Catalytic Hydrogenation Using Cationic Rhodium Complexes. 3. The Selective Hydrogenation of Dienes to Monoenes

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Abstract: Norbornadiene (NBD), 1,3-butadienes, and 1,3-cyclohexadienes are hydrogenated specifically to monoolefins with catalysts prepared by reacting $[Rh(NBD)L_2]^+A^-$ with molecular hydrogen (L = PPh_3, A^- = PF_6^-, for example). With proper choice of L the yield of monoolefin after absorption of 1 mol of hydrogen is essentially quantitative. Rapid, selective diene hydrogenation is successful since hydrogen attacks $[Rh(diene)L_2]^+$ (the sole species in solution with any significant concentration) at a rate which is remarkably rapid compared to the rate of similar "unsaturate" routes with other homogeneous hydrogenation catalysts. Hydrogen adds both 1,2 and 1,4 to conjugated dienes; the product ratio can be reversed in one instance (from 4:1 to 1:4) by changing L. In the presence of acid the rate of diene hydrogenation is unchanged while subsequent monoolefin isomerization and hydrogenation is slowed. Hydrogenation in the presence of acid is therefore a preferred, but not an essential, procedure.

Several years ago, we prepared a large class of complexes of the type $[Rh(diene)L_n]^+A^-$ (**1**; for example, diene = norbornadiene, L = $PPhMe_2$, n = 3, A^- = PF_6^-).[2] They react readily with hydrogen to give the corresponding saturated hydrocarbon and solutions which contain active catalysts for the hydrogenation of olefins, alkynes, dienes, and ketones under mild conditions (25°, 1 atm of H_2).[2a,d,3] The fact that two catalytically active species are actually present in a typical catalyst system in an equilibrium which can be controlled by addition of acid (H^+A^-) or base (NEt_3) and the fact that L can be varied at will make these catalysts versatile, useful, and, at present, unique in several ways. In this paper, the last of this series,[3] we examine closely the selective hydrogeneration of certain dienes under mild conditions, and discuss several aspects of selective hydrogenation which may not only be pertinent to this particular catalyst system, but to selective hydrogenation in general.[4] This will complete the outline of the general aspects of hydrogenation of three basic types of molecules containing unsaturated carbon-carbon bonds with cationic catalyst precursors of type **1**.

Results and Discussion

General Considerations. In Part 1[3a] we discussed fully the general principles of the catalytic system which results from exposure of the catalyst precursors, **1**, to hydrogen. Equations 1-3 show three important details and Scheme I the pathways for olefin hydrogenation which revolve about the equilibrium between the two known catalytically active species, **3** and **4** (x, y, and z unknown; S = solvent).

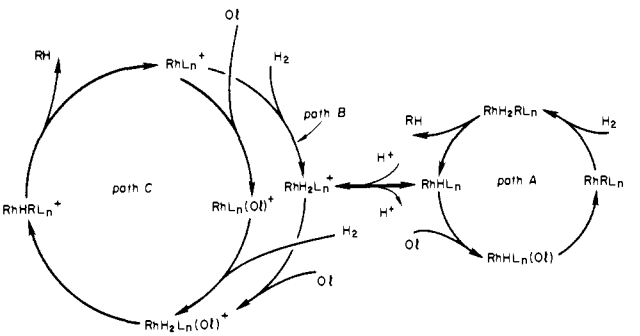
$$\underset{\mathbf{1}}{[Rh(diene)L_n]^+} + 2H_2 \longrightarrow \text{alkane} + \underset{\mathbf{2}}{[RhL_nS_z]^+} \quad (1)$$

$$\underset{\mathbf{2}}{[RhL_nS_z]^+} + H_2 \rightleftharpoons \underset{\mathbf{3}}{[RhH_2L_nS_x]^+} \quad (2)$$

$$\underset{\mathbf{3}}{[RhH_2L_nS_x]^+} \overset{-H^+}{\rightleftharpoons} \underset{\mathbf{4}}{RhHL_nS_y} \quad (3)$$

The major findings so far are the following: (i) the activity of **3** and **4** depends strongly on the nature of L; (ii) **3** is a good olefin hydrogenation catalyst and a poor olefin isomerization catalyst; (iii) **4** is an excellent olefin hydrogenation *and* isomerization catalyst; and (iv) **3** and **4** both selectively reduce alkynes to cis olefins at comparable rates. Both **3** and **4** are present under normal conditions. For example, when L = $PPhMe_2$, n = 3, and S = 2-methoxyethanol, we have estimated the ratio of **3** to **4** as 4:1 at 25°. On addition of 1-2 mol of acid per Rh (perchloric acid for example) the equilibrium shifts to give a solution which contains primarily **3**; on addition of base (NEt_3) the solution contains primarily **4**.

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).



