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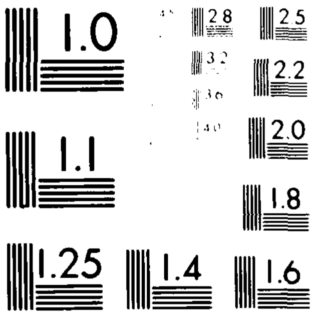

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A STUDY OF OXIDE-SUPPORTED HOMOGENEOUS CATALYSTS

A Final Report

David M. Hercules

September 19, 1980

U.S. Army Research Office

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The analog of $RhCl(CO)(PPh_3)_2$ was supported on both silica and alumina. Infrared and ESCA were used to study changes which occur when the complex reacts with CO. On silica, initially a square planar dicarbonyl complex is formed and at higher CO pressures a dimeric species. On alumina both the square planar and penta-coordinated dicarbonyls are formed. Dimeric species are formed from each kind of dicarbonyl and can be distinguished by their infrared spectra. (continued)

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20. Abstract

The supported complex listed above was used to study the liquid phase hydroformylation of 1-hexene. The observed activity and selectivity correlate with the nature of the Rh species on both silica and aluminum supports, as characterized by ESCA and IR. Under mild hydroformylation conditions the concurrent isomerization of olefin is catalyzed by the Rh complex and not by the support. Free phosphene in solution completely eliminates isomerization. The support influences the species that initiates the hydroformylation reaction and consequently influences the products of the reaction.

ESCA evidence has been presented that Wilkinson's catalyst, $RhCl(PPh_3)_3$ consists of two components: Rh(+1) and Rh(_3) species. It has been shown that this conclusion is consistent with chemical studies in solution. Hydrogenation studies have shown that the Rh(+3) species is an inactive catalyst. Elemental analyses suggest that the Rh(+3) species is not $RhCl_3(PPh_3)_3$ but an as of yet unknown Rh(+3) complex.

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2. List of Illustrations and Tables

3. Body of Report

The work performed has been in four areas, each of which will be summarized in detail below. We have approached the study of supported homogeneous catalysts from three directions: first, a study of the silanes used to attach the catalysts to oxides; second, spectroscopic characterization of appropriate homogeneous catalysts; and third, spectroscopic and chemical characterization of oxide-supported homogeneous catalysts.

A. Reactions of Oxide-Supported Chlorocarbonyl-bis(triphenylphosphine) Rhodium(I) with CO and H_2.

There has been much recent attention to supported Rh complexes as homogeneous catalysts. Many studies have been carried out with complexes supported on organic materials;[1-6] only a few have used inorganic supports.[7-9] In most cases, workers have been more concerned with catalytic activity of the supported homogeneous catalysts rather than the nature of the species on the support. This stands in contrast to studies of comparable homogeneous complexes in solution.[10-14]

We have studied an analog of $RhCl(CO)(Ph_3P)_2$ supported on alumina and silica to elucidate the different species present under conditions close to those used for hydroformylation. We have been particularly interested in seeing how these species vary with the support. Behavior was observed analogous to the homogeneous complexes in solution, although affected by the support. Species were observed that are unstable in the solid state and are likely intermediates in the catalytic reaction.

Appropriate structures are shown in Figure 1. Complex 1 was synthesized by reaction of $RhCl(Ph_3P)_3$ with CO according to the method of Wilkinson.[10] The complex, 2 [ν_{CO} 1962 cm^{-1}, m.p. 96-101°C (dec)] was prepared by reaction of $[RhCl(CO)_2]_2$ and 3 according to the procedure of the BP group.[15,16] Complex 2 was supported on silica gel (surface area 700 m^2/g, pore volume 1.0 cc/g) and on γ-alumina (surface area 200 m^2/g, pore volume 0.6 cc/g) by the method of the BP group,[17] modified as follows. Silica gel (5.0 g) dried in vacuo 24 hours at 100°C was suspended in benzene (30 ml) and 2 (1.0 g) in benzene (20 ml) was added. The mixture was refluxed for 20 hours. During this time most of the benzene was distilled away. After cooling, the solid was transferred to a soxhlet apparatus and extracted with benzene for 22 hours. Finally, the silica complex was dried in vacuo for 22 hours at 60°C (Rh content 2.0%). The method for alumina was the same except for the use of 0.25 g of complex and 1.25 g of alumina (Rh content 1.6%). Our modification of the BP procedure gave complexes having higher Rh content. All preparations were carried out in a [illegible] oxygen-free atmosphere. Solvents were degassed with nitrogen before u[illegible] CO and H_2 used were purchased from Union Carbide. Bulk Rh content of the catalysts was determined by x-ray fluorescence.

Reaction of the supported complexes with CO and CO + H_2 were carried out in an autoclave (Parr reactor) equipped with automatic temperature control and pressure indicator. All samples were evacuated 2 hours at 50°C before the gas was introduced.

Figure 1. Structures Appropriate to this Report

$RhCl(CO)(Ph_3P)_2$

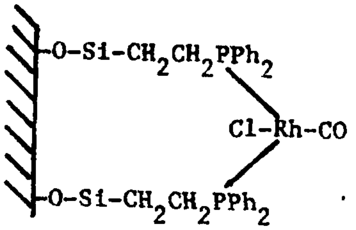
1

$RCl(CO)[Ph_2PCH_2CH_2Si(OEt)_3]_2$

2

$Ph_2PCH_2CH_2Si(OEt)_3$

3



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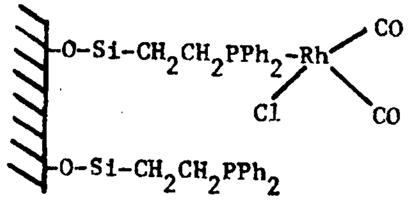

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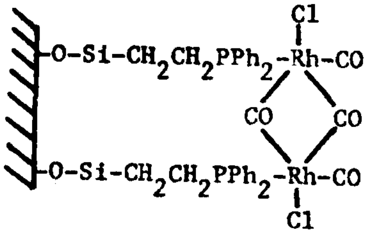

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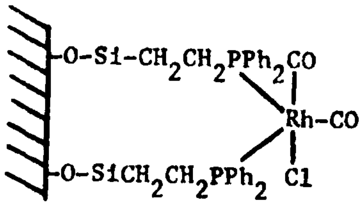

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Infrared spectra of 2 supported on silica gel (SiRh) and alumina (AlRh) were obtained as a function of CO exposure. Typical results for silica gel are shown in Figures 2 and 3. The data obtained for both SiRh and AlRh are given in Tables 1 and 2.

Silica Support. Complex 2 links to both silica and alumina retaining its trans configuration. This produces a supported complex having structure 4. This species gives a single CO stretching band at 1983 cm^{-1} on silica and 1978 cm^{-1} on alumina. Treatment with CO or CO + H_2 results in the formation of 5. In this case coordination with one phosphine ligand is replaced by coordination with CO. This cis-dicarbonyl complex is responsible for the two infrared bands at approximately 2080-2090 and 2010-2020 cm^{-1}. The same cis-dicarbonyl complex was obtained by the BP group using a different method of synthesis and shows infrared bands having the same frequencies.[16]

Under more extreme conditions the appearance of an 1800 cm^{-1} band indicates formation of a bridged structure involving at least two rhodium atoms. By analogy with Wilkinson's results[11] structure 6 is postulated as the bridging carbonyl species. Wilkinson observed that reaction of $RhH(CO)(PPh_3)_3$ in solution with CO gave first the dicarbonyl, $RhH(CO)_2(PPh_3)_2$ and then the dimer $[Rh(CO)_2(PPh_3)_2]_2$.

