termined as low-spin iron ($S = \frac{1}{2}$) while monoimidazolehemin was reported as high-spin iron ($S = \frac{5}{2}$).

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# Catalytic Homogeneous Hydrogenation of Arenes. 6.[1]
# Reaction Scope for the $\eta^3$-C$_3$H$_5$Co[P(OCH$_3$)$_3$]$_3$ Catalyst

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**Abstract:** The scope and selectivity of $\eta^3$-C$_3$H$_5$Co[P(OCH$_3$)$_3$]$_3$ as a catalyst precursor for the homogeneous hydrogenation of arenes at room temperature and low pressure (1–3 atm) have been examined for a variety of substituted benzenes and polycyclic aromatic and heterocyclic compounds. Pronounced stereoselectivity for the cis addition of H$_2$ and the formation of cis ring junctions has been observed. For example, benzene + D$_2$ gave ≥95% all cis C$_6$H$_6$D$_6$, naphthalene + H$_2$ gave *cis*-decalin with no detectable trans isomer, and anthracene + H$_2$ gave >95% of the *cis-syn-cis*-perhydroanthracene. The scope of the reaction is reasonably large. Catalytic hydrogenation was demonstrated for benzenes with substitutent groups that include –R, –OR, –COOR, –COR, –CH=CHR, –C≡CR, and –NR$_2$. The catalyst system is subject to steric inhibition by ring substituents on the arene ring. Electron-withdrawing and nucleophilic substituents such as halogen, –NO$_2$, and –CN also inhibit the reaction. The selectivity for arene vs. olefin hydrogenation in competitive systems is discussed. Comparisons are drawn with metal surface catalyzed hydrogenation.

## Introduction

A chemoselective and stereoselective hydrogenation of aromatic regions of complex organic molecules remains a major synthetic challenge. Catalytic hydrogenation of aromatic hydrocarbons has long been dominated by metallic heterogeneous systems; nickel, Raney nickel, palladium, platinum, and rhodium are especially active catalysts for these hydrogenation reactions.[2] Hydrogenation of aromatic hydrocarbons with metallic catalysts provides a modest degree of stereoselectivity with an essential cis orientation in the hydrogen addition steps. The stereoselectivity of such catalysts in the hydrogenation of xylenes, mesitylene, and naphthalene is illustrated in Table I. In chemoselectivity, the metallic catalysts fail in a general fashion simply because the reactivity of the substituent groups toward the metal surface is so high as to engender either substituent group hydrogenation or gross destruction of the substituent group, a more facile process than the hydrogenation of the aromatic system.[3]

In recent years, a number of ostensibly homogeneous reaction mixtures have been described as catalysts for the hydrogenation of aromatic hydrocarbons. Those reported through 1974 were reviewed in a previous paper of this series. Not covered in the earlier review was the report that (pyridine)$_2$-(dimethylformamide)RhCl$_2$(BH$_4$) is a catalyst for the hydrogenation of pyridine and quinoline.[4] Recent claims to homogeneous catalytic arene hydrogenations include the following: cobalt and nickel acetylacetonates react with LiAlH$_4$ to give homogeneous black solutions which catalyze the hydrogenation of benzene at 30 °C and 1 atm H$_2$ in tetrahydrofuran.[5] Klabunde has found that $\eta^6$-CH$_3$C$_6$H$_5$Co(C$_6$F$_5$)$_2$ and $\eta^6$-CH$_3$C$_6$H$_5$Ni(C$_6$F$_5$)$_2$ catalyze the hydrogenation of benzene at ~35 atm but these are both short-lived catalysts.[6] Also [Rh($\eta^5$-C$_5$Me$_5$)Cl$_2$]$_2$ has been reported to be an effective catalyst for the hydrogenation of benzene and substituted benzenes at moderate temperatures and pressures.[7a] The latter compound is of interest in that it displays a significantly dif-

