Catalytic Hydrogenation of Aromatic Hydrocarbons. Stereochemical Definition of the Catalytic Cycle for η^3-C$_3$H$_5$Co(P(OCH$_3$)$_3$)$_3$

J. R. Bleeke and E. L. Muetterties*

Contribution from the Departments of Chemistry, University of California, Berkeley, California 94720, and Cornell University, Ithaca, New York 14853. Received July 23, 1980

Abstract: The η^3-C$_3$H$_5$Co(P(OCH$_3$)$_3$)$_3$-catalyzed hydrogenations with D$_2$ of a series of unsaturated organic molecules, including cyclohexenes, cyclohexadienes, and arenes, have been investigated. Complete cis stereoselectivity was observed in the addition of deuterium to the unsaturated ring systems. When alkyl-substituted arenes were reduced with D$_2$, the hydrogen atoms in the alkyl chains underwent H–D exchange as long as each successive carbon atom in the chain possessed at least one hydrogen atom. Hence, extensive H–D exchange occurred in *n*-alkyl side chains while the *tert*-butyl side chain was deuterium free. When alkyl-substituted arenes were hydrogenated in the presence of olefins such as 1-hexene, a variety of isomeric alkylcyclohexenes and alkenylcyclohexanes were observed. The relative concentrations of these isomeric species provided information about the relative stabilities of the (olefin)cobalt species in the catalytic cycle. Further mechanistic information was obtained from other competitive reactions, i.e., hydrogenation reactions involving equimolar quantities of two different unsaturated molecules. The proposed initiation steps of the catalytic cycle have been revised on the basis of a study of η^3-C$_8$H$_{13}$Co(P(OCH$_3$)$_3$)$_3$ as a catalyst precursor. The cyclooctenyl–cobalt bond was cleaved by hydrogen early in the reaction, leaving the highly coordinatively unsaturated hydride, HCo(P(OCH$_3$)$_3$)$_3$, which is probably the true catalytic species.

Introduction

In 1973, η^3-C$_3$H$_5$Co(P(OCH$_3$)$_3$)$_3$ was shown to be a catalyst precursor for the homogeneous hydrogenation of arenes under mild conditions of temperature and pressure.[1,2] The complete[3] cis stereoselectivity in the cyclohexane products distinguishes this system from all known solid-state and solution-state catalysts. We describe here further evidence for the uniqueness of this homogeneous system from an investigation of the η^3-C$_3$H$_5$Co-(P(OCH$_3$)$_3$)$_3$-catalyzed hydrogenations with D$_2$ of a series of unsaturated organic molecules, including arenes, cyclohexadienes, and cyclohexenes. In addition, mechanistic features of the catalytic reaction have been probed through a study of the allylcobalt cleavage reaction and through the use of competitive reactions, i.e., hydrogenation reactions with two different unsaturated organic molecules. Stereochemical features of the catalytic reaction defined by the deuterium experiments and the complementary features of the competitive reactions now provide a definitive characterization of a major fraction of the catalytic cycle.

Experimental Section

Reagents and Solvents. η^3-C$_3$H$_5$Co(P(OCH$_3$)$_3$)$_3$,[4,5] η^3-C$_8$H$_{13}$Co-(P(OCH$_3$)$_3$)$_3$,[6] and η^3-C$_6$H$_5$CH$_2$Co(P(OCH$_3$)$_3$)$_3$[4] were prepared and purified as described previously. Arene reagents, pentane, and hexane were dried with sodium benzophenone and vacuum distilled. Olefin and cyclohexadiene reagents were dried with CaH$_2$ and vacuum distilled. Ultrahigh purity H$_2$ (99.999%) and CP D$_2$ (99.5%) were purchased from Matheson and used as received.

Physical Measurements. Gas chromatography (GC) was performed on a Perkin-Elmer 990 or a Perkin-Elmer Sigma 3 instrument equipped with a flame ionization detector. Peaks were recorded and integrated by using a Houston Instruments omniscribe recorder. Quantitative measurements were not corrected for response factor variations. The following columns were used: (A) 12 ft × $^1/_8$ in. 15% OV-17 on Chromosorb W, (B) 12 ft × $^1/_8$ in. 15% dimethylsulfolane on Chromosorb P, (C) 12 ft × $^1/_8$ in. 10% Carbowax 20M on GasChrom Q, and (D) 7 ft × $^1/_8$ in. 20% ethyl *N,N*-dimethyloxamate on Chromosorb P joined to 12 ft × $^1/_8$ in. 15% dimethylsulfolane on Chromosorb P.

Mass spectrometry was performed by using a Finnegan 4000 gas chromatograph/mass spectrometer (GC/MS) interfaced with a Finnegan/INCOS data system. The following columns were employed: (a) 30 m SP2100 (WCOT), (b) 6 ft × $^1/_4$ in. 3% Carbowax 20M on 100/20 Supelcoport, (c) 30 m SP2250 (WCOT), (d) 250 ft OV-17 (stainless steel WCOT), and (e) 30 m SP1000 (WCOT). Low ionizing voltages (15–18 eV) were employed to minimize C–H and C–D fragmentation in the parent ions. Blank runs with protioarenes and protiocyclohexanes proved that C–H bond cleavage in the parent ions was negligible under the experimental conditions. Since heavy (deuterium-rich) species were eluted from the columns slightly more rapidly than light (hydrogen-rich) species, the mass spectra taken at the front of a peak contained more of the heavy species and less of the light species than spectra taken at the rear of a peak. For a determination of the relative amounts of the various species in an entire peak, mass spectra were taken throughout the elution of the peak and then summed. All of the data reported here are summed spectra. In the analyses of the data, ^{13}C contributions to the ion mass intensities were taken into consideration but all experimental mass spectra presented in the figures are uncorrected. A complete set of experimental mass spectra are included in the supplementary material, Figures 11–48.

^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a modified Bruker 42 kG multinuclear pulse-FT NMR spectrometer equipped with Nicolet Technology Corporation software. ^{1}H and ^{13}C chemical shifts are reported in ppm units from internal tetramethylsilane. ^{31}P shifts are referenced to external H$_3$PO$_4$.

Hydrogenation Reactions. Hydrogenations were carried out in a glass reaction tube ($\sim$100 mL volume) equipped with a Kontes adjustable Teflon stopcock and a ball joint for attachment to a vacuum line. The tube was loaded with catalyst precursor (η^3-C$_3$H$_5$Co(P(OCH$_3$)$_3$)$_3$) for all of the experiments summarized in Tables I–III, substrate, and solvent in an inert atmosphere drybox. A typical run involved 20 mg of η^3-C$_3$H$_5$Co(P(OCH$_3$)$_3$)$_3$ (4.24 × 10^{-5} mol), 1.06 × 10^{-3} mol of unsaturated organic compound (for a 25:1 unsaturated organic compound:catalyst precursor ratio), and 2–3 mL of pentane or hexane solvent. After being loaded, the tube was removed from the drybox and attached to a vacuum line where the solution was frozen at –196 °C. The tube was evacuated and then refilled with 1–3 atm of H$_2$ or D$_2$. The solution was warmed to room temperature and stirred magnetically for periods of time ranging from several hours to several days. Products were isolated by vacuum distillation. Hydrogenation reactions of various arenes, cyclohexadienes, and cyclohexenes are summarized in Tables I and II.

Competitive hydrogenation reactions typically involved 12.5 mol of each unsaturated organic compound/mol of catalyst precursor, for a total unsaturated organic compound:catalyst presursor ratio of 25:1. Table III summarizes the results of the competition experiments.

Cleavage of the η^3-Allyl (Benzyl) Ligand with D$_2$. A 500-mg (1.06 × 10^{-3} mol) sample of η^3-C$_3$H$_5$Co(P(OCH$_3$)$_3$)$_3$ in 2.36 mL (2.66 × 10^{-2} mol) of neat benzene was stirred under 1 atm of D$_2$ at room temperature

(1) L. S. Stuhl, M. Rakowski Dubois, F. J. Hirsekorn, J. R. Bleeke, A. E. Stevens, and E. L. Muetterties, *J. Am. Chem. Soc.*, **100**, 2405 (1978).

(2) E. L. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 4063 (1974).

(3) Complete in the context of the sensitivity of the analytical procedures.

(4) E. L. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 7920 (1974).

(5) M. C. Rakowski, F. J. Hirsekorn, L. S. Stuhl, and E. L. Muetterties, *Inorg. Chem.*, **15**, 2379 (1976).

(6) K. D. Tau and E. L. Muetterties, to be submitted for publication.

