

- the definition above and (ii) this description most accurately and concisely describes the overall process (the diene is reduced and thereby eliminated from the coordination sphere).
- (14) (a) Another method of generating related Rh catalysts involves protonation of an acetate ligand in a neutral Rh(I) or Rh(II) complex.^{7c,14b,c} Catalytic hydrogenation systems based on this method behave similarly in many respects to those based on the cationic complexes discussed here. (b) P. Legzdins, R. W. Mitchell, G. L. Rempel, and G. Wilkinson, *J. Chem. Soc. A*, 3322 (1970). (c) R. W. Mitchell, A. Spencer, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 846 (1973).
 - (15) (a) Tetraphenylborate ion can coordinate to the cation once the diene is removed.^{15b} The resulting neutral species are relatively inactive under the mild conditions employed here. (b) R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, **9**, 2339 (1970).
 - (16) We will write S_x (or S_y, etc.) in all formulas of nonisolated species which almost certainly contain "coordinatively labile" solvents, though the number, of course, is unknown.
 - (17) Formation of unstable dihydrides containing other bound solvents has been observed; e.g., [RhH₂(PPh₃)₂(THF)₂]⁺ may be obtained as an unstable cream colored powder from concentrated THF solutions of [Rh(NBD)(PPh₃)₂]⁺ under hydrogen. Metal-hydrogen stretching frequencies are evident in an infrared spectrum of this complex in Nujol but poorly resolved. The ease of isolation of [RhH₂(PPh₃)₂S₂]⁺ appears to increase roughly in the order S = THF < ethanol ~ acetone < CH₃CN.
 - (18) B. F. Susz and P. Chalandan, *Helv. Chim. Acta*, **41**, 1332 (1958).
 - (19) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y., 1959, p 223.
 - (20) M. Orchin, *Adv. Catal.*, **16**, 1 (1966).
 - (21) J. W. Byrne, H. U. Blaser, and J. A. Osborn, *J. Am. Chem. Soc.*, **97**, 3871 (1975).
 - (22) (a) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **93**, 3089 (1971). (b) The existence of [Rh(P(OPh)₃)₂S_x]⁺ may be shown by (e.g.) the essentially quantitative yield of [Rh(NBD)(P(OPh)₃)₂]⁺ on addition of norbornadiene.^{22a} Note that catalysts prepared from [Rh(NBD)(P(OPh)₃)₂]⁺ isomerize olefins rapidly (see Table Ia).
 - (23) Flushing consisted of evacuation to ca. 200 mm total pressure followed by introduction of nitrogen to 1 atm; this was repeated three times.
 - (24) All experiments were conducted with 0.12 mmol of catalyst in 10 ml of solvent under ca. 200 ml of molecular hydrogen (deuterium).
 - (25) Complete equilibration of H₂O and D₂ would yield 93% H₂, 7% HD, and a trace of D₂.
 - (26) (a) G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970); (b) *ibid.*, **8**, 113 (1975).
 - (27) The catalyst solution was taken to dryness, dissolved in dichloromethane, and stirred with KCN in water for 24 h. The dichloromethane solution was dried and taken to an oil in vacuo. A 220-MHz ¹H NMR spectrum (in C₆D₆) of the triphenyl phosphite thus isolated showed that 65% of the ortho-hydrogen atoms had been replaced by deuterium atoms. H in the gas is 70% of that which would be found on complete exchange of ortho-H with D.
 - (28) (a) D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 3133 (1968); (b) C. O'Connor and G. Wilkinson, *ibid.*, 2665 (1968); (c) G. Yagupsky and G. Wilkinson, *ibid.*, 725 (1969); (d) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *ibid.*, 3143 (1968); (e) S. T. Wilson and J. A. Osborn, *J. Am. Chem. Soc.*, **93**, 3068 (1971); (f) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, 1711 (1966).
 - (29) A neutral monohydride species could conceivably be produced by other means such as ortho proton abstraction from the phenyl ring of L²⁶ or by some reaction involving the solvent. Though the former occurs in these systems (see eq 7) it is probably not a major source of monohydride since [Rh(NBD)(PMe₃)₃]⁺ produces an effective olefin isomerization catalyst after exposure to hydrogen. (Proton abstraction from an alkyl group in a *nonbulky* phosphine³⁰ is extremely rare.²⁶) The latter is also unlikely since isomerization is rapid in THF, a solvent which is normally inert. Also note that there is no induction period for isomerization or hydrogenation of 1-hexene or *cis*-2-hexene and the rate of isomerization of 1-hexene in the absence of hydrogen is first order with respect to the olefin (see Figure 2).
 - (30) See, however, J. M. Duff, B. E. Mann, B. L. Shaw, and B. Turtle, *J. Chem. Soc.*, 139 (1974), and references therein.
 - (31) E. K. Barefield and G. W. Parshall, *Inorg. Chem.*, **11**, 964 (1972).
 - (32) Possibly a trihydride (cf. CoH₃(PPh₃)₃) is present in solution but the catalytic chemistry almost certainly will arise from the monohydride.
 - (33) D. F. Shriver, *Acc. Chem. Res.*, **3**, 231 (1970).
 - (34) K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, **7**, 546 (1968).
 - (35) An analogous reaction of this type has been reported for Rh(COD)(C₆H₅)(PPh₃)₂; M. Takesada, H. Yamazaki, and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **41**, 270 (1968). See also ref 2a, p 272.
 - (36) These results are best regarded as only semiquantitative since it would appear the behavior of 4b is not exactly that expected; i.e., it is not intermediate between 4a and 4c. Most likely 4a is not completely correct; a side reaction when the concentration of RhH(PPh₂Me)₂S_x is high could alter the catalytic behavior.
 - (37) (a) We want to stress again that we are interested only in a broad mechanistic interpretation here. One could postulate an even more elaborate scheme involving less obvious, but not necessarily less important, kinetic intermediates (cf. the Wilkinson catalyst system^{37b,c}). However, at this time and for our purpose, Scheme I is adequate. (b) J. Halpern and C. S. Wong, *J. Chem. Soc., Chem. Commun.*, 629 (1973). (c) C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 2762 (1974).
 - (38) C. A. Tolman, *Inorg. Chem.*, **11**, 3128 (1972).
 - (39) Note that Figure 2 shows "hydrogen-free" olefin isomerization in acetone. In 2-methoxyethanol, where the rate of hydrogenation is only one-tenth as fast (Table III), the rate could conceivably deviate from first-order behavior.
 - (40) We suppose the forward step of eq 13 to be rapid even in the presence of olefin. However, we cannot be assured that RhH(PPhMe₂)₃S_x can freely enter into the reverse in the presence of olefin, i.e., formation of a relatively stable metal alkyl, RhR(PPhMe₂)₃S_x, may slow the rate at which (13) is attained while still allowing rapid olefin isomerization.
 - (41) J. R. Shapley, Ph.D. Thesis, Harvard University, 1971.