Our more detailed studies so far have dealt with monodentate substrates (olefins and alkynes).[3] Conjugated dienes, on the other hand, or those which can attain the proper configuration (norbornadiene or 1,5-cyclooctadiene for example), of course can coordinate to a metal through both double bonds. Therefore, the mechanism by which they are reduced need not be identical with that by which monodentate substrates are reduced. For example the reduction of norbornadiene (NBD) with $Rh(PPh_3)_3Cl$ in benzene is extremely slow compared to the rate of reduction of monoolefins.[5a] Since $Rh(NBD)(PPh_3)Cl$ can be isolated from the catalyst solution it is presumably the energetically favored species under catalytic conditions and evidentally does not react readily with molecular hydrogen (eq 4).

$$Rh(PPh_3)_3Cl \xrightarrow{NBD} Rh(NBD)(PPh_3)Cl \xrightarrow[\text{very slow}]{H_2} \text{norbornene} \quad (4)$$

On the other hand, the method of preparing the catalysts which we are discussing here (eq 1) is an example where hydrogen reacts *rapidly* with a diene complex. Therefore, we can at least be assured that this catalyst system will not be "poisoned" similarly.

In the following sections we discuss the catalytic hydrogenation of several dienes which are known[2b] to form complexes of type **1**. The object is to illustrate the principles of hydrogenation of these particular dienes and thereby to show under what circumstances similar results might be expected for other

Table I. The Hydrogenation of Norbornadiene in Acetone[a]

Run	Catalyst	R_{diene}	R_{ene}	Max % ene
1a	$[Rh(NBD)(PPh_3)_2]^+PF_6^-$	0.22	0.03	97
1b	1a with 3.0 mol of $HClO_4$	0.21	0.05	92
1c	1a with D_2	0.22	(b)	(b)
1d	1a with 2.0 mol of Et_3N and D_2	~0.21 (initial)[c]	(b)	80
2	$[Rh(NBD)(PPh_2Me)_2]^+PF_6^-$	0.16	0.12	97
3[d]	$[Rh(NBD)(PPhMe_2)_2]^+PF_6^-$	0.14	0.19	90

[a] In 10.0 ml of acetone, 1.0 ml of NBD, 30.0 ± 0.5°, 1 atm total pressure of H_2, 0.026 mmol of catalyst precursor, R = rate in mmol/min. [b] Not measured. [c] A markedly nonlinear rate was observed. The behavior was more nearly first order in olefin ($k = 4.4 \times 10^{-4}$ s^{-1}). [d] Catalyst precursor = 0.053 mmol.

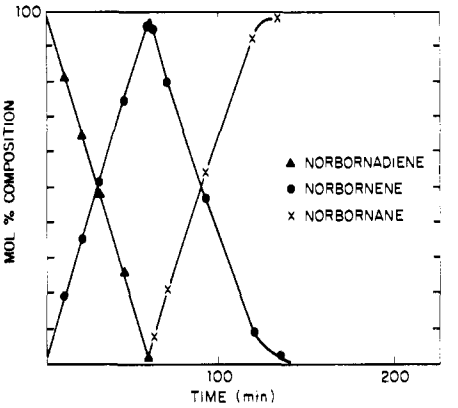


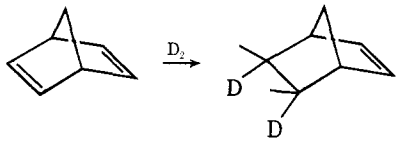
Figure 1. The catalytic hydrogenation of norbornadiene in acetone (run 2, Table I).

dienes. In each case the catalytic systems were prepared by stirring a solution of $[Rh(NBD)L_n]^+$ under hydrogen in a polar solvent. The diene (1.0 ml) was then injected and the composition monitored by GLC methods as described previously.[3a]

The Reduction of Norbornadiene. Table I shows the results of several runs using $[Rh(NBD)L_2]^+$ type catalyst precursors in acetone,[10] and Figure 1 a reaction profile of run number 2. Since the rates of disappearance, first of NBD, then norbornene, are nearly constant, they are tabulated in units of millimoles per minute of substrate reduced.

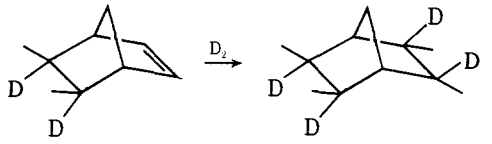
The data clearly show that norbornadiene is reduced selectively to norbornene. Since the rates of reduction are comparable, norbornadiene must compete effectively with norbornene for coordination sites on metal complexes in solution. This is consistent, of course, with the fact that all known complexes in the catalytic system have at least two available (solvated) coordination sites.

That *both* double bonds of NBD are indeed coordinated before a hydride (or hydrides) transfers to it is suggested by the fact that the norbornene-d_2 product in runs 1c and 1d is solely endo-d_2 (eq 5).[6a] A hydrogenation identical with run 1c



(5)

was allowed to proceed to the alkane stage; the product was solely *endo*-2,3-*exo*-5,6-norbornane-d_4 (eq 6).[6b] A metal is known to coordinate in the exo position in norbornene complexes.[7] Therefore hydrogenation of 2,3-disubstituted norbornenes gives *endo*-2,3-disubstituted-norbornane[8] and D_2 of course adds exo to norbornene (eq 6). However, the metal is



(6)

also exo in the known complexes containing monodentate NBD.[7,9] Therefore only if both double bonds are coordinated can D_2 add first specifically endo to NBD (eq 5).

