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Anchored Wilkinson Catalyst

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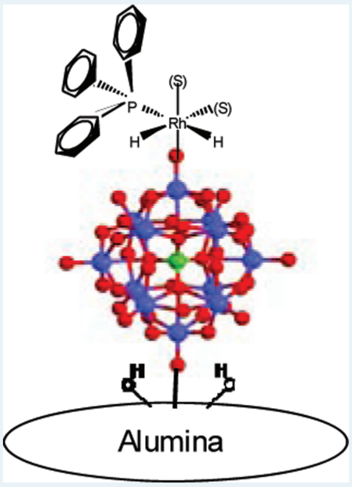
ABSTRACT: A series of Anchored Wilkinson's Catalysts were prepared by the reaction of the homogeneous Wilkinson catalyst with alumina/heteropoly acid support materials. It was found that the catalytically active species from these materials were unique in that they had only a single triphenylphosphine and a heteropoly acid as ligands giving these catalysts distinctive steric and electronic characteristics. These catalysts were used to promote the hydrogenation of 1-hexene and limonene with substrate to catalyst ratios of 10,000 and 7,500 respectively. The results were compared with those obtained using the homogeneous Wilkinson and 1% Rh/Al_2O_3 catalysts with respect to catalyst activity and stability as well as the reaction selectivity as measured by the amount of double bond isomerization observed. The observed rates of hydrogen uptake and double bond isomer formation in the hydrogenations of both 1-hexene and limonene follow the same order with respect to the nature of the heteropoly acid ligand used to anchor the Wilkinson catalyst to the alumina: silicotungstic acid > phosphotungstic acid > phosphomolybdic acid > silicomolybdic acid for hydrogen addition and the reverse for isomerization. This consistency provides a measure of the electronic character of these Keggin heteropoly acids when acting as ligands. In contrast to the reactions observed with the anchored catalysts the homogeneous Wilkinson catalyst was incapable of completing these high substrate/catalyst ratio hydrogenations. It became deactivated at about 85% 1-hexene conversion and only 10% limonene hydrogenation. As compared with the anchored catalysts the supported Rh promoted more isomerization of 1-hexene and limonene while the hydrogenation of the trisubstituted double bond in *p*-menthene was more difficult over the supported metal catalyst than with the sterically more accessible anchored Wilkinson catalysts.



KEYWORDS: hydrogenation of alkenes, anchored homogeneous catalysts, heteropoly acid effect, alkene isomerization, alkene hydrogenation, 1-hexene hydrogenation, 1-hexene isomerization, limonene hydrogenation, limonene isomerization, Wilkinson catalyst

INTRODUCTION

The first successful organometallic homogeneous hydrogenation catalyst, $RhCl(P\Phi_3)_3$, (**1**), was developed by Wilkinson in 1966.[1] Extensive research in subsequent years led to the generally accepted mechanism for alkene hydrogenation shown in Scheme 1, in which the initial step is dissociation to give the bisphosphine intermediate, **2**. Addition of hydrogen forms the dihydride, **3**, which then reacts with an alkene. Transfer of one hydrogen produces an organometallic intermediate, **4**, which then gives the alkane after the second hydrogen transfer. Initially, it was proposed that the two hydrogens were added almost simultaneously[2,3]but double bond isomerization and deuterium scrambling data indicated a two step addition mechanism was operating, especially in an ethanol solvent.[4,5]

While homogeneous catalysts such as **1** are generally selective and capable of promoting a variety of synthetically useful reactions, their use is hampered by the need to remove them from the product mixture. Not only can this present a separation problem but, when the more expensive platinum metal chiral complexes are used, there is also an economic factor leading to the need to recover the catalyst, not only the metal but also the ligand which is frequently more expensive than the metal itself. Since heterogeneous catalysts are more readily separated from the reaction mixture, it was considered that by immobilizing a homogeneous catalyst on a solid support the resulting material would have the activity and selectivity of the homogeneous species combined with the ease of separation of the heterogeneous moiety. It only took a few years after the discovery of the Wilkinson catalyst before reports began to appear in the literature describing the preparation of an immobilized Wilkinson catalyst.[6−10] These early reports described the modification of polystyrene by the introduction of a diphenylphosphine moiety and the use of this heterogeneous ligand to prepare the "heterogenized" Wilkinson catalyst.

Later methods used to immobilize the Wilkinson catalyst include the preparation of a ROMPgel containing the triphenylphosphine moiety[11] and attachment of an alkyldiphenylpho-

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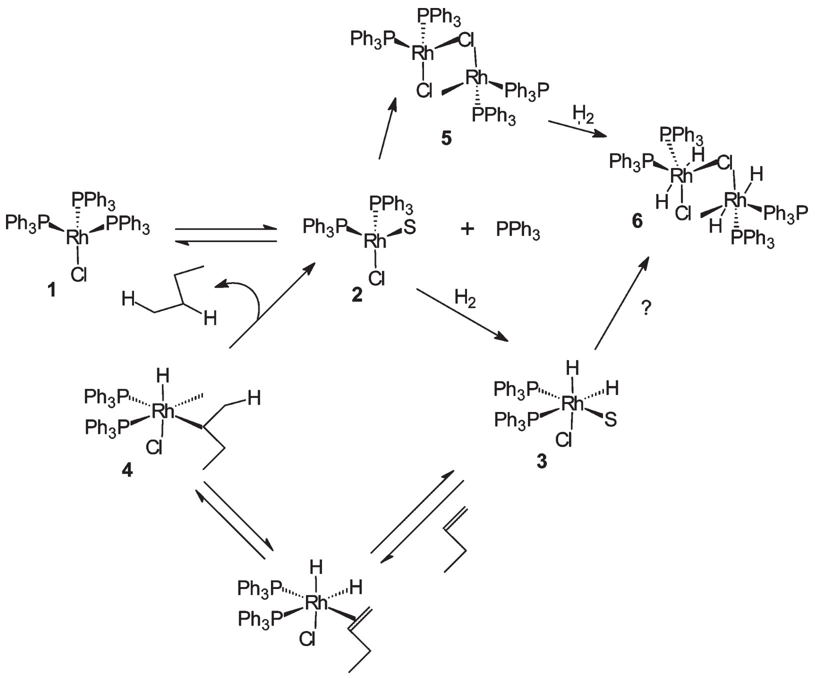
Scheme 1



sphine ligand onto oxide supports using siloxane “tethers”.[12−14] More direct approaches used the adsorption of the complex onto mesopourous SBA-15,[15] intercalation in clays[16,17] or, even, incipient wetness adsorption on alumina or carbon.[18,19] Most of this work involved the use of low substrate to catalyst ratios (turnover numbers, TONs) for catalytic hydrogenations along with little or no information concerning the possible loss of rhodium during the reaction nor any comparison with the homogeneous **1**.

With the Anchored Homogeneous Catalyst (AHC) technology the catalytically active complex was attached to an oxide support using a heteropoly acid (HPA) as the anchoring agent.[20,21] Early work in this area established that even though other supports such as montmorilonite and lanthana could be used, γ-alumina was the support of choice when these AHCs were used in liquid phase reactions such as hydrogenations.[20] No loss of HPA or Rh complex was observed with these systems. Since more acidic supports such as silica were not effective, it was considered that the anchoring took place by the interaction between the HPA and the basic sites on the alumina. It was further shown that all three components of the AHC were needed; the support, the HPA, and the complex. No interaction between the alumina and the complex was ever observed.[27] These anchored catalysts have been used for a variety of chiral and achiral hydrogenations, many at high substrate to catalyst ratios, with no observable leaching of the complex.[20−39] Since the AHC catalysts were prepared by the interaction between a supported HPA and a cationic Rh or Ru complex there was some thought that the resulting catalysts were ion pairs. However, UV[22,27] and ^{17}O NMR[40] evidence support the concept that the metal ion of the complex is directly bonded to an oxygen on the surface of the HPA.