*To whom correspondence should be addressed at the University of California.

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Table I. Hydrogenation Reactions of Alkyl-Substituted Arenes: Experimental Conditions and Products

arene	arene:cat. precur	time, h	convsn to alkylcyclo-hexane, %	GC separation		GC/MS anal.		
				column	temp, °C	column	temp, °C	ion. volt., eV
benzene	25:1	93	45	A	50	c	30	17
toluene	25:1	93	50	A	55	a	40	17.4
ethylbenzene	50:1	46.5	10	A	70	a	90	15
n-propylbenzene	50:1	46.5	10	A	70	a	90	15
n-butylbenzene	25:1	107	35.5	A	110	a	100	17
n-pentylbenzene	25:1	94	54.8	A	120	a	100	17
isopropylbenzene	50:1	46.5	5	A	70	b	60	17 (sat) 15 (unsat)
tert-butylbenzene	25:1	110	25	A	110	b	60–90	17 (sat) 15 (unsat)
neopentylbenzene	25:1	116.5	30	A	125	a	90	17
1-methyl-4-propylbenzene	25:1	112	15	A	115	a	115	17
o-xylene	25:1	97	45	A	70	c	45–150	17 (sat) 15 (unsat)
m-xylene	25:1	97	27	A	70	c	45–150	17 (sat) 15 (unsat)
p-xylene	25:1	97	29	A	70	c	50–130	17 (sat) 15 (unsat)
m-diethylbenzene	25:1	96	20	A	120	a	85	17
p-diethylbenzene	25:1	96	13	A	120	a	90	17

Table II. Hydrogenation Reactions of Olefins and Dienes: Experimental Conditions and Products

org compd	org compd:cat. precur	time, h	% products	GC separation		GC/MS anal.		
				column	temp, °C	column	temp, °C	ion. volt., eV
cyclohexene	25:1	10.5	18 cyclohexane	A	45	e	60	17
cyclohexene	25:1	24	42.2 cyclohexane	A	45	e	60	17
cyclohexene	25:1	91	87 cyclohexane	A	45	d	30–60	16
1,3-cyclohexadiene	25:1	24	7.6 cyclohexane 48.3 cyclohexene	B	40	e	40	17
1,3-cyclohexadiene	25:1	82	65.6 cyclohexane 34.4 cyclohexene	A	45	a	20	16.6
1,4-cyclohexadiene	25:1	8	10.4 cyclohexane 11.9 cyclohexene	B	40	e	80	17
1,4-cyclohexadiene	25:1	24	56.7 cyclohexane 36.7 cyclohexene	B	40			
1-methylcyclohexene	25:1	73	24.9 methylcyclohexane	A	55	e	60	18
3-methylcyclohexene	25:1	73	73.5 methylcyclohexane	A	55	e	80	18
styrene	25:1	20.5	0.3 ethylcyclohexane 2.8 vinylcyclohexane 3.7 3- and/or 4-ethylcyclohexene 1.5 ethylbenzene	C	70			
vinylcyclohexane	25:1	12.5	33.9 ethylcyclohexane 1.0 3- and/or 4-ethylcyclohexene 1.0 ethylidenecyclohexane	C	70			

for 22.5 h. The volatile products were vacuum distilled and analyzed by gas chromatography. Analysis for C_6 hydrocarbons (benzene/cyclohexane) was performed on column A at 50 °C, while C_3 hydrocarbons (propane/propene) were analyzed on column D at room temperature.

The solid-state residue that remained after vacuum distillation of the volatile products was treated with 0.41 mL (5.3×10^{-3} mol) of CF_3CO-OH in several milliliters of pentane and stirred for 1 h. The volatile fraction was vacuum transferred onto CaH_2 to destroy excess CF_3COOH and then off of the CaH_2 for GC analysis. The C_3 hydrocarbons were analyzed on column D at room temperature. The 17-eV GC/MS analyses of the C_3 hydrocarbons were performed on column a at 0 °C. Results of these reactions are summarized in Table IV.

In an analogous reaction, 200 mg (3.70×10^{-4} mol) of η^3-C_8H_{13}Co-$(P(OCH_3)_3)_3$ in 0.85 mL (9.57×10^{-3} mol) of benzene was stirred under D_2 for 3.75 h. The volatile products were vacuum distilled and analyzed by gas chromatography. The C_6 hydrocarbons were analyzed on column A at 50 °C while the C_8 hydrocarbons were analyzed on column C at 85 °C. The 17-eV GC/MS analysis of the cyclooctane was performed on column c at 40–70 °C. Similarly, 200 mg (3.83×10^{-4} mol) of η^3-$C_6H_5CH_2$Co($P(OCH_3)_3)_3$ in 1.34 mL (9.58×16^{-3} mol) of n-propylbenzene was stirred under D_2 for 2 h. The volatile products were vacuum distilled and analyzed by GC on column A at 75–100 °C. The 17-eV GC/MS analysis was performed on column C at 60–160 °C. These results are also summarized in Table IV.

NMR Studies of the Initiation Steps of the Catalytic Cycle. The early stages of the η^3-C_8H_{13}Co($P(OCH_3)_3)_3$-catalyzed hydrogenation of toluene were monitored by ^{31}P and ^{1}H NMR spectroscopy. Reactions were run in a glass tube similar to the one described earlier, but possessing an attached NMR tube. In a typical reaction, the vessel was charged with 80 mg of η^3-C_8H_{13}Co($P(OCH_3)_3)_3$ and 1 mL of toluene-d_8 and pressurized with ~1 atm of H_2. The solution was stirred at room temperature for periods of time ranging from 0.5 to 5 h. Hydrogenations were stopped by pouring the solution from the reaction tube into the attached NMR tube, freezing, and sealing the NMR tube under ~0.5 atm of H_2. NMR tubes were packed in dry ice until the spectra were run. Sharp ^{31}P and ^{31}P{^{1}H} spectra could only be obtained at temperatures below −50 °C. Broadening at higher temperatures probably resulted from the quadrupolar cobalt center. Standard samples of η^3-C_8H_{13}Co(P-$(OCH_3)_3)_3$, $HCo(P(OCH_3)_3)_4$, $HCo(P(O-i-C_3H_7)_3)_4$, and $H_3Co(P(O-i-C_3H_7)_3)_3$ were prepared. These exhibited ^{31}P{^{1}H} resonances (−50 to −65 °C) at 169.8, 176.1, 165.9, and 172.7 ppm, respectively.

Results

Background. Established in these and earlier studies of the fully homogeneous, catalyzed hydrogenation of aromatic hydrocarbons using as catalyst precursors η^3-C_3H_5Co($P(OR)_3)_3$, η^3-C_3H_5Co-($PR_3)_3$, η^3-C_8H_{13}Co($P(OR)_3)_3$, and η^3-$C_6H_5CH_2$Co($P(OR)_3)_3$ were certain essential and unique features of the reaction cycle.[2,5–9]

(7) F. J. Hirsekorn, M. C. Rakowski, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 237 (1975).

(8) M. C. Rakowski and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 739 (1977).
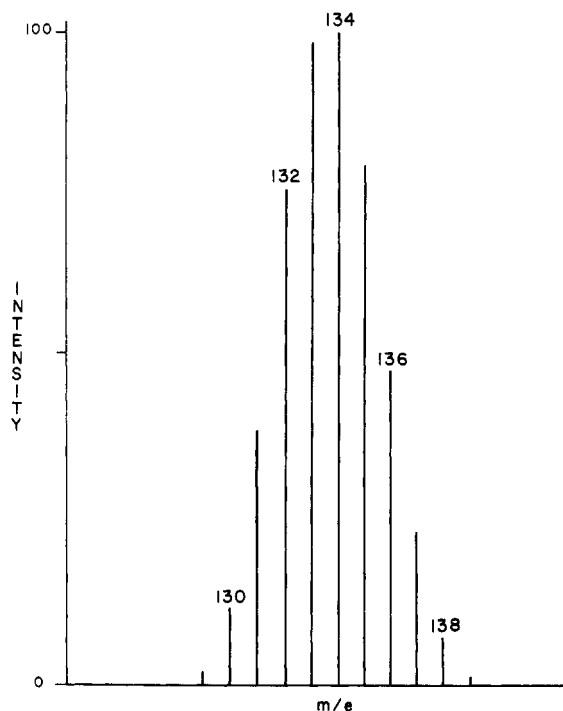
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Figure 1. Parent ion region of the mass spectrum of *n*-propylcyclohexane produced in the reaction of *n*-propylbenzene with D_2. Highest mass species (m/e 139) is due to $C_6H_5D_6C_3D_7$. The peaks at m/e 129–131 are due to species possessing less than six deuterium atoms. These hydrogen-rich molecules are produced when aromatic rings are reduced with *hydrogen* atoms released from the side chains of other molecules during H–D exchange.

