Hydrogenation of Arenes by the $RhCl_3$–Aliquat 336 Catalyst. 4. Hydrogen–Deuterium Exchange and Other Mechanistic Features[1]

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The ion pair generated from $RhCl_3$ and Aliquat 336 in an aqueous–organic two-phase medium was shown to catalyze the hydrogenation and deuteration of arenes at 30 °C and 0.9 atm under apparently homogeneous conditions. The rate of the reductions was preceded by characteristic induction periods. Substrates with electron-attracting groups proved to have shorter induction periods and higher reaction rates than those with electron-donating substituents. Sterically hindered benzenes yielded both cyclohexane and cyclohexene derivatives. Hydrogenation of deuteriated arenes and deuteriation of unlabeled benzenes were found, by mass spectral analysis, to be associated with both side-chain and ring-proton H–D exchange. Recovered starting material underwent hydrogen exchange as well, but only if the substrate had an α proton in the side chain. The water proved essential for the reduction and played an important part in the H–D exchange. Comparative experiments were carried out with the labile η^3-$C_3H_5Co[P(OCH_3)_3]_3$ arene hydrogenation catalyst precursor. The cobalt- and rhodium-promoted processes were found to have several common features and were assumed to follow similar mechanisms.

The solvated ion pair $[(C_8H_{17})_3NCH_3]^+[RhCl_4]^-$, formed from aqueous $RhCl_3$ and Aliquat 336,[2] has been shown to be an efficient, long-lived catalyst precursor for the hydrogenation of arenes under exceedingly mild conditions of temperature and pressure.[3] The complex has already proved useful for the preparative-scale synthesis of cyclohexanes from a variety of benzene derivatives,[3] for the transformation of naphthalenes to tetralins and *cis*-decalins,[4] and for the partial reduction of many polycyclic aromatics in a highly regio- and stereoselective manner.[1] In addition, the ion pair was found to promote selective hydrogenation of nonaromatic C–C double and triple bonds[3,5] and to serve as a recyclable catalyst in some unique hydrogen-transfer processes.[6]

We now extend the studies on arene hydrogenation to include competitive reactions, reduction of labeled arenes, deuteriations, comparative experiments with Muetterties' η^3-allylcobalt tris(trimethyl phosphite) catalyst,[7] and other investigations from which some mechanistic information of the catalysis could be obtained.

Results and Discussion

Physical Nature of the Catalyst System. Occasionally, during the very initial stages of our hydrogenations, small amounts of dark particles (which dissolved in hot DMF and hot Me_2SO) separated. The quantity of the precipitation could be reduced easily or even eliminated completely by addition of up to 4 equiv of trioctylamine/equiv of rhodium, depending on the substrate employed. Filtration of the solid particles under exclusion of air (ca. 15–20 min after hydrogenation had begun) gave clear solutions that did not deteriorate any further.

Since some well-known arene hydrogenations by soluble metal catalysts[8,9] were shown to proceed, in fact, under heterogeneous conditions, we found it imperative to examine carefully the physical nature of the organic phase of our rhodium catalyst system.

The solid particles that separated from the reaction mixture of the benzene and anisole hydrogenations, respectively, were examined and found inactive. The filtrates, however, absorbed hydrogen exactly at the same rate as that observed before filtration. They showed no traces of precipitation when subjected to filtration tests for heterogeneity[10] and did not scatter He-Ne laser beams.[13] Mercury, which had been reported to selectively inhibit heterogeneous hydrogenation processes,[14] had no effect on the reaction rate, while dibenzo[*a*,*e*]cyclooctatetraene—the inhibitor of *homogeneous* systems[14]—practically stalled hydrogenation of anisole. The reaction was resumed, however, when the tricyclic additive itself had been reduced. These tests, and the fact that the

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[1] Part 3: Amer, I.; Amer, H.; Ascher, R.; Blum, J.; Sasson, Y.; Vollhardt, K. P. C. *J. Mol. Catal.* **1987**, *39*, 185.

[2] Sasson, Y.; Zoran, A.; Blum, J. *J. Mol. Catal.* **1981**, *11*, 293.

[3] Blum, J.; Amer, I.; Zoran, A.; Sasson, Y. *Tetrahedron Lett.* **1983**, *24*, 4139.

[4] Amer, I.; Amer, H.; Blum, J. *J. Mol. Catal.* **1986**, *34*, 221.

[5] Azran, J.; Buchman, O.; Amer, I.; Blum, J. *J. Mol. Catal.* **1986**, *34*, 229.

[6] Blum, J.; Pri-Bar, I.; Alper, H. *J. Mol. Catal.* **1986**, *37*, 359.

[7] Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 324.

[8] E.g.: (a) Maitlis, P. *Acc. Chem. Res.* **1978**, *11*, 301. (b) Rajca, I. *Pol. J. Chem.* **1981**, *55*, 775. (c) Januszkiewicz, K. R.; Alper, H. *Organometallics* **1983**, *2*, 1055.

[9] Maitlis' (pentamethylcyclopentadienyl)rhodium complexes were shown to form solid particles during arene hydrogenation and to give positive filtration tests,[10a] the (anthranilato)- and (phenylanthranilato)-rhodium catalysts were reported recently[11,12] to decompose into black solids, and Alper's chloro(1,5-hexadiene)rhodium dimer[8c] is now believed to act as a fine colloid.

[10] (a) Hamlin, J. E.; Hirai, K.; Millan, A.; Maitlis, P. M. *J. Mol. Catal.* **1980**, *7*, 543. (b) Lain, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 252.

[11] Borowski, A. F. *Transition Met. Chem. (Weinheim, Ger.)* **1983**, *8*, 226.

[12] Borowski, A. F.; Rajca, I. *Transition Met. Chem. (Weinheim, Ger.)* **1984**, *9*, 109.

[13] Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.

[14] Anton, D. R.; Crabtree, H. *Organometallics* **1983**, *2*, 855.

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kinetic measurements performed with the filtered reaction mixtures were highly reproducible, indicated that the organic layer in our catalytic system behaves in every respect as a homogeneous solution.

Activation of Catalyst Precursor: Effect of Hydrogen and Aromatic Substrate. We have already shown (ref 3; Table I) that the $RhCl_3$–Aliquat 336 ion pair promotes smooth hydrogenation of a variety of benzene derivatives. Common substituents such as alkyl, alkoxy, trifluoroalkyl, and amino groups were found not to undergo hydrogenolysis nor to lead to other side reactions except H–D exchange (which will be discussed below). The progress of the hydrogenations followed first-order kinetics, both in the substrate (until at least 60% conversion) and in the catalyst, as long as the concentration of catalyst was <0.35 mM. At higher catalyst concentrations, the rate dependence was found to level off and the kinetics to approach the pseudo zero order. It should, however, be noted that none of the reduction processes started right away. The beginning of hydrogenation was preceded by induction periods of characteristic length for every substrate. In general, longer induction periods were observed for substrates with electron-donating and bulky substituents than for those with electron-attracting groups.

Treatment of $RhCl_3$–Aliquat 336 solution with an aromatic substrate and 2–3 equiv of argon-diluted hydrogen/equiv of rhodium for a period of 50 min *prior* to the hydrogenation either shortened the induction time or eliminated it completely. Pretreatment with an arene but without H_2 had, however, no effect on the process. Brief hydrogenation of the catalyst precursor in the absence of substrate also reduced the length of the induction periods. Under such conditions however, the greater part of the ion pair decomposed into inactive metallic rhodium. In any event, these experiments suggest that the activation of the catalyst precursor is associated with the formation of a rhodium–arene hydride, via the "hydride" rather than the "unsaturate" route. During this activation, two of the four chlorine atoms were found, by elemental analysis, to be expelled from the rhodium complex as water-soluble Cl^-. It should be noted that once the catalyst precursor had been activated it functioned right away without necessitating an induction period, even when the catalyst was recycled or treated with a totally different aromatic substrate at a later stage of the catalysis.

