Homogeneous catalysis in the reactions of olefinic substances. XI. Homogeneous catalytic hydrogenation of short-chain olefins with dichlorobis(triphenylphosphine) platinum (II)-Tin...

Homogeneous Catalysis in the Reactions of Olefinic Substances.[1a,b] XI. Homogeneous Catalytic Hydrogenation of Short-Chain Olefins with Dichlorobis(triphenylphosphine)platinum(II)–Tin(II) Chloride Catalyst[1c]

R. W. Adams, G. E. Batley, and John C. Bailar, Jr.

Contribution from the William Albert Noyes Laboratory of Chemistry, University of Illinois, Urbana, Illinois 61801. Received April 24, 1968

Abstract: Homogeneous hydrogenation with $PtCl_2(PPh_3)_2$ and $SnCl_2 \cdot 2H_2O$ catalyst mixtures has been further studied with short-chain olefins. Monoolefins are found to hydrogenate rapidly only when the double bond is terminal. Hydrogenation of hexadiene and pentadiene isomers has shown that reduction does not necessarily stop at the monoene stage as previously believed. Dienes have the greatest reactivity when both double bonds are terminal and, in these cases, small percentages of saturate are formed. In these molecules it was found that conjugation is not a necessary prior step to hydrogenation, and short-chain conjugated diene isomers were found to inhibit further reaction. In contrast, long-chain conjugated dienes are reduced since the larger size of the diene prevents the formation of stable catalyst–diene complexes. Unsaturated nitriles are hydrogenated when the double bond is terminal and not hindered by substituent groups on the β-carbon atom. The cyanide group remains intact.

The growing interest in the application of metal complexes as homogeneous catalysts for the hydrogenation and isomerization of olefins has been reflected in several recent review articles.[2] Complexes such as $RhCl(PPh_3)_3$,[3] $IrClCO(PPh_3)_2$,[4] $IrHCl_2(PPh_3)_3$,[5] and $[Co(CN)_5]^{3-}$ [6] have been shown to be very effective hydrogenation catalysts. It is of interest to compare the selectivity of hydrogenation for some of these complexes. The pentacyanocobaltate system[6] does not hydrogenate isolated double bonds, but conjugated double bonds as in butadiene are reduced to the monoene stage; $RhCl(PPh_3)_3$[3] is a very effective catalyst for the hydrogenation of monoenes with the exception of ethylene, but not for conjugated double bonds; $IrClCO(PPh_3)_2$[4b] slowly hydrogenates ethylene at 40–60°. The catalyst composed of chloroplatinic acid and tin chloride rapidly reduces ethylene, but hydrogenations become more difficult with increasing substitution about the double bond.[7,8] The catalytic activity of these complexes is associated with the ability of the metal to form a sufficiently labile complex containing both hydrogen and olefin coordinated to the metal. A π-acceptor ligand, by enhancing coordination of hydride or olefin, may dramatically heighten the catalytic activity. Such a ligand, $SnCl_3^-$, has been used with success in Pt–Sn systems. Cramer[9] observed that $SnCl_2$ increases the rate of formation of Zeise's complex after it was discovered[10] that a mixture of H_2PtCl_6 and $SnCl_2$ made an efficient hydrogenation catalyst.

The catalyst formed from $PtCl_2(PPh_3)_2$ and $SnCl_2$ has been the subject of several earlier publications.[11] In the hydrogenation of polyolefinic esters, this catalyst appears to be unique in that hydrogenation does not proceed beyond the monoene stage.[12] This is unusual since, for simple monoenes, the chloroplatinic acid–$SnCl_2$ catalyst system catalyzes hydrogenation to saturated species.[7,8,10,13] We have examined the $PtCl_2(PPh_3)_2$–$SnCl_2$ catalyst with a series of simple mono- and diolefins and have found that the degree of hydrogenation is very much dependent on the stereochemistry of the olefin and, in certain cases, polyolefins may be reduced to saturated species. This paper describes experiments designed to determine the conditions which will give rise to saturated species.

Experimental Section

1. Apparatus. Hydrogenation experiments were conducted in a Magne-Dash autoclave as previously described.[1b] Reactions at atmospheric pressure were performed in a conventional manometric apparatus.

Infrared absorption spectra were run on liquid films between NaCl plates using a Perkin-Elmer 521 infrared spectrophotometer. Nuclear magnetic resonance spectra were run on a Varian A-60A instrument in $CDCl_3$ solution with trimethylsilane as an internal standard.

2. Gas Chromatography. A Varian-Aerograph (Model 1520-B) gas chromatograph and a flame ionization detector were used

(1) (a) Part X: *Inorg. Nucl. Chem. Lett.*, **4**, 455 (1968); (b) part IX: H. A. Tayim and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **89**, 4330 (1967). (c) A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract was supervised by the Northern Utilization Research and Development Division of the Agricultural Research Service.

