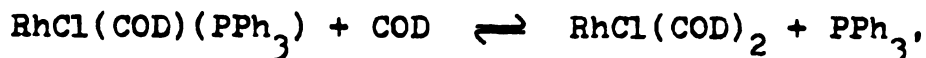
Although the hypothesis that $\text{RhCl}(\text{COD})_2$ is present with $\text{RhCl}(\text{PPh}_3)_3$ and free PPh_3 in solution II does account for the observed ^{31}P nmr spectra, it contradicts the proposed interpretation of the ^1H nmr spectra. This interpretation requires that $\text{RhCl}(\text{COD})(\text{PPh}_3)$ be present at low temperature, along with free PPh_3 .^{64,70} The existence of $\text{RhCl}(\text{PPh}_3)_3$ in II defies this interpretation based on problems of stoichiometry, although it may be possible that the vinyl protons of $\text{RhCl}(\text{COD})_2$ have the same chemical shifts as those of $\text{RhCl}(\text{COD})(\text{PPh}_3)$.

The discrepancies between the ^1H and ^{31}P nmr results are difficult to rationalize. The preparation of the compounds and solutions is essentially the same. The concentrations of the solutions used for the ^1H and ^{31}P nmr studies were of the same magnitude. Elucidation of the nature of the $\text{RhCl}(\text{COD})(\text{PPh}_3)$ plus PPh_3 system probably requires a more rigorous, independent ^1H , ^{31}P and perhaps ^{13}C nmr study in addition to conventional product separation and analysis.

Addition of hydrogen to solution II produces solution III. The temperature dependent ^{31}P nmr spectra of III

are reproduced in Figure 7. The -28° spectrum may be characterized in the following way. The downfield incompletely resolved doublet of doublets at $\delta P_t = -40.1$ ppm ($J_{P_tRh} = 115$ Hz, $J_{P_tP_c} = 18$ Hz) and the upfield unresolved doublet of triplets at $\delta P_c = -19.4$ ppm ($J_{P_cRh} = 90$ Hz) are characteristic of $RhH_2Cl(PPh_3)_3$ (lit.^{47c} $\delta P_t = -40.3$ ppm, $\delta P_c = -20.7$ ppm, $J_{P_tRh} = 114$ Hz, $J_{P_tP_c} = 18$ Hz and $J_{P_cRh} = 90$ Hz). Chemical shifts and coupling constants were taken from expanded scale spectra. The doublet centered at $\delta P = -30.6$ ppm ($J_{PRh} = 151$ Hz) is characteristic of $RhCl(COD)(PPh_3)$ (see Section III. A). Alternative peak assignments are difficult to rationalize. The temperature dependence of the spectrum of $RhH_2Cl(PPh_3)_3$ is well known.^{47c} The line broadening and loss of coupling at 28° is due to exchange of the labile phosphine cis, P_c , to the two trans phosphines, P_t .

Apparently, hydrogen adds directly to $RhCl(PPh_3)_3$ to form $RhH_2Cl(PPh_3)_3$. Although a gc analysis for reduction products of COD was not made, the presence of $RhCl(COD)(PPh_3)$ at both high and low temperatures indicates that the equilibrium,



is not operative. $RhH_2Cl(PPh_3)_3$, most likely in the highly active dissociated form, $RhH_2Cl(PPh_3)_2$, probably acts as a catalyst for the reduction of the free mole of COD in the solution.

Addition of a quantity of 1-hexene sufficient for ten

Figure 7. Temperature dependent ^{31}P nmr spectra of $\text{RhCl}(\text{COD})(\text{PPh}_3) + \text{PPh}_3 + x\text{H}_2$. 0.03 M in CH_2Cl_2 .

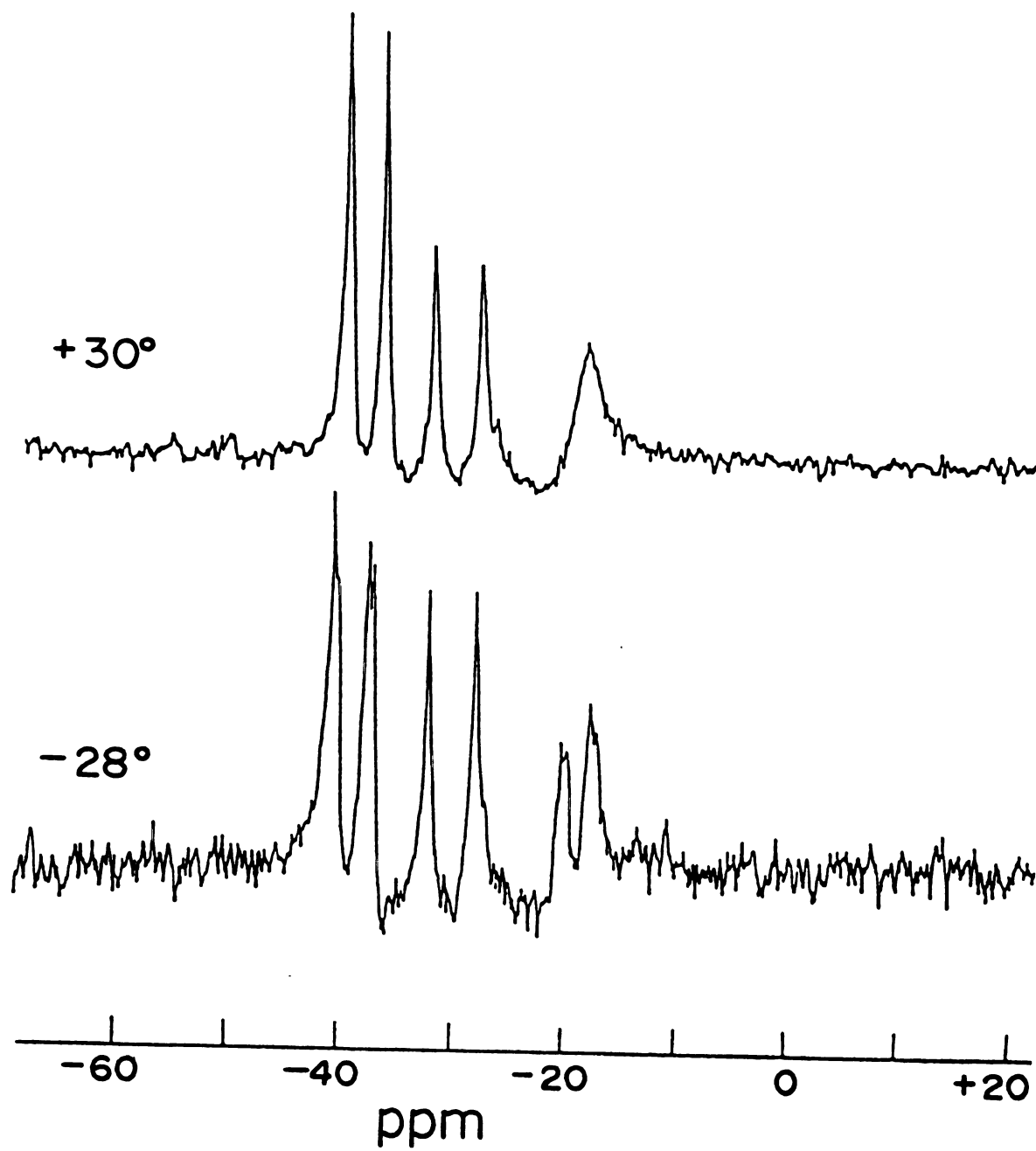


FIGURE 7

catalyst turnovers under oxygen free conditions followed by addition of H_2 until no more uptake was observed on a hydrogenation apparatus produced solution IV. The temperature dependent ^{31}P nmr spectra of IV are shown in Figure 8. In the -61° spectrum the upfield distorted doublet of doublets at $\delta P_t = -31.0$ ppm ($J_{PtRh} = 146$ Hz, $J_{PtP_c} = 39$ Hz) and the slightly obscured doublet of triplets at $\delta P_c = -47.6$ ppm ($J_{P_cRh} = 192$ Hz) are characteristic of $RhCl(PPh_3)_3$. The large doublet downfield at $\delta P = -51.5$ ppm ($J_{PRh} = 195$ Hz) is characteristic of chloride bridged dimeric species such as $[RhCl(PPh_3)_2]_2$ and $[RhCl(olefin)(PPh_3)]_2$. (See later in this section.) The absence of hydridic species indicates that the reduction of 1-hexene was incomplete so that there is probably residual olefin in solution IV.

The fact that $RhCl(PPh_3)_3$ remains as one of the major species is a surprise. For a phosphine to rhodium ratio of 2:1 it was expected that the major species in solution would contain only two phosphines in the metal's coordination sphere. The tris phosphine complex is apparently relatively more stable than the other bis and mono phosphine complexes possible in this solution.

The complex upfield patterns in the higher temperature spectra of IV are difficult to interpret based on first order spectral analysis. The equilibrium process illustrated below might account for the observed temperature dependence as well as the stoichiometry of the system, although it is difficult to say with any certainty what the $RhCl(L)(S)$

Figure 8. Temperature dependent ^{31}P nmr spectra of $\text{RhCl}(\text{COD})(\text{PPh}_3) + \text{PPh}_3 + x\text{H}_2 + y(1\text{-hexene})$ 0.03 M in CH_2Cl_2 . The $+30^\circ$, -42° and -61° spectra were taken at twice the instrument gain of the $+1^\circ$ and -21° spectra.