The Wilkinson catalyst, **1**, is non-cationic so it was of interest to ascertain how it would interact with a supported HPA to, possibly, produce an anchored catalyst. The reaction of alumina/HPA with **1** took place almost as readily as did the reaction with a cationic Rh complex. In an initial report on the use of this anchored species it was shown to be superior to the homogeneous **1** for alkene hydrogenations, especially at high TONs.[26] However, these reactions were run in a toluene/EtOH solvent in the mistaken belief that some toluene was needed to stabilize the anchored catalyst. Another preliminary report briefly described a comparison of the HPA anchored Wilkinson catalysts with the homogeneous **1** and a 1% Rh/Al_2O_3 catalyst for the hydrogenation of 1-hexene.[28] This report showed that with the reactors used, stirring rates above 1600 rpm were sufficient to minimize mass transport limitations in these reactions. This was further supported by the finding that the Anchored Wilkinson (AHC Wilk) catalyzed reaction had an activation energy of 36.4 kJ/mol, a value sufficiently close to that commonly accepted for reactions run in the kinetic regime (40 kJ/mol) so that, when considered in conjunction with the stirring effect data, it can reasonably be assumed that mass transport was not significant in these reactions. It was also determined that the hydrogenation was first order in hydrogen, and at the higher substrate concentrations used, it approached pseudo zero order in alkene.[28]

Another factor of interest was the effect which the HPA exerts on the activity and selectivity of the anchored catalyst. A previous report found that the Keggin HPAs can have an influence on the outcome of low TON hydrogenations run over AHCs.[25] However, since this study involved the use of rhodium and ruthenium complexes containing several different chiral and achiral bisphosphine ligands it was not possible to draw any definitive conclusions concerning the relative influence which the HPAs have on the hydrogenations studied. Nothing definitive could be drawn from the partial data in the preliminary report cited above[28] since there was only a one point comparison provided and that was the composition of the reaction mixtures when 70% of the 1-hexene had reacted, either by hydrogenation or by

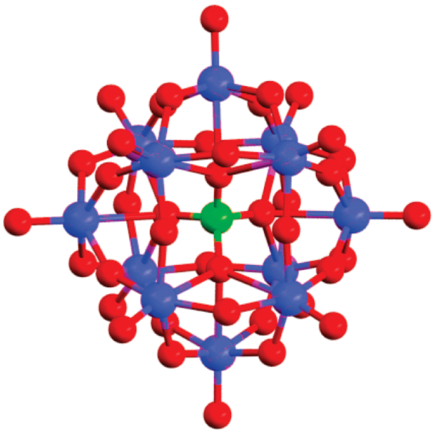


Figure 1. Keggin heteropoly acid with central tetrahedron and surrounding octahedra.

isomerization. The diverse compositions of these samples made any direct comparison tenuous, at best.

The common uses of HPAs have been as acid or oxidation catalysts.[41−43] In most of the systematic studies in these areas, especially acid catalysis, the well characterized Keggin acids have been the HPAs of choice. In the AHCs, the HPA acts as a ligand on the immobilized complex, an aspect of HPA chemistry which has been investigated to only a limited extent.[40,44−46]

It should be noted that the electronic characteristics of the HPAs are more complex than those of simpler ligands. As depicted in Figure 1, the Keggin heteropoly acids are composed of a central tetrahedron surrounded by 12 linked octahedra. The overall charge of the central tetrahedron is delocalized over the entire structure so the electronic properties of the HPA are dependent on both the nature of the central atom and the surrounding oxide shell.[47] These are the components which determine the ability of the HPA to complex with the rhodium, in this case, and to influence the activity of the resulting catalyst.

It was considered important for the future development of the AHCs that a more detailed comparison be made between the HPA anchored Wilkinson catalysts, the homogeneous **1**, and a supported metal catalyst, Rh/Al_2O_3. The effect which the different Keggin HPAs have on the catalytic activity of the anchored species would also be determined. To obtain the optimum data for such comparisons high TON hydrogenations/isomerizations of 1-hexene and limonene were studied with attention given to both the overall reaction rates as well as the monitoring of reaction intermediate formation during the reactions. These comparisons became even more interesting when it was found that the activated form of the anchored Wilkinson catalysts contained only one triphenylphosphine and was, thus, different from the active intermediate from **1**. The presence of only one triphenylphosphine on the rhodium complex minimized steric factors, and the HPA ligand was expected to impart unique electronic properties to the anchored complex so it was important to see the similarities and differences between the anchored catalysts, homogeneous **1**, and the supported metal. It is also important that these reactions be run in a "real world" manner by using reasonably high substrate to catalyst ratios (TONs) of at least 5,000 to 10,000.

RESULTS AND DISCUSSION

Table 1. HPA and Rh Content Found for Anchored Wilkinson Catalysts

HPA	μmoles HPA/g catalyst	%Rh	μmoles Rh/g catalyst	Rh/HPA
STA	46.5	0.52	50.5	1.08
SMA	49.7	0.47	45.6	0.92
PTA	46.8	0.44	42.7	0.91
PMA	49.1	0.48	46.6	0.95

Table 2. Percent Phosphorous Calculated and Found for Anchored Wilkinson Catalysts As Prepared and after Hydrogen Treatment

	calculated			found	
HPA	3 phosphines	2 phosphines	1 phosphine	AHC/Wilk	after H_2[a]
STA	0.47	0.31	0.16	0.43	0.11
SMA	0.42	0.28	0.14	0.35	0.10
PTA	0.53	0.40	0.26	0.48	0.22
PMA	0.58	0.43	0.29	0.55	0.25

[a] After a 2 h pre-hydrogenation or use in a hydrogenation reaction.

Catalyst Composition. The HPA used as the initial anchoring agent was silicotungstic acid (STA, $H_4SiW_{12}O_{40}$), with 46.5 μmoles adsorbed per gram of alumina (Table 1). After reaction with **1**, Inductively Coupled Plasma (ICP) analysis of the resulting anchored catalyst found 0.52% Rh which corresponds to 50.5 μmoles of Rh per gram of catalyst or about 5% of **1** in the anchored catalyst. The next consideration was the determination of the fate of the chloride present on the homogeneous Wilkinson catalyst. A baseline was developed by first measuring the amount of chlorine still present in the alumina after adsorption of the STA. To this end, samples from two separate preparations of STA/Al_2O_3 were analyzed by ICP and found to contain 0.15% and 0.18% residual chlorine, respectively. The anchored Wilkinson (STA/Wilk) catalysts prepared from these batches of STA/Al_2O_3 were found to have 0.19% and 0.17% chlorine, respectively, showing that the chlorine initially present on the Wilkinson complex was removed, apparently replaced by the STA.