(2) J. A. Osborn, *Endeavour*, **26**, 144 (1967); J. Halpern, *Ann. Rev. Phys. Chem.*, **16**, 103 (1965); M. Orchin, *Advan. Catalysis*, **16**, 1 (1966); S. Carra and R. Ugo, *Inorg. Chim. Acta Rev.*, **1**, 49 (1967).

(3) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, 1711 (1966); F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 1574 (1967).

(4) (a) G. G. Eberhardt and L. Vaska, *J. Catalysis*, **8**, 183 (1967); L. Vaska, *Inorg. Nucl. Chem. Lett.*, **1**, 89 (1965); (b) L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, **87**, 4970 (1965).

(5) M. Yamaguchi, *Kogyo Kagaku Zasshi*, **70**, 675 (1967); *Chem. Abstr.*, **67**, 99542 (1967); related complexes reported by R. S. Coffey, *Chem. Commun.*, 923 (1967).

(6) J. Kwiatek, *Catalysis Rev.*, **1**, 37 (1967).

(7) R. V. Lindsey, Jr., private communication.

(8) G. C. Bond and M. Hellier, *J. Catalysis*, **7**, 217 (1967).

(9) R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).

(10) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).

(11) Reference 1b and references therein.

(12) J. C. Bailar, Jr., and H. Itatani, *J. Am. Chem. Soc.*, **89**, 1592 (1967).

(13) L. P. Van't Hof and B. G. Linsen, *J. Catalysis*, **7**, 295 (1967).

throughout this work. Gas chromatograph analyses of hexene and pentene isomers (together with their hydrogenation products) were resolved on a 20 ft × 0.25 in. copper column packed with 40% tricresyl phosphate on Chromosorb P (60–80 mesh). Analysis of reaction products from 1- and 2-butene was achieved on a 10 ft × 0.25 in. copper column packed with 20% silicone oil (No. 200) on activated alumina (48–60 mesh). A similar 10 ft × 0.25 in. column containing di-*n*-decyl phthalate on Chromosorb P was used for substituted butenes and some of the hexene isomers. Analyses of the products from reactions of 1,5-hexadiene were accomplished by using two columns: (a) 20 ft × ⅛ in. copper column packed with 20% TCP on Chromosorb W (100–120 mesh) and (b) 34 ft × ⅛ in. copper column packed with 20% TCEP on Chromosorb W (100–120 mesh).

The reaction products from the hydrogenation of methyl linoleate and methyl 9,11-octadecadienoate were analyzed on a 10 ft × 0.25 in. copper column packed with 20% DEGA on Chromosorb W (60–80 mesh).

Preparative gas chromatography on the DEGA column was used to separate the final product of isomerization of 1,5-hexadiene (2,4-hexadiene) from solvent (benzene and methanol) and traces of other isomers. Analyses of the nitrile reaction products were carried out on a 10 ft × ⅛ in. copper column packed with 20% FFAP on Chromosorb W (100–120 mesh).

Column temperatures and gas flow rates were varied until good resolution of the components was obtained.

3. **Chemicals and Syntheses.** Liquid olefins were obtained from Aldrich Chemicals and Chemical Samples Ltd. (research grade). Gaseous olefins and deuterium gas were obtained from Matheson Co. and Phillips Petroleum (research grade). Methanol-d_1 (99.5%) was obtained from Stohler Isotope Chemicals. α-Chloroacrylonitrile and (*cis* and *trans*) β-chloroacrylonitrile were kindly donated by American Cyanamid Co. Research Laboratories. The purity of each chemical was checked by gas chromatography before use. Solvents were of analytical grade.

cis-Dichlorobis(triphenylphosphine)platinum(II)[14] was prepared as previously described.

Results and Discussion

Monoene Hydrogenation. Cramer, *et al.*,[10] have previously reported the hydrogenation of ethylene using a chloroplatinic acid–tin chloride catalyst mixture. This reaction proceeds readily at room temperature under 1 atm of hydrogen. The same catalyst has been used by other authors for the hydrogenation of 1-pentene[8] and 1-hexene,[13] and these olefins give significant proportions of isomerized monoenes together with small percentages of saturated compounds. In contrast, 2-pentene, with the same catalyst, showed little tendency to reduce or isomerize.[8] It was observed that terminal double bonds could be reduced much more easily than internal double bonds.