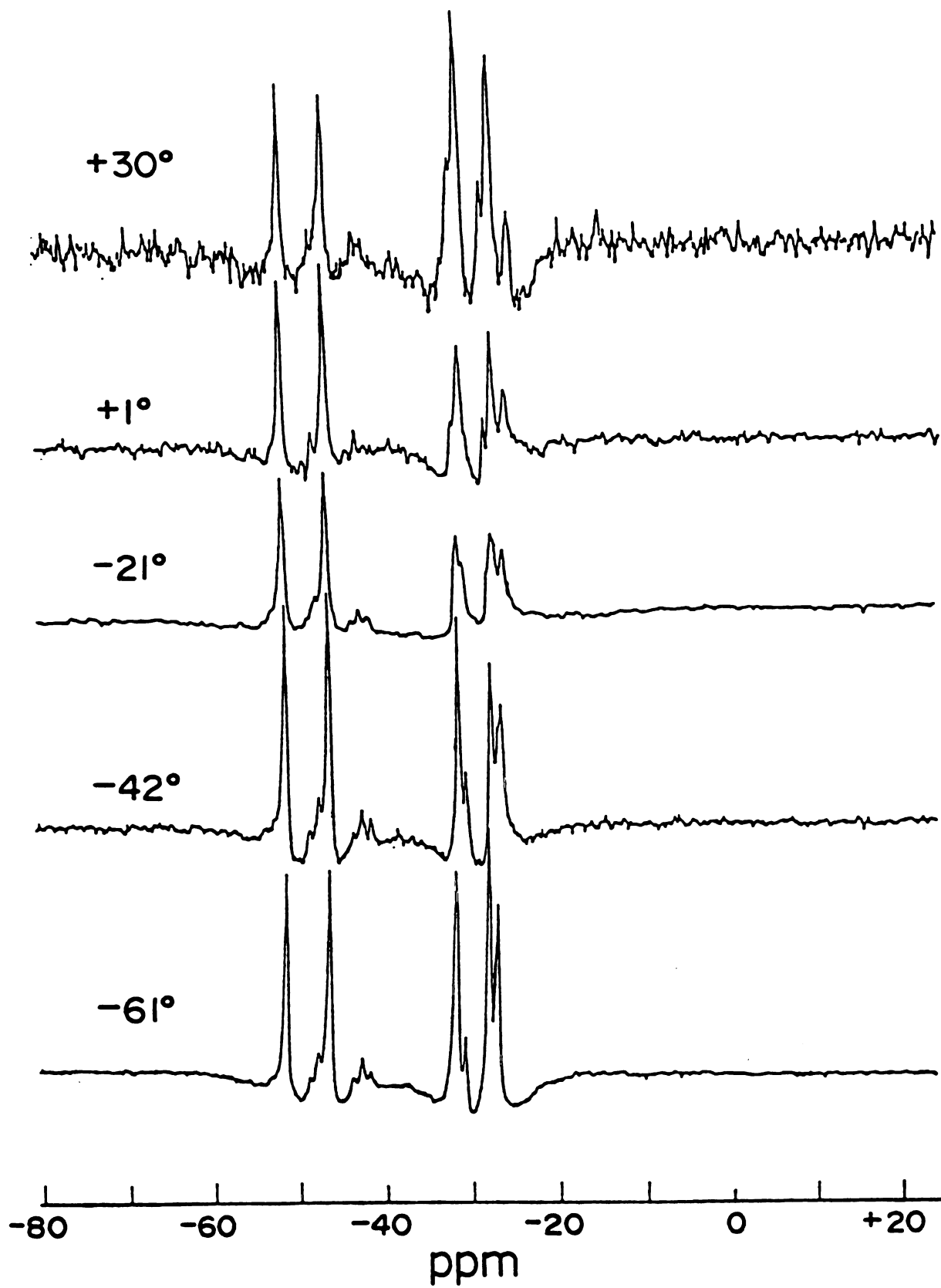
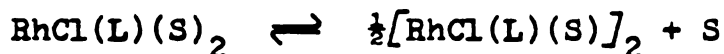


FIGURE 8

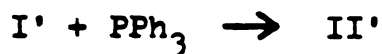
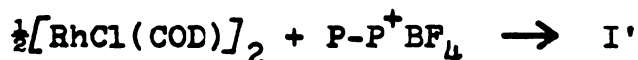
species may be because the composition of this solution has not been adequately elucidated.



S may be solvent or residual olefin. It is interesting to note that the complexes $\text{RhCl}(\text{COD})(\text{PPh}_3)$ ($\delta\text{P} = -30.6$ ppm, $J_{\text{PRh}} = 151$ Hz) and $\text{RhCl}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ ($\delta\text{P} = -35.7$ ppm, $J_{\text{PRh}} = 128$ Hz)^{47c} would both give rise to resonances in the vicinity of the complex upfield pattern of IV.

Despite the fact that $\text{RhCl}(\text{PPh}_3)_3$ and $[\text{RhCl}(\text{PPh}_3)(\text{S})]_2$ appear to be the major species in the solution they are probably not the actual catalytic species. They are probably in dissociative/associative equilibrium with the highly active species $\text{RhCl}(\text{PPh}_3)_2$ and/or $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$ which have been invoked by numerous authors to account for the observed kinetics in analogous catalyst systems.⁴⁷

A ^{31}P nmr study of the 1:1:1 catalyst system was undertaken in order that a comparison might be made with the analogous 0:2:1 catalyst system just described. The 1:1:1 catalyst is generated by the sequential addition of $\text{P-P}^+\text{BF}_4$, PPh_3 , H_2 and 1-hexene to $[\text{RhCl}(\text{COD})]_2$ as represented below.



As described in Section III. A, the addition of one equivalent of $\text{P-P}^+\text{BF}_4$ to $\frac{1}{2}[\text{RhCl}(\text{COD})]_2$ produces

$[\text{RhCl}(\text{COD})(\text{P}-\text{P}^+)]\text{BF}_4$, (I'), analogous to the preparation of I, $\text{RhCl}(\text{COD})(\text{PPh}_3)$.

Addition of one equivalent of PPh_3 to I' produced solution II'. The temperature dependent ^{31}P nmr spectra of II' are reproduced in Figure 9. The addition of PPh_3 to $[\text{RhCl}(\text{COD})]_2$ followed by addition of $\text{P}-\text{P}^+\text{BF}_4$ produces a solution whose ^{31}P nmr spectra resemble those of solution II'. The spectra are too complex to allow direct assignment of the peaks; however, certain major features of the spectra deserve comment. The large peaks near -27 ppm are in the region expected for the phosphonium group resonances of the cationic ligand. The two multiplets found between -40 and -50 ppm are reminiscent of the doublet of triplets found for $\delta_{\text{P}_c} = -47.8$ ppm of solution II and are therefore indicative of tris phosphine complexes in II'. The resonances between -20 and -35 ppm, aside from those due to the phosphonium group, are found where the trans phosphines of RhClL_3 complexes should resonate as well as the phosphine resonances due to $\text{RhCl}(\text{COD})\text{L}$ complexes. Like the spectra for II, II' shows the presence of free phosphine as the temperature is lowered, although this occurs at much lower temperature. It may be inferred from these generalizations that solution II' is similar to solution II in many ways, but the species present are much more complex since there are a number of ways in which the two different phosphine ligands may be distributed among them.

Addition of hydrogen to solution II' produces

Figure 9. Temperature dependent ^{31}P nmr spectra of $[\text{RhCl}(\text{COD})(\text{P}-\text{P}^+)]\text{BF}_4 + \text{PPh}_3$. 0.03 M in CH_2Cl_2 .