Structure 6 is unusual in the sense that normally binuclear platinum-metal complexes containing halogens tend to bridge via the halogens rather than by carbonyl ligands. However, such structures are not without precedent. Balch *et al.*[18] found a bridging carbonyl in a binuclear Pd-halogen complex, and Kubiah and Eisenberg[19] reported CO bridging in a binuclear Rh-halogen complex. Other factors support the assignment of structure 7. First, on the basis of ESCA results, the Rh remains in the (+1) oxidation state, and the chlorine content remains constant. Second, on standing, the complex reverts to 5 which requires only simple cleavage of the CO bridge bonds.

Another factor arguing for the presence of a bridged rhodium structure is that formation of structure 6 is reversible. The silica dimer 6 was suspended in benzene/ethanol and bubbled with N_2. In a short time, only the dicarbonyl species 5 was observed. An interesting parallel can be drawn with Wilkinson's dimer.[11] The latter is formed from the dicarbonyl species with loss of hydrogen, so the reaction can not be reversed without external hydrogen. When Wilkinson's dimer in solution is bubbled with N_2 it decomposes in benzene, but undergoes a solvent substitution reaction in a donor solvent. However, our dimer is formed without loss of ligands so the reaction can be reversed by itself and the solvent dimer is not formed.

Alumina Support. The AlRh data in Table 2 can be accounted for partly by species similar to those of SiRh. First, a square planar monocarbonyl complex (4) accounts for the band at 1978 cm^{-1}. Second, a square planar dicarbonyl complex (5) accounts for the bands at 2080 and 2000 cm^{-1}. Complex 5 forms the dimer (6) accounting for the bands at 1800 and 2080 cm^{-1}.

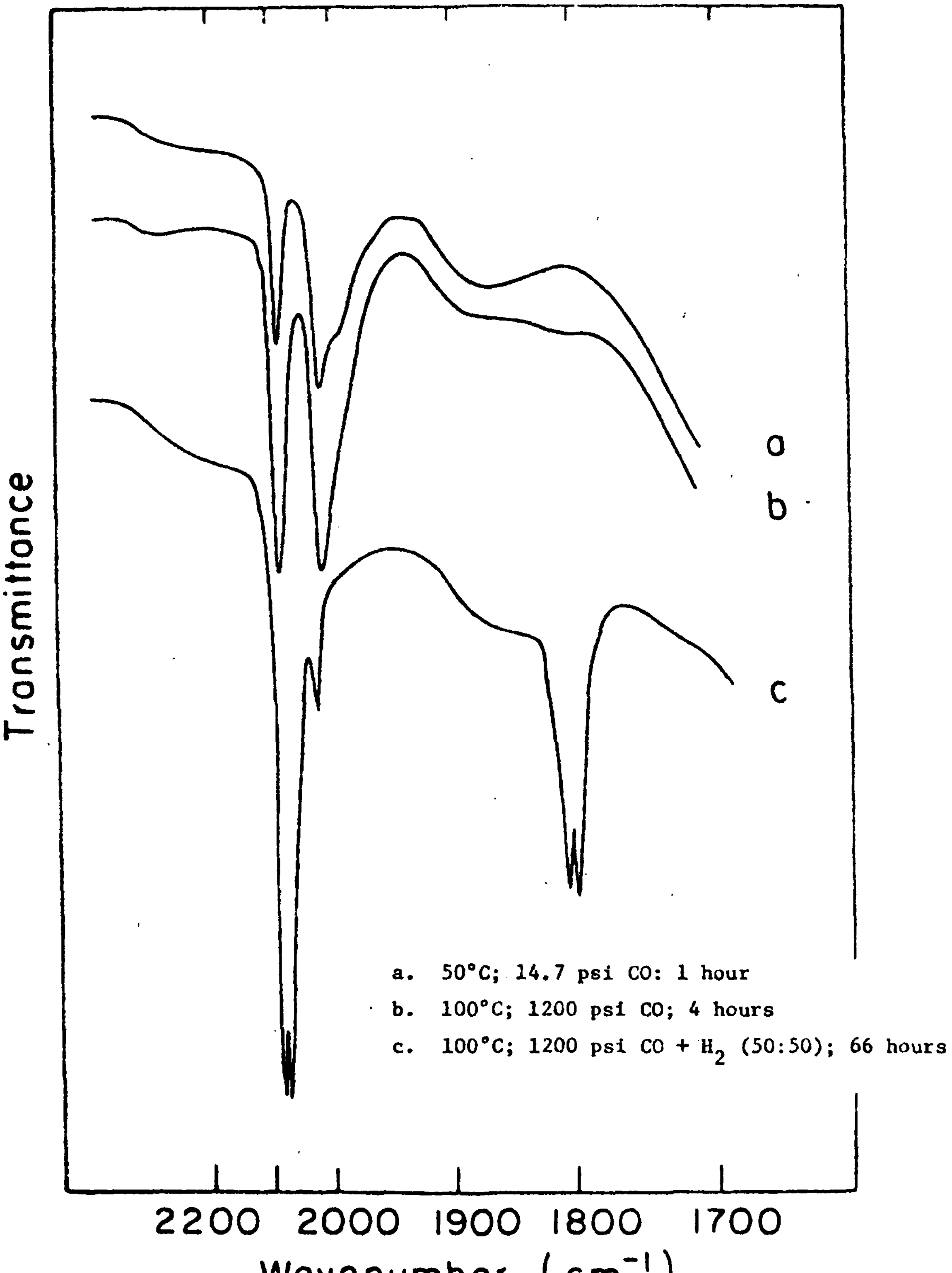

Figure 2 Infrared Spectra of Chlorocarbonyl-bis(Triphenylphosphine) Rhodium(I) Catalysts Supported on Silica