These are restated to provide a basic background to the presentation of new results and for a holistic discussion of the stereochemical features of the hydrogenation and H–D exchange reactions. (1) At 25 °C and 1–2 atm of H_2, arenes were hydrogenated at rates comparable to those of olefins. (2) In the absence of olefinic functions, arenes were fully hydrogenated; no cyclohexenes were produced. However, when olefinic functions were present in the reaction system, both cyclohexenes and cyclohexanes were produced. (3) The hydrogenations of arenes were stereoselective; all H (or D) atoms were added to one side of the ring to produce *cis*-cyclohexanes.

Hydrogen–Deuterium Exchange. In the catalytic reaction of C_6H_6 with D_2, the only hydrogenation product was all *cis*-$C_6D_6H_6$. Reactions of D_2 with alkyl-substituted benzenes in which the alkyl group was linear yielded alkylcyclohexanes with extensive deuterium incorporation in the alkyl side chain. The alkylcyclohexane products contained a statistical distribution of species with differing proportions of H and D. The highest mass species was $C_6H_5D_6(C_nD_{2n+1})$, where *n* is the length of the alkyl side chain (see Figure 1). The five ring hydrogen atoms on the alkylbenzene molecule did not undergo H–D exchange during the hydrogenation process. $^{13}C\{^1H\}$ NMR studies of the methylcyclohexane produced in the reaction of toluene with D_2 showed that the ring carbons possessed either zero or one deuterium but never two deuterium atoms, confirming that the ring hydrogen atoms on the starting toluene do not undergo H–D exchange (see Figure 2). No H–D exchange at either aliphatic or aromatic sites was observed in the unreduced arenes recovered from the catalytic reaction systems.

Catalytic reactions of D_2 with alkyl-substituted benzenes in which the alkyl substituent was branched provided obvious mechanistic information about the exchange process. (A) With *tert*-butylbenzene, there was no deuterium incorporation into the *tert*-butyl substituent. (B) With neopentylbenzene, a maximum of two deuterium atoms were introduced into the neopentyl group. (C) With isopropylbenzene, there was extensive deuterium in-
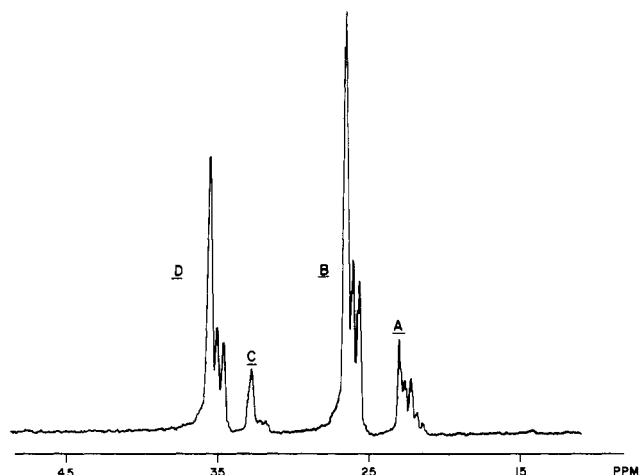
(9) Earl L. Muetterties and John R. Bleeke, *Acc. Chem. Res.*, **12**, 324 (1979), and references therein.

Figure 2. $^{13}C\{^1H\}$ NMR spectrum of methylcyclohexane produced in the reaction of toluene with D_2. Peaks are due to the following carbon atoms: (A) methyl, (B) meta and para, (C) tertiary (ring junction), (D) ortho. Peaks B and D each consist of a singlet due to CH_2 and a 1:1:1 triplet (one peak obscured by singlet) due to CHD. Quintets due to CD_2 are absent. Similarly, peak C consists of overlapping singlet and 1:1:1 triplet due to C–H and C–D; its small size relative to the other peaks results from absence of nuclear overhauser enhancement. Peak A consists of overlapping singlet, 1:1:1 triplet, and 1:2:3:2:1 quintet due to CH_3, CH_2D, and CHD_2, respectively. This spectrum supports the assertion that each ring carbon atom is attached to at most one deuterium atom.
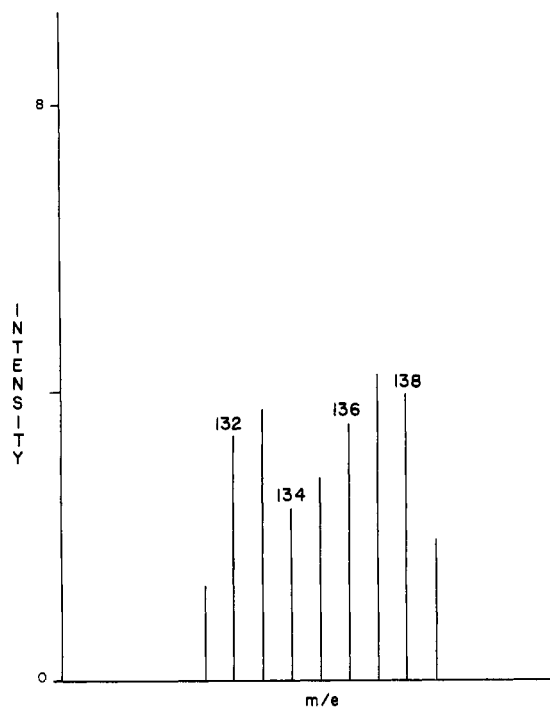
Figure 3. Parent ion region of the mass spectrum of isopropylcyclohexane produced in the reaction of isopropylbenzene with D_2. Highest-mass species (m/e 139) is due to $C_6H_5D_6C_3D_7$. Maxima in intensity occur at d_7 and d_{11}.

corporation throughout the side chain. Quantitatively, there was more deuterium exchange than for the isomeric *n*-propylbenzene. Furthermore, the deuterium distribution was bimodal, the most abundant species being $C_6H_5D_6(i$-$C_3DH_6)$, $C_6H_5D_6(i$-$C_3D_5H_2)$, and $C_6H_5D_6(i$-$C_3D_6H)$ (see Figure 3).

For disubstituted alkylbenzenes such as the xylene isomers and 1-methyl-4-*n*-propylbenzene, H–D exchange was found in both alkyl groups yet total cis stereochemistry was maintained (see Figure 4). Distribution of deuterium in the xylene hydrogenation (with D_2) products was not detectably different for any of the isomers.

Table III. Competitive Hydrogenation Reactions: Experimental Conditions and Products

org compds	org compd:cat. precur	time, h	% products	GC separation		GC/MS anal.		
				column	temp, °C	column	temp, °C	ion. volt., eV
benzene	12.5:1	9.5	1.5 cyclohexane 5.8 cyclohexene	A	45			
+								
1-hexene	12.5:1		16.4 n-hexane 17.2 trans-2-hexene 8.3 cis-2-hexene	B	25			
toluene	25:1		12.2 methylcyclohexane 4.6 methylenecyclohexane 3.3 3- and/or 4-methylcyclohexene	B	40	a	33	17
+		35						
1-hexene	25:1		29.3 n-hexane and isomeric hexenes	B	25			
1-methylcyclohexene	25:1		11.8 methylcyclohexane 1.8 methylenecyclohexane and 3- and/or 4-methylcyclohexene	A	55	c	50	17
+		36						
1-hexene	25:1		48.7 n-hexane and isomeric hexenes	B	40			
1,3-cyclohexadiene	12.5:1							
+		12	cyclohexane:methylcyclohexane: cyclohexene (1:0.24:6.88)ᵃ	B	40			
toluene	12.5:1							
1,3-cyclohexadiene	12.5:1							
+		30	cyclohexane:methylcyclohexane: cyclohexene (1:0.44:2.83)ᵃ	B	40			
toluene	12.5:1							
1,4-cyclohexadiene	12.5:1							
+		12	cyclohexane:methylcyclohexane: cyclohexene (1:0.53:1.52)ᵃ	B	40			
toluene	12.5:1							
allylbenzene	12.5:1		8.2 ring hydrogenation products 10.3 n-propylbenzene 1.8 cis-propenylbenzene 17.0 trans-propenylbenzene	A and C	100 and 90			
+		13.5						
benzene	12.5:1		0.4 cyclohexane 0.9 cyclohexene	A	45			
styrene	12.5:1		17.3 ethylcyclohexane and vinylcyclohexane 12.8 3- and/or 4-ethylcyclohexene 4.9 ethylbenzene					
+		29.5		A	45–80			
benzene	12.5:1		0 cyclohexane 0.7 cyclohexene					
ethylbenzene	25:1		36.0 ethylcyclohexane 3.5 3- and/or 4-ethylcyclohexene 0.7 vinylcyclohexane 0.7 ethylidenecyclohexane	C	70			
+		40						
1-hexene	25:1							

ᵃ Ratios of products.