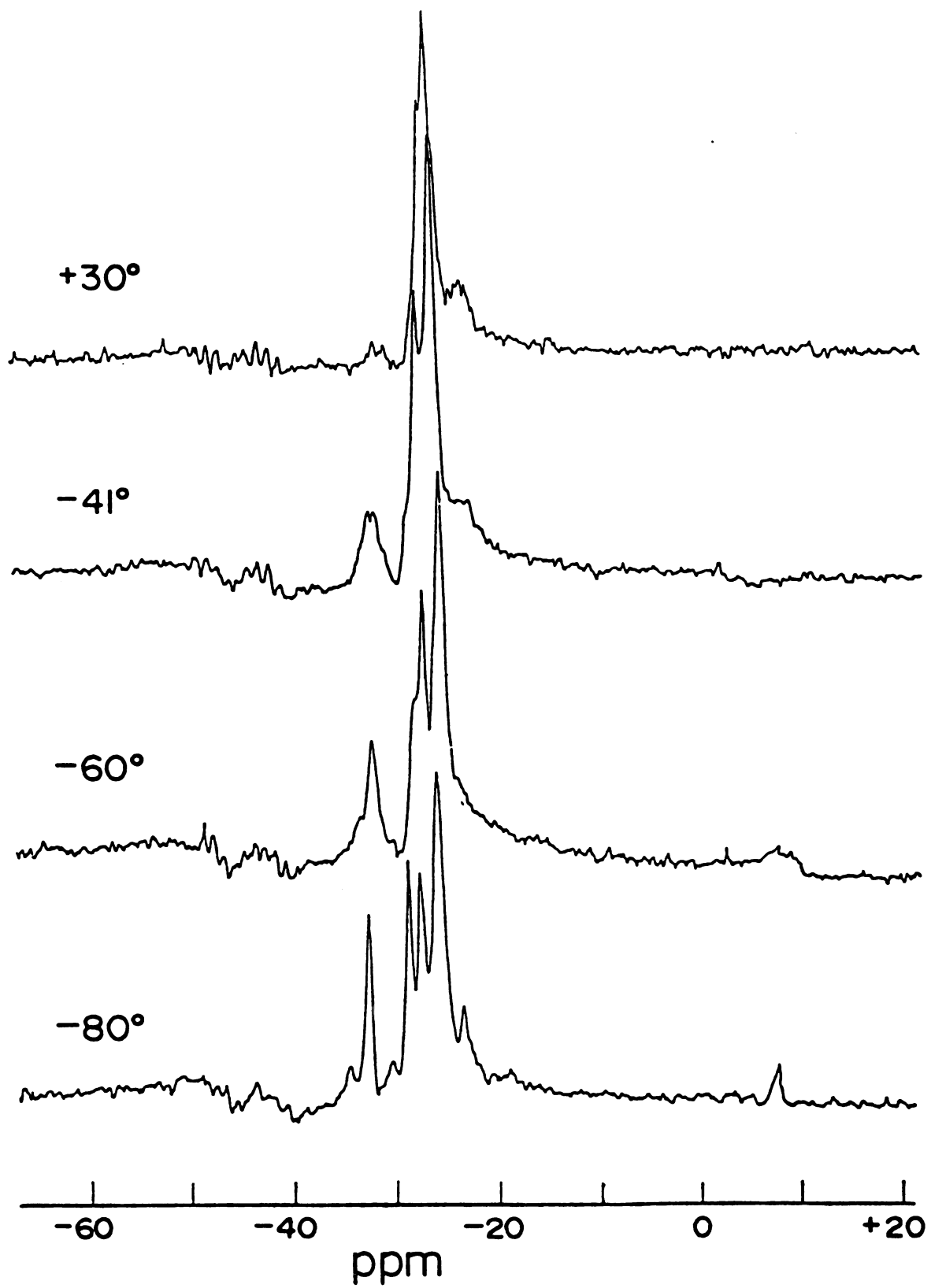


FIGURE 9

solution III'. The temperature dependent ^{31}P nmr spectra of III' are reproduced in Figure 10. These spectra are also too complex to be able to make specific peak assignments but just as the spectra of II' had certain features in common with II, III' appears to mimic the properties of III. The large central peaks near -27 ppm may be attributed to the phosphonium group of the cationic ligand. The broad multiplets near -41 ppm as well as those near -19 ppm may well indicate the presence of RhH_2ClL_3 complexes, where L is PPh_3 and/or $\text{P-P}^+\text{BF}_4$. There are also peaks centered about -30 ppm which may be due to $\text{RhCl}(\text{COD})\text{L}$ complexes. As with II', it is difficult to determine precisely which species are present in solution III', but the appearance of the spectra is suggestive of complexes similar to those found in solution III and probably containing mixed phosphine ligands.

Addition of 1-hexene to III' caused immediate precipitation of most of the rhodium containing material from the solution. The residual catalyst hydrogenated the 1-hexene only very slowly. The precipitation of most of the cationic catalyst precluded meaningful analysis of the ^{31}P nmr spectra of this solution.

Although $[\text{RhCl}(\text{COE})_2]_2$ was not used as a homogeneous catalyst precursor in this study, it was of interest to compare its reactivity toward PPh_3 and $\text{P-P}^+\text{BF}_4$ with that of $[\text{RhCl}(\text{COD})]_2$. Addition of one equivalent of PPh_3 to

Figure 10. Temperature dependent ^{31}P nmr spectra of $[\text{RhCl}(\text{COD})(\text{P}-\text{P}^+)]\text{BF}_4 + \text{PPh}_3 + \text{H}_2$. 0.03 M in CH_2Cl_2 .

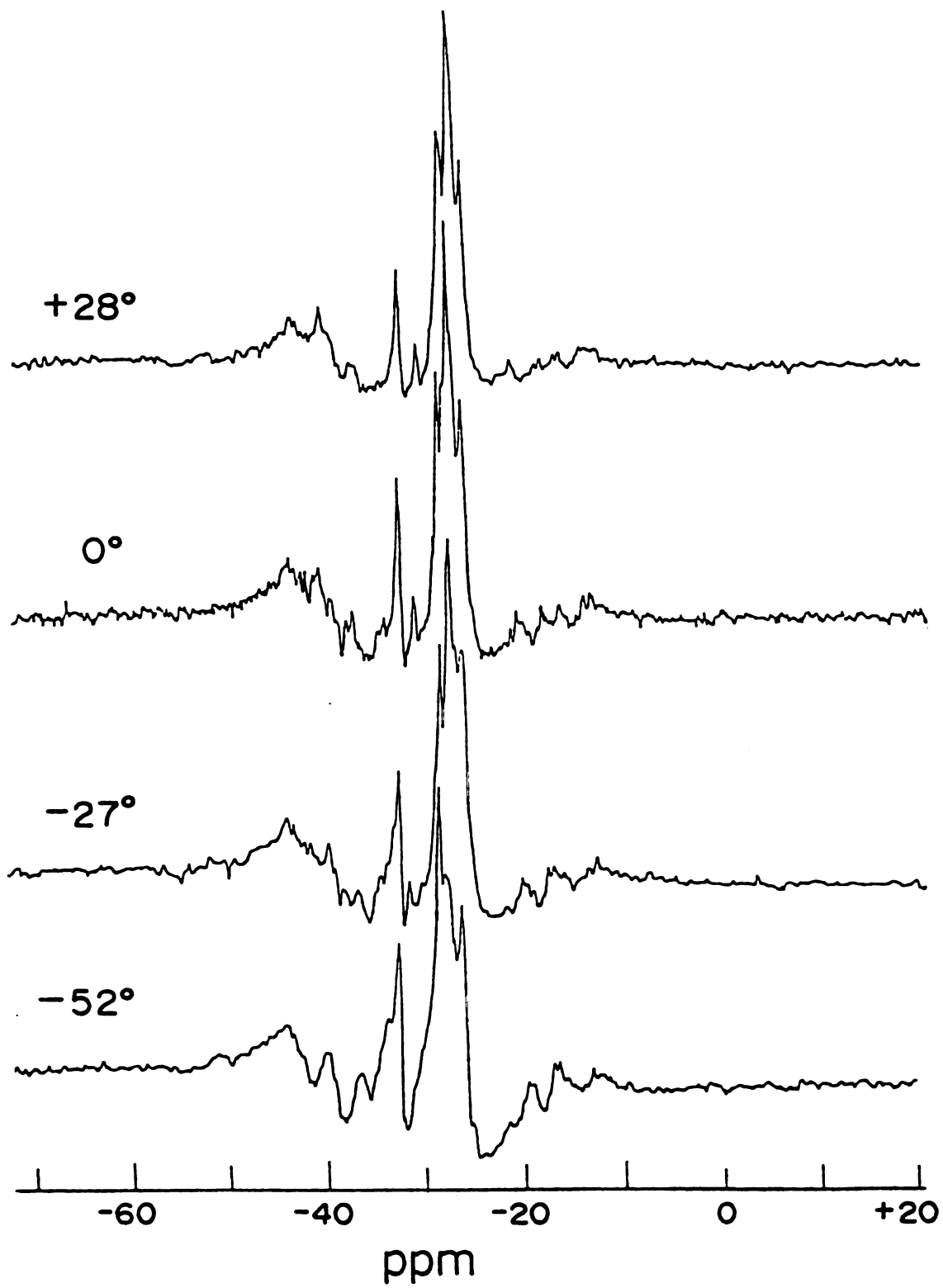


FIGURE 10

$\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2$ is known to cause displacement of one equivalent of COE by PPh_3 ,⁷⁴ not chloride bridge cleavage as is the case for $[\text{RhCl}(\text{COD})]_2$.

$\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2 + \text{PPh}_3 \rightarrow \frac{1}{2}[\text{RhCl}(\text{COE})(\text{PPh}_3)]_2 + \text{COE}$
 The ^{31}P nmr spectrum of $[\text{RhCl}(\text{COE})(\text{PPh}_3)]_2$ is shown in Figure 11 A. $\delta\text{P} = -55.2$ ppm and $J_{\text{PRh}} = 194$ Hz. It is assumed that one equivalent of COE is displaced from each rhodium center in the dimer. It is not known whether the configuration of the two phosphines about the $\text{Rh}(\text{Cl})_2\text{Rh}$ linkage is cis or trans.

Addition of two equivalents of PPh_3 to $\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2$ is known to cause displacement of two equivalents of COE by PPh_3 .^{47c,74}

$\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2 + 2\text{PPh}_3 \rightarrow \frac{1}{2}[\text{RhCl}(\text{PPh}_3)_2]_2 + 2\text{COE}$
 The ^{31}P nmr spectrum of $[\text{RhCl}(\text{PPh}_3)_2]_2$ is displayed in Figure 11 B. $\delta\text{P} = -51.5$ ppm and $J_{\text{PRh}} = 199$ Hz. This dimer is not very soluble in CH_2Cl_2 or benzene ($\sim 3 \times 10^{-5}$ M),^{47c} and it began to precipitate from the 0.05 M solution within one hour following preparation. The ^{31}P nmr data for the much more soluble complex $(\text{RhClL}_2)_2$, where $\text{L} = \text{P}(\text{p-tolyl})_3$, are $\delta\text{P} = -49.5$ ppm and $J_{\text{PRh}} = 196$ Hz.^{47c}

Addition of three equivalents of PPh_3 to $\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2$ not only displaces two equivalents of COE but also cleaves the chloride bridge of the dimer forming $\text{RhCl}(\text{PPh}_3)_3$.