Following catalyst activation, the various benzene derivatives reacted at different rates depending on both the structural and electronic nature of the substrates. While steric hindrance had a very pronounced influence on the rate, electronic factors had a much smaller, though clearly distinguishable, effect. The steric effect was demonstrated by a set of experiments in which benzene, durene, and hexamethylbenzene were hydrogenated to an extent of 4% under identical conditions of concentration, temperature, pressure, and stirring rate. The time required for completion of the test with the three substrates was <1, 22, and 100 h, exclusive of the induction periods. The effect of the electronic nature of the substrate was shown by comparison of the hydrogenation rates of unsubstituted benzene, as well as toluene, anisole, and benzotrifluoride. In some typical experiments (see Figure 1), the corresponding maximum rates were $(3.51 \pm 0.16) \times 10^{-3}$, $(2.36 \pm 0.12) \times 10^{-3}$, $(3.04 \pm 0.15) \times 10^{-3}$, and $(4.20 \pm 0.16) \times 10^{-3}$ mmol L^{-1} min^{-1}.

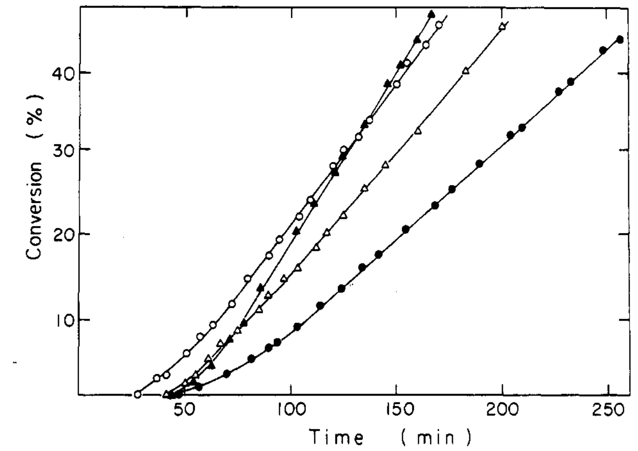

Figure 1. Conversion–time profiles for hydrogenation of benzene (○), toluene (●), anisole (△), and benzotrifluoride (▲). Reaction conditions: 1 mmol of substrate, 3.79×10^{-2} mmol of $RhCl_3{\cdot}3H_2O$, 22 mg of Aliquat 336, 50 μL of trioctylamine, 0.5 mL of H_2O, 0.5 mL of 1,2-dichloroethane, stirring rate 400 rpm, reaction temperature 30 °C, 0.9 atm H_2.

An additional factor that has been found to affect the reaction rate is the nature of the *initial* unsaturated substrate employed in activation of the catalyst precursor. When, e.g., toluene was reduced in the presence of the $RhCl_3$–Aliquat 336 catalyst that had been activated by styrene (i.e., styrene was reduced by the catalyst prior to addition of toluene), it reacted 1.4 times faster than in an experiment in which the rhodium complex was exposed right from the beginning only to toluene.[15] This peculiar effect of catalyst activation was further demonstrated by a set of three competitive experiments in which equimolar amounts of benzene and toluene, benzene and anisole, and benzene and benzotrifluoride were hydrogenated under the conditions given in the Experimental Section. In each of these experiments, both substrates reacted approximately at the same maximum rate (mmol L^{-1} min^{-1}) which was, however, different for each pair: $(0.58 \pm 0.02) \times 10^{-3}$, benzene–toluene; $(0.63 \pm 0.02) \times 10^{-3}$, benzene–anisole; $(1.19 \pm 0.05) \times 10^{-3}$, benzene–benzotrifluoride. Consequently, the rate of benzene hydrogenation was 1.1 times greater when admixed with benzotrifluoride and 1.9 times slower than when reacted together with toluene than in the absence of the second substrate under comparable conditions.

Rate enhancement in arene hydrogenation by addition of an olefinic substrate has previously been observed during application of Muetterties' η^3-$C_3H_5Co[P(OCH_3)_3]_3$ catalyst.[16] However, while the cobalt complex continued to affect the aromatic substrate in the presence of excess alkene,[17] a similar operation in the rhodium-promoted reductions stopped the process when the amount of olefin (or acetylene) surpassed 1 equiv/equiv of metal. Thus, toluene hydrogenation stopped immediately, even upon addition of traces of styrene to the reaction mixture. Resumption of the original process occurred only after complete conversion of the styrene into ethylbenzene. Likewise, when toluene was added to a reaction mixture in which styrene was hydrogenated, arene hydrogenation started only after complete consumption of the vinylic compound. Typical reaction profiles for the latter process are given in Figure 2.

Just as olefins were found to prevent arene hydrogenation, acetylenes inhibit the rhodium-promoted alkene reduction. Thus, in spite of the fact that olefins reacted

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[15] The figure 44 given in our preliminary communication[3] is a typographical error.

[16] Bleeke, J. R.; Muetterties, E. L. *J. Am. Chem. Soc.* 1981, *103*, 556.

[17] Benzene hydrogenation by η^3-$C_3H_5Co[P(OCH_3)_3]_3$ was reported also to be inhibited by styrene, but it proceeded well in the presence of other olefins.[16]

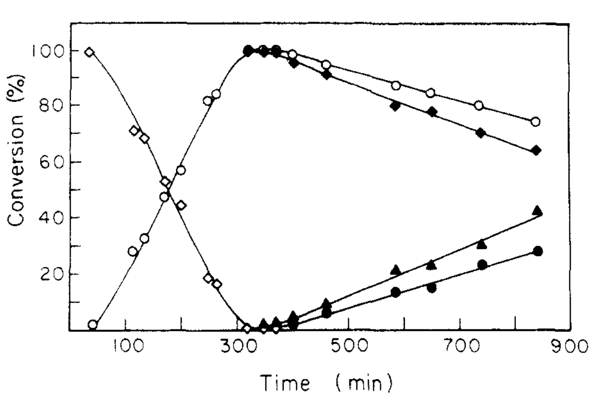

Figure 2. Conversion–time profiles for hydrogenation of a mixture of 0.5 mmol of styrene (◇) and 0.5 mmol of toluene (◆) under the conditions of Table I to give ethylbenzene (○), methylcyclohexane (▲), and ethylcyclohexane (●).

much faster than alkynes,[3] stepwise hydrogenation of arylacetylenes could be carried out by our catalyst system. In constrast to the hydrogenation of phenylacetylene by Muetterties' cobalt catalysts, we were able to obtain styrene, ethylbenzene, and ethylcyclohexane as single products (reaction 1) just by adjusting the reaction time of the

$$C_6H_5C{\equiv}CH \xrightarrow{H_2} C_6H_5CH{=}CH_2 \xrightarrow{H_2} C_6H_5C_2H_5 \xrightarrow{3H_2} C_6H_{11}C_2H_5 \quad (1)$$

process.[18,19] We explain this behavior of the rhodium catalyst system by initial formation of a relatively stable acetylene complex that inhibits olefin hydrogenation, followed by generation of an alkene complex that interferes with the reduction of aromatic rings.

Comparison of our catalyst system with the short-lived η^3-$C_3H_5Co[P(OR)_3]_3$ complexes revealed that the stable rhodium catalyst (which could even be recycled when worked up under exclusion of air) has a much wider scope of activity. It proved to promote selective reduction of mono- and polycyclic arenes with alkyl, alkoxy, amine, carbonyl, halogen, hydroxy, and mercapto functions,[1,3,4] while the cobalt catalysts failed to promote both selective partial hydrogenation of polycyclics[19] as well as the reduction of hydroxy-, halo-, and nitrobenzenes.[19,20]

In general, hydrogenation of benzenes did not give partially hydrogenated products (cyclohexenes and cyclohexadienes). Cyclohexene derivatives were, however, isolated when sterically hindered compounds were reduced. Durene, e.g., afforded, in addition to the isomeric 1,2,4,5-tetramethylcyclohexanes, 2,3,5,6-tetramethylcyclohexene (major side product) and 1,2,4,5-tetramethylcyclohexene (small amount). The cyclohexanones[3] and tetralones[4] formed from phenol and naphthols, respectively, can also be regarded as partially hydrogenated products, as they are the keto tautomers of 1-cyclohexenol and dihydronaphthols. These results imply the intermediacy of coordinated cyclohexenes, which are liberated when steric and electronic factors destabilize the complexes and prevent further transformation.