Reductions of Cyclohexene and Cyclohexadienes with D₂. The reaction of cyclohexene with D₂ yielded primarily cyclohexane-d_6 (see Figure 5). In the early stages of the reaction (low conversion to cyclohexane), the *unreduced* cyclohexene was essentially free of deuterium. However, as the hydrogenation proceeded, deuterium was slowly incorporated into the unreduced cyclohexene.

1,3-Cyclohexadiene and 1,4-cyclohexadiene reacted with D₂ to yield both cyclohexane and cyclohexene. When the reactions were stopped after short reaction times to minimize interactions of the displaced cyclohexene with the catalyst, the cyclohexane contained species with up to six deuterium atoms and the cyclo-

hexene contained species with up to four. The unreduced cyclohexadiene contained no deuterium and was not isomerized. 1,3-Cyclohexadiene yielded a far greater proportion of cyclohexene than did 1,4-cyclohexadiene.

The competitive hydrogenation of equimolar amounts of 1,4-cyclohexadiene and toluene yielded methylcyclohexane, cyclohexane, and cyclohexene. Similar results were obtained from the competitive hydrogenation of 1,3-cyclohexadiene and toluene.

Nature of Cyclohexenes Produced in the Hydrogenation of Arene–Olefin Mixtures. When toluene was hydrogenated in the presence of 1-hexene, two olefin peaks were detected by gas

Table IV.   Reactions of Catalyst Precursors, η^3-L-Co(P(OCH$_3$)$_3$)$_3$ (L = Allyl, Cyclooctenyl, Benzyl), with Hydrogen: Experimental Conditions and Organic Products

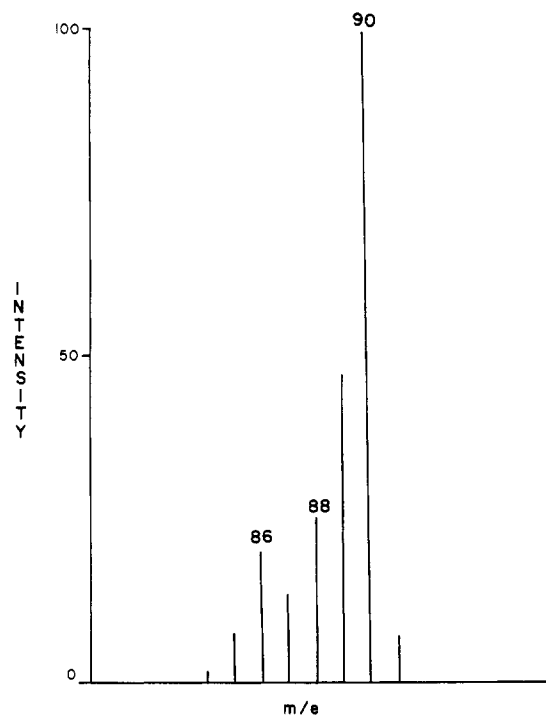| cat. precur	arene:cat. precur	time, h	% products of arene + H$_2$	% products of cat. precur + H$_2$	% products of residue + CF$_3$COOH
η^3-C$_3$H$_5$Co(P(OCH$_3$)$_3$)$_3$	25:1	22.5	8.6 cyclohexane 0.3 cyclohexene	100 propane	6.6 propane 93.4 propene
η^3-C$_8$H$_{13}$Co(P(OCH$_3$)$_3$)$_3$	25:1	3.75	4.3 cyclohexane 0.9 cyclohexene	93.0 cyclooctane 7.0 cyclooctene	
η^3-C$_6$H$_5$CH$_2$Co(P(OCH$_3$)$_3$)$_3$	25:1	2	0.3 n-propylcyclohexane	30.5 methylcyclohexane 69.5 toluene	
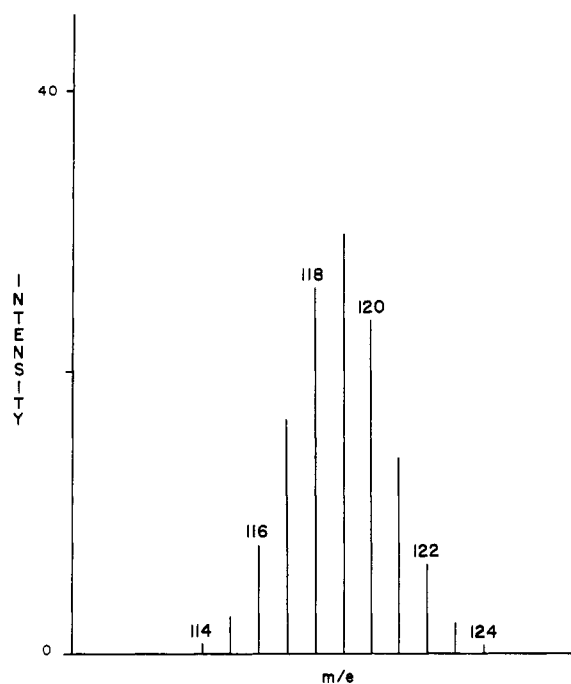
Figure 4. Parent ion region of the mass spectrum of 1,4-dimethylcyclohexane produced in the reaction of p-xylene with D$_2$. Highest mass species (m/e 124) is due to C$_6$H$_4$D$_6$(CD$_3$)$_2$.

Figure 5. Parent ion region of the mass spectrum of cyclohexane produced in the reaction of cyclohexene with D$_2$. Large peak at m/e 90 is due to C$_6$H$_6$D$_6$. Peak at m/e 91 is the ^{13}C contribution of the peak at m/e 90 (^{12}C$_5$^{13}CH$_6$D$_6$) and is of the expected intensity.

chromatography: 3- and/or 4-methylcyclohexene and methylenecyclohexane. No 1-methylcyclohexene was detected. The olefins contained deuterium while the unreduced toluene did not. 1-Methylcyclohexene was shown to react with D$_2$ to yield methylcyclohexane containing all isotopic species from C$_6$H$_{11}$CH$_3$ to C$_6$H$_5$D$_6$CD$_3$. The unreduced 1-methylcyclohexene contained no deuterium. 3-Methylcyclohexene reacted with D$_2$ to yield methylcyclohexane, and in this case, the unreduced 3- and/or 4-methylcyclohexene contained deuterium. When 1-methylcyclohexene reacted with D$_2$ in the presence of 1-hexene, small quantities of 3- and/or 4-methylcyclohexene and methylenecyclohexane were produced. The unreduced 1-methylcyclohexene contained no deuterium.

When ethylbenzene was hydrogenated in the presence of 1-hexene, three olefin peaks were detected by gas chromatography: 3- and/or 4-ethylcyclohexene, ethylidenecyclohexane, and vinylcyclohexane. No 1-ethylcyclohexene was detected. The hydrogenation of vinylcyclohexane yielded small quantities of 3- and/or 4-ethylcyclohexene and ethylidenecyclohexane as well as ethylcyclohexane.

Competitive Hydrogenation of Benzene and Alkenylbenzenes. The hydrogenation of equimolar amounts of styrene and benzene yielded ethylcyclohexane, vinylcyclohexane, 3- and/or 4-ethylcyclohexene, and ethylbenzene, but virtually no cyclohexene or cyclohexane. Analogously, the competitive hydrogenation of allylbenzene and benzene yielded only allylbenzene hydrogenation and isomerization products. In contrast, competitive hydrogenations of *cis*- or *trans*-propenylbenzene and benzene yielded cyclohexane and cyclohexene as well as propenylbenzene hydrogenation products.