$\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2 + 3\text{PPh}_3 \rightarrow \text{RhCl}(\text{PPh}_3)_3 + 2\text{COE}$
 The ^{31}P nmr spectrum of $\text{RhCl}(\text{PPh}_3)_3$ is reproduced in Figure 11 C. $\delta\text{P} = -31.5$ ppm, $\delta\text{P} = -48.3$ ppm,

Figure 11. ^{31}P nmr spectra of CH_2Cl_2 solutions containing: A, $\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2 + \text{PPh}_3$; B, $\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2 + 2\text{PPh}_3$; and C, $\frac{1}{2}[\text{RhCl}(\text{COE})_2]_2 + 3\text{PPh}_3$. A and B, $+28^\circ$; C, -34° .

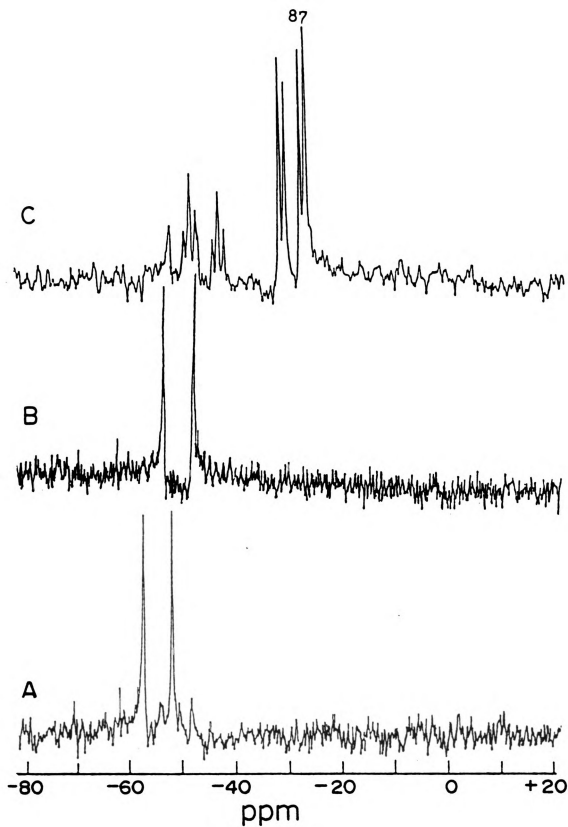


FIGURE 11

$J_{P_tRh} = 145 \text{ Hz}$, $J_{P_cRh} = 194 \text{ Hz}$ and $J_{P_tP_c} = 38 \text{ Hz}$.

Tolman has shown that $(RhClL_2)_2$ and $RhClL_3$ may be generated in an analogous fashion from the addition of phosphine to Cramer's complex, $[RhCl(C_2H_4)_2]_2$.^{47c} $(RhClL_2)_2$ adds one equivalent of hydrogen to produce $H_2(RhClL_2)_2$ which is an active hydrogenation catalyst and is in dissociative equilibrium with the highly active species " $RhClL_2$ " and RhH_2ClL_2 . $RhClL_3$ adds one equivalent of hydrogen to produce RhH_2ClL_3 , which dissociates one equivalent of L to form the catalytically active intermediates. Although the 2:1 PPh_3 :Rh catalyst generated from $[RhCl(COD)]_2$ contains $RhCl(PPh_3)_3$ as well as dimeric species, this presents little problem for the catalyst since active species containing two equivalents of PPh_3 are easily obtained. Overall hydrogenation rates may be affected, however. It would be interesting to see whether $RhCl(PPh_3)_3$ species are generated in 2:1 PPh_3 :Rh catalyst solutions obtained from $[RhCl(COE)_2]_2$.

The cationic ligand, $P-P^+BF_4$, appears to mimic the behavior of PPh_3 in the $[RhCl(COE)_2]_2$ system. Addition of one equivalent of $P-P^+BF_4$ to $\frac{1}{2}[RhCl(COE)_2]_2$ produces $\frac{1}{2}[RhCl(COE)(P-P^+)]_2(BF_4)_2$.



The ^{31}P nmr spectrum of $[RhCl(COE)(P-P^+)]_2(BF_4)_2$ is shown in Figure 12. $\delta P = -51.8 \text{ ppm}$, $\delta P^+ = -27.1 \text{ ppm}$, $J_{PRh} = 195 \text{ Hz}$ and $J_{PP^+} = 45 \text{ Hz}$. It is not known whether the configuration of the two phosphines about the $Rh(Cl)_2Rh$ linkage is cis

Figure 12. ^{31}P nmr spectrum of $[\text{RhCl}(\text{COE})(\text{P-P}^+)]_2(\text{BF}_4)_2$
at $+28^\circ$, 0.05 M in CH_2Cl_2 .

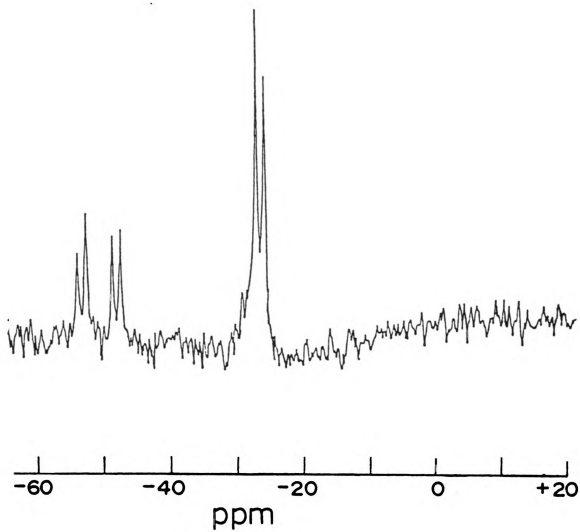


FIGURE 12

or trans.

D. Heterogeneous Systems II. Hydrogenations Employing
1:1:1/Hect, 0:2:1/Hect, $\text{Rh}(\text{COD})(\text{PPh}_3)_2^+/\text{Hect}$,
2:0:1/Hect and 3:0:1/Hect

The system employing a $\text{P}-\text{P}^+\text{BF}_4:\text{PPh}_3:\text{Rh}$ ratio of 1:1:1 appeared to be best suited for use as a cationic catalyst since the 1:0:1, 2:0:1 and 3:0:1 systems failed to function, the 2:1:1 system appeared to undergo constitutional change during reaction and the 1:2:1 and 2:2:1 systems probably contain too high a concentration of neutrally charged species. It was felt that generation of the hydride of the homogeneous catalyst prior to exchange with hectorite would allow a more legitimate comparison between the homogeneous and heterogeneous systems, since the nature of the reduction of the COD precursors might be altered within the mineral environment. Methanol was used as the solvent system to maintain consistency between the heterogeneous and homogeneous catalyst environments.

As may be seen in Table 7, the 1:1:1 homogeneous catalyst, when exchanged on hectorite, 1:1:1/Hect, is an active catalyst for the hydrogenation of 1-hexene. In fact, the supported catalyst is much more active than the homogeneous system. In general, the rate decrease of the 1:1:1/Hect system during the reaction parallels that of the solution catalyst. No desorption of the catalyst occurred during the reaction (color). Independent tests of filtrates taken from the reactions at $\text{CT} = 750$ and $\text{CT} = 1300$ for

Table 7. TO#'s for 1:1:1/Hect, 1:1:1, 0:2:1 and Rh(COD)(PPh₃)₂⁺ Hydrogenation Catalysts. MINTO#'s for 0:2:1/Hect and Rh(COD)(PPh₃)₂⁺/Hect

Hydrogenation Catalysts

Catalyst	100	200	300	400	500	600	700	800	900
1:1:1/Hect	147	183	187	191	153	189	135	95	66
1:1:1	95	90	97	93	84	79	71	64	58
0:2:1/Hect*	525	493	495	462	412	335	124	49	NA
0:2:1	536	528	463	374	284	216	147	99	52
Rh(COD)(PPh ₃) ₂ ⁺ /Hect*		149		195		150		22	
Rh(COD)(PPh ₃) ₂ ⁺		165		107		25		13	
2:0:1/Hect	(NO RXN)								
3:0:1/Hect	(NO RXN)								

Y:X:1 = P-P⁺, PPh₃:Rh, TO# (ml H₂/min/mmol Rh). Substrate = 1-Hexene, 1 M (CH₃OH), 30 ml total volume, 25°, 740 torr. 0.02 mmol Rh(I), 1-Hexene:Rh = 1500:1.

*Catalyst desorption was observed for these systems.

olefin hydrogenation activity gave negative results.

The fact that the rates of the heterogeneous and homogeneous systems parallel one another is significant. It indicates that the species responsible for the catalytic activity in both systems are probably very similar in composition. It is interesting to note that the composition of the 1:1:1/Hect catalyst determined by chemical analysis gave a Rh:P:Cl ratio of 1.00:3.17:0.76, very close to the ratio of 1.00:3.00:1.00 expected for the overall composition of the homogeneous catalyst.

