

Lawrence Berkeley National Laboratory

Recent Work

Title

REGIOSELECTIVE HYDROGENATION OF POLYNUCLEAR HETEROAROMATIC COMPOUNDS CATALYZED BY POLYMER-SUPPORTED TRANSITION METAL COMPLEXES: INITIAL RATES, MECHANISM OF REDUCTION, MODEL COAL LIQUID EXPERIMENT, ROLE OF P-CRESOL IN RATE ENHANCEMENT OF NITROGEN RING...

Permalink

<https://escholarship.org/uc/item/8491n818>

Authors

Fish, R.H.

Heinemann, H.

Publication Date

1985-06-01

2



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

RECEIVED
 FROM THE LIBRARY
 JUN 13 1985
 LIBRARY AND
 DOCUMENTS SECTION

Presented at the Tenth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, CA, April 23-25, 1985

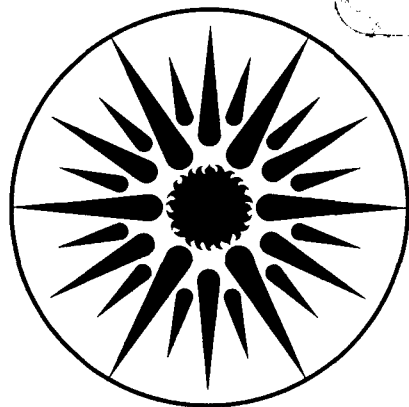
REGIOSELECTIVE HYDROGENATION OF POLYNUCLEAR HETEROAROMATIC COMPOUNDS CATALYZED BY POLYMER-SUPPORTED TRANSITION METAL COMPLEXES: Initial Rates, Mechanism of Reduction, Model Coal Liquid Experiment, Role of P-Cresol in Rate Enhancement of Nitrogen Ring Reduction, Catalytic Transfer Hydrogenation

R.H. Fish and H. Heinemann

June 1985

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.



**APPLIED SCIENCE
DIVISION**

LBL-19694
 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

REGIOSELECTIVE HYDROGENATION OF POLYNUCLEAR HETEROAROMATIC COMPOUNDS
CATALYZED BY POLYMER-SUPPORTED TRANSITION METAL COMPLEXES:
INITIAL RATES, MECHANISM OF REDUCTION, MODEL COAL LIQUID
EXPERIMENT, ROLE OF P-CRESOL IN RATE ENHANCEMENT OF
NITROGEN RING REDUCTION, CATALYTIC TRANSFER HYDROGENATION

Richard H. Fish and Heinz Heinemann

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

ABSTRACT

This research program focused on the utilization of polymer-supported (polystyrene-divinylbenzene, PS-DVB) transition-metal catalysts in the selective catalytic hydrogenation of polynuclear heteroaromatic compounds that are known to be present in coal and coal liquids. We found that the polymer-supported chloro(tristriphenylphosphine)rhodium(I) was the most efficient catalyst for the regiospecific reduction of the nitrogen containing ring in model coal compounds such as quinoline, 5,6 and 7,8-benzoquinoline, and acridine, and in one case, a heteroaromatic sulfur compound, benzothiophene.

Interestingly, the polymer-supported rhodium catalyst was more active than the corresponding homogeneous analogue by relative rate factors of 10 to 20 depending on the substrate studied in the reduction. More importantly, a model coal liquid was found to have a relative rate of reduction of quinoline to 1,2,3,4-tetrahydroquinoline (THQ) that was 2.2 times faster than a similar experiment without the coal liquid constituents consisting of pyrene, tetralin, methylnaphthalene, p-cresol, quinoline and 2-methylpyridine. Further experimentation clearly showed that the model coal liquid constituent, p-cresol, was responsible for the relative rate enhancement in the highly regiospecific (no other model coal liquid constituent was hydrogenated) reduction of quinoline to THQ. Nuclear magnetic resonance spectroscopy (NMR) experiments have given some insight into this rate enhancement phenomena. We also found that 9,10-dihydrophenanthridine was an excellent catalytic transfer hydrogenation reagent in the presence of several homogeneous and polymer-supported transition-metal catalysts to transfer hydrogen to such acceptors as quinoline and acridine. We also evaluated dihydroquinoline as a hydrogen transfer reagent, since THQ has been used as a donor solvent in coal liquifaction experiments.

CONTENTS

<u>SECTION</u>	<u>PAGE</u>
1. INTRODUCTION	1-1
2. REGIOSELECTIVE REDUCTION OF POLYNUCLEAR HETEROAROMATIC COMPOUNDS WITH POLYMER-SUPPORTED TRANSITION METAL CATALYSTS: INITIAL AND RELATIVE RATES; PARAMETERS THAT AFFECT RATES; AND MECHANISTIC ASPECTS	2-1
3. SELECTIVE REDUCTION OF QUINOLINE, IN A MODEL COAL LIQUID CATALYZED BY POLYMER-SUPPORTED CHLOROTRIS-(TRIPHENYLPHOSPHINE)RHODIUM(I) AND ROLE OF P-CRESOL IN THE RATE ENHANCEMENT OF QUINOLINE HYDROGENATION	3-1
4. CATALYTIC TRANSFER HYDROGENATION: SATURATED POLYNUCLEAR HETEROAROMATIC NITROGEN COMPOUNDS AS HYDROGEN DONORS CATALYZED BY TRANSITION METAL COMPLEXES	4-1
5. CONCLUSIONS	5-1
CONTRIBUTORS	5-1
REFERENCES	5-2

Section 1 INTRODUCTION

The utilization of hydrogen gas, in the hydroprocessing of synthetic fuels is well known to be the economically limiting factor in this upgrading process as well as in the important removal of nitrogen and sulfur atoms from these complex matrices. Previous studies by the Mobil Research and Development Corporation clearly showed that saturated nitrogen polynuclear heteroaromatic compounds are beneficial to coal liquefaction via their ability to transfer hydrogen to other coal compounds (1). Recently, we found that a wide variety of transition-metal compounds catalyzed the regioselective reduction of polynuclear heteroaromatic nitrogen and sulfur compounds under extremely mild homogeneous hydrogenation conditions (350 psi H₂ and 85 to 150 °C) (2,3,4,5). These latter results are important, since selective hydrogenation will lower hydrogen consumption; and furthermore, the homogeneous hydrogenation studies were carried out at much lower temperatures and H₂ pressures than are used in conventional industrial processing.