The rates of hydrogenation of benzene and benzene-d_6 were compared under a variety of conditions. In no case was the reduction rate of the deuteriated compound lower than that of the unlabeled substrate. Under the conditions of Figure 1, we observed even a negative isotope effect of rate (C_6H_6)/rate (C_6D_6) = 0.83. We attribute this effect to the extensive H–D exchange during the hydrogenation of unsubstituted benzene (vide infra).

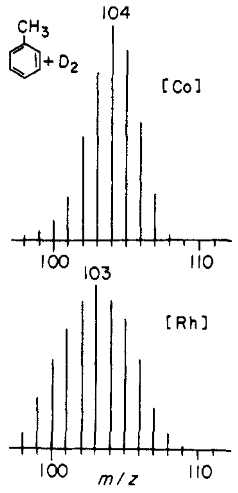

Figure 3. Parent ion region of the 17-eV EI mass spectra of methylcyclohexane produced in the reaction of toluene with D_2: upper spectrum, catalysis performed by Bleeke and Muetterties;[16] lower spectrum, catalysis performed under the conditions given in Table I.

A rate dependence on the hydrogen was observed in experiments in which the gas was diluted with argon to a partial pressure of 0.1–0.9 atm. At the lower limit, the hydrogenation of anisole proved to approach pseudo-first order. Substitution of the hydrogen gas by deuterium indicated no measurable isotope effect.

Hydrogen–Deuterium Exchange. Deuterium labeling experiments indicated substantial H–D exchange in many of our experiments. Since the cobalt–phosphite–catalyzed hydrogenations were reported to be likewise associated with such an exchange,[16] we carried out comparative studies in which both our rhodium complex and Muetterties' cobalt catalysts were used. Typical product distributions obtained in deuteriation of toluene by the two catalyst systems was deduced from the 17-eV EI mass spectra shown in Figure 3.[21] Although the spectra of the rhodium-catalyzed deuteriation and the η^3-$C_3H_5Co[P(OCH_3)_3]_3$-promoted catalysis were not taken at the same conversions, they suggest H–D exchange to nearly the same extent. The peaks of m/z 104 that correspond to $C_7H_8D_6^{\bullet+}$ are accompanied in both cases by peaks of higher masses of $C_7H_7D_7^{\bullet+}$, $C_7H_6D_8^{\bullet+}$, and $C_7H_5D_9^{\bullet+}$ (and in our catalysis also by a small signal of $C_7H_4D_{10}^{\bullet+}$), as well as by peaks of lower masses that *have been proven* to result from the deterium-deficient cation radicals $C_7H_9D_5^{\bullet+}$, $C_7H_{10}D_4^{\bullet+}$, $C_7H_{11}D_3^{\bullet+}$, $C_7H_{12}D_2^{\bullet+}$, and $C_7H_{13}D^{\bullet+}$ and from deuterium-free $C_7H_{14}^{\bullet+}$.

Further evidence for the H–D exchange was found in mass spectral data for various deuteriation products of benzene and of some of its derivatives formed under *comparable* conditions (see Table I). Table I indicates that both side-chain *and* ring protons were exchanged. The highest degree of proton exchange was found in unsubstituted benzene owing to the absence of any steric effect. Under the conditions of Table I, the introduction of deuterium in the side chain was shown (a) to take place only

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[18] The cobalt catalysts η^3-$C_3H_5Co[P(OR)_3]_3$ promoted the transformation of styrene into a mixture of ethylbenzene and vinyl- and ethylcyclohexanes, and 1-phenylpropyne gave a mixture of propynyl-, allyl-, propyl-, *cis*-propenyl-, and *trans*-propenylcyclohexane.

[19] Stuhl, L. S.; Rakowski-DuBois, M.; Hirsekorn, F. J.; Bleeke, J. R.; Stevens, A. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 2405.

[20] Cf. our account on the selective hydrogenation of nitrobenzenes and other unsaturated nitro compounds by the $RhCl_3$–Aliquat 336 catalyst: Amer, I.; Bravdo, T.; Blum, J. *Tetrahedron Lett.* **1987**, *28*, 1321.

[21] The mass spectrum of the cobalt-catalyzed reaction mixture was given to us by the late Professor Earl L. Muetterties and published together with our mass spectrum according to his suggestion.

Table I. Mass Spectral Data for Products and Recovered Starting Materials in Deuteriation of Various Benzene Derivatives RC_6H_5 by the $RhCl_3$–Aliquat 336 Catalyst under Comparable Conditions[a]

	deuterium distrib in products, m/z (rel intens)[b]												deuterium distrib in rec starting matl, m/z (rel intens)[b]					
R	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_0	d_1	d_2	d_3	d_4	d_5
H			87	88	89	90	91	92	93	94	95	96	78					
			(1)	(4.5)	(17)	(30)	(17)	(11)	(9)	(6)	(3)	(1.5)	100					
CH_3		100	101	102	103	104	105	106	107	108			92	93	94	95	96	97
		(3.5)	(7)	(12)	(17)	(19)	(24.5)	(9)	(5)	(3)			(2)	(10)	(29.5)	(32.5)	(19)	(7)
CH_3CH_2				116	117	118	119	120	121	122				107	108	109	110	111
				(4)	(10)	(20)	(30)	(21)	(10)	(5)				(13)	(33)	(35)	(15)	(4)
$CH_3(CH_2)_2$			129	130	131	132	133	134	135	136			120	121	122	123	124	
			(8)	(14)	(23)	(25)	(15)	(8)	(6)	(1)			(7)	(30)	(47)	(13)	(3)	
$(CH_3)_2CH$				130	131	132	133	134	135	136			120	121	122	123	124	
				(1)	(15)	(33)	(22)	(16)	(11)	(2)			(11)	(54)	(19)	(10)	(6)	
$(CH_3)_3C$						146							134					
						(100)							(100)					
CF_3	153	154	155	156	157	158							146					
	(10)	(15)	(20)	(26)	(18)	(11)							(100)					
CH_3O[c]				118	119	120							108					
				(12.5)	(46.5)	(30)							(100)					
naphthalene[d]			135	136	137								128					
			(12)	(87)	(1)								(100)					

[a] Reaction conditions: 1 mmol of substrate, 3.79×10^{-2} mmol of $RhCl_3{\cdot}3H_2O$, 5.4×10^{-2} mmol of Aliquat 336, 0.23 mmol of trioctylamine, 1 mL of 1,2-dichloroethane, and 1 mL of H_2O hydrogenated to an extent of 50% with D_2 at 0.9 atm; 30 ± 0.5 °C; constant stirring rate of 400 rpm. [b] The data given are corrected for natural ^{13}C contributions and expressed in percent of the sum of the molecular ion intensities. The mass spectra were taken under such conditions (17 eV) that hydrogen elimination from the molecular ions does not take place. [c] In addition to methoxycyclohexanes, 3% deuteriated cyclohexanone was formed. [d] The mass spectrum was recorded at 18% conversion.

Table II. Mass Spectral Data for Products and Recovered Starting Material in $RhCl_3$–Aliquat 336 Promoted Hydrogenation of Some Deuterium-Labeled Benzenes under Comparable Conditions[a]

	deuterium distrib in products, m/z (rel intens)[b]										deuterium distrib in rec starting matl, m/z (rel intens)[b]					
substrate	d_{n-4}	d_{n-3}	d_{n-2}	d_{n-1}	d_n	d_{n+1}	d_{n+2}	d_{n+3}	d_{n+4}	d_{n+5}	d_{n-5}	d_{n-4}	d_{n-3}	d_{n-2}	d_{n-1}	d_n
benzene-d_6 ($n = 6$)	86	87	88	89	90	91	92	93	94							84
	(2)	(4)	(10)	(14.5)	(28)	(29)	(10)	(2)	(0.5)							(100)
toluene-d_8 ($n = 8$)	102	103	104	105	106	107	108	109	110	111	95	96	97	98	99	100
	(1)	(4)	(8)	(19)	(20)	(21)	(13)	(10)	(3)	(1)	(5)	(14)	(28)	(29)	(21)	(3)
ethylbenzene-d^{10} ($n = 10$)	118	119	120	121	122	123	124	125	126	127	111	112	113	114	115	116
	(1.5)	(5)	(9.5)	(18)	(24.5)	(18.5)	(15)	(8)	(1)	(0.5)	(3)	(10)	(20)	(34)	(26)	(7)[c]

[a] Reaction conditions: quantities of substrate, $RhCl_3{\cdot}3H_2O$, Aliquat 336, trioctylamine, 1,2-dichloroethane, and water as in Table I; hydrogenation at 0.9 atm H_2; 30 ± 0.5 °C; constant stirring rate of 400 rpm, until 50% conversion. [b] See footnote b in Table I. [c] 300-MHz ^1H NMR spectra indicated that ca. 85% of the hydrogen in the side chain was replaced by deuterium.