That the catalyst exhibits larger TO#'s in the supported environment is unusual for Wilkinson type catalysts, which generally exhibit decreased activity when immobilized.⁹ The solution-like environment expected for the catalyst within the hectorite interlayers should allow the catalyst to behave as it would in the homogeneous environment, but although this is no doubt a major factor, it cannot explain the increase in catalytic activity. However, each of the following rationalizations may be contributing factors, either in part or in combination. It is possible that in the mineral environment steric congestion at the metal center may be relieved if strong electrostatic attraction of the silicate sheets for the phosphonium group causes the cationic ligand to undergo conformational change about the ethylene bridge by pulling the phosphonium group away from the coordination sphere. In addition, it is possible that the randomly distributed sites of negative charge

within the mineral, at a catalyst loading of only 14% that of the cation exchange capacity, affect the distribution of dimeric species in the overall catalyst composition. Separation of the rhodium centers through phosphonium group association with the negatively charged sites of hectorite would promote dimer separation and inhibit dimer formation. This should result in a higher concentration of the more active monomeric species, " RhClL_2 " and RhH_2CLL_2 .

As shown in Table 7, 0:2:1/Hect and $\text{Rh}(\text{COD})(\text{PPh}_3)_2^+/\text{Hect}$ were tested for catalytic activity in comparison with their homogeneous counterparts. 0:2:1/Hect begins to desorb catalyst immediately upon suspension in the solvent. Early in the work it was feared that the negatively charged silicate sheets might promote chloride ion dissociation from the rhodium center in the Wilkinson type catalysts. The fact that the 0:2:1 catalyst is readily desorbed from hectorite, which was the case for the $\text{RhCl}(\text{PPh}_3)_3/\text{Hect}$ system as well (see Section III. B. 1), indicates that the complexes involved maintain their neutrality in the physisorbed state.

The cationic complex $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]^+ \text{X}^-$, where $\text{X}^- = \text{ClO}_4^-$, PF_6^- or BF_4^- , is a known olefin hydrogenation catalyst.³⁵ Schrock and Osborn attribute the reactivity of this homogeneous catalyst to the presence of two species.^{35c} The cationic dihydride, $[\text{RhH}_2(\text{PPh}_3)_2]^+$, which is formed following reduction of COD, is an active olefin hydrogenation catalyst but a poor olefin isomerization catalyst. This

complex is in pH dependent deprotonation equilibrium with a neutrally charged monohydride complex, $\text{RhH}(\text{PPh}_3)_2$, which is also an active hydrogenation catalyst but is also very active for olefin isomerization as well.



As a result, as shown by the TO#'s in Table 7, the homogeneous catalyst hydrogenates 1-hexene at a fair rate in the early stages of the reaction, but as the concentration of the isomerization product 2-hexene increases, the overall rate of olefin hydrogenation decreases because 2-hexene is reduced much more slowly than 1-hexene.

Desorption of catalyst from $\text{Rh}(\text{COD})(\text{PPh}_3)_2^+/\text{Hect}$ was observed visually at $\text{CT} = 975$. The desorbed species is probably the neutrally charged monohydride catalyst. From the rate data for $\text{Rh}(\text{COD})(\text{PPh}_3)_2^+/\text{Hect}$ it might be inferred however, that the degree of monohydride formation in the mineral environment is less than that in homogeneous solution. High hydrogenation rates are maintained longer during the reaction with the supported catalyst, indicating that the extent of 1-hexene isomerization is less and thus the concentration of the monohydride is lower. The generally acknowledged higher acidity of the mineral environment compared to methanol solution³⁸ is most likely the major factor contributing to this effect.

As expected based on the results presented in Section III. B. 1 for the phosphinated hectorite systems and in Section III. C. 2 for the 2:0:1 and 3:0:1 homogeneous

catalysts, both the 2:0:1/Hect and 3:0:1/Hect systems proved inactive as catalysts for olefin hydrogenation.

IV. CONCLUSIONS AND RECOMMENDATIONS

As described in the results and discussion section, this dissertation has shown that a positively charged ligand can be employed to produce an active cationic transition metal catalyst. The 1:1:1, $P-P^+BF_4:PPh_3:Rh$, catalyst is active both in solution and when situated between the negatively charged sheets of the mica-like silicate hectorite. It is of considerable importance to note that, when in the mineral environment and under the reaction conditions employed here, the activity of the catalyst is increased. The 1:1:1 catalyst is a mixture of two or more cationic mixed phosphine ligand rhodium(I) chloride complexes which probably act in concert to generate highly active intermediates for olefin hydrogenation. The support appears to exert a positive effect on the catalytic activity of the 1:1:1 system. This effect may be attributed to the solution-like environment within the support and the ability of the large negatively charged silicate sheets to alter the stoichiometry and geometry of the complexes employed.

These results have some significant implications. Cationic catalysts might be prepared in a simple, convenient manner. Judicious choice of appropriate ligands and

reaction conditions could produce complexes which might possess a number of different oxidation states. These compounds would have the potential for binding to a variety of anionic supports. In particular, swelling, layered silicates seem ideal supports for immobilization of such species.

Certain aspects of this dissertation deserve additional comment. Although the cationic ligand, $P-P^+BF_4$, was relatively easy to prepare and manipulate and it mimics the behavior of PPh_3 up to a point, its large size and complexity relative to commonly used phosphine ligands probably preclude its use in other catalyst systems. A simpler, smaller cationic phosphine ligand comparable to PPh_3 would find more general application since problems associated with ligand steric bulk and the need for mixed phosphine ligand systems would be minimized.

Most of the known cationic phosphine ligands mentioned in Section I. D, would be no better than $P-P^+BF_4$ as far as size is concerned, although the methyl substituent on the quaternized phosphorus in the ligand $(Ph_2PCH_2CH_2PPh_2CH_3)^+$ is an improvement. The smaller ligands $[P(CH_2O)_3PCH_3]BF_4$ ⁵² and $(Ph_2PCH_2CH_2NR_2H)X$ ^{50b} would be more suitable, although the former may be too basic for many applications and in the latter the protonated amine suffers from pH restrictions and the ethylene bridge still allows ligand conformations which would crowd metal coordination sites.

The neutral ligands $(p-Me_2NC_6H_4)PPh_2$, $(p-Me_2NC_6H_4)_2PPh$

and $(p\text{-Me}_2\text{NC}_6\text{H}_4)_3\text{P}$ should possess the same steric bulk as PPh_3 and are known to mimic its behavior in certain catalytic systems.⁷⁵ Quaternization of one or more of the amine groups would produce cationic phosphine ligands capable of substitution for PPh_3 in the preparation of a variety of transition metal complexes. However, these complexes should exhibit different catalytic reactivities than the PPh_3 systems since one expects that the cationic phosphine ligands would be significantly poorer bases than PPh_3 , due to the strongly electron withdrawing trialkylammonium groups attached to the phenyl rings. The cationic ligand $(\text{Me}_2\text{N}^+\text{CH}_2\text{C}_6\text{H}_4)\text{PPh}_2$ is as yet unknown, but it should possess electronic and steric properties that are similar to those of PPh_3 and/or $\text{P}(p\text{-tolyl})_3$. $(\text{H}_3\text{N}^+\text{CH}_2\text{C}_6\text{H}_4)_3\text{P}$ is a known ligand,⁷⁶ but it would only be useful in acidic media.

The phosphinated hectorites employed in this study appeared to bind rhodium complexes, but these materials were not successful catalyst precursors presumably because of the bulkiness of the cationic ligand. Analogous phosphinated hectorites prepared with smaller cationic phosphine ligands, possibly at lower concentration within the intracrystal space, might well serve as catalyst supports. These materials might also find uses as molecular sieves and/or as metal ion or complex trapping agents. A simple method of phosphinated hectorite preparation might be found in the protonation of the amine groups of $(p\text{-Me}_2\text{NC}_6\text{H}_4)_3\text{P}$ by the acid exchanged mineral, H^+/Hect .

The surface catalyzed disproportionation of $[\text{RhCl}(\text{COE})_2]_2$ deserves further study. It would be of interest to determine the species produced from the reaction and establish a plausible mechanism.

The chemistry associated with the preparation and utilization of silylated montmorillonite and hectorite should also be investigated. These materials may prove very useful as supports for the immobilization of moisture sensitive catalysts and may extend the uses of smectites to systems whose reactivities are inhibited by the presence of protonated solvents and/or hydroxyl groups. The use of ligand functionalized silane coupling agents in place of $(\text{CH}_3)_3\text{SiX}$ in the silylation reaction might allow the preparation of dual purpose supported catalysts. It is feasible that two different catalysts could be supported on the same mineral, one within the interlayers and the other attached to edge sites via the silane coupling agent.