The above results do not predict in detail the manner in which NBD is reduced since NBD can coordinate in a bidentate fashion to any species in solution as long as it does so before any hydride transfers to C=C. Therefore we must consider all three major possible routes. In the first, A, NBD attacks **4**; in the second, B, NBD attacks **3**; and in the third, C, the so-called "unsaturate route", hydrogen attacks **1**.

The data in Table I clearly show that the rate of hydrogenation of norbornene (R_{ene}) increases as L varies in the order $PPh_3 < PPh_2Me < PPhMe_2$ (runs 1a, 2, and 3, respectively). This result is analogous to that found for reduction of other monoolefins by catalyst systems of this type and there is no reason to suspect that the gross mechanism of norbornene hydrogenation is not essentially identical with that of other monoolefins. The above variation in R_{ene} with L is, in fact, a general feature of several homogeneous hydrogenation systems which contain metal-phosphine complexes as catalysts where such a study is possible.[5a]

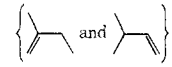
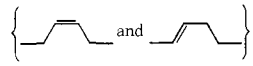
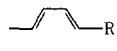
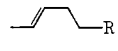
In contrast, however, note that the rate of reduction of NBD (R_{diene}) varies with L in the *opposite sense;* i.e., the catalyst precursor containing PPh_3 gives the *most active* system for reducing NBD. One might therefore suspect that to a large extent the mechanism by which NBD is hydrogenated is significantly different from that (paths A and B) by which monoolefins are hydrogenated,[3] i.e., that path C might operate in this case.

A likely, though not required, consequence of reduction via path C is that $[Rh(NBD)L_2]^+$ is the predominant, if not the only, species with any appreciable concentration under catalytic conditions. Several observations are consistent with this postulate: (i) the rate of diene reduction is independent of NBD concentration until near the endpoint (1 mol of H_2 absorbed); (ii) during the course of catalytic reduction of NBD to norbornene the solution color is qualitatively that of $[Rh(NBD)L_2]^+$; and, most importantly, (iii) the rate at which H_2 reacts with $[Rh(NBD)L_2]^+$ qualitatively parallels R_{diene} in Table I; i.e., $[Rh(NBD)(PPh_3)_2]^+$ reacts much more rapidly with H_2 than $[Rh(NBD)(PPhMe_2)_2]^+$ under identical conditions (acetone, 25°, 1 atm of H_2) as shown by the rate at which the color due to $[Rh(NBD)L_2]^+$ is discharged and by the rate at which norbornene is produced (monitored by GLC).

Further support for this postulate derives from the fact that R_{diene} in the presence of acid (run 1b) is identical (and constant with time) with that without added acid (run 1a). Since R_{diene} using a solution containing primarily **4** (1d) is not constant, the only reasonable explanation why R_{diene} is the same and constant with time in runs 1a and 1b is that *essentially no $RhHL_2S_x$ exists in solution during diene hydrogenation.* Therefore, the lack of an acid effect (either an increase or a decrease in the rate of hydrogenation) could be taken as positive evidence that a monohydride species is not present, i.e., that K_{eq} for formation of $RhHL_2S_y$ is not large. Significantly, there is an acid effect *after the endpoint* in run 1b (a rate increase) and in the systems dealing with hydrogenation of olefins[3a] and alkynes[3b] (a rate decrease).

We therefore suggest that NBD is hydrogenated largely, if not entirely, via path C. In retrospect this seems plausible since, in contrast to ostensibly more weakly bonded olefins and alkynes, NBD bonds strongly to the metal and can thereby effectively shift solution equilibria to form $[Rh(NBD)L_2]^+$,

Table II. The Catalytic Reduction of Substituted Butadienes[a]

Run	Catalyst precursor	Solv.	Diene	Rate	Products[b]			Max % total product
								
1a	$[Rh(NBD)(diphos)]^+(ClO_4^-)$	acet		0.14	43		57	99
1b	$[Rh(NBD)(diphos)]^+(BF_4^-)$	acet		0.15	46		54	99[c]
1c	1b with 2.0 mol of $HClO_4$	acet		0.14	43		57	99
1d	1b with 1.0 mol of Et_3N	acet		0.08[f]	51		49	(d)
2	$[Rh(NBD)(diphos)]^+$	2Me		0.08	39		61	99[c]
3	$[Rh(NBD)(diphos)]^+$	THF		0.06[e]	45		55	(d)
4a	$[Rh(NBD)(arphos)]^+$	acet		0.18	17		83	99
4b	4a with 1.0 mol of Et_3N	acet		0.19[f]	23		77	95
5a	$[Rh(NBD)(dpae)]^+$	acet		0.16	80[g]		20	90
5b	$[Rh(NBD)(dpae)]^+(BF_4^-)$[h]	acet		0.14	78		22	99[c]
5c	5a with 3.1 mol of $HClO_4$	acet		0.13	78[g]		22	98
								
