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Appendix 1

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Appendix to

FIRST ANNUAL TECHNICAL REPORT

July 1, 1973 - June 30, 1974

LONG RANGE MATERIALS RESEARCH

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Synthesis and Characterization of Supported Organometallic Rhodium (I) Catalysts

by Donald Nilan Marquardt

CENTER FOR MATERIALS RESEARCH

STANFORD UNIVERSITY • STANFORD, CALIFORNIA

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Synthesis and Characterization of Supported Organometallic Rhodium (I) Catalysts

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The Ph. D. dissertation by Don Marquardt serves as the Annual Technical Report for the work on hybrid homogeneous-heterogeneous catalysts supervised by Professor Collman with consultation by Professor Boudart. The chelating silated phosphine mentioned in the last Quarterly Report has been prepared and catalysts derived from it have been studied kinetically. This work represents the best comparison to date between homogeneous and heterogeneous catalysts. During the first part of the next year, this work will be extended to chelating arsines and the kinetic results amplified. Arrangements have been made at Yale University with Professor Jack Faller for a collaborative study using X-ray photoelectron spectroscopy (ESCA). Preliminary results are very encouraging and through the use of this technique, we hope to further clarify classic heterogenous catalysts.

I. INTRODUCTION

The work described herein is a novel approach to the problem of catalysis. With recent advances in both homogeneous and heterogeneous catalysis, the need to compare both their related and their individual aspects is crucial to a better understanding of each. This thesis deals with the continuing effort to chemically bind well defined homogeneous organometallic catalysts on the surface of the inert support and to study their behavior. As such, the work involves a broad spectrum of scientific endeavor from organic synthesis through organometallic chemistry to catalysis. Each field, in itself, has a vast literature, special techniques, and voids pertaining to this problem. Although no pretense of completely filling any void can be claimed, the author hopes the chemistry presented here will stimulate greater insight into various aspects of this multi-disciplinary problem.

Since background is helpful in understanding this problem, the following topics are discussed in this introduction: recent advances in homogeneous catalysis, present theories on heterogeneous catalysis, the effects of catalyst poisons, and recent attempts to support organometallic homogeneous catalysts on inert supports. This thesis describes the synthesis of a new chelating ligand for binding homogeneous catalysts to silica surfaces, a new method using poisons for distinguishing conventional heterogeneous catalysts from the newer supported organometallic catalysts, and several comparisons between homogeneous, heterogeneous, and bound organometallic catalysts. Details of these experiments are found in the experimental section. The results presented herein show unequivocally that the bound organometallic catalysts are different from classical heterogeneous catalysts, the former behaving like their free homogeneous analogues rather than metallic heterogeneous systems.

A. Homogeneous Hydrogenation by Rhodium(I) Complexes

Homogeneous catalysts have both served and plagued alchemists and chemists since work began with solutions. Catalytic amounts of trace minerals, acids, and bases are commonly employed to promote a myriad of chemical reactions. Indeed, long before the first studies of synthetic reactions, life's functions employed homogeneous catalysts and membrane-bound catalysts.[1,2]

Catalytic processes, however important, have proven to be the most difficult to study because the catalysts represent such a small component in the entire system. Such may be the explanation of this unfortunately typical example of events in understanding a homogeneous catalysis, which began in 1909 when Ipatieff and Werchowsky[3] noticed that cupric acetate is reduced in aqueous soltuions to cuprous oxide under mild conditions. Later, Calvin (1938)[4] reported that cuprous acetate catalyses the reduction of cupric acetate under one atmosphere hydrogen; but it was not until 1954 that the kinetics of this reaction were studied by Halpern and Dakers.[5]

The events of particular importance to the present work* evolved following the work by Wilkinson on rhodium complexes in the 1960's.

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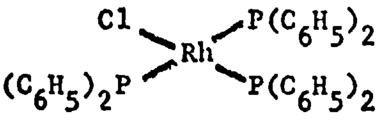
*Homogeneous catalysis is an immense field. Even narrowing the field to homogeneous hydrogenations, one is confronted with a vast array of literature and excellent reviews[6,7] and books.[8,9,10,11,12] The role of transition metals in homogeneous catalysis is likewise rich in literature and reviews.[13,14,15,16] Since any attempt at a complete review of either field would be as frustrating as it would be futile, readers are recommended to the appropriate references.

His earlier efforts centered on rhodium(III) compounds and hydrides,[17-21] none of which were derived from molecular hydrogen and none of which have been economically used as hydrogenation catalysts. However, in 1965, Wilkinson reported, "We have demonstrated the connection between hydride formation and homogeneous hydrogenation by using a new compound, tris(triphenylphosphine)chlororhodium(I)..."[21,22] Although discovered independently by R. S. Coffey[23] and synthesized at the same time by several other groups,[24,25] Wilkinson's succession of papers[26-29] established that tris(triphenylphosphine)chlororhodium(I) (1) was, indeed,



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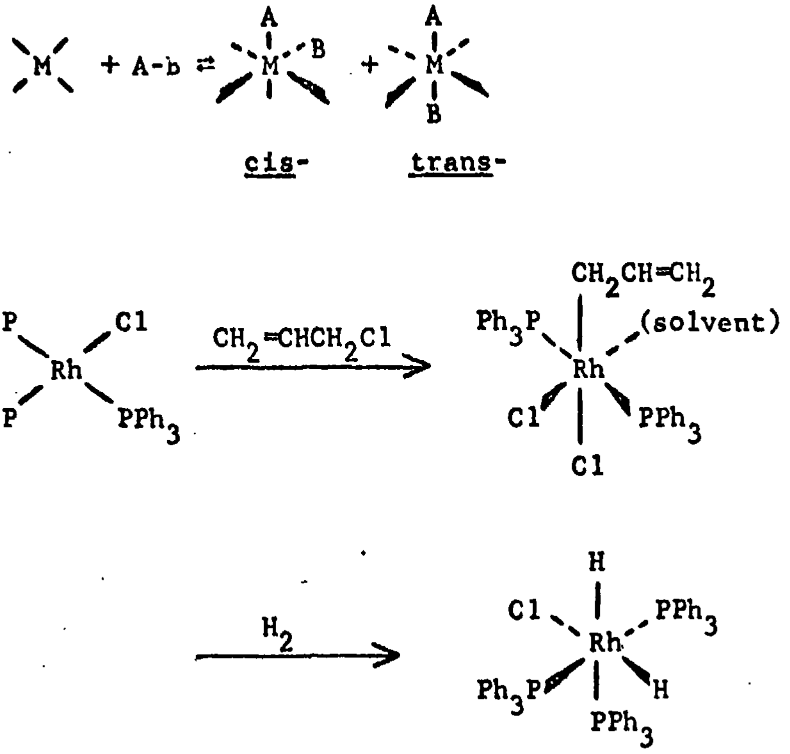
"Wilkinson's hydrogenation catalyst."

A myriad of other homogeneous catalysts have been investigated especially hydridocarbonyltris(triphenylphosphine)rhodium(I) which was first synthesized and investigated as a hydrogenation catalyst by Vaska and co-workers[30,31] and was later fully explored by Wilkinson's laboratory as a hydrogenation and hydroformylation catalyst.[32-43] However, for the purposes of this work, a fuller discussion of Wilkinson's first catalyst, tris(triphenylphosphine)chlororhodium(I), is more pertinent.

Homogeneous catalysts must be capable of activating both substrate and hydrogen, as well as stabilizing the highly reactive intermediates as soluble complexes.[9] In order to accomplish the activations the compound must have vacant binding sites for these interactions. This generally requires the ability to dissociate some of its ligands in order to accommodate the reactive species.

Tris(triphenylphosphine)chlororhodium(I) is a d^8 species and, though relatively stable, can undergo the addition of several covalent molecules. Both the general case as well as specific examples of such addition reactions are illustrated in Figure 1.



Reference
14, 44

45

49

Figure 1. Oxidative Addition to d^8 Complexes.

Termed as "oxidative addition" by Collman,[44] in this process the square planar, d^8 complex of Rh(I) is formally oxidized to an octahedral, d^6 complex of Rh(III).

An apparently vital feature of a homogeneous catalyst is the presence of a vacant site in its coordination sphere. Wilkinson noted in his first paper[26] that there is an equilibrium in solution

$$RhCl(PPh_3)_3 \underset{PPh_3}{\overset{solvent}{\rightleftharpoons}} RhCl(PPh_3)_2 + PPh_3 \qquad (1)$$

and believed the dissociation to be complete in chloroform and benzene. Although later investigations[46-49] proved that rigorous exclusion of oxygen leads to no detectable dissociation of the $\underline{d}^8$ Rh(I) species, it is certain that the $\underline{d}^6$ tris(triphenylphosphine)dihydridochlororhodium(III) species has a labile phosphine (Wilkinson indicated this by the presence of the solvent molecule in the coordination sphere, as in Figure 1(b)). This leads to "coordinative unsaturation" which allows for activation of the substrate, and subsequently, hydrogenation.

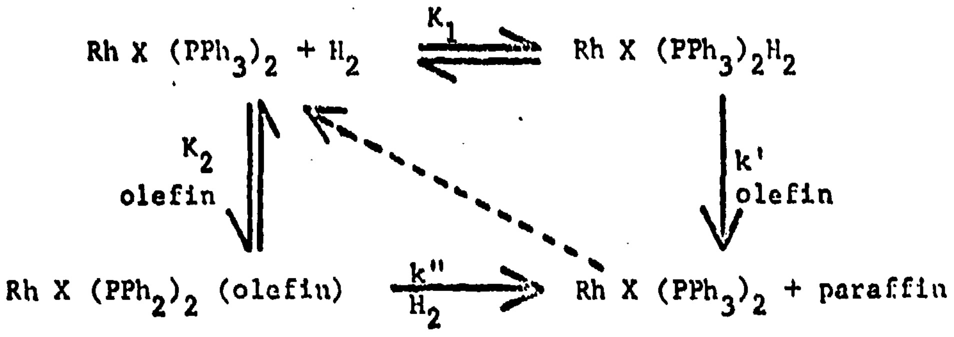
One problem with coordinative unsaturation, however, is that undesirable side reactions may occur at these vacant sites. This occurs with Wilkinson's catalyst, and dimer formation

$$2\ \mathrm{RhCl(PPh_3)_2} \rightleftarrows [\mathrm{RhCl(PPh_3)_2}]_2 \qquad (2)$$

was first described by Wilkinson[26] and was later substantiated by Meakin with ^{31}P NMR.[49] Such dimers generally exhibit little, if any, catalytic activity and, for this reason, kinetics are often performed with excess triphenylphosphine to inhibit the dimer formation.

The relative importance of the species actually involved in hydrogenation has a significant effect on the description of the rate law. Wilkinson originally proposed the mechanism shown in Figure 2.[26] More detailed mechanistic studies, necessitated by the evidence that Wilkinson's catalyst is very little dissociated in solution, have been described by Halpern with the results shown in Figure 3.[50]

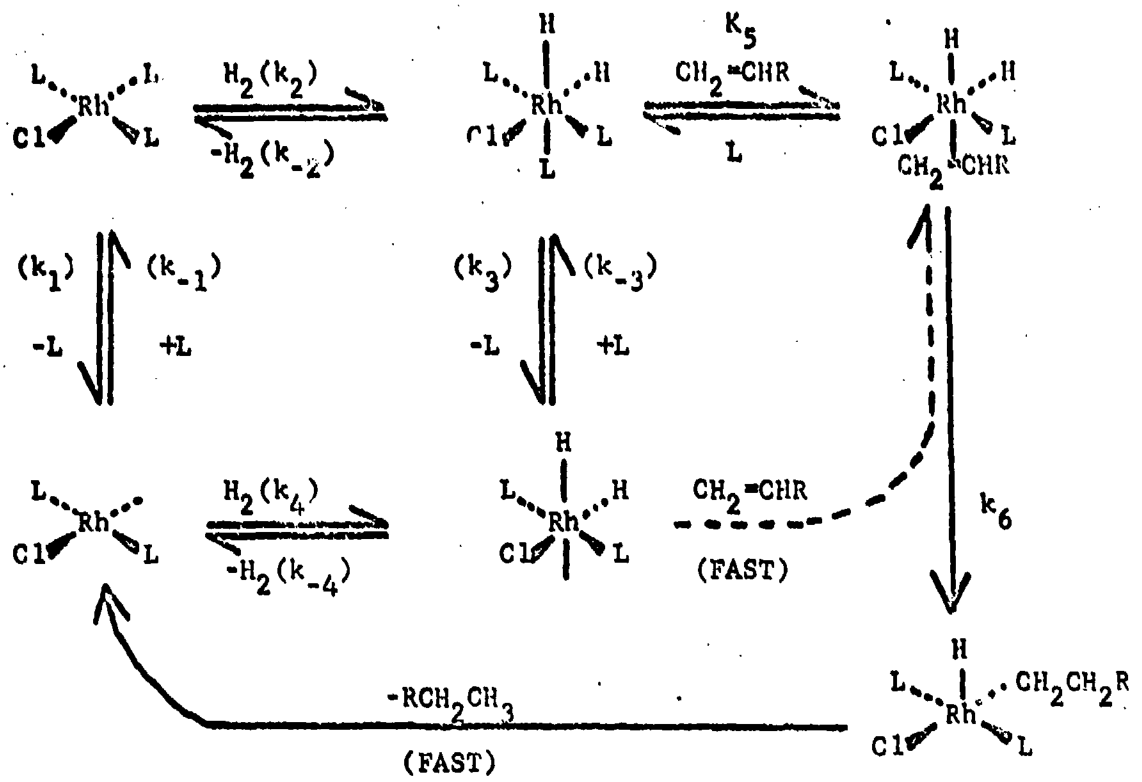
Halpern's recent kinetic studies more completely define the mechanism for catalytic hydrogenation by Wilkinson's complex. In the same study,[50] Halpern makes several other interesting points:



$$R = \frac{k'K_1P_{H_2}[\text{olefin}][\text{Rh X (PPh}_3)_2]}{1 + K_1P_{H_2} + K_2[\text{olefin}]}$$

(The k" pathway is much slower than the k' pathway if not totally inoperative under most catalytic conditions.)

Figure 2. Wilkinson's Scheme for Hydrogenation with Tris(triphenylphosphine)chlororhodium(I)[26]



For L = PPh_3, reduction of cyclohexene in benzene yields these constants (25°):

$k_1 = 0.7\ sec^{-1}$ $k_{-1} \geq 7 \times 10^4\ \underline{M}^{-1}\ sec^{-1}$ $K_1 = k_1/k_{-1} \leq 10^{-5}\ \underline{M}$
$k_2 = 4.8\ \underline{M}^{-1}\ sec^{-1}$ $k_{-2} = 2.8 \times 10^{-4}\ sec^{-1}$ $K_2 = k_2/k_{-2} = 1.7 \times 10^4\ \underline{M}^{-1}$
$k_3 = 3.1 \times 10^2\ sec^{-1}$ $k_4 \geq 7 \times 10^4\ \underline{M}^{-1}\ sec^{-1}$
$K_5 = 1.6 \times 10^{-3}$ $k_6 = 1.2 \times 10^{-1}\ sec^{-1}$

$$\frac{-d[RhClL_3]}{dt} = \left[k_1 + \frac{k_2 k_3}{k_{-2}[L] + k_3[H_2]}\right][H_2][RhClL_3]$$

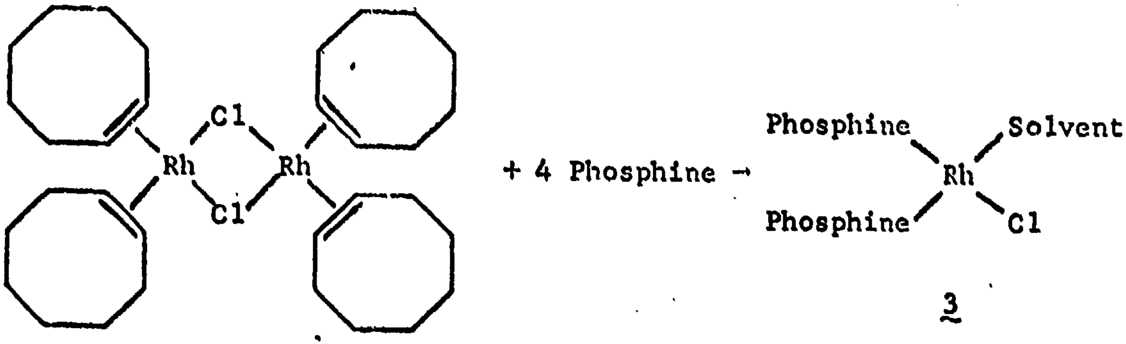
under most conditions, this simplifies to

$$\frac{-d[H_2]}{dt} = \frac{k_6 K_5 [Rh]_{total}[RCH=CH_2]}{K_5[RCH=CH_2] + L}$$

Figure 3. Halpern's Scheme for Hydrogenation with Tris(triphenylphosphine)chlororhodium(I)[50]

1) the kinetically dominant path for H_2 addition appears to be through the doubly coordinatively unsaturated bisphosphine complex (a 14 electron system) in spite of the fact that the trisphosphine complexes are more stable; 2) experiments with *p*-substituted styrenes show that the electronic properties of the olefin have minimal net effect on the overall rate, since the electron withdrawing groups stabilize the olefin complex but decrease the rate of hydrogen insertion; and 3) $k_6[Rh]_{total}$ is the limiting rate and is readily attainable in solution (~ 1 *M* olefin, $\leq 10^{-3}$ *M* PPh_3). Thus a modification of the catalyst to the $RhCl(PPh_3)_2$ form would offer only little advantage.

In earlier work, Wilkinson[29] showed that by preparing the catalyst *in situ* from a tetraolefin-μ,μ'-dichlororhodium(I) species, 2, by adding phosphine to split the bridge, a more active catalyst may be obtained (Eq. 3). This catalytic species is hypothesized to be what is shown as 3 but has never been characterized.



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(3)

Measuring the rate vs. amount of added phosphine, a plot (Figure 4) shows that optimal catalyst efficacy is obtained when approximately two phosphines per rhodium are added. In addition, this graph strikingly demonstrates that variation in the π-donor qualities of the phosphine ligand drastically affect the functioning of the ligand. This effect has been the subject of other studies.[59,60]

Furthermore, comparison of different halides produces similar changes. Although no tabulated data were presented on the rates, Wilkinson did report that the catalyst increased in ability to promote hydrogenation in the order I > Br > Cl.[26] Later[27] it was noted that there is a significant difference in the enthalpy and entropy of activation for the halogen catalysts

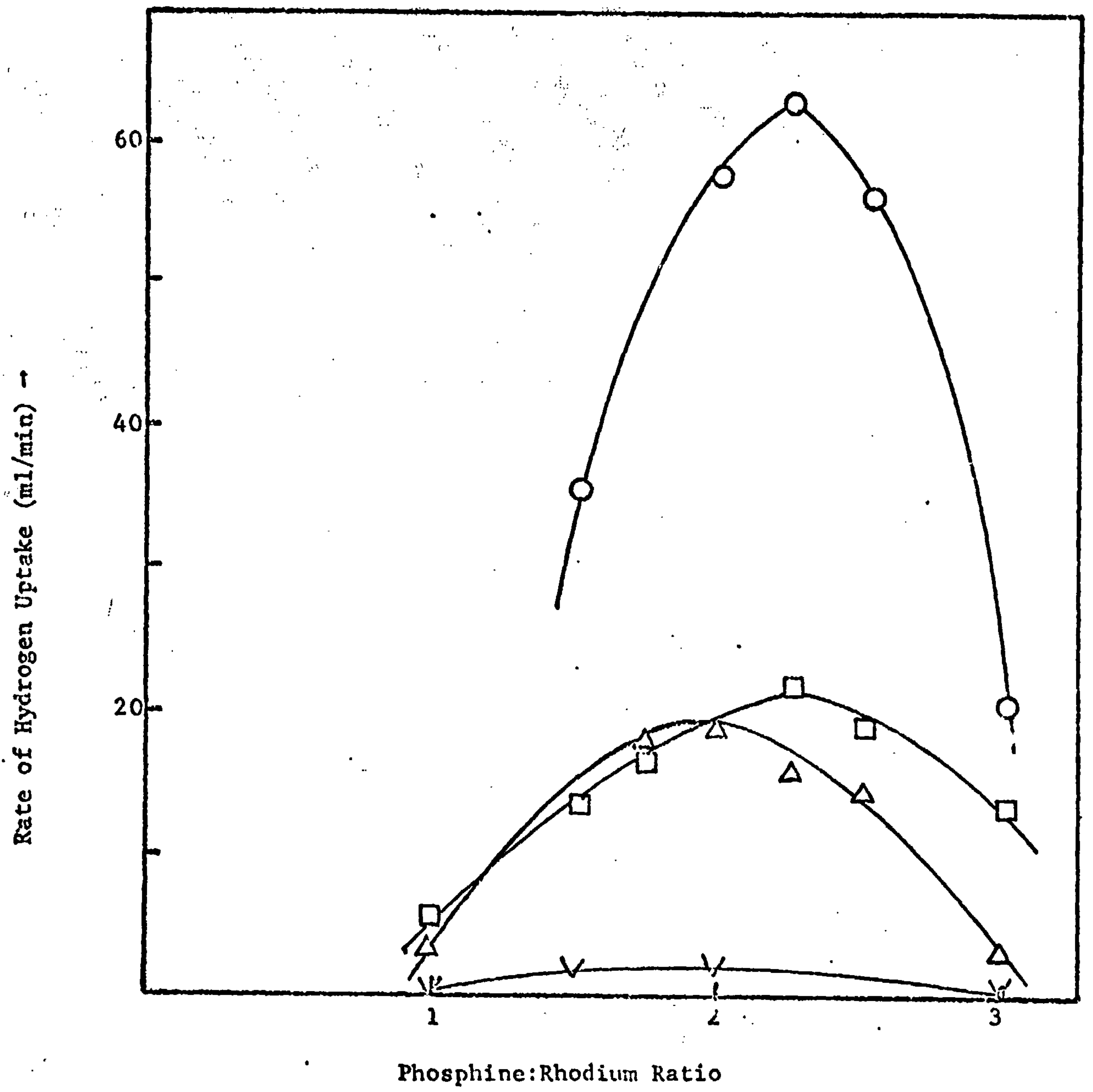
Cl: $\Delta H^{\ddagger}$, 23.3 kcal/mole; $\Delta S^{\ddagger}$, 12.9 eu

Br: $\Delta H^{\ddagger}$, 19.4 kcal/mole; $\Delta S^{\ddagger}$, 4.1 eu .

Similar differences in rates and activation parameters are also observed[27] with changes in solvents, for example, with $RhCl(PPh_3)_3$:

Ethyl methyl ketone-hexane:	$\Delta H^{\ddagger}$, 16.6 kcal/mole; $\Delta S^{\ddagger}$, -5.3 eu; k', 29.6 ℓ/mole-sec
Benzene-hexane:	$\Delta H^{\ddagger}$, 23.3 kcal/mole; $\Delta S^{\ddagger}$, 12.9 eu; k', 15.0 ℓ/mole-sec
Benzene:	$\Delta H^{\ddagger}$, 18.6 kcal/mole; $\Delta S^{\ddagger}$, 1.3 eu; k', 31.6 ℓ/mole-sec.

Finally, steric factors control the rate of hydrogenation of various substrates. Many sources[26,27,29,51-53] yield data on this point, but much of this is difficult to compare because of different conventions in reporting rate data. Table I attempts to put in perspective some of these data pertinent to this work.



Catalyst: 1.25 m$\underline{M}$ catalyst with: O $(\underline{M}eO)C_6H_4)_3P$
□ Ph_3P
Δ Ph_2EtP
V Et_3P

Conditions: 0.6 $\underline{M}$ cyclohexane in benzene 25°, 50 cm H_2

Figure 4. Rate of Hydrogenation with Wilkinson's Catalyst prepared *in situ* With Different Phosphines *vs.* Molar Ratio of Phosphine to Rhodium[29]

Table I.

Rates of Hydrogenation of Olefins by $RhCl(PPh_3)_3$ in Benzene at 25°.

Substrate (Concentration in M)	Pressure of H_2	[Catalyst] ($M \times 10^3$)	Rate of Uptake of Hydrogen (mmol/min)	Reference
Cyclohexene (1.25)	50 cm	1.25	0.08	27
2,3-Dimethylbut-2-ene (1.25)	50 cm	1.25	0.01	27
Acrylamide (1.25)	50 cm	1.25	0.22	27
Allyl Alcohol (1.25)	50 cm	1.25	3.02	27
Styrene (1.25)	50 cm	1.25	2.56	27
Penta-1,3-diene (1.25)	50 cm	1.25	0.06	27
Cyclohexene (1.10)	760 mm	2.4	0.148	53
1-Methylcyclohexene (0.94)	760 mm	2.4	0.0014	53
1,4-Dimethylcyclohexene (0.82)	760 mm	2.4	0.0001	53
1,3-Dimethylcyclohexene (0 82)	760 mm	2.4	0*	52
1,2-Dimethylcyclohexene(0.6)	760 mm	2.4	0*	52
Norbornene (1.22)	760 mm	2.4	0.048	53

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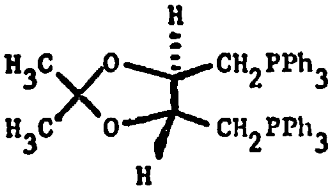
*Hydrogenation performed in 3:1 benzene:ethanol solvent, generally faster than straight benzene.

Through Wilkinson's work, there exist several alternatives to determine the "homogenosity" (or degree of similarity to the "standard" homogeneous catalyst) of Wilkinson-type catalysts. Mentioned so far are rate law determinations, dependence on phosphine, dependence on the halide, and finally the large differences in hydrogenations of substituted olefins.