We have made a more detailed study of simple monoenes using the PtCl₂(PPh₃)₂–SnCl₂ catalyst system, and the results are shown in Table I. This catalyst was found to be effective in the hydrogenation of short-chain monoenes, the yield of saturated compound being dependent primarily on whether the olefin has a terminal double bond. Where the double bond is not terminal, the degree of both hydrogenation and isomerization is small. The size of the monoene also appears to significantly affect the amount of reaction, since ethylene hydrogenates to a greater extent than propylene or 1-butene. For monoenes larger than propylene, where isomerization can lead to the removal of the double bond from the terminal position, the degree of reduction appears to be independent of chain length.

The significance of steric factors on the degree of hydrogenation has been demonstrated with a series of substituted butenes (Table II). Introduction of substituent

(14) K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **229**, 225 (1936).

Table I. Catalytic Hydrogenation of Monoenes (46 mmoles) with PtCl₂(PPh₃)₂ (0.25 mmol) and SnCl₂·2H₂O (2.5 mmoles) in Benzene–Methanol (50 ml, 3:2)[a]

	Glpc analysis, %				
Monoene	1 isomer	—2 isomer— cis	trans	3 isomer	Satd hydro- carbon
Ethylene	0	...	...	...	100[b]
Propylene	66.0	...	...	...	34.0
1-Butene	12.0	30.3	46.4	...	11.3
cis-2-Butene	0	71.1	27.3	...	1.6
trans-2-Butene	0	9.8	89.6	...	0.6
1-Pentene	11.0	30.2	47.2	...	11.6
2-Pentene (cis 47.9%, trans 52.1%)	3.0	27.7	67.5	...	1.8
1-Hexene	12.5	28.5	41.6	5.4	12.0
2-Hexene	No observable hydrogenation				
3-Hexene	No observable hydrogenation				

[a] Under 34 atm of H₂ at 90° for 3 hr. [b] 97.0% after 1 hr.

Table II. Hydrogenation of Substituted Butenes (10 mmoles) in Methylene Chloride Solvent[a] Using PtCl₂(PPh₃)₂ (0.25 mmole) + SnCl₂·2H₂O (2.5 mmoles)

	Glpc analysis, %			
	3-Methyl-1-butene	2-Methyl-2-butene	2-Methyl-1-butene	2-Methyl-butane
2-Methyl-1-butene	...	87.6	12.2	0.2
3-Methyl-1-butene	8.9	56.9	7.4	26.8

[a] At 90°, 34 atm of H₂, after 3 hr.

methyl groups near the terminal double bond in 1-butene significantly lowers the yield of saturate.

Hydrogenation and Isomerization of Isomeric Hexadienes. In a preceding publication,[1b] the results of hydrogenation of 1,5-hexadiene using the PtCl₂(PPh₃)₂–SnCl₂ catalyst were described. These experiments have now been carefully repeated, and the reaction products have been more fully characterized. The results are shown in Table III and Figure 1. It is now

Table III. Catalytic Hydrogenation of Isomeric Hexadienes (10 mmoles) with PtCl₂(PPh₃)₂ (0.25 mmole) and SnCl₂·2H₂O (2.5 mmoles) in Benzene–Methanol (50 ml, 3:2)[a]

	Glpc analysis, %								
Diene	1-Hex-ene	2-Hexene cis	trans	3-Hexene	n-Hex-ane	Hexadiene 1,5	1,4	1,3	2,4
1,5	0.8	5.8	12.2	1.0	2.5	0	17.0	2.0	58.7
1,4	0	5.0	12.5	0	0	0	5.7	3.6	73.2
1,3	0	0	0	7.5	0	0	0	73.1	19.4
2,4	0	0.9		0	0	0	1.3	1.8	96.0

[a] Under 34 atm of hydrogen at 90° for 3 hr.

apparent that, in addition to formation of monoenes, a small quantity of fully saturated material is produced from the hydrogenation of 1,5-hexadiene; *i.e.*, the reaction does *not* stop at the monoene stage. On the other hand, hydrogenation of 1,4- and 1,3-hexadiene yields 2-hexene and 3-hexene, respectively. We have already shown that these two monoenes are not reduced any further (Table I), and so, unlike the 1,5 isomer, we should not expect either 1,4-hexadiene or 1,3-hexadiene to be reduced beyond the monoene stage.