6	$[Rh(NBD)(diphos)]^+$	acet		0.28	31[i]		69	99[c]
7	$[Rh(NBD)(arphos)]^+$	acet		0.20[j]	10[k]		90	99[c]
8	$[Rh(NBD)(arphos)]^+$	2ME		0.15	8[l]		92	99[c]
								
9	$[Rh(NBD)(arphos)]^+$	2ME		0.10	16		84[m]	97[c]
								
10	$[Rh(NBD)(diphos)]^+$	acet		0.20[f]	15[n]	43	42[n]	96[c]
11	$[Rh(NBD)(arphos)]^+$	acet		0.22	3[n]	55	42[n]	96[c]
								
12	$[Rh(NBD)(arphos)]^+$	2ME		0.022				
							(R = CO_2CH_3)	
13	$[Rh(NBD)(diphos)]^+$	acet		<0.005				

[a] Catalyst concentration = 5.3 mM; 10.0 ml of solvent; 1.0 ml of substrate (diene); rate in units of mmol of diene min^{-1}; 30.0 ± 0.5 °C; 1 atm total pressure; diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, arphos = $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$, dpae = $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$; anion is PF_6^- unless otherwise noted. [b] Average % product in total product mixture. The values are constant to ±3% or less to >90% reduction unless otherwise noted. [c] Terminated at the endpoint. [d] Reaction terminated at >50% but <100% completion. [e] A fine precipitate appeared in the catalyst solution before injection of diene. It did not dissolve readily as hydrogenation proceeded. [f] Rate of reduction nonlinear. [g] This value decreased by ca. 5% during the course of the reaction. [h] Catalyst prepared in situ from $[Rh(NBD)_2]^+BF_4^-$ (ref 1c) and dpae. [i] Ratio of 13 to 18% or vice versa. [j] Rate calculated from uptake data only. [k] Ratio of 3 to 7% (or vice versa). [l] Ratio of 2.5 to 5.5% (or vice versa). [m] Products inseparable by GLC. If *trans*-2-hexene ≃ *cis*-2-hexene then *cis*-3-hexene (the 1,4-addition product) ≃ 66%. [n] Isomer identification based on ^1H NMR data.

even in the presence of H_2. This can be seen qualitatively by addition of NBD to the pale solution containing **3** and **4** under H_2; within time of mixing the solution turns the red color characteristic of **1**. Therefore **1** must form more rapidly than the rate at which it reacts with hydrogen. Consequently the rate determining step of catalytic NBD hydrogenation is likely to be the rate at which H_2 reacts with **1**. Interestingly, this fact could, in part, account for the observed variation of R_{diene} with L. Though no similar observations in a catalytic system are known to us, there is some parallel between these data and that of Strohmier and Onada[11] who studied the rate of addition of H_2 to *trans*-$IrL_2(CO)X$. They found that for X = Cl and T = 30°, the rate of hydrogen uptake to give $IrH_2L_2(CO)X$ decreases when L varies in the order L = PPh_3 (R = 2.10) > $P(\eta\text{-}C_4H_9)_3$ (R = 1.29) > $P(OPh)_3$ (R = 0.26).

The above findings suggest that other dienes with large complexation constants should also coordinate strongly to give predominantly **1** under catalytic conditions, and they should be reduced largely, if not entirely, also via path C. That **1** is the predominent species in solution under catalytic conditions could, in theory, be proven by visible-uv spectroscopy. However, a rough indicator is simply the ease of isolating species of type **1** on addition of diene to prepared catalyst solutions. This is in fact the method of preparing **1** when the diene is a conjugated diene such as 1,3-butadiene or its 2,3-dimethyl derivative.

The Reduction of Butadiene Derivatives. The characteristics of a typical hydrogenation of a conjugated diene are similar to those of an NBD hydrogenation (see Table II and Figure 2); i.e., the rates at which diene is consumed and products appear are essentially constant up to at least the point where about 90% of the diene has been reduced, and the color of the solutions rapidly changes from red to yellow at the endpoint (1 mol of H_2 absorbed). The products, monoenes which result from overall 1,2 and 1,4 addition of H_2 to the diene, are formed nearly quantitatively. Since the product distribution is constant within experimental error during diene hydrogenation, they are formed directly from the diene. (Product distribution is also independent of the anion; compare run 1a and 1b.) After the endpoint, however, the terminalll olefin isomerizes to the internal olefin and one or both are hydrogenated to the alkane. This behavior is analogous to that in other monoolefin hydrogenation studies discussed elsewhere.[3a] Therefore hydrogenation in the presence of acid might be preferred if one is

Table III. The Catalytic Reduction of Cyclohexadienes in Acetone[a]

