is approaching a maximum.

In the final case we examined, the saturated 2-norbornyl tosylate 4, it appears that $\sigma$ participation by the 6,1 bond falls well below the threshold above which participation can be enhanced. Consequently, this procedure is limited to those cases in which participation is at or above the borderline for observability. Whereas we could bring out previously unobserved participation by *p*-chlorophenyl, we could not elicit any response from the $\sigma$ bond. The procedure is further limited in each case (1) by the choice of models for the absence of participation and (2) by the choice of models for unenhanced participation, e.g., (1) **20** or **21** and (2) **3** for double bond participation in **19**. The method is also limited by the assumption that the introduction of the electron-withdrawing group X brings only an inductive effect. The problem of a possible steric effect in the $\sigma$ bond series (**20, 23, 29, 30**) had to be examined carefully.

With these limitations, the method of inductive enhancement of solvolytic participation should be applicable to a host of further modes of participation. There are a number of different cases involving participation by lone pairs, such as halogens, ethers, thioethers, amines, etc. Triple bond and cyclopropane participation could be examined as further representations of the $\pi$ bond class. Whereas we have used only tosyloxy and acetoxy groups as the electron-withdrawing substituent, investigations could also include other functionalities such as cyano or trifluoromethyl.

Finally, it might be worthwhile to examine the effect of placement of the electron-withdrawing group X directly at the reactive site. The molecules of Gassman and of Brown (**11–17**) essentially served this purpose, but the electron demand achieved by the most electron-withdrawing aryl group at the $\alpha$ position was still less than that of tosyloxy or acetoxy at the $\beta$ position in our systems. It would be worthwhile to examine the placement of much more strongly electron-withdrawing groups, such as trifluoromethyl, directly at the reactive site. These experiments are among the future directions studies might take in the general field of inductive enhancement of neighboring group participation.

# Catalytic Hydrogenation of Aromatic Hydrocarbons

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The art and science of metal and metal oxide catalyzed arene hydrogenations have been significantly advanced since Sabatier's original findings.[1] These catalytic hydrogenations are utilized in present-day technology,[2] but substantive issues and challenges remain. Mechanistically, the reactions are not fully defined.[3-5] In addition, none of these solid-state catalysts exhibits chemoselectivity or stereoselectivity features that could be of more general synthetic utility to the organic synthetic chemist. Chemoselectivity here refers to the rate of arene ring hydrogenation relative to other functional group hydrogenation rates. Stereoselectivity refers to the degree to which all six hydrogen atoms added to benzene or a benzene derivative in a hydrogenation appear on the same side of the resultant cyclohexane ring.

In 1973, we[6] accidentally discovered that a simple organocobalt molecule, $\eta^3$-$C_3H_5Co[P(OCH_3)_3]_3$,[7,8] was a solution-state catalyst for the hydrogenation of aromatic hydrocarbons. Reaction conditions were quite temperate—1 atm of hydrogen and room temperature. Most significantly, this catalyst was stereoselective[9-11] and, to a degree, chemoselective.[9-11] These findings

(1) Phenol and aniline were the first aromatic systems to be catalytically hydrogenated. These reactions were carried out in 1904 by Sabatier and Senderens, using nickel metal as catalyst. Cf. Sabatier, P.; Senderens, J. B. *Soc. Chim. Fr., Bull.* 1904, [3] *31*, 101. The hydrogenation of benzene with a nickel catalyst was reported by Sabatier and Espil in 1914: Sabatier, P.; Espil, L. *Ibid.* 1914, [4], *15*, 228.

(2) Rylander, P. N. "Catalytic Hydrogenation over Platinum Metals"; Academic Press: New York and London, 1967; Chapter 18. Weissermel, K.; Arpe, H-J. "Industrial Organic Chemistry"; Verlag Chemie: New York, 1978; p 301.

(3) Early mechanistic proposals were made by Horiuti and Polanyi and by Farkas and Farkas: Horiuti, I.; Polanyi, M. *Trans. Faraday Soc.* 1934, *30*, 1164. Horiuti, I.; Ogden, G.; Polanyi, M. *Ibid.* 1934, *30*, 663. Farkas, A.; Farkas, L. *Ibid.* 1937, *33*, 678, 827.

(4) Crawford, E.; Kemball, C. *Trans. Faraday Soc.* 1962, *58*, 2452; Harper, R. J.; Kemball, C. *Proc. Int. Congr. Catal., 3rd*, 1964, *2*, 1145. Garnett, J. L.; Sollich, W. A. *J. Catal.* 1963, *2*, 350.

(5) For a review of proposed mechanisms of heterogeneous hydrogenation see: Siegel, S. *Adv. Catal.* 1966, *16*, 123.

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

(7) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* 1973, *95*, 5419; 1974, *96*, 7920.

(8) Muetterties, E. L.; Hirsekorn, F. J. *J. Chem. Soc., Chem. Commun.* 1973, 683.

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

(10) (a) Stuhl, L. S.; DuBois, M. Rakowski; Hirsekorn, F. J.; Bleeke, J. R.; Stevens, A. E.; Muetterties, E. L. *J. Am. Chem. Soc.* 1978, *100*, 2405. (b) Small amounts of other species were detected, but these were derived, in the experimental workup, from the decomposition of catalyst intermediates in which hydrogenation was incomplete. See discussion in ref 10a.

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

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presented the possibility of establishing mechanistic details for the catalytic reaction and also the possibility of logically designing a practical catalyst with chemoselectivity and stereoselectivity characteristics. We describe here our progress in unraveling mechanistic details and in developing a catalyst useful to the organic synthesis chemist. Recent preliminary studies by others of alternative coordination catalysts for arene hydrogenation are not discussed here because detailed information is not available for the stereo- and chemoselectivity and the mechanistic features of the catalytic systems.

## The Allylcobalt Catalyst

The organometallic complex, $\eta^3$-$C_3H_5Co[P(OCH_3)_3]_3$, catalyzed the hydrogenation of aromatic hydrocarbons at 20 °C.[6,9-12] This hydrogenation was complete, and no cyclohexene products were detected. Hydrogenation rates were low, about 1 turnover per hour for benzene, but substitution[9,10] of the trimethyl phosphite ligands by bulkier phosphites or phosphines raised the catalytic rates up to nearly a turnover per minute at 20 °C. There is a relatively broad scope[9,10] to the catalytic reaction. Arene-substituent limiting factors were steric, electronic, and protonic in character: four or more methyl groups in sequence lowered the rate to zero, strongly electron-withdrawing groups like F and $NO_2$ also deactivated the arene to this reaction, and protonic substituents like OH or COOH led to protonation at the cobalt centers and then destruction of the critical allyl functionality on the cobalt catalyst.[10]

Stereoselectivity was the distinguishing feature of this cobalt-catalyzed hydrogenation.[6,10-12] *cis*-Dimethylcyclohexanes were the only products from xylene hydrogenations.[6,10] *cis*-Decalin and *cis-syn-cis*-perhydroanthracene were the only detectable products from the parent condensed aromatic hydrocarbons.[10a,b] Most dramatically, the all-cis $C_6H_6D_6$ isomer was at least 95% of the product from the $D_2 + C_6H_6$ catalytic reaction.[11] This unique stereoselectivity in the cobalt-catalyzed reaction unequivocally defines the stereochemical character of the hydrogen addition steps—all hydrogen atoms are added to the same side (face) of the arene ring—and shows that free cyclohexenes are not free intermediates.