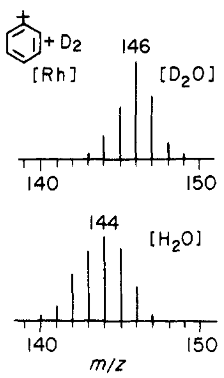

Figure 4. Parent ion region of the 17-eV EI mass spectra of *tert*-butylcyclohexane produced in the reaction of *tert*-butylbenzene with D_2 under the conditions of Table IV at *full* conversion: upper spectrum, reaction in the presence of D_2O; lower spectrum, reaction in the presence of H_2O.

in the presence of at least one proton at the α-position of the chain and (b) to be influenced by steric constraints. Both kinds of H–D exchange processes (in the ring and in the side chains) were found to depend strongly on the reaction periods. For example, while at 50% conversion of *tert*-butylbenzene deuteration no exchange at all could be observed, by the time that the reaction with deuterium had been completed, hydrogen scrambling was rather significant (Figure 4).

Formation of the deuterium-deficient products is assumed to result in part from the reaction of the arenes with either H_2 or HD generated during D_2-induced H–D exchange and in part from the water effect discussed below.

Hydrogen–deuterium exchange in hydrogenation of deuterated arenes was found to be even more pronounced than that observed in deuteration of unlabeled benzenes, seemingly due to a kinetic isotope effect associated with the exchange but not with the hydrogenation process. Examples for the exchange during hydrogenation of benzene-d_6, toluene-d_8, and ethylbenzene-d_{10} are given in Table II.

Since H–D exchange was reported to occur also in arene reductions by Muetterties' cobalt catalysts,[16] we were interested in comparing these results with those obtained with the $RhCl_3$–Aliquat 336 ion pair. We found, however, through numerous experiments, that Muetterties' arene hydrogenations are difficult to reproduce. Reduction of benzene and toluene at 20 °C and 1 atm H_2 by η^3-$C_3H_5Co[P(OCH_3)_3]_3$ (that had been prepared exactly as described in the literature[22,23]) proceeded significantly more slowly than reported.[16] In order to obtain the published yields, we had to raise the temperature to 60–80 °C and the hydrogen pressure to 3–6 atm. Furthermore, we observed that the activity of the cobalt catalyst is extremely sensitive to the quality of the reducing agent as well as to the purity of the trimethyl phosphite from which the catalyst precursor was synthesized. Although we had no difficulty (at 80 °C and 6 atm) in carrying out the hydrogenation of C_6H_6, C_6D_6, $CH_3C_6H_5$, and $CD_3C_6D_5$, *absolutely no deuteriation* took place unless the starting phosphite (Fluka's purum or Aldrich 97% grade) was vacuum distilled (1 mm) at least three successive times before use. Deuteration proceeded smoothly also when the D_2 gas (Matheson, Fluka, or Schuchardt; >99.5% isotopically pure) was doped with 1–2% H_2 (99.95%). At present we have no rational explanation for this peculiar behavior of η^3-$C_3H_5Co[P(OCH_3)_3]_3$, which has been found to be common to all 15 deuteriation experiments attempted within the framework of this study.

The results of some comparative hydrogenation and deuteriation experiments using the cobalt and rhodium complexes are summarized in Table III. The data indicate that the cyclohexanes formed in the presence of rhodium underwent more extensive H–D exchange than those obtained in the presence of the Co catalyst. For example, while the highest molecular ion in experiment 4 was found to be *m/z* 107 (probably corresponding to $CD_3C_6H_5D_6^{\bullet+}$), in experiment 5 the molecular mass extended up to *m/z* 108. This indicates that in the rhodium-catalyzed reaction at least one ring proton has been replaced by deuterium. Yet, we believe that the difference between the two catalyst systems is quantitative rather than qualitative. In spite of the report by Bleeke and Muetterties that no ring-proton exchange takes place in the presence of the cobalt complexes,[16] we found (albeit at 80 °C) that some exchange *does* occur both in deuteration of C_6H_6 and in hydrogenation of C_6D_6 even at low conversions (Table III, experiments 1 and 6, respectively). In fact, reinspection of the $^{13}C\{^1H\}$ NMR spectrum of the deuteration products of toluene reported by Bleeke and Muetterties in Figure 2 in ref 16, as well as the data for D_2 reduction of propylbenzene given in ref 10 of their paper, clearly indicates ring-proton exchange.

In addition to H–D exchange in the reduced products, we observed in the rhodium-catalyzed systems considerable exchange in the recovered starting material, provided it possessed at least one α-hydrogen atom in the side chain (see Tables I–III). Here too, we found that, in contrast to the report of Bleeke and Muetterties,[16] the cobalt catalyst promoted exchange in the recovered substrates, albeit to a much smaller extent (see, e.g., Table III, experiments 4 and 8).

The most important difference between Muetterties' and our catalysts is, of course, the existence of an aqueous phase in the latter system. While the cobalt catalysts are decomposed readily in the presence of moisture, water was shown to be essential for the rhodium catalysis. A minimum of 2 equiv of H_2O or D_2O (apart from the water of coordination in $RhCl_3{\cdot}3H_2O$)/equiv of the metal was required for the formation of a soluble ion pair and for allowing the reduction to take place. Thus, drying of the organic layer over $MgSO_4$ gave a completely inactive rhodium solution. We were able, however, to conduct the various H_2 and D_2 hydrogenation processes in a one-liquid instead of our two-liquid phase system in which wet THF was employed. Catalyses in a single phase gave, in general, products with the same deuterium distribution as in the presence of a separate aqueous layer. For example, deuteriation of $CF_3C_6H_5$ in D_2O-treated THF yielded under the conditions of method B (see the Experimental Section) (trifluoromethyl)cyclohexanes having the following 17-eV EI mass spectrum: *m/z* (relative intensity as defined in Table I) 156 (13), 157 (30), 158 (37), 159 (13), 160 (7). Under the conditions of method A (see the Experimental Section) the corresponding MS data were *m/z* 156 (8), 157 (32), 158 (45), 159 (11), and 160 (4). The small differences in the relative intensities are attributed to the difference in the effective D_2O concentration in the reacting phases (vide infra).

Since the water proved to be an essential component in the rhodium-promoted reductions, its involvement in the catalyses was investigated. The results summarized in Table IV as well as the data given in Table I–III show that