Cleavage of the η^3-Allyl (Benzyl) Ligand with D$_2$. The allyl group of the catalyst precursor, η^3-C$_3$H$_5$Co(P(OCH$_3$)$_3$)$_3$, was hydrogenated to propane containing a statistical distribution of species ranging from C$_3$H$_8$ to C$_3$D$_8$ (see Figure 6). However, η^3-C$_3$H$_5$Co(P(OCH$_3$)$_3$)$_3$ recovered after a catalytic run contained no deuterium in the allyl ligand. The cyclooctenyl group of the catalyst precursor, η^3-C$_8$H$_{13}$Co(P(OCH$_3$)$_3$)$_3$, was hydrogenated primarily to cyclooctane containing a statistical distribution of species terminating in C$_8$H$_8$D$_8$. The benzyl group of the catalyst precursor, η^3-C$_6$H$_5$CH$_2$Co(P(OCH$_3$)$_3$)$_3$, was hydrogenated to ~30% methylcyclohexane (statistical distribution of species terminating in C$_6$H$_5$D$_6$CD$_3$) and ~70% toluene (largely C$_6$H$_5$CH$_2$D).

NMR Studies of the Initiation Steps of the Catalytic Cycle. The early stages of the η^3-C$_8$H$_{13}$Co(P(OCH$_3$)$_3$)$_3$-catalyzed hydrogenation of toluene-d_8 were investigated by ^{31}P and ^{1}H NMR spectroscopy. The reaction solution was monitored after 0.5, 0.75, 1, 3, and 5 h. The ^{31}P signal due to η^3-C$_8$H$_{13}$Co(P(OCH$_3$)$_3$)$_3$ decreased rapidly in the early stages of the reaction and was accompanied by a rapid increase in the signal due to HCo(P(OCH$_3$)$_3$)$_4$. After 1 h, the ^{31}P resonance due to η^3-C$_8$H$_{13}$Co(P(OCH$_3$)$_3$)$_3$ was very small, and after 3 h, it had vanished completely. The ^{31}P{^{1}H} spectra for the 3- and 5-h reactions were virtually identical. The spectrum of the 3-h reaction solution is shown in Figure 7. The large peak labeled A is due to HCo(P(OCH$_3$)$_3$)$_4$. The small peak labeled B has been assigned to H$_3$Co(P(OCH$_3$)$_3$)$_3$; this assignment was based, in part, on a comparison with the analogous P(O-i-C$_3$H$_7$)$_3$ complex, since a
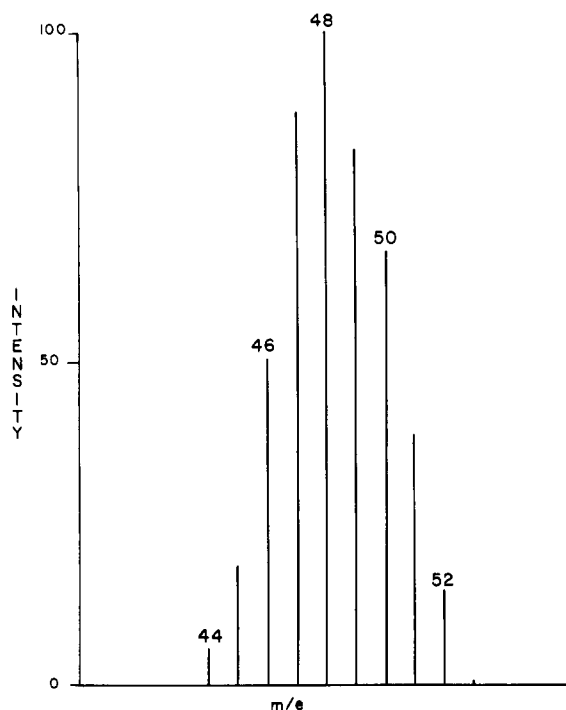
Figure 6. Parent ion region of the mass spectrum of propane produced in the reaction of η^3-$C_3H_5Co(P(OCH_3)_3)_3$ with D_2. Highest mass species (m/e 52) is due to C_3D_8.
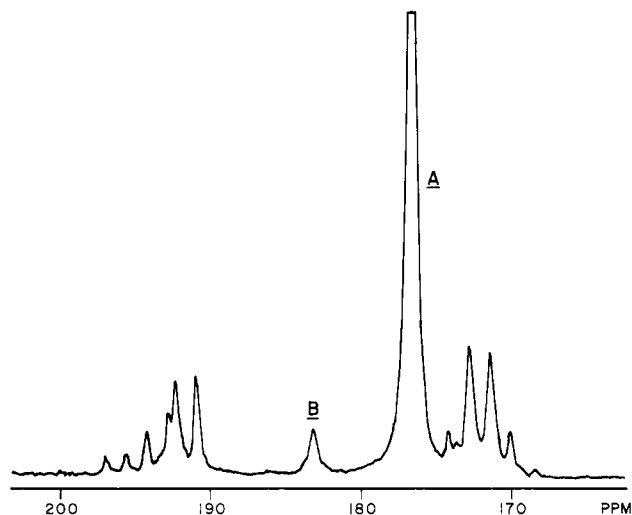
Figure 7. $^{31}P\{^1H\}$ NMR spectrum (−75 °C) of a catalytic solution formed by reacting η^3-$C_8H_{13}Co(P(OCH_3)_3)_3$ in toluene-d_8 with H_2 for 3 h. Resonance A is due to $HCo(P(OCH_3)_3)_4$; B is due to $H_3Co(P(OCH_3)_3)_3$. The other peaks can be explained by three different species, each with an AB spectrum (i.e., three doublets of doublets). Three of the doublets are clearly resolved in the 190–200-ppm region; their associated doublets are overlapping at 170–175 ppm.

standard sample of $H_3Co(P(OCH_3)_3)_3$ could not be prepared. The other peaks appear to consist of three pairs of doublets and are perhaps due to catalytic intermediates. The ^{1}H-coupled spectra yielded no additional information; line widths broadened somewhat, but no P–H splittings were observed. Although the resonance due to η^3-$C_8H_{13}Co(P(OCH_3)_3)_3$ was completely gone after 3 h, the solution was catalytically active for at least 20 h. In a typical benzene hydrogenation reaction using η^3-$C_8H_{13}Co$-$(P(OCH_3)_3)_3$ as catalyst precursor (25:1 benzene:catalyst precursor), only 5.2% of the benzene was reduced in 3.75 h (see Table IV) while 34.5% was reduced in 20 h.

^{1}H NMR spectra of a 3-h reaction solution were taken at temperatures ranging from −85 to +35 °C. The phosphite region of the spectrum (δ 3.3–3.7) was temperature dependent and rather complicated. The hydride region (δ −5 to −30) contained only

a large quintet at δ −15.9 (J_{P-H} = 18 Hz) due to $HCo(P(OCH_3)_3)_4$ and a small quartet at δ −12.8 (J_{P-H} = 27 Hz) due to H_3Co-$(P(OCH_3)_3)_3$.

Discussion

Stereoselectivity. All the deuterium studies show that without any exceptions the orientation of the ring with respect to the cobalt center is maintained throughout the hydrogenation of arenes, cyclohexadienes, and cyclohexenes. Exchange of ring hydrogen atoms for deuterium atoms occurs only on the side of the ring oriented toward the cobalt center. The cyclohexane produced in the reaction of D_2 with benzene, cyclohexadiene, or cyclohexene never contained more than six deuterium atoms. Exchange of ring hydrogen atoms is a facile process since the major product of the reaction of cyclohexene or cyclohexadiene with D_2 was $C_6D_6H_6$, in which all of the accessible hydrogen atoms were, in fact, replaced by deuterium atoms.

Surprisingly, the pervasive cis stereochemistry exhibited by this cobalt system is not the universal property of arene hydrogenation catalysts. In fact, all other known coordination complex or solid-state catalysts yield some trans products—e.g., dimethylcyclohexanes from xylenes—although all produce predominantly cis products. For coordination complex catalysts, trans stereochemistry seems explicable only if dissociation of partially reduced arene from the metal center is a kinetically significant process. This scenario appears to be appropriate for the (η^6-$C_6(CH_3)_6$)-$Ru(\eta^4$-$C_6(CH_3)_6$) complex which yields cyclohexene and cyclohexane products and is not an especially stereoselective catalyst.[23] However, Maitlis' catalyst,[24] generated from $(C_5(CH_3)_5RhCl_2)_2$ and an amine cocatalyst, produces no detectable cyclohexenes and yet it also is not particularly stereoselective—33% *trans*-1,4-dimethylcyclohexane from *p*-xylene. With respect to solid-state catalysts, no molecular features for arene hydrogenations have been defined. However, loss of cis stereoselectivity is easily rationalized only by again postulating the dissociation of a partially reduced aromatic ring. Dissociation can be unequivocally established only for those systems in which cyclohexenes are detectable products. Some,[31] but not all, solid-state catalysts produce small quantities of cyclohexenes in the arene hydrogenation reaction.