One of the most remarkable features of the unique allylcobalt catalysts is their ability to complex and hydrogenate arenes at about the same rate as olefins for olefin–benzene mixtures.[10,12] In direct competitive reactions, 1-hexene was hydrogenated slightly more rapidly than benzene while cyclohexene was hydrogenated more slowly than benzene (rates based on product formation, not on hydrogen consumption). No other coordination catalyst and no solid-state catalyst have shown this property—with metals we find that olefins are selectively hydrogenated in olefin–arene mixtures.[13] Although no cyclohexenes are produced in arene hydrogenations with the cobalt catalyst, cyclohexenes and cyclohexanes are produced in hydrogenations where olefins are present. Thus, an olefin but not an arene can displace the complexed cyclohexene intermediate from the cobalt center.[14]

Dienes completely blocked the cobalt-catalyzed arene hydrogenation reaction. For example, benzene in a benzene–norbornadiene mixture was not hydrogenated. Benzene hydrogenation was also blocked by allylbenzene; only hydrogenation of the allyl group of the allylbenzene was initially observed.[10] However, the presence of *cis*- or *trans*-propenylbenzene did not substantially affect the benzene hydrogenation rate. In fact, the major products from the hydrogenation of a benzene–propenylbenzene mixture were cyclohexane, propenylcyclohexane, propylcyclohexane, and propylbenzene.[10] For interaction with a metal center, both propenylbenzene and allylbenzene are potential pseudodienes, 1 and 2, respectively, by utilizing the



1        2
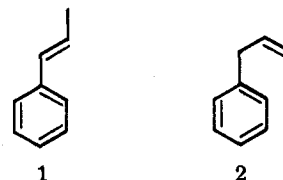
olefin and an arene C–C bond; the only difference is that allylbenzene is a nonconjugated diene and propenylbenzene a conjugated diene. (Any arene is a potential conjugated diene ligand.)

There is hydrogen atom transfer from the cobalt catalyst center not only to the arene molecules but also to the allyl ligand. Through the latter transfer, a destruction of the catalyst occurs with the elimination of propylene and the formation of a hydride complex that is inactive as an arene hydrogenation catalyst.[9] Thus the lifetimes of the allylcobalt catalysts are limited; effectively the average total turnovers are about 20–40. This deleterious side reaction is irreversible. Attempts to find other allylmetal complexes more resistant to this reductive cleavage have been unsuccessful. Although the allyl group is a necessary functionality in our cobalt complexes' activity in arene hydrogenation, it is a flawed ligand for this chemistry simply because of the ease, albeit variable in character from one complex to the next, with which hydrogen transfer to the allyl ligand occurs.

## Reaction Mechanism

Structural features of the allylcobalt complex are shown in Figure 1.[15] These coordinately saturated allylcobalt phosphite complexes do not *detectably* undergo phosphite ligand dissociation in solution at concentrations as low as $10^{-6}$ M (UV and NMR studies).[16a] Similarly, there was no evidence of interaction between these complexes and arenes.[6,12] A common dynamic process in allylmetal complexes is a facile $\eta^3 \rightleftharpoons \eta^1$ ($\pi \rightleftharpoons \sigma$) rearrangement. We postulated this re-

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

(13) These include ruthenium, rhodium, Raney cobalt, and platinum. Bleeke, J. R.; Muetterties, E. L., to be published.

(14) In the cobalt system, a cyclohexene intermediate, $C_3H_5Co$-$P(OR)_3$-$\eta^2$-$C_6H_{10}$, may react with hydrogen to yield the product cyclohexane (see Figure 2). Olefins but not arenes compete with this hydrogen addition step and ultimately cyclohexene dissociates from the complex.

(15) Tau, K. D.; Muetterties, E. L.; Fredrich, M. F.; Day, V. W. To be published.

(16) (a) L. S. Stuhl, Cornell University, Thesis, 1978, presents the details of the UV studies. (b) The formation constants for olefin–metal complexes are orders of magnitude greater than for $\eta^2$-arene–metal complexes. For example, in the most thoroughly studied $Ag^+$ system, the formation constant for $AgL^+$ (25 °C, $\mu$ = 1.0) in aqueous solution is 85.3 for L = $C_2H_4$[16d] and 2.41 for L = $C_6H_6$.[16e] Note also the lability of the $d^{10}$ Ni–$\eta^2$-arene complexes.[16f] (c) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (d) Trueblood, K. N.; Lucas, H. J. *J. Am. Chem. Soc.* **1952**, *74*, 1338. (e) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1949**, *71*, 3644. (f) Jonas, K. *J. Organomet. Chem.* **1974**, *78*, 273.
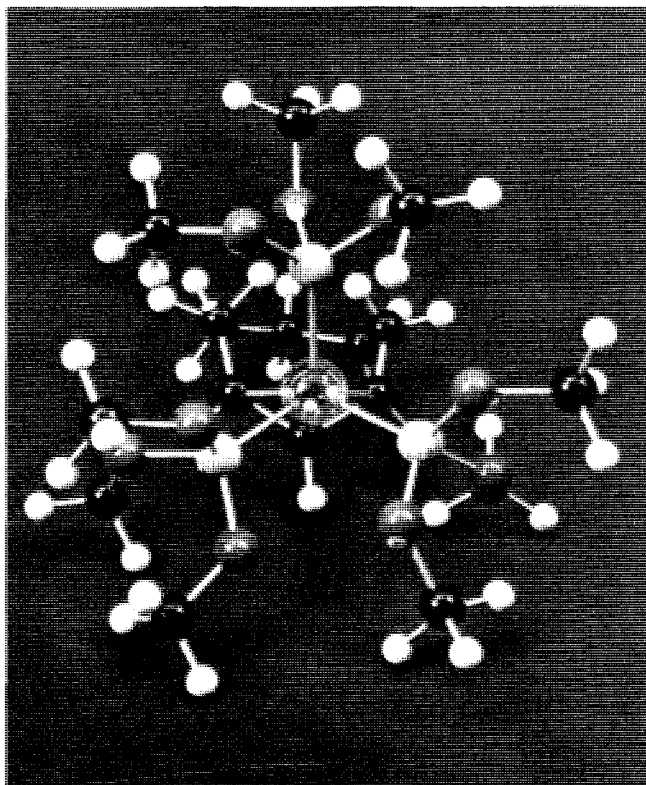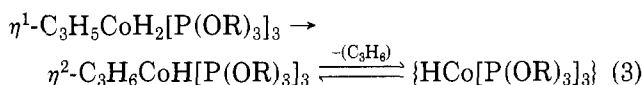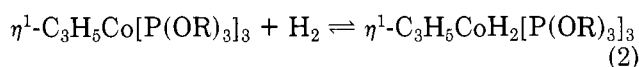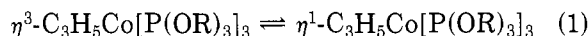
**Figure 1.** A ball and stick model of $\eta^3$-cyclooctenylcobalt tris(trimethyl phosphite) looking down a near-threefold axis of the molecule. The clear large sphere represents the cobalt atom.[15] To the left, to the right, and just below (and all to the back of) the cobalt sphere are the three allylic carbon atoms. This particular view of the molecule emphasizes the similarity of the molecular geometry to an idealized structure involving a basically tetrahedral array of the three phosphorus atoms and the $C_3$ centroid of the allylic ligand. In fact, the molecular geometry is closer to another idealized representation in which there is a pseudo-5-coordinate coordination sphere of square-pyramidal form with the allylic ligand, considered as a pseudobidentate ligand, residing at two adjacent basal sites in the square pyramid.