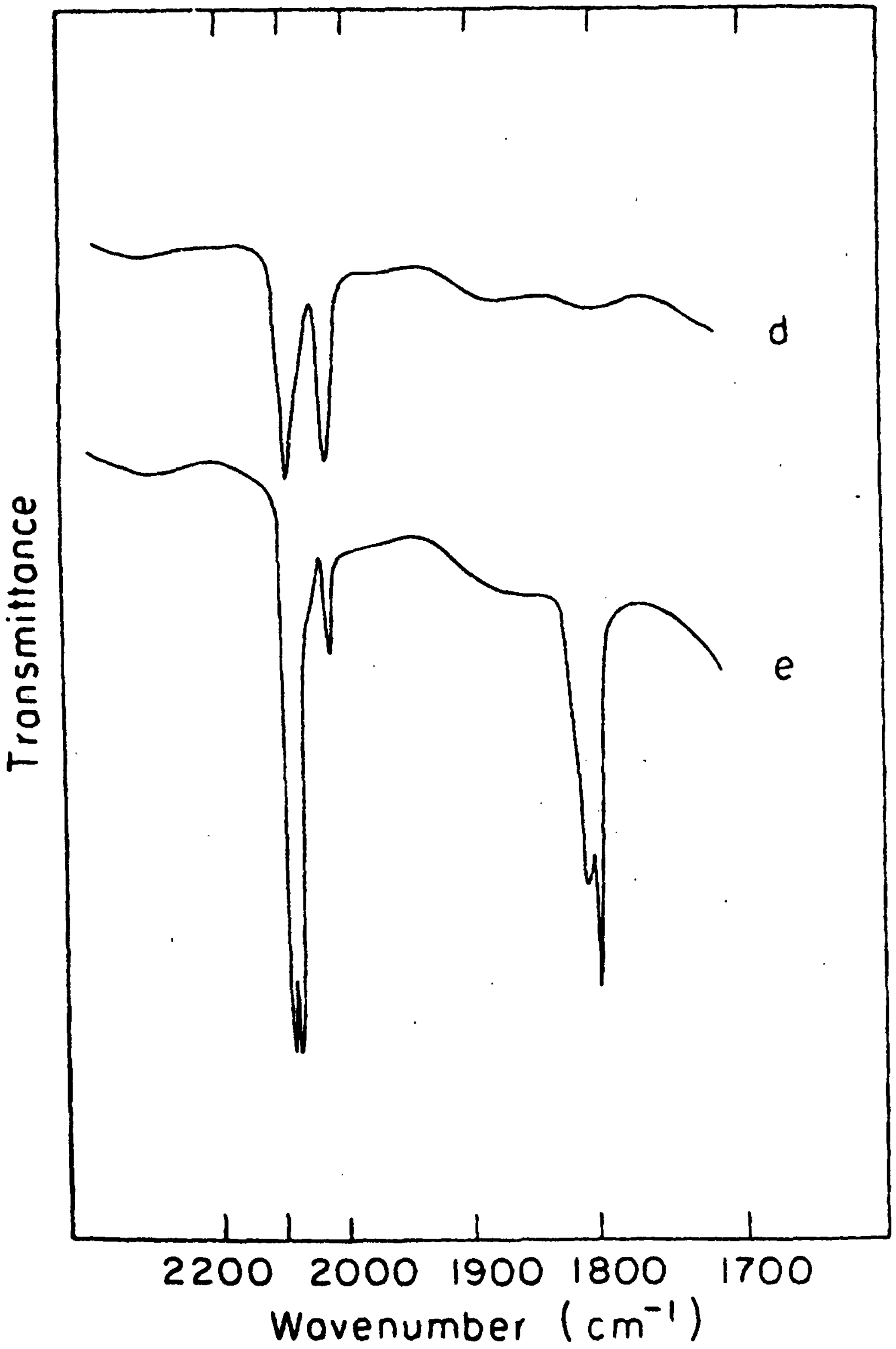

Figure 3 Infrared Spectra of Chorocarbonyl-bis(Triphenylphosphine) Rhodium(I) Catalysts Supported on Silica

d. sample c (Fig. 2) after 30 days

e. sample d at 100°C; 1400 psi CO; 70 hours

TABLE 1

Carbonyl Stretching Frequencies for SiRh Samples Treated with CO or CO + H_2.

Sample	Temperature °C	Pressure psi	Time hrs	Infrared Frequencies (cm^{-1})[a]	
				Terminal CO	Bridge CO
- SiRh	After Preparation			1983w	
2a SiRh	50	14.7	1	2090m 2020m 1985sh	
2b SiRh	100	1200	4	2082s 2012s	
2c SiRh	100	1200	66	2078d,vs 2024w	1804d,s
3d Sample c	after 30 days			2085m 2022m	
3e Sample d	100	1400	70	2078d,vs 2022w	1804d,s

[a] Abbreviations: vs: very strong; s: strong; m: medium; w: weak; sh: shoulder; d: doublet.

TABLE 2

Carbonyl Stretching Frequencies for AlRh Samples Treated with CO or CO + H_2.

Sample	Temperature °C	Pressure psi	Time hrs	Infrared Frequencies (cm^{-1})[a] Terminal CO	Bridge CO
- AlRh	After preparation			1978s	
4a AlRh	50	20	4	2080m 2052s 2022m 2000s 1981m	
4b AlRh	120	1400	52	2080m 2052sh 2020vs	1840m 1800sh
4c Sample b	After 15 days			2080m 2000m	
4d Sample c	100	1400	70	2078d,vs 2052m 2022sh 2000s	1800d,vs

[a] Abbreviations: vs: very strong; s: strong; m: medium; sh: shoulder, d: doublet

Because the entire alumina complex can be converted to the dicarbonyl form it is unlikely that steric restrictions are responsible for additional species. Therefore the bands at 2052 and 2022 cm^{-1} must be due to a different complex than the square dicarbonyl. We propose structure 7 for the new species found on alumina. This is a dicarbonyl pentacoordinate rhodium complex formed by coordination of an extra CO ligand with the starting square planar monocarbonyl complex. A similar kind of complex has been postulated for CO attack on the square-planar hydride species in Wilkinson's[20] hydroformylation mechanism. Structure 7 requires that both phosphine groups remain coordinated to the rhodium when the complex is supported on alumina. This is consistent with the fact that the band of the starting carbonyl, structure (4), which has both phosphine groups coordinated, is stronger and persists longer on CO treatment for alumina than for silica. Another argument for this complex is that pentacoordinated rhodium(I) chloride complexes have been reported widely in the literature.[12,21]

Complex 7 can lose a phosphorus ligand to form a dimer with bands at 2020 and 1840 cm^{-1}. We assume the latter dimer is similar to 6 but with the terminal CO trans to the chlorine. This postulate is supported by the lower frequency for the terminal CO and the higher frequency for the CO bridge compared with the CO frequencies for complex 6.

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B. Hydroformylation of 1-Hexene by SiRh and AlRh Catalysts.

The hydroformylation of olefins under homogeneous conditions has been widely studied. Heck and Breslow[22] proposed a mechanism that accounts for the observed activity, selectivity and effect of pressure on the products from the cobalt-catalyzed reactions. Changes in activity and selectivity induced by particular compounds (principally phosphines) was rationalized by Wilkinson[20] with his mechansim. Both mechanisms, however, appear to be essentially identical. The use of these complexes on a support allows one to preserve the great selectivity and activity associated with homogeneous systems, while the catalyst is easily recovered from reaction products. The open question, then, is to verify to what extent the properties of the supported catalysts parallel those of the homogeneous catalysts.

Hydroformylation reactions have been studied by many authors using complexes supported on polymers and on inorganic solids.[1,2,7,23,24] The results generally have been interpreted in terms of homogeneous mechanisms. The support appears to influence the catalytic system in remarkable ways, but this influence does not always appear to be well understood. Differences in behavior are found between different supports.

We have characterized different structures that exist for analogs of the $RhCl(CO)(PPh_3)_2$ anchored to alumina and silica, under conditions used for hydroformylation. We have studied the activity, selectivity, temperature- and pressure-dependence of the catalyst, along with the influence of the support, in the liquid phase hydroformylation of 1-hexene.

It is known that α-olefin isomerization occurs in many catalytic systems, concurrent with hydroformylation.[1,7] This causes some difficulty comparing the present data with literature results and limits the possibility of investigating the reaction mechanism using selectivity to normal aldehyde as a probe. To distinguish the aldehydes produced by Markownikov and anti-Markownikov addition to α-olefins from those produced by hydroformylation of the internal olefin, we studied the concentrations of reaction products as a function of time.