In addition to the positively charged ligands discussed in this dissertation, there exists a number of other cationic and zwitterionic ligands of variable functionality which might be employed to synthesize cationic complexes of catalytic interest. Some examples of positively charged nitrogen ligands are the amines, $\text{R}_2\text{NCH}_2\text{CH}_2\text{N}^+\text{R}_3$,⁷⁷ $\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}^+\text{R}$ ⁷⁸ and $\text{N}(\text{CHCH})_2\text{N}^+\text{CH}_3$ ⁷⁹ and the nitrile, $\text{NCC}(\text{CHCH})_2\text{N}^+\text{CH}_3$.⁸⁰ An arsine is known, $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{As}^+\text{Ph}_2\text{R}$,⁸¹ and a sulfonium ligand, Me_3S^+ , has been reported recently.⁸² Zwitterionic carboxylate ligands such as $(\text{Me}_3\text{N}^+\text{CH}_2\text{CO}_2^-)$

have been studied for some time for their biochemical interest.⁸³ Organometallic ligands containing positive charge are also known, such as the cyclopentadienyl ligand $C_5H_4P^+Ph_3$,⁸⁴ the carbanion $(PhMe_2P^+CH_2CH^-)$,⁸⁵ the cyclo-octatetraenyl ligand $C_8H_7CH_2N^+Me_3$,⁸⁶ and the allyl ligand $Ph_3P^+CH(CH)_2CH$.⁸⁷

Finally, the following list of complexes, which are known homogeneous catalysts, probably only hints at the number and variety of systems which might be rendered cationic through the judicious utilization of positively charged ligands in their preparation (see Table 8).

Table 8. Some Known Homogeneous Catalysts Potentially
Suitable for Modification by Positively Charged
Ligands*

<u>Complexes</u>	<u>Selected Uses</u>	<u>Type of Cationic Ligand Needed</u>
$Ti(Cp)_2(CO)_2$	ol H_2	cyclopentadienyl
$MnCp(CO)_2(PPh_3)$	H_2/CO	cyclopentadienyl or phosphine
$Fe(Et)_2dipy)_2$	olig, poly	amine
$Fe(CO)_4(PPh)_3$	H_2/CO	phosphine
$[Co(CO)_3L]_2$	H_2/CO , ket H_2	phosphine
$Co(\eta^3-C_3H_5)[P(OMe)_3]_3$	ar H_2	phosphite
$Ni(PPh_3)_3$	XPh/HCN	phosphine
$Ni(CO)_2(PPh_3)_2$	olig, poly	phosphine
$NiCl_2(PEt_3)_2$	isom, olig	phosphine
$Ni(COD)(PPh_3)_3$	olig	phosphine
$Ni(PPh_3)_4$	dimer	phosphine
$Ni(Et)(dipy)_2$	olig, poly	amine
$Mo(CO)_5(PPh_3)$	H_2/CO	phosphine
$RuCl_2L_4$	H_2/CO , ol H_2	phosphine
$RhCl(CO)L_2$	H_2/CO	phosphine
$RhH(CO)L_3$	H_2/CO	phosphine
$Rh_6(CO)_{16-n}L_n$	ol H_2	phosphine
$RhCl_n(NR_3)$	HS1	amine
$RhCl_n(NCR)$	HS1	nitrile
$PdCl_2(PPh_3)_2$	HOPh/ NR_2 , ol H_2 , olig	phosphine

Table 8. (cont'd).

$\text{Pd}(\text{PPh}_3)_4$	olig	phosphine
$\text{IrI}(\text{CO})\text{L}_2$	ol H_2	phosphine
$\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{py})$	HS1	amine
$\text{PtCl}_2(\text{NCR})_2$	HS1	nitrile
PtCl_2L_2	ol H_2	phosphine

*The literature referred to in the preparation of this table may be found in references 7c,d,f, 9g,h and 88. ar H_2 = arene hydrogenation, dimer = ethylene dimerization, H_2/CO = hydroformylation, HOPh/NR_2 = amination of aromatic hydroxyl groups, HS1 = hydrosilation, isom = alkene isomerization, ket H_2 = ketone hydrogenation, ol H_2 = olefin hydrogenation, olig = oligomerization (many types possible), poly = polymerization, and XPh/HCN = cyanation of halogenated arenes.

BIBLIOGRAPHY

BIBLIOGRAPHY

- 1a. R. F. Heck, Advan. Organometal. Chem., 4, 243 (1966).
- b. H. Lemke, Hydrocarbon Process., 45, 27 (1966).
- c. J. Falbe, "Synthesen mit Kohlen Monoxyd", Springer Verlag, 1967.
- d. A. J. Chalk, R. F. Harrod, Advan. Organometal. Chem., 6, 119 (1968).
- e. I. Wender, P. Pino, eds., "Organic Synthesis via Metal Carbonyls", Vol. 1, Interscience-Wiley, 1968.
- f. R. Kummer, H. J. Nienburg, H. Hohenschutz, M. Strohmeyer, Advan. Chem. Ser., 132, 19 (1974).

2. G. Szonyi, Advan. Chem. Ser., 70, 53 (1968).
3. J. Smidt, Chem. Ind. (London), 54 (1962).
4. G. C. Bond, Advan. Chem. Ser., 70, 25 (1968).
5. R. G. Shultz, D. E. Gross, Advan. Chem. Ser., 70, 97 (1968).

- 6a. Monsanto Co., Brit. Pat., 1,233,121 (1968).
- b. J. F. Roth, J. H. Craddock, A. Hershman, F. E. Paulik, Chemtech, Oct., 600 (1971).
- c. R. P. Lowry, A. Aguilo, Hydrocarbon Process., Nov., 103 (1974).
- d. Chem. Eng. News, June 30, 7 (1975).
- e. D. Forster, J. Am. Chem. Soc., 98, 846 (1976).

- 7a. J. P. Collman, Accounts Chem. Res., 1, 136 (1968).
- b. R. Cramer, Accounts Chem. Res., 1, 186 (1968).
- c. J. Halpern, Advan. Chem. Ser., 70, 1 (1968).
- d. F. A. Cotton, G. Wilkinson, "Advanced Inorganic Chemistry, A Comprehensive Text", 3rd Ed., Interscience Publishers, New York, NY, 1972, ch. 24.
- e. C. A. Tolman, J. P. Jesson, Science, 181, 501 (1973).
- f. M. M. Taqui Khan, A. E. Martell, "Homogeneous Catalysis by Metal Complexes", Academic Press, Inc., New York, NY, 1974.

8. A. W. Adamson, "Physical Chemistry of Surfaces", 3rd Ed., John Wiley and Sons, New York, NY, 1976.

- 9a. J. Manassen, Platinum Metals Rev., 15, 142 (1971).
- b. D. G. H. Ballard, Advan. Catal., 23, 269 (1973).
- c. C. U. Pittman, G. O. Evans, Chemtech, Sept., 560 (1973).
- d. J. C. Bailar, Jr., Cat. Rev. -Sci. Eng., 10, 17 (1974).
- e. Z. M. Michalska, D. E. Webster, Chemtech, Feb., 117 (1975).
- f. Yu. I. Yermakov, Cat. Rev. -Sci. Eng., 13, 77 (1976).
- g. R. H. Grubbs, Chemtech, Aug., 812 (1977).
- h. F. R. Hartley, P. N. Vezey, Advan. Organometal. Chem., 17, 189 (1977).
10. G. W. Parshall, J. Am. Chem. Soc., 94, 8716 (1972).
- 11a. L. Cassar, M. Foci, A. Gardano, J. Organometal. Chem., 121, C55 (1976).
- b. Y. Dror, J. Manassen, J. Mol. Catal., 2, 219 (1977).
12. L. W. Gosser, CRD, E. I. DuPontdeNemours and Co., unpublished results.
13. E. Bayer, V. Schurig, Angew. Chem. Int. Ed., 14, 493 (1975).
14. W. D. Bonds, Jr., C. H. Brubaker, Jr., E. S. Chandrasekaran, S. Gibbons, R. H. Grubbs, L. C. Kroll, J. Am. Chem. Soc., 97, 2128 (1975).
15. R. H. Grubbs, L. C. Kroll, J. Am. Chem. Soc., 93, 3062 (1971).
16. W. Dumont, J. C. Poulin, T. P. Dang, H. B. Kagan, J. Am. Chem. Soc., 95, 8295 (1973).
- 17a. P. R. Rony, J. Catal., 14, 142 (1969).
- b. P. R. Rony, J. F. Roth, J. Mol. Catal., 1, 12 (1975/76).
18. W. O. Haag, D. D. Whitehurst, Belgian Pat., 721,686 (1969).
- 19a. P. Legzdins, G. L. Rempel, G. Wilkinson, Chem. Commun., 825 (1969).
- b. P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, G. Wilkinson, J. Chem. Soc. (A), 3322 (1970).
20. R. L. Lazcano, J. E. Germain, Bull. Chem. Soc. Fr., 1869 (1971).
- 21a. T. J. Pinnavaia, P. K. Welty, J. F. Hoffman, Proc. Intern. Clay Conf., Mexico City, 373 (1975).
- b. T. J. Pinnavaia, P. K. Welty, J. Am. Chem. Soc., 97, 3819 (1975).