Run	Catalyst precursor	Diene	Rate H_2	Rate D_2[b]	Max % Monoene(s)
1	$[Rh(NBD)(diphos)]^+$		0.29[c]	0.25[c]	98
2	$[Rh(NBD)(PPh_3)_2]^+$ with 2.2 mol of $HClO_4$		0.20[c]	(d)	99
3a	$[Rh(NBD)(PPh_2Me)_2]^+$		0.23	0.21[c]	98
3b	3a with 2.2 mol of $HClO_4$		0.22	(d)	99
4	$[Rh(NBD)(diphos)]^+$		(d)	0.18[c]	98
5	$[Rh(NBD)(PPh_2Me)_2]^+$		0.07	(d)	98
6	$[Rh(NBD)(diphos)]^+$		0.13[c]	(d)	98[e,f]
7	$[Rh(NBD)(PPh_2Me)_2]^+$		0.12[c]	(d)	91[g]

[a] Conditions and terminology as described in Table II. [b] The gas above the solution at the endpoint in all cases consisted of >98% D_2. [c] Hydrogenation was terminated at the endpoint. [d] Not done. [e] 3-Me (3-methylcyclohexene) and 4-Me are inseparable by GLC; their relative amounts were estimated by NMR. 1-Me and a mixture of 3- and 4-Me were formed in a constant ratio (±3%) up to >90% reduction. [f] (3-Me + 4-Me)/1-Me = 87:13; 3-Me/4-Me ≃ 2:3, by NMR. [g] (3-Me + 4-Me)/1-Me = 79:21; 3-Me/4-Me ≃ 1:1, by NMR.

interested in slowing the rate of isomerization and hydrogenation of the primary products. As found in the case of NBD (preceding section), the rate of diene reduction does not change significantly on addition of acid (1c vs. 1a or 1b; 5c vs. 5a or 5b).

It should be noted that the most successful catalyst precursors are those containing bidentate phosphine or arsine ligands. $[Rh(NBD)L_2]^+$ (L = PPh_3, PPh_2Me, and $P(OPh)_3$) or $[Rh(NBD)(AsPhMe_2)_3]^+$ precursors gave catalyst solutions which, a few seconds to several minutes after injecting diene, turned nearly colorless and absorbed no more hydrogen to any significant extent over several hours. In one case (L = PPh_3, diene = 1,3-butadiene) very pale yellow crystals could be isolated. ^1H NMR and elemental analyses[2b] support formulation of this product as $[Rh(1,3\text{-butadiene})_2(PPh_3)]^+$. A solution of $[Rh(1,3\text{-butadiene})_2(PPh_3)]^+$ and 2,3-dimethyl-1,3-butadiene in acetone under molecular hydrogen did not take up hydrogen to any significant extent in 4 h under standard conditions. We conclude, therefore, that formation of $[Rh(diene)_2L]^+$ is responsible for deactivating the catalytic system.[12] Since a chelating ligand prevents ready formation of analogous complexes, $[Rh(NBD)(chelate)]^+$ catalyst precursors are preferred for diene reductions.[13]

All the arguments in the preceding section which led to the conclusion that the sole significant pathway for NBD hydrogenation consists of H_2 attack on $[Rh(NBD)L_2]^+$ apply equally well here (where L_2 = a chelating ligand) since the complexation constant of a 1,3-diene which can attain an *S*-cis configuration is likewise probably large. (Note that the rate of reduction of a diene which cannot attain the *S*-cis configuration (run 13) is comparatively slow under similar catalytic conditions.) In that case the 1,2 and 1,4 hydrogenation product mixture from the stoichiometric reaction of H_2 with $[Rh(2,3\text{-dimethyl-}1,3\text{-butadiene})(diphos)]^+ClO_4^-$ should not differ greatly from that obtained catalytically. The results of one such experiment (see Experimental Section) showed this to be the case. Stoichiometric hydrogenation gave 51% 2,3-dimethyl-1-butene and 49% tetramethylethylene while 43 and 57% (respectively) were obtained in the corresponding catalytic experiment (Table II).

One of the most interesting aspects of conjugated diene hydrogenations is the often striking variation in product ratios on varying slightly the nature of the chelating ligand. For example, the percentage of 2,3-dimethyl-1-butene vs. tetramethylethylene obtained on reduction of 2,3-dimethyl-1,3-butadiene varies from ca. 40:60 (L-L = diphos) to ca. 20:80 (L-L = arphos) to ca. 80:20 (L-L = dpae). Yet, closely