As a brief postscript to Wilkinson's work, it should be mentioned that increasing interest in homogeneous catalysis has been generated through the possibilities of asymmetric induction through reduction by homogeneous catalysts having chiral phosphines. This was first tried by Knowles and Sabackey[54] using a $L^{*}_{3}Cl_{3}Rh(III)$ system and hypothesizing (as previously suggested for several systems but yet unproven[7]) that a Rh(I) species is involved in the active intermediate. A Wilkinson catalyst having chiral phosphines was tried later,[55] but Morrison[56] discovered that chirality need not necessarily be at the phosphorus itself, but could be located in a carbon on the phosphine. The greatest degree of optical purity obtained at that time, however, was found by Dang and Kagan[57] using (-)-2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((-)-DIOP) (4),



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One of the major factors cited in DIOP's capability to induce such high optical purity was its ability to bind the rhodium with two phosphines and hence be present throughout the several catalytic steps.

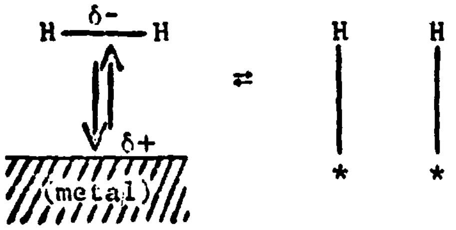
Dang and Kagan prepared this complex in situ using the method described earlier of splitting a dichlororhodium dimer (Eq. 3). The catalyst was not recovered and characterized. The problems of using a bisphosphine ligand with rhodium complexes is suggested by a recent review on bidentate phosphine ligands,[58] which shows no Wilkinson's catalyst analogs with bidentate phosphine ligands. A few neutral species involving carbonyls exist with bisphosphine ligands,[61,62] but the majority are "ill defined products" or precipitate from organic solutions as salts.

B. Heterogeneous Hydrogenation Catalysts

Heterogeneous catalysis is a surface phenomenon, characterized by the fact that at least some of the intermediates are absorbed on or chemisorbed (or chemically bonded) to a solid phase. Although an asset in many respects, this property makes study of heterogeneous catalysts even more difficult than the study of homogeneous catalysts; not only are the active catalytic species present in relatively minute quantities, but the heterogeneous are inseparable from the bulk of their support. Recent progress has been made into the study of the properties of the physisorbed or chemisorbed species; direct infrared,[63], magnetic,[64] surface potential,[65,66] radiochemical,[67] and electron spin resonance[68] techniques have yielded information about the nature of these species. However, isolation and observation of the intermediates has heretofore been infeasible, and the active species during the catalytic process are known only by speculation and inference from kinetic data and reaction products.

Heterogeneous catalysis is much too broad a topic to be discussed in this work,* but an introduction to the basic theories of this type of catalysis is in order before commenting specifically on rhodium heterogeneous catalysts.

Classically, heterogeneous catalysts were considered to activate hydrogen by weakening the H-H bond resulting from the interation of the metal d-band with molecular hydrogen. This results in a dipole, and the molecule of hydrogen is believed to split, yielding two hydride species on the surface (Figure 5).



where * = active metal site

Figure 5. Hydrogen Activation by Metal[6]

This might be compared with the hydrogen activation of organometallic homogeneous catalysts. With Wilkinson's catalyst, 1, a hydrogen molecule is added in the process of oxidative addition, formally reducing the hydrogen to two hydrides and oxidizing the d^8 rhodium(I) complex

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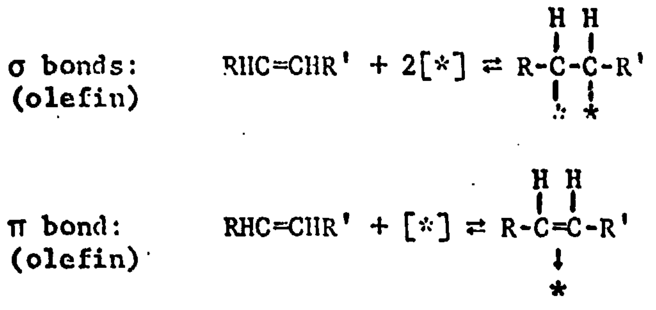
[*] Heterogeneous catalysis of olefin hydrogenation by transition metals has been reviewed many times recently.[6,69-72] Insights into the theory of heterogeneous catalysis[73] and current theories of the effect of metal structure on catalytic activity[74] are available in recent publications. The references are recommended for further information in the respective field of investigation.

to a $\underline{d}^6$ rhodium(III) complex (Figure 1). With heterogeneous catalysts, the analogous reactions are much harder to study and several important issues remain much less well understood: even the number of hydrogens bonded to active metal sites is not certain, particularly with sites on corners or edges of crystallites capable of binding several hydrides. It is generally assumed that there is a single hydride on each surface metal site: the standard method for determination of catalytic surface area developed by Benson and Boudart[151] assumes that the oxide on the surface of the metal (M-O) is reduced and replaced by the hydride (M-H) by the stoichiometry 1 M-O + 3/2 $H_2 \rightarrow$ 1 M-H + 1 H_2O.

The interactions involved in the activation of organic compounds by the metal is even more complex, even to the point of being referred to as an "organometallic zoo" by Burwell.[72] In theory, there are several possibilities depending on the orbitals available for interaction, commonly formulated as σ-bonded and π-bonded structures (Figure 6).



$$\sigma \text{ bonds: (olefin)} \quad RHC{=}CHR' + 2[*] \rightleftharpoons R\text{-}\overset{H}{\underset{*}{C}}\text{-}\overset{H}{\underset{*}{C}}\text{-}R'$$

$$\pi \text{ bond: (olefin)} \quad RHC{=}CHR' + [*] \rightleftharpoons R\text{-}\overset{H}{C}{=}\overset{H}{C}\text{-}R' \; (\downarrow *)$$

Figure 6. σ- and π-Olefin-Metal Complexes[70]

It may be noted that the olefin π-bonded to the metal site is apparently similar to the activation of an olefin by organometallic catalysts, and it is believed that strong parallels exist between the nature of these activated species. It is also interesting that heterogeneous "cracking" catalysts can activate saturated hydrocarbon compounds, but this phenomenon has not been directly observed with organometallic catalysts probably because they cannot be used under similarly rigorous conditions.

The examples in Figure 6 are quite simple, but the systems become much more complex as the number of carbons and metals involved in a reaction increase. With organometallic catalysts, there is a practical limit to the number of carbons that can interact with the single metal center (this limit generally being six carbons, as in arene π complexes), but heterogeneous catalysts have adjacent sites available for multiple interactions. In fact, the activity of a catalyst for a particular reaction may vary with the nature (i.e., proximity or spatial arrangement) of metal sites in that catalyst. In a particularly well-chosen example, Boudart and co-workers studied two parallel reactions of neopentane on platinum catalysts: isomerization to isopentane and hydrogenolysis to isobutane and methane.[76] Although most previous work had shown that specific activity (activity per unit surface area) of various platinum catalysts was insensitive to the particle size and nature of support, Boudart showed that these studies were performed with "structure insensitive" or "facile" reactions that are dependent only on a single parameter (the type of available orbitals at the metal surface). For "structure sensitive" or "demanding" reactions, however, a second parameter is required: a particular spatial arrangement or proximity of active sites. Boudart found that by varying the structure of the catalyst by means of its preparation and pretreatment, the specific activity of the isomerization of neopentane varied by a factor of 15 whereas the specific activity of hydrogenolysis changed by a factor of 300. In presently accepted terminology, the isomerization is considered "structure insensitive" and the hydrogenoloysis is "structure sensitive". Thus, by varying the pretreatment of the catalyst, and hence the relative numbers of specific configurations of active sites, it is possible to vary the rates of structure sensitive reactions. Similar studies with ethane hydrogenolysis on rhodium catalysts show similar differences in specific activity for demanding reactions.[81]

In heterogeneous catalysts, structure has definite influence on the rates of reactions, much more in "demanding" than in "facile" reactions. Generally speaking, hydrogenations of olefins are facile and are usually described by a rate law that is first order in the quantity of catalyst and first order in hydrogen, but zeroth (or slightly negative) order in substrate:[53,75]

$$\text{Rate} = k[H_2]^1[\text{Rh}_{\text{active surface}}]^1[\text{olefin}]^0 \qquad (4)$$

This rate law agrees with the findings that olefins are strongly bound to the metal (hence not rate determining) whereas the hydrogen is more weakly adsorbed.[77] With rhodium supported on either alumina or silica, the mechanism for hydrogenation of 1-butene is proposed as:[77]

$$\begin{aligned} &C_4H_8(g) + [*] \rightleftharpoons C_4H_8(a) \\ &H_2(g) + 2[*] \rightleftharpoons 2H(a) \\ &C_4H_8(a) + H(a) \rightleftharpoons C_4H_9(a) + [*] \\ &C_4H_9(a) + H(a) \rightarrow C_4H_{10}(g) + 2[*]. \end{aligned} \qquad (5)$$

This mechanism requires a minimum of two neighboring metal sites in order for the last three steps to proceed.

Rhodium catalysts behave differently from most other supported catalysts with regard to isomerization of olefins. Compared to other Group VIII metal catalysts, rhodium shows an anomalously high temperature dependence of isomerization[70,75,77] and above 40° the rate of isomerization dramatically increases for 1-butene.[77] In further work, it was postulated that this isomerization is dependent on participation of surface hydroxyl groups of the support since up to 80% poisoning of the active sites has a dramatic effect on hydrogenation but no effect on isomerization.[80]

Rhodium heterogeneous catalysts also have the distinction of showing the highest rate of hydrogen exchange between C_6H_6 and C_6D_6 (the full order being Rh > Ir > Mo > Re > W = Co > Ni = Fe > Pt > Mn > Cr > Pd > Ta > V > Ti > Ag >>> Cu, Au).[78] This may be correlated to the percentage of d character in the metallic bonds and hence ability to π-bond the aromatic ring. The ability to scramble hydrogen in aromatic systems also gives rhodium the capability to hydrogenate same when hydrogen is supplied. The proposed mechanism for this hydrogenation has been described as shown in Figure 7. For benzene reduction, as for olefin reduction, the rate is first order in hydrogen and zeroth order in benzene.[78]

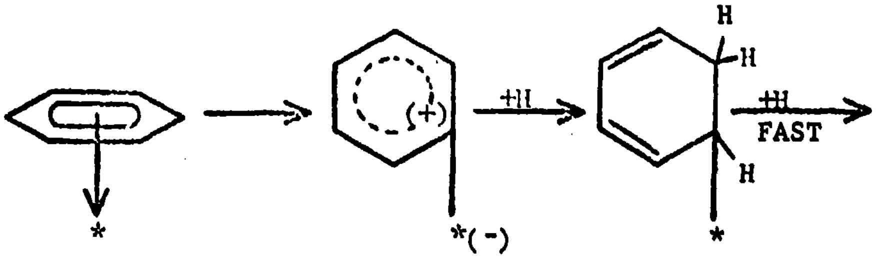
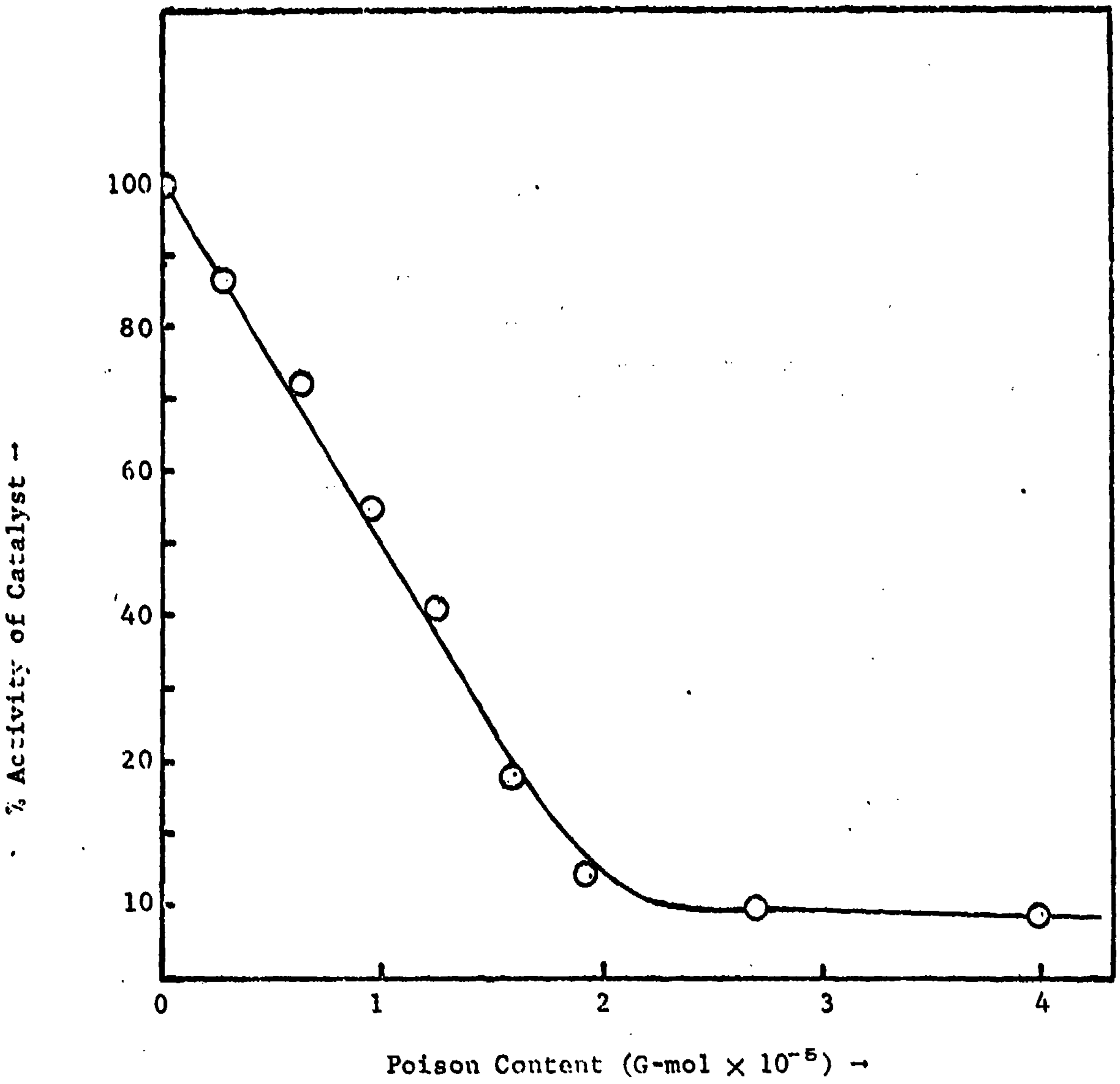


Figure 7. Mechanism of the Hydrogenation of Benzene[79]

Another method of studying a catalyst surface is to observe the deactivation of that surface as a function of poison added to the system. In a recent review of the subject, Butt noted "catalyst deactivation appears to be one of the darker areas of an art (catalysis) which, more often than not, assumes various magical (and always mysterious) characteristics."[82] He defined poisoning as the action of compounds binding strongly to the active sites on the catalyst and stated poisoning should be distinguished from both fouling (some product degrading on the surface) and aging (sintering or other decrease in active surface area). In discussing types of poisons often found in metallic catalyst systems, Butt distinguished between three groups: 1) molecules containing elements of groups Vb and VIb or the free elements (except N_2), 2) compounds of catalytically toxic metals and metallic ions (especially mercury and its salts), and 3) molecules containing multiple bonds that are strong sorbates, as CO and benzene.[82]

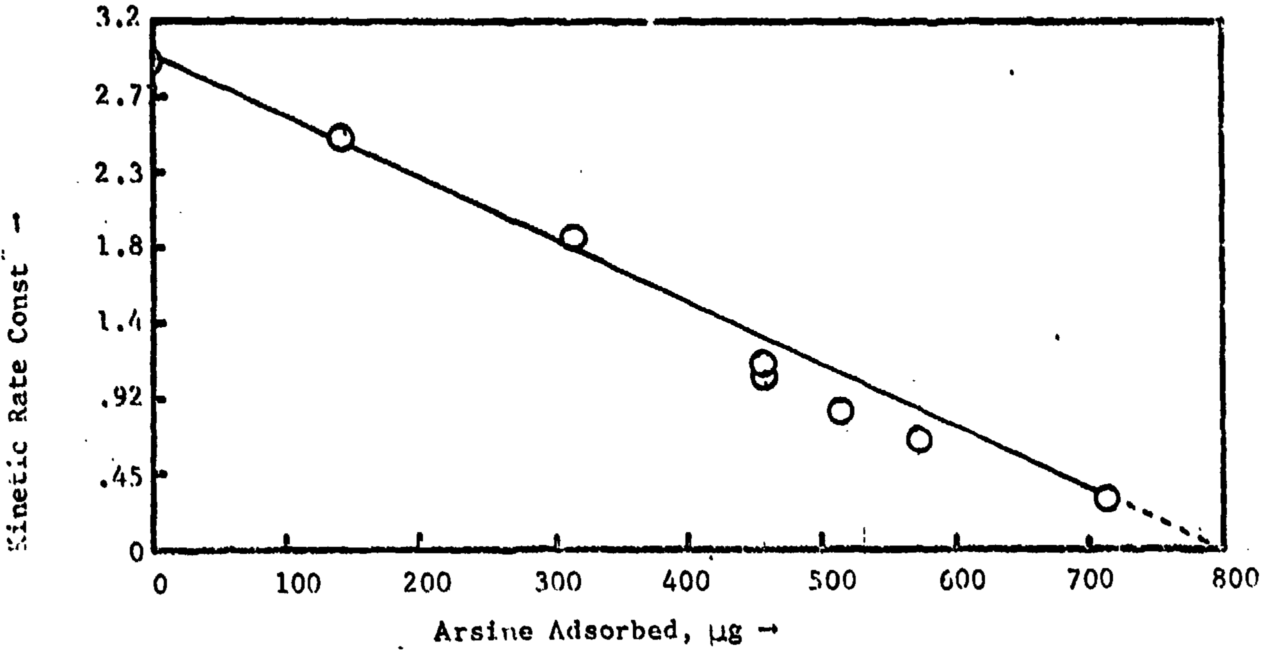
Early work by Maxted showed "typical" poisoning curves for supported platinum catalysts (Figure 8a).[83] Using pyridine, thiophene, mercury, and other poisons, he obtained similar and apparently linear deactivation over a broad region of the poisoning. More recent work has shown other linear poisoning curves for a platinum film catalyzed cyclopropane hydrogenoloysis being deactivated by arsine (Figure 8b).[84] The authors proposed the formation of $PtAs_2$ thus destroying the active surface area in direct proportion to the amount of arsine. More recent work tried to correlate nonlinearities in poisoning curves with physical phenomena, especially "pore mouth poisoning" where relatively small amounts of poison are adsorbed near the mouth of the pore and seal off the majority of active catalyst further inside the pore.[85]



Catalyst: 0.05 g stock platinum black

Conditions: 10 ml 1 N solution cyclohexene in cyclohexane, 27°

Figure 8a. Maxted's Experiment Showing the "Toxicity of Water-Free Pyridine Toward a Platinum Catalyst in the Hydrogenation of Cyclohexene"[83]



*Kinetic Rate Const = $\frac{kA}{V} \times 10^3$, min^{-1}

Catalyst: Platinum film

Conditions: Hydrogenolysis of Cyclopropane 25°, 1 atm H_2

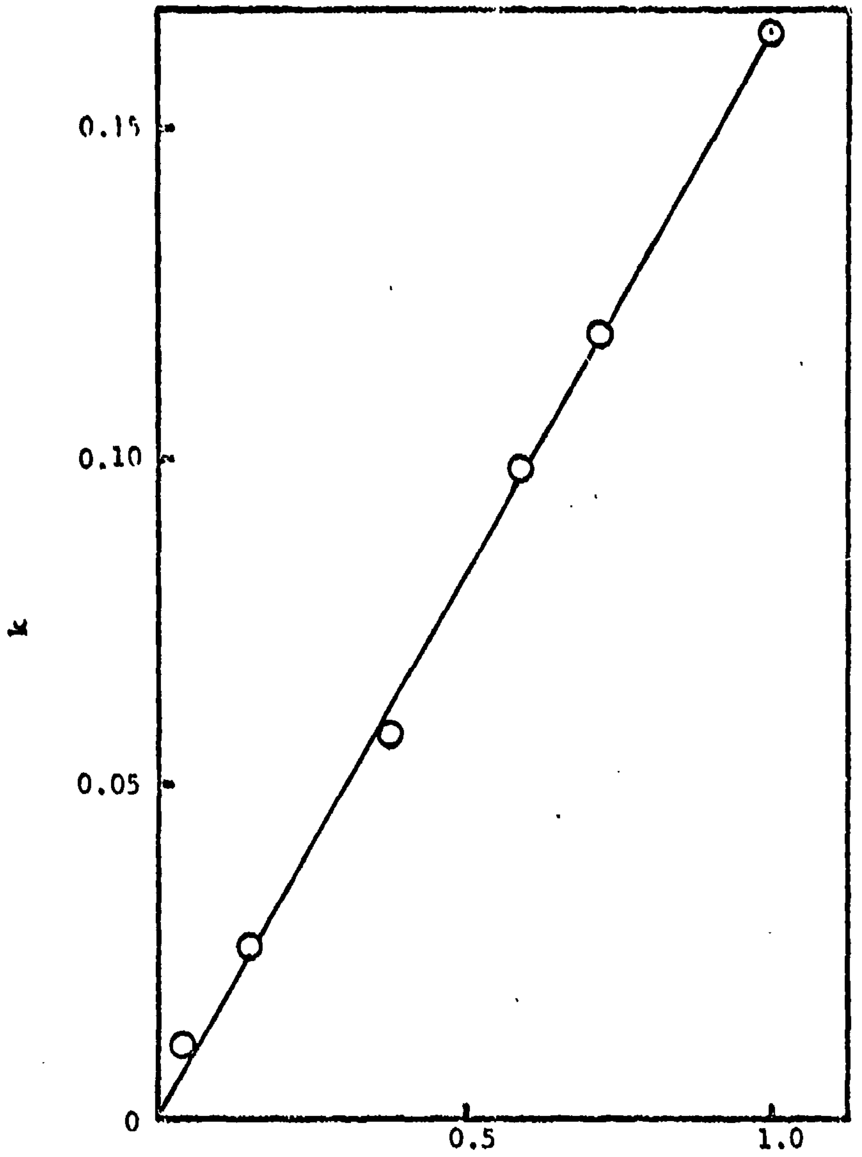
Figure 8b. Clay and Petersen's Experiment Showing "Kinetic Rate Constants as a Function of the Quantity of Arsine Adsorbed on [Platinum] Film"[84]

Two other recent papers have shown that valuable information can be obtained about the active sites of a reaction and the mechanism of catalysis through poisoning experiments. In one paper, Kral reported that he could selectively poison different types of sites on palladium supported on carbon using thiophene.[86] In a second paper, Brill and Tauster used hydrogen sulfide to poison iron/alumina catalyst systems used for producing ammonia. In this work, they found a nonlinear poisoning which, significantly, showed a linear relationship between the rates of ammonia formation and S^2, where $S = [1-(\text{quantity of poison added}/\text{quantity of poison required to totally deactivate the catalyst})]$ (Figure 8c).[87] They used this in support of the mechanism proposed by Ozake, Taylor, and Boudart requiring two adjacent sites for catalyst activity.[88] It appears, then, that poisoning can help elucidate the catalytic mechanisms.

So far, it is clear that heterogeneous catalysts behave by very different mechanisms than homogeneous catalysts, with significantly different rate laws. Heterogeneous catalysts are notably less specific than homogeneous catalysts for the reduction of terminal vs. hindered olefins,[89] and the rhodium systems are capable of reducing not only olefins but also ketones (which are not affected by Wilkinson's catalyst) and aromatic systems.[90] It appears, then, that significant distinctions can be drawn between the homogeneous Rh(I) and heterogeneous systems.

C. Supported Organometallic Catalysts

The practicality and benefits of chemically binding otherwise homogeneous catalysts on supports were first realized by living systems.



$$S^2 = \left(1 - \frac{\text{quantity poison added}}{\text{quantity poison required to totally deactivate}}\right)$$

Catalyst: Fe + 3% Al_2O_3

Conditions: conversion of N_2 to NH_3 at 300°

Poison: H_2S

Figure 8c. Brill and Tauster's Experiment Showing "Dependence of the Reaction Constant on the Square of the Active Sites"[87]

By fixing enzymes to membranes, these systems could be ordered for maximum efficiency and chemically active intermediates could be shielded from interaction with one another by their own immobility. Even with man-made systems, early efforts and significant progress have been made in biochemical and enzyme engineering fields.[91,92]

In chemical applications, Merrifield pioneered the use of polystyrene resins in polypeptide synthesis,[93] making isolation of product, removal of by-products, and elimination of unwanted side reactions much easier. Other chemical operations have been performed with polystyrene-bound species, including macrocycle and threaded chain compounds,[94] Dieckmann cyclization with mixed esters,[95] preparation of a multipurpose trisubstituted phosphine dichloride reagent,[96] and others.[97]

The possibilities of chemically binding an organometallic homogeneous catalyst to a solid support has generated a significant amount of interest recently.* The possibilities of a catalyst with the specificity and reproducibility of a homogeneous catalyst yet with the stability and ease of removal from reaction media of a heterogeneous catalyst are indeed attractive.