**Table I**

| Catalyst (temp,[a] °C) | % trans[b] | Catalyst (temp,[a] °C) | % trans[b] |
|---|---|---|---|
| *o*-Xylene | | *p*-Xylene | |
| Ni/Al₂O₃ (180) | ~50[d,h] | Ni (180) | ~80[d,i,k] |
| Os/asbestos | 29[d,i] | Pt black (200) | ~80[d,k] |
| PtO₂ (85) | 12.7[c,e] | Rh/C (100) | 36.4[c] |
| Rh/C (100) | 10.8[c] | PtO₂ (85) | 33.4[c,e] |
| Ru/C (100) | 7.4[c] | Ru/C (100) | 30.3[c] |
| PtO₂ | 5[d,j] | PtO₂ | 28[d,j] |
| | | Pt black | 20[d,k] |
| *m*-Xylene | | Mesitylene | |
| Rh/C (100) | 26.3[c] | Pt or Ni (175) | 10[d,l] |
| Ni (180) | ~20[d,k] | Naphthalene | |
| Pt black | 20[d,k] | Pd/C (100) | 52[f] |
| PtO₂ (85) | 19.0[c,e] | Rh/Al₂O₃ | 16[f] |
| Ru/C (100) | 15.5[c] | Ir/C (115) | 12[c] |
| PtO₂ | 15[d,j] | Ir/C | 6[f] |
| | | Ru/C | 4[f] |
| | | Anthracene | |
| | | Ni/Cr (180) | ~30[g] |

[a] Room temperature if not otherwise indicated. [b] Total of all isomers other than the all-cis isomer. [c] P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals", Academic Press, New York, N.Y., 1967, pp 324–325. [d] R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957). [e] R. D. Schuetz and L. R. Caswell, *J. Org. Chem.*, **27**, 486 (1962). [f] A. W. Weitkamp, *Adv. Catal.*, **18**, 2 (1968). [g] M. M. Podorozhanskii, E. M. Zeidlits, V. P. Sukhowkova, and I. I. Eru, *Koks Khim.*, 38 (1969); *Chem. Abstr.*, **71**, 38639u (1969). [h] O. Miller, *Bull. Soc. Chim. Belg.*, **42**, 238 (1933). [i] N. D. Zelinskii and E. I. Margolis, *Ber.*, **65**, 1613 (1932). [j] S. Siegel and M. Dunkel, International Congress on Catalysis, Philadelphia, Pa., 1956, Lecture 4. [k] O. Miller, *Bull. Soc. Chim. Belg.*, **44**, 513 (1935). [l] G. Chiurdoglu, *ibid.*, **60**, 39 (1951); G. Chiurdoglu, P. J. C. Fierens, and C. Henkart, *ibid.*, **59**, 161 (1950).

ferent response to ring substituents than that reported herein for $\eta^3$-C₃H₅Co[P(OCH₃)₃]₃; it unfortunately lacks the stereoselectivity we have observed for our catalyst.

Our discovery that $\eta^3$-C₃H₅Co[P(OCH₃)₃]₃ is a catalyst precursor[7b] for the hydrogenation of aromatic hydrocarbons was a signal advance for several reasons: (1) the system was unequivocally homogeneous, (2) the hydrogenation conditions were quite mild, (3) there was a remarkably high cis stereoselectivity, and (4) the catalyst after the initial hydrogen addition step[7c] exhibited a reactivity toward arenes that was nearly equivalent to that toward terminal olefins. However, the $\eta^3$-C₃H₅Co[P(OCH₃)₃]₃ catalyst and its close analogues are seriously flawed in a practical context because hydrogen atom transfer to the allyl group which produces propylene and inactive cobalt hydrides occurs at a rate such that the practical lifetime of all the allylcobalt complexes is no greater than about 25 turnovers of benzene. A substantially larger catalyst lifetime has not been achieved by electronic or steric redesign of L in $\eta^3$-C₃H₅CoL₃ nor by conventional substitution in the allyl group.[8] Our studies to date clearly indicate that the allylcobalt catalyst system minimally requires modification at the metal center in order to reduce the deleterious allyl group cleavage reaction. To facilitate a logical design of a practical catalyst, we have attempted a delineation of the reaction mechanistic details of this allylcobalt catalyst since the stereoselective features are unique for this catalyst. We describe here the reaction scope for the arene hydrogenation reactions catalyzed by $\eta^3$-C₃H₅Co[P(OCH₃)₃]₃ which outlines the chemoselectivity and stereoselectivity of the reaction and which provides incisive details that must be fully explicable for any mechanistic proposal.