Catalytic Hydrogenation Using Cationic Rhodium Complexes. II. The Selective Hydrogenation of Alkynes to Cis Olefins

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Abstract: The cationic dihydride, [RhH₂L_nS_x]⁺ and the neutral monohydride, RhHL_nS_y, which are present in equilibrium in solutions of [Rh(NBD)L_n]⁺A⁻ after exposure to molecular hydrogen, both catalyze the reduction of alkynes to cis olefins at comparable rates (*n* = 2 or 3, *x* and *y* unknown, A⁻ = (e.g.) PF₆⁻, NBD = norbornadiene, S = (e.g.) acetone). When L is a more electron donating phosphine like PPhMe₂ (*n* = 2 or 3) and the alkyne is 2-hexyne the reduction is rapid and selective; after absorption of 1 mol of H₂ the solution contains ca. 99% *cis*-2-hexene. Employing [RhH₂L_nS_x]⁺, the predominant catalytically active species in the presence of H⁺A⁻, isomerization of the olefin is negligible. In either case the reaction can be quenched at the endpoint and pure *cis*-2-hexene recovered by standard techniques. Selective reductions of several substituted alkynes have been equally successful. In one direct comparison, a system based on a cationic catalyst precursor was shown to be far superior to the Lindlar-type heterogeneous catalyst.

Several years ago we prepared a large class of complexes of the type [Rh(diene)L_n]⁺A⁻ (**1**; for example, diene = norbornadiene, L = PPhMe₂, *n* = 3, A⁻ = PF₆⁻).² They react readily with molecular hydrogen to give the corre-

sponding saturated hydrocarbon and solutions which contain active catalysts for the hydrogenation of olefins, alkynes, dienes, and ketones.^{2a,d,3} The fact that one can vary L at will allowed close examination of how L influences the

Scheme I. Pathways for Olefin Hydrogenation and Isomerization ($n = 2$ or 3 , Ol = olefin, R = alkyl, RH = alkane, L = ligand, S_x and S_y omitted)