Since the three triphenylphospines (TPPs) on **1** cause a sterically induced distortion of the molecule which is relieved in a homogeneous hydrogenation by the loss of one triphenylphosphine (Scheme 1), attention was directed toward the determination of what happens to the three triphenylphosphines present on **1** after being anchored to the larger HPA molecule. Analysis of the STA/Wilk showed that there were still three triphenyl-phosphines on the complex after anchoring (Table 2). By analogy with the hydrogenation mechanism established for the homogeneous **1** (Scheme 1), it was expected that on exposure to hydrogen and a solvent the STA/Wilk would also lose one TPP to give a catalytically active species having two TPPs. However, phosphorus analysis of the catalyst recovered after either a 2 h pre-hydrogenation or use in a high TON hydrogenation indicated that the active entity had only one TPP ligand present (Table 2).

The complex, **1**, was also anchored to alumina using the other, commercially available, HPAs, silicomolybdic acid (SMA, $H_4SiMo_{12}O_{40}$), phosphotungstic acid (PTA, $H_3PW_{12}O_{40}$), and phosphomolybdic acid (PMA, $H_3PMo_{12}O_{40}$). As shown by the data in Table 1, all of these HPAs interact with the alumina support to about the same extent and in every case the HPA/Rh ratio is about 1. As with STA/Wilk, the other anchored Wilkinson catalysts all retain three triphenylphosphines on anchoring and lose two of them on exposure to hydrogen (Table 2) when suspended in a solvent.

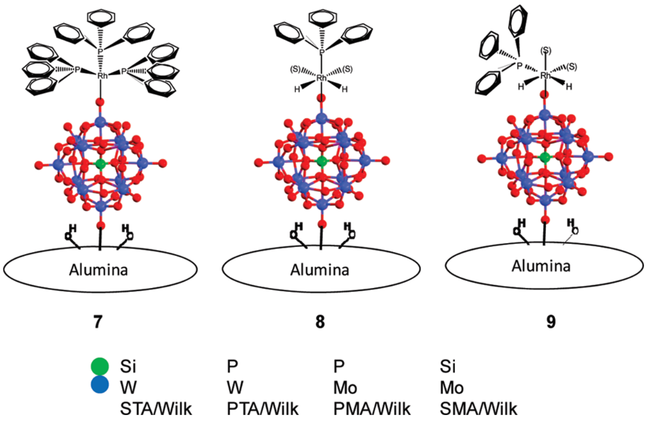
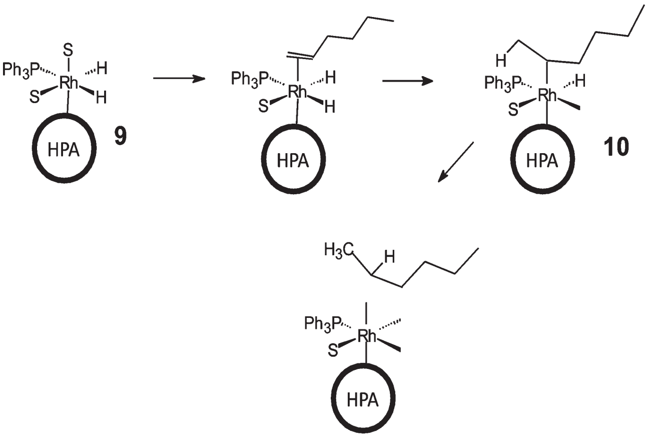


Figure 2. Anchored Wilkinson catalysts.

Scheme 2



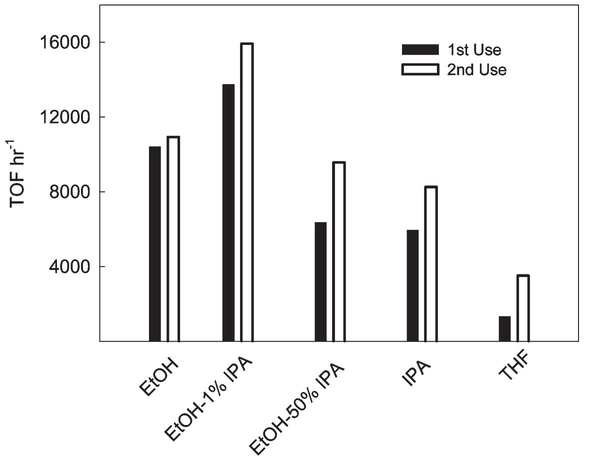
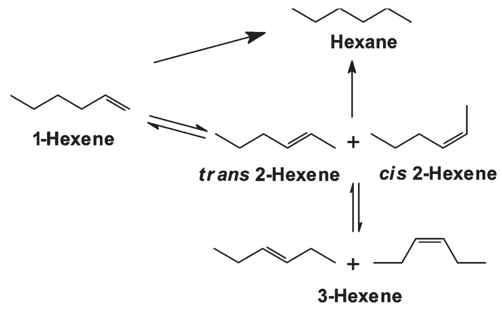


Figure 3. Effect of solvent on the pre-hydrogenation of STA/Wilk in the hydrogenation of 1-hexene.

Scheme 3



Examination of the drawing, **7**, in Figure 2 shows that because of the size of the STA, some severe crowding is apparently taking place in the initially formed STA/Wilk. Loss of two phosphines and the addition of two hydrogens would give a monotriphenylphosphine dihydrido rhodium(III) species which is expected to exist in an octahedral arrangement, probably with two molecules of solvent occupying the vacant ligand sites. On consideration only of steric effects the HPA and the phosphine were initially proposed to occupy positions trans to each other as in **8**.[28] However, as discussed later, the nature of the HPA has an effect on both the activity and the selectivity of the catalyst in 1-hexene and limonene hydrogenations. If these two ligands were trans to each other, a trans influence between the HPA and either an adsorbed hydrogen or alkene would not be possible. It seems probable, then, that the preferred arrangement would be one with these two groups cis to each other as in **9**. This species would then follow the reaction path shown in Scheme 2 in which each of the ligands can have an influence on the adsorption and reactivity of the hydrogens and the alkene. With one triphenylphosphine and an HPA ligand on the rhodium, **9** represents a unique type of catalytic material, one having different electronic characteristics than **2** while exerting minimal steric constraints on the substrate.

The drawings in Figure 2 depict the Rh as being bonded to one of the external oxygens of the Keggin HPA. However, Finke and co-workers[40] have shown by X-ray crystallography and NMR spectrometry that $Rh(COD)_2$ and $Ir(COD)_2$ were bonded to a niobium oxide containing Dawson-type HPA using three of the surface oxygens which were also bonded to the Nb atoms. It is possible that a similar multiple bonding could also be present in the AHC species but, lacking any data concerning this aspect of the structure a single Rh—O bond is depicted for simplicity.

Obviously, pre-hydrogenation of the HPA/Wilk catalysts is needed to form the active species, something which has been necessary with virtually all other AHC catalysts.[22−28] Initially, the pre-hydrogenation of the STA/Wilk was accomplished by stirring the catalyst overnight at room temperature in the reaction solvent under 35−50 psi of H_2. It was later found that a two or three hour pre-hydrogenation under these conditions was usually sufficient for catalyst activation. However, successive hydrogenations over the same catalyst sometimes resulted in an increase in the initial rate after the first reaction. For instance, three successive 10,000 TON hydrogenations of 1-hexene over the same STA/Wilk catalyst which had been prehydrogenated for 2 h resulted in an increase in the initial rate of hydrogen uptake from 3.01 mmol/min for the first reaction to 3.39 mmol/min for the second and third use of the catalyst. The data in Figure 3 show the effect of the solvent on catalyst activity as well as the efficiency of the 2 h pre-hydrogenation procedure. In all of these solvents, except ethanol, the turn-over frequency (TOF) for the second use of the catalyst was significantly higher indicating that the 2 h pre-hydrogenation was not sufficient for activating the catalyst in these solvents.