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

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

Table III. Comparison of Cobalt and Rhodium Catalysts: Mass Spectral Data for H_2 and D_2 Hydrogenation of Some Labeled and Unlabeled Arenes by η^3-$C_3H_5Co[P(OCH_3)_3]_3$ [Co] and by the $RhCl_3$–Aliquat 336 System [Rh][a]

expt	reactants (*n*)	catalyst system	conversn, %	deuterium distrib in products, m/z (rel intens)[b]												deuterium distrib in rec starting matl, m/z (rel intens)[b]					
				d_{n-5}	d_{n-4}	d_{n-3}	d_{n-2}	d_{n-1}	d_n	d_{n+1}	d_{n+2}	d_{n+3}	d_{n+4}	d_{n+5}	d_{n+6}						
1	C_6H_6, D_2 (6)	[Co]	20				88 (10)	89 (32)	90 (55)	91 (3)						78 (100)					
2	C_6H_6, D_2 (6)	[Rh]/H_2O	50			87 (1)	88 (4.5)	89 (17)	90 (30)	91 (17)	92 (11)	93 (9)	94 (6)	95 (3)	96 (1.5)	78 (100)					
3	$CH_3C_6H_5$, D_2 (6)	[Co]	8					103 (10)	104 (27)	105 (35)	106 (17)	107 (11)				92 (100)					
4	$CH_3C_6H_5$, D_2 (6)	[Co]	20		100 (2)	101 (5)	102 (11)	103 (19)	104 (25)	105 (22)	106 (12)	107 (4)				92 (98)	93 (2)				
5	$CH_3C_6H_5$, D_2 (6)	[Rh]/H_2O	50		100 (3)	101 (7)	102 (12)	103 (17)	104 (19)	105 (25)	106 (9)	107 (5)	108 (3)			92 (2)	93 (10)	94 (29)	95 (33)	96 (19)	97 (7)
6	C_6D_6, H_2 (6)	[Co]	5				88 (0.5)	90 (2)	90 (97.5)							84 (100)					
7	C_6D_6, H_2 (6)	[Rh]/H_2O	10		86 (1)	87 (12)	88 (16)	89 (19)	90 (26)	91 (21)	92 (5)					84 (100)					
8	$CD_3C_6D_5$, H_2 (8)	[Co]	8			103 (1.5)	104 (9)	105 (31)	106 (55)	107 (3.5)								97 (0.5)	98 (4)	99 (18.5)	100 (77)
9	$CD_3C_6D_5$, H_2 (8)	[Rh]/H_2O	26	101 (4)	102 (10)	103 (19)	104 (26)	105 (22)	106 (13)	107 (13)	108 (2)					95 (4)	96 (14)	97 (32)	98 (35)	99 (13)	100 (2)

[a] Reaction conditions for experiments 1, 3, 4, 6, and 8: 5 mmol of substrate, 0.105 mmol of η^3-$C_3H_5Co[P(OCH_3)_3]_3$; 6 atm H_2 or D_2 at 25 °C; reaction temperature 80 °C; magnetically stirred autoclave. Reaction conditions for experiments 2, 5, 7, and 9 as given in Table I except that either H_2 or D_2 was used and the conversion was as given in column 4. [b] See footnote *b* in Table I.

Table IV. Effect of Water: Mass Spectral Data for Some $RhCl_3$–Aliquat 336 Promoted Hydrogenations and Deuteriations of Toluene and of Benzotrifluoride in the Presence of H_2O and D_2O[a]

expt	substrate	hydrogen. agent (*n*)	aq phase	deuterium distrib in rec starting matl, m/z (rel intens)[b]						deuterium distrib in products, m/z (rel intens)[b]											
				d_0	d_1	d_2	d_3	d_4	d_5	d_{n-5}	d_{n-4}	d_{n-3}	d_{n-2}	d_{n-1}	d_n	d_{n+1}	d_{n+2}	d_{n+3}	d_{n+4}	d_{n+5}	d_{n+6}
1	$CH_3C_6H_5$	H_2 (0)	D_2O	92 (67)	93 (31)	94 (2)									98 (56)	99 (27)	100 (14)	101 (2)			
2	$CH_3C_6H_5$	D_2 (0)	H_2O	92 (2)	93 (10)	94 (30)	95 (32)	96 (19)	97 (7)		100 (3)	101 (7)	102 (12)	103 (17)	104 (19)	105 (25)	106 (9)	107 (5)	108 (3)		
3	$CH_3C_6H_5$	D_2 (6)	D_2O	92 (5)	93 (16)	94 (37)	95 (39)	96 (2.5)	97 (0.5)				102 (4)	103 (8)	104 (15)	105 (25)	106 (22)	107 (12)	108 (8)	109 (4)	110 (2)
4	$CF_3C_6H_5$	H_2 (0)	D_2O	146 (100)											152 (51)	153 (25)	154 (24)				
5	$CF_3C_6H_5$	D_2 (6)	H_2O	146 (100)						153 (10)	154 (15)	155 (20)	156 (26)	157 (18)	158 (11)						
6	$CF_3C_6H_5$	D2 (6)	D_2O	146 (100)									156 (8)	157 (32)	158 (45)	159 (11)	160 (4)				

[a] Reaction conditions: 1 mmol of substrate, 3.79×10^{-2} mmol of $RhCl_3 \cdot 3H_2O$, 5.4×10^{-2} mmol of Aliquat 336, 0.23 mmol of trioctylamine, 1 mL of 1,2-dichloroethane, and 1 mL of either H_2O or D_2O hydrogenated to an extent of 50% conversion with either H_2 or D_2; 0.9 atm; 30 ± 0.5 °C. [b] See footnote *b* in Table I.

the water takes part in H–D exchange both in the products and in the recovered starting material. Table IV reveals that water-induced exchange is generally slower than that caused by H_2 and D_2. It is, however, effective in some cases where the reducing agent is not. Thus, while at low conversions (<50%) H_2 and D_2 were shown not to cause H–D exchange in cyclohexanes that do not have an α-hydrogen or α-deuterium atom in the side chain (e.g., methoxy- and (trifluoromethyl)cyclohexane), the water protons did induce substantial exchange in such molecules. Therefore, deuteriation of anisole and benzotrifluoride in the presence of H_2O did not yield products with excess deuterium atoms but led to deuterium-deficient products (see Tables I and IV). When the deuteriation of $CF_3C_6H_5$ was conducted in D_2O (Table IV, experiments 4 and 6), compounds with more than six deuterium atoms could be identified. The water affected even the sterically hindered *tert*-butylbenzene, albeit only after very long reaction periods (see Figure 4).

The effect of the water on recovered starting material was much smaller, though not negligible (Table IV, experiment 1), and it did not lead to any detectable exchange in arenes with no α-hydrogen atoms. Owing to the existence of a deuterium isotope effect, the H–D exchange by H_2O proceeded faster and to a greater extent than by D_2O.

While the water proved to play an important role in the H–D exchange, it did not contribute to the hydrogenation processes. Blank experiments with toluene as substrate in which the H_2 or D_2 was omitted gave only *unchanged* starting material, even when the rhodium catalyst was pretreated for 30 min with 3 equiv of H_2 (or D_2) and an excess of D_2O.

The participation of water in H–D exchange processes resulted, of course, also in parallel exchange in the water itself. Thus, when naphthalene was deuteriated in tetrahydrofuran-d_8 according to method B (see the Experimental Section) in the presence of D_2O, a small broad water singlet at 4.024 ppm appeared immediately after initiation of the reduction. The signal gradually grew, sharpened, and shifted to 4.878 ppm, where the resonance peak of a reference solution of naphthalene, $RhCl_3{\cdot}3H_2O$, tetrahydrofuran-d_8, trioctylamine, and *H_2O* appeared.

Hydrogen–deuterium exchange was observed also during the rhodium-promoted deuteriation of cyclohexenes and cyclohexadienes. Saturated cyclohexanes, however were not affected even when added to reaction mixtures in which aromatics or olefins had been deuteriated. Deuteriation of cyclohexene in the presence of H_2O gave a mixture of cyclohexanes with d_0 to d_7. Typical 17-eV EI mass spectral data for full conversion of cyclohexene are as follows: m/z (relative intensity as defined in Table I) 84 (14), 85 (32.5), 86 (28), 87 (14), 88 (7), 89 (3), 90 (1), 91 (0.5). As the corresponding data for the same reaction in the presence of D_2O are m/z 84 (8), 85 (21), 86 (32), 87 (15), 88 (9), 89 (8), 90 (4.5), 91 (1.5), and 92 (1), it can be concluded that the water takes part in this H–D exchange to a much smaller extent than in that associated with arene hydrogenation. Partial deuteriations of cyclohexene revealed that in the recovered starting material hardly any H–D exchange took place (even after 50% conversion). In this context it should be recalled that the deuteriation of cyclohexene by Muetterties' cobalt catalyst gave $C_6H_6D_6$ (m/z 90) as the major product, and the recovered starting material was found to be deuterium free only at the early stages of the process.[16]

Both 1,3- and 1,4-cyclohexadiene reacted with D_2 in the presence of $RhCl_3$–Aliquat 336 and D_2O to give a mixture of cyclohexanes-d_0 to -d_{10}. The main product was $C_6H_8D_4$ (cf. ref 16). In addition to cyclohexanes, substantial quantities of deuterium-free benzene were formed as a result of both disproportionation (eq 2) and dehydrogenation (eq 3) of the dienes.

$$2C_6H_8 \rightarrow C_6H_6 + C_6H_{10} \qquad (2)$$

$$C_6H_8 \rightarrow C_6H_6 + H_2 \qquad (3)$$

The two processes that were not noticed in the cobalt-catalyzed hydrogenation of cyclohexadienes[16] were shown to take place at 30–70 °C in the presence of the ion pair $[(C_8H_{17})_3NCH_3]^+[RhCl_4]^-$ and also in the absence of H_2 or D_2. In these reactions, the ion pair proved to serve as the actual catalyst rather than as the catalyst precursor,[24] as it could be recovered unchanged and be recycled by the method described previously.[2,6] In any event, reaction 2 cannot be part of the catalytic cycle of arene hydrogenation.