Homogeneous catalysts have their own limitations in that recovery is often difficult or impossible. In addition, thermal stability and solubility may also present problems in practical applications. The use of polymer-supports, such as cross-linked polystyrene-divinylbenzene (PS-DVB), as well as silica and alumina, to anchor homogeneous transition-metal catalysts and overcome some of the difficulties mentioned above, has been the subject of intensive research over the last fifteen years (6,7,8,9,10,11,12,13). We will present evidence for the potential utilization of polymer-supported transition metal catalysts on 2% or 20% cross-linked phosphinated PS-DVB in synthetic fuel hydroprocessing applications. We will compare the initial rates of hydrogenation of the polymer-supported catalyst, chloro(tris(triphenylphosphine)rhodium(I)) on 2% PS-DVB, with the homogeneous analogue for the selective reduction of polynuclear heteroaromatic nitrogen and sulfur compounds. We will also address the effect of cross-linking, diffusion rates into the PS-DVB beads and surface mass transfer effects. Mechanistic aspects of the reduction of one of the model coal compounds, quinoline, was carried out with deuterium gas in place of hydrogen gas in conjunction with high field nuclear magnetic resonance spectroscopy and mass spectrometry analysis (14,15).

In order to evaluate the practical application of these polymer-supported catalysts, we studied the selectivity for the reduction of the nitrogen heterocyclic ring with quinoline in a model coal liquid consisting of pyrene, tetralin, methylnaphthalene, p-cresol and 2-methylpyridine. We will present some nuclear magnetic resonance spectroscopy experiments that will help define the role of p-cresol in its effect on the rate enhancement of quinoline hydrogenation in the above-mentioned model coal liquid experiment.

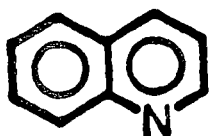
Finally, we will address the role of transition-metal catalysts in the catalytic transfer of hydrogen from saturated polynuclear heteroaromatic nitrogen compounds, known to be present in coal and coal liquids, to other polynuclear heteroaromatic nitrogen compounds. The importance of these findings relates to the use of 1,2,3,4-tetrahydroquinoline as a donor solvent in coal liquefaction experiments (1).

Section 2

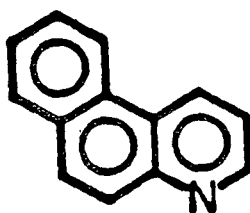
REGIOSELECTIVE REDUCTION OF POLYNUCLEAR HETEROAROMATIC COMPOUNDS WITH POLYMER-SUPPORTED TRANSITION METAL CATALYSTS: INITIAL AND RELATIVE RATES; PARAMETERS THAT AFFECT RATES; AND MECHANISTIC ASPECTS

The reduction of polynuclear heteroaromatic compounds of nitrogen and sulfur (Chart 1) with 2% cross-linked phosphinated polystyrene-divinylbenzene beads modified with chloro(tristriphenylphosphine)rhodium(I) was compared to the homogeneous analogue (Table I). The polymer-supported catalyst, \boxed{P} — $\text{PH}_2\text{Rh}(\text{Ph}_3\text{P})_2\text{Cl}$, (Equation 1) had initial rates of hydrogenation that were 10 to 20 times faster than the homogeneous equivalent. Cross-linking of the polymer-supported catalyst also affected hydrogenation rates, but diffusion into the bead and surface mass transfer effects were not rate limiting. The mechanism of reduction of the nitrogen heterocyclic ring was investigated by substituting deuterium gas for hydrogen gas. The lack of aromatic hydrogen exchange in the polymer-supported catalyst versus its homogeneous analogue is evidence for steric effects being highly important at the rhodium metal center.

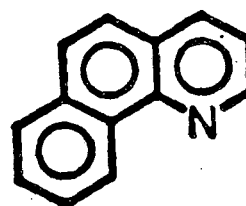
Chart 1



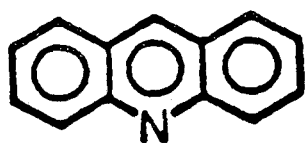
1



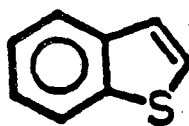
2



3



4



5

Table 1
COMPARISON OF INITIAL AND RELATIVE RATES OF HYDROGENATION OF SUBSTRATES 1-5 USING BOTH
POLYMER-SUPPORTED AND HOMOGENEOUS $(\text{Ph}_3\text{P})_3\text{RhCl}$ AS CATALYST^a

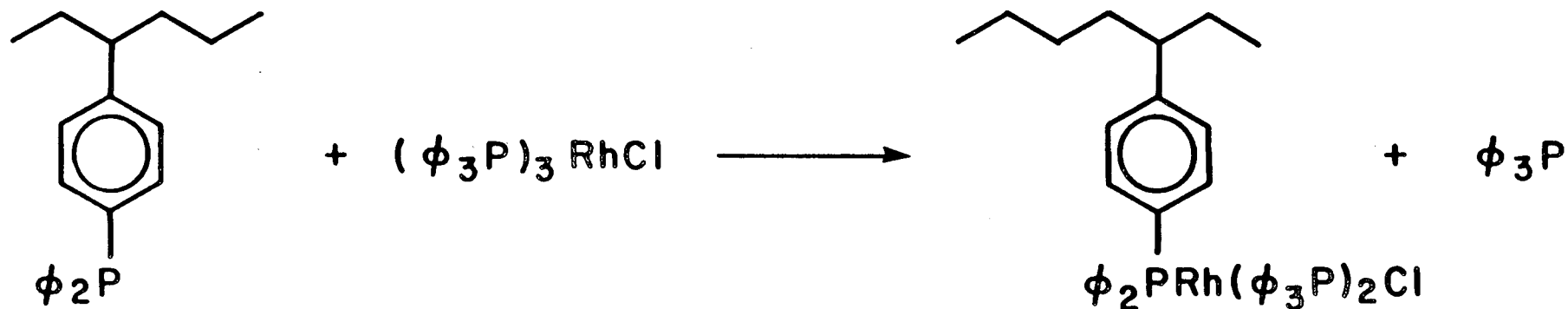
<u>Substrate</u>	<u>Product</u> ^b	<u>Polymer-Supported Rates</u> ^c		<u>Homogeneous Rates</u>		<u>PS/H Rate Ratio</u>
		<u>Initial</u> (%/min)	<u>Relative</u>	<u>Initial</u> (%/min)	<u>Relative</u>	
1, Quinoline	1,2,3,4 Tetrahydro-	.29	1	.013	1	22
2, 5,6 Benzoquinoline	1,2,3,4 Tetrahydro-	.14	.48	.0065	.5	22
3, 7,8 Benzoquinoline	1,2,3,4 Tetrahydro-	.024	.08	.0012	.09	20
4, Acridine	9,10 dihydro-	!4	!1.4	!04	!3	10
4, Acridine	1,2,3,4 Tetrahydro-	0	0	.047	3.6	0
5, Benzothiophene	2,3 Dihydro	!06	!2	.044	3.4	1.4

^a Reaction conditions were as follows: $P_{\text{H}_2} = 310$ psi, $T = 85$ °C, sub./Cat. = 91/1, Benzene (20 ml), 1 mmole substrate in each case, with either 10.2 mg of homogeneous $(\text{PPh}_3)_3\text{RhCl}$ or 52 mg of polymer-supported $(\text{P}_3\text{P})_3\text{RhCl}$ [2% cross-linked, 1.9% P, 2.19% Rh, initial P/Rh = 2.9 (Strem Chemical Co.), P/Rh after reaction with substrate 1, -5, !3.3] contained in a wire basket attached to the end of the dip-tube of the kinetic apparatus.