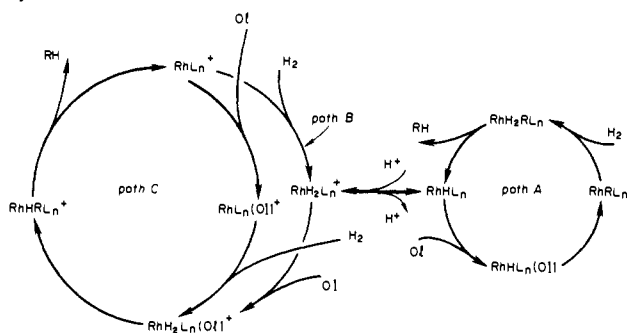


Table I. The Catalytic Hydrogenation of 2-Hexyne and 1-Hexyne^a

(a) 2-Hexyne				
Run	Catalyst precursor	Solv	Rate	Max % <i>cis</i> -2-hexene
1	[Rh(NBD)(PPh ₃) ₂] ⁺	Acet	0.01 ^b	30
2	[Rh(NBD)(diphos)] ⁺	Acet	0.09	81
3	[Rh(NBD)(PPh ₂ OMe) ₂] ⁺	Acet	0.11	90
4a	[Rh(NBD)(PPhMe ₂) ₃] ⁺	Acet	0.47	98
4b	4a plus 1.0 mol of HClO ₄	Acet	0.22	99
5	[Rh(NBD)(PPhMe ₂) ₃] ⁺	2ME	0.78	99
6	[Rh(NBD)(PPhMe ₂) ₂] ⁺	Acet	0.39	97
7a	[Rh(NBD)(PPh ₂ Me) ₂] ⁺	2ME	0.33	98
7b	7a plus 1.6 mol of HClO ₄	2ME	0.14	93
8	[Rh(NBD)(PPh ₂ Me) ₂] ⁺	THF	0.26	95
9	[Rh(NBD)(PPh ₂ Me) ₂] ⁺	Acet	0.17	92
10	[Rh(NBD)(PPh ₂ Me) ₂] ⁺	CH ₃ NO ₂	0.02	
11	[Rh(NBD)(PPh ₂ Me) ₂] ⁺	CH ₃ CN	ca. 0	

(b) 1-Hexyne				
Run	Catalyst precursor	Concn (mM)	Solv	Rate ^c
12	[Rh(NBD)(PPh ₃) ₂] ⁺	2.6	Acet	0.08 ^d
13	[Rh(NBD)(PPhMe ₂) ₃] ⁺	2.6	Acet	0.03 ^d
14	[Rh(NBD)(PPh ₂ Me) ₂] ⁺	5.3	(ClCH ₂) ₂	0.12 ^e
15	[Rh(NBD)(PPh ₂ Me) ₂] ⁺	5.3	2ME	0.08

^a 5.3 mM catalyst concentration; Acet = acetone, 2ME = 2-methoxyethanol, THF = tetrahydrofuran; the anion is ClO₄⁻ or PF₆⁻ (no significant differences in activity were found); rate in units of (mmol of substrate)/min unless otherwise noted. ^b Employing 0.029 mmol of catalyst in 10.0 ml of solvent and 1.0 ml of substrate. ^c Only the initial rate is given. ^d Rate rapidly decreases. ^e Catalyst deactivated after the endpoint (tested at 240 min with 1-hexyne).

process of catalytic hydrogenation and isomerization.⁴ But the most important finding was that two catalytically active hydridospecies are actually present in an equilibrium which can be controlled simply by addition of acid (H⁺A⁻) or base (NEt₃).⁴ Since these catalysts are so efficient and the catalyst precursors easy to make, and since homogeneous hydrogenation systems based on cationic catalyst precursors are rare,⁵ we undertook what is normally a routine study of alkyne hydrogenation. In this paper we present the results and briefly discuss their significance.

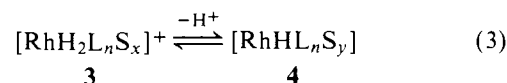
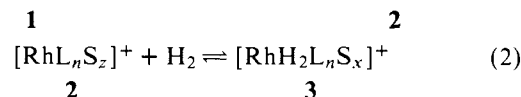
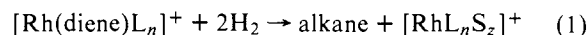
Experimental Section

Part I⁴ describes the hydrogenation apparatus, hydrogenation procedure, and method of product analysis. Catalyst precursors were prepared by previously discussed methods.² The one starting with [Rh(NBD)Cl]₂ and Ag⁺X⁻ in THF^{2c} is the most versatile and best for preparing several small samples of [Rh(NBD)L_n]⁺A⁻ with L different in each. In preparative work one need not isolate [Rh(NBD)L_n]⁺A⁻ but can prepare it in situ in the solvent of choice (acetone or 2-methoxyethanol are both suitable). [Rh(NBD)Cl]₂ and several of the cationic catalyst precursors are available commercially (Strem Chemicals).