arrangement as the first step in the catalytic cycle for the cobalt complexes, although the presumed rearrangement is not sufficiently rapid to be detected by proton NMR studies up to 100 °C.[6,12]

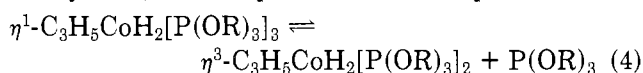Hydrogen reacts with $\eta^3$-C$_3$H$_5$Co[P(OCH$_3$)$_3$]$_3$ at 20 °C to form propylene at a higher rate than if an arene is present. Low-temperature phosphite studies of the H$_2$-cobalt system showed the presence of a hydride. This hydride resonance, a quartet due to H-P spin–spin coupling, is consistent with the fluxional complex, $\eta^1$-C$_3$H$_5$CoH$_2$[P(OCH$_3$)$_3$]$_3$.[10] On these grounds, we write the first two steps in the catalyst cycle and the key catalyst destruction sequence as (1)–(3). Attempts to

$$\eta^3\text{-C}_3\text{H}_5\text{Co[P(OR)}_3]_3 \rightleftharpoons \eta^1\text{-C}_3\text{H}_5\text{Co[P(OR)}_3]_3 \quad (1)$$

$$\eta^1\text{-C}_3\text{H}_5\text{Co[P(OR)}_3]_3 + \text{H}_2 \rightleftharpoons \eta^1\text{-C}_3\text{H}_5\text{CoH}_2\text{[P(OR)}_3]_3 \quad (2)$$

$$\eta^1\text{-C}_3\text{H}_5\text{CoH}_2\text{[P(OR)}_3]_3 \rightarrow$$

$$\eta^2\text{-C}_3\text{H}_6\text{CoH[P(OR)}_3]_3 \xrightarrow{-(\text{C}_3\text{H}_6)} \{\text{HCo[P(OR)}_3]_3\} \quad (3)$$
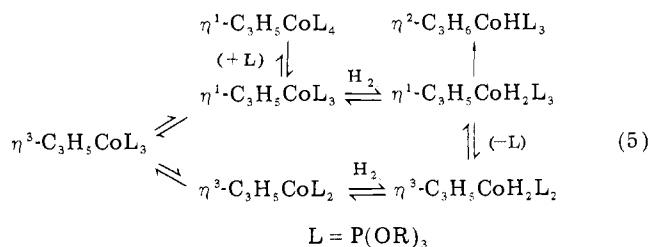
spectroscopically detect later catalytic intermediates have failed. The first step of reaction 3 is irreversible because there was no deuterium incorporation in the allyl group of the recovered catalyst after an extended D$_2$-C$_6$H$_6$ reaction.

The allylcobalt hydride intermediate is coordinately saturated, and phosphite ligand dissociation is a requisite process if any unsaturated molecule is to be
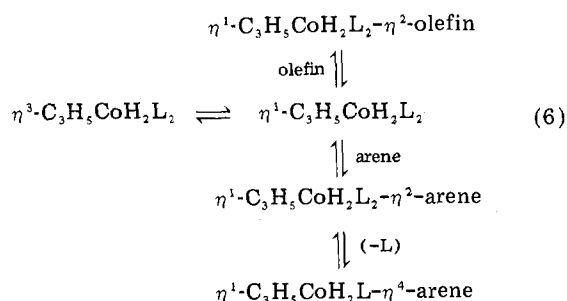
complexed and then hydrogenated. This phosphite loss may be enhanced through a $\sigma \rightleftharpoons \pi$ allyl conversion in the hydride, (4). All potential initial steps are outlined

$$\eta^1\text{-C}_3\text{H}_5\text{CoH}_2\text{[P(OR)}_3]_3 \rightleftharpoons \\ \eta^3\text{-C}_3\text{H}_5\text{CoH}_2\text{[P(OR)}_3]_2 + \text{P(OR)}_3 \quad (4)$$

in (5); phosphite ligand exchange steps are included

$$\begin{array}{ccc}
\eta^1\text{-C}_3\text{H}_5\text{CoL}_4 & & \eta^2\text{-C}_3\text{H}_6\text{CoHL}_3 \\
(+\text{L}) \updownarrow & & \uparrow \\
\eta^1\text{-C}_3\text{H}_5\text{CoL}_3 & \xrightarrow{\text{H}_2} & \eta^1\text{-C}_3\text{H}_5\text{CoH}_2\text{L}_3 \\
\eta^3\text{-C}_3\text{H}_5\text{CoL}_3 \nearrow & & \updownarrow (-\text{L}) \quad (5) \\
\searrow \eta^3\text{-C}_3\text{H}_5\text{CoL}_2 & \xrightarrow{\text{H}_2} & \eta^3\text{-C}_3\text{H}_5\text{CoH}_2\text{L}_2
\end{array}$$
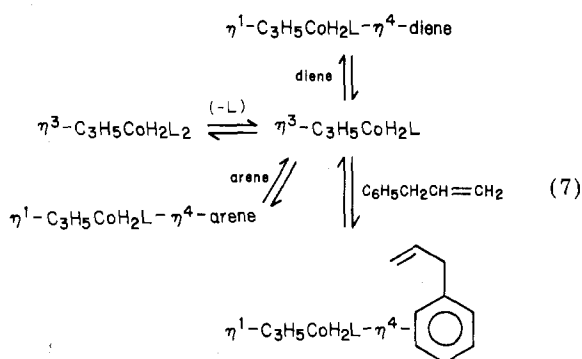
$$\text{L} = \text{P(OR)}_3$$

because phosphite ligand exchange does occur slowly in $\eta^3$-C$_3$H$_5$Co[P(OCH$_3$)$_3$]$_3$.[9] Further reaction of the bisphosphite complex, produced in (4), with either an olefin or an arene complex could follow the sequences outlined in eq 6. Sequences presented in (6) are plausible, although competition for the bis(phosphite) complex of an arene subsequently bound as an $\eta^2$ ligand with an olefin should not be significant[16b]—yet olefins and arenes are, in fact, hydrogenated at roughly the same rate. If equilibrium between $\eta^3$-C$_3$H$_5$CoH$_2$L$_2$ and the $\eta^2$-olefin complex and the $\eta^4$-arene complex were rapidly established, then perhaps a more or less even competition is plausible. However, we now have evi-

$$\eta^1\text{-}C_3H_5CoH_2L_2\text{-}\eta^2\text{-olefin}$$

$$\text{olefin} \updownarrow$$

$$\eta^3\text{-}C_3H_5CoH_2L_2 \;\rightleftharpoons\; \eta^1\text{-}C_3H_5CoH_2L_2 \qquad (6)$$

$$\updownarrow \text{arene}$$

$$\eta^1\text{-}C_3H_5CoH_2L_2\text{-}\eta^2\text{-arene}$$

$$\updownarrow \;(-L)$$

$$\eta^1\text{-}C_3H_5CoH_2L\text{-}\eta^4\text{-arene}$$

dence from H–D exchange reactions that an olefin is predominantly hydrogenated by an allylcobalt intermediate that is not the same as the intermediate operative in arene hydrogenation. Accordingly, sequence 6 appears to be applicable only to olefins.