Figure 4 shows changes in product composition as a function of time for the silica supported complex. At 80°C and 45 atm of CO/H_2 (1:1) both silica (SiRh) and alumina (AlRh) supported complexes show an initial inhibition period necessary to form the active complex by hydrogenolysis of the Rh-Cl bond.[20] 2-Hexene, arising from isomerization of the starting olefin, is also observed. Under these conditions it is evident that all 1-hexene has reacted after 3 hrs, and the increase of aldehydes after 3 hrs originates from 2-hexene conversion to produce only iso-aldehyde as the slopes in Figure 1 suggest (compare lines marked o and x after 3 hrs).

Table 3 compares the results for silica and alumina supported complexes and for SiRh in the presence of triphenylphosphine. The maximum amount of the internal olefin (2-hexene) produced by AlRh is lower than that for SiRh, and the rate of reaction is faster for SiRh (see column marked "Partial Time" in Table 3). No difference in selectivity to normal aldehyde is found. In the presence of PPh_3, SiRh loses the tendency to form an internal olefin and so the absolute selectivity to normal aldehyde is increased. The 1-hexene conversion versus time for the SiRh catalyst in the presence of PPh_3 is shown in Fig. 5. No internal olefin is produced, but the rate of reaction is significantly lower.

The effects of temperature, pressure of CO/H_2 and pretreatment with CO on the activity and selectivity of the silica supported complex were studied. Pretreatment does not produce substantially different activity and selectivity either at higher temperature or at lower pressure. The effect of increasing temperature, on the other hand, is very evident. At 130°C the rate of 1-hexene conversion appears to be exceptionally fast; there is a large increase of internal olefin which is reflected in a lower selectivity to normal aldehyde. About 10% of alcohols (1-heptanol, 2-methyl-1-hexanol are also produced. In contrast, at 55°C, after 20 hrs, only 22% of 1-hexene has reacted yielding almost exclusively aldehydes.

Pressure also strongly influences the distribution of products. At low pressure (12 atm) a large increase of internal olefin is found, while at 95 atm aldehyde formation is significantly enhanced. The selectivity to normal aldehyde is also pressure dependent, being largest at low pressure. In all cases alcohols are produced only at high temperature.

In part 1 a square-planar monophosphine dicarbonyl **5** was obtained exclusively by carbon monoxide treatment and it was not possible to recoordinate the phosphine group. On alumina, in addition to the monophsophine complex, a pentacoordinated diphosphine **7** was formed.

TABLE 3

Hydroformylation of 1-Hexene by Silica and Alumina Supported Catalysts.

	1-hexene[a] %	max 2-hexene %	partial aldehydes[b] %	partial time (hrs)[b]	selectivity n-aldehyde[b,c]	absolute aldehydes[a] %	absolute time (hrs)	absolute selectivity n-aldehyde[a,c]
SiRh[e]	0	40.0	56.2	2.5[b] (1.4)[f]	2.7	100	20	0.8
AlRh	0	27.8	45.4	7.5[b] (5.0)[f]	2.7	79.4	22	1.3
SiRh + PPh_3[d,e]	5.0	---	---	--- (11.0)[f]	---	95.0	25	2.7