It had also previously been assumed that isomerization to the conjugated molecule was necessary before hydro-
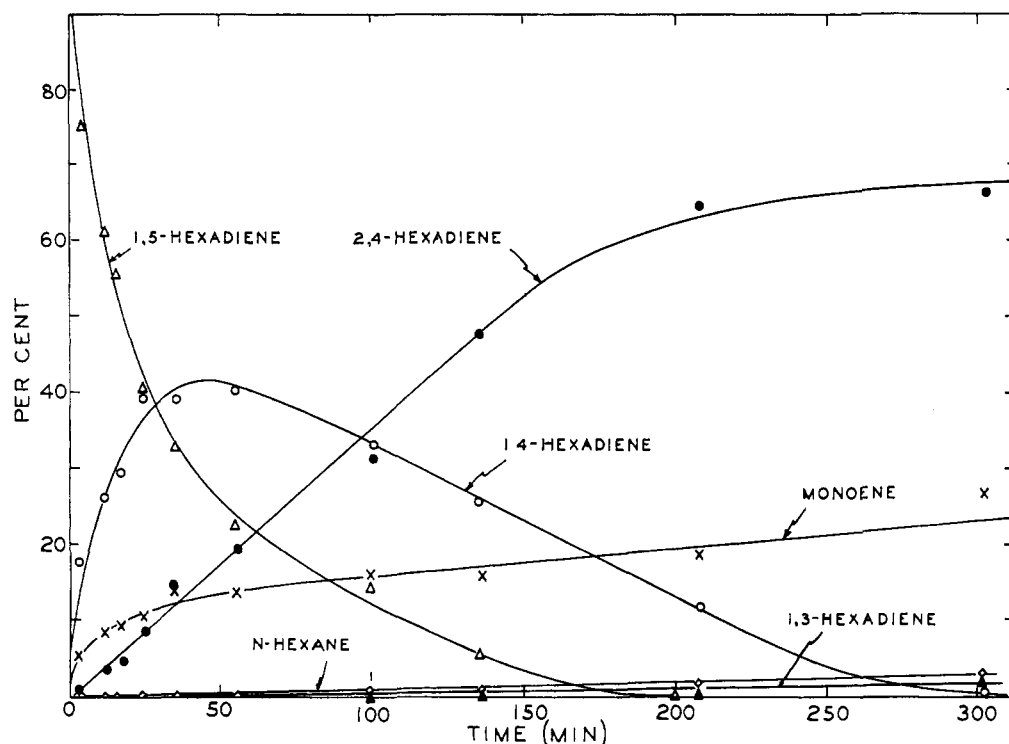
Figure 1. Catalytic hydrogenation of 1,5-hexadiene in benzene–methanol solvent under 34 atm of H_2 at 90°, using $PtCl_2(PPh_3)_2$–$SnCl_2$ catalyst.

genation could occur.[1b] However, the attempted reduction of the conjugated 2,4-hexadiene gives only traces of monoenes, while 1,5-, 1,4-, and 1,3-hexadiene all undergo reduction to varying degrees, the 1,5 isomer being the most reactive (Table III). From measurements of the per cent monoene produced under identical experimental conditions, an approximate order of reactivity can be adduced: 1,5 > 1,4 > 1,3 >> 2,4. Again, it appears that a terminal double bond is more susceptible to reduction, and also that the hydrogenation of a short-chain conjugated diene which has no terminal double bond is very difficult to achieve.

from reduction of 1,5-, 1,4-, or 1,3-hexadiene will be correspondingly higher.

The results presented in Table III and Figure 1 show that isomerization of dienes may occur concurrently with hydrogenation. Thus, 1,5-, 1,4-, and 1,3-hexadiene all give high percentages of the 2,4 isomer. By using milder conditions, it has been possible to study the isomerization reaction independent of hydrogenation. The results of the isomerization of 1,5-hexadiene under different experimental conditions are shown in Table IV and Figure 2. The reaction is effected by a mixture of $PtCl_2(AsPh_3)_2$ and $SnCl_2 \cdot 2H_2O$ in the pres-

Table IV. Isomerization of 1,5-Hexadiene (2.2 ml) under Various Conditions

Expt	Reaction time, hr	Catalyst (g)	Solvent (ml)	Gas (atm)	Temp, °C	Glpc analysis, %			
						1,5	1,4	1,3	2,4
1	3.5	PtCl₂(AsPh₃)₂ (0.22) + SnCl₂·2H₂O (0.57)	Benzene (15) + methanol (10)	H₂ (1)	39	4.5	22.9	2.3	70.3
2	3.5	PtCl₂(PPh₃)₂ (0.25) + SnCl₂·2H₂O (0.50)	Benzene (15) + methanol (10)	H₂ (1)	39	70.6	28.5	. . .	0.9
3	3.5	PtCl₂(AsPh₃)₂ (0.22) + SnCl₂·2H₂O (0.57)	Benzene (15) + methanol (10)	Argon (1)	39	1.2	27.8	. . .	71.0
4	3.5	PtCl₂(AsPh₃)₂ (0.22) + SnCl₂·2H₂O (0.57)	Benzene (15) + methanol (10)	H₂ (1)	60	1.8	4.0	2.3	91.9
5	4.0	PtCl₂(AsPh₃)₂ (0.22) + SnCl₂·2H₂O (0.57)	Methylene chloride (25)	Argon (1)	40	No isomerization			