## Experimental Section

**Reagents and Solvents.** The catalyst was prepared and purified as described previously.[8] In some earlier experiments, the chromatographic purification of the catalyst was omitted. Generally, rates of hydrogenation were higher with the purified catalyst, provided that care was taken to ensure the absence of excess trimethyl phosphite.

THF was purified as described previously; other solvents were dried with CaH₂ or Na/benzophenone. Prepurified hydrogen (99.5%) was purchased from Matheson and Co. and used as received. Benzene, the methylbenzenes, anisole, furan, cyclohexene, 1,3-cyclohexadiene, 1-hexene, thioanisole, and 1-phenyl-1-propane were vacuum distilled from lithium aluminum hydride. Acetonitrile, chlorobenzene, fluorobenzene, aniline, and pyridine were vacuum distilled from P₄O₁₀. Styrene, cyclohexenone, and methyl vinyl ketone were vacuum distilled from activated alumina. Allylbenzene was purified by vacuum distillation from LiAlH₄ followed by passage through an activated alumina column and redistillation. Benzaldehyde, cyclooctatetraene, and 1,5-cyclooctadiene were vacuum distilled. Phenol and benzoic acid were recrystallized from THF. Ethyl benzoate was washed with Na₂CO₃ and CaCl₂ solutions, dried over K₂CO₃, and vacuum distilled from P₄O₁₀. Naphthalene, anthracene, and pyrene were zone refined. *N,N*-Dimethylbenzamide was sublimed at ~90 °C (0.05 mm) and tetrapropylammonium benzoate was recrystallized from tetrahydrofuran.

Other liquids were dried by vacuum distillation from CaH₂; other solids were used as received. Decolorizing carbon (Norit A) was extracted with refluxing cyclohexane for 3 days and then was vacuum dried.

**Physical Measurements.** Gas chromatography was performed on Perkin-Elmer 990 instruments equipped with flame ionization or thermal conductivity detectors. All quantitative measurements were performed using the flame ionization detector and are not corrected for response factor variations. The following columns were used: (A) 12 ft × 1/8 in. 3% squalene on Chromosorb P joined to 7 ft × 1/8 in. 20% ethyl *N,N*-dimethyloxamate on Chromosorb P; (B) 12 ft × 1/8 in. 15% OV-101 on Chromosorb W; (C) 7 ft × 1/8 in 20% ethyl *N,N*-dimethyloxamate on Chromosorb P; (D) 12 ft × 1/8 in. 15% OV-17 on Chromosorb W; (E) 6 ft × 1/8 in. 3% SE-30 on Chromosorb W; (F) 12 ft × 1/8 in. 3% Carbowax 20M on Chromosorb P; (G) 12 ft × 1/8 in. 3% squalane on Chromosorb P; (H) 6 ft × 1/8 in. 3% OV-225 on Gas-Chrom Z; (I) 6 ft × 3/8 in. 20% OV-17 on silanized Chromosorb PAW; (J) 6 ft × 1/8 in. 10% Apiezon L on Gas-Chrom Q; (K) 6 ft × 1/8 in. 3% OV-101 on Gas-Chrom Q; (L) 6 ft × 1/8 in. Chromosorb 103; (M) 6 ft × 1/8 in. 3% OV-17 on Gas Chrom Q.

A Finnegan 3300 GC/MS interfaced with a System Industries System 150 was used for positive identification of chromatographic peaks when authentic samples of products were not available. Columns for this spectrometer were all 3% loading on Chromosorb WHP. ¹H NMR spectra were recorded on Varian A-60A or Brucker HX-90 spectrometers. Infrared spectra were recorded on Perkin-Elmer 137 or 337 instruments.