Early work performed in this laboratory[105-107] and others[108-112] showed that modified polystyrene resins could also be used as supports

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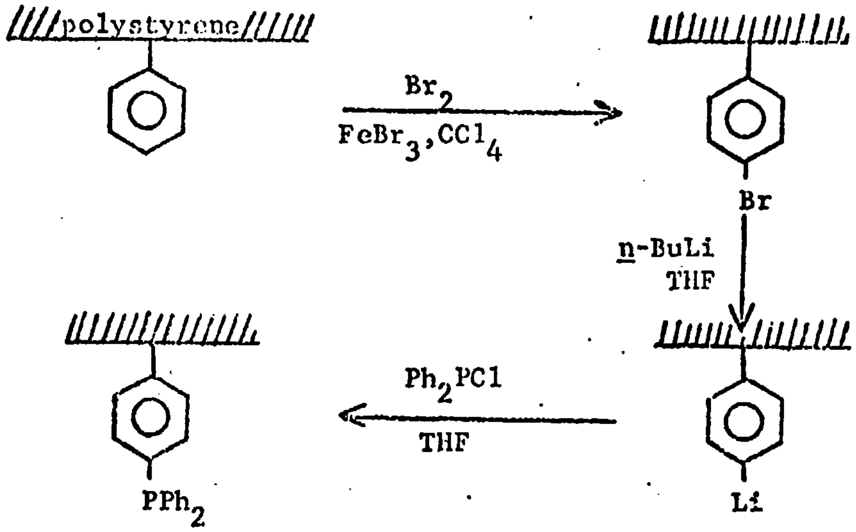
*Three reviews of the uses of "heterogenized" homogeneous catalysts have recently been written.[98-100] Readers are referred to these for a full background on this work. Successful efforts have been reported by Monsanto's laboratories at preparation of hydroformylation catalysts from bis(triphenylphosphine)chlorocarbonylrhodium(I) physically supported on alumina and carbon.[101-104] These catalysts are not chemically bound and the reactions take place between the vapor and solid phases in a fixed bed reactor and, hence, are not directly comparable to other work presented here.

for several organometallic species active in homogeneous catalysis. The original approach taken in this laboratory involved bromination of 2% crosslinked polystyrene resin ("Biobeads SX2," Bio Rad, Inc., Richmond, CA) then conversion to a polystyrene-bound analogue of triphenyl phosphine (Eq. 6). Unfortunately results indicated that, even with only 10% functionalization of the available benzene rings,

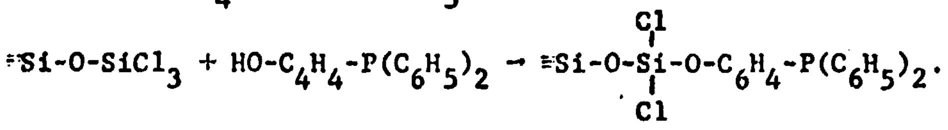


(6)

the bound phosphines were capable of acting as chelating ligands and were not isolated and immobilized sites, as indicated by the liberation of two moles of free triphenylphosphine per bis(triphenylphosphine)-ethylenechlororhodium(I) added to the resin.[106] The fact that crosslinked polystyrene, when solvent swelled, behaves much like soluble, non-crosslinked polystyrene has been recently established by ESR techniques.[113] Grubbs[112] has shown that metal centers on 20% crosslinked macroreticular polystyrene appear to be noninteracting, but the nonstatistical properties of macroreticular supports make them a poor alternative.

Silicas attracted significant interest because of their high surface area-to-mass ratio, thus facilitating the high degree of functionalization necessary for any form of analysis. Early work in this laboratory studied attachment of alcohols to silica surfaces* pretreated with silyl chlorides (Eq. 7).[115,116]

$$\equiv Si\text{-}OH + SiCl_4 \rightarrow \equiv Si\text{-}O\text{-}SiCl_3$$



$$\equiv Si\text{-}O\text{-}SiCl_3 + HO\text{-}C_4H_4\text{-}P(C_6H_5)_2 \rightarrow \equiv Si\text{-}O\text{-}\overset{Cl}{\underset{Cl}{Si}}\text{-}O\text{-}C_6H_4\text{-}P(C_6H_5)_2. \qquad (7)$$

Unfortunately, the resulting silicon-oxygen-carbon linkages are subject to hydrolysis and alcoholysis under mild conditions and this approach was abandoned. Another approach, following the scheme of Paar and Grohman (Eq. 8),[117] was tried but yielded insufficient functionalization in preliminary experiments in this laboratory.[120]

$$\equiv SiOH + Cl_3Si\text{-}C_6H_4\text{-}CH_2Br \rightarrow \equiv Si\text{-}O\text{-}Si(Cl)_2C_6H_4\text{-}CH_2Br \qquad (8)$$

$$\equiv Si\text{-}O\text{-}Si(Cl)_2C_6H_4\text{-}CH_2Br + LiPPh_2 \rightarrow \equiv Si\text{-}O\text{-}Si(Cl)_2C_6H_4\text{-}CH_2PPh_3.$$

Following an approach used by Allum,[118] work in this laboratory continued synthesizing ligands with siloxy functional groups which could then be attached to silica <u>via</u> a stable silicon-oxygen-silicon-carbon linkage (Eq. 9), using organic functional groups (R') containing both thiols[119,121] and phosphines.[120,121]

$$\equiv Si\text{-}OH + (RO)_3Si\text{-}R' \xrightarrow[\text{reflux}]{\text{toluene}} \equiv Si\text{-}O\text{-}Si(OR)_2R' \qquad (9)$$

---

*Silica surfaces normally contain several monolayers of water adsorbed to the surface hydroxyls. Most of these waters are lost by heating under vacuum (see the Experimental Section) and dried silica surfaces will be referred to as $\equiv Si\text{-}OH$ in this work.

The silica with sulfur ligands yielded a method to obtain a wide variety of supported metal species (metal = Rh, Cr, Re, Nb, Ir, Pb, Au, Co, Fe) often with high concentrations of metals, but characterizing the nature of the species present on the surface was nearly impossible without the capability to produce analogs free from the support.[119]

Work with the siloxy phosphine ligands, however, proved more rewarding. As noted by Allum,[118] organometallic complexes can be made with the siloxy phosphine ligands which can then be added to the silica surface. Makoto Takeda,[121] in this laboratory, prepared several interesting compounds [6, 7, 8 (6 had been previously prepared)[118]]. These compounds, when attached to silica via Eq. 9, are then discrete organometallic species bound on the silica surface.

$L_2Rh(CO)Cl$

L = L' or L"

6

$L_1ClRh(COD)$

COD≡cycloocta-1,5-diene

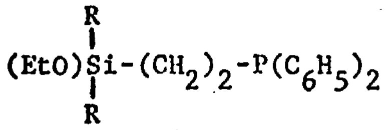
L = L' or L"

7

$L_2Rh_4(CO)_{10}$

L = L"

8



$$(EtO)\underset{R}{\overset{R}{Si}}-(CH_2)_2-P(C_6H_5)_2$$

L':R = -OEt

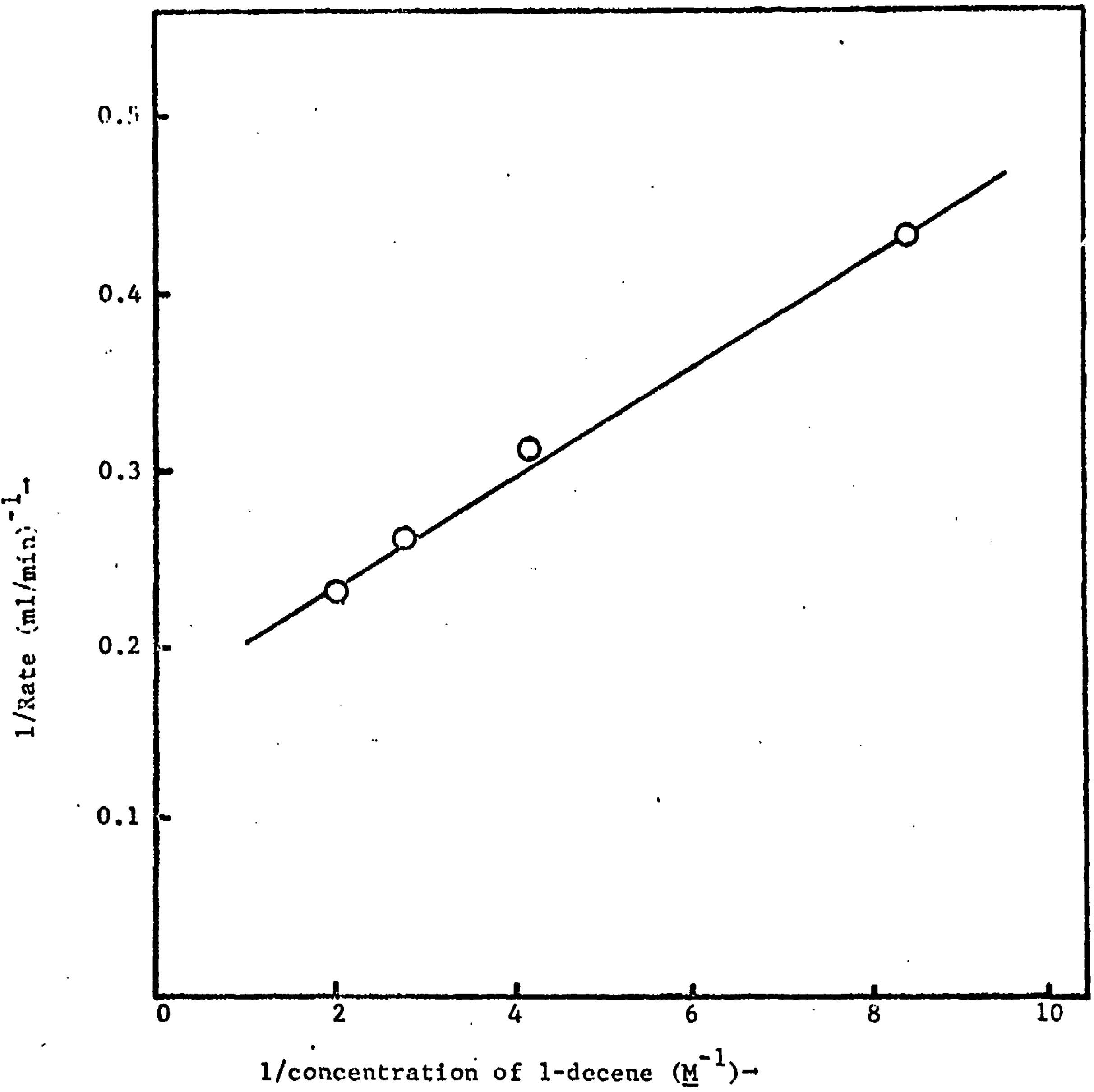
L": R = -Me

5

None of the triphenylphosphine analogues of these species are used as homogeneous hydrogenation catalysts either because of low activity or lack of stability under hydrogen. However, once supported on silica, species 7 and 8 can be used as hydrogenation catalysts under ambient conditions. Unfortunately, concomitant to the hydrogenation is a color change to grey/black and often times reduction of benzene is observed,[121] both of which are indicative of an alteration in the catalyst from the organometallic complex originally bound on the surface to a more classical metallic heterogeneous catalyst. Neither the color change nor the hydrogenation of benzene were reported by Allum[118] who used heat (50-55°, or up to 140° with bound species 6) and pressures of hydrogen (13.8 atm) to accomplish these catalyses.

Most of the preliminary studies with the catalysts prepared by Takeda suggest that a classical heterogeneous catalyst is present, although there exist experiments which support the presence of an organometallic catalyst. Figure 9 shows the linear relationships which Takeda found between reciprocal rate and reciprocal olefin, suggesting that the catalyst obeys a rate law similar to Halpern's rate law for the hydrogenation by Wilkinson's catalyst (Figure 3). More evidence indicating an organometallic catalyst in Takeda's catalysts is the dramatic difference between the rate of hydrogenation of 1-decene and 1-methylcyclohexene (3.88 to 0.08, respectively) which is similar to the selectivity characteristic of homogeneous catalysts.

Other studies with Takeda's catalysts, however, suggest the presence of heterogeneous catalysts. Electron microscopy shows metal particles[122] and ESCA shows the presence of Rh(III) species and no Rh(I) after hydrogenation then exposure to air.[123] Furthermore, Takeda also found a first order linear dependence between the rate of hydrogenation and the pressure of hydrogen (Figure 10)[121] which concurs with

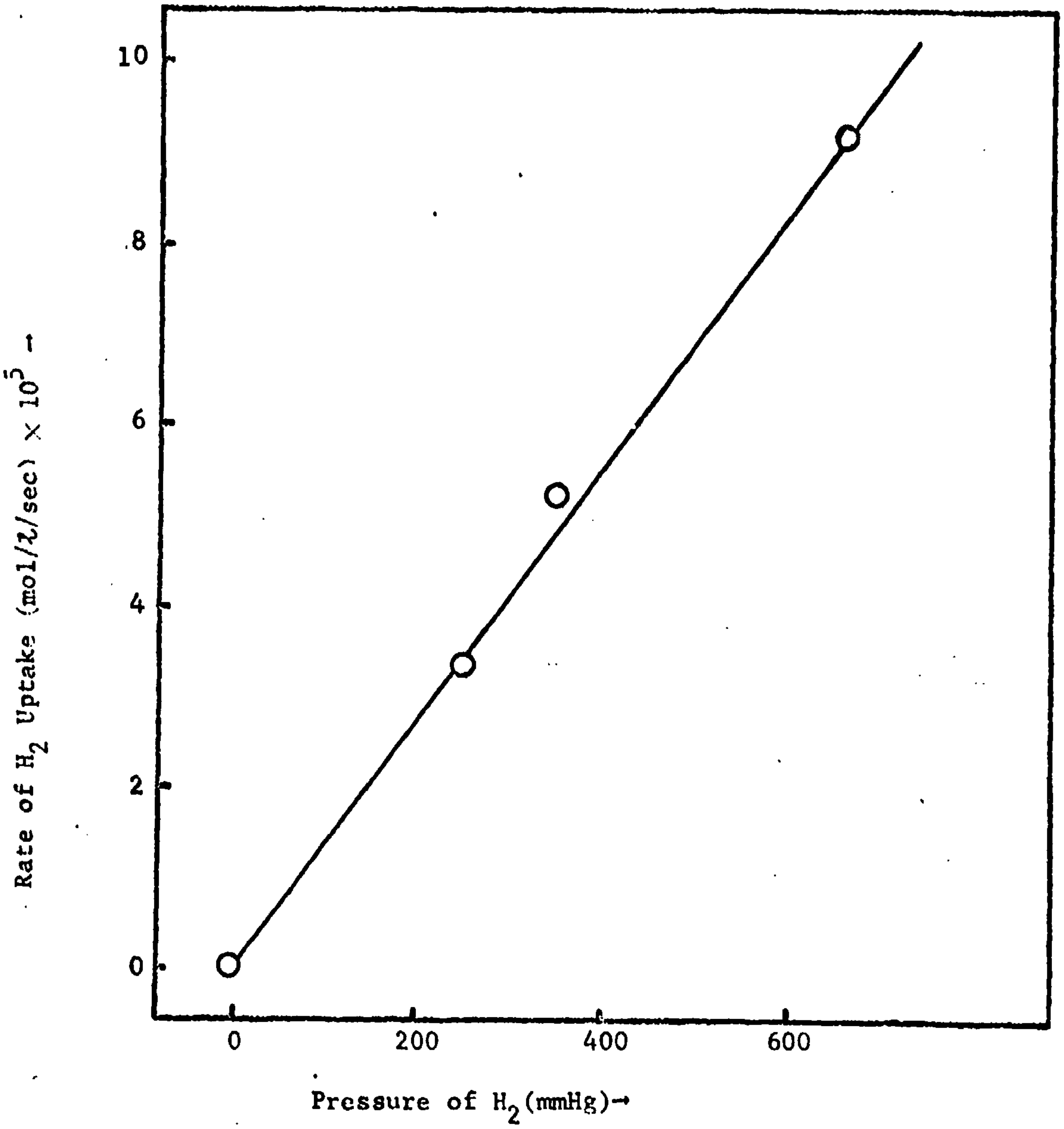


Catalyst: porous silica supported 7

Conditions: 25°, 665 mm H_2

1.19 m$\underline{M}$ Rh in 21 ml benzene

Figure 9. Dependence of Rate of Hydrogenation by Silica Supported-L RhCl(COD) on Concentration of Olefin[121]



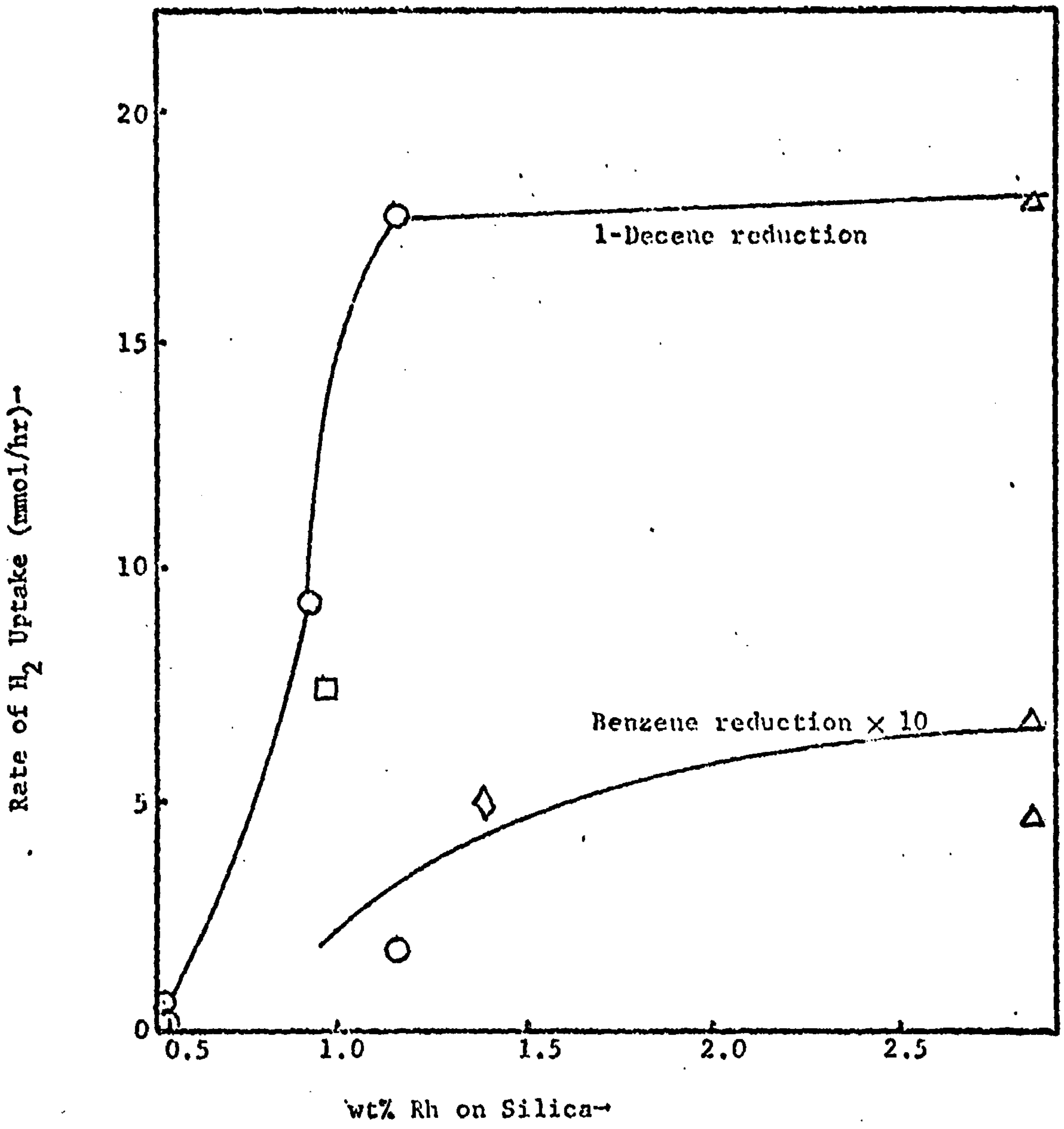
Catalyst: porous silica supported 7

Conditions: 25°, 0.238 M 1-decene
1.19 M Rh in 20 ml benzene

Figure 10. Dependence of Rate of Hydrogenation by Silica Supported-L RhCl(COD) on Pressure of Hydrogen[121]

heterogeneous mechanisms but not with the classical Wilkinson's catalyst that shows a linear recriprocal rate *vs*. reciprocal hydrogen pressure dependence.[26] Activation is required for Takeda's catalyst (up to a day under one atmosphere pressure of hydrogen, less under $\sim$3 atm hydrogen) and it is unclear in what form the rhodium exists after activation. This activation is a difficult process to follow and generally the first rate is not reproducible, whereas the activity generally becomes reproducible after the second run as a catalyst. Finally, Takeda noticed an unusual dramatic increase in catalytic activity when the concentration of rhodium on the silica reached 0.5% (Figure 11).[121] This is not observed with either homogeneous catalysts or immobilized organometallic catalysts, but would be consistent with the possibility that a sufficient concentration of rhodium is necessary so that, during activation, the reduced rhodium may migrate to form catalytically active metallic crystallites.

It is unclear that the active catalysts in Takeda's organometallic complexes bound to silica are still similar to their homogeneous analogs, several experiments suggesting that metal crystallites are the active catalysts. Through the work presented in this paper, the author hopes to show that a chelating bisphosphine ligand bound to the silica is more successful at maintaining the integrity of immobilized organometallic catalysts.



Conditions: 2.5 mmol 1-decene in 10 ml benzene
46 psi H_2 (similar results at 1 atm H_2)

Catalysts: 2.5 × 10^{-6} mol Rh
○ CAB-O-SIL supported 7 (with L")
☐ porous silica supported 7 (with L")
△ CAB-O-SIL supported 5 + $[RhCl(COD)]_2$
◊ CAB-O-SIL supported 7 (with L')

Figure 11. Dependence of Rate of Hydrogenation by Silica Supported-L RhCl(COD) Catalysts on Surface Concentration of Rhodium[121]

II. RESULTS AND DISCUSSION

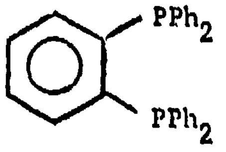
In the introductory part of this work, several comparisons were drawn between homogeneous and heterogeneous catalysts: their selectivity and rate laws are significantly different, and homogeneous catalysts are more subject to alteration by changing ligands or solvent. In addition, recent efforts at supporting homogeneous catalysts on inert materials show that, although some of these species show increased activity or specificity, the active catalyst is not always clearly an organometallic complex. The great analytical problems that confront those who study heterogeneous catalysts also plague those who attempt to characterize the supported organometallic species.

The present work describes a new silated bisphosphine ligand which is capable of chelating low valent metals. In this way, this ligand binds the metal more strongly and prevents formation of metal crystallites noted in earlier work. This ligand has a triethoxysilyl functionality and is capable of binding to silica surface hydroxyl groups and thus holding these organometallic centers immobile and incapable of interacting with one another. Through comparisons of this new supported organometallic catalyst to both classical homogeneous and heterogeneous catalysts, this work shows that the active catalyst bound to silica by this new ligand is organometallic in nature.

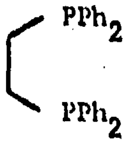
The remainder of this section describes the synthesis of this ligand and the preparation of a rhodium catalyst with this ligand supported on silica. This catalyst is compared to classical catalysts in nine ways: 1) selectivity of the catalyst in reducing terminal vs. hindered olefins; 2) dependence of the catalytic rates on olefin concentration (and implications on the form of the rate law); 3) effect of solvent on the rates of catalysis; 4) effect of surface concentration of rhodium on the catalytic rate; 5) relative turnover rates; 6) isomerization phenomena in the bound organometallic catalysts; 7) poisoning experiments on heterogeneous and supported organometallic catalysts; 8) electron microscopy as evidence against metal crystallites in the supported organometallic catalysts, and 9) ESCA (Electron Spectroscopy for Chemical Analysis) as a method of determining the oxidation state of the rhodium catalyst.

A. Synthesis of 2(3-triethoxysilylpropyl)-1,3-bis(diphenylphosphino)-propane [SiP_2]

After it became evident that the monodentate 2-triethoxysilylethyldiphenylphosphine employed by Allum[117] and Takeda[121] may allow the metal species to migrate when in a reduced state and to form metal crystallites, work began on a new ligand that would have bisphosphine functionality for chelating the organometallic species as well as a siloxy group for attachment to silica surfaces. Although the ideally stable phosphine would be a siloxy derivative of o-phenylene(bisdiphenylphosphine), 9, even the nonderivatized compound was difficult to prepare, affording only a 2% yield.[126] Our efforts were thus directed at the synthesis of an analog of 1,2-bis(diphenylphosphino)ethane or "diphos," 10.[127]

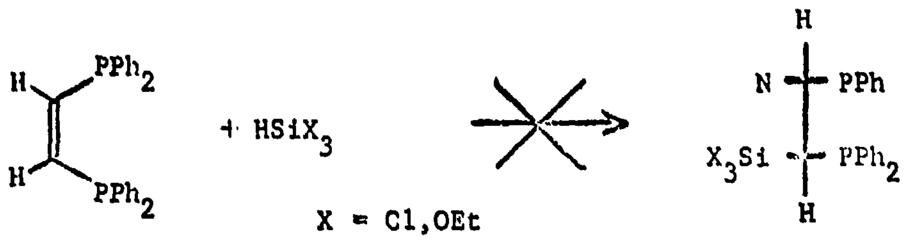


9



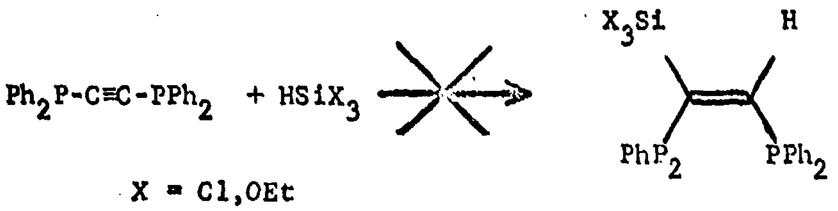
10

Four pathways were considered before a successful method was found for preparing a siloxybisphosphine. The first two methods depended on hydrosilylation of an unsaturated bis(diphenylphosphino) derivative, either cis-1,2-vinylenebis(diphenylphosphine)[128]



(10)

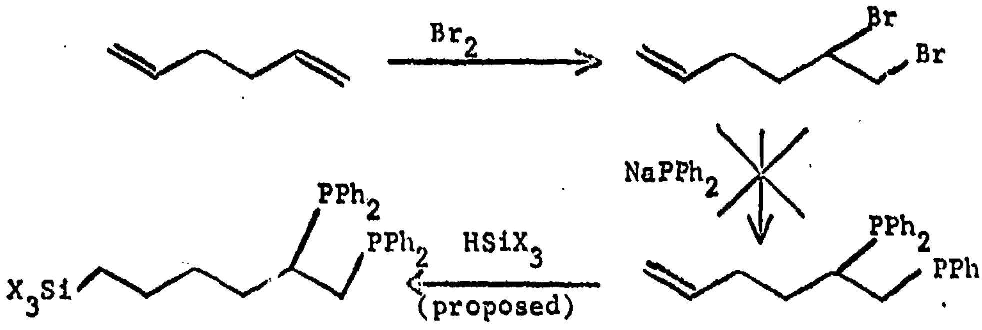
or acetylene(bis(diphenylphosphine)acetylene.[129]



(11)

Unfortunately, both reactions represented in Eq. 10 and Eq. 11 fail to proceed under a variety of conditions normally conducive to free radical additions of hydrosilates,[129,130] including irradiation by ultraviolet light, elevated temperatures (up to 350°) in sealed tubes, and free radical initiators (up to 10 mol·% AIBN, azobisisobutylnitrile). Platinum catalysts are commonly used to aid the addition but the concentration of phosphines present in these reactions would quickly render the platinum ineffective.