It is of interest to note that if methylene chloride is substituted for benzene–methanol as the solvent, the yield of monoene is markedly increased.[1b] This observation is in line with our experiments on the isomerization of 1,5-hexadiene when it was found that the formation of 2,4-hexadiene is very much more rapid in benzene–methanol than in methylene chloride (Table IV). Obviously, if the formation of the relatively inert 2,4 isomer is slow, then the yield of monoene obtained

ence or absence of hydrogen using a benzene–methanol solvent. The arsine catalyst at 39° under 1 atm of hydrogen after 3.5 hr yields over 70% of the 2,4 isomer. In contrast, the phosphine is a much poorer catalyst and yields only 0.9% of 2,4-hexadiene under the same conditions.

In order for isomerization to take place, a source of hydride ions such as hydrogen gas or methanol must be present; no reaction was detected when methylene
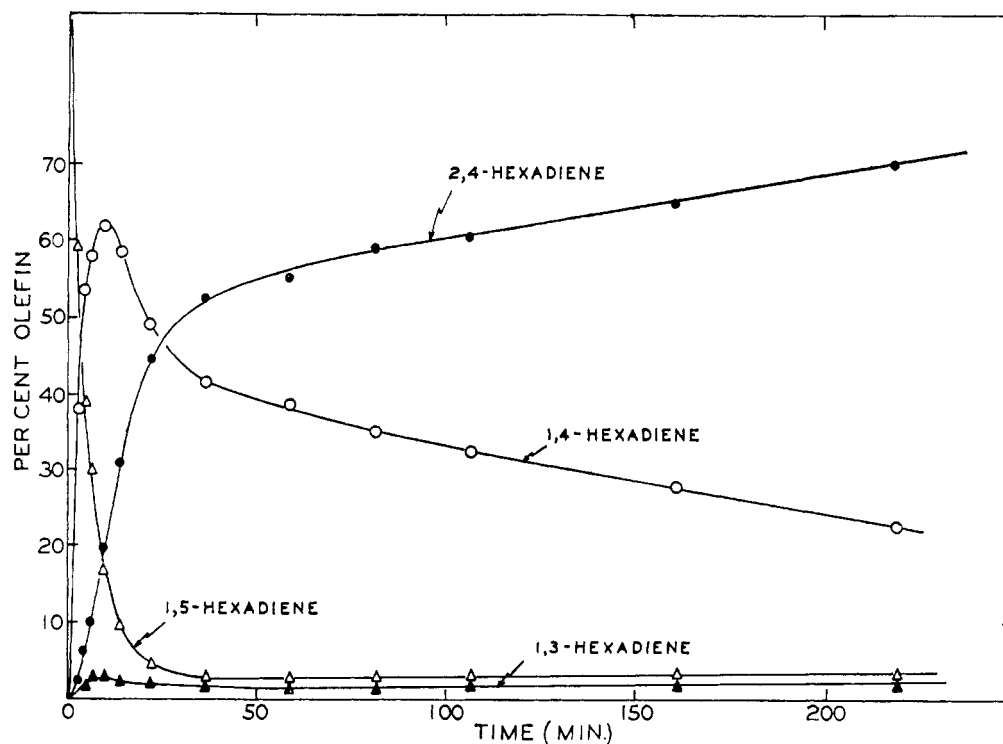
Figure 2. Catalytic isomerization of 1,5-hexadiene in benzene–methanol solvent under 1 atm of H_2 at 39° using $PtCl_2(AsPh_3)_2$–$SnCl_2$ catalyst.

chloride was used as a solvent in an atmosphere of argon.[15] The yield of isomerized material obtained from reaction in benzene–methanol solvent is only slightly increased when hydrogen is replaced by argon (expt 1 and 3, Table IV). Further, we have shown that if 1,5-hexadiene is catalytically isomerized in d_1-methanol under deuterium, deuterated 2,4-hexadiene is obtained as the final product (Table V). Infrared

zation even when hydrogen gas is present. It is of interest to note that extensive deuteration of 1-butene in CH_3OD by the catalyst H_2PtCl_4–$SnCl_2$ was observed by Cramer and Lindsey.[17] The utilization of the α-hydrogen atoms in alcohols to form metal hydride complexes is well known.[18,19] An intermediate platinum hydride might then react with olefin to give a hydride–π-olefin complex which could then rearrange to a σ-

Table V. Isomerization of 1,5-Hexadiene in Methanol-d_1[a]