- 22a. K. A. Windhorst, J. H. Lunsford, J. C. S. Chem. Comm., 852 (1975).
 b. W. B. Williamson, D. R. Flentge, J. H. Lunsford, J. Catal., 37, 258 (1975).
 c. J. H. Lunsford, Catal. Rev. -Sci. Eng., 12, 137 (1975).
23. E. Mantovani, N. Palladino, A. Zanobi, J. Mol. Catal., 3, 285 (1977/78).
24. J. P. Candlin, H. Thomas, Advan. Chem. Ser., 132, 212 (1974).
- 25a. G. K. Acres, G. C. Bond, B. J. Cooper, J. Dawson, J. Catal., 6, 139 (1966).
 b. N. Takahashi, I. Okura, T. Keii, J. Am. Chem. Soc., 97, 7489 (1975).
- 26a. L. J. Boucher, A. A. Oswald, L. L. Murrell, Preprints, Div. Petr. Chem. ACS, Los Angeles, 162 (1974).
 b. K. G. Allum, R. D. Hancock, I. V. Howell, S. McKenzie, R. C. Pitkethly, P. J. Robinson, J. Organometal. Chem., 87, 203 (1975).
 c. K. G. Allum, R. D. Hancock, I. V. Howell, T. E. Lester, S. McKenzie, R. C. Pitkethly, P. J. Robinson, J. Organometal. Chem., 107, 393 (1976).
- 27a. A. J. Moffat, J. Catal., 18, 193 (1970).
 b. A. J. Moffat, J. Catal., 19, 322 (1970).
 c. M. Capka, P. Svoboda, M. Kraus, J. Hetflejš, Chem. Ind. (London), 650 (1972).
 d. W. O. Haag, D. D. Whitehurst, Proc. Int. Cong. Catal., 5th, 465 (1972).
 e. L. D. Rollman, Inorg. Chim. Acta, 6, 137 (1972).
 f. R. H. Grubbs, C. Gibbons, L. C. Kroll, W. D. Bonds, Jr., C. H. Brubaker, Jr., J. Am. Chem. Soc., 95, 2373 (1973).
 g. Y. Inaki, K. Kimura, K. Takemoto, Makromol. Chem., 171, 19 (1973).
 h. I. Dietzmann, D. Tomanova, J. Hetflejš, Coll. Czech. Chem. Commun., 39, 123 (1974).
 i. A. T. Jurewicz, L. D. Rollmann, D. D. Whitehurst, Advan. Chem. Ser., 132, 240 (1974).
 j. K. Kimura, Y. Inaki, K. Takemoto, Makromol. Chem., 175, 83 (1974).
 k. K. Kimura, Y. Inaki, K. Takemoto, Makromol. Chem., 175, 95 (1974).
 l. M. Kraus, Coll. Czech. Chem. Commun., 39, 1318 (1974).
 m. M. Kraus, D. Tomanova, J. Polym. Sci., Polym. Chem. Ed., 12, 1781 (1974).
 n. M. Mejstrikova, R. Hericha, M. Kraus, Coll. Czech. Chem. Commun., 39, 135 (1974).
 o. Y. Nakamura, H. Hirai, Chem. Lett., 645 (1974).
 p. Y. Nakamura, H. Hirai, Chem. Lett., 809 (1974).

- 28a. M. Capka, J. Hetflejš, Coll. Czech. Chem. Commun., 39, 154 (1974).
- b. R. D. Hancock, I. V. Howell, R. C. Pitkethly, P. J. Robinson, "Catalysis: Heterogeneous and Homogeneous", B. Delmon, G. Jannes, eds., Elsevier, Amsterdam, 1975, p. 361.
- c. K. G. Allum, R. D. Hancock, I. V. Howell, R. C. Pitkethly, P. J. Robinson, J. Catal., 43, 322 (1976).
- d. R. Jackson, J. Raddlesden, D. J. Thompson, R. Whelan, J. Organometal. Chem., 125, 57 (1977).
- e. F. R. W. P. Wild, G. Gubitosa, H. H. Brintzinger, J. Organometal. Chem., 148, 73 (1978).
29. N. Kawata, T. Mizoroki, A. Ozaki, M. Ohkawara, Chem. Lett., 1165 (1973).
- 30a. M. Capka, P. Svoboda, M. Cerný, J. Hetflejš, Tetrahedron Lett., 4787 (1971).
- b. K. G. Allum, T. D. Hancock, S. McKenzie, R. C. Pitkethly, Proc. Int. Cong. Catal., 5th, 477 (1972).
- c. British Petroleum Co. Ltd., British Pat., 1,295,675 (1972).
- d. H. S. Bruner, J. C. Bailar, J. Amer. Oil Chem. Soc., 49, 533 (1972).
- e. V. Bazant, M. Capka, M. Tscherný, J. Hetflejš, M. Kraus, P. Svoboda, German Pat., 2,245,187 (1973).
- f. H. S. Bruner, J. C. Bailar, Inorg. Chem., 12, 465 (1973).
- g. M. Capka, P. Svoboda, J. Hetflejš, Coll. Czech. Chem. Commun., 38, 1242 (1973).
- h. R. G. Muratova, R. Z. Khairullina, S. Y. Shulyndin, B. E. Ivanov, R. I. Izmailov, Kinet. Katal., 15, 137 (1974).
- i. F. G. Young, German Pat., 2,330,308 (1974).
- j. K. G. Allum, R. D. Hancock, I. V. Howell, R. C. Pitkethly, P. J. Robinson, J. Organometal. Chem., 87, 189 (1975).
- 31a. R. H. Grubbs, L. C. Kroll, E. M. Sweet, J. Macromol. Sci. Chem., A7, 1047 (1973).
- b. C. U. Pittman, L. R. Smith, R. M. Hanes, J. Am. Chem. Soc., 97, 1742 (1975).
- 32a. G. Strukul, M. Bonivento, M. Graziani, E. Cernia, N. Palladino, Inorg. Chim. Acta, 12, 15 (1975).
- b. F. Pinna, M. Bonivento, G. Strukul, M. Graziani, E. Cernia, N. Palladino, J. Mol. Catal., 1, 309 (1975/76).
- c. G. Strukul, P. D'Olimpio, M. Bonivento, F. Pinna, M. Graziani, J. Mol. Catal., 2, 179 (1977).

- 33a. J. Manassen, Isr. J. Chem., 8, 5 (1970).
 - b. J-C. Poulin, W. Dumont, T-P. Dang, H. B. Kagan, C. R. Acad. Sci., Ser. C, 277, 41 (1973).
 - c. L. C. Kroll, Ph. D. Dissertation, Department of Chemistry, Michigan State University, 1974.
 - d. R. H. Grubbs, S. G-H. Su, Preprints, Div. Petr. Chem. ACS, Chicago, 1193 (1977).
 - e. R. H. Grubbs, E. M. Sweet, J. Mol. Catal., 3, 259 (1977/78).
 - f. J. Conan, M. Bartholin, A. Guyot, J. Mol. Catal., 1, 375 (1975/76).
34. J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, D. N. Marquardt, J. Am. Chem. Soc., 94, 1789 (1972).
- 35a. J. R. Shapley, R. R. Schrock, J. A. Osborn, J. Am. Chem. Soc., 91, 2816 (1969).
 - b. R. R. Schrock, J. A. Osborn, J. Am. Chem. Soc., 93, 3089 (1971).
 - c. R. R. Schrock, J. A. Osborn, J. Am. Chem. Soc., 98, 2134 (1976).
 - d. R. R. Schrock, J. A. Osborn, J. Am. Chem. Soc., 98, 2143 (1976).
 - e. R. R. Schrock, J. A. Osborn, J. Am. Chem. Soc., 98, 4450 (1976).
- 36a. R. Raythatha, M. S. Thesis, Department of Chemistry, Michigan State University, 1978.
 - b. This work, Section II. D. 3 and Section III. D.
37. F. Farzaneh, T. J. Pinnavaia, unpublished results.
- 38a. R. E. Grim, "Clay Mineralogy", 2nd Ed., McGraw-Hill Book Co., New York, NY, 1968.
 - b. H. van Olphen, "An Introduction to Clay Colloid Chemistry", John Wiley & Sons, Inc., New York, NY, 1977.
 - c. B. K. G. Theng, "The Chemistry of Clay - Organic Reactions", John Wiley & Sons, Inc., New York, NY, 1974.
- 39a. D. M. Clementz, T. J. Pinnavaia, M. M. Mortland, J. Phys. Chem., 77, 196 (1973).
 - b. M. McBride, T. J. Pinnavaia, M. M. Mortland, Am. Mineralogist, 60, 66 (1975).
 - c. T. J. Pinnavaia, "Magnetic Resonance in Colloid and Interface Science", ACS Symp. Ser., 34, H. A. Resing, C. G. Wade, eds., 1976, p. 94.

- 40a. M. B. McBride, J. Phys. Chem., 80, 196 (1976).
- b. M. B. McBride, "Magnetic Resonance in Colloid and Interface Science", ACS Symp. Ser., 34, H. A. Resing, C. G. Wade, eds., 1976, p. 123.
- c. M. B. McBride, Clays Clay Minerals, 25, 6 (1977).
41. M. Bartholin, CH. Graillat, A. Guyot, G. Coudurier, J. Bandiera, C. Naccache, J. Mol. Catal., 3, 17 (1977/78).
- 42a. S. Teichner, E. Pernoux, Clay Minerals Bull., 1, 145 (1951).
- b. J. J. DeLange, Notes, J. Sci. Instr., 24, 20 (1947).
- c. R. N. Shreve, J. A. Brink, Jr., "Chemical Process Industries", 4th Ed., McGraw-Hill Book Co., 1977, p. 683.
- 43a. H. E. Swift, E. R. Black, I and EC Product Research and Development, 13, No. 2106 (1974).
- b. P. G. Bercik, K. J. Metzger, H. E. Swift, Preprints, Div. Petr. Chem. ACS, Anaheim, 775 (1978).
- 44a. H. E. Doner, M. M. Mortland, Science, 166, 1406 (1969).
- b. M. M. Mortland, T. J. Pinnavaia, Nature Phys. Sci., 229, 75 (1971).
- c. T. J. Pinnavaia, M. M. Mortland, J. Phys. Chem., 75, 3957 (1971).
- d. D. B. Fenn, M. M. Mortland, T. J. Pinnavaia, Clays Clay Minerals, 21, 315 (1973).
45. P. Peigneur, A. Cremers, 2nd Meeting European Clay Groups, Strasbourg, Abstracts, 31 (1974).
46. S. I. Zones, M. R. Palmer, J. G. Palmer, J. M. Doemeny, G. N. Schrauzer, J. Am. Chem. Soc., 100, 2113 (1978).
- 47a. B. R. James, "Homogeneous Hydrogenation", John Wiley & Sons, Inc., New York, NY, 1973, ch. 11.
- b. G. Dolcetti, N. W. Hoffman, Inorg. Chim. Acta, 9, 269 (1974).
- c. C. A. Tolman, P. Z. Meakin, D. L. Lindner, J. P. Jesson, J. Am. Chem. Soc., 96, 2762 (1974).
- d. J. Halpern, T. Okamoto, A. Zakhariev, J. Mol. Catal., 2, 65 (1977).
- e. C. Rousseau, M. Evrard, F. Petit, J. Mol. Catal., 3, 309 (1977/78).
- f. S. Montelatici, A. van der Ent, J. A. Osborn, G. Wilkinson, J. Chem. Soc. (A), 1054 (1968).
- g. J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, J. Chem. Soc. (A), 1711 (1966).
48. K. Ohno, J. Tsuji, J. Am. Chem. Soc., 90, 99 (1968).