Stereochemical Features. While η^3-$C_3H_5Co[P(OCH_3)_3]_3$ was reported to catalyze benzene deuteriation in a highly selective manner to give over 95% *all cis*-cyclohexane-d_6,[25] the H–D exchange associated with our rhodium-promoted catalysts did not permit isolation of just a single stereoisomer. In fact, it seems to us that even in the cobalt-catalyzed process the high stereoselectivity is restricted to extremely low conversion: Already at 5% conversion, substantial hydrogen scrambling was found to take place. Yet, in all rhodium-catalyzed reductions, cis-hydrogenated compounds proved to be either the major or the sole products. We already reported that *p*-xylene and tetralin yield at 40% conversion 72 and 91% of *cis*-1,4-dimethylcyclohexane and *cis*-decalin, respectively,[3] that ethyl 1-naphthoate gives a single *cis*-decalin derivative as the final product,[4] and that 2,3-dimethylnaphthalene forms *cis*-1,2,3,4-tetrahydro-2,3-dimethylnaphthalene free of any trans isomer.[4] Among the various substrates that were found to give practically a single stereoisomer upon deuteriation (in the presence of H_2O) were some methoxylated arenes. Veratrol was shown by virtue of the 50-MHz $^{13}C\{^1H\}$ NMR spectrum to form almost pure *cis*-1,2,3,4,5,6-hexadeuterio-1,2-dimethoxybenzene[26,27] [21.956 (t, J = 19 Hz, C4, C5), 26.657 (t, J = 19 Hz, C3, C6), 56.842 (s, OCH_3), 79.226 (t, J = 23 Hz, C1, C2) ppm] contaminated with just traces of a CH_2-containing compound showing singlets at 22.290 and 27.018 ppm. Likewise, 2-methoxynaphthalene was found to form highly isomerically pure 1,2,3,4-tetradeuterio-6-methoxynaphthalene [50-MHz $^{13}C\{^1H\}$ NMR ($CDCl_3$) 22.863 (t, J = 19 Hz, C6), 23.525 (t, J = 19 Hz, C7), 28.752 (t, J = 20 Hz, C5), 29.909 (t, J = 19 Hz, C8), 55.921 (s, OCH_3), 112.470 (s, C4), 114.419 (s, C3), 128.970 (s, C4a), 129.953 (s, Cl), 138.191 (s, C2), 138.832 (s, C8a) ppm] contaminated with very little CH_2-containing products that showed up at 29.127 (s) and 30.289 ppm (s). The deuterium-deficient compounds were identified also by the MS peaks of low intensities at m/z 164 and 165.

Possible Hydrogenation and H–D Exchange Mechanisms. The close similarity between the rhodium- and cobalt-catalyzed arene hydrogenation in respect to the intermediacy of cyclohexenes, the ring and side-chain H–D

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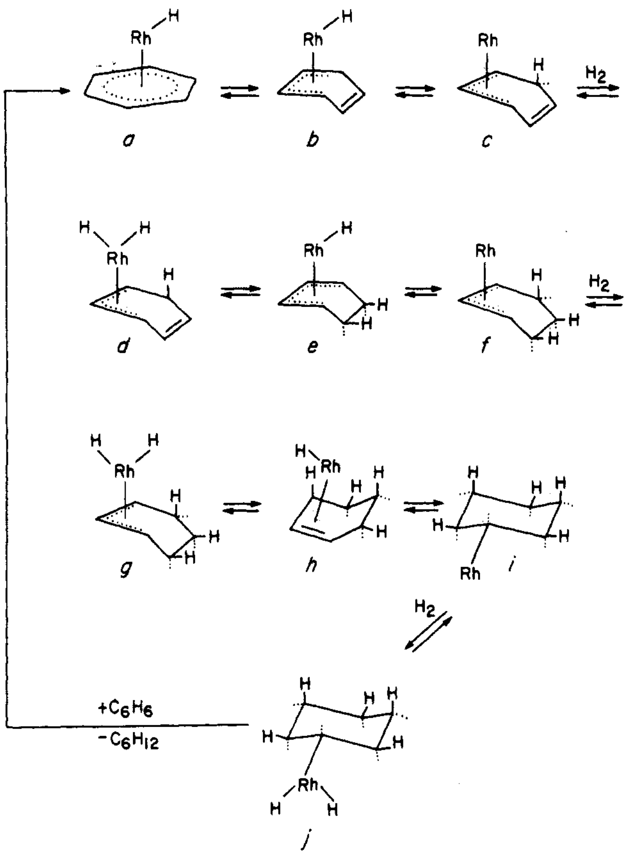
(24) Full details on the rhodium-catalyzed disproportionation and dehydrogenation of cyclohexadienes will be reported in a separate paper.

(25) Muetterties, E. L.; Rakowski, M. C.; Hirsekorn, F. J.; Larson, W. D.; Basus, V. J.; Anet, A. L. *J. Am. Chem. Soc.* **1975**, *97*, 1266.

(26) Winkler, J.; Grützmacher; H.-F. *Org. Mass Spectrom.* **1970**, *3*, 1139.

(27) Cf. the similar 50-MHz $^{13}C\{^1H\}$ NMR spectrum of unlabeled *cis*-1,2-dimethoxycyclohexane [($CDCl_3$) 21.801 (C4, C5), 26.568 (C3, C6), 56.190 (OCH_3), 78.641 (C1, C_2) ppm] and the different spectrum of the trans isomer reported by: Zefirov, N. S.; Somoshin, V. V.; Baranenkov, I. V.; Subbotin, O. A.; Sergeev, N. M. *Zh. Org. Khim.* **1977**, *13*, 2232.

Scheme I[a]



[a] Proposed mechanism for benzene hydrogenation by $RhCl_3$–Aliquat 336. The exact nature of the other ligands on the rhodium is unknown, and they have therefore been omitted.

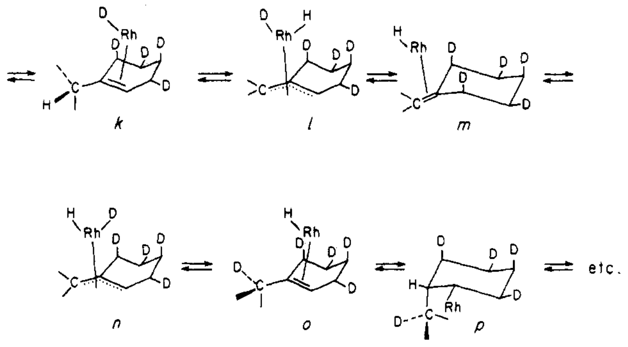
exchange, and the preferential formation of cis products led us to assume that both processes follow closely related pathways. The mechanism proposed by Muetterties and Bleeke[7,16] for benzene hydrogenation by their cobalt catalysts appears to be a reasonable candidate also for our system and is formulated as shown in Scheme I.[28]

The η^6-arene complex *a* (or an analogous dihydride) is assumed to be formed during the induction period, which was shown to vary in length in accord with the substrate employed. As this period could be shortened or eliminated completely by pretreatment with H_2 and an aromatic substance, but not with the arene alone, a "hydride route" is proposed for the generation of *a*. The formation of several metal hydride intermediates during the process has been proven by conducting the hydrogenation of naphthalene in a Wilmad's pressure valve NMR tube. The low-field 300-MHz FT NMR spectrum consisted of three triplets at −22.354 (J = 7.6 Hz), −23.122 (J = 9.1 Hz), and −24.289 (J = 7.6 Hz) ppm and of one unresolved mutliplet at 22.780 ppm.