**Hydrogenation Reactions.** The procedure described earlier[8] for the hydrogenation reactions was used under the conditions indicated in Table II. Volatile products were isolated by vacuum distillation on a high-vacuum line. Nonvolatile products were isolated by opening the reaction mixture to air, stirring until precipitation was complete, and filtering off the oxidized catalyst residues. When the latter procedure was followed in reactions with high catalyst to substrate ratios (e.g., anthracene) the formation of partially hydrogenated species in amounts approximately equal to the amount of catalyst present was noted. This material is believed to represent compound bound to the catalyst at the time the oxidative workup was commenced.

Competition experiments between benzene and norbornadiene or allylbenzene were performed as above using 1:1 mixtures and an overall catalyst to reactant ratio of 1:20. The benzene/allylbenzene reaction was analyzed after 4 h and after 24 h on 10 ft × 1/8 in. 5% QF-1 on Chromosorb W and 6 ft 80/100 Chromosorb 104 GC columns. After 4 h, no cyclohexane or propene was detected, and only a small amount of allylbenzene reaction; after 24 h, there was still no cyclohexane, only <1% cyclohexene and extensive allylbenzene isomerization being observed. The benzene/norbornadiene reaction was analyzed after 6 h on column D. No cyclohexane and only traces of benzene partial hydrogenation products and norbornadiene hydrogenation products were observed. The catalyst was recovered from the allylbenzene/benzene experiment and was shown by ¹H NMR to be unaltered. The ¹H NMR of catalyst plus allylbenzene in the absence of hydrogen is that expected for a mixture of the two compounds without interaction.

Tables II and III summarize the results of this investigation. One point that requires comment is the percent conversions reported. The catalyst was very sensitive to the presence of free trimethyl phosphite and other impurities which may act as ligands, suggesting that ligand dissociation is a relatively unfavorable step in the mechanism of hydrogenation. The purification procedure previously reported is of value only if care is taken to ensure that the alumina column is washed completely free of the phosphite before the catalyst is chromatographed, and exposure of the purified catalyst to phosphite is scrupulously avoided. In the course of more exact rate studies to be reported later, we have found that even the presence of traces of trimethyl phosphite in the glove-box atmosphere can significantly perturb the hydrogenation rate. Since no extreme precautions were taken to use catalyst of constant activity over the course of this study of scope, the conversion values reported should be taken as semiquantitative indications of rates only.

The second point of note is that we chose to use $\eta^3$-$C_3H_5Co$-$[P(OCH_3)_3]_3$ rather than the more active analogues reported in the previous paper of this series. We have found that, although the trimethyl phosphite derivative is the least active catalyst examined, it is also the most resistant to the side reaction involving loss of propene leading to catalyst death. The trimethyl phosphite compound also represented a good compromise in terms of ease of preparation and cost of materials.

## Results and Discussion

The pervasive and distinctive feature of the $\eta^3$-$C_3H_5Co$-$[P(OCH_3)_3]_3$ catalyzed hydrogenation of aromatic hydrocarbons is the cis stereoselectivity in the hydrogen atom addition to the aromatic ring system. Thus, benzene and $D_2$ yielded >95% of the all-cis isomer of $C_6H_6D_6$,[9] the *o*-, *m*-, and *p*-xylenes gave only the corresponding *cis*-dimethylcyclohexanes, and mesitylene formed only *cis,cis*-trimethylcyclohexane. No cyclohexenes were produced in these reactions. Naphthalene yielded *cis*-decalin and no detectable amounts of the trans isomer. Anthracene formed *cis-syn-cis*-perhydroanthracene with possibly small amounts of other isomers. Larsen and Chang in independent studies detected (GC analysis) a single isomeric hydrogenation product from naphthalene, anthracene, and phenanthrene with the allylcobalt catalyst.[10] These catalytic results are to be compared with typical heterogeneous metallic catalysts (Table I) where substantial amounts (5–15%) of the trans isomers are produced, and with $[C_5(CH_3)_5RhCl_2]_2$ which yielded 14–33% trans isomers with the xylenes. The invariant and complete cis stereoselectivity and the absence of cyclohexenes in these reactions requires a reaction mechanistic scheme in which the arene once complexed and initially hydrogenated is not displaced from the metal center and in which the metal atom remains on normals to one face of the arene ring until the hydrogenation is complete.