H–D Exchange in Alkyl-Substituted Arenes. When an alkyl-substituted arene was reacted with D_2, the hydrogen atoms in the alkyl chain underwent exchange as long as each successive carbon atom in the chain possessed at least one hydrogen atom. Thus, H–D exchange occurred throughout a linear alkyl side chain but occurred only on the α-carbon of a neopentyl side chain and did not occur at all in a *tert*-butyl side chain. The *n*-alkylcyclohexane produced in the reaction of an *n*-alkylbenzene with D_2 contained a statistical distribution of deuterium, and the major product was not the totally deuterated species; e.g., the major *n*-propylcyclohexane species produced in the D_2 reduction of *n*-propylbenzene was $C_6H_5D_6(n$-$C_3H_5D_2)$[10] not $C_6H_5D_6(n$-$C_3D_7)$. The contrast between the *major* deuterated species produced in (a) the cyclohexene + D_2 reaction and (b) the *n*-propylbenzene + D_2 reaction is notable—the former was $C_6H_6D_6$ where all of the accessible hydrogen atoms (those cis to the cobalt atom) were exchanged for deuterium, while the latter was $C_6H_5D_6(n$-$C_3H_5D_2)$ where five accessible hydrogen atoms (those in the side chain) were not exchanged. This suggests that exchange of endo ring hydrogen atoms is more facile than exchange of hydrogen atoms in an alkyl side chain.

The isopropylcyclohexane molecules obtained from the reaction of isopropylbenzene with D_2 contained an unusual distribution of deuterium. There were two maxima in the deuterium distribution, one at d_7 and the other at d_{10}-d_{11}. The data suggest that the catalyst is inhibited from entering the methyl groups of the

(10) From the mass spectral data, the positions of the eight deuterium atoms in the molecule could not be determined. Most likely, these atoms were distributed among the thirteen possible positions (six on the ring and seven in the *n*-propyl side chain). Thus, some of the *n*-propylcyclohexane-d_8 molecules had composition $C_6H_6D_5(n$-$C_3H_4D_3)$, $C_6H_7D_4(n$-$C_3H_3D_4)$, ... , or $C_6H_{10}D(n$-$C_3D_7)$ rather than $C_6H_5D_6(n$-$C_3H_5D_2)$.
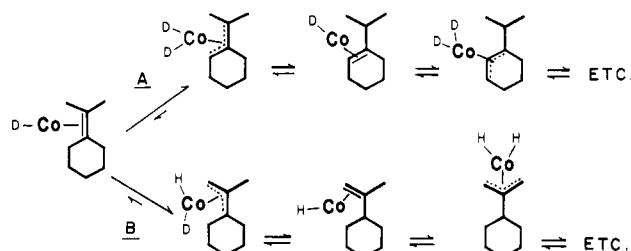
Figure 8. Proposed mechanism for H–D exchange in the reaction of isopropylbenzene with D_2. Pathway A results in a maximum at d_7 in the isotopic distribution of product isopropylcyclohexane, while pathway B results in a maximum at d_{10}–d_{11}. The unfavorable isopropylidenecyclohexane intermediate is avoided. Phosphite ligands have been omitted for clarity.

isopropyl side chain (preponderance of d_7 product); however, once it does enter these methyl groups, it encounters a barrier to returning to the ring (preponderance of d_{10}–d_{11} products). The reluctance of the catalyst to leave the ring and enter the side chain (and vice versa) is perhaps due to unfavorable energetics for the isopropylidenecyclohexane complex (see Figure 8), a likely intermediate in any such process. As will be discussed in more detail later, (olefin)metal complexes involving highly alkyl-substituted olefins are unfavorable on both steric and electronic grounds.

When a dialkyl-substituted benzene was reacted with D_2, the exclusive product was the corresponding cis-dialkylcyclohexane,[11] which contained deuterium in both alkyl side chains. The retention of stereochemistry is required: As the cobalt center leaves the ring to enter the side chain, the ring–cobalt stereochemistry is fixed by the hydrogen (deuterium) atom that is transferred to the tertiary ring carbon atom (Figure 9, K → L). On return of the cobalt center to the ring, that same hydrogen must be abstracted and replaced by cobalt with consequent retention of stereochemistry (Figure 9, L → K). Note that these arguments are unaffected by rapid rotation about the C_α(alkyl chain)–C(ring) bond.

The allyl and benzyl ligands of the catalyst precursors were hydrogenated to products in much the same way as the arene molecules discussed above. For example, the cyclooctenyl ligand of η^3-$C_8H_{13}Co(P(OCH_3)_3)_3$ was hydrogenated to cyclooctane molecules containing a statistical distribution of deuterium. Only the hydrogen atoms on one side of the ring underwent H–D exchange, so the highest mass species observed was $C_8H_8D_8$. Similarly, the methylcyclohexane produced from the benzyl ligand of η^3-$C_6H_5CH_2Co(P(OCH_3)_3)_3$ contained a maximum of nine deuterium atoms (six ring deuterium atoms and three methyl deuterium atoms). Interestingly, about 70% of the benzyl ligand was hydrogenated to toluene (mostly d_1).[12] This result suggests that in an alkylbenzene hydrogenation sequence alkylbenzene molecules do not initially bind to the catalyst through a benzyl interaction; if they did, some of the unreduced alkylbenzene molecules recovered at the end of a reaction with D_2 should contain deuterium in the α-position. In fact, deuterium was never observed in recovered unreduced alkylbenzenes.

Mechanism for H–D Exchange. A mechanism for the hydrogenation of arenes and the exchange of hydrogen for deuterium atoms in the alkyl side chains is proposed in Figure 9. For simplicity, the phosphite ligands have been excluded. The relative stabilities of the intermediates proposed in Figure 9 are unknown, and the reversibility of some steps has not been demonstrated.

Initial complexation of the arene probably occurs away from the alkyl side chain for steric reasons. As shown in Figure 9, the ring is probably hydrogenated before the side chain is entered.[13]

(11) Our studies included the three isomeric xylenes, m- and p-diethylbenzene, and 1-methyl-4-propylbenzene (see Table I). In each case, standard samples of the cis- and trans-dialkylcyclohexanes were produced by reacting the arene with H_2 in the presence of the heterogeneous catalyst, 5% Rh/C (Strem). Separations of these isomers were effected by using the GC conditions listed for the corresponding arenes in Table I.

(12) When hydrogen is transferred to the methylene carbon, the toluene remains bound to the cobalt center in an η^2 fashion. This mode of binding is unfavorable, and toluene readily dissociates.
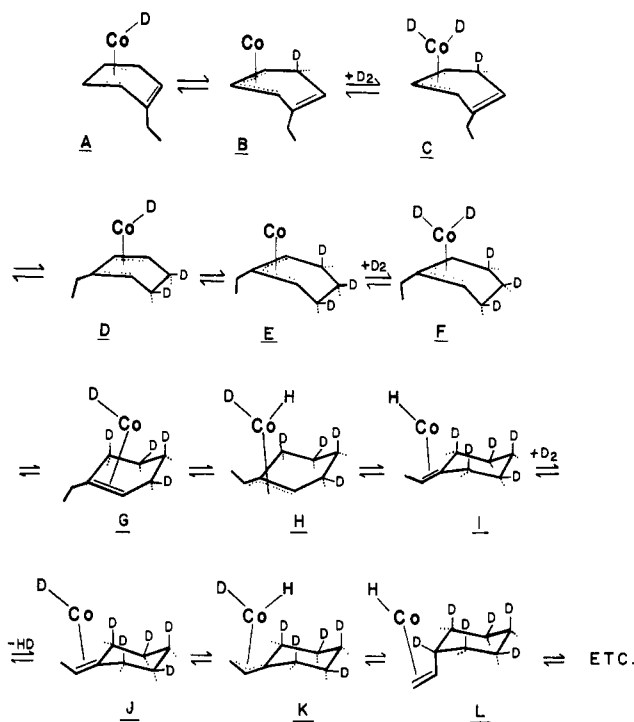
Figure 9. Proposed mechanisms for arene hydrogenation and H–D exchange in alkyl side chains. Phosphite ligands have been omitted for clarity.