^b Analysis by gas chromatography.

^c Plots of % conversion vs. time provided initial (pseudo zero order) rates. Rates are relative to quinoline (1.0). Substrates, 1-5, were reacted with the same beads for all initial rates reported.

Synthesis of Polymer - Supported Chlorotris (triphenylphosphine) Rhodium (I)



2% Cross-linked PS - DVB

2.19% Rhodium

P/Rh = ~ 2.9

Equation 1

Section 3

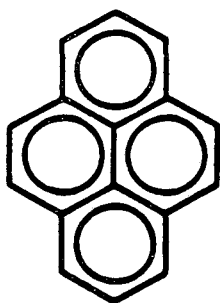
SELECTIVE REDUCTION OF QUINOLINE, IN A MODEL COAL LIQUID CATALYZED BY POLYMER-SUPPORTED CHLOROTRIS(TRIPHENYLPHOSPHINE)RHODIUM(I) AND ROLE OF P-CRESOL IN THE RATE ENHANCEMENT OF QUINOLINE HYDROGENATION

Regioselectivity for the nitrogen heterocyclic ring, in the presence of other model coal liquid constituents such as pyrene 6, tetralin 7, methylanthralene 8, p-cresol 9, and 2-methylpyridine 10 (Chart 2) verifies the potential of anchored catalysts in hydroprocessing applications.

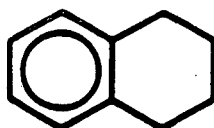
In the coal liquid experiment, it was also found that p-cresol 9, increased the initial rate of quinoline hydrogenation by a factor of ~ 3 . Recent ^1H nmr experiments tentatively show that p-cresol can hydrogen bond to free triphenylphosphine, (Figure 1 and 2) but does not assist in the dissociation of a phosphine ligand from the rhodium metal center (Figure 3 and 4). However, ^{31}P nmr spectroscopy does demonstrate that quinoline can displace an axial phosphine ligand from the octahedral dihydrido-chloro(tristriphenylphosphine)rhodium (III) complex (Figure 5). Thus, p-cresol may enhance the quinoline initial hydrogenation rate by shifting the equilibrium toward the quinoline-rhodium complex (Equation 2).

Chart 2

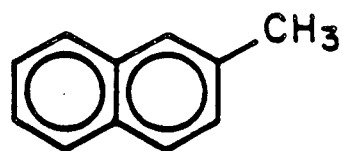
Model coal liquid constituents



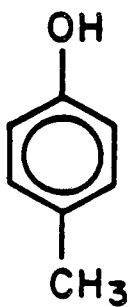
6



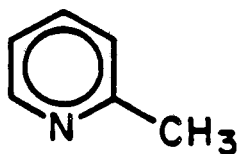
7



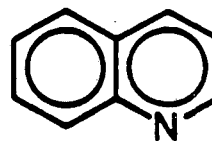
8



9



10



11

Figure 1

^1H nmr spectrum of p-cresol.