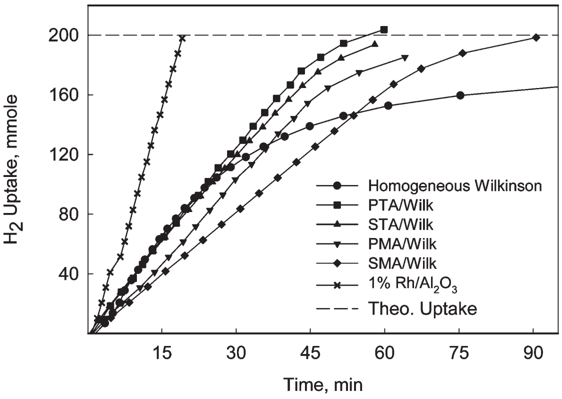


Figure 4. Hydrogen uptake curves for the hydrogenation of 1-hexene over homogeneous and anchored Wilkinson catalysts and 1% Rh/Al_2O_3.

Hydrogenation of 1-Hexene. As depicted in Scheme 3, hydrogenation of 1-hexene to hexane can be accompanied by the parallel formation of the 2- and 3-hexene isomers, materials which can be further hydrogenated to hexane. Information concerning both the overall rate of hydrogenation as well as the extent of isomer formation can provide a means of differentiating between the various catalysts used in this study. The hydrogen uptake curves for 10,000 TON hydrogenations of 1-hexene over the four HPA/Wilk catalysts, homogeneous **1**, and 1% Rh/Al_2O_3 are shown in Figure 4, and the reaction rate data are listed in Table 3.

With the homogeneous complex, **1**, as the catalyst the first 50% of the hydrogenation was completed in about 25 min and 70% in about 45 min, but the uptake of the last five mmoles of hydrogen took over 50 min, indicating a significant deactivation of this catalyst. This catalyst was almost completely deactivated at about 85% conversion leaving a product mixture composed of 14.5 mmol of 1-hexene, 162.5 mmol of hexane, 13 mmol of trans 2-hexene, 7.5 mmol of cis 2-hexene, and 2.5 mmol of 3-hexene. The composition profile for this reaction is shown in Figure 5. With all of the other catalysts the hydrogenation went to completion giving >98% hexane. The presence of unreacted 1-hexene in the final reaction mixture from **1** precluded the possibility that the deactivation was the result of the complete hydrogenation of the more active 1-hexene leaving only the less active 2- and 3-hexenes. Instead, the most apparent reason for this deactivation was the formation of the inactive dichlorodimer, **5** (Scheme 1) or its tetrahydro derivative, **6**, since it has been shown that **5** was about 1000 times less active than the bis phosphine, **2**.[48] When the substrate concentration was decreased sufficiently so that the adsorption of the alkene was slow, the dimerization of **2** and/or **3** could take place.[3] With the anchored catalysts such dimerization cannot occur.

The most active AHC catalyst was STA/Wilk followed by PTA/Wilk with both catalysts promoting the hydrogenation at rapid rates. The molybdate containing AHCs, PMA/Wilk, and SMA/Wilk were less reactive with the SMA/Wilk being the least active of all. The Rh/Al_2O_3 catalyst was the most active, almost one and a half times as active as STA/Wilk. ICP analysis of the product solutions from the PTA, STA, and SMA anchored catalysts showed that less than 1 ppm of Rh was present and only 2 ppm of Rh was found in the product solution from the PMA/Wilk catalyzed hydrogenation.

Aliquots were taken at intervals from these hydrogenation reaction mixtures, and the amounts of the isomerized alkenes present at 50% and 70% of the theoretical hydrogen uptake are listed in Table 4. At the 50% hydrogenation level the isomeric alkenes formed from the Homo/Wilk catalyzed reaction were near equal amounts of the trans and cis 2-hexenes along with a small amount of 3-hexene. The formation of near equal amounts of trans and cis 2-pentene was also reported for the hydrogenation of 1-pentene over **1**.[4] Over the anchored catalysts the amount of 2- and 3-hexene isomers formed was inversely related to the rate of hydrogen uptake; STA/Wilk < PTA/Wilk < PMA/Wilk < SMA/Wilk. The STA/Wilk and PTA/Wilk promoted reactions gave isomer compositions similar to those observed for the Homo/Wilk catalyzed hydrogenation. The trans/cis 2-hexene ratios were the same for all of the anchored catalyst promoted reactions with the exception of the PMA/Wilk catalyzed reaction which gave a slightly higher isomer ratio. The product mixture from the Rh/Al_2O_3 catalyzed reaction was similar to that observed with SMA/Wilk but with a lower amount of cis 2-hexene and, thus, a higher trans/cis ratio. At 70% hexane formation the longer contact of the alkenes with the catalysts resulted in more isomerization taking place as well as slightly higher trans/cis isomer ratios. Again, the PMA/Wilk promoted reaction mixture had a slightly higher isomer ratio.

With the ease of hydrogenation being terminal ene > cis ene > trans ene, one can provide an understanding of the sequence of reactions taking place during this hydrogenation (Scheme 2).

Table 3. Reaction Rate Data for 1-Hexene Hydrogenations Depicted in Figure 4

catalyst	init. rate mmol/min[a]	TOF[b] hr^{-1}
homogeneous[c]	5.28	3,400
STA/Wilk	4.83	12,500
PTA/Wilk	4.77	10,900
PMA/Wilk	3.37	7,700
SMA/Wilk	3.15	6,600
1% Rh/Al_2o_3	7.05	18,800

[a] Calculated from the first 30% of the hydrogen uptake curve. [b] Calculated from the time and composition of the reaction mixture at theoretical hydrogen uptake. [c] Catalyst deactivates at about 85% conversion.

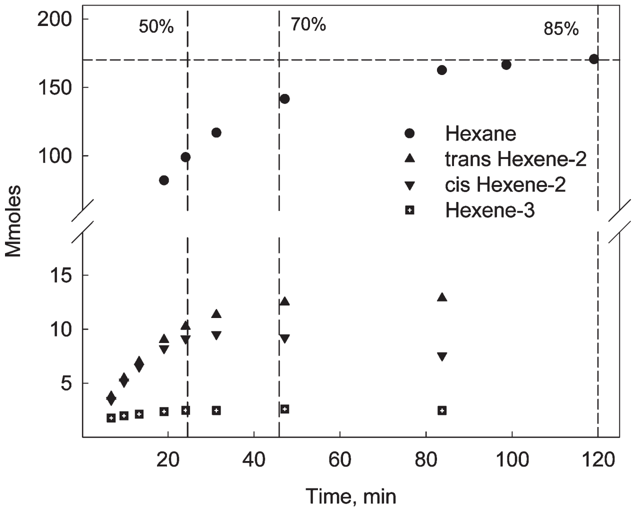
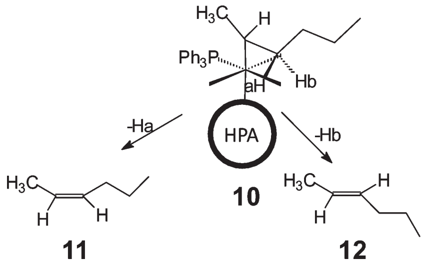


Figure 5. Reaction mixture composition in the hydrogenation of 1-hexene over the homogeneous Wilkinson catalyst.