49. C. Ercolani, J. V. Quagliano, L. M. Vallarino, Inorg. Chim. Acta, 3, 421 (1969).
- 50a. W. V. Dahlhoff, T. R. Dick, S. M. Nelson, J. Chem. Soc. (A), 2919 (1969).
b. R. C. Taylor, R. A. Kolodny, Chem. Commun., 813 (1970).
c. R. C. Taylor, R. A. Kolodny, Inorg. Nucl. Chem. Letters, 7, 1063 (1971).
- 51a. D. Berglund, D. W. Meek, J. Am. Chem. Soc., 90, 518 (1968).
b. D. Berglund, D. W. Meek, Inorg. Chem., 8, 2602 (1969).
52. R. D. Bertrand, D. A. Allison, J. G. Verkade, J. Am. Chem. Soc., 92, 71 (1970).
- 53a. R. L. Keiter, D. P. Shah, Inorg. Chem., 11, 191 (1972).
b. R. L. Keiter, L. W. Cary, J. Am. Chem. Soc., 94, 9232 (1972).
54. R. C. Taylor, R. L. Keiter, L. W. Cary, Inorg. Chem., 13, 1928 (1974).
55. J. A. Connor, J. P. Day, E. M. Jones, G. K. McEwen, J. Chem. Soc. (D), 347 (1973).
56. D. D. Traficante, J. A. Sims, M. Mulcahy, J. Magn. Res., 15, 484 (1974).
57. A. van der Ent, A. L. Onderdelinden, Inorg. Syn., 14, 92 (1973).
58. J. Chatt, L. M. Venanzi, J. Chem. Soc. (A), 4735 (1957).
59. R. R. Schrock, J. A. Osborn, J. Am. Chem. Soc., 93, 2397 (1971).
60. "Handbook of Chemistry and Physics", 52nd Ed., R. C. Weast, ed., The Chemical Rubber Co., Cleveland, 1971.
- 61a. H. -G. Horn, K. Sommer, Spectrochim. Acta, 27A, 1049 (1971).
b. R. M. Silverstein, G. C. Bassler, "Spectrometric Identification of Organic Compounds", 2nd Ed., John Wiley & Sons, Inc., New York, 1967, ch. 3.
62. M. Green. T. A. Kuc, S. H. Taylor, J. Chem. Soc. (A), 2334 (1971).
- 63a. D. Brodzki, G. Pannetier, J. Organometal. Chem., 63, 431 (1973).
b. M. A. Bennett, R. J. H. Clark, D. L. Milner, Inorg. Chem., 6, 1647 (1967).

- 64a. K. Vrieze, H. C. Volger, J. Organometal. Chem., 11, P17 (1968).
b. K. Vrieze, H. C. Volger, A. P. Praat, J. Organometal. Chem., 14, 185 (1968).
65. E. D. Becker, "High Resolution NMR - Theory and Chemical Applications", Academic Press, New York, 1969, ch. 7.
66. P. N. Rylander, "Catalytic Hydrogenation over Platinum Metal", Academic Press, New York, NY, 1967.
67. P. K. Welty, Ph. D. Dissertation, Department of Chemistry, Michigan State University, 1976.
68. W. Skupinski, S. Malinowski, J. Organometal. Chem., 99, 465 (1975).
69. C. A. Tolman, Chem. Rev., 77, 313 (1977).
70. B. Denise, G. Pannetier, J. Organometal. Chem., 148, 155 (1978).
71. H. C. Volger, H. Hogeveen, Recueil, 86, 1066 (1967).
72. L. Porri, A. Lionetti, G. Allegra, A. Immirzi, Chem. Commun., 336 (1965).
73. H. C. Volger, M. M. P. Gaasbeek, H. Hogeveen, K. Vrieze, Inorg. Chim. Acta, 3, 145 (1969).
74. W. Partenheimer, E. F. Hoy, J. Am. Chem. Soc., 95, 2840 (1973).
75. R. B. King, C. R. Bennett, Advan. Chem. Ser., 132, 124 (1974).
76. P. A. Bartlett, B. Bauer, S. J. Singer, J. Am. Chem. Soc., 100, 5085 (1978).
- 77a. J. V. Quagliano, J. T. Summers, S. Kida, L. M. Vallarino, Inorg. Chem., 3, 1557 (1964).
b. K. P. Beaumont, C. A. McAuliffe, Inorg. Chim. Acta, 14, L9 (1975).
c. V. L. Goedken, L. M. Vallarino, J. V. Quagliano, Inorg. Chem., 10, 2682 (1971).
d. R. Romeo, S. Lanza, M. L. Tobe, Inorg. Chem., 16, 785 (1977).
e. J. D. Petersen, F. P. Jakse, Inorg. Chem., 16, 2845 (1977).

- 78a. A. K. Banerjee, L. M. Vallarino, J. V. Quagliano, Coord. Chem. Rev., 1, 239 (1966).
b. V. L. Goedken, J. V. Quagliano, L. M. Vallarino, Inorg. Chem., 8, 2331 (1969).
c. J. V. Quagliano, A. K. Banerjee, V. L. Goedken, L. M. Vallarino, J. Am. Chem. Soc., 92, 482 (1970).
d. B. B. Garrett, V. L. Goedken, J. V. Quagliano, J. Am. Chem. Soc., 92, 489 (1970).
e. L. M. Vallarino, V. L. Goedken, J. V. Quagliano, Inorg. Chem., 11, 1466 (1972).
f. W. J. Rozell, J. S. Wood, Inorg. Chem., 16, 1827 (1977).
- 79a. J. E. Figard, J. D. Petersen, Inorg. Chem., 17, 1059 (1978).
b. D. W. Franco, H. Taube, Inorg. Chem., 17, 571 (1978).
c. J. M. Malin, R. C. Koch, Inorg. Chem., 17, 752 (1978).
80. J. E. Figard, J. V. Paukstelis, E. F. Byrne, J. D. Petersen, J. Am. Chem. Soc., 99, 8417 (1977).
81. C. Ercolani, J. V. Quagliano, L. M. Vallarino, Chem. Commun., 1094 (1969).
- 82a. C. A. Stein, H. Taube, J. Am. Chem. Soc., 100, 336 (1978).
b. R. D. Adams, D. F. Chodosh, J. Am. Chem. Soc., 100, 812 (1978).
- 83a. J. V. Quagliano, S. Kida, J. Fujita, J. Am. Chem. Soc., 84, 724 (1962).
b. R. S. McEwen, J. C. S. Chem. Commun., 68 (1973).
84. D. Cashman, F. J. Lalor, J. Organometal. Chem., 24, C29 (1970).
- 85a. M. R. Churchill, B. G. DeBoer, J. R. Shapley, J. B. Keister, J. Am. Chem. Soc., 98, 2357 (1976).
b. M. R. Churchill, B. G. DeBoer, Inorg. Chem., 16, 1141 (1977).
86. C. A. Harmon, D. P. Bauer, S. R. Berryhill, K. Hagiwara, A. Streitwieser, Jr., Inorg. Chem., 16, 2143 (1977).
87. A. Efraty, S. S. Sandhu, Jr., R. Bystrek, D. Z. Denney, Inorg. Chem., 16, 2522 (1977).

- 88a. L. Marko, B. Heil, S. Vastag, Advan. Chem. Ser., 132, 27 (1974).
- b. L. Cassar, S. Ferrara, M. Foa, Advan. Chem. Ser., 132, 252 (1974).
- c. W. Rupilius, J. J. McCoy, M. Orchin, Ind. Eng. Chem. (Prod. Res. Devel.), 10, 142 (1971).
- d. A. Andreeta, G. F. Ferrari, J. Organometal. Chem., 30, 387 (1971).
- e. E. L. Muettert, F. J. Hirsekorn, J. Am. Chem. Soc., 96, 4063 (1974).
- f. F. J. Hirsekorn, M. C. Rakowski, E. L. Muettert, J. Am. Chem. Soc., 97, 237 (1975).

MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 03175 6630