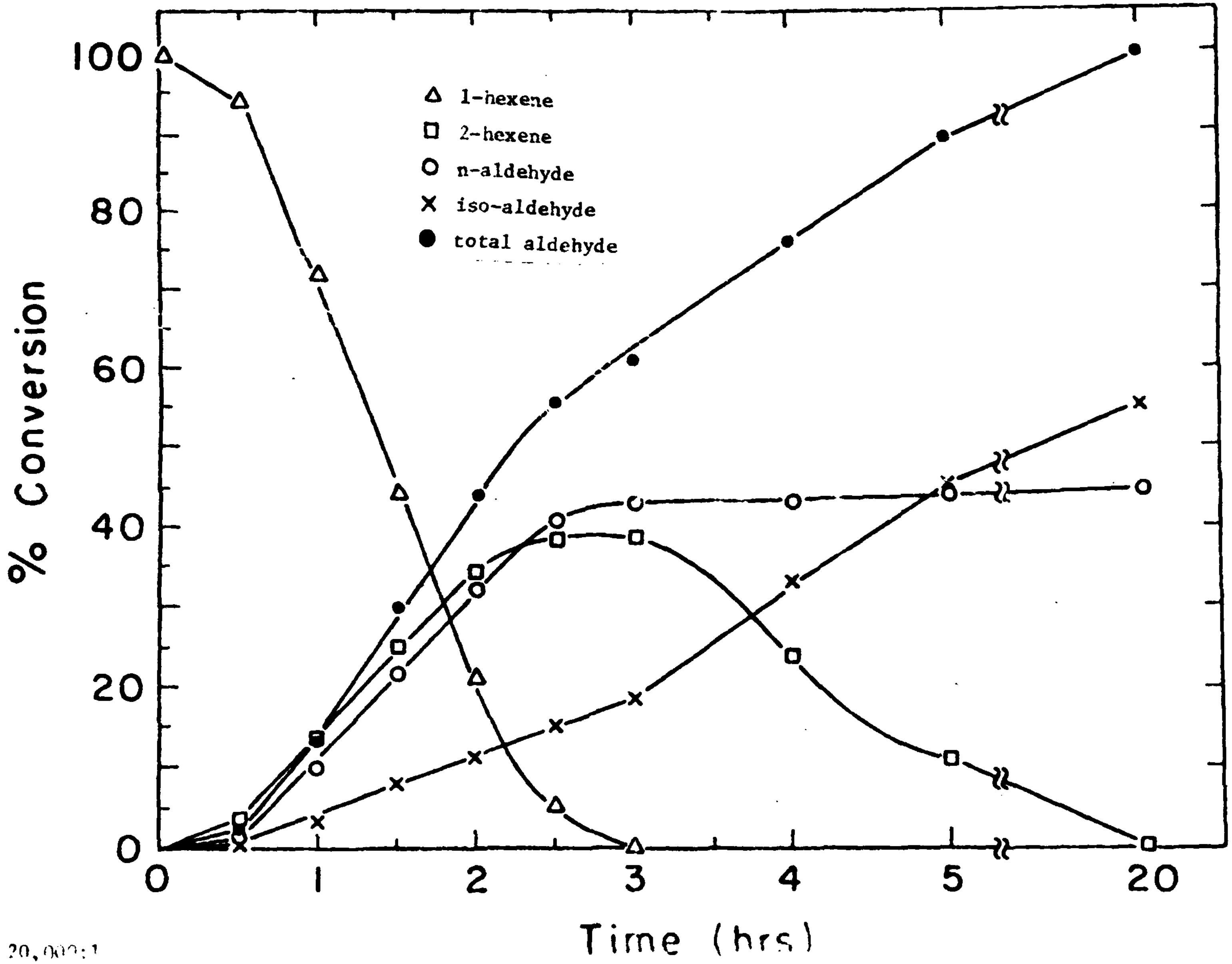
[a] End of reaction

[b] At max 2-hexene production

[c] Selectivity is defined as n-aldehyde/iso-aldehyde ratio

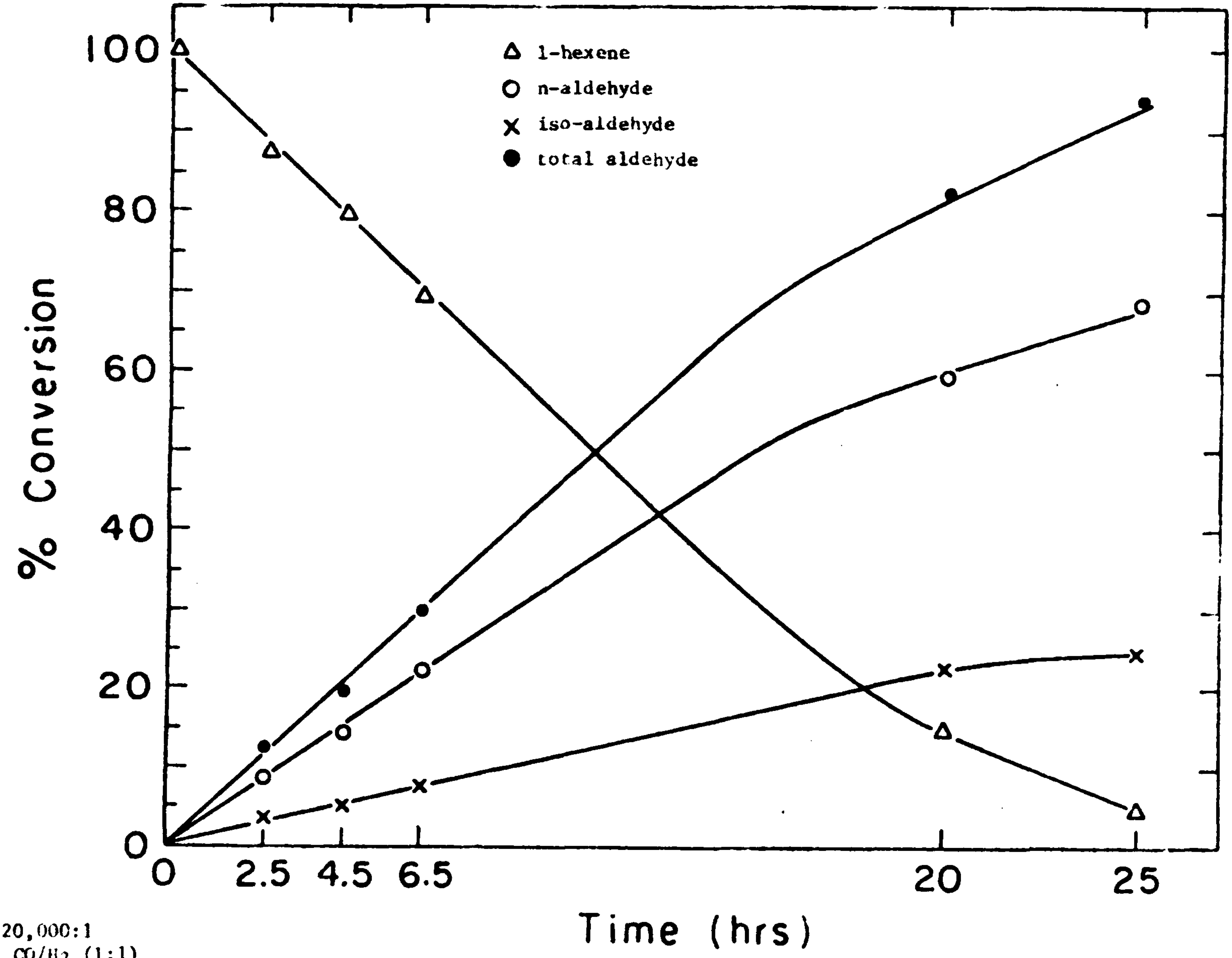
[d] PPh_3:Rh = 5:1

[e] Ratio olefin:Rh = 20,000:1, olefin in n-heptane 1:2 by volume, conditions: 80°C at 45 atm CO/H_2 (1:1)



Conditions:

olefin:Rh = 20,000:1



Conditions:

olefin:Rh = 20,000:1
80°C, 45 atm CO/H_2 (1:1)
olefin in n-heptane 1:2 by volume

Figure 5 - Hydroformylation of 1-hexene by SiRh + [illegible] catalyst

The activity and selectivity of both the silica (SiRh) and alumina (AlRh) supported complexes shown in Table 1 are consistent with our postulated structures. Thus the silica supported complex, changing under hydroformylation conditions into the monophosphine complex, 5, loses its selectivity for exclusive formation of aldehydes and internal olefins are produced. This result and the selectivity to normal aldehyde are consistent with the behavior of analogous monophosphine complexes under homogeneous conditions.[7] On an alumina support, the pentacoordinate complex, does not yield an internal olefin;[20] therefore the quantity of 2-hexene produced by our alumina-supported catalyst is lower than for silica. The lower rate of reaction for alumina-supported complexes orginates from the fact that complexes having greater numbers of phosphine ligands have lower reaction rates.[25]

Addition of PPh_3 in solution to the SiRh catalyst transforms all complexes into the diphosphine dicarbonyl pentacoordinated form, $RhCl(CO)_2[\quad PPh_2](PPh_3)$, 8; under these conditions no internal olefin is found. That complex 8 is formed for SiRh catalysts treated with PPh_3 is shown from increased ESCA intensity ratios for P/Si and P/Rh. The almost constant Rh/Si ESCA ratio with or without PPh_3 means that PPh_3 substitutes for only one PPh_2 ligand; if substitution of both PPh_2 ligands occurred, the Rh/Si ratio should be much lower for PPh_3 treated catalysts. The rate of reaction is still lower in the presence of PPh_3 because an excess of phosphine is known to inhibit the reaction.[20]

Some authors have indicated that the inorganic support is largely responsible for olefin isomerization.[7,26] Our results for SiRh treated with PPh_3 suggest that isomerization of the olefin is not caused by the hydroxyl group of the support at 80°C. As a test of this, using only silica in the presence of 1-hexene at 80°C, 45 atm CO/H_2 for 4 hrs, no trace of 2-hexene was found. Thus, isomerization of the olefin is caused exclusively by a supported rhodium complex.

We found that ∿10% of alcohol is produced at high temperatures. Under homogeneous conditions with analogous complexes more severe conditions are required for alcohol production.[27] For supported catalysts, alcohols are found when nitrogen ligands are present.[1]

This work has been submitted for publication: Journal of Physical Chemistry

C. Studies on Wilkinson's Catalyst

Among homogeneous catalysts, Wilkinson's catalyst[28,29] is one of the best hydrogenation catalysts. It is easy to use. Its activity on a metal-weight basis is greater than many well known heterogeneous catalysts. It performs rapidly under mild conditions. It is highly specific for the hydrogenation of olefins, polyenes, conjugated polyenes (except aromatics) and acetylenes, and shows some selectivity within this group of substrates. It lends itself to detailed mechanistic studies. It has been possible to isolate and study some of the intermediates which occur in the catalytic cycle and show how various inhibitors and poisons operate at a molecular level.