After H–D exchange in the side chain is effected, the catalyst can return to the ring and, in the case of disubstituted arenes, enter the other side chain. H–D exchange in the side chain is proposed to occur through a series of reversible $\eta^3 \leftrightarrows \eta^2$ steps (e.g., G $\leftrightarrows$ H and J $\leftrightarrows$ K in Figure 9);[14] however, $\eta^1 \leftrightarrows \eta^2$ interconversions may also play a role in this reaction.[15]

Displacement of Olefins from Catalytic Intermediates. In the absence of olefins, arenes were fully hydrogenated to cyclohexanes. However, when olefinic functions were present, cyclohexenes were produced in addition to cyclohexanes. The cyclohexene products probably result from displacement of catalyst-bound cyclohexene (see, for example, intermediate G in Figure 9) by free olefin. Olefins vary widely in their ability to displace other complexed olefins. Sterically unhindered terminal olefins such as 1-hexene are highly effective displacing agents; cyclohexene is intermediate in effectiveness and the sterically hindered 1-methylcyclohexene is totally ineffective.

Four (olefin)cobalt complexes are likely intermediates in the reduction of toluene to methylcyclohexane. These include the three isomeric (methylcyclohexene)cobalt species and (methylenecyclohexane)cobalt. As discussed above, catalyst-bound olefin

(13) If the catalyst were to enter a side chain before completing hydrogenation of the ring, unsaturated products would result. For example, if
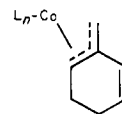
were an intermediate in the hydrogenation of toluene, methylcyclohexene would almost certainly be produced.

(14) The facile reversibility of the $\eta^2 \leftrightarrows \eta^3$ step is supported by the observation that η^3-$C_3H_5Co(P(O$-i-$C_3H_7)_3)_3$ isomerized 1-hexene in the absence of H_2 gas. (J. R. Bleeke and E. L. Muetterties, unpublished results.)

(15) $\eta^1 \leftrightarrows \eta^2$ interconversions are of the type
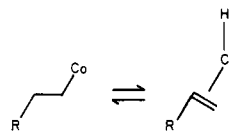
molecules can be displaced by free olefins such as 1-hexene; hence, one might expect the three isomeric methylcyclohexenes and methylenecyclohexane to be produced when toluene is reacted with hydrogen in the presence of 1-hexene. In fact, 3- and 4-methylcyclohexane and methylenecyclohexane were observed, but 1-methylcyclohexene was not. This absence of 1-methylcyclohexene can be understood in light of established thermodynamic features for (olefin)metal complexes. The mixture of olefin products is a kinetic mixture;[16] therefore, it must reflect the relative stabilities (i.e., concentrations) of the various olefin(cobalt) complexes.[17] The 1-methylcyclohexene complex is less favorable than the complexes of the other isomers on both steric and electronic grounds—sterically unfavorable because the double bond is trisubstituted and electronically unfavorable because the bond is electron rich and hence less effective in π-back-bonding.[18] Both Rh(I)[19] and Ag(I)[20,21] have been shown to form less stable complexes with alkyl-substituted olefins than unsubstituted olefins.

When the reaction of cyclohexene with D_2 was terminated at the stage of low conversion to cyclohexane, the unreduced cyclohexene was free of deuterium and the cyclohexane contained no species with more than six deuterium atoms. As reaction time (and conversion to cyclohexane) was increased, (a) deuterium began to appear in the cyclohexene and (b) cyclohexane molecules with more than six deuterium atoms were observed. The deuterium found in the cyclohexene is due to molecules that were displaced from cyclohexene(cobalt) complexes after undergoing some H–D exchange. Since cyclohexene is only a moderately effective displacing olefin, long reaction times are required before there is a significant concentration of these displaced cyclohexene molecules. The cyclohexane molecules with more than six deuterium atoms result from hydrogenation of displaced, deuterium-containing cyclohexene molecules.

3-Methylcyclohexene is comparable to cyclohexene in its ability to displace complexed olefins. Hence, the unreduced olefins recovered at the end of a long reaction of 3-methylcyclohexene with D_2 contained deuterium. In contrast, the sterically congested 1-methylcyclohexene is an ineffective displacing olefin, and the unreduced olefins were deuterium free, even after long reaction times.

Unlike arenes, cyclohexadienes were hydrogenated to both cyclohexenes and cyclohexanes. This suggests that dienes as well as olefins are able to displace catalyst-bound cyclohexenes. However, the cyclohexadienes clearly are not behaving simply as conjugated olefins. Olefins can be displaced after undergoing H–D exchange and/or isomerization. In contrast, cyclohexadienes are not displaced; the unreduced cyclohexadienes contained no deuterium and were not isomerized. These observations indicate that cyclohexadienes are bound as dienes, not as olefins. 1,3-Cyclohexadiene yielded a far greater proportion of cyclohexene than does 1,4-cyclohexadiene suggesting that 1,3-cyclohexadiene is the better displacing agent. Perhaps 1,3-cyclohexadiene binds initially through one double bond, and then in a second, rapid step displaces the cyclohexene to form a stable cyclohexadiene complex. The 1,4-cyclohexadiene is less favorably set up for this displacement.

Competitive Hydrogenation Reactions. The hydrogenation of benzene was blocked by added alkenylbenzenes such as styrene or allylbenzene (see Figure 10). As noted above, it seems probable that dienes bind to the catalyst in a stepwise fashion—first one
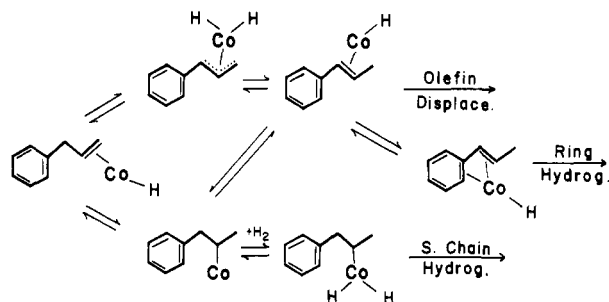
Figure 10. Proposed mechanisms for some reactions of allylbenzene. Phosphite ligands have been omitted for clarity.

double bond and then the other.[22] The ability of styrene and allylbenzenes to bind so effectively (and hence block the hydrogenation of benzene) is perhaps due to the fact that these molecules possess (1) an unhindered double bond that can initially bind to the catalyst and (2) a second double bond in close proximity to the first that can subsequently bind to generate a stable 1,3-diene complex. *cis*- and *trans*-propenylbenzene do not block the hydrogenation of benzene, probably because these molecules do not possess an unhindered double bond for initial binding to the catalyst. Similarly, the hydrogenation of toluene is not blocked by 1,3- or 1,4-cyclohexadiene.

Cleavage of the η^3-Allyl Ligand—The Initiation Step. In catalytic hydrogenations with the η^3-$C_3H_5Co(P(OR)_3)_3$ (R = CH_3, C_2H_5, and i-C_3H_7) complexes, the allyl ligand was lost as propane. Complete loss of the allyl ligand closely coincided with the essential cessation of catalytic hydrogenation. For this reason, it was assumed early in our studies that the allyl ligand on the cobalt remained intact through the hydrogenation cycle. Strongly supportive of this characterization was the observation that the isolable "decomposition" product from η^3-$C_3H_5Co(P(O$-i-$C_3H_7)_3)_3$, the hydride $H_3Co(P(O$-i-$C_3H_7)_3)_3$, was completely inactive as a catalyst or catalyst precursor for arene hydrogenation from 20 to 65 °C.[8] However, the previous characterization of the allyl ligand role in arene hydrogenation is incorrect as shown from studies of η^3-$C_8H_{13}Co(P(OCH_3)_3)_3$ as a catalyst precursor.

The η^3-cyclooctenyl ligand in η^3-$C_8H_{13}Co(P(OCH_3)_3)_3$ was quickly and quantitatively converted to a mixture of cyclooctane and cyclooctene—yet the catalytic hydrogenation proceeded for an extended period beyond the loss of all cyclooctenylcobalt species. The true catalytic species must initially be a hydride. It cannot be $HCo(P(OR)_3)_4$ or $HCo(P(OR)_3)_3$ (in equilibrium with $H_3Co(P(OR)_3)_3$), since both classes of hydrides have been shown to be catalytically inactive for benzene hydrogenation.[5,7,8] We propose that the initially formed hydride is monomeric $HCo(P(OR)_3)_2$[25] (eq 1). This highly coordinately unsaturated complex

$$\eta^3\text{-}C_3H_5Co(P(OR)_3)_3 \ \rightleftharpoons \ \eta^3\text{-}C_3H_5Co(P(OR)_3)_2 \ + \ P(OR)_3 \quad (1)$$

$$\Big\downarrow H_2$$

$$HCo(P(OR)_3)_2 \ + \ C_3H_8$$
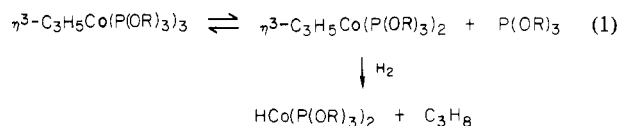
will, of course, react with free phosphite to ultimately yield the

(16) 1-Methylcyclohexene is the most thermodynamically stable olefin product.