Table 4. Millimoles of 2- and 3-Hexene Formed at 50% and 70% Hexane Formation during the Hydrogenation of 1-Hexene over Homogeneous 1, Anchored Wilkinson Catalysts, and 1% Rh/Al_2O_3

	catalyst					
	1	STA/ Wilk	PTA/ Wilk	PMA/ Wilk	SMA/ Wilk	Rh/ Al_2O_3
			hexane formation = 50%			
trans 2-hexene	10.3	11.2	12.1	15.7	18.3	18.9
cis 2-hexene	9.2	8.7	9.3	10.4	12.6	9.0
trans/cis	1.1	1.3	1.3	1.5	1.3	2.1
3-hexene	2.5	1.8	1.9	2.4	2.3	2.2
			hexane formation = 70%			
trans 2-hexene	12.4	15.5	16.7	20.9	25.5	25.5
cis 2-hexene	9.2	11.2	11.6	11.8	15.2	10.3
trans/cis	1.3	1.4	1.4	1.8	1.4	2.5
3-hexene	2.6	2.2	2.3	3.1	3.0	3.3

Scheme 4



After adsorption of the 1-hexene and transfer of the first hydrogen the secondary metal alkyl, **10**, is formed. Transfer of the second hydrogen gives the saturated alkane. However, if this second hydrogen transfer is slow, the reaction can reverse by abstracting a hydrogen from C-3 to produce an adsorbed 2-hexene. The stereochemistry of this isomer depends on which hydrogen is removed from C-3 (Scheme 4). If H_a is removed, the cis isomer, **11**, is formed and the trans isomer, **12**, by removal of H_b. Since these two hydrogens are almost equally accessible to the rhodium, a trans/cis isomer ratio close to 1 would be expected as long as 1-hexene is the predominant alkene in the reaction mixture. Otherwise the isomeric alkenes, initially the cis 2-hexene, can become complexed on the rhodium. Hydrogenation to hexane would decrease the amount of this isomer and change the isomer ratio. Alternately, the complexed cis 2-hexene could isomerize to the trans isomer. A further aspect is the fact that trans alkenes are more stable than the cis isomers, so if the hydrogen abstraction step is sufficiently slow some differentiation between the transition states leading to the two isomeric alkenes can lead to the formation of more of the trans isomer and a higher trans/cis ratio.

The isomeric alkene compositions in the aliquots taken from the STA/Wilk catalyzed reaction are shown Figure 6. In this reaction, the amount of the cis isomer began to decrease at about 70% hexane formation. At this point the reaction mixture contained about 25 mmol of 1-hexene and 35 mmol of the isomeric hexenes. Since cis alkenes are more readily hydrogenated than the trans isomers, at this time some cis 2-hexene hydrogenation began along with further 1-hexene saturation. At about 80% conversion, the reaction mixture contained about 10 mmol of 1-hexene and 30 mmol of isomerized hexenes, so the selective hydrogenation of 1-hexene and/or the cis 2-hexene became less favored and the trans 2-hexene and the 3-hexenes were hydrogenated to give, eventually, hexane as the sole product. The trans/cis 2-hexene ratio remained relatively constant to about 60% hexane formation and increased to about 1.6 at 80% conversion and 3.1 at about 95% conversion.

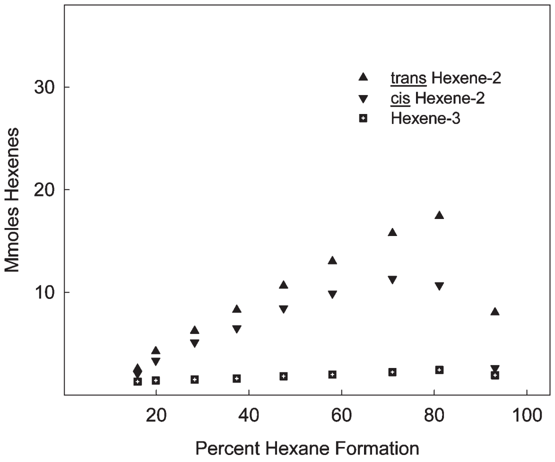


Figure 6. Isomer formation during the hydrogenation of 1-hexene over STA/Wilk.

The PTA/Wilk catalyzed hydrogenation had product distributions very similar to those shown in Figure 6 for STA/Wilk. The product compositions from the PMA/Wilk and SMA/Wilk catalyzed hydrogenations contained more of the 2-hexenes, particularly the trans isomer. Since these hydrogenations were the slowest they may have been favoring product formation as determined by transition state differentiation. The Rh/Al_2O_3 catalyzed hydrogenation produced about the same amount of the trans 2-hexene as was formed in the SMA/Wilk promoted reaction, but the product mixture contained significantly less of the cis isomer. In every case isomerization was observed as taking place parallel to hydrogenation throughout the reaction indicating that the addition of the second hydrogen to the metal alkyl intermediate, **10**, did not take place instantaneously so the abstraction of a C-3 hydrogen to give the 2-hexene isomers could occur.

With all of the catalysts the trans/cis ratio remained relatively constant to about 60% completion of the reaction and then increased when the hydrogenation of the isomeric alkenes became more dominant. As illustrated in Figures 5 and 6, the extent of 3-hexene formation was about two to three mmoles throughout most of these reactions. This was found with all of the AHC/Wilk catalysts as well as the Rh/Al_2O_3 and the homogeneous **1**.

It was considered that at least some isomerization could have been promoted by the catalyst support materials so the reactions were repeated under an inert atmosphere using STA/Al_2O_3, STA/Wilk, and 1% Rh/Al_2O_3 as the catalysts. No isomerized alkenes were formed in any of these reactions.

Hydrogenation of Limonene. As depicted in Scheme 5 the hydrogenation of limonene (**13**) presents a different type of selectivity from that associated with the saturation of 1-hexene. Limonene has two double bonds with different substitution

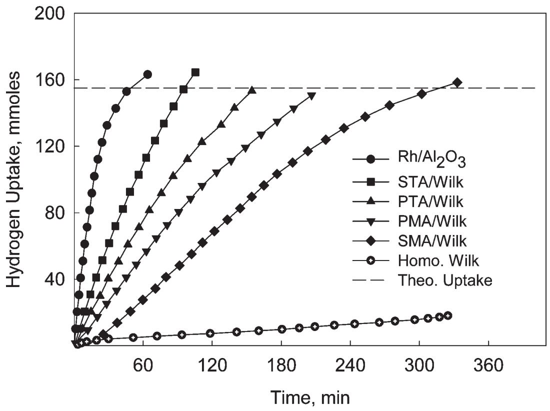
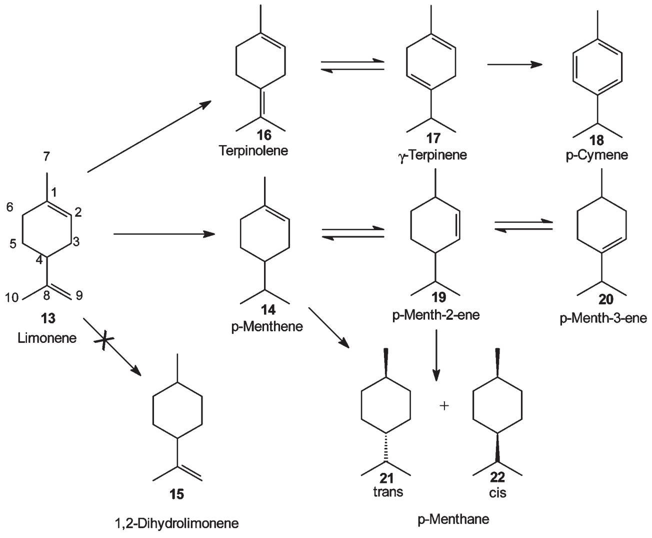


Figure 7. Hydrogen uptake curves for the hydrogenation of limonene over homogeneous and anchored Wilkinson catalysts as well as 1% Rh/Al_2O_3.