Another unique feature of the allylcobalt catalyst is the virtual absence of H–D exchange for reaction systems based on nonsubstituted aromatic hydrocarbons plus deuterium or perdeuterioarenes plus hydrogen. As noted earlier, the reaction of $C_6D_6$ + $H_2$ or $C_6H_6$ + $D_2$ in the presence of the allylcobalt catalyst yielded only (>95%) $C_6H_6D_6$. The reaction of naphthalene and deuterium gave $C_{10}H_8D_{10}$; within the experimental errors of the mass spectral analysis no $C_{10}H_7D_{11}$ was produced. Small amounts of $C_{10}H_9D_9$ and $C_{10}H_{10}D_8$ were detected and are ascribed to hydrogen impurity in the $D_2$ used. Precise establishment of this point will require kinetic studies to examine the possibility of an isotope effect being operative. The $n + 1$ peak of the recovered naphthalene was slightly larger than that of a naphthalene standard. However, this difference was within the limits of experimental error for the mass spectral analysis. Thus in the cobalt system there is an essential irreversibility in the hydrogen addition steps. This sharply contrasts with heterogeneous metallic catalyst systems where H–D exchange is extensive in arene plus $D_2$ reactions as well as in other soluble catalyst systems such as the one described by Maitlis et al.[7a]

The reaction of toluene with $D_2$ in the presence of allylcobalt catalyst yielded significant amounts of $d_6$, $d_7$, $d_8$, and $d_9$ methylcyclohexanes, while the more deuterated methylcyclohexanes ($d_{10}$ and above) were produced in much smaller quantities. This result suggests facile H–D exchange in the methyl group of the methylcyclohexane product. Mass spectral analysis of the unreacted toluene showed no deuterium incorporation. The reaction of *p*-xylene with $D_2$ in the presence of allylcobalt catalyst generated $d_6$ through $d_{12}$ *p*-dimethylcyclohexanes, while the more highly deuterated *p*-dimethylcyclohexanes ($d_{13}$ and above) were absent. This is further evidence for H–D exchange in the methyl groups of the product. There was no deuterium incorporation in the unreacted *p*-xylene. The absence of deuterium incorporation in the recovered toluene and xylene is consistent with the general observation for the cobalt catalyst that an arene once complexed does not dissociate until hydrogenated. A catalyzed H–D exchange in the methyl groups of toluene and xylenes and their hydrogenation products has been observed[1] for the $\eta^6$-$C_6(CH_3)_6Ru$-$\eta^4$-$C_6(CH_3)_6$ homogeneous arene hydrogenation catalyst.

Catalyst recovered after a 12-h deuteration of benzene showed no deuterium incorporation in the allyl group. Thus, hydrogen transfer to the allyl ligand which is the first step in the sequence that leads to propylene formation and catalyst destruction is an irreversible step.

Within the class of polycyclic aromatic hydrocarbon hydrogenations, the scope of reaction for the allylcobalt catalyst is limited. Although naphthalene, anthracene, and phenanthrene are fully and selectively hydrogenated with the cobalt catalyst, the rates fall significantly in going from benzene to naphthalene and anthracene. Pyrene proved inert,[11] a finding independently confirmed by Larsen and Chang.[10] An extension to coal, especially with the ubiquitous sulfur and nitrogen components that would probably deactivate the catalyst, would not seem feasible. Attempts to hydrogenate carbon black (a "purified Norit") were unsuccessful with the cobalt catalyst. Larsen and Chang found that a typical coal sample and a variety of coal and petroleum derived asphaltenes were not hydrogenated with this catalyst.[10]