Since a separate pathway is required for arene complexation, we propose the plausible sequence 7

$$\eta^1\text{-}C_3H_5CoH_2L\text{-}\eta^4\text{-diene}$$

$$\text{diene} \updownarrow$$

$$\eta^3\text{-}C_3H_5CoH_2L_2 \;\overset{(-L)}{\rightleftharpoons}\; \eta^3\text{-}C_3H_5CoH_2L$$

$$\text{arene} \nparallel \quad \updownarrow C_6H_5CH_2CH=CH_2 \qquad (7)$$

$$\eta^1\text{-}C_3H_5CoH_2L\text{-}\eta^4\text{-arene}$$

$$\eta^1\text{-}C_3H_5CoH_2L\text{-}\eta^4\text{-}\langle\text{(allyl)}\rangle$$

wherein $\eta^3\text{-}C_3H_5CoH_2L_2$ loses a phosphite ligand to generate $C_3H_5CoH_2L$ which has the capability of reacting with dienes and arenes (as pseudodienes). Since the cobalt(III) hydride intermediate, $C_3H_5CoH_2L$, has a $d^6$ configuration, complexation of nonconjugated dienes should be favored over conjugated dienes.[16c] This electronic facet would explain the preferential binding of allylbenzene as a nonconjugated pseudodiene, structure 3, which would lead to hydrogenation



**3**  **4**  **5**
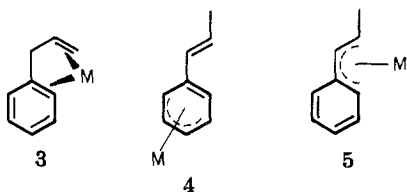
of the olefinic function and not the ring. In contrast, propenylbenzene can only bind as a conjugated pseudodiene in either of two forms, 4 and 5, which would then lead to either olefinic bond hydrogenation or to ring hydrogenation. Benzene, which can bind only as a conjugated pseudodiene, would compete effectively for coordination sites with propenylbenzene but not allylbenzene.

Potential intermediates in the hydrogen-transfer sequence have been described earlier[12,14] (Figure 2). The $\eta^4$-arene intermediate postulated in (6) and (7) has a well-established precedent, $\eta^6\text{-}C_6(CH_3)_6Ru\text{-}\eta^4\text{-}C_6\text{-}(CH_3)_6$, which is itself a catalyst for arene hydrogenation (vide infra). We call special attention to the intermediate labeled F in Figure 2. This intermediate is coordinately unsaturated and is shown in this figure to add molecular hydrogen. Other potential two-electron donors could compete for intermediate F. An olefin
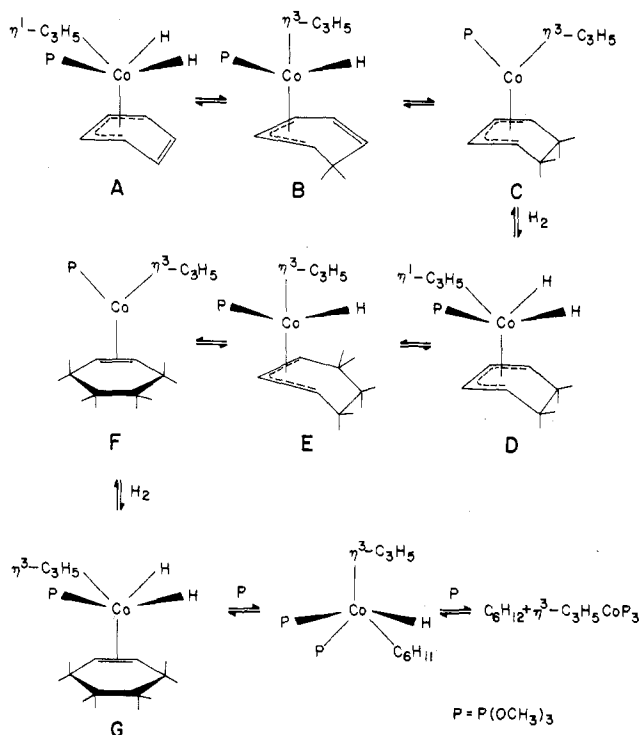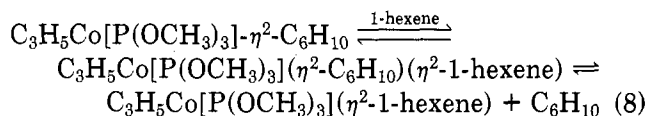


**Figure 2.** A proposed reaction sequence for the hydrogen transfer from cobalt to the complexed arene ligand as first reported by Hirsekorn, Rakowski, and Muetterties.[12] In this proposed sequence, hydrogen transfer from cobalt to the $C_3H_5$ ligand is not shown. Were this to occur, an allylic cobalt complex, e.g., cyclohexenyl or cyclohexadienyl, would be formed and would function as a catalyst in the reaction system. (The cleavage rates of substituted-allyl–cobalt complexes are, however, substantially higher than for the $C_3H_5$ ligand itself.) Note that intermediate F is coordinately unsaturated and may react with hydrogen as depicted in the subsequent reactions or may react with an olefin as discussed in the text (see reaction 8) and that the overall reaction cycle depicted above could achieve a stereoselective hydrogenation of an arene.

fulfills this specification, and we have observed experimentally that hydrogenation of arenes by the cobalt catalyst in the presence of olefins leads to cyclohexene formation. Explicitly, this competition reaction is shown in (8).

$$C_3H_5Co[P(OCH_3)_3]\text{-}\eta^2\text{-}C_6H_{10} \overset{1\text{-hexene}}{\rightleftharpoons}$$

$$C_3H_5Co[P(OCH_3)_3](\eta^2\text{-}C_6H_{10})(\eta^2\text{-}1\text{-hexene}) \rightleftharpoons$$

$$C_3H_5Co[P(OCH_3)_3](\eta^2\text{-}1\text{-hexene}) + C_6H_{10} \qquad (8)$$

No hydrogen–deuterium exchange occurred between aromatic C–H and $D_2$ in the cobalt-catalyzed $D_2$ addition to either benzene or naphthalene; recovered unreacted arene contained essentially no deuterium, and products were $C_6H_6D_6$ and $C_{10}H_8D_{10}$, respectively. However, methyl-substituted benzenes showed a distinctly different behavior. Deuterium incorporation in the *methyl* groups of the resultant methylcyclohexanes was extensive.[10] The hydrogenation product of toluene was not solely $C_7H_8D_6$ but included $C_7H_7D_7$, $C_7H_6D_8$, and $C_7H_5D_9$, and an analogous distribution, $d_6$–$d_{12}$, was found in the *p*-xylene hydrogenation product. Recovered arenes contained no deuterium.[17] The