(17) The olefins are the result of just one encounter with the catalyst, since they contain at most seven deuterium atoms (four on the ring and three in the side chain). If multiple encounters had occurred, higher mass isotopes would have been observed.

(18) Further evidence for the instability of the 1-methylcyclohexene complex with respect to the complexes of the other isomers comes from the reaction of 1-methylcyclohexene with D_2 in the presence of 1-hexene, a good displacing olefin. Here again displaced 3- and 4-methylcyclohexene and methylenecyclohexane were observed while displaced 1-methylcyclohexene (i.e., 1-methylcyclohexene containing deuterium) was not.

(19) R. Cramer, *J. Am. Chem. Soc.*, **89**, 4621 (1967).

(20) F. R. Hepner, K. N. Trueblood, and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 1333 (1952).

(21) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962).

(22) Consistent with this proposed stepwise addition is the fact that substantial quantities of propenylbenzenes were produced in the allylbenzene–benzene reaction. This isomerization must occur while the alkenylbenzene is bound simply through the olefin in the side chain, since only olefins (not dienes) are displaceable.

(23) (a) J. W. Johnson and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 7395 (1977); (b) M. Y. Darensbourg and E. L. Muetterties, *ibid.*, **100**, 7425 (1978).

(24) (a) M. J. Russell, C. White, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 427 (1977); (b) D. S. Gill, C. White, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 617 (1978).

(25) The analogous rhodium species are isolable; they form a robust dimer for $P(O$-i-$C_3H_7)_3$ and trimers for $P(O$-n-alkyl)$_3$. Fragmentation of these rhodium dimers and trimers to monomers is not a significant process. Hence, these compounds are not very effective catalyst precursors for arene hydrogenation.[26]

(26) A. J. Sivak and E. L. Muetterties, *J. Am. Chem. Soc.*, **101**, 4878 (1979).

very stable $HCo(P(OR)_3)_4$ (eq 2).[27] Thus, every two molecules

$$HCo(P(OR)_3)_2 \xrightarrow{P(OR)_3} HCo(P(OR)_3)_3 \xrightarrow{P(OR)_3} HCo(P(OR)_3)_4 \quad (2)$$

$$\downarrow H_2$$

$$H_3Co(P(OR)_3)_3$$

of allylcobalt complex will yield one molecule of $HCo(P(OR)_3)_2$ and one of $HCo(P(OR)_3)_4$. In the absence of donor molecules, $HCo(P(OR)_3)_2$ decomposes probably through a first step of dimerization, but in the presence of donor molecules (L) like olefins, dienes, and arenes, relatively stable $HCo(P(OR)_3)_2L_{1\,or\,2}$ molecules are initially formed. For benzene, the first species formed should be $HCo(P(OR)_3)_2(\eta^4\text{-}C_6H_6)$. Transfer of hydrogen to benzene would yield $\eta^3\text{-}C_6H_7Co(P(OR)_3)_2$, hydrogen addition would then give $\eta^3\text{-}C_6H_7CoH_2(P(OR)_3)_2$, etc.[28]

Formation of $HCo(P(OCH_3))_4$ and $H_3Co(P(OCH_3)_3)_3$ from $\eta^3\text{-}C_8H_{13}Co(P(OCH_3)_3)_3$ and hydrogen in toluene was unequivocally established by ^1H and ^{31}P NMR studies.[29] No other hydrides were detected by FT ^1H NMR. However, the ^{31}P NMR studies showed a set of resonances that could be explained by three different species each with an AB ^{31}P spectrum. Thus, there appear to be cobalt species present that contain two phosphite ligands. Since no hydride resonances were detected, these phosphite-containing species could be allylic intermediates (see footnote 28) of the type $\eta^3\text{-}C_6H_6CH_3Co(P(OCH_3)_3)_2$ and $\eta^3\text{-}C_6H_8CH_3Co(P(OCH_3)_3)_2$. (For each of these, there are several isomers that have different phosphorus atom environments.)[30]

Rinze[34] has reported the synthesis of $HCo(P(C_6H_5)_3)_2(\eta^4\text{-}2,3\text{-dimethylbutadiene})$, a crystalline compound that is a close analogue of the first intermediate in our proposed benzene hydrogenation sequence, $HCo(P(OR)_3)_2(\eta^4\text{-}C_6H_6)$. The ^1H NMR spectrum of $HCo(P(C_6H_5)_3)_2(\eta^4\text{-}2,3\text{-dimethylbutadiene})$ is temperature dependent; the dynamic behavior is due to exchange of H between the metal center and one end of the butadiene ligand.[34] Hence, the behavior of $HCo(P(C_6H_5)_3)_2(\eta^4\text{-}2,3\text{-dimethyl-butadiene})$ in solution serves as a model for the first step in our proposed arene hydrogenation sequence, transfer of H from Co to the bound arene. We have demonstrated that $HCo(P(C_6H_5)_3)_2(\eta^4\text{-}2,3\text{-dimethylbutadiene})$ is a catalyst precursor for the hydrogenation of benzene, although the lifetime of the catalytic species produced in this system is very short.[35] $Fe(P(OCH_3)_3)_3(\eta^3\text{-cyclooctenyl})^{+\,36}$ is also a close analogue of our proposed first intermediate. In the solid state, this complex possesses a hydrogen atom that is bridging between the metal center and one of the carbon atoms adjacent to the allylic portion of the ring.[37] Hence, in the solid state, this complex also serves as a model for the first step in the proposed benzene hydrogenation sequence.

Supplementary Material Available: Complete set of experimental mass spectra (41 pages). Ordering information is given on any current masthead page.

(27) The stability of the $H_3Co(P(OR)_3)_3$ complexes, which are in equilibrium with $HCo(P(OR)_3)_3$, is R = $CH_3 \ll$ R = $i\text{-}C_3H_7$. In the case of R = $i\text{-}C_3H_7$, both $H_3Co(P(OR)_3)_3$ and $HCo(P(OR)_3)_3$ were isolated at the end of the hydrogenation reactions. For R = CH_3, NMR studies showed both species to be present in early stages of the catalytic hydrogenation reactions but only $HCo(P(OCH_3)_3)_4$ could be isolated after long reaction times; a paramagnetic product also formed after long reaction times.

(28) The full proposed sequence for benzene hydrogenation is η^3-$C_3H_5Co(P(OR)_3)_3 \rightarrow \eta^3\text{-}C_3H_5Co(P(OR)_3)_2 \xrightarrow{H_2} HCo(P(OR)_3)_2 \xrightarrow{C_6H_6} HCo(P(OR)_3)_2(\eta^4\text{-}C_6H_6) \rightarrow \eta^3\text{-}C_6H_7Co(P(OR)_3)_2 \xrightarrow{H_2} \eta^3\text{-}C_6H_7CoH_2(P(OR)_3)_2 \rightarrow HCo(P(OR)_3)_2(\eta^4\text{-}C_6H_8) \rightarrow \eta^3\text{-}C_6H_9Co(P(OR)_3)_2 \xrightarrow{H_2} \eta^3\text{-}C_6H_9CoH_2(P(OR)_3)_2 \rightarrow HCo(P(OR)_3)_2(\eta^2\text{-}C_6H_{10}) \rightarrow C_6H_{11}Co(P(OR)_3)_2 \xrightarrow{H_2} C_6H_{11}CoH_2(P(OR)_3)_2 \rightarrow C_6H_{12} + HCo(P(OR)_3)_2$. This sequence is formally analogous with the original proposed cycle and is fully consistent with all the experimental data.

(29) In the early stages of the hydrogenation (0.5 h) the ratio of $HCo(P(OCH_3)_3)_4$ to $H_3Co(P(OCH_3)_3)_3$ is ~3:1 and this ratio increases with time.

(30) The $Co(P(OR)_3)_2$ species are not necessarily catalytic intermediates. The effective intermediates may be in very low concentrations.

(31) For example, cyclohexene was observed during the early stages of a vapor-phase hydrogenation (flow system) of benzene over nickel films at 0–50 °C.[32] The formation of small concentrations of olefins has also been observed in the hydrogenation of aromatic hydrocarbons on several catalysts in the liquid phase.[33]

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