Reaction time, hr	Catalyst (g)	Solvent (ml)	1,5-Hexadiene, ml	Glpc analysis, %				Ir spectra of isomerization product in the C–D stretching region	
				1,5	1,4	1,3	2,4	ν, cm^{-1}	Tentative assignment
7.0	$PtCl_2(AsPh_3)_2$ (0.09) + $SnCl_2 \cdot 2H_2O$ (0.26)	CH_3OD (4.0) + benzene (40)	1.0	1.2	0.2	2.0	96.6	2218 (s) 2212 (sh) 2160 (m) 2140 (m)	C–D stretch of vinyl deuterium C–D stretch of methyl deuterium

[a] At 62° under 1 atm of deuterium gas. The nmr spectrum of the deuterated product is considerably different from that of nondeuterated 2,4-hexadiene; however, the complexity of the spectrum prevented unambiguous identification of all the resonances, and no attempt was made to measure the relative amounts of vinyl and methyl deuterium.

spectra of the deuterated 2,4 product in the C–D stretching region indicate that deuterium atoms are substituted on both the methyl and vinyl groups. No evidence of deuteration was found when the reaction was run in nondeuterated methanol even in the presence of deuterium gas. Thus, transfer of the acidic proton of CH_3OH to the olefin appears to accompany isomeri-

(15) This observation at first appears to be in conflict with experiments involving isomerization of 1,5-cyclooctadiene[16] where it was found that isomerization occurs in CH_2Cl_2 under a nitrogen atmosphere. However, in this case the reaction was performed with the phosphine, not the arsine, catalyst and under 600 psi of nitrogen at 90°. In addition, we cannot assume that a cyclic diene will behave in the same manner as a linear diene.

(16) H. A. Tayim and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **89**, 3420 (1967).

bonded complex by transfer of hydrogen from the metal to the bonded olefin.[20] This type of hydride addition–elimination mechanism has already been invoked to account for the isomerization of olefins by various catalysts.[2] The stepwise migration of double bonds in 1,5-cyclooctadiene catalyzed by $PtCl_2(PPh_3)_2$ + $SnCl_2$ has already been fully described in these terms in a previous report.[16]

Hydrogenation of Isomeric Pentadienes. The results of catalytic hydrogenation of 1,4- and 1,3-pentadiene

(17) R. Cramer and R. V. Lindsey, Jr., *ibid.*, **88**, 3534 (1966).

(18) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

(19) L. Vaska, *J. Am. Chem. Soc.*, **83**, 756 (1961).

(20) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc.*, 190 (1968).

Table VI. Hydrogenation of 1,3-Pentadiene and 1,4-Pentadiene with PtCl₂(PPh₃)₂ (0.25 mmole) and SnCl₂·2H₂O (2.5 mmoles) in Methylene Chloride (50 ml)[a]

| Olefin (ml) | Glpc analysis, % | | | | |
| | —Diene— | | —Monene— | | n- |
	1,4	1,3	1	2	Pentane
1,4-Pentadiene (1.0)	28.0	2.9	2.3	63.4	3.4
1,3-Pentadiene (1.0)	0	97.0	0	3.0	0

[a] At 90° under 34 atm of H₂ for 3 hr.

Table VII. Hydrogenation of Fatty Acid Esters[a]

	Time, hr	Linoleate	cis–trans conj diene	trans–trans conj diene	cis–cis conj diene	Monoene
1. Methyl linoleate	0	98.9	0.2	0.2	0	0.4
	3	70.2	16.4	8.2	0	5.1
2. Conjugated cis– trans diene[b]	0	2.5	91.3	3.4	1.3	1.0
	3	0.9	65.0	26.7	0	7.1
3. Conjugated trans– trans diene[b]	0	0.7	0.1	97.2	0	1.0
	3	0	9.4	81.4	0	9.2

[a] At 90° under 34 atm of hydrogen in benzene–methanol solvent. [b] Methyl 9,11-octadecadienoate.

(Table VI) with PtCl₂(PPh₃)₂ + SnCl₂·2H₂O are similar to those of the hexadiene system. Again, the nonconjugated isomer, 1,4, with two terminal double bonds, appears more reactive than the 1,3 isomer. A small quantity (3.4%) of saturated material is produced by reduction of 1,4-pentadiene, but no pentane is produced from hydrogenation of 1,3-pentadiene, and 2-pentene, which we have already shown to be relatively inert (Table I), is the only product.

Reactivity of Conjugated Dienes. In catalysis by PtCl₂(PPh₃)₂ + SnCl₂·2H₂O, it was believed that conjugation was an essential prerequisite to hydrogenation.[1b] However, the reduction of the diene, 2,3,3-trimethyl-1,4-pentadiene, which cannot isomerize to a conjugated molecule, with both the arsine– and phosphine–tin chloride catalysts, yields two reduction products in significant quantities. The gc retention times of these products are close together but different from the retention time of 2,3,3-trimethylpentane, so they are very probably 2,3,3-trimethyl-1-pentene and 3,3,4-trimethyl-1-pentene. It therefore appears that conjugation does not necessarily have to occur before hydrogenation can begin. In the case of this diene, hydrogenation can occur readily and independently at each of the terminal double bonds.