Results and Discussion

The Catalyst System. Part I⁴ discusses fully the catalytic principles, reaction of the catalyst precursors with hydrogen, isolation of catalytically active complexes, and how a study of olefin isomerization and hydrogenation led to discovery of the essential features of the catalyst system. It is convenient, however, to briefly summarize here some of the more significant findings.

Equations 1–3 show how catalytically active solutions (S = solvent) result on exposure of 1 to molecular hydrogen. The most important aspects which will concern us here are



the two catalytically active complexes, 3 and 4, and the equilibrium between them. For example, in the case where L = PPhMe₂, n = 3, and S = 2-methoxyethanol, we have estimated that the ratio of 3 to 4 is about 4:1⁴ at 25°. Similar data for other L, n, and S are not available at this time but undoubtedly the ratio will depend strongly on one or more of these variables. Significantly, the equilibrium can be displaced by adding acid (H⁺A⁻) to give a solution containing mainly 3 or base (NEt₃) to give one containing mainly 4. Convincing evidence suggests that solutions containing essentially 100% 3 are easily prepared but we are presently less certain that sufficient NEt₃ will generate solutions containing only 4 or that side reactions are negligible.

Injecting an olefin such as 1-hexene into solutions containing both 3 and 4 (solutions to which no base or acid has been added) under hydrogen results in hydrogenation and isomerization of 1-hexene by 4 and hydrogenation only by 3. The relative amounts of 3 and 4 probably change when olefin is added but this will not concern us here. Scheme I shows the most obvious mechanism, one which will serve the purpose of demonstrating the basic catalytic cycles and how they are related.

In the presence of acid, only hydrogenation by 3 occurs, and in the presence of base, both hydrogenation and isomerization by 4. One rough estimate⁴ (L = PPhMe₂, n = 3, S = 2-methoxyethanol) suggests that 4 isomerizes 1-hexene 25 times more rapidly than 3 hydrogenates 1-hexene. 4 also hydrogenates 1-hexene more rapidly than 3 but no quantitative data are yet available.

In the sections which follow we will study the hydrogenation of alkynes by techniques entirely analogous to those described in Part I.

The Hydrogenation of 2-Hexyne and 1-Hexyne. We began by studying the hydrogenation of 2-hexyne and 1-hexyne since the fates of the primary products, *cis*-2-hexene and 1-hexene, are already known.⁴

Table I lists some representative results and Figures 1 and 2 three reaction profiles. In most cases the rate of alkyne hydrogenation was nearly constant until near the endpoint. Rates are therefore given in millimoles per minute of alkyne reduced rather than calculated in terms of a first-order rate constant. There is no induction period and the maximum amount of the corresponding *cis*-olefin was present after the absorption of 1 mol of hydrogen.

Several general observations can be made based on the data in Table Ia: (i) 2-hexyne is hydrogenated at a rate which is much greater than the rate at which *cis*-2-hexene subsequently is hydrogenated and isomerized; (ii) the maxi-

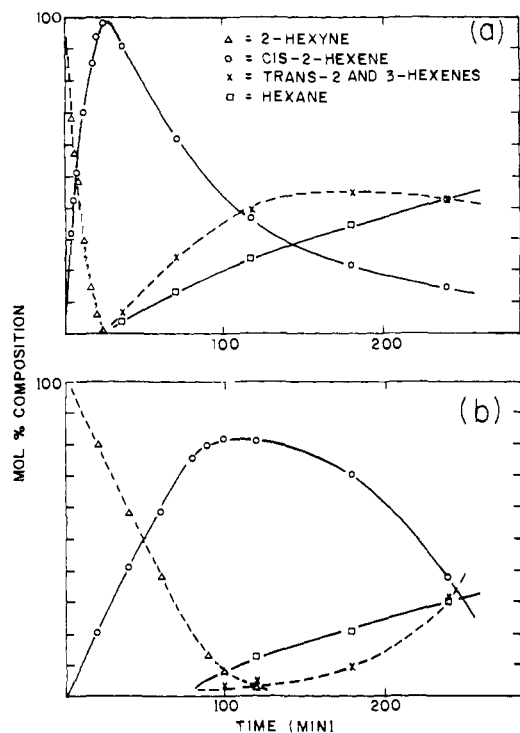
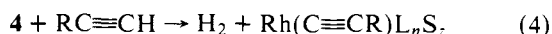