It appeared that the phosphine substituted on the olefin somehow inhibits the free radical addition. For this reason hydrosilylation was attempted on an olefin more remote from the phosphine group, following the pathway outlined below (Eq. 12).

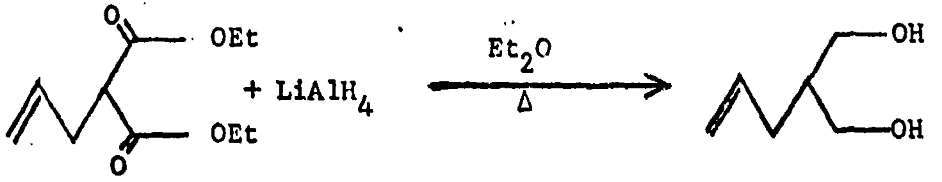


(12)

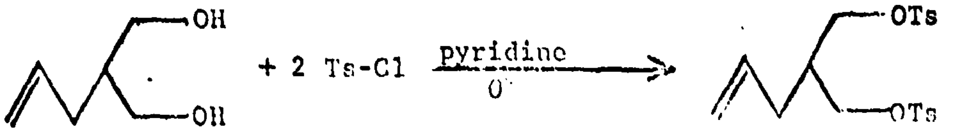
The first step, 1,2-dibromination of 1,5-hexadiene, is in the literature[131] and 1,2-dibromoethane has been successfully converted to the bisphosphine using sodium diphenylphosphide. Unfortunately the 5,6-dibromohexa-1-ene proved more difficult to substitute with the phosphine and this pathway was abandoned when evidence (presented later) suggested even an olefin removed from phosphines by four carbons would be difficult to hydrosilylate.

The pathway that eventually proved successful involved a series of well-known reactions giving moderate to good yields:

(13)[132]

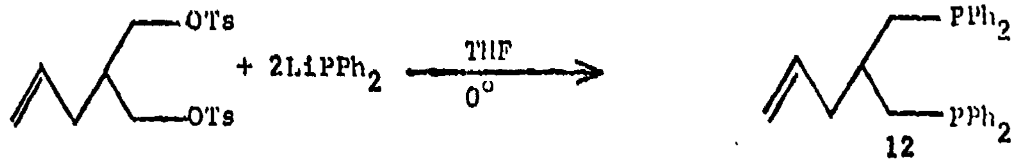


(14)[133]



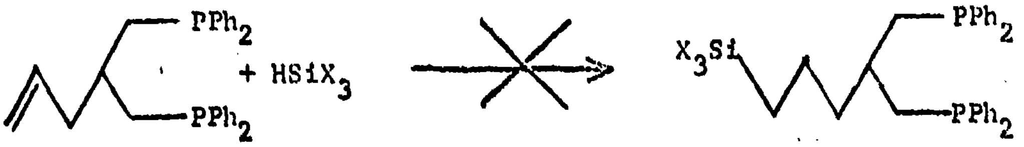
(15)[134]

$-Ts = -SO_2C_6H_4CH_3$



12

(16)

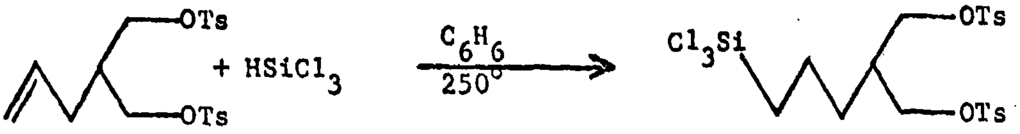


(17)

X = Cl, OEt

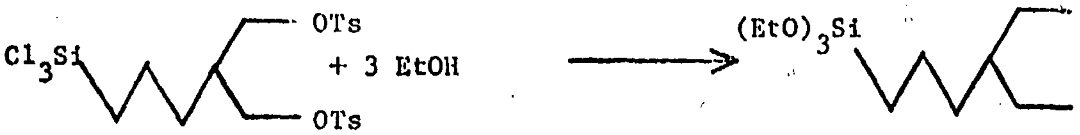
The reactions represented by Eqs. 13-16 proceeded with no problems, yielding crystalline 2-allyl-1,3-bis(diphenylphosphino)propane, 12, in 36% overall yield on the first attempt. As mentioned earlier, hydrosilylation of this olefin, even when removed by four carbons from the phosphines, proved to be most difficult. Under ultraviolet light, in the presence of radical initiator (up to 10% AIBN), or in sealed tubes at 250°, the allylbisphosphine, 12, was not hydrosilylated. Nonetheless, the allylbisphosphine is a new compound and is useful as a model and homogeneous analog of the desired siloxybisphosphine.

A variation on this pathway was implemented to avoid hydrosilylating in the presence of phosphine: first, hydrosilylate the allylbis(tosylate), then replace the tosylate functionality with phosphines (Eqs. 18-20).

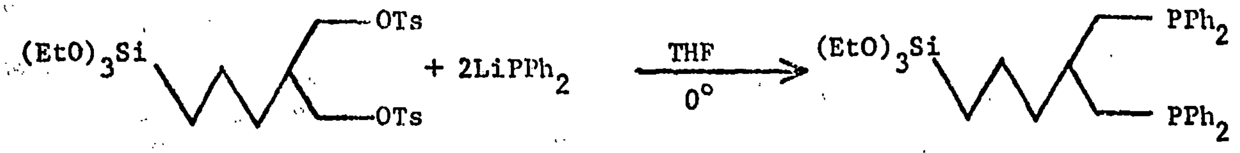


11

(18)



(19)

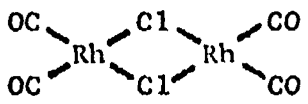


(20)

13 = SiP$_2$

These reactions all proceeded smoothly to give the desired product, 2-(3-triethoxysilylpropyl)-1,3-bis(diphenylphosphino)propane, 13, SiP$_2$, in approximately 30% yield. The disadvantage of this route is the inability to isolate products from Eq. 18, 19, and 20 before proceeding with the next step. For example, SiP$_2$ is molecular weight 616 and cannot be distilled or sublimed before decomposing; it cannot be successfully chromatographed because of hydrolysis of the siloxy functionality; and it appears to be an oil, at least in the presence of the major contaminate diphenylphosphine (identified by ^{31}P-NMR, +41.1 ppm from H_3PO_4).[135]

As noted earlier, even well characterized bisphosphine ligands that have the most stable ring size (5 atoms when coordinated to the metal) do not generally give characterizable, neutral metal complexes.[58,61,62] Reactions of bisphosphines with chlorobis(cyclooctene)rhodium(I) generally give "ill defined solids,"[61] although Hieber and Kummer[62] report three complexes of 1,2-bis(phosphino)ethane, 10, with μ,μ'-dichlorotetracarbonylrhodium(I), 14, depending on the molar ratio of the reactants:



14

$Cl(OC)_2RhP(Ph_2)C_2H_4(Ph)_2PRh(CO)_2Cl$

15

$Cl(OC)Rh(PPh_2CH_2)_2$

16

$[Rh\{(PPh_2)_2C_2H_4\}_2]Cl$

17

With 1:1 dirhodium 14:bisphosphine 10, compound 15 was obtainable, but not in as pure form as its iridium analog, and was identified only by its IR spectrum (reported as three bands in the carbonyl region, 2081 cm^{-1}, 2068 cm^{-1}, and 1989 cm^{-1}). The product formed by reacting 1:2 dirhodium 14:bisphosphine 10, yields 16, which is an easily recrystallizable yellow compound with a single CO band in the infrared (2010 cm^{-1}) and giving a good analysis and molecular weight. Product 17 forms on the addition of an excess of bisphosphines (1:4 dirhodium 14:bisphosphine 10), and is well defined, with no CO band in the IR, good analysis, and, as expected for a salt, molecular conductivity of μ = 116 cm/Ω·mol.

Attempts were made to characterize a complex of the Rh(I) with the allylbisphosphine 12, prepared by the methods of Hieber and Kummer.[62] The reaction of 1:1 dirhodium 14:allylbisphosphine 12 yielded a yellow powder which gave a similar infrared spectrum (2075, 2000, 1960 cm^{-1}) but analyzed poorly. The reaction of 1:2 dirhodium 14:bisphosphine 12 in benzene gave an orange solution with a single CO stretch in the IR (1920 cm^{-1}), but attempts to crystallize (by either reducing the volume of benzene or adding diethyl ether) resulted in precipitation of a brown powder which analyzed poorly for either an analog of 16 or 17 and demonstrated no CO band in the IR.

On the basis of these results, no further efforts were made to prepare a characterizable complex with the siloxybis(phosphine), 13, SiP_2. SiP_2 complexes would be even more difficult to make and purify because of 1) the size of the metal chelate ring is 6 atoms (like 12 but larger than 10), 2) the reaction of the siloxy groups with traces of water or alcohol would tend to increase the number of impurities and make compound isolation and characterization more difficult, and 3) the triethoxysilyl group is extremely soluble and would probably make the complexes even more difficult to crystallize.

B. Organometallic Catalysts Supported on Silica

Inorganic oxides have long been used as supports for metallic heterogeneous catalysts and, in many reactions, as catalysts themselves.[136-138] Even silica and alumina, generally considered to be "inert" supports for metallic catalysts, have been implicated in hydrogenation and isomerization reactions especially when poisons are involved.[80,139]

To exclude possibilities of pore effects and diffusion problems, the author has chosen to work solely with CAB-O-SIL[140] silica, grade HS-5. This exists as a very fine powder, containing relatively uniform 70 Å (diameter) silica spheres and exhibits a surface area of 325 ± 25 m^2/g.

Silicas* have acidic surface hydroxyl groups which, under ambient conditions, hydrogen bond several monolayers of water. Various methods for drying and annealing silicas have been tried,[142-145] and significant work has been performed to characterize the chemistry of these "dry" silica surfaces,[146] which will be represented by ≡Si-OH in this work.

Reviewing the above-mentioned studies, it appears that drying the silica at 380° under 10^{-5} torr vacuum for 24 hr is sufficiently rigorous for exposing reactive surface hydroxyls. From these studies, it appears approximately 4.6 hydroxyl groups/100 $Å^2$ exist after partial drying, but of these only 1.4 OH/100 $Å^2$ are free ≡Si-OH, the other 3.2 OH/100 $Å^2$ are hydrogen bonded pairs and are much less reactive.[143,144] These figures agree reasonably with Chien's[147] recent work on CAB-O-SIL showing, for fully hydroxylated surfaces, ~ 4 m<u>M</u> OH/g (~ 6 OH/100 $Å^2$) and, for dehydroxylated (dried at 700°) silicas, ~ 0.7 m<u>M</u> OH/g (~ 1.1 OH/100 $Å^2$). Half of these hydroxyls are free, the others existing as hydrogen-bonded pairs.

By adding dried CAB-O-SIL to varying quantities of the SiP_2 ligand, the concentration on the surface seems to be linearly dependent on the amount of ligand added but saturates the surface at ~ 3% P/g silica which corresponds to ~ 0.9 molecule SiP_2/100 $Å^2$ surface (Figure 12). This is

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*For an excellent overview of silicas, see <u>The Colloid Chemistry of Silica and Silicates</u> by Iler.[141]

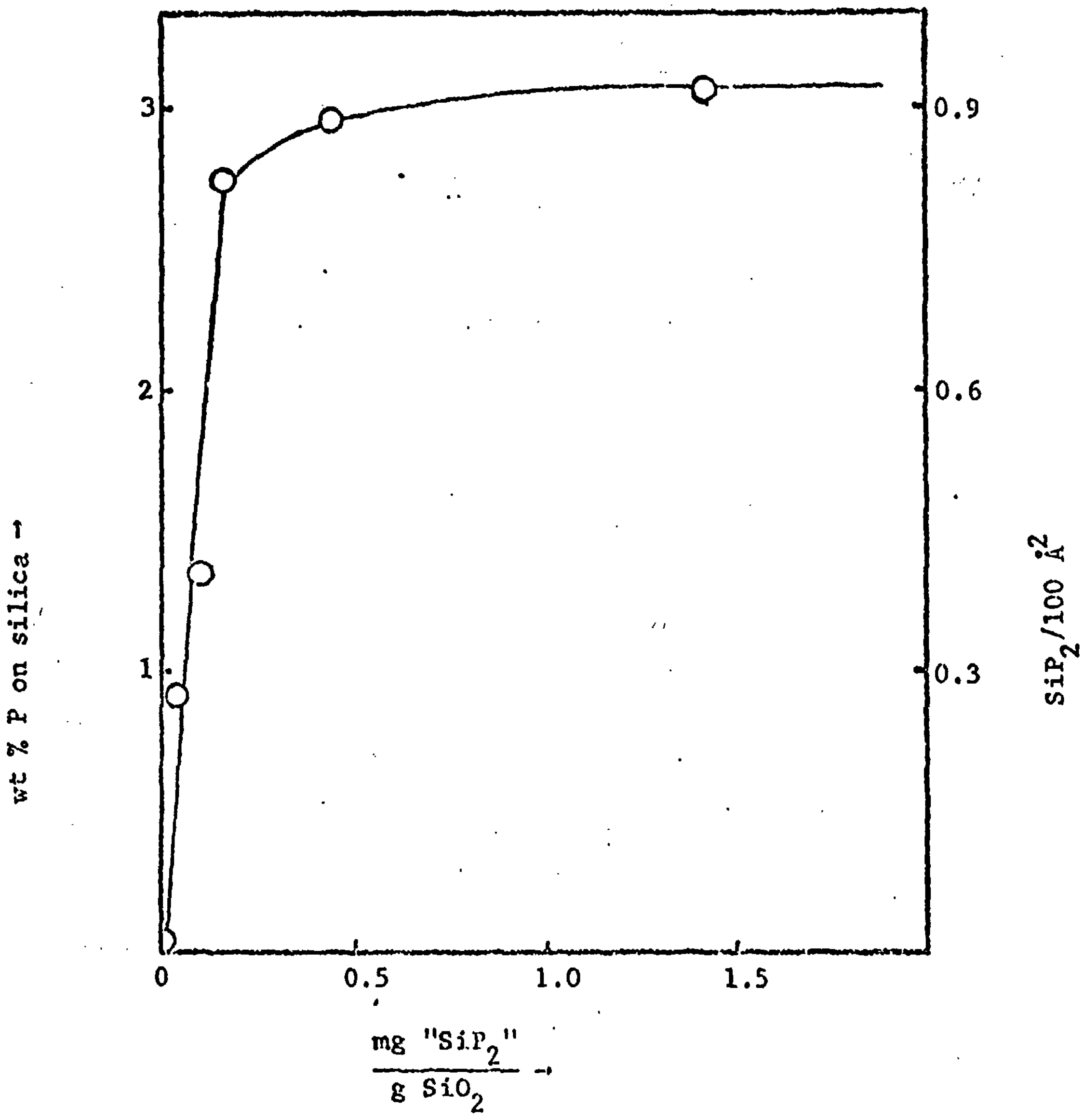

Figure 12. Dependence of the Concentration of Phosphorus on Silica on the Amount of SiP_2 Treated with the Silica

consistent with the methods of drying, being between fully hydroxylated (~ 3 active OH/100 Å^2) and dehydroxylated silica (~ 0.5 active OH/100 Å^2).

Since it was not possible to form well-defined organometallic complexes with SiP_2 and rhodium, it was necessary to form them <u>in situ</u> following Wilkinson's method[29] of adding the phosphine (in this work, silica supported SiP_2) to chlorobis(cyclooctene)rhodium(I), as previously described (Eq. 3). In these experiments, it was most convenient to place the silica-SiP_2 and olefin complex in the solid state in the hydrogenation vessel, then evacuate. After purging the system several times with hydrogen, olefin substrate was added, then the solvent. (If solvent was added before the olefin while under hydrogen, the rhodium species decomposed very rapidly to a black species that resembled heterogeneous catalysts, in character as well as color, much more than homogeneous catalysts.)

Elemental analysis shows a roughly linear correlation between the weight percent phosphorus in the original silica-SiP_2 and the weight percent rhodium in the catalyst after filtering from the reaction, washing with solvent, and vacuum drying (Figure 13). The reaction solvent, filtered from the silica, contains roughly 13 ppm rhodium, or about 1.3×10^{-7} <u>M</u> rhodium. This represents less than 3% of the total rhodium present, and is an upper limit of rhodium species free in solution since there is great probability of significant silica (aggregates of 70 Å silica particles) passing through the (200 Å pore diameter) millipore filter.

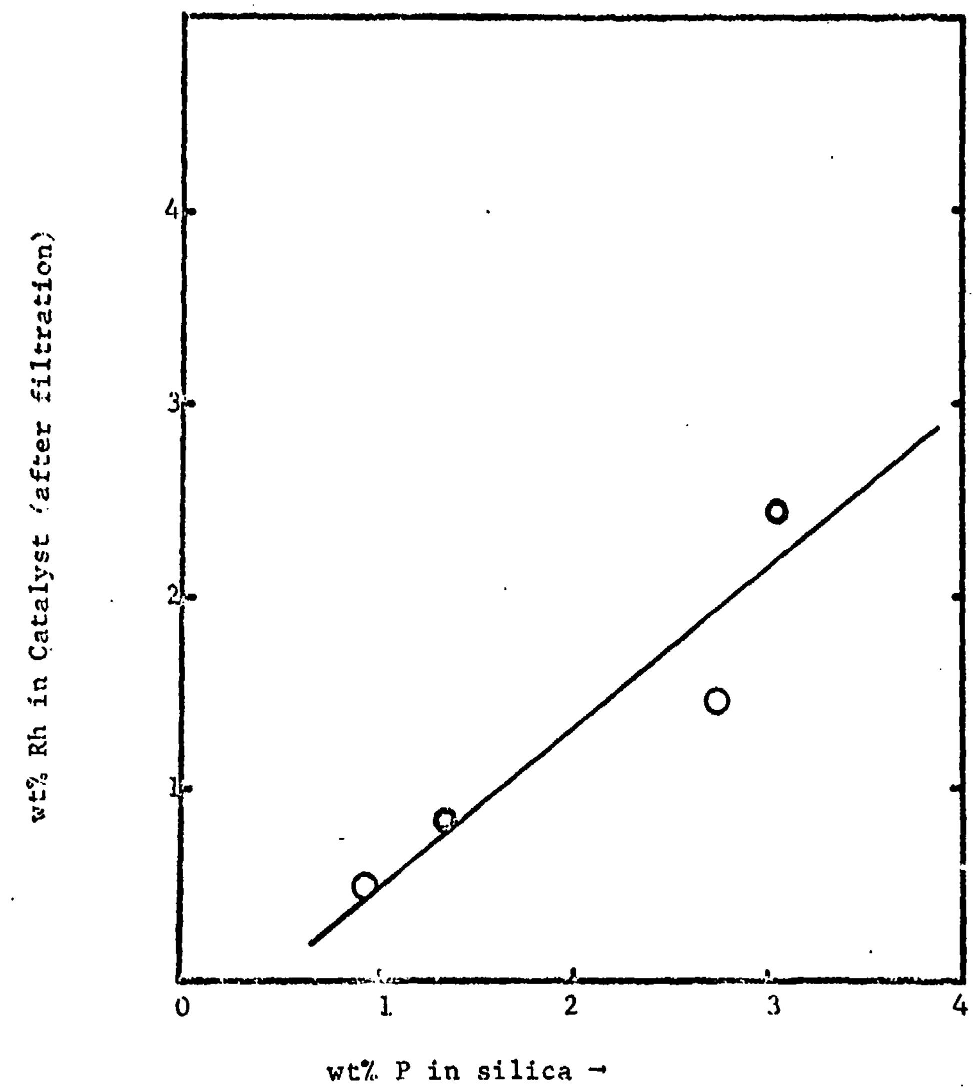

Figure 13. Dependence of the % Rh in Supported-SiP_2-Rh Catalysts on the % P in starting Silica-SiP_2.

It should also be noted from Figure 12 that there is approximately a three-fold excess of SiP_2 for each Rh: the theoretical ratio of weight percent (2 phosphorus:1 rhodium) is ~ 0.6, where as the line represented in the figure is ~ 1.6. The reason for this is not known, perhaps some SiP_2 sites are inaccessible or oxidized, but nonetheless this is an argument that the species are rigidly bound. Solution studies show catalytic activity decreases rapidly when the molar ratio $P/Rh > 2$ (cf. Figure 4), and these supported systems maintain good activity at $P/Rh \approx 6$.

It should also be noted that this catalyst is recoverable; it can be filtered from the reaction mixture in air, and reused with only minimal loss in activity. (Most of this loss in activity appears to be due to mechanical loss while handling the silica supported catalyst.)

In some respects, this catalyst appears similar to the polystyrene supported (-)DIOP catalyst developed by Dang and Kagan and co-workers.[125] It takes significantly less time for the silica-SiP_2 to react with the chlorobis(cyclooctene)rhodium(I) (since the rate of the polystyrene bound phosphine is limited by diffusion through the resin) but the handling of the catalysts, once made, seem virtually identical. The two are compared in further detail in the next sections.

C. Comparisons between Homogeneous, Heterogeneous, and Supported Organometallic Catalysts

This work is concerned primarily with synthesis and characterization of silica supported organometallic catalysts. In order to fully characterize the active catalyst, however, comparisons with both heterogeneous and homogeneous catalysts are necessary. The literature contains many experiments involving Wilkinson's hydrogenation catalyst, $(PPh_3)_3$-RhCl, 1, and its several analogues utilizing different ligands and methods of preparation: this body of data on the Wilkinson and related catalysts is not entirely consistent but generally quite sufficient for purposes of comparison.

Data for heterogeneous rhodium catalysts, at least for conditions and experiments studied here, are quite rare in literature. Comparisons have necessitated work in this laboratory to establish how "classical" heterogeneous rhodium species perform. For these purposes, a commercial[149] 5% Rh/Al_2O_3 catalyst was used and determined to be 4.3% Rh by weight with a dispersion* of 43%.[150]

To be certain the supporting material would not affect the result of the experiments, an experimental 5% Rh/SiO_2 catalyst was obtained as $RhCl_3 \cdot 3H_2O$ impregnated on CAB-O-SIL.[153] The catalyst was treated by the method employed by Yates and Sinfelt[81] for maximum dispersion. The resultant catalyst contained 4.75% Rh by weight with a 59% dispersion.[154] This Rh/SiO_2 catalyst showed a somewhat slower rate of hydrogenation (Table V) but was not significantly different from the Rh/Al_2O_3 catalyst, a result verified in literature.[80]

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*

$$\% \text{ dispersion} = \frac{\text{number of surface active sites}}{\text{total number of metal atoms}}$$

Dispersion is determined by a "hydrogen titration" of surface oxide method, originally developed by J. Benson and M. Boudart[151] for platinum catalysts. Although this method may not be directly applicable to rhodium catalysts with very high dispersion,[152] the result gives sufficient accuracy for the results reported here.

The comparisons that follow will show much greater difference between heterogeneous and organometallic catalysts (bound or homogeneous) than between heterogeneous rhodium catalysts.

1) Table II presents data for several catalysts comparing the rate of hydrogenation of terminal olefins (which is approximately equal to the rate of hydrogenation of cyclohexene) to the rate of hydrogenation of a hindered olefin (1-methylcyclohexene).

The ratios of the turnover number* for reduction of unhindered olefin over the turnover number for reduction of hindered olefin for the different catalysts are shown in Table III.

Table III. Ratios of Turnover Number for Hydrogenation of Unhindered Olefins over Turnover Number for Hydrogenation of 1-Methylcyclohexene†

Catalyst/Ref.	Olefins (hindered | unhindered)		Ratio $\left(\frac{\text{turnover unhindered}}{\text{turnover hindered}}\right)$
5% Rh/Al_2O_3/this work	1-methylcyclohexene	1-decene	1.9
0.52% Pt/Al_2O_3/ (53)	1-methylcyclohexene	cyclohexene	1.9
$(Ph_3P)_3RhCl$/(52)	1-methylcyclohexene	cyclohexene	34
SiP_2-Rh/this work	1-methylcyclohexene	1-decene	6

†Full reaction conditions reported in Table II.

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*

$$\text{Turnover number} = \frac{\text{mol } H_2 \text{ consumed}}{\text{mol metal sites} \cdot \text{sec}}$$

Turnover number is a commonly used measure of rate for heterogeneous catalysts. Since this work deals with a supported catalyst, and the concept of concentration of catalytic species is difficult to interpret with this system, the author felt it was best to use turnover numbers to compare all rate data rather than rate constants. Note should be taken that heterogeneous catalyst activity is independent of olefin concentration, but homogeneous activity is not, thus the turnover numbers for homogeneous catalysts apply for a specific olefin concentration.