The literature on Wilkinson's catalyst reports that it consists of a single species, $RhCl(PPh_3)_3$, **9**. In this paper we report evidence that the standard preparation of Wilkinson's catalyst yields a mixture of two species; the active Rh(I) species, **9**, and an inactive Rh(III) species. Further, we demonstrate that it is possible to prepare pure **9** and that it is more active than Wilkinson's catalyst (WC).

Speciation - The Rh 3d ESCA spectrum of Wilkinson's catalyst is not the expected doublet. Figure 6 shows a comparison of spectra for Wilkinson's catalyst and another Rh(I) complex. The deconvoluted spectrum of Wilkinson's catalyst indicates that two species are present. An extensive compilation of Rh 3d binding energies suggests that the lower binding energy doublet is due to a Rh(I) species, and the higher doublet is characteristic of a Rh(III) species.[30-32] The spectrum shown in Fig. 1 is typical of the spectra observed for all samples of Wilkinson's catalyst (both red and orange forms) which have been obtained from a vareity of sources, including our own preparation. A wide scan of the sample showed no elements present other than rhodium, chlorine, phosphorus and carbon. Further, the intensity ratio of the high energy doublet to the lower energy doublet was always approximately 2:3, regardless of source.

X-ray Effects - To determine if exposure to x-rays in the ESCA source was causing possible decomposition of Wilkinson's catalyst a time study was conducted. Spectra were obtained at different times while the sample was continuously exposed to an x-ray power of 400 watts. Even after 20 hours in the instrument under x-ray exposure there was no appreciable change from the initial spectrum. Therefore, it was concluded that no decomposition is occurring in the spectrometer source.

Oxidation-Reduction of the Catalyst - To determine the nature of the Rh(III) species in Wilkinson's catalyst oxidation and reduction reactions were carried out as shown in Figure 7. First, chorine was bubbled through a benzene solution of WC yielding a solid which gave the spectrum shown in Fig. 7B. This treatment caused the rhodium to be totally oxidized to the Rh(III) species. Another portion of WC solution was reacted with sodium borohydride causing total reduction to the Rh(I) species as shown in Fig. 7C. The atomic ratios for these compounds indicate that the Rh(III) species has three times as much chlorine as the Rh(I) species. Further, the amounts of carbon and phosphorus are approximately equal in both compounds. This leads to the conclusion that the high binding energy Rh species in Wilkinson's catalyst is probably the octahedral complex $RhCl_3(PPh_3)_3$.

Preparation of the Rh(III) and Rh(I) Species - To further confirm the nature of the Rh(III) species preparation of both $RhCl_3(PPh_3)_3$ and $RhCl(PPh_3)_3$ was accomplished via independent synthetic routes. The octahedral complex is prepared in a manner very similar to that of Wilkinson's catalyst. Both preparations start with $RhCl_3$ and PPh_3. However, in the trichloro preparation stoichiometric amounts of the two starting reagents are used and the temperature is lower by about 30°C. We have not been able to prepare the Rh(III) species with less than 10% contamination by the Rh(I) compound. Pure Rh(I) species was prepared by the following reaction:

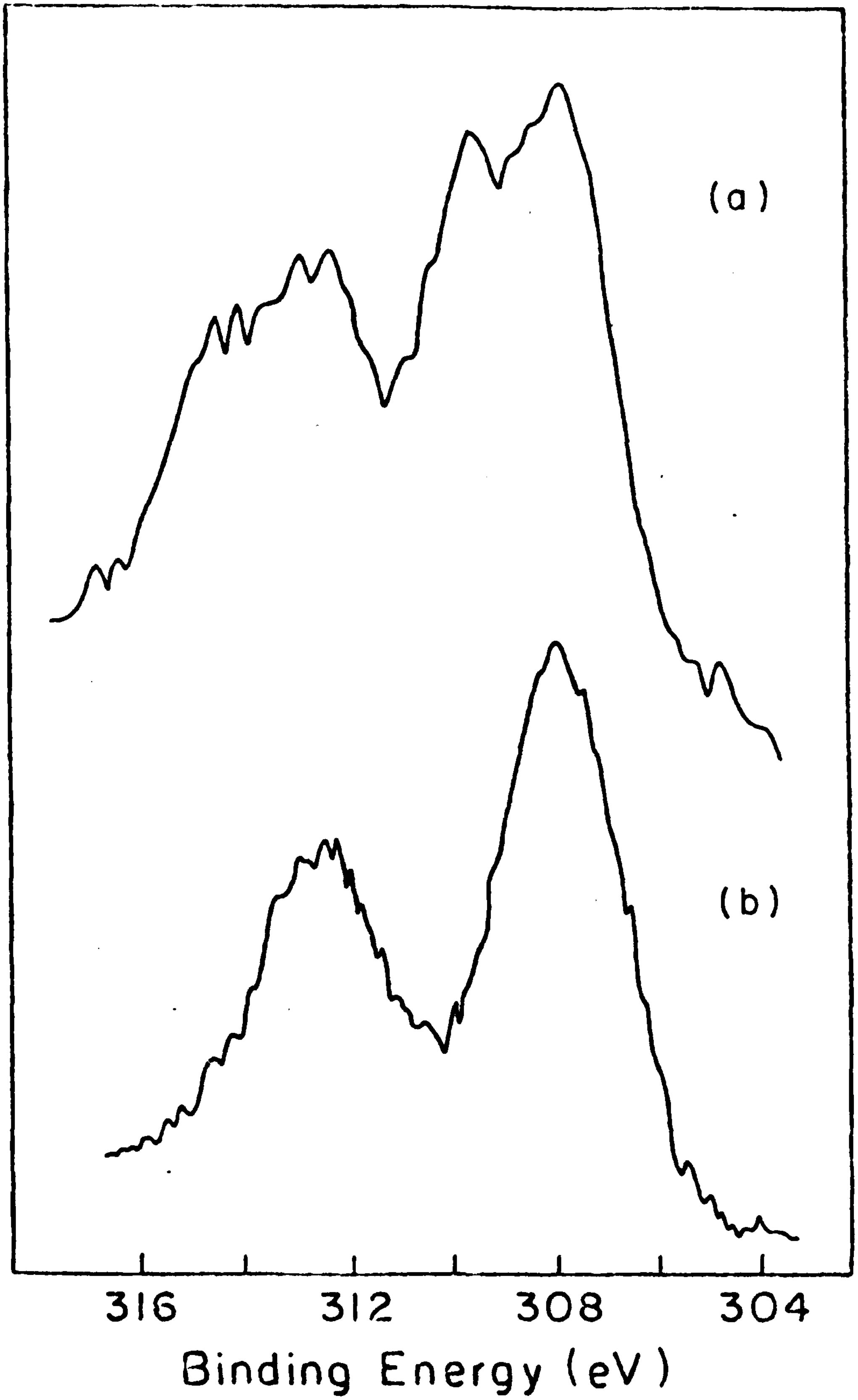


Figure 6. Rhodium 3d spectra of Wilkinson's catalyst (a) compared with the Rh(I) compound $[RhCl(C_2H_4)_2]_2$ (b).