We have examined the reactivity of some internally conjugated dienes and have found that certain low molecular weight dienes are not reduced and are also able to hinder the reduction of other olefins. For example, 1,3-butadiene, which is relatively inert to hydrogenation, is able to completely prevent the reduction of 1-butene and 1,5-hexadiene. Thus, attempted hydrogenation of 1,3-butadiene (46 mmoles) at 90° under 34 atm of H₂ with PtCl₂(PPh₃)₂ (0.25 mmole) and SnCl₂·2H₂O (2.5 mmoles) in benzene–methanol after 3 hr yielded only 0.2% of 2-butene. Similar experiments were performed on mixtures of 1-butene–1,3-butadiene (22%) and 1,5-hexadiene–1,3-butadiene (22%), and it was found that neither reduction nor isomerization took place in either case. It is of interest to note that Cramer[21] has already demonstrated that the Rh(III)-catalyzed isomerization of 1-butene can be effectively

stopped by adding 1,3-butadiene to the system, and that isomerization of 1,4-hexadiene is retarded through formation of the product conjugated diene.[22] In each case, the conjugated diene may inhibit both the isomerization and hydrogenation steps simply by coordinating so strongly to the metal that both the elimination of reduced or isomerized olefins and the approach of other monoenes to the metal is prevented. The results obtained for the hydrogenation of these short-chain olefins appear to be quite different from those obtained for the soybean oil methyl ester system[12] in which reduction occurs despite the fact that there are no terminal carbon–carbon double bonds and that conjugated isomers are formed as intermediate products.[23]

An examination of some conjugated diene isomers of methyl linoleate has shown them to be effectively reduced in the presence of the PtCl₂(PPh₃)₂–SnCl₂ catalyst (Table VII), unlike the corresponding short-chain internally conjugated dienes (Table III). Thus, cis,-trans-9,11-octadecadienoic acid methyl ester yields 7.1% monoene after 3 hr of reaction at 90° and 34 atm of hydrogen, whereas 2,4-hexadiene yields only 0.9% monoene in the same time. It is possible that the presence of the ester group could be responsible for the increased reactivity of conjugated double bonds in the long-chain polyolefinic esters. We have found that, while 2,4-hexadiene is relatively unreactive, the corresponding ester, methyl 2,4-hexadienoate (ethyl sorbate), gave 9% monoene after 3 hr of hydrogenation under similar conditions. It seems unlikely that an ester group as far removed from the double bonds as it is in methyl linoleate could affect the ease of reduction. Experiments are in progress to further examine olefinic esters.

The reactivity of internally conjugated dienes depends on the instability of the diene–catalyst complex intermediate. With short-chain olefins, the bond between the conjugated diene and the metal atom is not labile, but with long-chain olefins this bond is weakened by the steric effect imposed by the chain length and the olefins are thus more reactive. When reduction of internally conjugated dienes occurs, the product is an internal monoene which we have shown is not reactive. Hydrogenation of dienes with PtCl₂(PPh₃)₂–SnCl₂ therefore does not proceed beyond the monoene stage unless the diene contains terminal double bonds which may be reduced independently of each other.

Hydrogenation of Unsaturated Nitriles. In order to investigate the possible influence of a cyanide sub-

(21) R. Cramer, J. Am. Chem. Soc., 88, 2272 (1966).

(22) R. Cramer, ibid., 89, 1633 (1967).
(23) E. N. Frankel, E. A. Emken, H. Itatani, and J. C. Bailar, Jr. J. Org. Chem., 32, 1447 (1967).

Table VIII. Hydrogenation of Unsaturated Nitriles[a]

Expt	Catalyst (mmoles)	Nitrile (mmoles)	Glpc analysis (%)
1	$PtCl_2(AsPh_3)_2$ (1.5) + $SnCl_2 \cdot 2H_2O$ (15.0)	CH_2=CHCN (90)	CH_3CH_2CN (94.4) CH_2=CHCN (5.6)
2	$PtCl_2(PPh_3)_2$ (1.5) + $SnCl_2 \cdot 2H_2O$ (15.0)	CH_2=CHCN (90)	CH_3CH_2CN (94.0) CH_2=CHCN (6.0)
3	$PtCl_2(AsPh_3)_2$ (1.5) + $SnCl_2 \cdot 2H_2O$ (15.0)	ClCH=CHCN (90)	No hydrogenation
4	$PtCl_2(AsPh_3)_2$ (1.5) + $SnCl_2 \cdot 2H_2O$ (15.0)	CH_2=CCl(CN) (90)	No hydrogenation
5	$PtCl_2(AsPh_3)_2$ (1.5) + $SnCl_2 \cdot 2H_2O$ (15.0)	CH_3CH=CHCN (90)	No hydrogenation

[a] At 80° under 55 atm of hydrogen in CH_2Cl_2 (150 ml) for 5 hr.

stituent attached to the olefin, a number of unsaturated nitriles were subjected to hydrogenation experiments. The results for acrylonitrile, α-chloroacrylonitrile, and a mixture of cis- and trans-β-chloroacrylonitrile are presented in Table VIII.