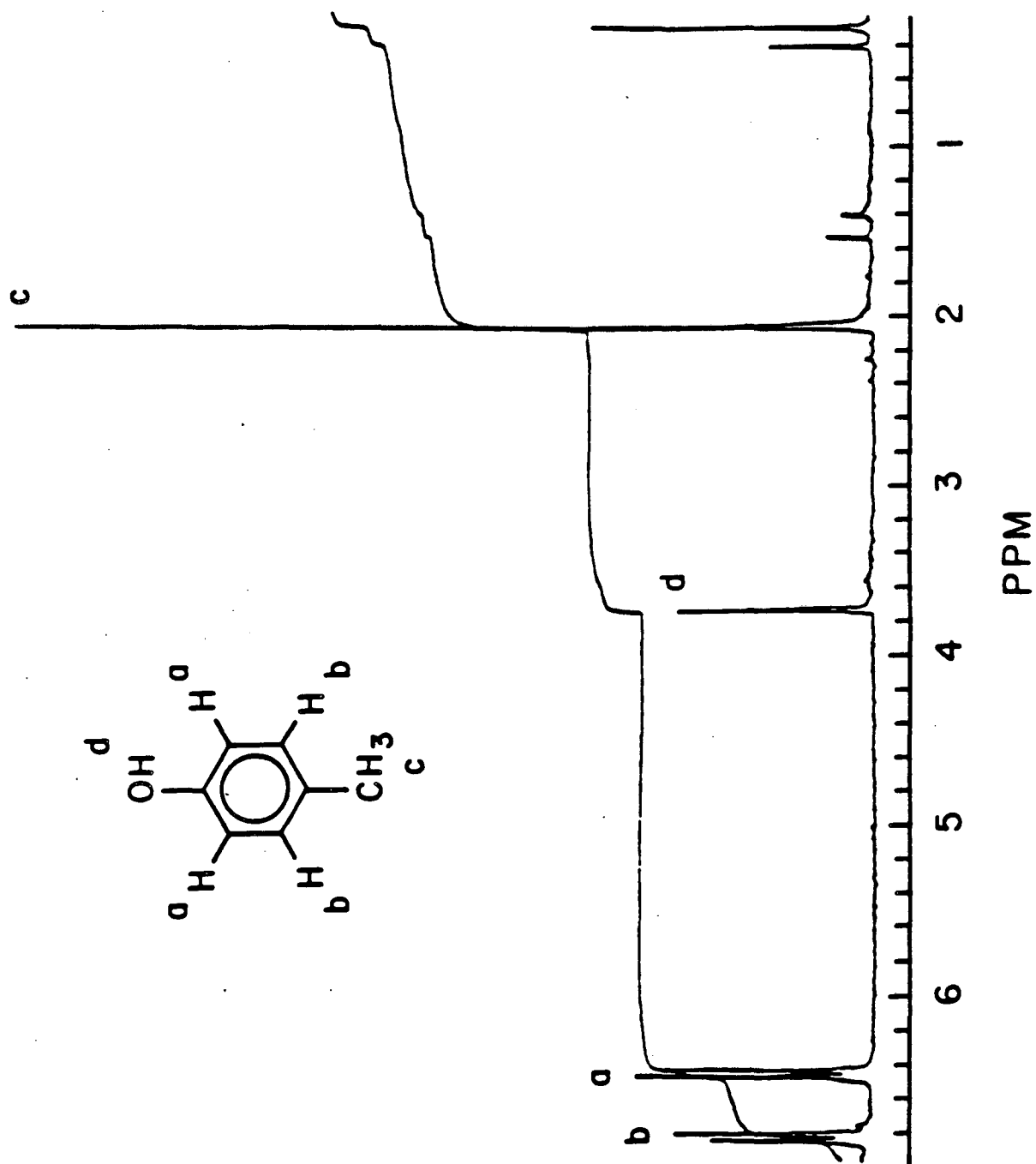
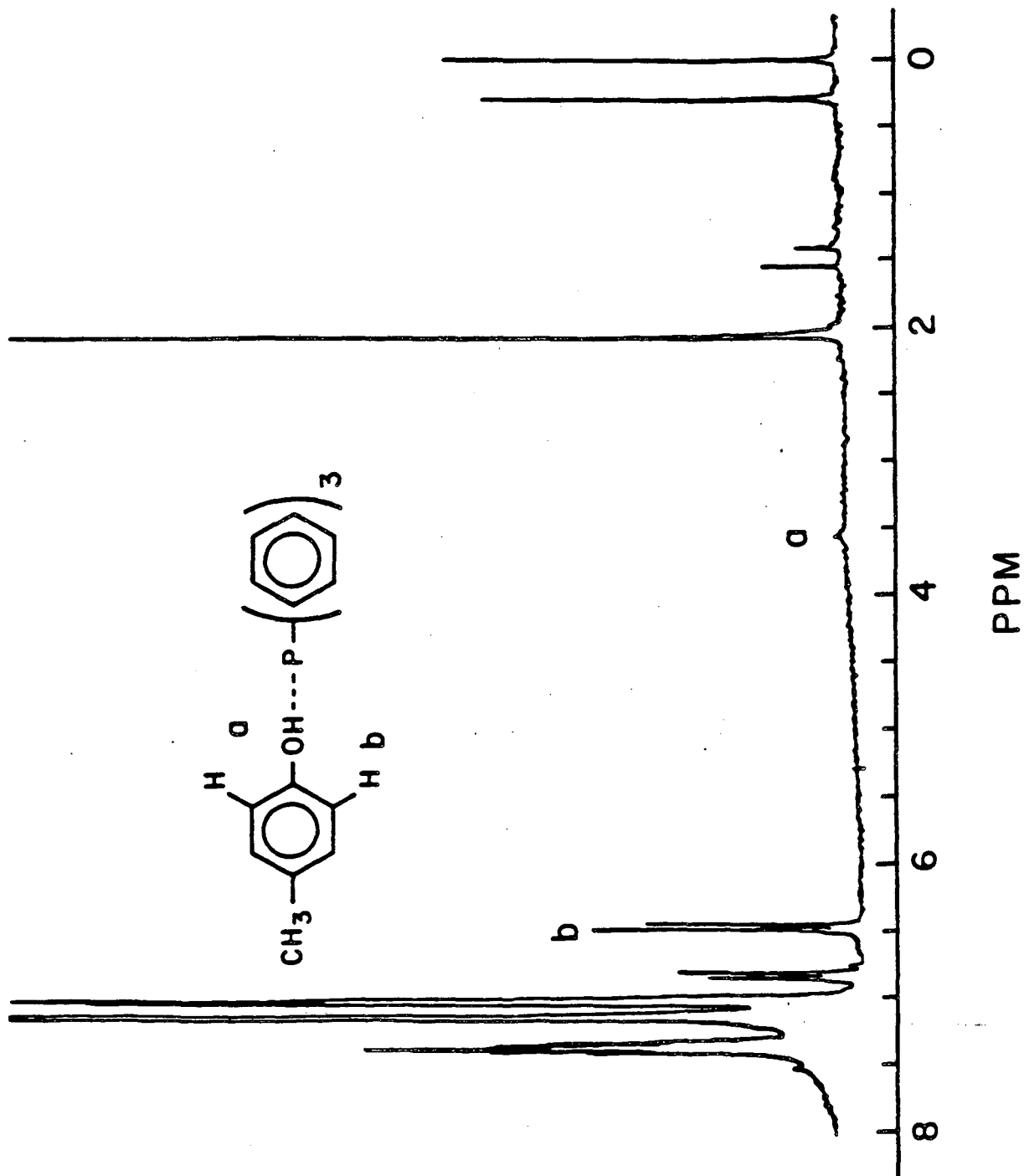


Figure 2

^1H nmr spectrum of p-cresol hydrogen bonded to Triphenylphosphine.