(17) This observation and the pervasive cis stereoselectivity of the cobalt catalyst support the thesis that once the hydrogenation of the arene begins there is no dissociation of the hydrocarbon from the cobalt center until cyclohexane is eliminated from the complex.

mechanism of this hydrogen–deuterium exchange in the arene methyl groups is experimentally undefined but is believed to involve an initial, intramolecular $\alpha$-C–H oxidative addition of a methyl-substituted arene ligand to give a benzylcobalt hydride. In the ethyl- and *n*-propylbenzene reactions with $D_2$, there was deuterium incorporation at all carbon positions of the side chain of the alkylcyclohexane products but none in the *tert*-butylbenzene reaction. Exchange phenomena appear to be common in coordination catalysis of arene hydrogenation.[18]

## What Features Are Critical for Coordination Catalysis of Arene Hydrogenation?

In the allylcobalt catalyst precursor, the most distinctive features are (a) the allyl ligand which through facile $\eta^3 \rightleftharpoons \eta^1$ transformations may generate empty coordination sites and (b) ready accessibility of a $d^6$-cobalt(III) state through hydrogen oxidative addition. In addition, there is a *postulated* catalytic intermediate, an allylcobalt(III) dihydride, with an $\eta^4$-arene ligand—a presumed more readily reduced (hydrogenated) type of arene ligand than an $\eta^2$- or $\eta^6$-arene ligand. Which, if any, of these features are necessary for catalytic activity in a coordination complex in arene hydrogenation? Some, particularly condition b and the $d^6$–$d^8$ couple, may be necessary only to chemoselectivity and stereoselectivity since *there is no basis to presume that only one reaction mechanism will prevail for coordination catalysis of arene hydrogenation.*
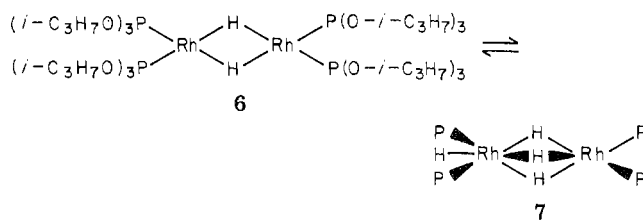
Without equivocation, we can note that an allyl ligand is neither a necessary nor sufficient coordination condition. Many allylmetal complexes, including the analogous allylrhodium phosphite complexes, have been examined, and none to date has been found to be a catalyst.[19-22] Even allylmetal complexes with arene ($\eta^6$) ligands, e.g., $[\eta^3\text{-}C_3H_5Mo(\eta^6\text{-}C_6H_5CH_3)Cl]_2$ and $\eta^3$-$C_3H_5Ru(\eta^6\text{-}C_6H_6)Cl$, were inactive—allyl cleavage was the only detectable reaction at higher temperatures with the hydrogen molecule.[21] Furthermore, a number of complexes that contain no allyl ligand have been shown to be catalysts.[23] An accessible metal$^{n+}$ $\rightleftharpoons$ metal$^{n+1\,or\,2}$ + 1 or 2 e$^-$ couple is an obvious requirement in the catalyst precursor for the $H_2$ reaction. Most of the active complexes we have discovered are or appear to be based on metal$^{n+}$ $\rightleftharpoons$ metal$^{n+2}$ + 2 e$^-$ couples and specifically on the $d^8$ $\rightleftharpoons$ $d^6$ couple.[24]

A most intriguing issue is the necessary character of the arene bonding in the catalytic intermediate. Is it possible for hydrogen to be added directly (through the

agency of the metal atom) to an $\eta^6$-arene ligand or to an $\eta^2$-arene ligand? An $\eta^4$-arene ligand requires a noncoplanar $C_6$ skeleton, and such a highly perturbed aromatic system may be more susceptible to hydrogenation than an $\eta^6$- or $\eta^2$-arene ligand—but is this a necessary condition?

## A Rhodium Catalyst, $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$

Allylrhodium phosphite analogues of the cobalt catalyst are too short-lived in the presence of hydrogen to effect significant arene hydrogenation.[19,27] However, the hydrogen cleavage product of one of the analogues, $\eta^3$-$C_3H_5Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$, is an arene hydrogenation catalyst. This cleavage product is a hydride-bridged rhodium dimer, 6, which reacts reversibly with hy-



drogen to form a tetrahydride dimer whose NMR spectra are fully consistent with the triply hydride bridged dimer structure 7.[27] The tetrahydride, 7, reacts instantaneously with olefins to give alkanes and is thus an extraordinarily active catalyst for the hydrogenation of olefins. In addition, 7 is the catalyst *precursor* for the arene hydrogenation reaction.

Benzene and alkylbenzene hydrogenations are catalyzed by 7 at 20 °C and 1 atm at rates that decrease with the degree of methyl substitution—in full analogy to the allylcobalt system. The rhodium catalyst is, however, not stereoselective; substantial amounts of *trans*-dimethylcyclohexanes were formed in xylene hydrogenations—as high as 30% in the case of *p*-xylene. The catalyst is fully chemoselective, but to olefins, simply because 7 catalyzes hydrogenation of olefins at rates that are $\sim 10^5$ greater than for hydrogenation of arenes. Explicably, then, no cyclohexenes were produced in the catalytic reaction.

With arene–$D_2$ mixtures, the rhodium catalyst effected substantial H–D exchange which was in evidence in both the recovered arene and in the cyclohexane products. Thus, unlike cobalt, an arene can complex with the rhodium, undergo H–D exchange, and then be eliminated as an arene-$d_x$ species. With methyl-substituted arenes, the rate of H–D exchange was much higher for aliphatic than for aromatic C–H, and with *n*-propyl- and ethylbenzene, H–D exchange was primarily evident in the $\alpha$-$CH_2$ position.

For the rhodium catalyst system, a possible but as yet nondetectable process is the cleavage of the triply hydride-bridged dimer, 7, by hydrogen to yield the mononuclear $d^6$ $H_3Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ which would be isoelectronic to the postulated $\eta^1$-$C_3H_5CoH_2[P(OR)_3]_2$ intermediates.

## The Chemistry of Arene–Transition-Metal Complexes

Arene complexation is an obvious and crucial step in any catalytic hydrogenation cycle.[28] For hydrogen

(18) We have encountered extensive H–D exchange at aliphatic C–H sites for $D_2$–methylbenzene reaction mixtures as catalyzed by {HRh-[P(O-*i*-$C_3H_7)_3]_2\}_2$ and by $\eta^6$-$C_6(CH_3)_6Ru$-$\eta^4$-$C_6(CH_3)_6$ (vide infra).

(19) Day, V. W.; Fredrich, M. F.; Reddy, G. S.; Sivak, A. J.; Pretzer, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* 1977, *99*, 8091.

(20) Stuhl, L. S.; Muetterties, E. L. *Inorg. Chem.* 1978, *17*, 2148.

(21) Muetterties, E. L.; Schaffer, H.; Mink, R. I.; Darensbourg, M. Y.; Millar, M.; Groshens, T.; Klabunde, K. *J. Inorg. Chem.* 1979, *18*, 883.

(22) $\eta^3$-$C_3H_5Ni[P(OR)_3]_3^+$ is not a catalyst for these reactions: L. S. Stuhl, Cornell University, Thesis, 1978.