The catalyst composed of $PtCl_2(MPh_3)_2$ and $SnCl_2 \cdot 2H_2O$ (M = P, As) is a good catalyst for the hydrogenation of the double bond in CH_2=CHCN. The cyanide group remains intact. However, both CH_2=CCl(CN) and cis- and trans-CHCl=CHCN remain unreduced under the same experimental conditions. Since crotononitrile, CH_3CH=CHCN, also fails to hydrogenate, this effect is likely to arise from steric rather than electronic considerations. Substitution of groups on the α- and β-carbon atoms of acrylonitrile may be sufficient to prevent approach of a platinum–hydride species to the double bond so that subsequent transfer of hydrogen cannot occur.

Although there is some evidence for coordination of acrylonitrile to the platinum–tin catalyst, no complexes of definite composition could be isolated.

Electrochemistry of Open-Cage Boron-10 Species[1a]

J. Q. Chambers, A. D. Norman, M. R. Bickell, and S. H. Cadle[1b]

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. Received May 8, 1968

Abstract: The electron-transfer and proton-transfer reactions which interrelate the open-cage B-10 hydrides in acetonitrile have been determined. The electrochemical reduction of decaborane(14) in acetonitrile yields the dianion, $B_{10}H_{14}^{2-}$, in an irreversible two-electron step. In a similar manner, $B_{10}H_{14}$ is produced by the oxidation of $B_{10}H_{14}^{2-}$. In either case, the kinetically important reaction following charge transfer is a proton transfer between $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$. The rate of this reaction is approximately $5 \times 10^4 M^{-1} sec^{-1}$ at $24 \pm 2°$. The over-all products of either the reduction of $B_{10}H_{14}$ or the oxidation of $B_{10}H_{14}^{2-}$ are $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$ in an equimolar mixture as confirmed by [11]B nmr analysis. This mixture constitutes a "one-electron" oxidation state between $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$. The formal reduction potential for the $B_{10}H_{14} | B_{10}H_{14}^{2-}$ couple is -0.78 ± 0.02 V vs. sce. The electrochemical behavior of $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$ in acetonitrile is compared with that in 1,2-dimethoxyethane. A significant solvent effect on the oxidation–reduction mechanistic pathways is indicated.

The electrochemical behavior of decaborane(14) in nonaqueous solvents and the electron-transfer and proton-transfer reactions which interrelate the open-cage B-10 species in acetonitrile have been determined and compared to the behavior in monoglyme. Mechanisms for the reduction of $B_{10}H_{14}$ and the oxidation of $B_{10}H_{14}^{2-}$ are proposed, and the chemical and electrochemical kinetic parameters have been determined in acetonitrile at room temperature. The results of this study are of significance to an understanding of redox reactions of the open-cage B-10 compounds.

Previous work on the reduction of decaborane includes that of Toeniskoetter,[2] who carried out sodium

reductions in ammonia, ether, and tetrahydrofuran, the work of Hough and Edwards,[3] who carried out sodium amalgam reductions in ether, and that of Rupp, Smith, and Shriver,[4] who investigated the electrochemical reduction in monoglyme (1,2-dimethoxyethane). The sodium reductions[2,3] give a mixture of products, including $Na_2B_{10}H_{14}$ and $NaB_{10}H_{13}$, which varies with solvent and reaction time. This paper reports on experiments which further characterize the reduction of decaborane. Quantitative single-sweep cyclic voltammetry and double-potential-step electrochemical measurements were carried out over a wide time scale. Although this work is in qualitative agree-

(1) (a) This work was supported by grants from the Research Corporation, the Petroleum Research Fund, and the National Science Foundation. (b) Phillips Petroleum undergraduate research fellow.
(2) R. H. Toeniskoetter, Ph.D. Thesis, St. Louis University, 1958.

(3) M. V. Hough and L. J. Edwards, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p 184.
(4) (a) E. B. Rupp, D. E. Smith, and D. F. Shriver, *J. Am. Chem. Soc.*, **89**, 5562 (1967); (b) *ibid.*, **89**, 5568 (1967).