Figure 1. The hydrogenation of 2-hexyne: (a) 5.3 mM $[\text{Rh}(\text{NBD})(\text{PPh}_2\text{Me})_3]^+\text{PF}_6^-$ in 2-methoxyethanol (run 5, Table Ia); (b) 5.3 mM $[\text{Rh}(\text{NBD})(\text{diphos})]^+\text{ClO}_4^-$ in acetone (run 2, Table Ia).

imum percent *cis*-2-hexene varies directly with the rate of hydrogenation of 2-hexyne. Both are maximized by employing catalysts containing more basic or less sterically demanding phosphine ligands or solvents (compare runs 7–11) which probably coordinate weakly to the metal. Of course, the most striking result is that in some cases 2-hexyne can be selectively reduced to *cis*-2-hexene in essentially quantitative yield. On a larger scale the reaction can be quenched with diphos (1,2-bisdiphenylphosphinoethane) at the endpoint⁴ and *cis*-2-hexene isolated by vacuum transfer and distillation. The product distribution does not change during this time; the isolated product is ~99% *cis*-2-hexene.

1-Hexyne cannot be reduced successfully to 1-hexene with as many catalysts. In many cases the normally orange solution turned brown as 1-hexyne was consumed; in one case (run 14) the catalyst was apparently deactivated during the run as determined by injection of 1-hexyne at $t = 240$ min. The rate of 1-hexyne hydrogenation is also often not constant. These observations all suggest that a side reaction destroys the active catalyst. Since terminal alkynes are fairly acidic, one possibility is that shown in eq 4. In spite of these difficulties, 1-hexyne can be successfully and selectively reduced to 1-hexene under the right conditions (run 15, Table Ib, Figure 2).



The selective reduction of alkynes is rare and no catalyst, homogeneous or heterogeneous, produces the olefin in yields which equal the best results observed here. For example, Candlin and Oldham⁶ report that $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ reduces 1-hexyne to 1-hexene with 95% selectivity in 1/1 benzene/phenol. (In benzene alone they found $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ nonselective; note that $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ can be protonated.⁷) The most widely used palladium catalysts (among them the Lindlar catalyst) have been known for two decades,⁸ but selectivity rarely exceeds 90%. Since homogeneous hydrogenation systems which employ discrete transition metal catalysts and which operate under mild conditions are not yet

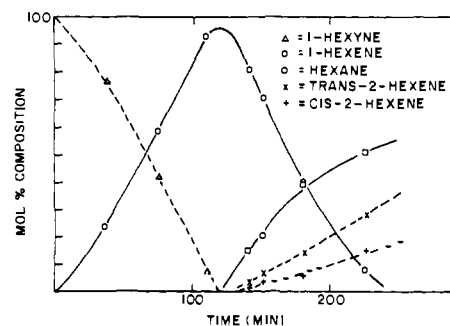


Figure 2. The hydrogenation of 1-hexyne by 5.3 mM $[\text{Rh}(\text{NBD})(\text{PPh}_2\text{Me})_2]^+\text{PF}_6^-$ in 2-methoxyethanol (run 15, Table Ib).

commonplace, and cationic catalysts are rare, we chose to study the selective reduction of 2-hexyne in greater detail in order to determine why these particular catalysts are so successful.

The Origin of Selectivity. The metal-catalyzed hydrogenation of 2-hexyne by any reasonable mechanism can only give *cis*-2-hexene as the primary reaction product. Assume for the sake of argument that two hydrides transfer sequentially to coordinated 2-hexyne. Transfer of the first hydride most reasonably would yield a *cis* vinyl ligand. The second hydride should transfer to the vinyl α -carbon with retention of the *cis* geometry about the double bond. Alternatives have no precedent and seem considerably less likely, especially in view of the selective production of *cis*-2-hexene observed in this study.

Since *cis*-2-hexene is the only reasonable primary product, selectivity must arise from the fact that coordinated *cis*-2-hexene is immediately displaced by 2-hexyne before it can isomerize or be hydrogenated to hexane. The mechanism by which *cis*-2-hexene is formed is unimportant. Therefore, in theory, mechanisms (substituting alkyne for olefin in Scheme 1) analogous to path A, B, or C, or any combination, could be the means by which 2-hexyne is reduced selectively.