The intermediacy of a π-allyl complex has already been shown to explain our observation that β-substituted naphthalenes give tetralins with unsubstituted saturated rings in higher selectivity than the α-substituted compounds.[4]

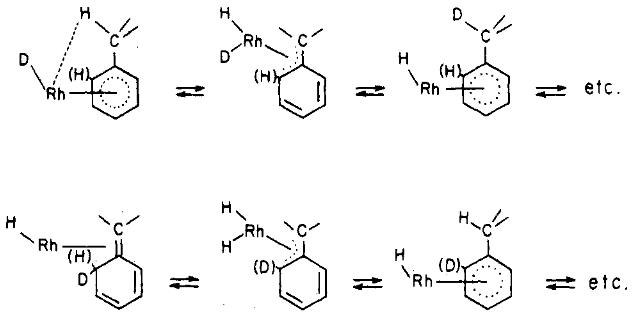
In no case did we isolate any cyclic dienes. We found, however, some indirect evidence for the intermediacy of complexes of type *e* in the hydrogenation and deuteriations of 1,3-cyclohexadiene. Experiments conducted at 20 °C yielded, after 50% conversion, 13% benzene, 10% cyclohexene, and 27% cyclohexane. Since reactions 2 and 3 proved not to take place at 20 °C, it may be assumed that the benzene results from the reverse process of arene hydrogenation, i.e., via steps *e* → *d* → *c* → *b* → *a*.

Scheme II[a]



[a] Part of a proposed mechanism for side-chain and ring H–D exchange in deuteration of alkylbenzenes with α-hydrogen protons. The unchanged ligands on the rhodium have been omitted.

Scheme III[a]



[a] Possible mechanism for H–D exchange in recovered starting material during deuteration of alkylarenes having α protons.

The isolation of cyclohexene derivatives during hydrogenation of durene and of some other overcrowded arenes suggests the intermediacy of η^2 complexes of type *h*. Such complexes with several alkyl groups are, however, expected to be unstable on both steric and electronic (electron-withdrawing substituents) grounds[16,29] and, therefore, tend to release the cycloalkene ligand.

The final stages in the catalytic cycle are proposed to have the features well-known for alkene hydrogenation and include hydride transfer ($\eta^2 \rightarrow \eta^1$ conversion) and reductive elimination of the product.

Muetterties and Bleeke[7,16] presented their mechanism (Scheme I, Co instead of Rh) as an appropriate explanation for the very high stereoselectivity and for their observation that H–D exchange is limited to alkylcyclohexanes with α protons. They proposed that the reaction proceeded through intermediates *a*–*g* (Co instead of Rh) without any exchange, in spite of the fact that stage *h* can undergo the transformations shown in Scheme II (Co instead of Rh).

As the combined mechanisms (Schemes I and II) involve both exocyclic and endocyclic $\eta^3 \rightleftharpoons \eta^2$ interconversions, this may provide, in our opinion, ring-proton exchange just as well as H–D exchange in the side chain (provided the addition of D_2 to intermediate *o* is not followed by the selective HD elimination shown in Figure 9 of ref 16, for which we have not found any evidence).

Although the mechanism is described as a series of reversible steps, the lack of H–D exchange in unreacted starting material from several reactions in which exchange

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(28) The evidence at hand is equally compatible with a mechanism in which the first intermediate is a rhodium *di*hydride followed by analogous steps to those shown in Scheme I.

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

in the products *did* take place indicates that under the conditions of the catalysis some reverse processes are in fact insignificant.

The differences between the exchange in recovered substrate with and without α protons imply that α protons already assist exchange in an early stage of the process. α-Proton abstraction in the η^6 complex *a* shown in Scheme III is a plausible mechanism.

It should be noted that exchange in the side chain is always more pronounced than that in the ring and is the first to take place. Therefore, the recovered starting material from hydrogenation of $CD_3C_6H_5$ (in the presence of H_2O) consisted of a mixture with ^1H NMR signals at 2.429 (s), 2.413 (t, J = 2.5 Hz), and 2.398 (quint, J = 2.2 Hz) ppm, corresponding to CH_3, CH_2D, and CHD_2 resonances, respectively. The pattern of the aromatic protons differed only slightly from those of the original toluene-d_3. Inspection of the $^{13}C\{^1H\}$ NMR spectrum of the recovered substrate led to the same conclusion. The corresponding signals for the CH_3, CH_2D, CHD_2, and CD_3 groups were centered at 21.364 (s), 21.087 (t, J = 19 Hz), 20.804 (quint, J = 19 Hz), and 21.000 (m) ppm, and the aromatic ^{13}C resonances showed up at 125.289, 128.200, and 129.014 ppm as in the original deuteriated toluene.

The water in our system was shown to play hardly any role in the hydrogenation process (no hydrogenation took place in the absence of H_2 or D_2) but to be associated with H–D exchange in the reaction products. This exchange differed from that induced by the reducing agents and varied widely in its effect, in accord with the nature of the substrates. Deuteriation of benzotrifluoride led to deuterium-deficient products when the reaction was conducted in the presence of H_2O, and deuterium-rich compounds were formed in D_2O, regardless of whether H_2 or D_2 had been used for the reduction (Table IV, experiments 4–6). Substrates with α protons also underwent some H–D exchange in recovered starting material (Table IV, experiment 1). On the other hand, the water had hardly any effect on some methoxy-substituted compounds, hence the high stereochemical purity of 1,2-dimethoxycyclohexane-d_6 observed in the deuteriation of veratrol in H_2O and of 1,2,3,4-tetradeuterio-6-methoxynaphthalene obtained by this method from nerolin. As hydrogen–deuterium exchange in the water itself was found (by NMR) to take place only when the rhodium ion pair was treated with both the arene and the reducing agent, we assume the effect of the water to be exerted at the final stages in the hydrogenation (e.g., with an intermediate of type *h*). Water had occasionally been reported to serve as a hydride source both via oxidative addition[30] and via nonoxidative addition mechanisms.[31] As the rhodium catalyst may act as a low-valent complex, it is likely to form a series of hydrido hdyroxy species[30] as shown in eq 4, where M represents the rhodium nucleus with unspecified ligands.

$$\begin{aligned}(H)M(C_6H_{10}) &\rightleftharpoons (H)M(C_6H_{10})(D_2O) \rightleftharpoons \\ (H)(D)M(OD)(C_6H_{10}) &\rightleftharpoons (D)M(C_6H_{10})(HDO) \rightleftharpoons \\ &D(M)(C_6H_{10}) \rightleftharpoons \text{etc.}\end{aligned} \qquad (4)$$

In conclusion, we assume that the hydrogenation and proton-exchange processes by the cobalt and rhodium catalysts proceed via similar mechanisms in which structural factors cause quantitative, rather than qualitative, differences. The H–D exchange is believed to take place at various stages of the hydrogenation processes and to be governed mainly by steric factors in the organometallic intermediates and, in the rhodium catalyses, also by the water. Under certain conditions that can be achieved more easily with the cobalt-catalyzed than with the rhodium-catalyzed reactions, the proton exchange is small in comparison with the hydrogenation processes, and consequently, very high stereoselectivities are observed.