Scheme 5



patterns, a methylene group between C-8 and C-9 and a trisubstituted double bond at C-1. It would appear that the difference in reactivity between these two double bonds could be determined by measuring the relative amounts of the two potential dihydro compounds, **14** and **15**, formed in the hydrogenation. However, the literature pertaining to the hydrogenation of limonene is interesting in that there is no identification of the 1,2-dihydro product, **15**, in any of the reported hydrogenation reactions.[49−51] This compound is not even mentioned in a review of limonene reactions[49] nor in a comprehensive study of the Pd catalyzed hydrogenation of limonene.[50] The only report of its formation was by a Zn/$NiCl_2$ reduction of limonene which gave predominantly *p*-menthene with about 1% of **15** isolated from the reaction mixture.[52] Another report cites the relative rates in the hydrogenation of limonene to **14** and **15** over supported Pd aminosilane complexes but does not provide any evidence for the actual formation of **15**.[53]

Not only does the hydrogenation of the C-8,9 double bond take place preferentially, but there are also double bond isomerization and further saturation aspects to consider. There are two isomerization pathways shown in Scheme 5. One involves the direct conversion of limonene to terpinolene, (**16**) and/or γ-terpinene (**17**), which are precursors in the formation of *p*-cymene (**18**). The second pathway involves the isomerization of *p*-menthene (**14**) to give *p*-menth-2-ene (**19**) and *p*-menth-3-ene (**20**). Also, further hydrogenation of menthene and/or its double bond isomer, **19**, gives the trans (**21**) and cis (**22**) menthanes. Thus, with limonene as the substrate, catalyst comparisons can be based not only on the overall rate of hydrogen uptake but also

Table 5. Reaction Rate Data for Limonene Hydrogenations Depicted in Figure 7

catalyst	init. rate mmol/min[a]	TOF[b] hr^{-1}
homogeneous	na	na
STA/Wilk	2.05	4,800
PTA/Wilk	1.28	3,000
PMA/Wilk	0.80	2,200
SMA/Wilk	0.61	1,500
1% Rh/Al_2O_3	5.02	7,100

[a] Calculated from the first 30% of the hydrogen uptake curve. [b] Calculated from the time and composition of the reaction mixture at theoretical hydrogen uptake.

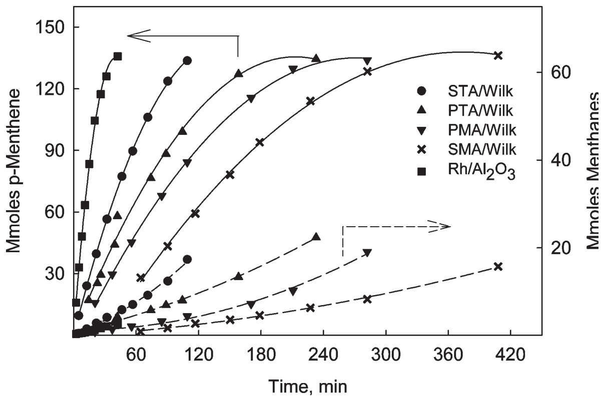


Figure 8. Influence of the HPA anchoring agent on the formation of *p*-menthene and the isomeric menthanes during the hydrogenation of limonene.

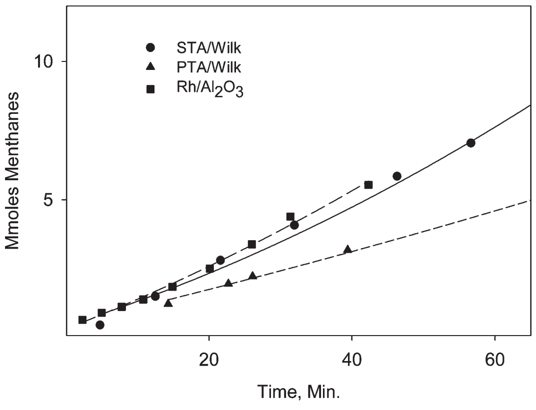
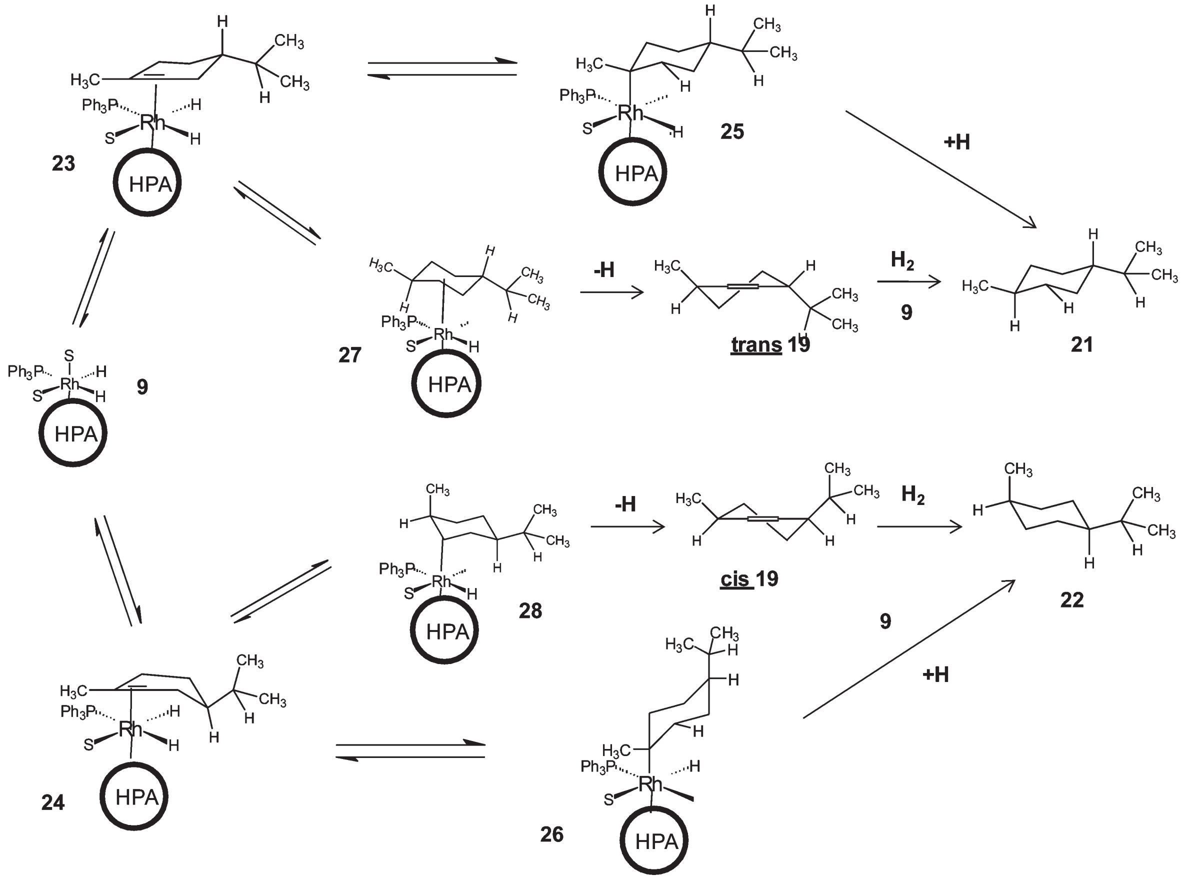


Figure 9. Menthane formation during the first 60 min of limonene hydrogenation over 1% Rh/Al_2O_3, STA/Wilk, and PTA/Wilk.