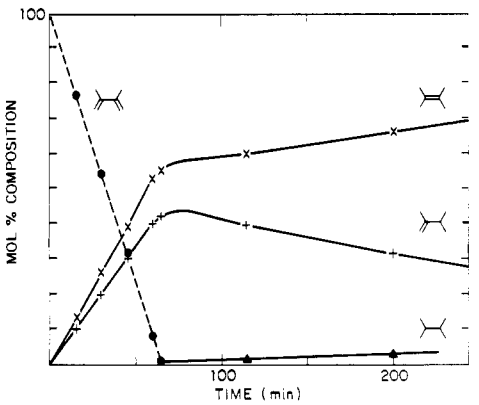


Figure 2. The catalytic hydrogenation of 2,3-dimethyl-1,3-butadiene in acetone with $[Rh(NBD)(diphos)]^+ClO_4^-$ (5.3 mM, run 1a, Table II).

similar product distributions are obtained on reduction of *trans,trans*-2,4-hexadienoic acid methyl ester with L-L = diphos or arphos. Therefore the product distribution may be determined in part by the nature of the substrate being reduced (as in the latter example) yet may also strongly depend on the nature of L-L (as in the former examples). More detailed studies are clearly needed in order to provide a more complete picture of how product ratios are determined.

The Hydrogenation of Cyclohexadienes. 1,3-Cyclohexadiene. The characteristics of the hydrogenation of 1,3-cyclohexadiene are essentially the same as those of norbornadiene and 1,3-butadienes. The rate of diene reduction is constant till near the endpoint (1 mol of H_2 absorbed) and cyclohexene is produced essentially quantitatively before it is hydrogenated to cyclohexane (cf. Figure 1). Table III lists some pertinent data. The findings that the addition of acid has little or no effect on the rate of diene hydrogenation and that catalysts containing more basic ligands (compare run 3b with 2) do not reduce the diene significantly more rapidly, of course, are analogous to results in the preceding sections.

Examination of the D_2 above the catalyst solution in runs 1a and 3a is a slightly different technique which was not used in preceding studies. Less than 1% H_2 and HD were found above the solution at the endpoint. The results described in part 1[3a] would suggest that significantly larger amounts (ca. 5%) of each should be formed during the time of the experiment (ca. 0.5 h) if **3** and **4** are present to any significant extent. That they are not is consistent with the proposal that **1** is the predominant species in solution.

Examination of the cyclohexene resulting in runs 1a and 3a by ^1H NMR[14] showed it to be a mixture of three parts of cyclohexene-*3,4-d*$_2$ and one part cyclohexene-*3,6-d*$_2$. Therefore D_2 adds 75% 1,2- to 1,3-cyclohexadiene in each case. These results differ somewhat from those obtained in the case of 2,3-dimethyl-1,3-butadiene hydrogenation with a $[Rh(NBD)(diphos)]^+$ type catalyst (run 1a, Table II) where slightly more (ca. 55%) 1,4 addition of H_2 to the diene was observed.

Finally, it should be noted that $[Rh(NBD)L_2]^+$ species (L monodentate) are successful catalyst precursors.[15] One might presume, therefore that $[Rh(1,3\text{-cyclohexadiene})_2L]^+$ complexes do not form irreversibly under the conditions of catalytic run.[12]

1,4-Cyclohexadienes. The data in Table III also include the results of hydrogenation of 1,4-cyclohexadiene and 1-methyl-1,4-cyclohexadiene. The reaction profiles are virtually identical with those of 1,3-cyclohexadiene except the rate of 1,4-cyclohexadiene reduction is, in general, markedly slower. A typical quenched sample[3] taken during the course of 1,4-cyclohexadiene reduction shows that ca. 1% 1,3-cyclohexadiene is present, an amount on the order of catalyst concentration. Furthermore, hydrogenation of 1-methyl-1,4-cyclohexadiene gave ca. 35% (run 6) and 40% (run 7) 3-methylcyclohexene as product.[16] These two observations imply that 1,4-cyclohexadiene isomerizes on the metal under catalytic conditions. We also find that 1,4-cyclohexadiene isomerizes stoichiometrically in the absence of molecular hydrogen to produce $[Rh(1,3\text{-cyclohexadiene})(PPh_3)_2]^+$ (eq 7).

$$[Rh(NBD)(PPh_3)_2]^+ \xrightarrow[3.\ 1,4\text{-cyclohexadiene}]{1.\ H_2,\ 2.\ N_2} [Rh(1,3\text{-cyclohexadiene})(PPh_3)_2]^+ \quad (7)$$

The product was identified by comparison with an authentic sample (ir, NMR)[2b] and by treatment with excess diphos which liberated 1,3-cyclohexadiene in quantitative yield.[17] Such an isomerization is well documented and occurs via an η^3-cyclohexadienyl metal hydride.[18] However, no free 1,3-cyclohexadiene was found in solution. Therefore eq 7 is not a catalytic reaction. This would imply that the 1,3-diene complex, once formed, is stable to dissociation, and the diene would only be removed by reaction with hydrogen under catalytic conditions. This is of course consistent with one of the requirements of path C; 1,3-cyclohexadiene does not readily dissociate from $[Rh(1,3\text{-cyclohexadiene})(PPh_3)_2]^+$.