(23) These include $\eta^6$-$C_6H_6M(C_6F_5)_2$ (M = Co, Ni),[30] HClRu($\eta^6$-$C_6$-$(CH_3)_6$)P($C_6H_5)_3$,[29] {$\eta^5$-$C_5(CH_3)_5RhCl_2\}_2$,[37] $\eta^6$-$C_6H_6TiAl_2Cl_8$,[21] and $\eta^6$-$C_6$-$(CH_3)_6Ru$-$\eta^4$-$C_6(CH_3)_6$.[31]

(24) There are, however, exceptions,[25] and the $d^8$ $\rightleftharpoons$ $d^6$ electronic couple may be essential[26] only to chemoselective and stereoselective catalysts.

(25) Examples are $\eta^6$-$C_6H_6TiAl_2Cl_8$,[21] apparently {$\eta^5$-$C_5(CH_3)_5RhCl_2\}_2$,[37] and $\eta^6$-$C_6H_6Co(C_6F_5)_2$.[30]

(26) A radical catalytic reaction is a possibility, and one may be the very high temperature (200 °C) reduction of benzene catalyzed by $HCo(CO)_4$. Cf.: Rathke, J. W.; Feder, H. M. *J. Am. Chem. Soc.* 1978, *100*, 3623.

(27) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* 1979, *101*, in press.

Table I
Metal-$\eta^6$-Arene Complexes: Hydrogen Reactions[a]

| complex | metal $d^x$ configuration | solvent | reaction temp, °C | result |
|---|---|---|---|---|
| $(\eta^6\text{-}CH_3C_6H_5)_2Ti$ | $d^4$ | toluene | 20 | slow decomposition |
| $[\eta^6\text{-}CH_3C_6H_5Mo(\eta^3\text{-}C_3H_5)Cl]_2$ | $d^4$ | benzene | 85 | decomposition |
| $\eta^6\text{-}CH_3C_6H_5MoH_2[PR_3]_2$ | $d^4$ | benzene | 95 | decomposition |
| $(\eta^6\text{-}C_6H_6)_2Cr$ | $d^6$ | benzene | 150 | no reaction |
| $(\eta^6\text{-}CH_3C_6H_5)_2Mo$ | $d^6$ | benzene | 150 | no reaction |
| $(\eta^6\text{-}CH_3C_6H_5)_2W$ | $d^6$ | benzene | 150 | no reaction |
| $\eta^6\text{-}CH_3C_6H_5Mo(CO)_3$ | $d^6$ | benzene | 120 | no reaction |
| $\eta^6\text{-}CH_3C_6H_5Mo[P(OR)_3]_3$ | $d^6$ | benzene | 120 | no reaction |
| $\eta^6\text{-}CH_3C_6H_5W(CO)_3$ | $d^6$ | benzene | 150 | no reaction |
| $\eta^6\text{-}C_6H_6Ru(\eta^3\text{-}C_3H_5)Cl$ | $d^6$ | benzene | 85 | decomposition |
| $\eta^6\text{-}C_6H_6Ru(1,5\text{-}C_8H_{12})$ | $d^8$ | toluene | 20 | slow decomposition |
| $[\eta^6\text{-}C_6(CH_3)_6]_2Co^+$ | $d^8$ | benzene-acetone | 20 | slow decomposition |
| $\eta^6\text{-}C_6(CH_3)_6Rh(\eta^4\text{-}C_6(CH_3)_6H_2)^+$ | $d^8$ | benzene-acetone | 20 | slow decomposition |

[a] In all cases, there was no detectable hydrogenation of arene ligand or of arene solvent.

atom transfer from metal to arene ring to occur, what is required? An arene molecule could be bound initially to a transition metal in an $\eta^6$, $\eta^4$, or $\eta^2$ form; the last is experimentally established only for $d^{10}$ metal complexes. In these three structural classes, loss of aromatic delocalization energy is probably greatest in an $\eta^4$ binding. Hydrogenation of an arene bound to a metal site may well be most facile in those instances where the $\eta^4$-arene–metal state is accessible since coplanarity of the arene is lost (vide infra). We found that most $\eta^6$-arene–transition-metal complexes do not possess the requisite features for either catalytic or stoichiometric hydrogenation of the arene ligand (see Table I). In particular, coordinately saturated and unsaturated bis(arene)–metal complexes with both arenes bound in an $\eta^6$ fashion were inactive, complexes with both an $\eta^6$-arene and an $\eta^3$-allyl ligand were inactive, and a complex with an $\eta^6$-arene and two hydride ligands was inactive. There are, however, five metal–arene complexes which have in the ground state $\eta^6$-arene–metal binding and which are reported to be catalytically active in arene hydrogenation: $\eta^6\text{-}C_6H_6TiAl_2Cl_8$,[21] described below, and $\eta^6\text{-}C_6(CH_3)_6RuHCl[P(C_6H_5)_3]$,[29a] $[\eta^6\text{-}C_6(CH_3)_6\text{-}Ru(\mu\text{-}H)_2(\mu\text{-}Cl)Ru\text{-}\eta^6\text{-}C_6(CH_3)_3]Cl$,[29b] $(C_6F_5)_2Co\text{-}\eta^6\text{-}C_6H_6$, and $(C_6F_5)_2Ni\text{-}\eta^6\text{-}C_6H_6$,[30] whose activities were briefly described in recent communications. Additionally, an $\eta^6$-arene–metal cluster complex, $CH_3C_6H_5Ru_6C(CO)_{14}$, reacted with hydrogen at 150 °C to produce methylcyclohexane, but the benzene solvent molecules did not capture the cluster fragment so as to produce a catalytic cycle.[31]

### The Chemistry of $\eta^4$-Arene–Metal Complexes: The Ruthenium System

One of the most remarkable organometallic structures is bis(hexamethylbenzene)ruthenium(0), which has one conventional $\eta^6$-arene ligand and one $\eta^4$-arene ligand

that is nonplanar with some consequent loss of the aromatic ring stabilization.[32] At 80 to 90 °C and 1–3 atm of hydrogen, bis(hexamethylbenzene)ruthenium is a long-lived catalyst for arene hydrogenation.[33] These catalytic reactions differ markedly from those based on allylcobalt catalysts. Most distinctive is the production of cyclohexenes in significant amounts: cyclohexene to cyclohexane ratios are 1:19 and 1:1 for benzene and $p$-xylene, respectively. In addition, there is limited stereoselectivity with $o$- and $p$-xylenes respectively producing 10 and 18% $trans$-dimethylcyclohexanes. This low stereoselectivity arises partially because at least some of the cyclohexene molecules are displaced from the metal center. Hydrogen–deuterium exchange is extensive in all $D_2$–arene reaction mixtures and, as in the cobalt and rhodium cases, the rate of aliphatic C–H centered exchange is greater than aromatic C–H. In the benzene–$D_2$ reaction, recovered benzene and recovered catalyst contain deuterium, and the cyclohexene and cyclohexane products contain deuterium in excess of that required for reduction.