Table II

Dependence of Catalytic Activity on Substrate with Various Catalysts (1 Atm H_2, 25°).

Catalyst (Reference)	Olefin (Molarity) Solvent	Reported Rate and Conditions	Turnover Number
A. Heterogeneous Catalysts			
5% Rh/Al_2O_2 (this work)	decene cyclohexane	7.4 ± .1 ml H_2min (5.5 mg catalyst, 42% dispersion)	5.6 ± .1
5% Rh/Al_2O_3 (this work)	1-methylcyclohexene cyclchexane	3.9 ± .3 ml H_2/min (5.5 mg catalyst, 42% dispersion)	2.9 ± .2
0.52% Pt/Al_2O_3 (53)	cyclohexene cyclohexane	1.3 ± 4 mol H_2/min/g·atom Pt	1.88 ± .06*
0.52% Pt/Al_2O_3 (53)	1-methylcyclohexene cyclohexane	1.3 ± 4 mol H_2/min/g·atom Pt	1.0 ± .1*
B. Homogeneous Catalysts			
$(Ph_3)_2RhCl$ (52)	cyclohexene**(1.1) 3 benzene:1 ethanol	1.8 × 10^{-4} mol H_2/min (2.4 m<u>M</u> Rh, 4.5 m/ solvent)	2.8 × 10^{-1}
$(Ph_3)_3RhCl$ (52)	1-methylcyclohexene (0.94) 3 benzene:1 ethanol	5.3 × 10^{-6} mol H_2/min (2.4 m<u>M</u> Rh, 4.5 ml solvent)	8.2 × 10^{-3}
C. Supported Organometallic Catalyst			
SiP_2·Rh (this work)	1-decene (1.1) benzene	0.32 ± .01 ml H_2/min (0.1 g catalyst, 0.59% Rh)	(4.2 ± .1) × 10^{-2}
SiP_2·Rh (this work)	1-methylcyclohexene (1.7) benzene	0.054 ± .008 ml H_2min (0.1 g catalyst, 0.59 % Rh)	(7 ± 1) × 10^{-3}

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[*] Authors did not report % dispersion on this catalyst. Calculations assume 100% dispersion, so turnover number may be higher.

[**] k' for hydrogenation of cyclohexene/k' for hydrogenation of 1-dodecene = 0.94 in benzene solution.[27]

As is expected, the specificity of heterogeneous systems is minimal and Wilkinson's hydrogenation catalyst exhibits nearly fifteen times the heterogeneous selectivity. The specificity of the bound organometallic catalyst is intermediate. One would expect some loss in specificity since the catalyst is less sterically hindered with the chelating bisphosphine and thus less selective.

2) Figure 14 demonstrates the dependence of rate of hydrogenation by the silica supported-SiP_2Rh catalyst on olefin concentration. With Wilkinson's classical homogeneous catalyst, Halpern's[50] data yields the following rate law:

$$\text{Rate} = \frac{-dH_2}{dt} = \frac{k_6K_5[\text{Rh}]_{\text{Total}}[\text{olefin}]}{K_5[\text{olefin}] + [\text{L}]}$$

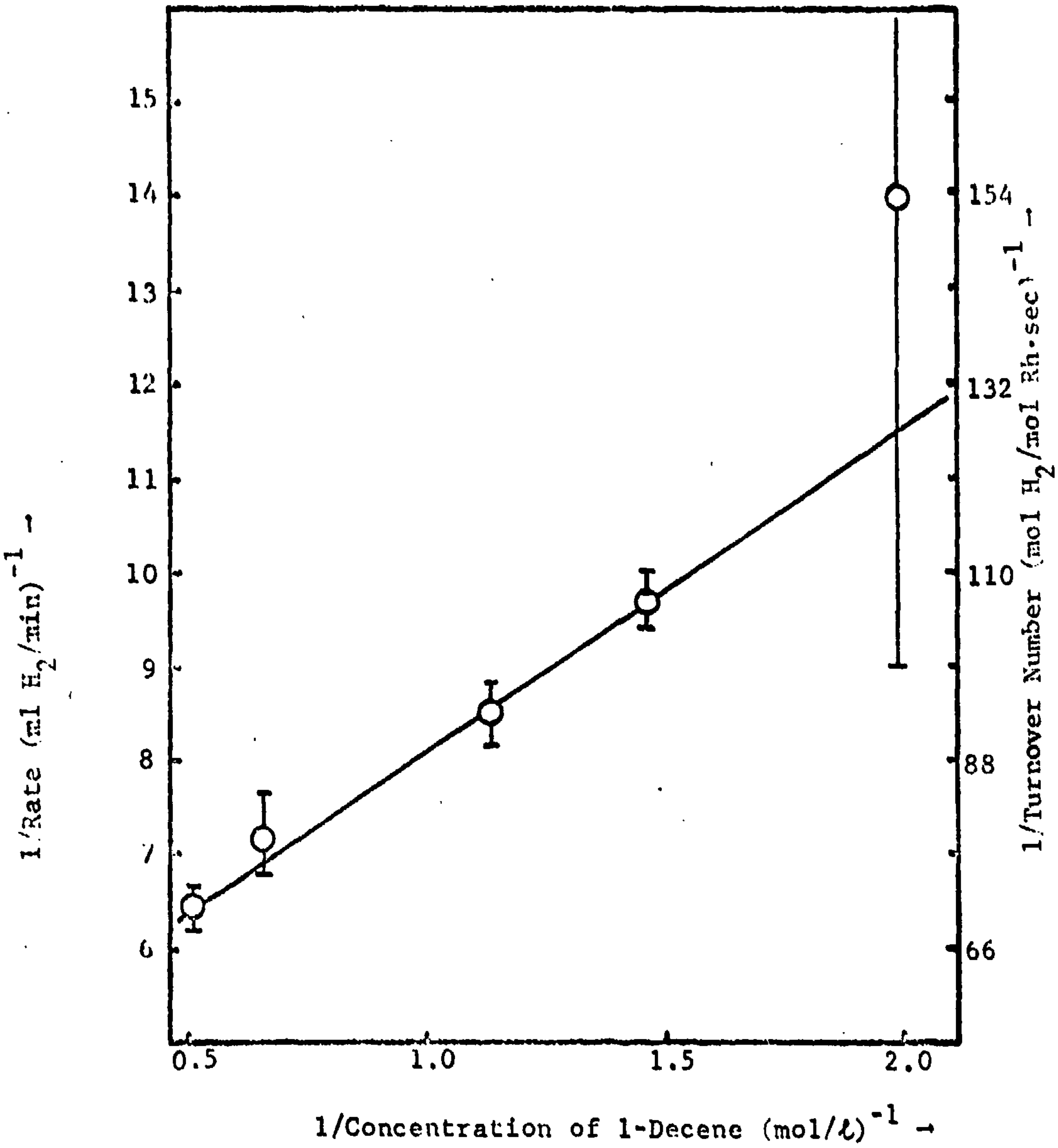
$$1/\text{rate} = \frac{K_5[\text{olefin}]}{k_6K_5[\text{Rh}]_T[\text{olefin}]} + \frac{[\text{L}]}{k_6K_5[\text{Rh}]_T[\text{olefin}]} \qquad (21)$$

$$1/\text{rate} = \frac{1}{k_6[\text{Rh}]_T} + \left(\frac{[\text{L}]}{k_6K_5[\text{Rh}]_T}\right)\frac{1}{[\text{olefin}]}$$

With the silica SiP_2-Rh catalyst, plot of (1/rate) vs. (1/[olefin]) in Figure 13 is definitely linear, suggesting that this system follows a homogeneous catalyst-type rate law.

It should be noted that the catalysts prepared by Takeda[121] also showed an apparently linear plot with these functions (Figure 9), but his plot was over a completely different (lower) olefin concentration range than shown in Figure 13 and also the range studied by Wilkinson.[26]

3) Table IV shows the dramatically different effects that solvent has on homogeneous and heterogeneous catalysts. As mentioned



Catalyst: 0.1 g Silica-SiP_2-Rh, 0.82% Rh, 8.0×10^{-6} mol Rh
Conditions: 25°, 5 ml benzene, 1 atm H_2

Figure 14. Dependence of Rate of Hydrogenation by Supported SiP_2-Rh Catalyst on Concentration of Olefin

Table IV

Dependence of Catalytic Activity on Solvent with Various Catalysts (1 atm H_2, 25°)

Catalyst (Reference)	Olefin (Molarity) Solvent	Reported Rate and Conditons	Turnover Number
A. Heterogeneous Catalyst			
5% Rh/Al_2O_3 (this work)	1-decene benzene	-31 ± 2 ml H_2/min (0.1 g catalyst, 42% dispersion)	1.3 ± .1
5% Rh/Al_2O_3 (this work)	1 decene cyclohexane	-7.4 ± .1 ml H_2/min (5.5 mg catalyst, 42% dispersion)	5.6 ± .1
B. Homogeneous Catalysts			
$(Ph_3P)_3RhCl$ (27)	cyclohexene (0.6) benzene	31.6 ℓ/mol-sec (1.25 m$\underline{M}$ Rh, 80 ml)	0.13 ± .01
$(Ph_3P)_3RhCl$	cyclohexene (0.6) 1 benzene:1 hexane	15 ℓ mol·sec (1.25 m$\underline{J}$ Rh, 80 ml)	0.06 ± .01
$(Ph_3)_3RhCl$ (52)	cyclohexene (1.1) 3 benzene:1 ethanol	1.8×10^{-4} mol H_2/min (2.4 m$\underline{M}$ Rh, 4.5 ml)	0.28
[(-)-DIOP]Rh (125)	α-ethylstyrene (1.3) benzene	0.75 ml H_2/min (0.06 mmol Rh)	0.009*
[(-)-DIOP]Rh (124)	α-acetamido- cinnamic acid (0.3) 1 benzene:2 ethanol	3.7 ml H_2/min 3 m$\underline{M}$ Rh, 20 ml, P/Rh ratio = 2.2	0.046
[(-)-DIOP]Rh	α-acetamido- cinnamic acid (0.3) 1 benzene:2 ethanol	0.0 ml H_2/min 3 m$\underline{M}$ Rh, 20 ml, P/Rh ratio = 4.4	0.0
$(PhP_3)_nRhCl$	α-acetamido- cinnamic acid (0.3) 1 benzene:2 ethanol	0.43 ml H_2/min 3 mM Rh, 20 ml n = P/Rh ratio = 2 or 3	0.005

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*Optical yield (homogeneous) 15%.

C. Supported Organometallic Catalysts

[(-)-DIOP]Rh (polystyrene) (125)	α-ethylstyrene(1.3) benzene	0.3 ml H_2/min (0.5 g catalyst, 0.06 mmol Rh)	0.004**
[(-)-DIOP]Rh (polystyrene) (125)	α-acetamido cinnamic acid(1.3) benzene:ethanol	0 (0.5 g catalyst, 0.06 mmol Rh)	0***
(SiP_2)Rh (this work)	1-decene(1.1) benzene	0.15 ± .01 ml H_2/min (0.2 g catalyst, 0.49% Rh)	0.012 ± .001
(SiP_2)Rh (this work)	1-decene(1.1) 1 benzene:1 ethanol	1.56 ± .03 ml H_2/min (0.2 g catalyst, 0.49% Rh)	0.12 ± .01
(SiP_2)Rh (this work)	1-decene(2.2) cyclohexane	0.013 ± .005 ml H_2/min (0.176 g catalyst, 0.25% Rh)	0.0022 ± .0008

** Optical yield (supported) 1.5%.

*** Authors noted: a) olefin insoluble in benzene, b) ethanol added to solubilize the olefin caused the polystyrene to contract.

by Butt,[82] benzene can be a "poison" to a heterogeneous catalyst hydrogenating olefins since benzene can also be adsorbed on the active sites. Heterogeneous catalysts, hence, function best in solvents that interact least with metal sites.

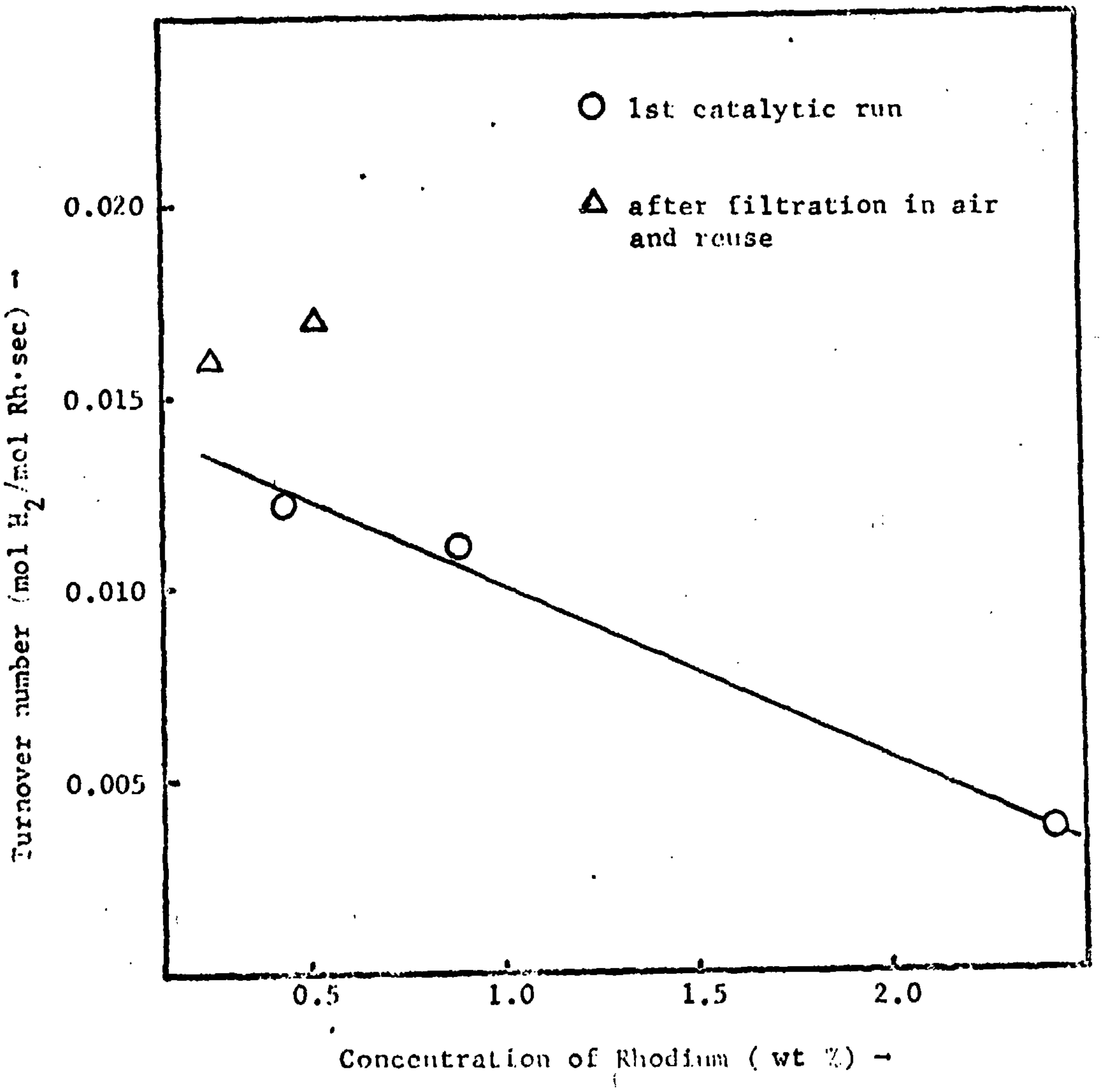
Homogeneous catalysts, however, have strong dependence on several solvent interactions, including solvation of the metal complex, as well as solvation of dissociated ligands and substrates.[27] The dielectric constant of the reaction medium also has an effect and the solvent may play a large role in migratory insertion steps where the stability of the coordinatively unsaturated product can be stabilized by the appropriate solvent, probably acting as a ligand. Wilkinson's catalyst is virtually insoluble in alkanes, hence quite inactive, but the rate is dramatically increased by benzene and, even more, by ethanol. (It may be noted here that the importance of the solvent as a "ligand" in homogeneous catalysts is underscored by the fact that, in hydrogenation in pure ethanol, Wilkinson's catalyst will slowly abstract carbon monoxide from the solvent and thus become deactivated.[26] The solvent appears intimately involved with the mechanism of hydrogenation in homogeneous catalysts.)

The silica supported SiP_2 catalysts are affected by solvents in the same way as homogeneous catalysts, but to a somewhat different magnitude. Opposite from the heterogeneous catalysts, the supported SiP_2-Rh complex does not hydrogenate rapidly in alkanes but has a discrete advantage over homogeneous Wilkinson's since it need not necessarily be soluble--it is already a molecular dispersion in suspension.

Similar to Wilkinson's catalyst, the silica supported SiP_2 catalyst shows much faster rates in benzene and a ten-fold increase in rate when ethanol is added.

One interesting note about solvent effects is apparent from previous work by Dang and Kagan and co-workers on supported (-)-DIOP compounds.[124,125] These show particular solvent dependence because the support, polystyrene, does not swell in polar solvents like ethanol and cannot be used on substrates insoluble in less polar solvents. The nonpolar microenvironment within polystyrene supports may be selective toward reduction of nonpolar substrates, but this has not been investigated. A similar physical phenomenon of support interaction was, however, reported by Grubbs and Kroll[109] who noticed a great selectivity toward reduction of unhindered substrates that can enter the polystyrene with least steric interference.

4) One of the most interesting observations in the catalysts that were made by Takeda[121] was the precipitous (almost 100-fold) drop in activity when rhodium passed from 1.0% to 0.5% by weight (Figure 11). Since crystallites of metal were observed in electromicrographs of his catalysts, it was hypothesized that a minimum concentration of 0.5% was necessary for the rhodium to be close enough to interact and form crystallites under reducing conditions. The supported SiP_2-Rh catalysts do not demonstrate this behavior and, to the contrary, have an increasing turnover number with decreasing weight percent rhodium (Figure 15). This may result because of the concomitant decrease in the surface concentration of phosphine in these silicas, hence less excess phosphine-rhodium interactions which kill activity in homogeneous systems (Figure 4)



Catalysts: Silica supported-SiP_2-Rh

Conditions: 25°, 1 atm H_2, 5 ml benzene, 1.2 M 1-decene

Figure 15. Dependence of Turnover Number in Decene Hydrogenation with Supported-SiP_2-Rh Catalysts on Surface Concentration of Rhodium

but evidently have a considerably smaller effect in these supported systems.

5) Turnover rates are also quite instructive for comparing the catalysts. It has been noted previously in this discussion that there are many different factors controlling the rates of hydrogenation of catalysts, especially solvents and the nature of the olefin. Table V brings together several examples of olefin hydrogenation by different catalysts.

It shall be noted that comparisons with Wilkinson's catalysts are tenuous since they can be made by various methods, with different P/Rh ratios, and even different ligands (not to mention the previously discussed effects of solvent, hindered olefins, and concentration of olefin). In spite of these problems, however, a few observations can be made:

a) Nowhere do the homogeneous or bound organometallic catalysts approach closer than an order of magnitude to the heterogeneous turnover rate.

b) It is apparent that the bound organometallic catalysts prepared by Takeda[121] have turnover numbers for both olefin and benzene hydrogenation that are approximately one-tenth that found with the standard heterogeneous catalysts. This would strongly suggest that these are similar to heterogeneous species only having one-tenth the active surface area per weight rhodium.*

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*Dispersion of these species could not be obtained by the standard hydrogen titration method.[154,155]

Table V

Turnover Numbers for Various Catalysts (1 Atm H_2, 25°)

Catalyst (Reference)	Substrate (Molarity) Solvent	Other Conditions	Turnover Number
A. Heterogeneous Catalysts			
5% Rh/Al_2O_3 (this work)	1-decene cyclohexane		5.6 ± .1
5% Rh/Al_2O_3 (this work)	benzene cyclohexane		0.18 ± .01
5% Rh/SiO_2 (this work)	1-decene cyclohexane		2.26 ± .06
B. Homogeneous Catalysts			
$(PPh_3)_nRhCl$ (29)	cyclohexene(0.6) benzene	n = P/Rh = 3 1.25×10^{-3} M Rh	0.092*
$(PPh_3)_nRhCl$ (29)	cyclohexene(0.6) benzene	n = P/Rh = 2 1.25×10^{-3} M Rh	0.21*
$(EtPPh_2)_nRhCl$ (29)	cyclohexene(0.6) benzene	n = P/Rh = 3 1.25×10^{-3} M Rh	0.013*
$(EtPPh_2)_nRhCl$ (29)	cyclohexene(0.6) benzene	n = P/Rh = 2 1.25×10^{-3} M Rh	0.13*
$(PPh_3)_3RhCl$ (52)	cyclohexene(1.1) 3 benzene:1 ethanol	2.4×10^{-3} M Rh	0.28
$(PPh_3)_3RhCl$ (52)	1-methylcyclohexene (0.94) 3 benzene:1 ethanol	2.4×10^{-3} M Rh	0.0082

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*Pressure of H_2 = 50 cm.

C. Bound Organometallic Catalysts

(-)-DIOP (polystyrene) (125)	α-ethylstyrene(1.3) benzene	0.5 g catalyst, 0.06 mmol Rh	0.004
L RhCl(COD) (silica) (121)	1-decene (2.5) benzene	2.5×10^{-5} mol Rh (catalyst 2.88% Rh)	0.16
L RhCl(COD) (silica) (121)	benzene benzene	2.5×10^{-5} mol Rh (catalyst 2.88% Rh)	0.0018
$L_2Rh_4(CO)_{10}$ (silica) (121)	1-decene(2.5) benzene	2.5×10^{-5} mol Rh (catalyst 8.13% Rh)	0.219
$L_2Rh_4(CO)_{10}$ (silica) (121)	benzene benzene	2.5×10^{-5} mol Rh (catalyst 8.13% Rh)	0.023
L RhCl(COD) (silica) (148)	1-decene(2.5) benzene	1.36×10^{-5} mol Rh	0.33
SiP_2Rh (this work)	1-decene(1.1) benzene	0.1 g catalyst, 0.59% Rh (approx. 10^{-3} $\underline{M}$ Rh)	0.042 ± .001
SiP_2Rh (this work)	1-decene(2.2) cyclohexane	0.18 g catalyst, 0.25% Rh	0.0022 ± .0008
SiP_2Rh (this work)	1-decene(1.1) benzene-ethanol	0.2 g catalyst, 0.49% Rh	0.12 ± .01
SiP_2Rh (this work)	1-methyl cyclohexene (1.7) benzene	0.1 g catalyst, 0.59% Rh	0.007 ± 0.001
SiP_2Rh (this work)	benzene benzene	50 psi H_2	$< 7 \times 10^{-4}$**

**Hydrogenation of benzene not normally observed if catalyst used at 1 atm H_2.

c) The SiP_2 ligand most closely resembles the bis(ethyldiphenylphosphino)chlororhodium(I) species formed in situ. The activity of the bound-SiP_2-Rh species is approximately one tenth the activity of this closest analog in homogeneous catalysis. It may be noted, however, that the bound-SiP_2-Rh species has activity very close to that of the tris(ethyldiphenylphosphine)chlororhodium(I), suggesting the possibility of interaction of some of the excess phosphines on the silica (noted earlier) with the catalytic species.

d) The SiP_2 bound catalyst has, within experimental error, the same rate as Wilkinson's hydrogenation catalyst with the hindered olefin, 1-methylcyclohexene. The bound catalyst thus appears to have potential for hydrogenating these more hindered olefins but still maintaining more selectivity than heterogeneous catalysts.

e) The bound SiP_2-Rh catalyst appears to be better for hydrogenations than the equivalent polystyrene-bound (-)-DIOP complex. The SiP_2 system makes no pretense of inducing optical activity in substrates, but the 1.5% optical yield reported with the bound (-)-DIOP is not significant.

f) Benzene reduction by the SiP_2-Rh system is usually not observed at 1 atm hydrogen pressure and, when observed, cyclohexane is barely at the detection limit of the glc (present in quantities 200 times smaller than reduced olefin). Even at 40 psi H_2, the quantity of cyclohexane is an order of magnitude less than that observed with the catalysts previously developed by Takeda.[121] These bound SiP_2-Rh systems seem much less like classical heterogeneous catalysts.

6) Isomerization is generally not reported by investigators using Wilkinson's hydrogenation catalyst under hydrogen. There are, however, many reports in the literature of Rh(I) species performing in this manner, as shown in Figure 16.

During the course of experiments with the bound SiP_2 system, it was noted that isomerization of 1-decene was occurring to give the thermodynamically favored ratio of cis-2-decene and trans-2-decene. This is a very unexpected result and has no parallel in heterogeneous rhodium catalysis except under severely poisoned conditions.[80]

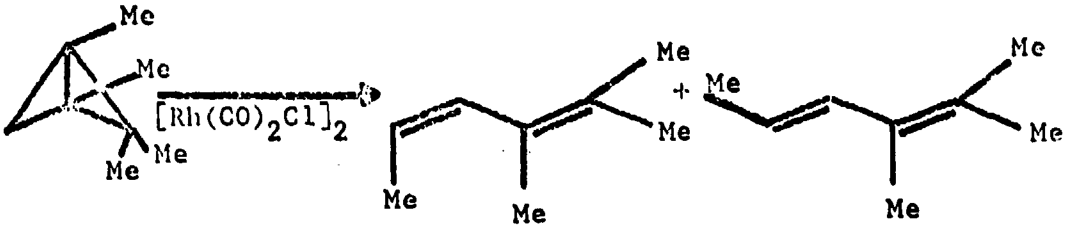
This isomerization, however, may be evidence for the true bound nature of this catalyst. Webb and MacNab,[80] looking at rhodium heterogeneous catalysts under the above-mentioned poisoning experiments, invoked interaction of the rhodium catalyst with the support's acidic surface hydroxyls to explain their result. In may be, then, that these bound organometallic catalysts are so intimately associated with the support that they demonstrate this isomerization under conditions that homogeneous and classical heterogeneous catalysts do not. In this respect, this bound organometallic is a new catalytic species having unique characteristics.