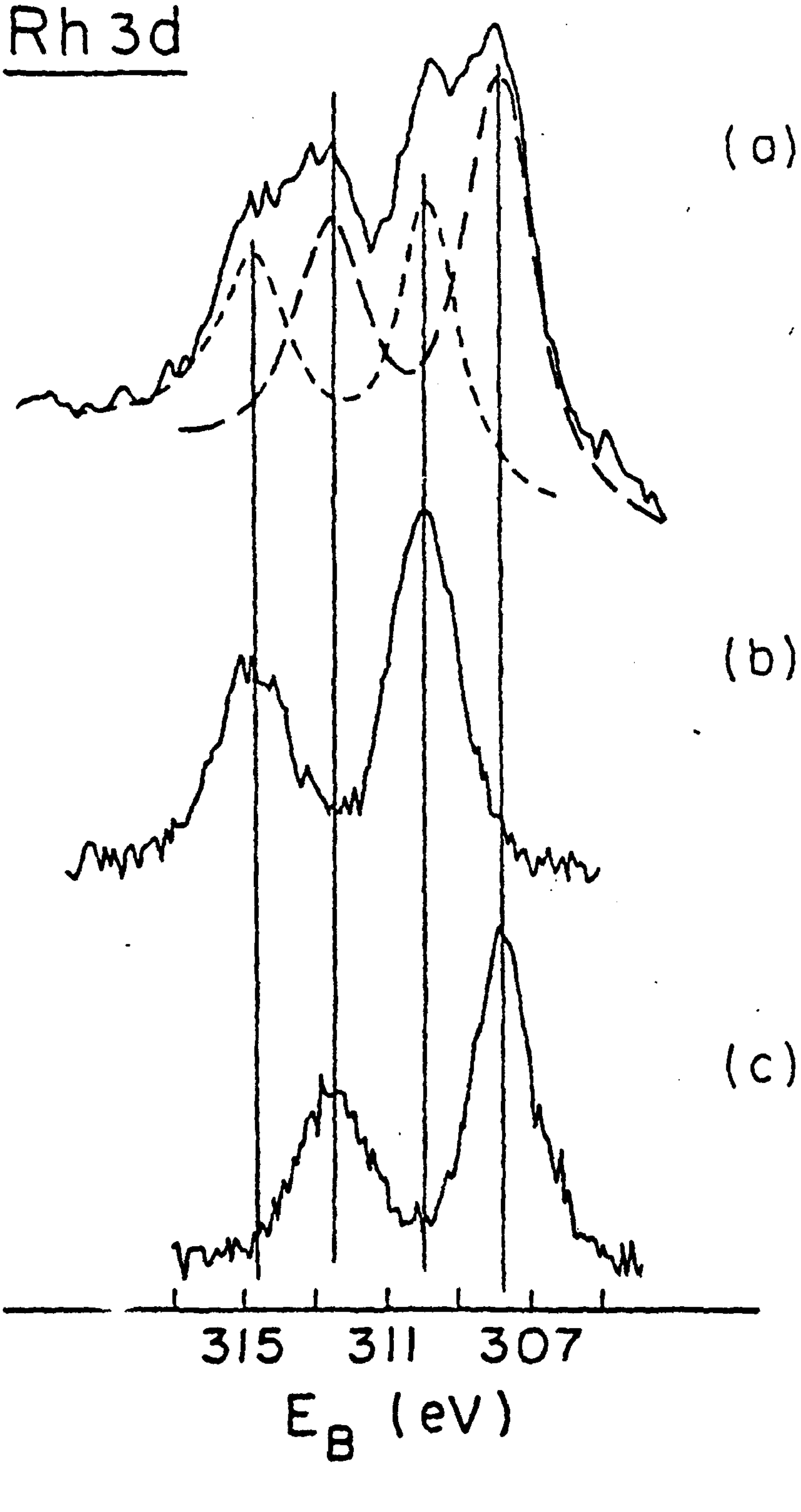


Figure 7. Oxidation and reduction behavior of Wilkinson's catalyst. a) Wilkinson's catalyst, b) Product of bubbling chlorine through a solution of Wilkinson's catalyst, c) Product of Wilkinson's catalyst reaction with $NaBH_4$.

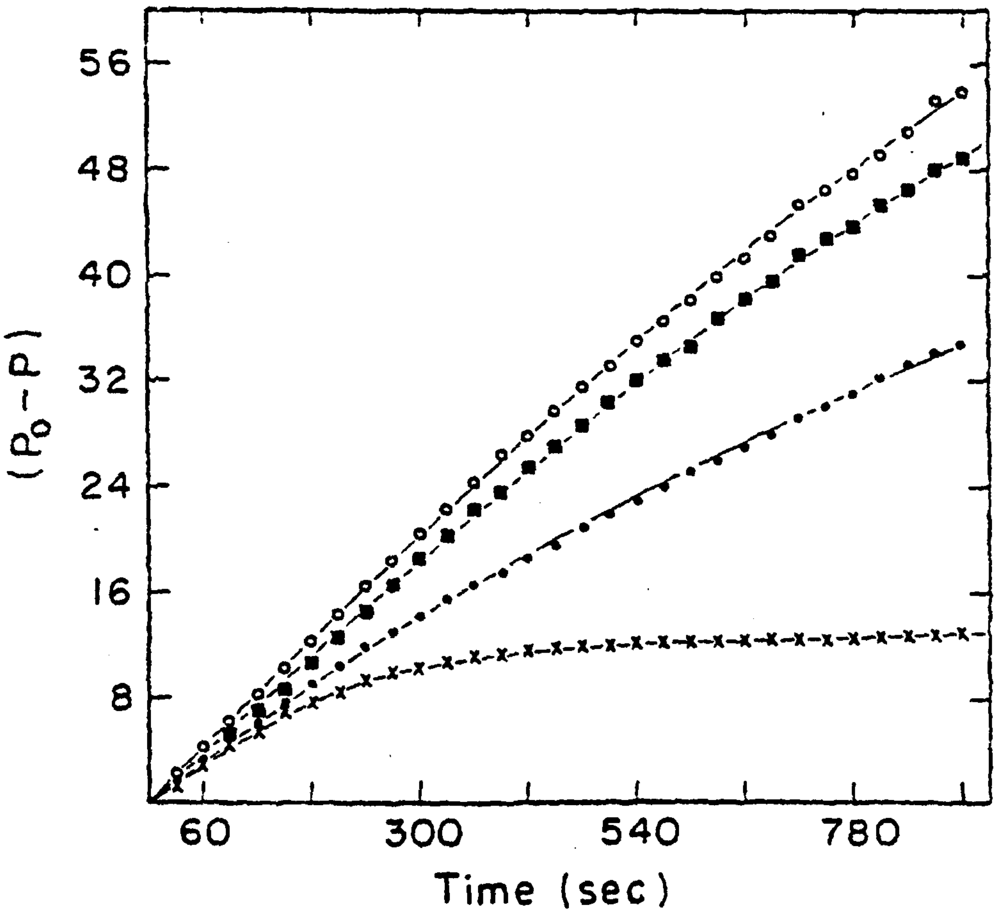
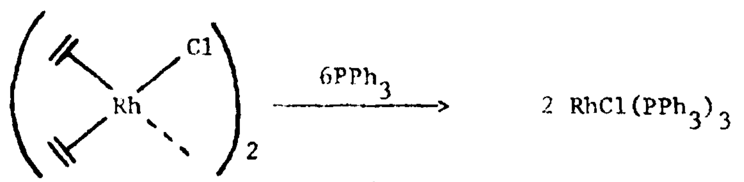


Figure 8. Qualitative comparisons of the rate of cyclohexene (10.0 ml - 9.86 x 10^{-2} moles) hydrogenation in benzene (25 ml) by 10^{-4} moles of: (o) $RhCl(PPh_3)_3$; (■) a ten-fold mole excess of $RhCl_3(PPh_3)_3$; (·) Wilkinson's catalyst; (x) $RhCl_3(PPh_3)_3$ contaminated by 10% $RhCl(PPh_3)_3$.