Bis(hexamethylbenzene)ruthenium(0) is a stereochemically nonrigid structure. A physical mechanism consistent with the established permutational character of the exchange involves a bis($\eta^4$-arene)ruthenium excited state (eq 9). The latter, a 16-electron complex,



$$\tag{9}$$
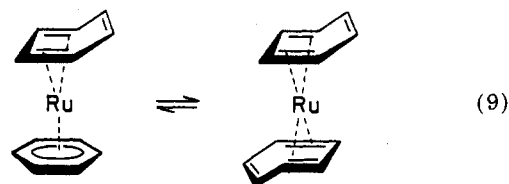
may react with hydrogen in what could be the first step (eq 10) in the catalytic sequence. Arene exchange to

$$\eta^6\text{-}C_6(CH_3)_6Ru\text{-}\eta^4\text{-}C_6(CH_3)_3 \rightleftharpoons Ru[\eta^4\text{-}C_6(CH_3)_6]_2 \rightleftharpoons H_2Ru[\eta^4\text{-}C_6(CH_3)_6]_2 \tag{10}$$

allow introduction of a reducible arene into the coordination sphere was presumed to be a subsequent step and probably rate determining. Exchange of hexamethylbenzene between $C_6(CD_3)_6$ and the ruthenium complex was nondetectable at 90 °C even in the presence of hydrogen.[33] However, if the forward and

(28) Chemically, key questions are (a) how are arene–metal complexes formed, (b) what is the mechanism of arene ligand exchange in arene–(arene)metal complex systems in nondonor solvents, (c) what are the *factors* affecting ($\eta^6$-arene)metal $\rightleftharpoons$ ($\eta^4$-arene)metal transformations, and (d) what are the factors affecting the ease of hydrogen atom transfer from metal to bound arene ligand?

(29) (a) Bennett, M. A.; Huang, Tai-Nang; Smith, A. K.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* 1978, 582. (b) Bennett, M. A.; Huang, Tai-Nang; Turney, T. W. *Ibid.*, 1979, 312.

(30) Klabunde, K. J; Anderson, B. B.; Bader, M.; Radonovich, L. J. *J. Am. Chem. Soc.* 1978, *100*, 1313.

(31) Johnson, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* 1977, *99*, 7395.

(32) Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B* 1972, *28*, 2049.

(33) Darensbourg, M. Y.; Muetterties, E. L. *J. Am. Chem. Soc.* 1978, *100*, 7425. Idem., unpublished data.

back rates for $[C_6(CH_3)_6]_2Ru + C_6H_6 \rightleftharpoons C_6(CH_3)_6Ru\text{-}C_6H_6 + C_6(CH_3)_6$ are low, then a $C_6(CH_3)_6RuC_6H_6$ species could effect many catalytic cycles and account for the arene hydrogenation (relatively low rate) in this system while the arene exchange rates would be sufficiently small to account for the experimental non-detection of exchange in the $[C_6(CH_3)_6]_2Ru\text{-}C_6(CD_3)_6$ system.[34]

Trimethylaluminum, which forms no detectable complex with $\eta^6\text{-}C_6(CH_3)_6Ru\text{-}\eta^4\text{-}C_6(CH_3)_6$ at temperatures as low as −80 °C, catalyzes the site exchange in the ruthenium complex.[33] In fact, this alane alters the very character of the exchange to a two-step process in which the lower energy step formally has the character of a 1,3 ring shift in the $\eta^4$-arene ligand. Even more significantly, this alane raises the rate of arene exchange in the $Ru[C_6(CH_3)_6]_2\text{-}C_6(CD_3)_6$ system to the detectable level and also raises the rate of the arene hydrogenation reaction in the catalytic system. These observations are not inconsistent with the original surmise that hexamethylbenzene ligand dissociation is rate determining in the ruthenium catalytic reaction. In addition, the alane appears to stabilize the catalyst, and it also completely suppresses cyclohexene formation in the catalytic reaction.[33]

The mechanistic role of the alane is unknown—yet the general efficacy of aluminum halides or alkyls in the synthesis of arene–metal complexes is well-known. It is also reported that aluminum chloride catalyzes arene exchange in chromium group–arene complexes. In addition, we[21] have found that a titanium(II)–arene complex, $C_6H_6TiAl_2Cl_8$, that structurally incorporates aluminum trichloride is an arene catalyst at 120 °C. All these observations raise a quite fundamental point. How does arene exchange occur? Does it unzip through a series of $\eta^6 \rightleftharpoons \eta^4 \rightleftharpoons \eta^2$ transformations accompanied (at some stage) by a "zipping up" of the incoming arene by a series of comparable processes? What is the alane's role—does it complex with the arene ligand or directly with the metal atom? These issues must be resolved before one can confidently discuss the mechanistic features of coordination complex catalyzed arene hydrogenation reactions.

## The Hydrogen–Deuterium Exchange Reaction

One pervasive feature of catalytic arene hydrogenation reactions effected either in solution or at metallic surfaces is hydrogen exchange at C–H sites. For reactions of alkyl-substituted arenes with deuterium, the rates of H–D exchange are higher for aliphatic than for aromatic sites, with the only exception being tungsten and rhodium metallic[4] surfaces. Exchange is evident in recovered arene and in product cyclohexanes with the exception of the allylcobalt-catalyzed reaction where the recovered arene is free of deuterium (vide supra). To date, studies of coordination catalysts show that H–D exchange in alkylbenzenes requires a hydrogen

atom on the α-carbon, a feature consistent with the following sequence (eq 11) in which a hydridometal–



$$\text{(11)}$$
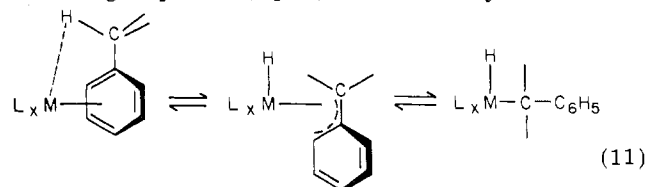
$\eta^3$-benzyl complex is formed from either an initial $\eta^6$- or $\eta^4$-arene complex. Deuterium addition to the latter can then lead to H–D exchange in the alkyl group. Similar cycles could occur at later stages in the arene hydrogenation sequence, especially at the $\eta^4$-cyclohexadiene–metal complex stage. (At this stage, a reversible sequence like (11), with C–$C_{phenyl}$ bond rotation, could lead to aromatic carbon–hydrogen H–D exchange.) Note that if the $\eta^3$-benzyl structure is in rapid equilibrium with an $\eta^1$-benzyl structure (eq 11), there is then a mechanism for the ultimate formation of non-cis arrays in the methylcyclohexanes derived from xylenes and tri- or tetramethylbenzenes.

Hydrogen–deuterium exchange also occurs at aromatic C–H sites in benzene itself with solid-state metallic catalysts[4] and with coordination catalysts. Only[35] the allylcobalt-catalyzed reactions do not exhibit this exchange.