7) Poisoning has presented some interesting information, particularly for heterogeneous catalysts. Hydrogenation by Rh/Al_2O_3 normally occurs at a relatively rapid rate, zeroth order in olefin concentration, as shown by hydrogen uptake curves in Figure 17. The slope of these lines gives the rate in ml H_2/sec which, knowing the amount of rhodium in the system, yields the turnover number.

Reference

156 $RhCl_3 \cdot 3H_2O$ + 1,3-cyclooctadiene → Rh_2Cl_2(1,5-cyclooctadiene)$_2$

157



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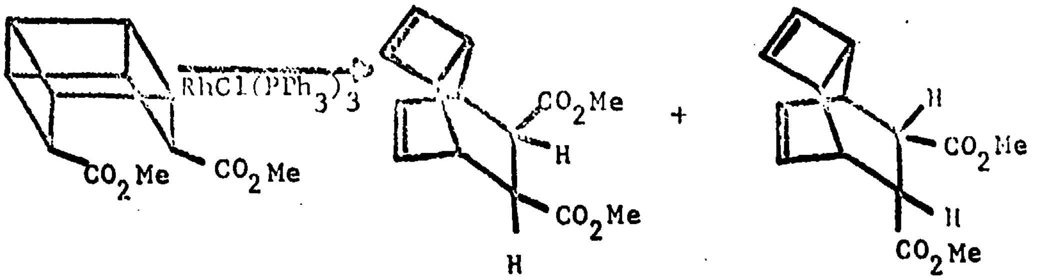

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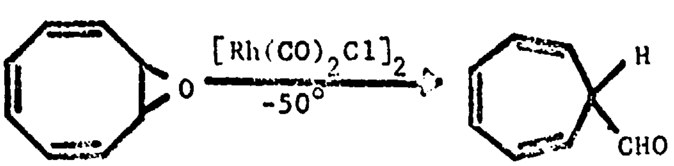

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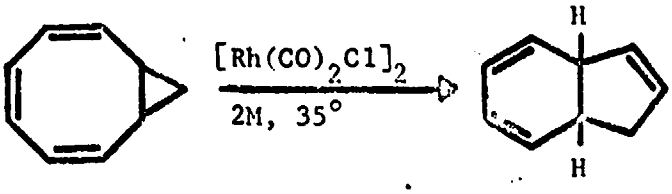
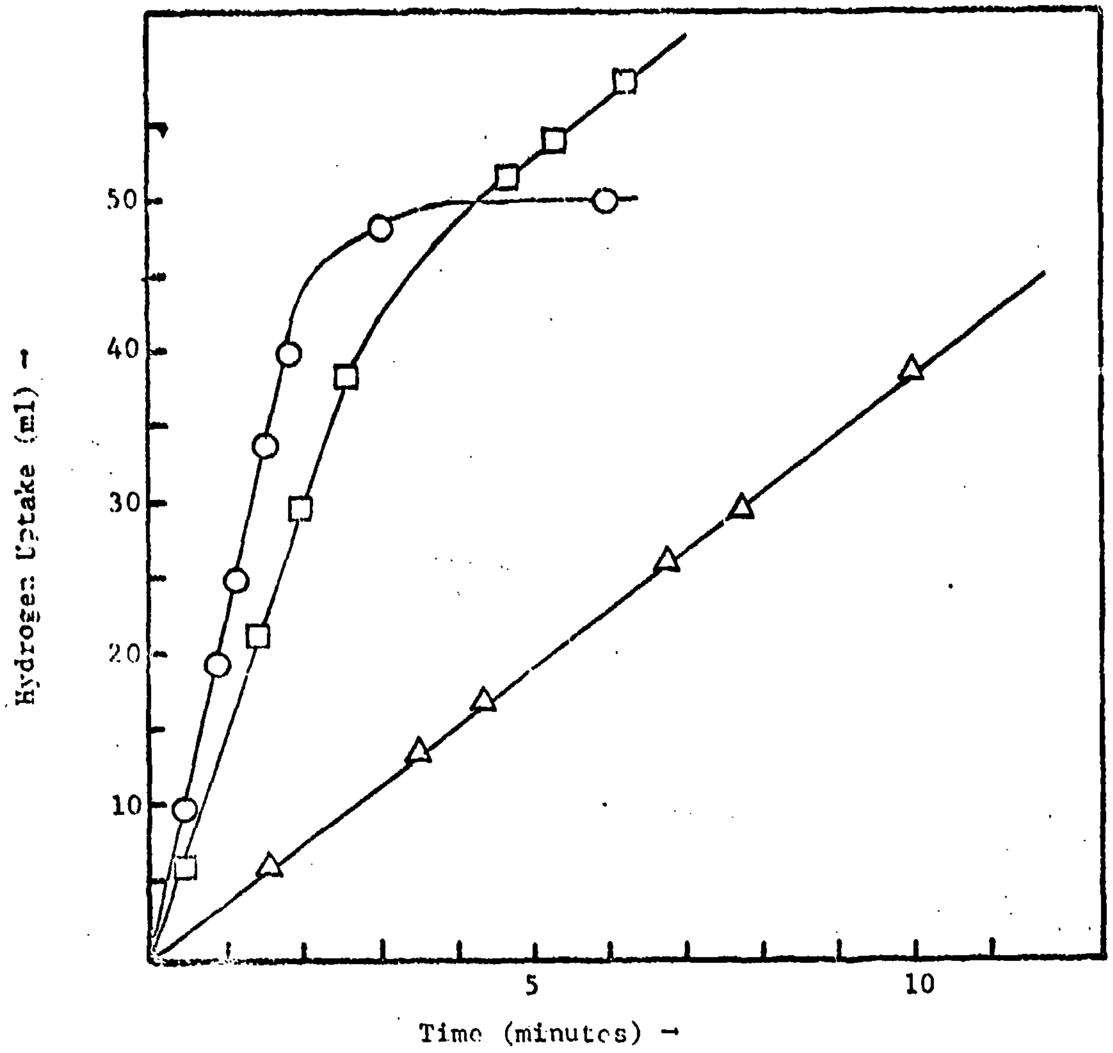


100% cis

Figure 16. Isomerization with Rh(I) Organometallic Complexes



Catalyst: 5% Rh/Al$_2$O$_3$

Conditions: 1 atm H$_2$, 25°
O 0.1 M 1-Decene in cyclohexane (0.02 g Rh/Al$_2$O$_3$)
□ 0.1 M 1-Decene in benzene (0.05 g Rh/Al$_2$O$_3$)
Δ 0.1 M benzene in cyclohexane (0.05 g Rh/Al$_2$O$_3$)

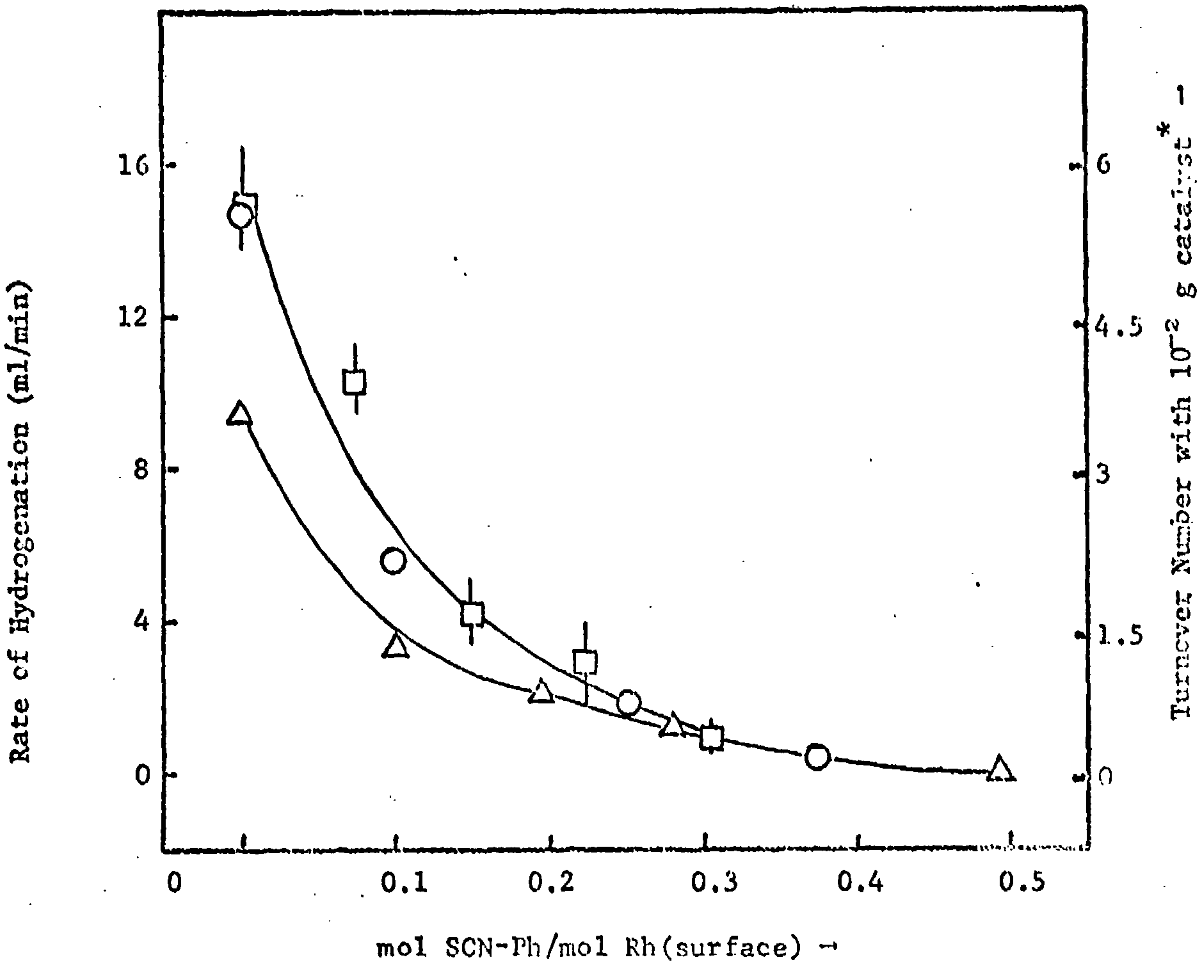
Figure 17. Hydrogen Uptake vs. Time During Hydrogenation of 1-Decene and Benzene by Rhodium on Alumina

If a poison, such as phenylthioisocyanate, C_6H_5NCS, is added, and the system is given adequate time to equilibrate (one-half hour in these studies), a slower rate of hydrogen uptake is observed. By plotting the turnover numbers of the catalyst, at various stages of poisoning, versus the amount of poison added, curves as in Figure 18 evolve. It may be noted, firstly, that the curves are not linear, demanding that the poison is affecting more than just the active site(s) it is occupying. Secondly, all hydrogenations appear to cease at about the stoichiometry of one poison molecule per two metal active sites, implying that the poison is binding two active sites.

If, as observed by Brill and Tauster,[87] a new function is defined as

$$S = \left(1 - \frac{q}{q_{max}}\right), \text{ where } \begin{array}{l} q = \text{quantity poison added} \\ q_{max} = \text{quantity poison required to poison all sites} \end{array}$$

then a plot of the turnover number *vs*. S^2 gives linear curves as shown in Figure 19. This would imply that each poison molecule binds two adjacent active sites and, by its presence, further inhibits activity at other neighboring sites. This is in agreement with the mechanism for hydrogenation by rhodium metal surfaces that show at least two neighboring sites as necessary for reduction (e.g., Eq. 5 shown in the Introduction). Interestingly, these data also show that similar sites, requiring about the same cooperativity from adjacent sites, are used for benzene reduction as for olefin reduction. These sites are poisoned at the same rates, implying that one is not necessarily more structure dependent than the other. This is consistent with the mechanism previously shown in Figure 7.

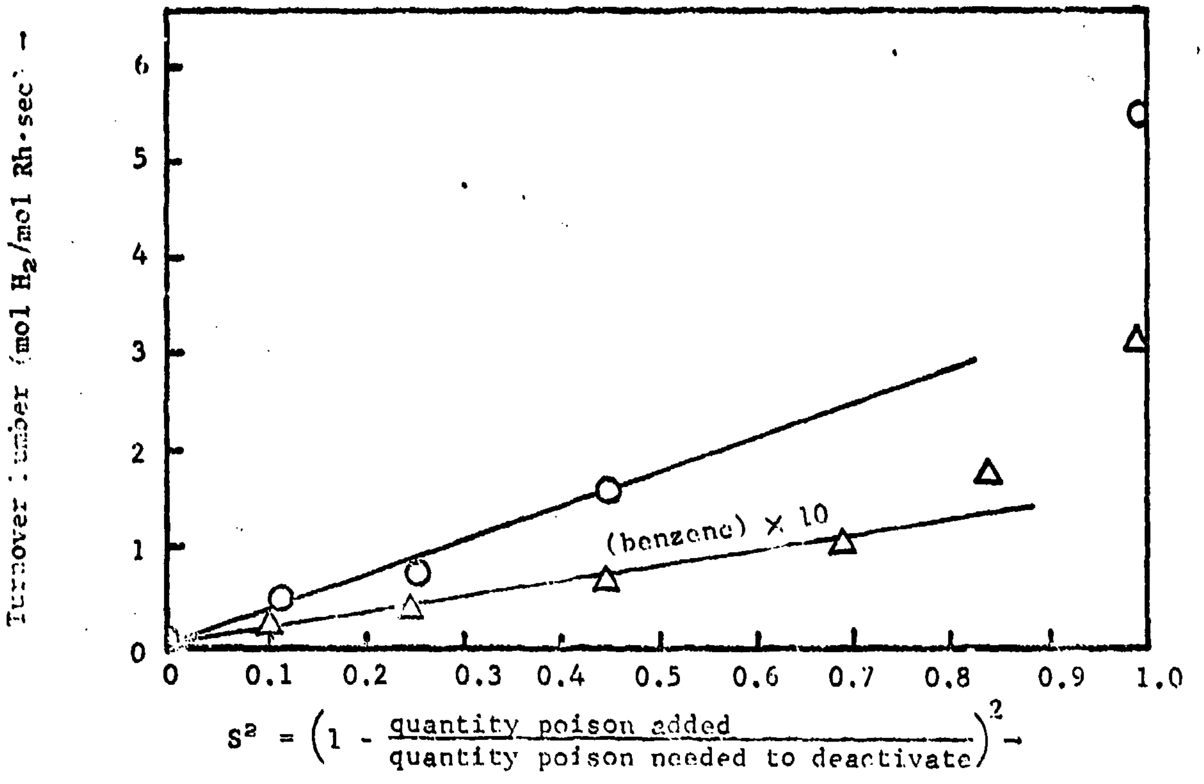


Catalyst: 5% Rh/Al_2O_3

Conditions: 25°, 1 atm H_2
○ 0.1 $\underline{M}$ 1-Decene in cyclohexane (0.01 g Rh/Al_2O_3)
□ 0.1 $\underline{M}$ 1-Decene in benzene (0.05 g Rh/Al_2O_3)
Δ Benzene (0.1 g Rh/Al_2O_3)

*Turnover number = $\frac{\text{mol } H_2}{\text{mol Rh}\cdot\text{sec}}$; scale shown for "O" points only with 10^{-2} g catalyst. Scale for "□", divide by 5; scale for "Δ", divide by 10.

Figure 18. Rate of Hydrogenation by Rhodium on Alumina vs. Poison/Surface Rhodium Ratio



Conditions: 25°, 1 atm H_2

O 0.1 M 1-Decene in cyclohexane (0.02 g Rh/Al_2O_3)

Δ 0.1 M benzene in cyclohexane (0.10 g Rh/Al_2O_3)

Figure 19. Quadratic Relationship between Active Sites Unpoisoned and Turnover Number on 5% Rh/Al_2O_3 Catalyst

Unfortunately, poisoning of the bound organometallic catalyst is not as easily explicable. The curve in Figure 20 shows the decrease in activity as a function of the amount of phenylthioisocyanate added. After an apparently linear and very dramatic change in activity, the effect of increased poison is minimal. This could be rationalized by a mechanism whereby the poison "saturates" the relatively small number of coordinatively unsaturated species first then slowly acts to poison even the coordinatively saturated catalytic species.

It might also be argued from this that there are, perhaps, a few heterogeneous sites that are much more active than the homogeneous sites, and that these are poisoned first. From this poisoning information there would have to be 10% such "heterogeneous sites." With even this number of heterogeneous sites, the selectivity would be much lower and the hydrogenation of benzene would be a significant event at atmospheric pressure. Neither of these is observed, so it seems improbable that there are even 10% heterogeneous sites.

8) Electron microscopy* is commonly used to identify metal crystallites in heterogeneous-type catalysts. It should be pointed out that electron microscopy, more than any other experimental method used in this work, offers indirect evidence because it does not study the system during catalysis and can only aid in description of the physical state of the catalyst. Furthermore, this is negative evidence since it is possible to have metal crystallites that are too small to be detected by electron microscopy (< 20 Å) but yet large enough to function as catalysts--thus absence of electron microscopic evidence for crystallites does not rule out their existence.

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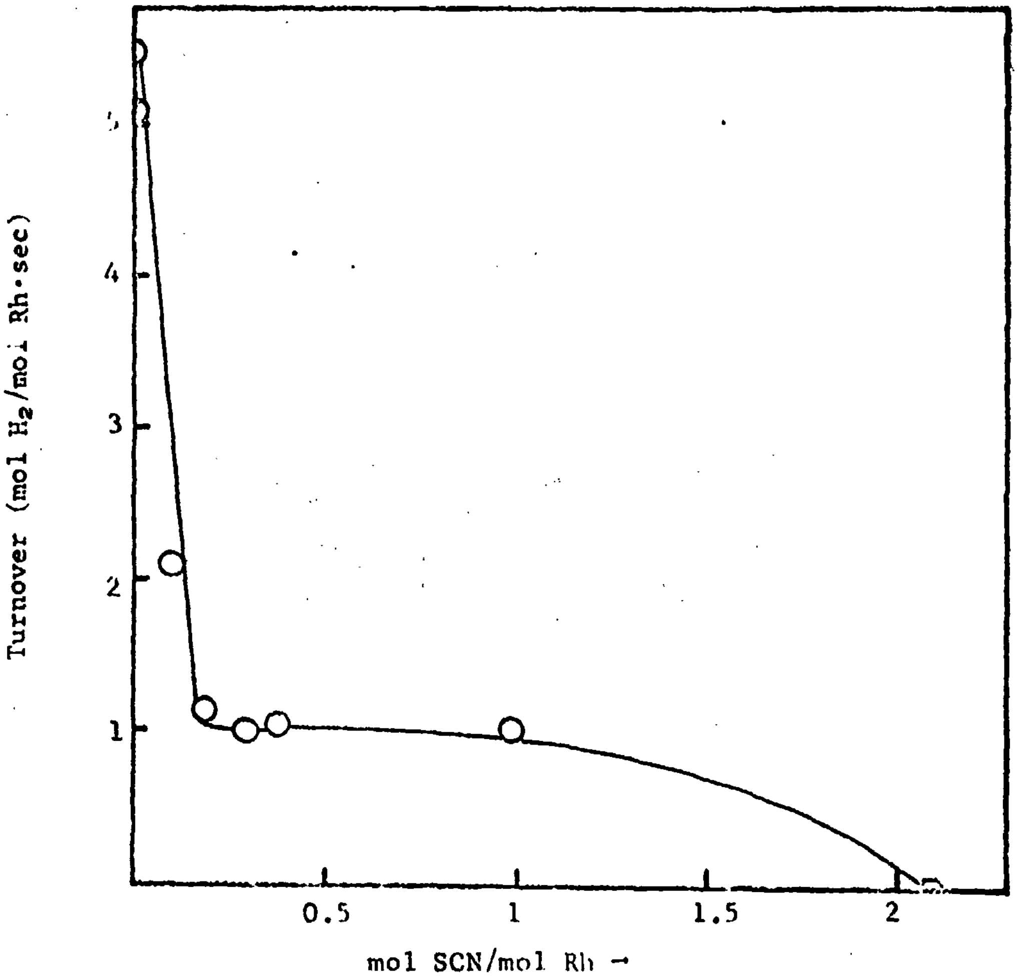
*The author is indebted to Matthew Marrocco, of this research group, for his generous assistance in producing these micrographs.



Catalyst: 0.08 g ≡Si-O-SiP$_2$Rh

Conditions: 1 atm H_2, 25°
1-Decene, 1.1 M in 5 ml benzene

Figure 20. Poisoning of Supported SiP$_2$-Rh Catalyst by Phenylthioisocyanate, Turnover Number on Rhodium *vs.* SCN/Rh Ratio

With these cautions, it is nevertheless interesting to note that electron microscopy shows metal crystallites in heterogeneous catalysts, Rh/Al_2O_3 (Figure 21) and Rh/SiO_2 (Figure 22), and bound catalysts previously prepared by Takeda (Figures 23 and 24). No crystallites, however, are observed in silica bound $L_2Rh(CO)Cl$(<u>6</u>) (Figure 25) or in supported-SiP_2-Rh catalysts, whether freshly prepared (Figure 26), used once (Figure 27), or filtered in air and reused (Figure 28). If care in preparation of the catalyst is not taken to add olefin before solvent under hydrogen atmosphere, the silica rapidly turns black and will reduce benzene. This catalyst <u>does</u> show metal crystallites under the electron microscope (Figure 29).

It is a positive sign, then, that no crystallites are found in the normal silica-SiP_2-Rh systems. This system does not appear to be a classical metallic heterogeneous catalyst, suggesting the organometallic complexes still exist and are functioning as the catalyst.

9) ESCA* is a particularly powerful tool for examining surfaces (several monolayers down) and analytically characterizing the oxidation state of the species present. Unfortunately, results are not complete, but preliminary evidence[123] shows primarily Rh(III) present on two catalysts prepared from LRh(CO)Cl(COD)(COD=1,5-cyclooctadiene) and $L_2Rh_4(CO)_{10}$ by Takeda.[121] In these same systems, all phosphorus seems to be present as phosphine oxide. Although more definite evidence from comparisons to other systems is desirable, this preliminary ESCA data tends to substantiate other evidence that these previously studied silica organometallics were not Rh(I) organometallic compounds during catalysis.

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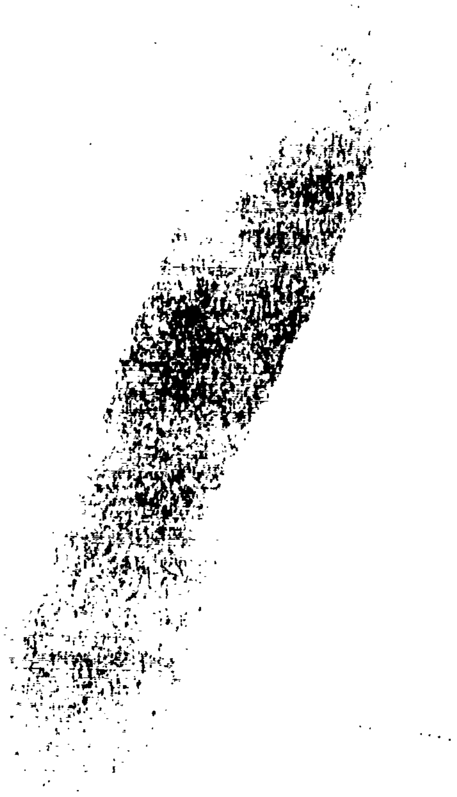
*The author is indebted to Professor Jack Faller at Yale University for his help with this technique.

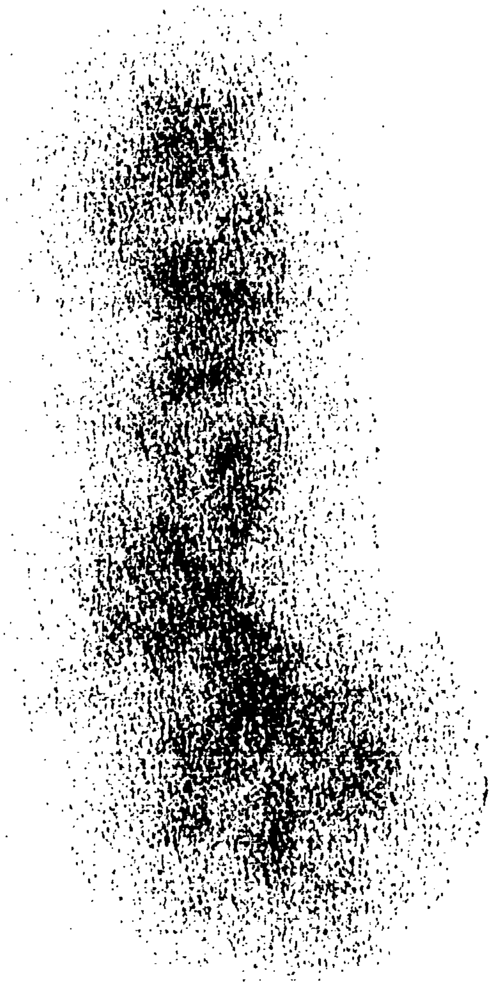
Dark areas are smaller crystallites dispersed on Alumina support.