Scheme 6



on the rate of formation of *p*-menthene and the fully saturated products, the initial isomerization of limonene, and the isomerization of the *p*-menthene product.

The hydrogen uptake curves for 7,500 TON hydrogenations of limonene over the four HPA/Wilk catalysts, homogeneous **1**, and 1% Rh/Al_2O_3 are shown in Figure 7, and the reaction rate data is listed in Table 5. The homogeneous catalyst was essentially inactive for this hydrogenation, stopping at about 10% conversion yielding *p*-menthene along with very small amounts of menth-3-ene and trans menthane as the products. The relative activities of the catalysts used for this reaction are the same as those observed in the hydrogenation of 1-hexene: Rh/Al_2O_3 > STA/Wilk > PTA/Wilk > PMA/Wilk > SMA/Wilk. The analysis of aliquots taken during these hydrogenations provided information concerning the changes in product composition which were taking place during the course of the reactions.

The hydrogenation uptake data shown in Figure 7 are a combination of both the formation of *p*-menthene and the further hydrogenation to the trans and cis menthanes. Figure 8 shows the extent of formation of *p*-menthene and menthane with time of reaction as taken from aliquot analyses. Both of these reactions follow the same order of activity as depicted in Figure 7. While *p*-menthene formation tends to level off, menthane formation increases with time. This was, most likely, the result of the hydrogenation of *p*-menthene and/or its isomer, *p*-menth-2-ene, which resulted in the formation of the menthanes while decreasing *p*-menthene concentration. While Rh/Al_2O_3 was the most active catalyst for *p*-menthene formation, it produced the lowest amount of menthane of all of these catalysts. The data in Figure 9, depicting menthane formation for the first 60 min of the reactions promoted by Rh/Al_2O_3, STA/Wilk, and PTA/Wilk, show that only about five mmoles of menthane are formed during the Rh/Al_2O_3 catalyzed hydrogenation. All of the HPA/Wilk catalysts produced the menthanes in the range of about 20 mmol to about 40 mmol. The AHC catalyst effect on the amount of menthane formation follows the overall hydrogen uptake results; STA/Wilk > PTA/Wilk > PMA/Wilk > SMA/Wilk.

The trans/cis menthane ratios were about one throughout all of the HPA/Wilk promoted hydrogenations of limonene indicating that there was little, if any, steric difference in the ease of adsorption of **14** for either the trans adsorption, **23**, or cis adsorption, **24**, as depicted in Scheme 6. This was a result of the relatively open environment around the Rh atom in the catalytically active entity, **9**. Hydrogen transfer from the Rh to the adsorbed alkene can take place to either the C-1 or the C-2 carbons of the double bond. Addition to C-2 leads to the formation of a tertiary C—Rh bond as in **25** or **26**. These intermediates can either reverse to regenerate the adsorbed alkenes, **23** or **24**, or their enantiomers, or form the isomeric menthanes, **21** or **22**, by the transfer of the second hydrogen from the rhodium. An alternate route involves the transfer of the first hydrogen to the tertiary carbon forming **27** or **28** which are less sterically hindered than **25** or **26**. Again, transfer of the second hydrogen will produce the **21** or **20**. Additionally,

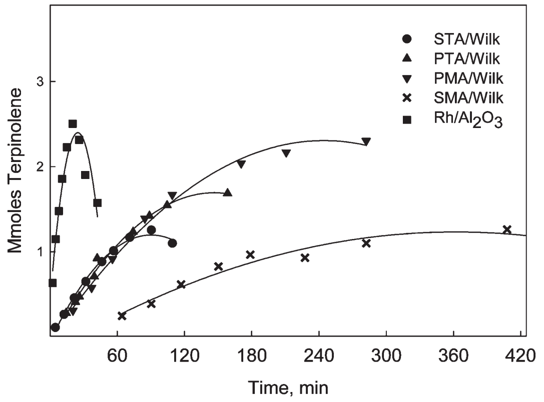


Figure 10. Influence of the catalyst on the formation of terpinoline during the hydrogenation of limonene.

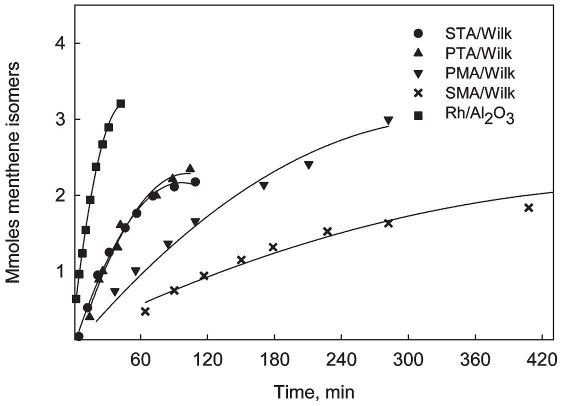


Figure 11. Influence of the catalyst on the formation of *p*-menthene isomers during the hydrogenation of limonene.

hydrogen abstraction from the C-3 carbon results in the formation of the isomeric menth-2-enes, trans and cis **19**, which can be further hydrogenated to **21** or **22**. Regardless of the reaction pathway used for menthane formation, the product stereochemistry is fixed by the mode of initial adsorption, **23** or **24**. Since the formation of the menthane isomers, **21** and **22**, as well as the menthene isomers, **19** and **20**, was detected in the very early reaction aliquots, it would seem that the reactions depicted in Scheme 6 were taking place in competition with the initial formation of *p*-menthene, **14.** Apparently a cis adsorbed species similar to **24** is favored over Rh/Al_2O_3 since cis menthane formation predominated over this catalyst with a trans/cis ratio of 0.6.

As discussed previously, two different isomerization paths are shown in Scheme 5, isomerization of the methylene double bond in limonene to produce terpinoline and the isomerization of the trisubstituted double bond in *p*-menthene giving menth-2-ene and menth-3-ene. Since these isomerizations are not related they should be considered separately. In Figure 10 is shown the extent of terpinoline formation during the hydrogenation of limonene. Clearly, Rh/Al_2O_3 promoted not only the most rapid hydrogenation but also the highest amount of terpinoline formation. As the amount of terpinoline increased, γ-terpinene and *p*-cymene were also formed to the extent of about 0.35 mmol of γ-terpinoline and 0.4 mmol of *p*-cymene being present at the end of the reaction. This was the only catalyst of those studied here where *p*-cymene was observed in the reaction mixture. The initial rates of terpinoline formation were almost identical in the STA/Wilk, PTA/Wilk, and PMA/Wilk catalyzed hydrogenations with the amount of terpinoline formed increasing in that order. SMA/Wilk was the least active catalyst.

The rates of formation of the menthene isomers, **19** and **20**, are depicted in Figure 11. Again, Rh/Al_2O_3 was the most active catalyst also giving the most menthene isomerization. The curves for the STA/Wilk and PTA/Wilk catalyzed reactions are almost identical while the PMA/Wilk catalyst promoted a slower reaction but gave the highest amount of isomerization of the HPA/Wilk catalysts. As seen before, the SMA/Wilk promoted reaction was the slowest giving the least amount of isomerization.