The Rh 3d binding energy of the Rh(III) compound matches that of the high energy doublet in Wilkinson's catalyst. Similarly, the Rh(I) compound has the same binding energy as the low energy doublet in Wilkinson's catalyst. The atomic ratios are consistent with the mono- and the chlorides.

To confirm the proposed idea of a mixture catalytic hydrogenation of cyclohexene was carried out. Comparisons of hydrogenation rates for the three compounds are shown in Figure 8. The data of Figure 8 confirm the speciation effect since Wilkinson's catalyst shows activity between that of $RhCl(PPh_3)_3$ and $RhCl_3(PPh_3)_3$. The turnover number for Wilkinson's catalyst was calculated from GC data to be 0.21 sec^{-1} which is in reasonable agreement with literature values.[33] The turnover number for $RhCl(PPh_3)_3$ is 0.30 sec^{-1} and 0.08 sec^{-1} for $RhCl_3(PPh_3)_3$. Given that the rate of hydrogenation is directly proportional to catalyst concentration,[28] in Fig. 5, the slope of the hydrogenation curve of Wilkinson's catalyst is approximately 60% of the slope for the hydrogenation curve of the Rh(I) species. This gives excellent confirmation of the ESCA results which also indicated that the Rh(I) species comprised about 60% of the total catalyst.

The lower curve in Figure 8 is for the hydrogenation of cyclohexene with $RhCl_3(PPh_3)_3$ as a catalyst. The activity of this catalyst probably is due to the ca. 10% contamination of $RhCl(PPh_3)_3$, shown by ESCA. The tendency of the curve to flatten out is presumably due to the excessively large substrate-to-catalyst ratio. To confirm this the catalyst amount was increased ten-fold, which has the effect of increasing the active species $(RhCl(PPh)_3)_3$ to the same level as used in the top curve of Figure 8. The plot is almost identical to that of the Rh(I) species as expected.

From the above discussion, it is clear that Wilkinson's catalyst consists of two compounds, probably the Rh(I) and Rh(III) compounds proposed. To further demonstrate this effect, we carried out two sets of experiments, one of which confirmed two components and the other giving rise to some confusion.

Samples submitted for elemental analysis gave the following data:

	percent					
	C	H	Cl	P	Rh	Total
Wilkinson's Catalyst	67.8	4.98	3.84	9.63	9.42	95.6
(theory)	68.1	4.80	6.5	9.7	10.8	---
$RhCl(PPh_3)_3$	65.8	4.76	4.07	9.31	9.11	93.1
(theory)	70.1	4.90	3.7	10.0	11.1	---
$RhCl_3(PPh_3)_3$	60.3	4.46	9.59	8.66	7.84	90.9
(theory)	65.1	4.60	10.7	9.3	10.3	---

*as a 60/40 mixture

Obviously the elemental analyses do not support the idea of a 40/60 mixture. However, the low total percentages lead one to question the validity of the results. We have submitted additional samples for analysis to measure the reproducibility of the above.

We have done some preliminary studies of the HPLC of Wilkinson's catalyst. In a CH_3CN/phosphate buffer, two major peaks of about equal intensity are observed. This supports the idea of a mixture. We are currently carrying out a more thorough HPLC study to compare Wilkinson's catalyst with authentic samples of $RhCl(PPh_3)_3$ and $RCl_3(PPh_3)_3$.

Once the HPLC study is completed and the results of elemental analysis have been resolved, the work will be submitted for publication.

D. Structural Studies of Silated Surfaces

We have obtained ESCA and SIMS spectra of silated surfaces. Interpretation of these spectra was difficult because of the lack of suitable reference spectra; for example, virtually no mass spectra of the silanes have been reported in the literature. Therefore, we did spectroscopic characterization of the silanes prior to attachment to the surfaces. The silanes which have been studied are:

$(CH_3CH_2O)_3Si(CH_2)_3NH_2$ (A-1100)
$(CH_3O)_3Si(CH_2)_3NHCH_2CH_2NH_2$ (A-1120)
$(CH_3O)_3Si(CH_2)_3NHCH_2H_2NHCH_2CH_2NH_2$ (H-5162)
Polyaminofunctional Silane (Z-6050)
$(CH_3O_3Si(CH_2)_3NHCH_3$ (XZ-2-2024)
$(CH_3O)_3Si(CH_2)_3NHC_6H_5$ (Y-5699)
$(CH_3O)_3Si(CH_2)_3N(CH_3)_2$ (Y-5822)
$(CH_3O)_3Si(CH_2)_3NH(CH_2)_3CH_3$ (Y-9020)

Our intent is to study the interaction of the amine functional group as a function of its substitution pattern. Control compounds consisting of a set of n-propyl and n-butyl amines with similar substitution patterns were also studied. The control amines allow for interferences from the amine-amine interactions.

Electron impact mass spectra (70 eV and 15 eV), proton NMR, ^{13}C NMR and IR spectra have been recorded for the bulk silanes. To date the mass spectra data have proved to be most interesting and indicate a nitrogen interaction between the head and tail of the compound. For the silanes Y-5669 ($-NHC_6H_5$) and Y-5822 ($-N[CH_3]_2$), where the phenyl and methyl groups are expected to prevent any amine-silicon interactions one sees simple 15 eV spectra with strong molecular ion peaks and $CH_2NHC_6H_5^+$ or $CH_2N(CH_3)_2^+$ as base peaks. For Y-9020 ($-NHCH_2CH_2CH_2CH_2$) and XZ-2-2024 ($-NHCH_3$) where the butyl and methyl groups are expected to block the amine, one also sees base peaks of $CH_2NHCH_2CH_2CH_2CH_3^+$ and $CH_2NHCH_3^+$, but without the strong molecular ion peaks.

For XZ-2-2024 and A-1100 (-NH_2) strong peaks occur for the loss of the entire organic chain and for the loss of CH_3O or CH_3CH_2O groups. For A-1120 (-$NHCH_2CH_2NH_2$), Y-5162 (-$NHC_2H_4NHC_2H_4NH_2$), and Y-9020, strong peaks are observed at 192 and 160 with the 160 peak being the base peak for A-1120 and Y-5162. The 192 peak is $(CH_3O)_3SiCH_2CH_2CH_2NHCH_2^+$, while the 160 peak is $(CH_3O)_2SiCH_2CH_2CHNHCH_2^+$. A-1120 and Y-5162 also show strong loss peaks for CH_2NH_2 and $CH_2NHCH_2CH_2NH_2$ and further loss of alkoxy fragments. Thus for amine silanes where the amine nitrogen is not sterically hindered there is a significant interaction between the amine group and the silica atom.

Infrared spectra were obtained for the silanes and showed no interesting first-order effects. A more thorough IR study is planned to see if the amine-silicon interaction can be detected.

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