Figure 3 shows the reaction profiles of two parallel experiments. One system contains both 3 and 4 (Figure 3a), the other essentially only 3, the result of adding acid (Figure 3b). After the endpoint no 2-hexyne remains and the fate and rate of disappearance of *cis*-2-hexene are identical with results described in Part I.⁴ At the endpoint the maximum percentages of *cis*-2-hexene are essentially the same. The most important feature is that, in the system containing only 3, the rate of 2-hexyne hydrogenation is approximately half that in the system containing both 3 and 4 (see Table Ib, runs 4a and 4b). A second parallel experiment (runs 7a and 7b) gave similar relative rates though the maximum percentage of *cis*-2-hexene declined somewhat, from 98% in run 7a to 93% in run 7b. These data suggest that (i) both 3 and 4 are active catalysts for the selective hydrogenation of 2-hexyne and (ii) the rate of hydrogenation with 4 is at least twice that with 3.

Figure 4 shows the reduction of 2-hexyne by the system in Figure 3a to which 1 mol of base has been added. The active catalyst is therefore largely $\text{RhH}(\text{PPh}_2\text{Me})_3\text{S}_y$. Note that 2-hexyne is still *selectively* reduced.⁹ Analogous experiments with $\text{RhH}(\text{PPh}_2\text{Me})_2\text{S}_y$, prepared from $[\text{Rh}(\text{NBD})(\text{PPh}_2\text{Me})_2]^+$, H_2 , and Et_3N or $\text{Rh}(\text{NBD})(\text{CH}_3)(\text{PPh}_2\text{Me})_2$ and H_2 , each in acetone, gave similar results to those shown in Figure 4. The rate of reduction was somewhat slower, however, consistent with the general trend (Table Ia) that RhHL_xS_y catalysts containing PPh_2Me do not reduce 2-hexyne as efficiently as those containing PPhMe_2 .

In view of the above results the possibility that 2-hexyne

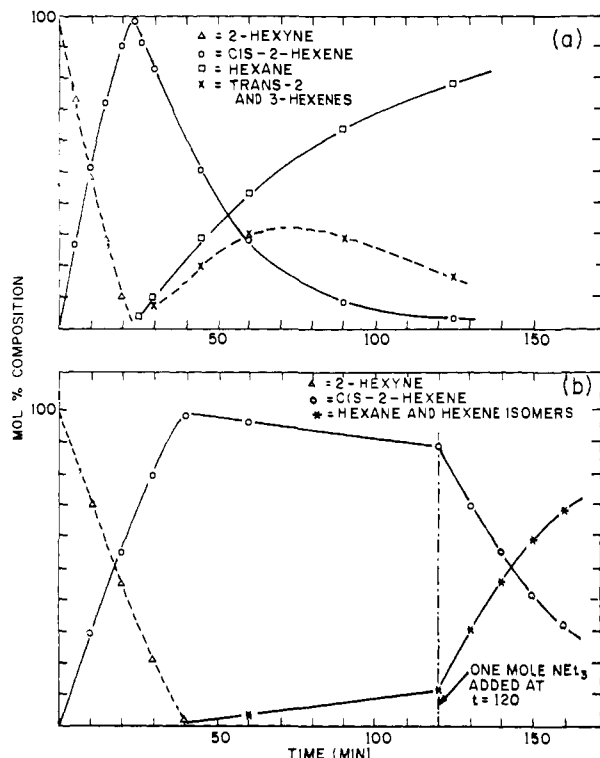


Figure 3. The hydrogenation of 2-hexyne in acetone, the effect of acid (Table Ia, runs 4a and 4b): (a) 5.3 mM $[\text{Rh}(\text{NBD})(\text{PPhMe}_2)_3]^+\text{PF}_6^-$, (b) 5.3 mM $[\text{Rh}(\text{NBD})(\text{PPhMe}_2)_3]^+\text{ClO}_4^-$ in the presence of 1.0 mol of HClO_4 .

is reduced to a significant extent by a mechanism analogous to path C (Scheme 1) would seem remote. The characteristics of a system in which path C is believed to play a major role (see Part III) are distinctive and significantly different from those of typical olefin or alkyne hydrogenations. However, we cannot discount the possibility that more strongly coordinating alkynes will be reduced to some extent by a mechanism analogous to path C.

Clearly **3** and **4** both selectively reduce 2-hexyne, and at rates which are roughly comparable. In some instances, however, hydrogenation in the presence of acid (i.e., with **3**) might be preferred since subsequent hydrogenation or isomerization of *cis*-2-hexene is comparatively slow (see Figure 3), thereby allowing more time to quench the reaction and giving, ultimately, a purer isolated product.