Figure 21. Electron Micrograph of 5% Rh/Al_2O_3, Commercial Catalyst[149]



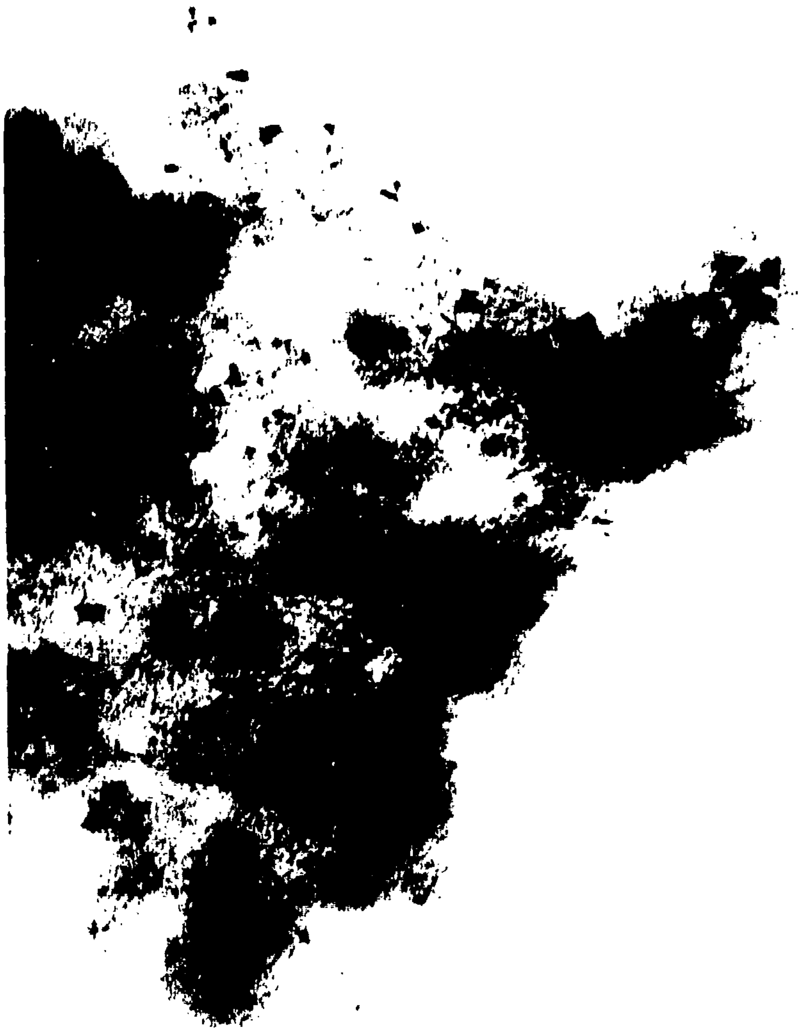
Single large crystallite found in Rh heterogeneous catalysts, at lower magnification.

Figure 22. Electron Micrograph of 5% Rh/SiO_2, Experimental Catalyst[153]



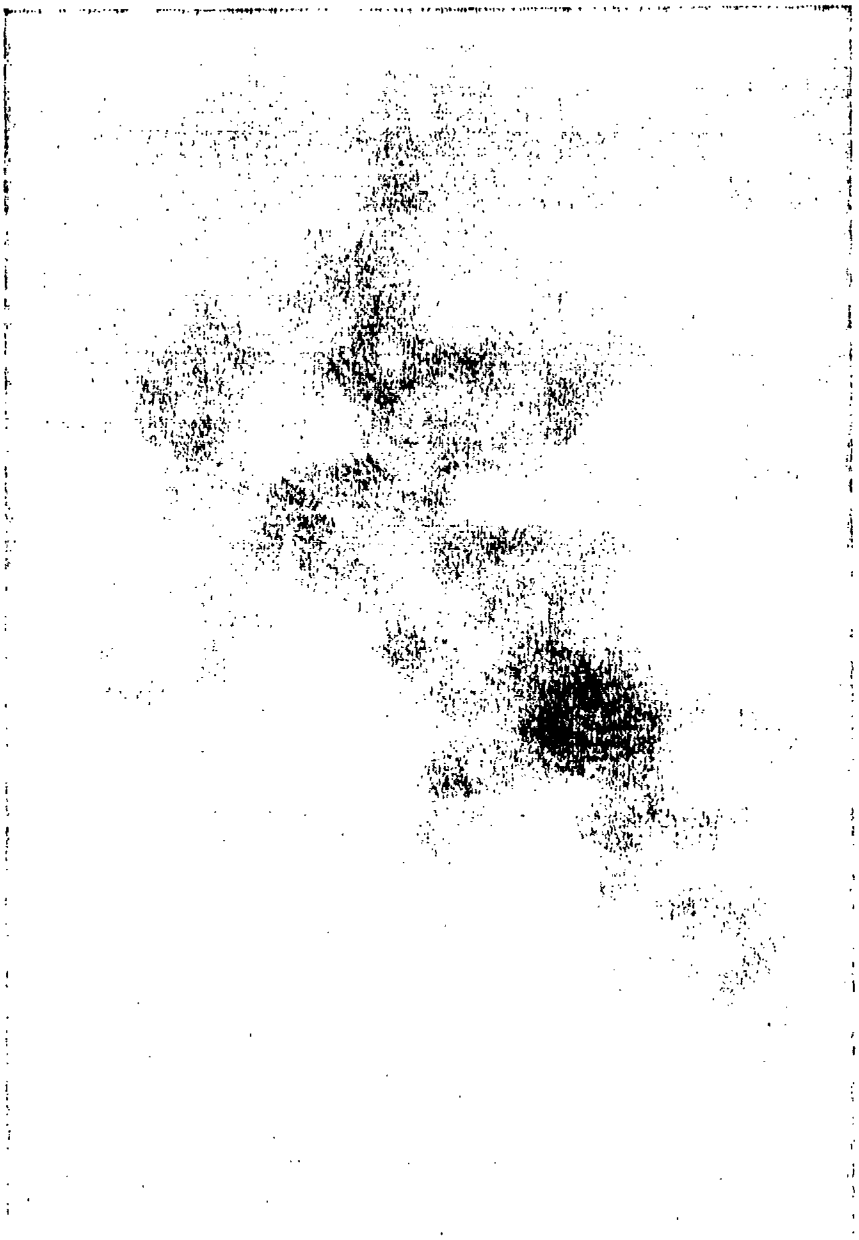
Crystallites visible as darker areas, high magnification.

Figure 23. Electron Micrograph of Silica Supported L Rh(COD)Cl,$\underset{\sim}{7}$, After Use as Hydrogenation Catalyst[122]



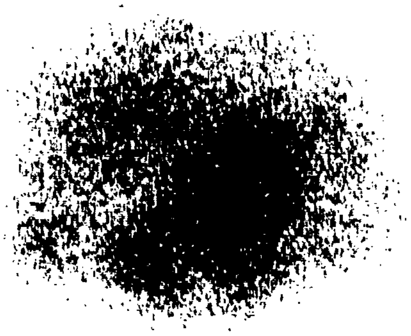
At low magnification, crystallites are evidence of metallic rhodium catalyst.

Figure 24. Electron Micrograph of Silica Supported $L_2Rh_4(CO)_{10}$, $\underset{\sim}{8}$, After Use as Hydrogenation Catalyst



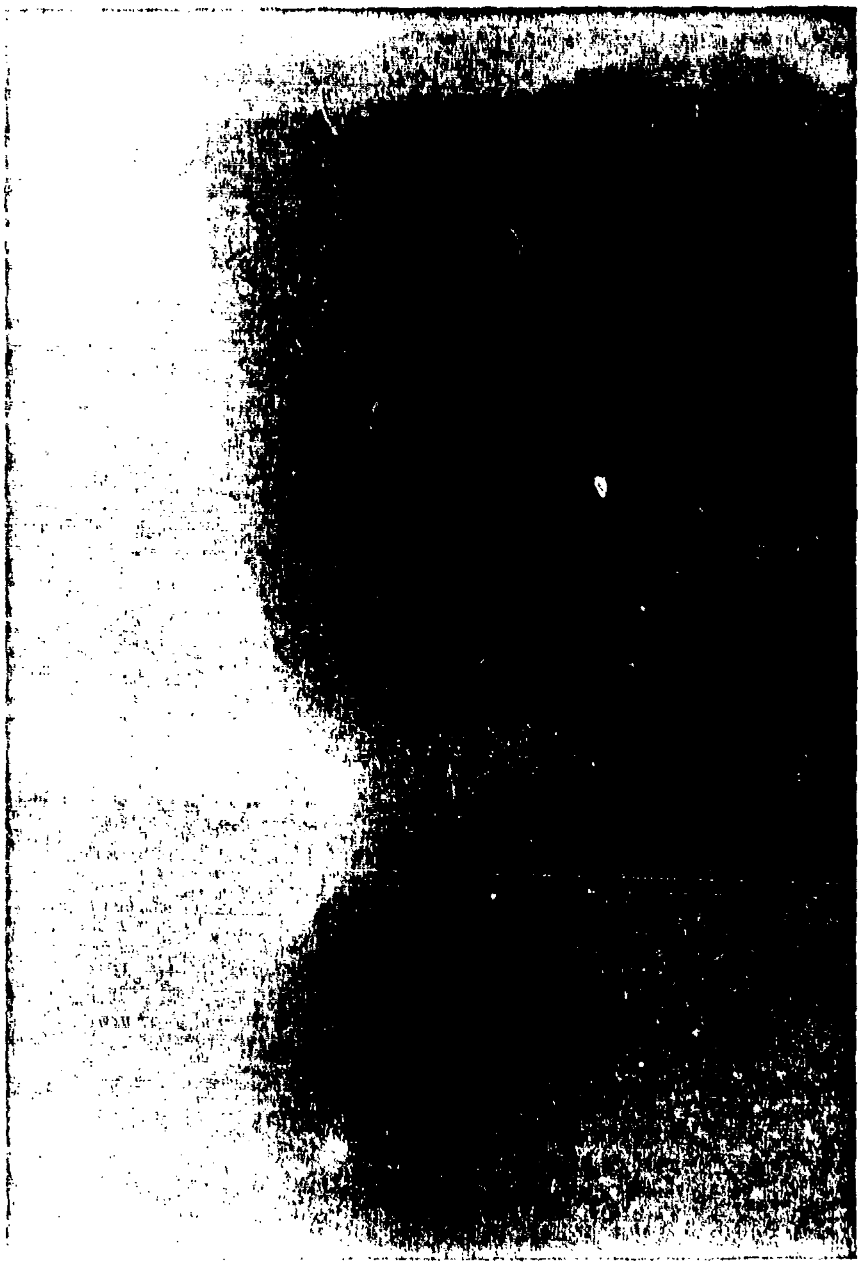
No crystallites visible.

Figure 25. Electron Micrograph of Silica Supported $L_2Rh(CO)Cl$, Never Used as Hydrogenation Catalyst[148]



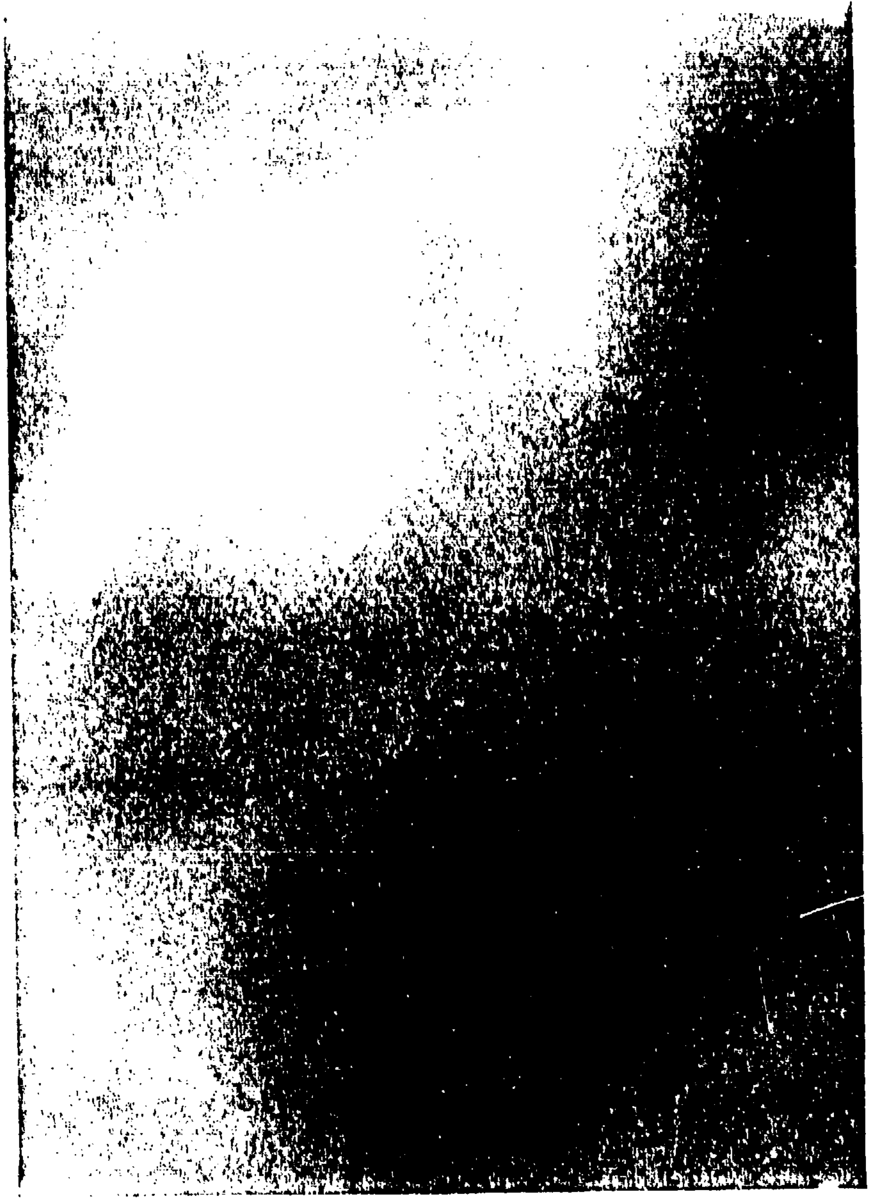
No crystallites visible.

Figure 26. Electron Micrograph of $\equiv Si-O-SiP_2Rh$, Never Used as Catalyst



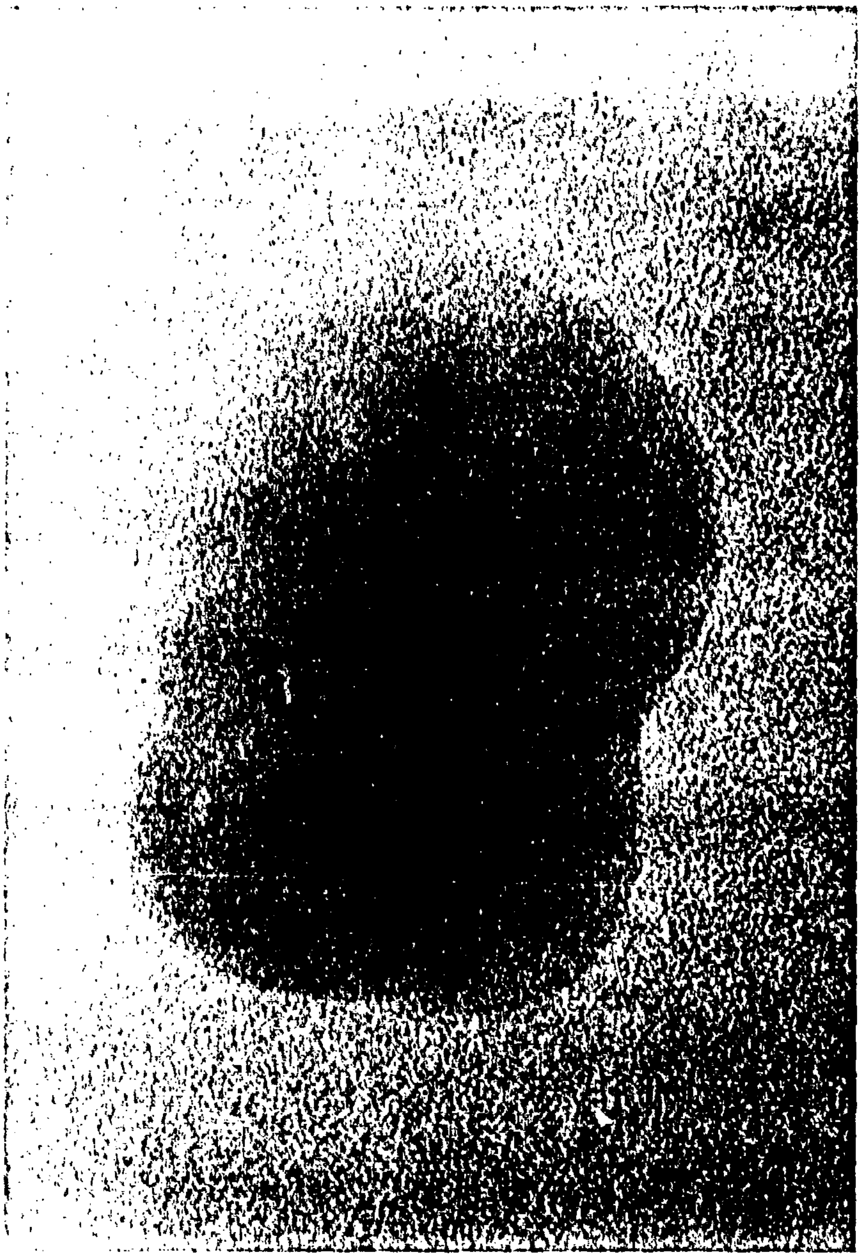
No crystallites visible.

Figure 27. Electron Micrograph of $\equiv$Si-O-SiP$_2$-Rh, Used Once as Hydrogenation Catalyst



No crystallites visible.

Figure 28. Electron Micrograph of $\equiv$Si-O-SiP$_2$-Rh, Used as Hydrogenation Catalyst, Filtered in Air, Dried in Vacuum, then Reused as Hydrogenation Catalyst



Crystallites visible as dark areas.

Figure 29. Electron Micrograph of Silica Supported-SiP$_2$ after treatment with Chlorobis(cyclooctene)rhodium(I) under Hydrogen (no Olefin present)

III. EXPERIMENTAL

Since phosphines are easily oxidized and silyl groups are easily hydrolyzed, care must be taken to dry all glassware and work in an oxygen-free environment. Solvents were carefully dried and deoxygenated, and transferred under positive nitrogen pressure. THF was distilled from benzophenone and sodium; benzene was distilled from sodium/potassium after being previously stirred for 10 hr with sulfuric acid to remove traces of thiophene; anhydrous diethylether was used as received from Mallinckrodt (St. Louis, Mo.) and absolute ethanol was dried over Linde type 4X molecular sieves. "Hi Pure Nitrogen", 99.99%, Liquid Carbonic, Chicago, Ill.) was further purified over BASF Catalyst R3-11 (BASF Ag, Ludwigshaven am Rhein).

Poisoning and kinetic experiments were performed with 99.99% hydrogen (Liquid Carbonic, Chicago, Ill.) and further purified to < 1 ppm O_2 by a "Deoxo" catalytic purifier (Englehard Industries, East Newark, NJ) and passed through molecular sieves. Cyclohexane solvent ("Chromatoquality Reagent 99+ mole%" from Matheson, Coleman, and Bell, Norwood, Ohio) was passed through activated alumina under nitrogen, then freeze/pump/thaw degassed before use. Aldrich 1-decene was passed through activated alumina under nitrogen and then distilled from lithium aluminum hydride under nitrogen before use. Aldrich phenylthioisocyanate was used as received.

^{1}H NMR spectra were recorded on a Varian T-60 and ^{31}P NMR spectra were obtained with a Varian XL-100 spectrometer. Analyses were performed by the Microanalytical Laboratory of this Department. Gas/liquid chromatography was performed on Hewlett-Packard 5750 Research

Chromatographs and integrated by a Vidar 6300 Digital Integrator.

The remainder of the Experimental Section will describe A) Synthesis of Phosphine ligands, B) Synthesis of Organometallic Compounds, C) Preparation of the Organometallic Catalyst Supported on Silica, and D) Determination of Rate of Hydrogenation at Constant Pressure.

A. Synthesis of Phosphine Ligands

2-Triethoxysilyl-1-diphenylphosphino ethane

Following the procedure of H. Niebergall[162] an equimolar mixture of diphenylphosphine (5.0 g, 2.7 × 10^{-2} mol) and triethoxyvinylsilane (5.1 g, 2.7 × 10^{-2} mol) were placed in a quartz tube. After freeze/pump/ thaw degassing, the sample was frozen, evacuated again, and closed (closure should be capable of withstanding moderate pressure generated by heating of the sample by irradiation). The tube was placed under a low pressure mercury ultraviolet lamp, and cooled by a stream of air directed at it, for two days (disappearance of vinyl protons was monitored by ^1H NMR). The mixture, distilled at 132-4° at 10 μ, yielded 8.7 g product (85%).

<u>^1H NMR</u> (60 MHz, $CDCl_3$) δ 7.2 (m, 10H), δ 3.7 (q, 6H), δ 1.2 (t, 9H), δ 0.8-0.3 (m, 4 H)

Analysis: calculated for $C_{20}H_{29}O_3PS_i$: C, 63.8; H, 7.76

found: C, 63.65; H, 7.89

2-Allyl-diethyl malonate

The method of Adams and Kamm[132] used for preparing 2-*n*-butyl-diethyl malonate was followed on approximately one-tenth scale. Clean sodium (14 g, 0.61 mol) was added slowly to 250 ml absolute ethanol in a 500 ml flask fitted with a condenser and then allowed to cool to 50°. Diethyl malonate (85 ml, 0.56 mol) was added over a period of one-half hr, followed by allyl bromide (72 g 0.59 mol) added over an additional 30 min. The solution was refluxed until neutral to moist litmus (two hr) and 200 ml ethanol was distilled off. Adding 150 ml water separated the crude product in the upper layer, which was then vacuum distilled (bp 82-5° at 50 μ) to yield 95.6 g (85%) of product.

<u>^{1}H NMR</u> (60 MHz in $CDCl_3$): δ 6.1-4.8 (m, 3 H), δ 4.18 (q, 4 H)
δ 3.4 (m, 1 H), δ 2.6 (m, 2 H), δ 1.15 (t, 6 H).

2-Allyl-1,3-propanediol

Following hints for use of lithium aluminum hydride (LAH) in Fieser and Fieser,[133] LAH (17.5 g, 0.45 mol) was dissolved in 250 ml refluxing diethyl ether in a three-neck 500 ml round bottom flask fitted with a powerful mechanical stirrer, a condenser dropping funnel, and an oil bath (preparations were also made for ice bath for cooling in case of vigorous reaction). At a dropping rate sufficient to generate a gentle reflux, the 2-allyl-diethyl malonate (55.3 g, 0.275 mol) was added and the mixture refluxed for an additional 30 min. Water (17.5 ml) was added slowly with stirring, providing for adequate venting of the H_2 generated. Aqueous 15% NaOH solution (17.5 ml) was added dropwise, followed by an additional 51 ml water. The white precipitate was filtered off and washed with five 20 ml portions of diethyl ether. The ether was removed from the filtrate on a rotary evaporater, yielding 15 ml (75%) of product after distillation (96-100° at 20 μ).

^{1}H NMR (60 MHz, $CDCl_3$): δ 6.1-4.8 (m, 3 H), δ 4.3 (5, 2 H),
δ 3.5 (m, 4 H), δ 1.9 (m, 3 H).

2-Allyl-1,3-propanediol-di-*p*-toluene sulfonate (2-Allyl-1,3-propanediol-ditosylate)

Following H. Lettre and U. Wölcke[134] 2-allyl-1,3-propanediol (24 g, 0.206 mol) was added to 160 ml dry pyridine and stirred at 0° in a 250 ml Erlenmeyer flask fitted with a septum. After the temperature had equilibrated, *p*-toluene sulfonyl chloride (80 g, 0.41 mol) was added slowly, carefully maintaining the temperature below 10°. The vessel was tightly capped, the mixture stirred an additional 2 hr under cooling and then 6 hr at room temperature. The reaction mixture was then poured into a 3 ℓ Erlenmeyer flask containing a mixture of 760 g of ice and 250 ml concentrated hydrochloric acid and stirred rapidly.

The product was extracted from the aqueous solution with 5 100 ml portions of benzene. The benzene solution was washed with 2 125 ml portions of 2 *M* HCl then dried over sodium sulfate. The benzene was removed on a rotary evaporator and the product crystalized from 250 ml absolute ethanol. (Care must be taken to cool slowly, as an oil is likely to form. This oil, however, solidified after several days at -22° and this was easily recrystallized from absolute ethanol.) Yield of recrystallized product was 80%.

^{1}H NMR (60 MHz, $CDCl_3$): δ 7.8-7.0 (AA'BB', 8 H), δ 5.4-4.6 (m, 3 H),
δ 3.9 (d, 4 H), δ 2.2 (s, 6 H), δ 2.0 (d, 3 H).

Analysis: calculated for $C_{20}H_{24}O_6S_2$: C, 56.7; H, 5.65
found: C, 56.9; H, 5.67

2-Allyl-1,3-bis(diphenylphosphino)propane

Lithium diphenylphosphide was prepared by placing lithium ribbon (4.9 g, 0.7 mol), cut into small pieces, in a 100 ml round bottom flask with magnetic stirrer and septum stopper. The flask was flushed with nitrogen and 50 ml dry THF was transferred by needlestock into the flask under positive nitrogen pressure. Chlorodiphenylphosphine (18.5 ml, 20.1 g, 0.10 mol) was added slowly and stirred at room temperature for 4 hr. CAUTION: This reaction is exothermic, so the addition was performed slowly to avoid generating excess pressure. As precautionary measures, 1) the reaction flask was placed in a water bath at ambient temperature and 2) the reaction was performed in a hood to avoid a hazardous situation should the chlorodiphenylphosphine escape.

A solution of 2-allyl-1,3-propanediol-ditosylate (17.1 g, 0.05 mol) in 100 ml dry THF was prepared in a 500 ml round-bottom flask and stirred at 0° under nitrogen. The lithium diphenylphosphide solution was transferred by needlestock into this vessel under nitrogen. The mixture was allowed to come to room temperature and heated to distill off 200 ml THF under nitrogen. Water (100 ml) and diethyl ether (100 ml) were added to separate products from lithium salts. CAUTION: Diphenylphosphine may be present and although not extremely volatile, it is toxic and unpleasant. All work was performed in a hood.