Experimental Section

General Procedure for Hydrogenation. Method A. Two identical three-necked reaction flasks provided with identical magnetic bars were connected to each other with a tap and a separable sintered glass filter coated with a sheet of fluoropore paper (FHLP, 0.5-μm pore size). One of the flasks was charged under argon through a neoprene seal with a mixture of 10 mg (3.79 × 10^{-2} mmol) of $RhCl_3 \cdot 3H_2O$ in 1 mL of triply distilled water (or 99.95% D_2O), 22 mg (5.4 × 10^{-2} mmol) of Aliquat 336, 100 μL (0.23 mmol) of trioctylamine, and 1 mmol of freshly purified substrate in 0.5 mL of 1,2-dichloroethane. The flasks were connected to a standard apparatus for catalytic hydrogenation at atmospheric pressure. The reaction mixture was frozen, the inert gas removed and replaced by H_2 or D_2, and the pressure adjusted to 690 mm. The system was inserted into an oil bath thermostated at 30 ± 0.5 °C and stirred at constant rate of 400 rpm. Gas absorption was recorded, and samples were withdrawn periodically with the aid of an air-tight syringe for GC analysis. If some precipitate was formed, the reaction mixture was forced through the fluoropore filter into the second reaction flask (usually after 90 min), which was now connected through the tap to the gas buret. The reaction was continued in the second flask under the same conditions as before the filtration until the desired conversion was obtained. The organic layer was usually filtered through acidic alumina and analyzed or separated on one of the following GC columns: 15% OV 17, 10% Carbowax 20 M, or 7% stabilized DEGS on Chromosorb WAW 60/90 mesh.

When recycling of the catalyst was required, the reaction flask was connected directly to a vacuum line and the product and solvents were distilled off at 1 mm. The residue was flashed with argon, and a new reaction mixture was injected into the flask with an air-tight syringe.

Method B. A two-necked reaction flask was connected to a hydrogenation apparatus and charged under argon with a solution of 10 mg of $RhCl_3 \cdot 3H_2O$ in 1 mL of freshly purified THF, 100 μL of trioctylamine, and 50 μL of water.[32] The mixture was frozen, the argon replaced by H_2 or D_2, and the hydrogenation conducted at 30 ± 0.5 °C as in method A.

Competitive Hydrogenation of Two Different Arenes. The hydrogenation flask described in method A was charged with a mixture of 3.79 × 10^{-2} mmol of $RhCl_3 \cdot 3H_2O$, 1 mL of triply distilled water, 1 mL of 1,2-dichloroethane, 5.4 × 10^{-2} mmol of Aliquat 336, 100 μL of trioctylamine, 1 mmol of benzene, 1 mmol of a second arene, and 100 μL of a suitable internal standard (e.g., *n*-octane). The mixture was stirred at 30 ± 0.5 °C at a rate of 400 rpm. The reaction flask was connected to a hydrogen source (H_2 pressure adjusted to 690 mm). The progress of the hydrogenation was monitored both by recording the rate of the hydrogen absorption and by GC analysis of the substrates and products in 2-μL samples withdrawn from the reaction mixture every 5–15 min.

The experiment was then repeated twice: once using 2 mmol of benzene and once using 2 mmol of the second substrate alone.

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(30) See, e.g.: Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941.

(31) For use of water as a source of hydride via a nonoxidative addition process, see: James, R. B. In *Comprehensive Organometallic Chemistry, The Synthesis, Reactions, and Structures of Organometallic Compounds*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 302.

(32) The same results were also obtained with 10 μL of water, but under these conditions, the rhodium trichloride dissolved over a very long period.

Registry No. $\mathrm{RhCl_3}$, 10049-07-7; η^3-$\mathrm{C_3H_5Co[P(OCH_3)_3]_3}$, 42603-27-0; $\mathrm{C_6H_4}$, 71-43-2; $\mathrm{CH_3C_6H_5}$, 108-88-3; $\mathrm{CH_3CH_2C_6H_5}$, 100-41-4; $\mathrm{CH_3CH_2CH_2C_6H_5}$, 103-65-1; $\mathrm{(CH_3)_2CHC_6H_5}$, 98-82-8; $\mathrm{(CH_3)_3CC_6H_5}$, 98-06-6; $\mathrm{F_3CC_6H_5}$, 98-08-8; $\mathrm{CH_3OC_6H_5}$, 100-66-3; $\mathrm{H_2O}$, 7732-18-5; $\mathrm{H_2}$, 1333-74-0; Aliquat 336, 63393-96-4; naphthalene, 91-20-3; methylcyclohexane, 108-87-2; ethylcyclohexane, 1678-91-7; *tert*-butylcyclohexane, 3178-22-1; benzene-d_6, 1076-43-3; toluene-d_6, 1076-43-3; ethylbenzene-d_{10}, 25837-05-2.

The Reactions of 1-Adamantyl Radicals with Acetonitrile and Their Bearing on the Oxidative Decomposition of 1,1′-Azoadamantane

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1-Adamantyl radicals (Ad$^\bullet$) have been generated photochemically from azo-1,1′-adamantane (AA) in acetonitrile (MeCN). Product analysis by GC accounted for 98% of the Ad groups as a mixture of adamantane (AdH), 1,1′-biadamantane (AdAd), and the coupling product (**5**) of Ad(Me)C=N$^\bullet$ with solvent-derived $^\bullet$CH$_2$CN. The remaining 57% of the $^\bullet$CH$_2$CN groups that could be found appeared as succinonitrile. Kinetic modeling of the product distribution shows that Ad$^\bullet$ abstracts hydrogen from MeCN roughly four times as fast as it adds to the nitrile carbon. In our previous work[7] on the oxidative decomposition of AA in MeCN, induced by the thianthrene cation radical (Th$^{\bullet+}$), very little AdH but significantly larger amounts of AdAd and AdCOMe were obtained. We propose, therefore, that virtually no free Ad$^\bullet$ is formed or survives oxidation in the oxidative decomposition of AA. Further, the AdAd found in the oxidative reaction cannot have come from the dimerization of free Ad$^\bullet$ but may have arisen, instead, from the biadamantane cation radical (AdAd$^{\bullet+}$), formed within a solvent cage.

Introduction

Acetonitrile (MeCN) is a solvent frequently used in electrochemistry[1] and in cation radical reactions.[2-5] While its reactions with carbocations are well documented,[6,7] many free-radical reactions have been carried out in MeCN solution without clear evidence of solvent participation. For example, in some now classical studies of the decomposition of di-*tert*-butyl peroxide[8] and of hydrogen atom abstraction by *tert*-butoxy radical,[9] MeCN functioned as one of a number of inert solvents. Again, in the superoxide-induced decomposition of *tert*-butyl hydroperoxide in MeCN, in which *t*-BuOO$^-$, *t*-BuOO$^\bullet$, and *t*-BuO$^\bullet$ all participate, *t*-BuOO$^-$ added to MeCN, but apparently, reactions of the radicals with the solvent did not occur.[10] Hydroxyl radical abstracted hydrogen atom from MeCN in aqueous solution, leading to an 18% yield of succinonitrile.[11] It is surprising that so little is known about the reaction of radicals with liquid MeCN, especially in view of the substantial radical-stabilizing ability of the cyano group.[12-17]

The present investigation arose from questions about radical reactions with MeCN that remained unanswered in the oxidative decomposition of azo-1,1′-adamantane (AA) by the thianthrene cation radical (Th$^{\bullet+}$) in MeCN.[7] Whereas 91% of the adamantyl (Ad) groups from AA appeared in cation-derived products, adamantane (AdH) and 1,1′-biadamantane (AdAd) were obtained only in 0.2% and 2.5% yield, respectively. Also, the Ad group was found in an unexpected product, adamantyl methyl ketone (AdCOMe, **1**), formed in 5.5% yield. We were puzzled as to why so little AdH but much more AdCOMe and AdAd were obtained. It seemed to us that if free Ad$^\bullet$ radicals were generated singly, for example, by single-electron transfer (SET) from AA to Th$^{\bullet+}$, and escaped oxidation to Ad$^+$, they should react preferentially with the solvent, so the yield of AdAd should be insignificant. Any AdAd observed, in that case, would suggest its formation in some sort of a cage reaction. Furthermore, we attributed the formation of AdCOMe to addition of Ad$^\bullet$ to the cyano group of MeCN and the subsequent hydrolysis by water adventitiously in the solvent or added during workup, of Ad(Me)C=NH (**2**) or Ad(Me)C=NH$_2^+$. If this hypothesis were correct, the ratio of addition of Ad$^\bullet$ at cyano group carbon to abstraction of a hydrogen atom from the methyl group of MeCN would be 5.5/0.2, that is, 27.5. These surprising results led us to investigate the reactions of Ad$^\bullet$, generated in a more conventional way, with MeCN. Ad$^\bullet$ is conveniently produced by irradiation of *trans*-AA.[18] The cis isomer, formed initially, undergoes thermolysis

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