The above evidence suggests that hydrogenation of 1,4-cyclohexadiene may proceed totally via the 1,3-cyclohexadiene complex. However, two observations indicate that this may not be the case. The fact that the color of catalytic solutions is much paler for the 1,4-diene than the 1,3-diene reductions under otherwise identical conditions would imply that the standing concentration of $[Rh(diene)L_2]^+$ (at least $[Rh(1,3\text{-cyclohexadiene})L_2]^+$) is greatly reduced during 1,4-diene catalysis, and/or that molecular hydrogen may compete with the 1,4-diene for the RhL_2^+ moiety under these conditions. Consequently part of the hydrogenation could proceed via paths A and B. Secondly, the reduced hydrogenation rate of the 1,4-diene (run 4) against the 1,3-diene (run 1) may also indicate that alternate, hydride routes are operative. However, no significant amount of HD or H_2 was detected in the residual gas during a run using D_2 (run 4). Therefore the concentration of neutral, monohydride species should be low and this particular hydride route[3] may only occupy a minor role.

Conclusion

The selective and rapid reduction of dienes (which can chelate strongly to rhodium) to monoenes can be facilitated by use of catalyst precursors of the type $[Rh(NBD)L_2]^+$. Both 1,2 and 1,4 addition of hydrogen are found, the ratio of which depends on the nature of L. Chelating phosphines or arsines are preferred as the stabilizing ligands, allowing the active catalytic species, $[Rh(diene)L_2]^+$, to predominate in solution. The fact that this complex forms readily and reacts rapidly with H_2 appears to be a major reason why these complexes successfully catalyze the selective reduction of dienes. If the reduction is arrested after 1 mol of hydrogen is consumed, essentially quantitative yields of monoene can be recovered. Any isomerization of the products after the endpoint can be slowed by addition of small quantities of acids (e.g., $HClO_4$ or HBF_4).

Experimental Section

Part 1[3a] describes the hydrogenation apparatus, hydrogenation procedure, and method of product analysis. Catalysts were prepared by previously discussed methods.[2] In preparative work one need not isolate $[Rh(NBD)L_n]^+A^-$ but can prepare it in situ in the solvent of choice (acetone[10] or 2-methoxyethanol are both suitable). $[Rh(NBD)Cl]_2$ and several of the cationic catalyst are availabe commercially (Strem Chemicals).

Reaction of [Rh(2,3-dimethyl-1,3-butadiene)(diphos)]$^+$ with H_2. $[Rh(NBD)(diphos)]^+ClO_4^-$ (275 mg) and two drops 70% aqueous perchloric acid were stirred in 10 ml of acetone under hydrogen for 2 h. The hydrogen was removed and substituted with nitrogen and 1.0 ml of 2,3-dimethyl-1,3-butadiene injected. A homogeneous red solution resulted after stirring overnight. The volume was reduced to ca. 2 ml to yield scarlet crystals of [Rh(2,3-dimethyl-1,3-butadiene)-(diphos)]$^+$ which were filtered off, washed with diethyl ether, and air dried; yield 120 mg.

A solution of 1 drop of 70% aqueous perchloric acid in 2 ml of acetone was injected onto 90 mg of [Rh(2,3-dimethyl-1,3-butadiene)(diphos)]$^+ClO_4^-$ under H_2 and the solution stirred vigorously until ca. 3.5 ml of hydrogen had been absorbed (ca. 2 min). Diphos (60 mg) was then added, and the contents were bulb-to-bulb distilled in vacuo. GLC analysis on a UC-W98 column showed 2,3-dimethyl-1-butene, 2,3-dimethyl-1,3-butadiene, and tetramethylethylene in a ratio of 25:2.1:24, respectively.

Preparation of [Rh(1,3-cyclohexadiene)(PPh$_3$)$_2$]$^+ClO_4^-$ from 1,4-Cyclohexadiene. $[Rh(NBD)(PPh_3)_2]^+ClO_4^-$ (500 mg) in 10 ml of degassed THF was treated with hydrogen till a pale yellow solution resulted (ca. 30 min). The solution was pumped on for 1 min then N_2 admitted to a pressure of 1 atm. 1,4-Cyclohexadiene (0.25 ml, GLC pure) was then injected causing the solution to become cherry red in 5–10 s. The red-orange crystals were filtered off after 10 min and dried in air. The product was identical with [Rh(1,3-cyclohexadiene)-$(PPh_3)_2]^+ClO_4^-$ (ir, NMR) prepared in a similar manner using 1,3-cyclohexadiene.[2b] The filtrate was bulb-to-bulb distilled in vacuo and analyzed by GLC (UC-W98). Norbornane, 1,4-cyclohexadiene, cyclohexene, and cyclohexane were present, but not 1,3-cyclohexadiene.

Samples of $[Rh(1,3\text{-cyclohexadiene})(PPh_3)_2]^+ClO_4^-$ were treated with diphos in acetone followed by bulb-to-bulb distillation in vacuo. GLC analysis indicated the presence of only 1,3-cyclohexadiene irrespective of whether 1,3-cyclohexadiene or 1,4-cyclohexadiene had been used to prepare the complex.