The gross mechanism of alkyne hydrogenation must be essentially that shown in Scheme 1 (substituting alkyne for olefin). We have learned little new in this respect. The reason why 2-hexyne is selectively reduced must be that postulated earlier. 2-Hexyne simply competes strongly with *cis*-2-hexene for coordination sites on **3** and **4**. In the most successful cases (runs 4b and 5 in Table Ia) one molecule of 2-hexyne must compete successfully with 99 molecules of *cis*-2-hexene. The catalyst's discrimination between the two is impressive.

The most obvious variable on which selectivity depends is the nature of L. The most successful catalysts are those in which L donates (in a relative sense) more electron density to the metal. Possibly this ensures that 2-hexyne is bound rapidly and significantly more strongly than *cis*-2-hexene. At this time we have no basis for stating that the catalyst systems described here are unique. Therefore other group 8 catalysts (e.g., RuHClL_3 ,¹⁰ $\text{RhH}(\text{CO})\text{L}_3$,¹¹ and RhL_3Cl ¹²) where L is PPhMe_2 , for example, should be examined carefully. Note, however, that their catalytic activity usually depends on dissociation of L;⁵ **3** and **4**, on the other hand, both

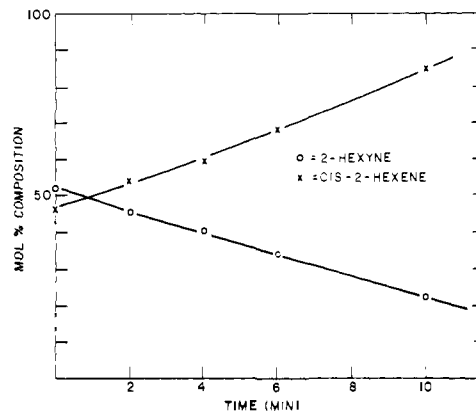
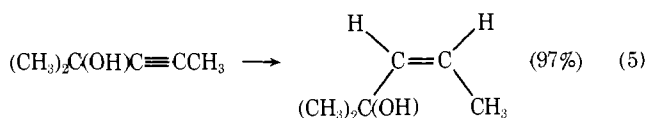


Figure 4. The selective reduction of 2-hexyne in a 2-hexyne-*cis*-2-hexene mixture with $\text{RhH}(\text{PPhMe}_2)_3\text{S}_x$ in acetone (5.3 mM $[\text{Rh}(\text{NBD})(\text{PPhMe}_2)_3]^+$ was treated successively with H_2 , 1.0 mol of Et_3N , and 1.0 ml of the mixture; no hexene isomers or hexane was observed).

contain at least one hydride and are both already "coordinatively unsaturated" in weak donor solvents.

Applications. We have so far been concerned only with a model alkyne. We have also briefly explored reduction of alkynes containing certain substituent groups.

2-Pentyne-4-methyl-4-ol (1.0 mmol) was cleanly reduced to *cis*-2-pentene-4-methyl-4-ol with 0.058 mmol of $[\text{Rh}(\text{NBD})(\text{PPhMe}_2)_3]^+\text{ClO}_4^-$ in 10.0 ml of acetone (eq 5). The olefin was separated by preparative GLC methods



and shown to be *cis* ($J_{\text{H-H}} \approx 3$ Hz). The initial rate (ca. 0.1 mmol/min) rapidly decreased so that complete reduction required ca. 6 h. No obvious catalyst decomposition took place; the color of the solution remained a pure yellow and no other products were detected. (We did not test whether more alkyne could be reduced at the initial rate after 6 h.)

The rate of reduction of 0.90 g of 2-butyne-1,4-diol with 0.058 mmol of $[\text{Rh}(\text{NBD})(\text{PPh}_2\text{Me})_2]^+\text{PF}_6^-$ under identical conditions was comparable to the initial rate above, but did not decrease with time. Negligible alkyne remained after absorption of 1 mol of H_2 per mole of alkyne. However, only ca. 60% of the alkyne was reduced to 2-butene-1,4-diol; ca. 40% was converted to an unidentified low boiling product. "Hydrogenolysis" of acetylenic alcohols during hydrogenation with heterogeneous catalysts is common.⁸ Since the amount of hydrogenolysis generally decreases if a base is added, it would be worthwhile to repeat this experiment in the presence of NEt_3 , i.e., with the $\text{RhH}(\text{PPh}_2\text{Me})_2\text{S}_x$ catalyst.

Attempts to selectively reduce the acetylenic bond in 1-octen-4-yne and 1-hexen-3-yne gave complex mixtures with no one product outstanding (by GLC; we did not attempt to identify products). This result is not surprising in view of the fact that the alkyne bonds are in the center of the chain and may not compete well with terminal olefinic bonds for metal coordination sites. Note also that reduction of 1-hexen-3-yne would yield a conjugated diene. As we shall see in Part III, conjugated dienes are also easily reduced to monoenes by a combination of 1,4- and 1,2-hydrogen addition.