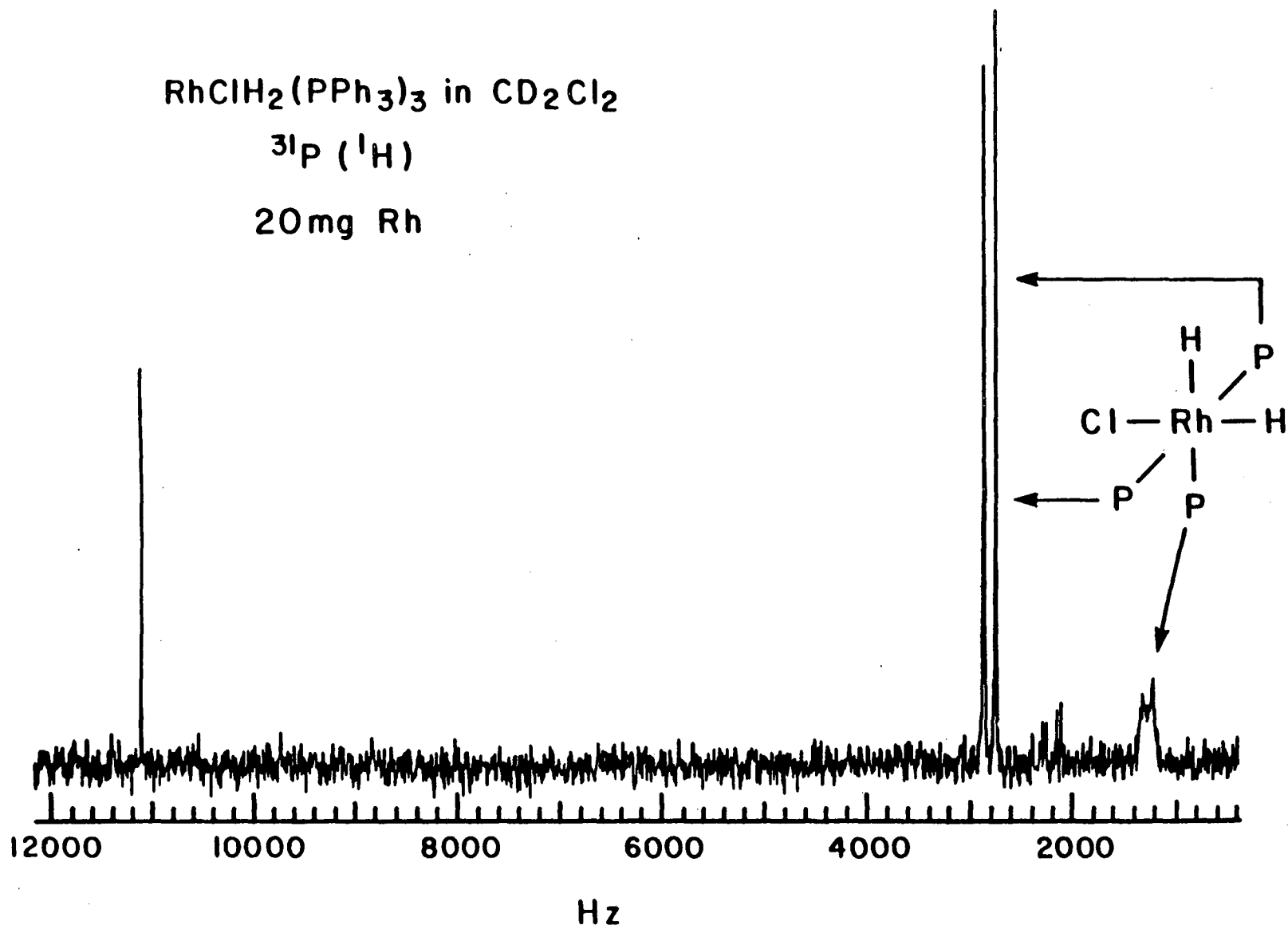
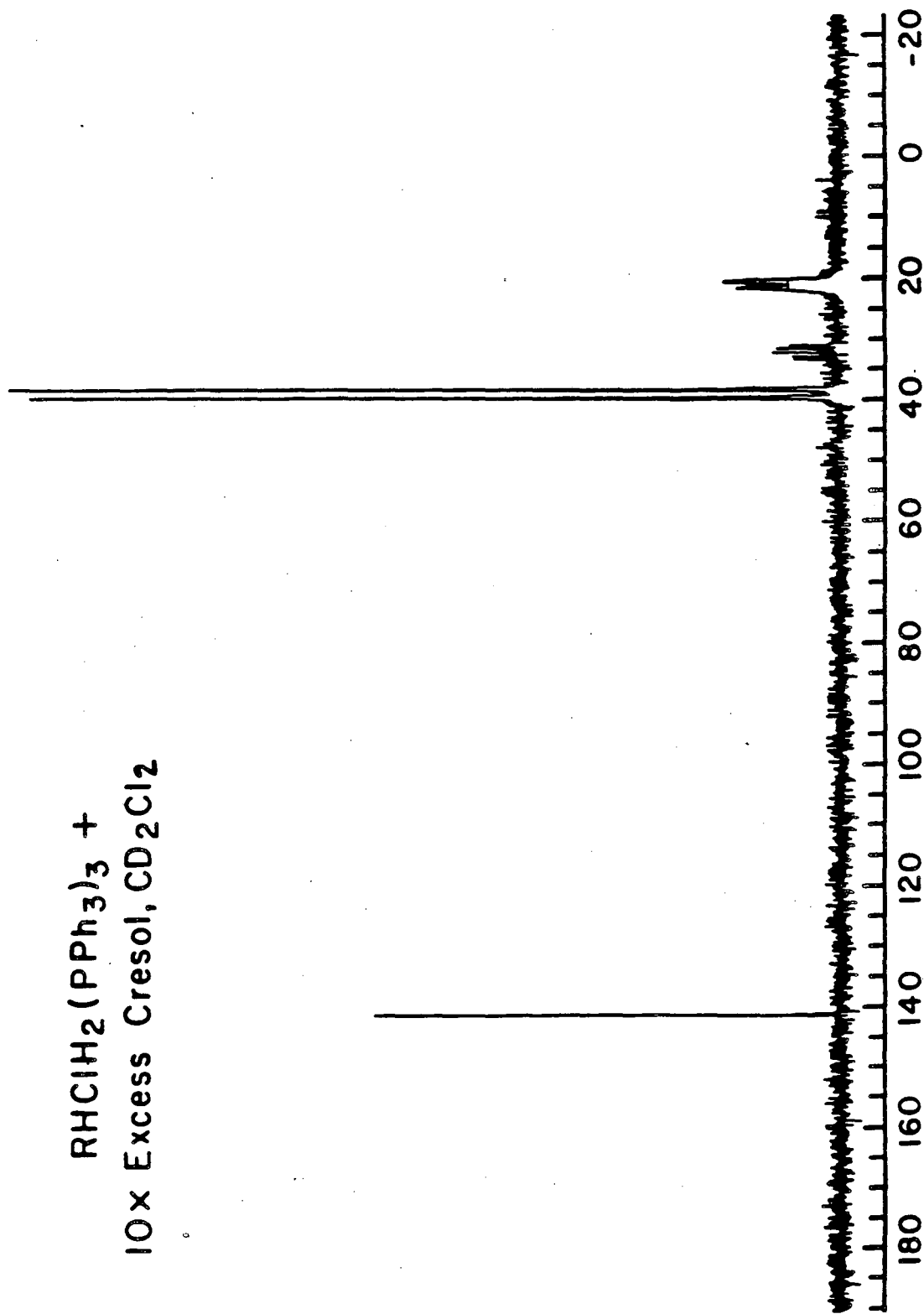