## Prospects

A number of substantive scientific issues in arene–transition-metal complexes have been raised in the specific context of coordination catalysis of arene hydrogenation.[36] Many of these issues can be resolved by rational design of experiments. In addition, information is needed about $\eta^2$-arene–metal complexes of $d^x$ ($x < 10$) configuration, an unknown but credible type of complex. All available data point to $\eta^4$-arene ligand binding as an intermediate in at least some hydrogenation sequence, although this is not to say that direct hydrogen atom transfer from a metal center to an $\eta^6$-arene or $\eta^2$-arene ligand is not feasible. In this respect, a dynamic variable important in the hydrogenation reaction is the effect of metal oxidation state and $d^x$ electronic configuration on the activation energy for the process of converting a metal–$\eta^6$-arene complex to a metal–$\eta^4$-arene complex—presently we only know that the barrier is about 16 kcal/mol for bis(hexamethylbenzene)ruthenium(0).

Returning to the practical question posed in the beginning of this Account—can a selective and long-lived coordination catalyst for arene hydrogenation be rationally designed? The answer is unequivocally yes for a long-lived catalyst.[38]    We have these, e.g.,

(34) Generally, arene exchange between an $\eta^6$-arene–metal complex and free arene is not a facile process unless a coordinating solvent such as acetone or a strong Lewis acid like an alane is present. Cf. the review of Silverthorn, W. E. *Adv. Organometal. Chem.* 1975, *13*, 47; Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* 1974, 233; and also Sievert, A. C.; Bleeke, J. R.; Muetterties, E. L. *J. Organomet. Chem.*, in press.

(35) Recently, M. A. Bennett described a ruthenium coordination catalyst for arene hydrogenation that showed no evidence of H–D exchange in the $C_6H_6 + D_2$ reaction (ACS/CSJ Chemical Congress, Inorganic Division, Honolulu, Hawaii, April 5, 1979).

(36) We defer comment on the various systems, reported to be homogeneous, which are based on aluminum or boron hydride or alkyl coreagents to yield *black* reaction mixtures. The complex reaction system reported by Maitlis et al.[37] is based on $(C_5(CH_3)_5RhCl_2)_2$ and a basic cocatalyst like an amine at 50 °C and 50 atm. The catalytic system is not stereoselective, and a hydrogen–deuterium exchange at aromatic CH sites does occur. Klabunde and co-workers[30] have shown that both $d^7$ $\eta^6\text{-}C_6H_6Co(C_6F_5)_2$ and $d^8$ $\eta^6\text{-}C_6H_6Ni(C_6F_5)_2$ are catalysts for benzene hydrogenation at 25 °C and 100 atm. More experimental and mechanistic details are required before substantive comments can be drawn about these results. In addition, $HCo(CO)_4$[26] (extreme temperature and pressure conditions) and $RuHCl[\eta^6\text{-}C_6(CH_3)_6]P(C_6H_5)_3$[29] are reported to be catalysts. Some of these may involve formal $M^+ \rightleftharpoons M^{2+} + e^-$ couples in the hydrogen oxidative-addition reaction.

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

$Ru[C_6(CH_3)_6]_2$ and $H_4Rh_2[P(OR)_3]_4$, but there is only one known selective catalyst, actually a class of catalysts, the allylcobalt tris(phosphite) complexes. Selectivity, specifically stereoselectivity, requires the absence of certain reaction cycles: (1) significant displacement of the partially hydrogenated arene as a cyclohexene and (2) significant lifetimes for intermediates derived from alkyl-substituted arenes in which transformations from $\eta^3$-benzylmetal to $\eta^1$-benzylmetal would allow for rotation about the metal–carbon $\sigma$ bond. We must design structures so as to disallow these processes. The presence of an electronically ambidentate ligand like the allyl ligand which can facilitate the generation of open coordination sites can also operate to minimize the formation of low hapticity interactions with a partially hydrogenated arene (e.g., $\eta^1$-benzylmetal) and also stabilize the last displaceable state before total hydrogenation, the cyclohexene state.

(38) There is no compelling technological need for longer-lived, more efficient or more active arene hydrogenation catalysts. Established solid-state catalysts meet present day practical needs.

We now seek alternative ambidentate ligands—e.g., chelate ligands that are more resistant to reduction.

Finally, we note here one of the most fascinating aspects of reactions catalyzed by discrete coordination compounds—and to us one of the most compelling reasons for studying such reactions. Many fundamental features of coordination chemistry can be revealed from the studies because of the multistepped character of the catalytic reactions. The allylcobalt class of complexes has been no exception to the generality—the number of elementary steps identified in the arene–hydrogen reaction catalyzed by the cobalt complexes is impressively large.

# Iridium Compounds in Catalysis

## ROBERT CRABTREE

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Why are metal surfaces (heterogeneous catalysts) so much more active than the metal complexes (homogeneous catalysts) which are their soluble counterparts? How can one set about the design of homogeneous systems that are much more active than those presently available?

These were the sort of questions that prompted us to look at the catalytic chemistry of some highly coordinatively unsaturated iridium species. These systems have proved to be far the most active homogeneous hydrogenation catalysts known. For example, they can reduce even tetrasubstituted olefins, such as $Me_2C{=}CMe_2$, at up to 4000 catalytic cycles per hour at 0 °C. These studies have also led to the isolation both of the first dihydrido olefin complexes, the active intermediates in catalysis, and of some unusual hydrogen-bridged cluster complexes formed in the deactivation of the catalysts.

High catalytic activity in an iridium-based system might be thought surprising, because transition metals of the third row had previously been found to be less active in catalysis than those of the first and, more especially, the second rows (see Figure 1). A char-

acteristic example is that of the complexes [MCl(PPh_3)_3]. Where the metal is rhodium, this complex is an efficient catalyst for the hydrogenation of unsaturated substrates.[1] The cobalt and iridium analogues are entirely inactive, but for different reasons. The cobalt complex fails to react with hydrogen,[2] while the iridium analogue reacts irreversibly with hydrogen to give a stable adduct $[IrClH_2(PPh_3)_3]$; this adduct, however, unlike the rhodium analogue, fails to dissociate $PPh_3$ to allow the substrate access to the active site.[3]

The mechanisms of olefin hydrogenation with [RhCl(PPh_3)_3], Wilkinson's catalyst, are known in some detail;[1,4] the major route is shown in Figure 2. Hydrogen addition (step a) gives a relatively unstable dihydride adduct in which solvent or $PPh_3$ (L') is labile, presumably due to the high trans effect of a hydrogen ligand. Solvent and substrate (step b) can compete for the available site. The presumed dihydrido olefin intermediate, which has never been observed, must undergo a hydride insertion, perhaps assisted by a ligand association (step c). A reductive elimination (step d) gives the product alkane and regenerates the catalyst.

Robert H. Crabtree was born in London in 1948. He studied at Oxford (B.A., M.A.), where he worked for a year with Malcolm Green, and then took his D.Phil with Joseph Chatt at the Unit for Nitrogen Fixation, Sussex University. With Hugh Felkin, at the Institut de Chimie des Substances Naturelles at Gif-sur-Yvette, near Paris, he was first a postdoctoral fellow, and then Attaché de Recherche. In 1977, he took up an assistant professorship in Inorganic Chemistry at Yale University.

(1) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).
(2) N. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **3**, 227 (1969).
(3) M. A. Bennett and D. A. Milner, *J. Am. Chem. Soc.*, **91**, 6983 (1969).
(4) P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Am. Chem. Soc.*, **94**, 3240 (1972); C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *ibid.*, **96**, 2762 (1974); J. Halpern and C. S. Wong, *Chem. Commun.*, 629 (1973).