The last example provides a direction comparison between one of the catalysts described here and a Lindlar-type catalyst. Studies concerning the mode of "oxidative addition" to Ir(I) complexes¹³ required a source of *cis*-ethyl cinnamate (*cis*-**5**). A 7.7-g sample of $\text{C}_6\text{H}_5\text{C}\equiv\text{CCO}_2\text{C}_2\text{H}_5$ in

30 ml of acetone containing 220 mg of $[\text{Rh}(\text{NBD})(\text{PPhMe}_2)_3]^+\text{PF}_6^-$ and 30 mg of 70% aqueous perchloric acid was stirred under H_2 until 95% of the theoretical amount of H_2 had been absorbed. The product mixture was distilled at 103° and 57 mm to give 7.4 g of *cis*-5 containing only a trace of $\text{C}_6\text{H}_5\text{C}\equiv\text{CCO}_2\text{C}_2\text{H}_5$ and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ and no *trans*-5. The attempted specific reduction with a Lindlar-type catalyst (5% Pd on BaSO_4) gave primarily $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$.

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Optical Spectra of the Difluoride, Dichloride, and Trichloride Ions in the Matrix-Isolated M^+F_2^- , M^+Cl_2^- , and M^+Cl_3^- Species

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Abstract: Alkali metal atoms were codeposited with fluorine and chlorine at high dilution in argon on a sapphire plate cooled to 17 K. Ultraviolet spectra contained strong absorptions near 300 nm for M^+F_2^- and 340 nm for M^+Cl_2^- which are assigned to the $\sigma \rightarrow \sigma^*$ transition of the dihalide anion. This transition for Cl_2^- occurs at half of the energy known for Cl_2 . The alkali metal effect on the absorption spectra is consistent with an ionic model of polarizable ion pairs. In addition, the strong ultraviolet band of the trichloride anion was observed at 250 nm with the metal-chlorine reactions and with the matrix reaction of CsCl and Cl_2 .

Very recently Howard and Andrews reported the observation of Raman signals near 460 cm^{-1} from argon-fluorine matrix samples codeposited with alkali atoms which were assigned to the intraionic F_2^- vibration in the M^+F_2^- species.² The first evidence for the difluoride radical anion came from ESR spectra of irradiated fluoride salts at 77 K.³ Subsequent work confirmed the ESR spectrum of F_2^- in solid LiF and recorded a strong optical band at 348 nm which was assigned to the ${}^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ transition of the F_2^- center.⁴ Hence, optical spectroscopic observation of F_2^- using the same reactions as the Raman experiments would provide support for this chemical preparation of the unstable species F_2^- .

On the other hand, the dichloride radical anion has been more widely studied. Cl_2^- has been observed in irradiated chloride salts at 77 K by ESR and optical spectroscopy,⁵ in irradiated 77 K glasses by optical⁶ and Raman methods,⁷ and as a transient species in aqueous chloride solutions by flash photolysis⁸ and pulse radiolysis.⁹ Laser-Raman studies of matrix samples prepared by codepositing chlorine with alkali atoms yielded strong resonance Raman progressions in the Cl_2^- vibration.^{10,11} The dependence of reso-

nance Raman spectra of Cl_2^- upon the wavelength of the exciting line required a near-ultraviolet optical band for the M^+Cl_2^- species which was one of the goals of this study.

Even though optical spectra of the more stable triiodide and tribromide ions have been studied extensively,¹² the limited spectral data on the less stable trichloride ion has not been well characterized. Aqueous solutions of Cl_2 and Cl^- exhibited broad absorptions near 230 nm which have been attributed to Cl_3^- .^{13,14} Upon warming irradiated $\text{NaCl-H}_2\text{SO}_4$ glasses, the Cl_2^- absorption decayed and a band assigned to Cl_3^- appeared at 230 nm.⁶ The M^+Cl_3^- species is produced as a secondary reaction product in the matrix reactions of alkali metal atoms with chlorine,¹¹ which has been confirmed by the matrix reaction of MCl salt molecules with chlorine.¹⁵ The optical spectrum of the trichloride ion in the M^+Cl_3^- species will also be presented in the following study.

Experimental Section

The vacuum vessel used for optical matrix-isolation studies was similar to that previously described for infrared work¹⁶ except for quartz optical windows and a Model 21 Cryodyne (Cryogenic