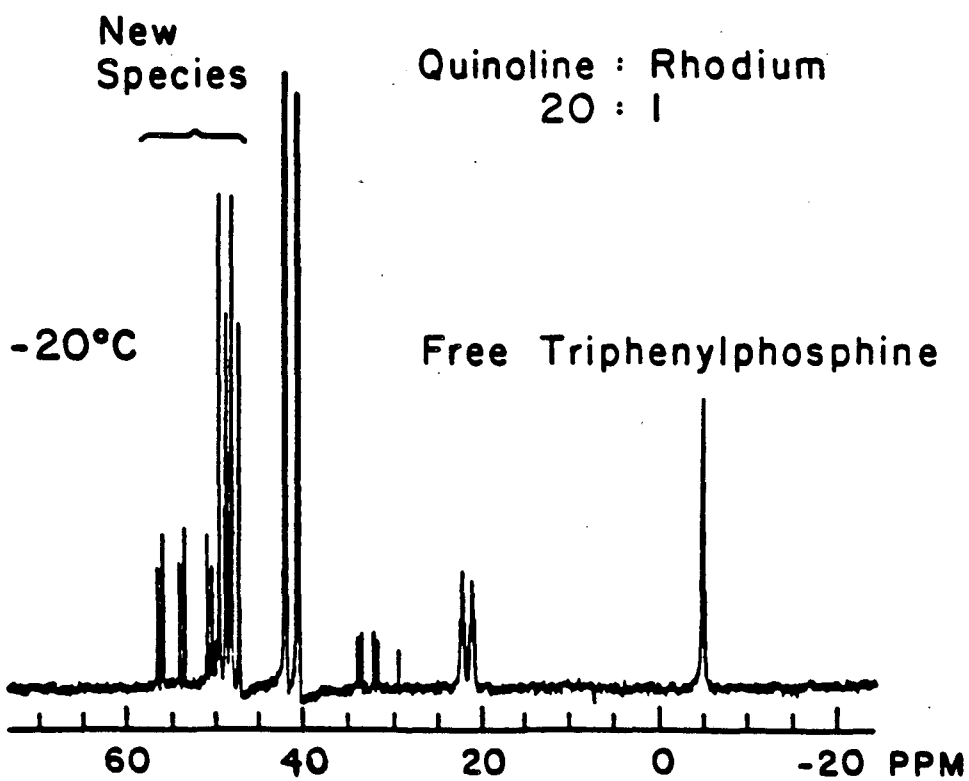
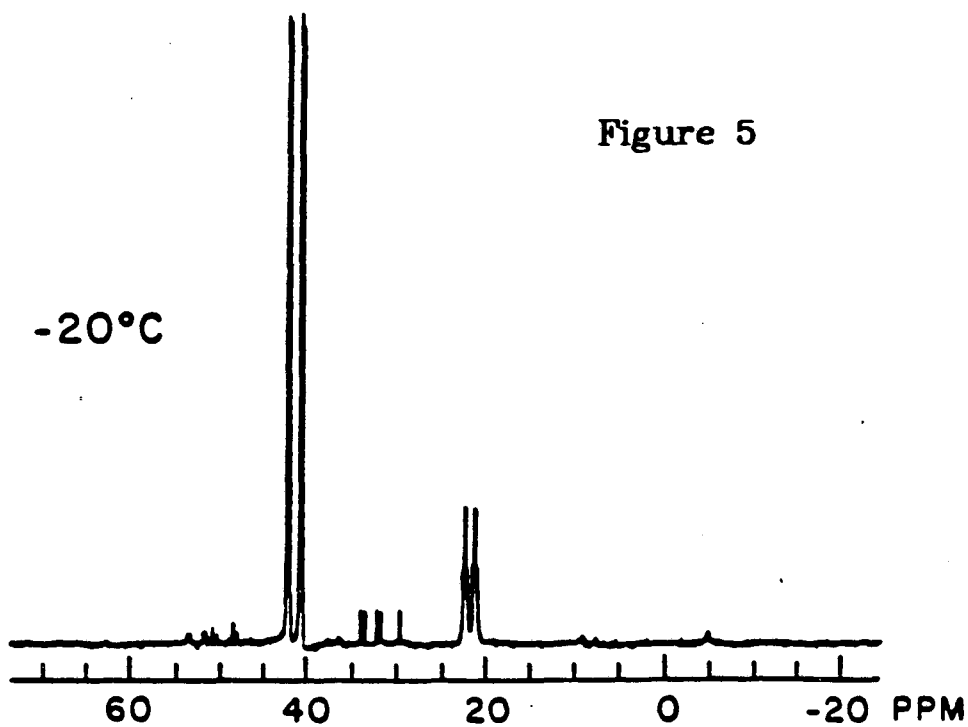
Figure 3

RHClH₂(PPh₃)₃ +
10x Excess Cresol, CD₂Cl₂



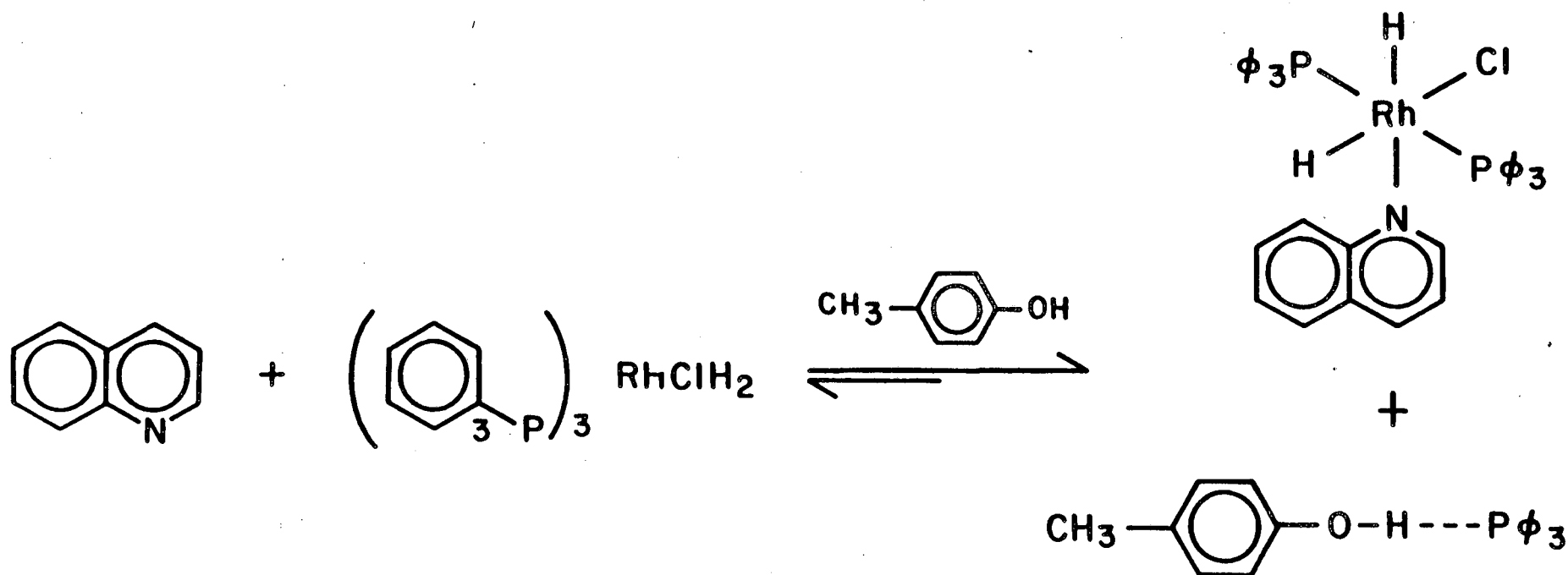
PPM
Figure 4

Figure 5



^{31}P nmr spectrum of $\text{RhClH}_2(\text{PPh}_3)_3$ (top) and Quinoline-Rhodium Complex (bottom).

Plausible Role of P-Cresol in the Rate Enhancement of Quinoline Hydrogenation



Equation 2

Section 4

CATALYTIC TRANSFER HYDROGENATION: SATURATED POLYNUCLEAR HETEROAROMATIC NITROGEN COMPOUNDS AS HYDROGEN DONORS CATALYZED BY TRANSITION METAL COMPLEXES

Catalytic transfer hydrogenation is an important component in the donor solvent coal liquefaction process. We discovered that saturated polynuclear nitrogen heterocyclic compounds, constituents in coal liquids, can transfer hydrogen to other polynuclear heteroaromatic compounds at low temperatures (80 °C) when transition metal complexes, both polymer-supported and homogeneous, are present as catalysts (Table 2 and Equations 3-6).