The ether was separated from the water layer and the latter washed with 50 ml additional ether. The combined ether extracts were dried over sodium sulfate and ether removed on a rotary evaporator. Recrystallization from absolute ethanol (see notes on recrystallizing 2-allyl-1,3-propanediol-ditosylate) yielded 15.5 g (67%) product, melting at 48-49°C.

<u>^{1}H NMR</u> (60 MHz, $CDCl_3$): δ 7.3 (5, 20 H), δ 5.6-48 (m, 3 H), δ 2.6-1.4 (m, 7 H).

<u>^{31}P NMR</u> (40.5 MHz, C_6D_6, H decoupled): + 22.8 ppm from H_3PO_4 1 ext).

<u>Analysis</u>: calculated for $C_{30}H_{30}P_2$: C, 79.9; H, 6.65; P, 13.65

found: C, 79.81; H, 6.57; P, 13.76

2-(3-Trichlorosilylpropyl)-1,3-propanediol-ditosylate

2-Allyl-1,3-propanediol-ditosylate (7.0 g, 2.05 × 10^{-2} mol) was loaded into a Carius tube (30 ml capacity) and 6 ml dry benzene was added. Trichlorosilane (5 ml, 3.8 g 0.028 mol) was "bulb-to-bulb" distilled (bp 31.8°) through needlestock into the cooled Carius tube under positive pressure of nitrogen. CAUTION: Trichlorosilane is rapidly hydrolyzed by slight traces of water liberating HCl--handle with care in a well-vented hood. The entire tube was then frozen in liquid nitrogen, evacuated, and sealed. After warming to room temperature, the tube was placed into a blast-proof furnace at 250° for 12-16 hr. The tube was cooled and opened (see CAUTION below), and the excess trichlorosilane and benzene were removed by evacuation. The resulting colorless oil gave only one spot on silica gel TLC with chloroform as elutant (r_f = 0.0 for the product, r_f = 0.4 for the starting allyl-ditosylate).

CAUTION: Noncondensable gases are evolved in this sealed tube reaction: the sealed tubes open <u>explosively</u>. The suggested opening procedure is to freeze the reaction mixture in one end of the sealed tube with liquid nitrogen, wrap this end in cloth and (behind a safety shield) score around the other end of the tube with a file. Clamp the tube with the cloth wrapping behind the safety shield in a hood and, using a gloved hand to hold a blunt instrument, gently knock off the top of the tube. Be prepared to salvage the product from the remains of the sealed tube before it melts, remembering that the excess trichlorosilane is rapidly hydrolyzed and unpleasant to work with.

^{1}H NMR (60 MHz, $CDCl_3$): δ 7.8-7.0 (AA'BB', 8 H), δ 4.0-3.2 (m, 2 H), δ 3.0-2.3 (m, 1.2 H), δ 2.2 (s, 6 H), δ 2.0-0.8 (m, 10 H)

2-(3-Triethoxysilylpropyl)-1,3-propanediol-ditosylate

Absolute ethanol (3.5 ml, 2.75 g, 6.15×10^{-2} mol) was added with vigorous stirring to the 2-(3-trichlorosilylpropyl)-1,3-propanediol-ditosylate (2.05×10^{-2} mol). Evolution of HCl was rapid and the reaction mixture was then evacuated to 5 μ for 2 hr at 50°. The remaining colorless oil showed a single spot on analytical silica gel TLC, r_f ± 0.1 in chloroform. The product decomposed and only a dark brown oil was collected after an attempt to bulb-to-bulb distill the product at 5 μ up to 150°.

^{1}H NMR (60 MHz, $CDCl_3$): δ 7.8-7.0 (AA'BB', 8 H), δ 4.2-3.6 (q, 6 H), δ 3.6-3.4 (d, 2 H), δ 2.4 (s, 6 H), δ 2.2-1.6 (m, 4 H), δ 1.2 (t, 10 H), δ 1.0-0.8 (m, 3 H)

2-(3-Triethoxysilylpropyl)-1,3-bis(diphenylphosphino)propane

Lithium diphenylphosphide (4.1×10^{-2} mol) was prepared as previously described under 2-allyl-1,3-bis(diphenylphosphino)propane. Fifty ml THF were added to the 2-(3-triethoxysilylpropyl)-1,3-propanediol-ditosylate and the lithium diphenylphosphide solution was transferred into the tosylate solution under positive nitrogen pressure. The dark red color of the phosphide anion disappeared immediately on mixing, with a light red color persisting at the end. The mixture was stirred for 4 hr at room temperature, and the addition of 0.05 ml absolute ethanol at this time quenched the remaining lithium diphenylphsophide. The solvent was removed by evacuation and 50 ml benzene was added to extract the product from the insoluble lithium salts. The product was filtered in an inert atmosphere and the precipitate washed with an additional 50 ml dry benzene. The benzene from the combined fractions was evaporated and the resulting light yellow oil was evacuated at 100°C at 5 μ for 12 hr. The product (4 g, 55% based on 2-allyl-1,3-propane-diol-ditosylate) gives 4 spots on analytical silica TLC in chloroform, 2 minor spots at $r_f = 0.95$ and $r_f = 0.53$, major product $r_f = 0.15$, and a smaller spot at $r_f = 0$. Further heating under vacuum removes the more volatile impurities that migrated fastest on the TLC, and dissolving in diethylether and filtering under inert atmosphere reduces the TLC stationary component. Bulb-to-bulb distillation was again unsuccessful, the product decomposing to a colorless oil which cooled to a white wax. The mass spectrum showed major components at 183 amu $[P(C_6H_5)]$ and 163 amu $[Si(OC_2H_5)_3]$ but nothing significant over 210 amu.

^{1}H NMR (60 MHz, $CDCl_3$): δ 7.1 (s, 20 H), δ 4.0-3.8 (m, 2 H),
δ 3.4 (q, 5 H), δ 2.4-1.5 (m, 5 H), δ 1.12 (t, 9 H),
δ 1.0-0.4 (m, 2 H)

^{31}P NMR (40.5 MHz, C_6D_6, H decoupled): + 22.6 ppm from H_3PO_4 (ext).

Analysis: calculated for $C_{36}H_{46}P_2O_3Si$: C, 70.5; H, 7.5; P, 10.0
found: C, 69.42; H, 7.3; P, 11.2.

B. Synthesis of Organometallic Compounds

Bis(cycloocta-1,5-diene)-μ,μ'-dichlorodirhodium(I)[$Rh_2Cl_2(COD)_2$]

Following the method of Chatt and Venanzi[163] $RhCl_3 \cdot 3H_2O$ (1 g, 3.8 mmol) was dissolved in 30 ml 95% ethanol, filtered, and boiled under reflux with the 1,5-cyclooctadiene (2 ml, 1.7 g, 16 mmol) for 3 hr. The solution is cooled and the yellow crystalline product (0.7 g, 75%) is filtered, washed, and recrystallized from ethanol or acetic acid.

Analysis: calculated for $C_{16}H_{24}Cl_2Rh_2$: C, 39.0; H, 4.9
found: C, 39.13; H, 4.50.

Cycloocta-1,5-dienetriphenylphosphinechlororhodium(I) [$RhCl(PPh_3)$-(COD)]

Following the method of Chatt and Venanzi[163], bis(cycloocta-1,5-diene)-μ,μ'-dichlorodirhodium(I) (0.5 g, 1 mmol) and freshly recrystallized triphenylphosphine (0.5 g, 4 mmol) are added to 5 ml benzene and stirred for 10 min. The solution is evaporated and the product is washed with methanol and recrystallized from ethanol. Yield is 0.86 g (83%).

Analysis: calculated for $C_{26}H_{27}ClPRh$: C, 61.4; H, 5.35
found: C, 61.19; H, 5.42.

Chlorobis(cyclooctene)rhodium(I)

Following the method of A. van der Ent and A. Onderdelinden[161] $RhCl_3 \cdot 3H_2O$ (2 g, 7.7 mmol) was dissolved in a mixture of 40 ml 2-propanol and 10 ml water. The solution was filtered into a 3-neck round-bottom flask fitted with magnetic stirrer and cyclooctene (6 ml, 43 mmol) added. The entire solution was freeze/pump/thaw degassed and placed under nitrogen and closed. The solution stood for 5 days, then filtered under nitrogen (using Schlenck tubes), and washed with 20 ml degassed ethanol, yielding 1.8 g (70%) orange powder.

The filtered solution was again placed under nitrogen and allowed to stand 1½ months and refiltered for another 0.5 g (total yield, 89%). Both products were stored under nitrogen in refrigerator.

Analysis: calculated for $C_{16}H_{28}ClRh$: C, 53.55; H, 7.8
found: C, 53.42; H, 7.74.

μ,μ'-Dichlorotetracarbonyldirhodium(I) [$Rh_2Cl_2(CO)_4$]

Following the method of E. O. Fischer and co-workers[164] $RhCl_3 \cdot 3H_2O$ (5 g, 19 mmol) is dissolved in 10 ml water and stirred with 20 g silica gel. This is dried overnight at 110° under vacuum from a water aspirator. This silica is poured into a glass tube and placed in a tube furnace and further dried at 150° with a stream of chlorine gas passing through it for 12 hr. Then carbon monoxide is passed through at a slow, even rate at 160°, generating $Rh_2Cl_2(CO)_4$ which sublimes and condenses on the tube outside the furnace. The product is collected in a pure state (2.6 g, 95%). Infrared adsorption spectrum (hexane solution) shows bands at 2105, 2089, 2080, 2030, and 2000 cm^{-1}.

Tetrarhodium(0)dodecarbanoyl [$Rh_4(CO)_{12}$]

Following the procedure of Chaston and Stone,[165] dichlorotetracarbonyldirhodium(I) (2 g, 5 mmol) and finely cut copper turnings (7.5 g, 120 mmol) are placed in a glass liner of an autoclave. After adding 70 ml hexane, the autoclave is flushed with carbon monoxide then pressured to 3000 psi CO and left at ambient temperature with constant stirring for four days.

After venting the autoclave, the solution of the product is filtered from the copper, which is then washed with five portions of 20 ml pentane (until filtrate is colorless). The resulting hexane/pentane solution of product was evaporated to dryness in a rotary evaporator at room temperature (heating above 25° causes formation of $Rh_6(CO)_{16}$). The product (1.35 g, 70%) is quite pure but may be recrystallized from pentane immediately before use. Infrared spectrum shows strong adsorptions (in hexane) at 2062, 2040, and 1883 cm^{-1}.

Analysis: calculated for $C_{12}O_{12}Rh_4$: C, 18.0 Rh, 57.9

found: C, 18.03; Rh, 57.3.

C. Preparation of the Organometallic Catalyst Supported on Silica

Preparation of Dry Silica

The silica employed in this work was CAB-O-SIL HS-5 (325 m^2/g, particle size = 70 Å).[140] The silica was dried under a vacuum of 10^{-5} torr at a temperature of 380° for 24 hours. The silica, once dried, was allowed to cool and transferred, still under vacuum, into an inert atmosphere dry box where it was stored until use.

CAUTION: CAB-O-SIL is a very fine silica and should be handled in a hood to avoid inhalation of powder. When handling on vacuum lines, precautions must be taken to prevent the silica from entering the line; for this work, a fine frit separated the flask containing the silica from the rest of the line.

Preparation of SiP_2 Supported on Silica [$\equiv Si-O-Si(OEt)_2CH_2CH_2CH-(CH_2P(C_6H_5)_2)_2$]

The desired quantity of dried silica was placed into a Fisher Porter pressure bottle, with a stir bar, and suspended in dry benzene. The amount of SiP_2 added to the silica is dependent on the concentration desired on the silica surface (see Figure 12); for example, 50 mg SiP_2 ligand may be added to 0.7 g CAB-O-SIL for approximately 1.3% by weight P on the resultant silica. The mixture is heated to 110° under pressure (~ 20 psi) and constant stirring for a minimum of 18 hours. The suspension is filtered through a medium frit and washed three times with a volume of benzene equal to that required to suspend the silica originally. The silica was then vacuum dried.

NOTE: An inert atmosphere dry box greatly facilitated these operations: all handling of dry silica should exclude even traces of water, and once the phosphine is attached to the surface it is very susceptible to air oxidation. If an inert atmosphere dry box is not available, all due consideration must be taken to preclude traces of moisture and oxygen from the system.

Preparation of supported-SiP_2Rh catalyst

Based on an analysis of the %P on the silica, the amount of chlorobis(cyclooctene)rhodium(I) was calculated to give a ratio of 1 SiP_2 per 1 Rh. For example, in a typical catalyst prepared in this laboratory, 0.1 g $\equiv Si\text{-}O\text{-}SiP_2$ with 3.03% P (0.49 mmol SiP_2/g silica, hence 4.9×10^{-5} mol ligand) was added to 8.6 mg (4.9×10^{-5} mol Rh) chlorobis(cyclooctene)rhodium(I). The two solids are weighed and placed together in the hydrogenation vessel.

NOTE: An inert atmosphere dry box should be used to handle the silica-SiP_2--it is very subject to oxidation.

The vessel is then sealed onto the hydrogenation apparatus (see next section) evacuated to 10 μ, then filled with hydrogen. Olefin substrate must be added first, then the solvent. The catalyst may take a 2-5 minute activation (the rhodium species is quite insoluble, so it takes a few minutes for it all to react) and the hydrogenation catalyst is ready.

The catalyst may be filtered in air and reused. Excess rhodium species are noted in the first filtrate, but the loss of these soluble species does not affect the rate on reuse.

The filtrate from the reaction contains 13 ppm rhodium, or about 1.3×10^{-7} M rhodium. This represents less than 3% of the total rhodium present, and is an upper limit of rhodium species free in solution since there is great probability of significant quantities of silica (aggregates of the 70 Å particles) passing through the (200 Å pore diameter) millipore filter.

D. Determination of Rate of Hydrogenation at Constant Pressure

The hydrogenation apparatus diagrammed in Figure 30 was modeled after a similar apparatus used by Professor Boudart's laboratory.[160] Designed for constant pressure, a photocell's light source (A) is cut by rising mercury as hydrogenation continues and mercury rises in the manometer (B). The photocell trips a relay (C) which opens a solenoid valve (D) allowing positive pressure to force mercury into a gas burette (E) thus equilibrating the internal pressure to 1 atmosphere.

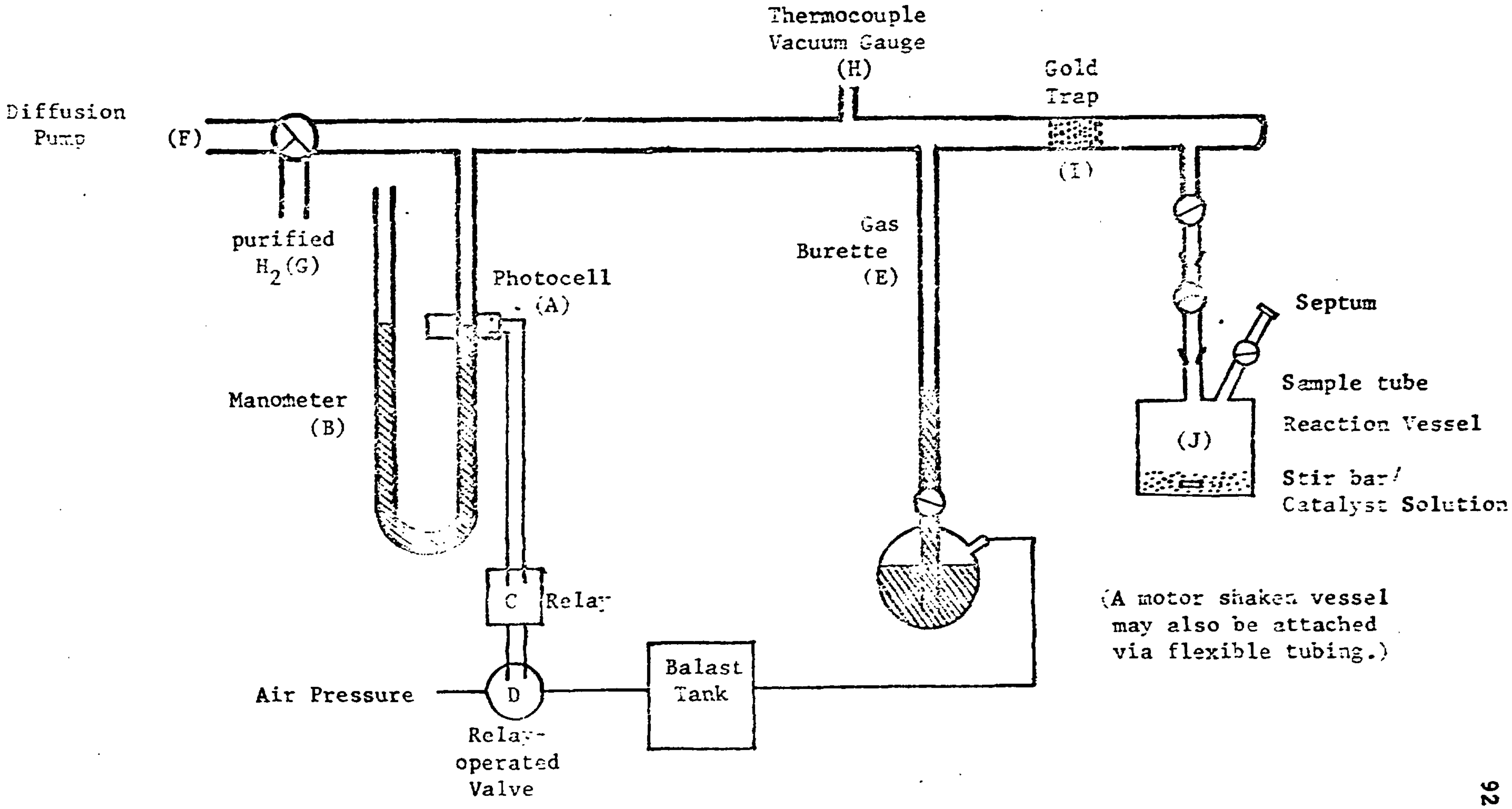
The line is attached to a diffusion pump (F), to remove traces of oxygen from the system before hydrogenation and also attached to a supply of purified hydrogen (G), to fill the line for hydrogenation. The line is fitted with a thermocouple vacuum gauge (H) and a gold (metal) powder trap to keep mercury vapor from the manometers from poisoning the catalyst (I).

The experiments performed in this work utilized both a motor driven shaker reaction vessel[160] when the rate of hydrogen uptake was greater than 8 ml/min (thus eliminating diffusion controlled steps as rate determining factors), or a magnetically stirred reaction vessel (J) used in slower reactions that would not be affected by diffusion controlled steps.

Using an electric timer, the mercury level in the gas burettes is monitored as a function of time.

Procedure for Hydrogenation:

1) Reaction vessel with silica-SiP_2 and rhodium cyclooctene complex are sealed onto apparatus and evacuated for two hours at 10 μ.



(A motor shaken vessel may also be attached via flexible tubing.)

Figure 30. Simplified Diagram of Hydrogenation Apparatus

2) Purified hydrogen is used to flush the system and again evacuated to 10 μ.

3) Purified hydrogen is added slowly to a pressure slightly greater than 1 atmosphere.

4) With internal positive pressure, pre-purified olefin and solvent are added by syringe through a sampling tube fitted with a septum.

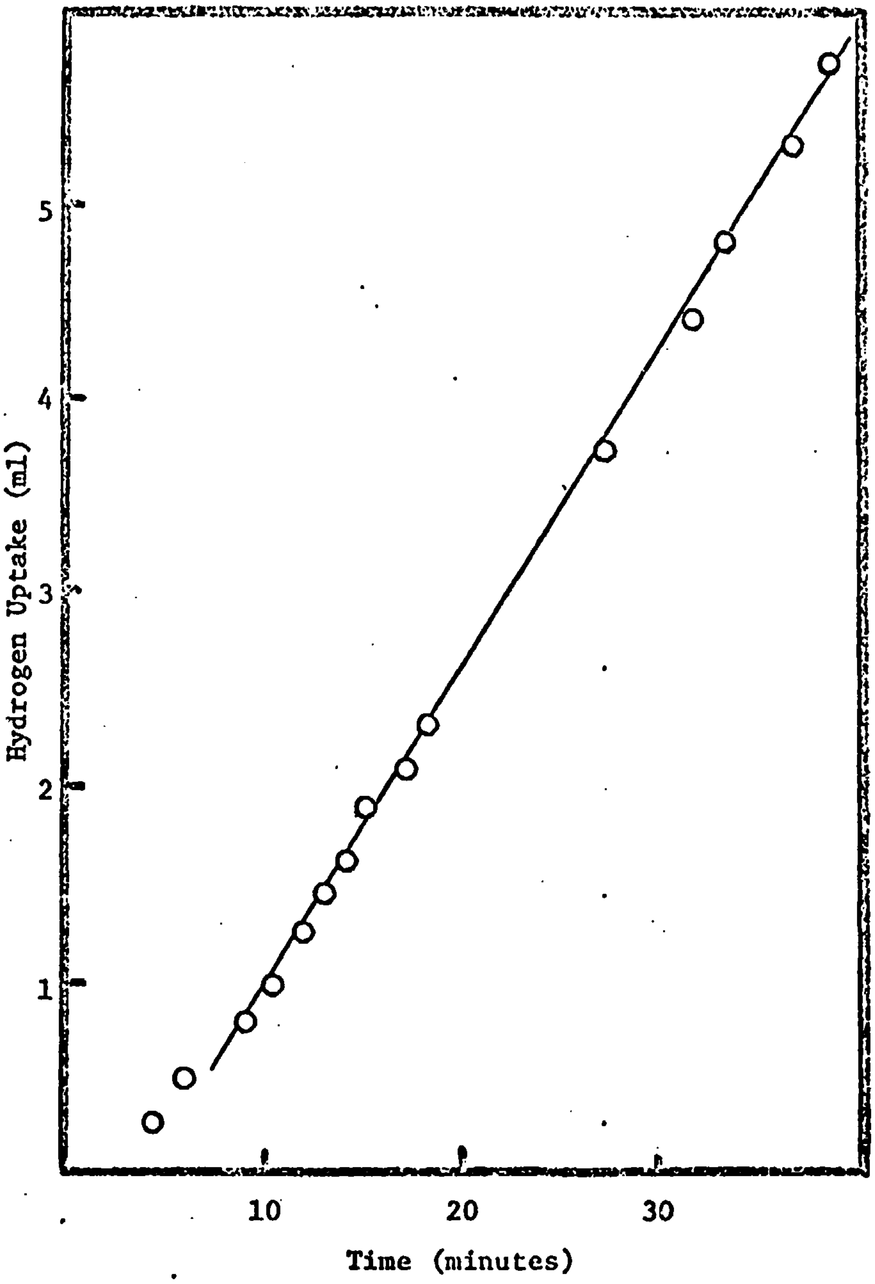
5) The apparatus is evacuated slightly to bring the internal pressure to 1 atmosphere.

6) Hydrogenation is ready to begin.

7) Whenever more substrate or poison is added, it is always added under positive hydrogen pressure.

Treatment of Kinetic Data

Figure 31 shows a typical hydrogenation run with the silica supported-SiP_2-Rh catalyst. The hydrogen uptake shows a linear, pseudo zeroth order rate over approximately 300 turnovers on the catalyst. This rate, analyzed by a least squares/linear regression analysis yields a reasonable slope (-0.171 ± .005 ml/min) which may be converted to turnover number (0.013± .001 mol H_2/mol Rh·sec).



reaction conditions: 25°, 1 atm H_2
5 ml benzene, 1.1 M 1-decene
0.2 g catalyst, 0.49% Rh (9.5×10^{-6} mol Rh)

Hydrogen uptake = 5 ml, 3×10^{-4} mol, or 300 turnovers on catalyst (Uptake during total experiment corresponds to hydrogenation of approximately 8% available olefin.)

slope = $-0.171 \pm .005$ ml/min, corresponding to
turnover number = $0.013 \pm .001$ mol H_2/mol Rh · sec

Figure 31. Rate of Hydrogenation with Silica Supported-SiP_2-Rh Catalyst.

III. SUMMARY

This work has shown that a chelating bisphosphine ligand [2-(3-triethoxysilylpropyl)-1,3-bis(diphenylphosphino)propane] can effectively support and immobilize an organometallic Rh(I) hydrogenation catalyst on a silica surface. Through a series of tests, this bound hydrogenation catalyst behaves in a manner expected of an analog of homogeneous organometallic Rh(I) catalysts and not like a metallic rhodium catalyst.

Eight tests on this new supported organometallic catalyst demonstrate: 1) selectivity in reducing hindered olefins at a significantly slower rate than unhindered olefins, 2) a linear correlation between the recriprocal rate of hydrogenation and the recriprocal olefin concentration, thus obeying rate laws for Wilkinson's tris(triphenylphosphine)chlororhodium(I) catalyst, 3) a dramatic solvent dependence of the supported organometallic catalyst paralleling an increased rate of hydrogenation of Wilkinson's catalyst with the increased ability of solvents to participate in stabilizing the coordinatively unsaturated catalytic intermediates, 4) a turnover number $\approx$ 0.4 mol H_2/mol Rh·sec (depending on conditions) which is consistent with homogeneous organometallic catalysts, 5) increasing catalyst activity as the rhodium becomes less concentrated on the silica surface, 6) some isomerization of 1-decene to 2-decenes, 7) a dramatically different rate of poisoning than demonstrated with heterogeneous catalysts, 8) and no metal crystallites visible in electron micrographs of this new supported organometallic catalyst. In at least one respect, isomerization, this new supported catalyst has unique catalytic properties not generally observed with either rhodium heterogeneous or homogeneous hydrogenation catalysts. This may be explained by the proximity of the close interactions with the silica support.

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