■ CONCLUSIONS

Exposing the HPA/Wilk catalysts to hydrogen produces the unique catalytically active entity, **9**, which has distinctive electronic and steric properties warranting a comparison with the homogeneous catalyst, **1**, on one hand and the heterogeneous supported metal, 1% Rh/Al_2O_3, on the other. Further, the influence of the HPA ligand in these catalysts was also of concern.

The observed rates of hydrogen uptake and double bond isomer formation in the hydrogenations of both 1-hexene and limonene followed the same order with respect to the nature of the HPA ligand used to anchor the Wilkinson catalyst to the alumina: STA/Wilk > PTA/Wilk > PMA/Wilk > SMA/Wilk for hydrogen addition and the reverse for isomerization. This consistency provided a measure of the electronic character of these Keggin HPAs when acting as ligands influencing the relative facility with which each of the two complexed hydrogens were added to the adsorbed alkene.

As discussed above, the electronic character of the Keggin HPAs is related to the nature of both the central tetrahedron and the surrounding octahedra. From the limited data presented here it would appear that since the STA and PTA containing catalysts were quite similar in activity the tungstate octahedral shell had more influence on the activity than the central tetrahedra. With the molybdates, though, the nature of the central tetrahedra also exerted an influence on the catalyst activity. These results may provide an opening into the use of HPAs as ligands in catalytically active complexes to fine-tune the activity and/or selectivity of a given reaction.

Since the deactivation of **1**, when used in the high TON hydrogenations reported here, was also observed in the high TON hydrogenation of cyclohexene,[26] it does not appear that **1** is a viable catalyst for use in high TON hydrogenations while none of the HPA/Wilk catalysts have this constraint. In other respects, though, the relationship between the HPA/Wilk catalysts and the homogeneous **1** and the Rh/Al_2O_3 catalysts appears to depend on the activity of the anchored catalyst. In the hydrogenation of 1-hexene the more active, STA/Wilk and PTA/Wilk promote product compositions which are similar to that found using **1** as the catalyst. The less active, PMA/Wilk and, specially, SMA/Wilk give products more like those obtained from the use of the Rh/Al_2O_3 catalyst, but with the supported metal giving less trans 2-hexene than the anchored catalysts.

In the hydrogenation of limonene comparisons with **1** were not possible because of the rapid deactivation of the catalyst. Comparison of the anchored catalysts with the supported Rh showed that the Rh/Al_2O_3 catalyst promoted more isomerization of the methylene group of limonene and the trisubstituted double bond in *p*-menthene. The production of the fully saturated menthanes by the hydrogenation of the trisubstituted double bond in *p*-menthene, though, was more difficult over the supported metal catalyst than with the sterically more accessible anchored Wilkinson catalysts. Further, the formation of more of the cis menthane over the Rh/Al_2O_3 indicated that more steric hindrance was present around the active sites of that catalyst.

EXPERIMENTAL SECTION

Materials. The phosphotungstic acid (PTA), phosphomolybdic acid (PMA), silicotungstic acid (STA), and silicomolybdic acid (SMA) were obtained from Sigma-Aldrich and used as received. The alumina used as the support was a neutral gamma alumina obtained from W.R. Grace and washed with ethanol to remove the fine particles before use. The 1-hexene and limonene were obtained from Sigma-Aldrich and distilled under argon before use. All solvents were distilled under argon and stored in air-tight containers fitted with septa through which all transfers were made. The Wilkinson's catalyst was obtained from Strem. The 1% Rh/Al_2O_3 was obtained from Johnson Matthey. The ICP analyses were obtained through Johnson Matthey.

Preparation of the Anchored Catalysts and Catalytic Hydrogenations. Freshly distilled air and moisture free solvents were used. All manipulations were carried out under an atmosphere of argon. All solvent transfers were carried out via cannula under positive argon pressure or by the use of gas-tight syringes.

The suspended stirrer jacketed glass reactor previously described[54] was used for all reactions. The procedures used for the preparation of the anchored Wilkinson catalysts and that used for the alkene hydrogenations were described previously.[20,27] The amount of each catalyst was adjusted so each reaction was run using 20 μmole of Rh. Care was taken in the use of these anchored catalysts not only to have oxygen-free solvents and substrates but, also to remove all of the air from the pores of the support. This must be done before placing any solvents in the reactor with the catalysts and was best accomplished by first placing the catalyst in the reactor and then pressurizing the reactor to about 50 psig with argon or nitrogen, holding at that pressure for about 5 min and then releasing the pressure. Repeating this cycle five times was usually sufficient to replace the air in the pores of the support with argon or nitrogen. The solvent can then be added to the reactor, preferably through a septum, and the catalyst prehydrogenated. After pre-hydrogenation, the catalyst was allowed to settle and the solvent removed using a cannula under a low pressure of hydrogen for the transfer. The solution of the substrate was then added through the septum using a gastight syringe, and the reaction initiated by starting the stirring.

The hydrogen uptake was measured by monitoring the pressure drop in the high pressure ballast and recording these values in 1 min intervals using a computer.[54] In this way, the reactions were run at constant volume and constant pressure. These data were then plotted, and the rate of hydrogenation and the TOF of each reaction calculated. In the preliminary report the rates were determined from the slopes of the first 10 data points for each curve, and the TOFs calculated from the time and composition after 90% hydrogen uptake. The more precise rates reported here were determined from the slopes of the first 30% of the uptake data for each curve, and the TOFs from the time and the composition of the reaction mixtures at theoretical hydrogen uptake.

1-Hexene (25 mL), 200 mmol, was hydrogenated in 15 mL of abs. EtOH at 35 °C under 50 psig of hydrogen using a stirring rate of 1800 rpm.

Limonene (25 mL), 150 mmol, was hydrogenated in 15 mL of abs. EtOH at 35 °C under 50 psig of hydrogen using a stirring rate of 1800 rpm.

Aliquots (100 μL) were taken using a gas-tight syringe at about 10% hydrogen uptake intervals, and the reaction mixtures analyzed using GC and GC-MS. The products were identified by comparison of their retention times with those of authentic samples or by comparison with data from the GC-MS library.

The GC analyses of the 1-hexene hydrogenation mixtures were done on an HP 5890 equipped with a DB-1 capillary column (100 m × 0.25 mm, 0.5 mkm thickness) and a flame ionization detector. Injector and detector temperatures were 180 and 240 °C respectively at a helium head pressure of 5 psi. The initial column temperature was started at 40 °C for 6 min then increased at a rate of 3 °C/min to 100 °C and held constant for 5 min. Retention times: 1-hexene-1 (21.41 min), *n*-hexane (21.76 min), 3-hexene (22.20 min), trans 2-hexene (22.46 min), and cis 3-hexene (23.35 min).

The GC-MS analyses of the limonene hydrogenation mixtures were carried out on an HP 5890 with a DB 624 capillary column (70 m × 0.53 mm, 3 mkm film thickness) and a 5971A Mass selective detector. Injector and detector temperatures were 180 and 240 °C respectively and helium head pressure of 10 psi. The initial column temperature was 100 °C, held for 2 min and followed by a ramp to 180 °C at a rate of 3 °C/min. Retention times: cis menthane (12.08 min), *p*-menth-3-ene (12.33 min), *p*-menth-2-ene (12.57 min), trans menthane (12.76 min), *p*-menthene (14.14 min), limonene (14.47 min), *p*-cymene (14.65 min), γ-terpinene (15.71 min), α-terpinolene (17.12 min).

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