Isomerization of 1-Methyl-1,4-cyclohexadiene to Yield a [Rh(diene)(PPh$_3$)$_2$]$^+ClO_4^-$ Species Containing Methyl-1,3-cyclohexadiene Isomers. $[Rh(NBD)(PPh_3)_2]^+ClO_4^-$ (1.0 g) in 20 ml of THF was treated with hydrogen for 45 min to yield a pale yellow solution. The hydrogen was pumped off and substituted with nitrogen. 1-Methyl-1,4-cyclohexadiene (1.0 ml) was injected into the solution. After 10 min the volume was reduced to ca. 5 ml. One volume of ethanol was added followed by diethyl ether as needed to cause crystallization. The product was filtered off, washed with diethyl ether, and air dried; yield 0.84 g; 500 mg of the product was dried thoroughly in vacuo and added to 1 ml of $CDCl_3$ containing 500 mg of diphos. The liquid was bulb-to-bulb distilled in vacuo. GLC analysis showed only one of the possible methyl-1,3-cyclohexadiene isomers to be present by comparison with a known mixture of isomers. A small amount of 1-methyl-1,4-cyclohexadiene (ca. 5%) was also present. NMR analysis showed the product to be either 1- or 2-methyl-1,3-cyclohexadiene.

The experiment was repeated employing acetone as the solvent; 1.10

g of the product was treated with 1.10 g of diphos in 2 ml of acetone and the liquid bulb-to-bulb distilled in vacuo. GLC analysis indicated the presence of two methyl-1,3-cyclohexadiene isomers in approximately a 1:3 ratio. The major isomer was the one found in the THF experiment above.

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References and Notes

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(13) Reduction of 2,3-dimethyl-1,3-butadiene with $[Rh(NBD)(PPhMe_2)_3]^+$ in acetone was successful though the rate of diene disappearance was not constant and the mechanism therefore possibly not analogous to that using $[Rh(NBD)(chelate)]^+$ precursors. For example, mechanistic complications related to the reduction of acetone could be significant in this case.[10]
(14) The ratios were estimated by ^1H NMR. The ratio of β:α:olefinic protons should be 3:3:2 for cyclohexene-3,4-d_2 and 4:2:2 for cyclohexene-3,6-d_2. The found ratio was 3.3:2.7:2.0.
(15) (a) $[Rh(NBD)(PPhMe_2)_2]^+$ was not successful, however, since disproportionation of 1,3-cyclohexadiene to cyclohexane and benzene predominates. This disproportionation is not uncommon and has been found in systems containing related Rh(I) cationic complexes.[15b] (b) M. Green and T. A. Kuc, *J. Chem. Soc., Dalton Trans.*, 832 (1972).
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Electron Spin Resonance of Electrochemically Generated Rhodium(0) Complexes[1a]

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Abstract: Cyclic voltammetry studies of 2,2′-dipyridyl (dip) and 1,10-phenanthroline (phen) complexes of Rh(III) have previously indicated the production of relatively stable Rh(0) having the general formula, $[RhL_2]^0$. A combined coulometry–electron spin resonance study has now been utilized to characterize these unusual paramagnetic Rh(0) complexes. Glassy acetonitrile solution spectra of chemically or electrochemically prepared $[Rh(L)_2]^0$ (77–200 K) produce an axially symmetric $S = ½$ spectra in the $g = 2$ region for both the phen and dip complexes and no spectra at room temperature. The sign and magnitude of the g factor anisotropy ($g_\perp = 2.01$, $g_\parallel = 1.98$ for $[Rh(dip)_2]^0$ and $g_\perp = 2.01$, $g_\parallel = 1.97$ for $[Rh(phen)_2]^0$) and the absence of resonance at room temperature are consistent with a "distorted square planar" structure for the Rh(0) complexes.

The low oxidation states in first transition series complexes (V(0), Cr(I), Fe(I), Fe(0)) of dipyridyl and its derivatives are frequently characterized by electron spin resonance studies.[2] Within the limitations of ligand field theory, two limiting case descriptions of the highest filled orbital are suggested: (1) a localized metal d type orbital or (2) a delocalized ligand type π orbital. That this ligand field model and the resulting limits are frequently inadequate is best evidenced by the contradictory conclusions obtained for $[Fe(dip)_3]^0$ (dip = 2,2′-dipyridyl) from electrochemical[3] and ESR data,[4] the former indicating a ligand localized radical and the latter a localized d orbital system for this paramagnetic species. For these same π ligands, complexation of a second series ion, with its higher energy d subshell, can produce mixing of d and π orbitals, even in the higher oxidation state complexes such that, for example, the ground and lowest excited states for $[Ru(dip)_3]^{2+}$ contain ligand character[5,6] and therefore cannot be described as localized d–d states. Electrochemical data obtained for this complex are consistent with the delocalized orbital character of the ground state of the $[Ru(dip)_3]^{2+}$,