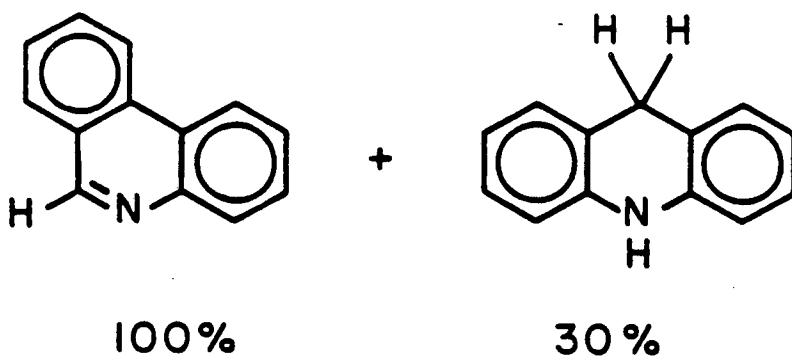
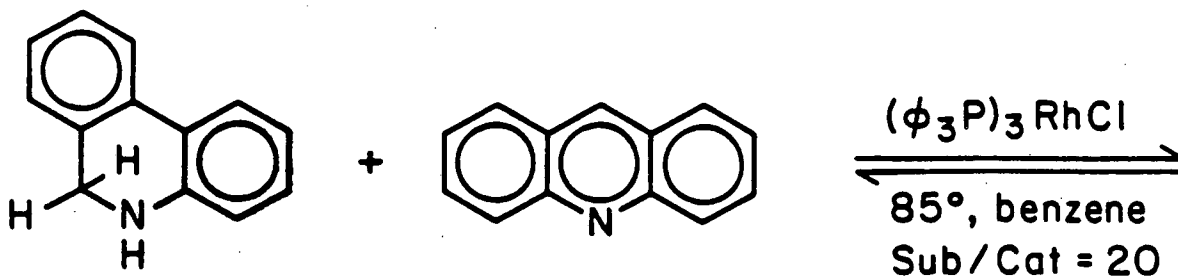
Table 2. Catalytic Transfer Hydrogenation Experiments Catalyzed by Transition-Metal Complexes ^{a,b,d}					
Donor	Acceptor	Temp (°C)	Catalyst	Product (%) ^c	
9,10-Dihydrophenanthridine	Acridine	85°	(ϕ_3P) ₃ RhCl	9,10-dihydroacridine	(30)
"	"	"	(ϕ_3P) ₃ RuCl ₂	"	(70)
"	quinoline	"	(ϕ_3P) ₃ RuCl ₂	THQ	(35)
"	"	"	(ϕ_3P) ₃ RhCl	"	(8)
"	"	"	NO Catalyst	"	(< 1)
"	"	"	[P]- $\phi_2PRh(\phi_3P)_2Cl$	"	(10)
"	7,8-Benzoquinoline	"	(ϕ_3P) ₃ RuCl ₂	1,2,3,4-Tetrahydro-5,6-benzoquinoline	(0)
1,2-Dihydroquinoline	Acridine	"	(ϕ_3P) ₃ RhCl	9,10-dihydroacridine	(10)
"	"	"	(ϕ_3P) ₃ RuCl ₂	"	(22)
9,10-Dihydroacridine	Phenanthridine	"	(ϕ_3P) ₃ RuCl ₂	9,10-dihydrophenanthridine	(30)
"	quinoline	"	(ϕ_3P) ₃ RuCl ₂	THQ (0), acridine	(48)

a) Benzene was the solvent.

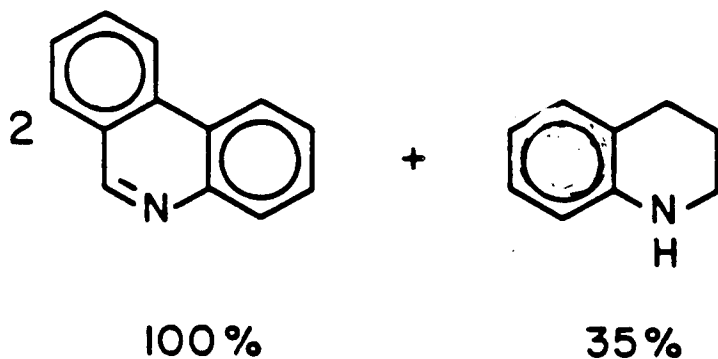
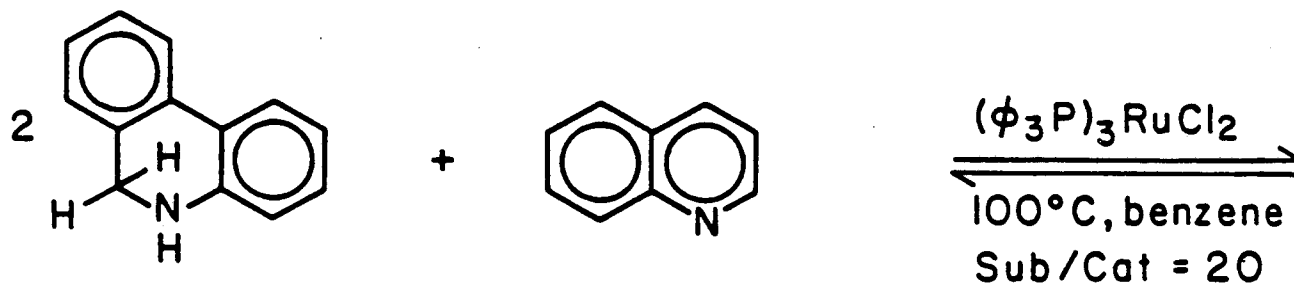
b) Substrate to catalyst = 20.

c) Capillary column gas chromatography analysis (digitized).

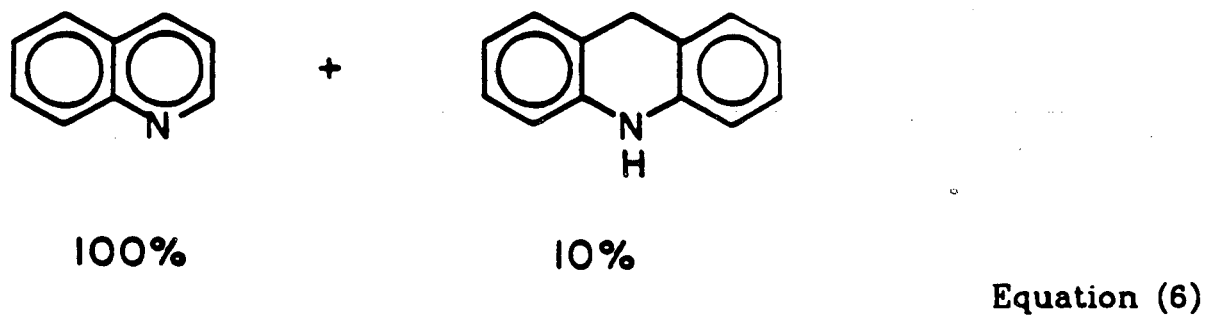
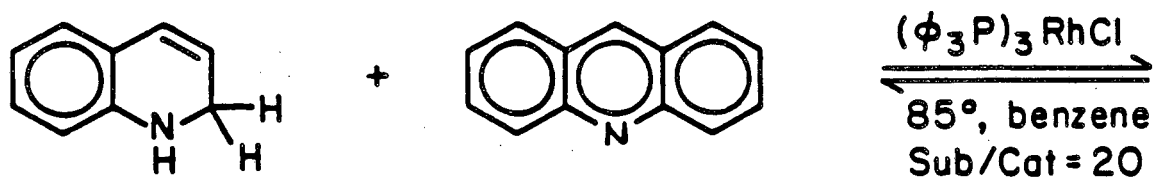
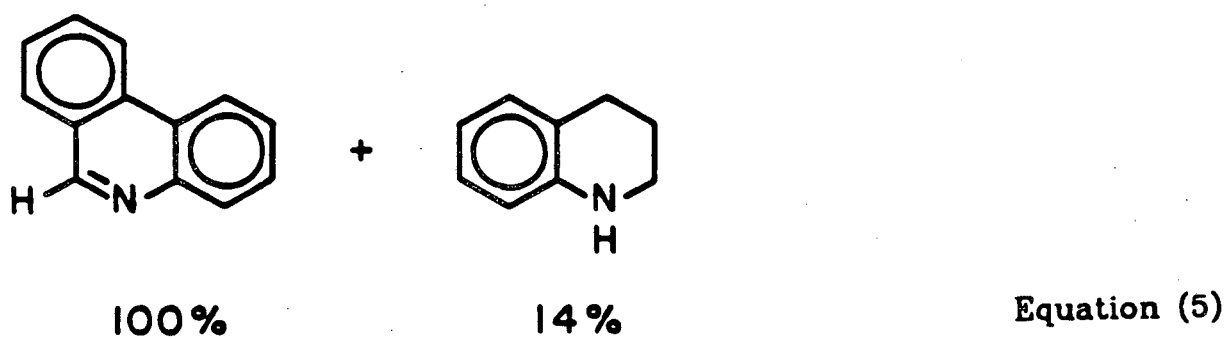
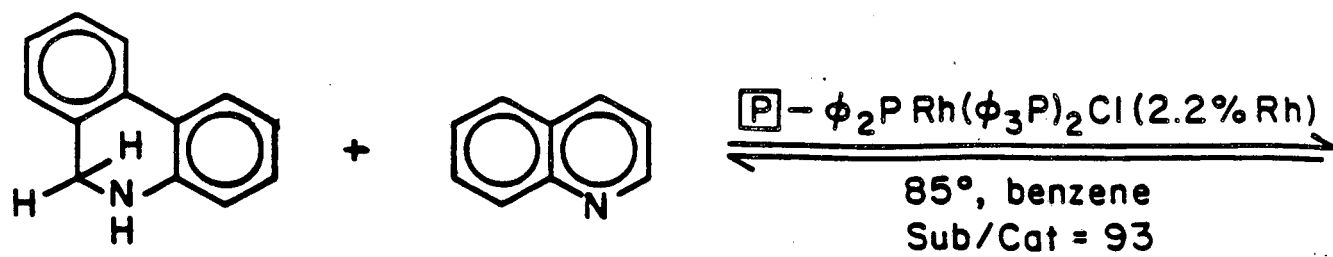
d) All reactions with 9,10-dihydrophenanthridine provided 100% phenanthridine, i.e., 100% dehydrogenation.



Equation (3)



Equation (4)



Section 5

CONCLUSIONS

The results we report indicate that low temperature hydrogenation of coal liquids with polymer-supported catalysts clearly provides a facile method for the regioselective reduction of the nitrogen containing ring in polynuclear heteroaromatic nitrogen compounds known to be present in these complex matrices. In addition, phenols enhance the initial rate of reduction of the nitrogen containing ring by affecting the formation of the nitrogen compound-metal complex. The observation that 9,10-dihydrophenanthridine can transfer hydrogen to other polynuclear heteroaromatic nitrogen compounds with catalysis by homogeneous and polymer-supported transition-metal complexes at temperatures of 100 °C and lower may pave the way to processes that degrade coal under extremely mild conditions.

CONTRIBUTORS

We wish to acknowledge the following students who performed all the experimental studies that are described in this EPRI proceedings. They are Arne D. Thormodsen and Michael Simmons, who studied the polymer-supported catalysts, and as well Arne Thormodsen performed the NMR experiments on the role of p-cresol in the rate enhancement of quinoline hydrogenation. Raja S. Tannous prepared several of the polymer-supported catalysts and Angelina Ausban did the experiments on catalytic transfer hydrogenation.

We also wish to acknowledge the Department of Energy under Contract No. DE-AC03-76SF00098 and the Electric Power Research Institute (Linda Atherton, project manager) for support of these studies.

REFERENCES

1. Fundamental Studies in the Conversion of Coal to Fuel of Increased Hydrogen Content. Electric Power Research Institute, November 1981. AP2117.
2. R. H. Fish, A. D. Thormodsen, and G. A. Cremer. J. Am. Chem. Soc. 104, 5234, 1982.
3. R. H. Fish, J. L. Tan, and A. D. Thormodsen. J. Org. Chem. 49, 4500, 1984.
4. R. H. Fish. Ann. N.Y. Acad. Sci. 415, 292, 1983.
5. R. H. Fish, J. L. Tan, and A. D. Thormodsen. Organometallics. 1985 (in press).
6. J. C. Bailar, Jr. Catal. Rev. 10, 17, 1974.
7. F. R. Hartley, and P. N. Vezey. Adv. Organometal Chem. 15, 189, 1977.
8. D. D. Whitehurst. Chemtech. 44, 1980.
9. F. Ciardelli, G. Braca, C. Carlini, G. Sbrana, and G. Valentini. J. Mol. Catal. 14, 1, 1982.
10. C. U. Pittman, Jr. Comprehensive Organometallic Chemistry. The Synthesis, Reactions and Structures of Organometallic Compounds. Pergamon Press, 1982, p. 553.
11. C. U. Pittman, Jr. Polymer-Supported Reactions in Organic Synthesis. New York: Wiley Press, 1980, p. 249.
12. Y. Chauvin, D. Commerenc, and F. Dawans. Prog. Polym. Sci. 5, 95, 1977.
13. C. U. Pittman, Jr., A. Hirao, C. Jones, R. M. Hanes, and Q. Ng. Ann. N.Y. Acad. Sci. 295, 15, 1977.
14. R. H. Fish, A. D. Thormodsen, and H. Heinemann. J. Mol. Catal. 1985 (in press).
15. R. H. Fish, and H. Heinemann. Selective Catalytic Hydrogenation of Polynuclear Heteroaromatic Compounds Using Polymer-Supported Transition Metal Compounds as Catalysts. EPRI Final Report. 1985 (to be published).

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*