Electronic and steric elements in the aromatic hydrocarbons present additional constraints in the hydrogenation reaction. Electron-withdrawing groups deactivate the arenes toward the hydrogenation cycle with the $\eta^3$-$C_3H_5Co[P(OCH_3)_3]_3$ catalyst (see Table III). Fluorine, cyano, and nitro groups rendered the benzene nucleus unreactive in this system. The $\pi$ donor capability of the arene must be relatively high for the hydrogenation cycle to commence. A high degree of nucleophilicity in the substituent group can also confound the desired hydrogenation cycle presumably through a catalyst-substituent binding that directly involves the substituent group or atom rather than the $\pi$ system of the arene, e.g., phenylacetonitrile, triphenylphosphine, and possibly benzonitrile, which were inert to the cobalt catalyst system. An oxidation-reduction couple between catalyst and substrate probably explains the fast irreversible reaction observed between chlorobenzene and the allylcobalt complex. The electron density on the cobalt atom in $\eta^3$-$C_3H_5Co[P(OCH_3)_3]_3$ is relatively high as documented in earlier studies and this feature unfortunately presents another limitation to the catalytic reaction because the protonated complex $\eta^3$-$C_3H_5CoH[P(OCH_3)_3]_3^+$ is unstable with respect to propylene elision;[12] this feature probably accounts for the absence of hydrogenation of phenol and benzoic acid.

The experimental results for alkyl-substituted benzenes show a significant steric inhibition feature of the hydrogenation reaction. Thus, the hydrogenation rate falls in the order benzene > toluene > xylenes > mesitylene > 1,2,4,5-tetramethylbenzene > 1,2,3-trimethylbenzene > 1,2,3,4-tetramethylbenzene and hexamethylbenzene (essentially inert). Three or
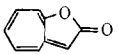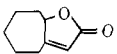
**Table II**

| Reactant (solvent) | Reaction duration, h | Catalyst/ reactant ratio | Product(s) | (GC column) | % conversion |
|---|---|---|---|---|---|
| Benzene | 24 | 1:100 | Cyclohexane[b] | | 16[a] |
| Benzene | 24 | 1:100 | Cyclohexane[b] | | 16.4 |
| Benzene | 10 | 1:100 | Cyclohexane[b] | | 5[a] |
| Benzene + $D_2$ | 10 | 1:100 | all-cis-$C_6H_6D_6$[c] | | 5[a] |
| Perdeuteriobenzene | 15 | 1:100 | all-cis-$C_6H_6D_6$[c] | | 8[a] |
| Toluene | 10 | 1:100 | Methylcyclohexane[b] | | 5[a] |
| o-Xylene | 10 | 1:100 | cis-1,2-Dimethylcyclohexane[b,d] | | 3 |
| o-Xylene | 48 | 1:100 | cis-1,2-Dimethylcyclohexane | (B) | 15 |
| m-Xylene | 10 | 1:100 | cis-1,3-Dimethylcyclohexane[b,d] | | 3 |
| m-Xylene | 48 | 1:100 | cis-1,3-Dimethylcyclohexane | (B) | 7 |
| p-Xylene | 10 | 1:100 | cis-1,4-Dimethylcyclohexane[b,d] | | 3 |
| p-Xylene | 49 | 1:100 | cis-1,4-Dimethylcyclohexane | (B) | 7 |
| Mesitylene | 15 | 1:100 | cis,cis-1,3,5-Trimethylcyclohexane[b,d] | | 1[a] |
| 1,2,3-Trimethylbenzene | 65 | 1:10 | cis,cis-1,2,3-Trimethylcyclohexane | (M) | 2 |
| 1,2,4,5-Tetramethylbenzene (THF) | 72 | 1:10 | cis,cis,cis-1,2,4,5-Tetramethylcyclohexane | (M) | 9.5 |
| Naphthalene (diethyl ether) | 168 | 1:10[f] | cis-Decalin Tetralin | (D) | 99 1 |
| Anthracene (diethyl ether) | 49 | 1:10 | cis-syn-cis-Perhydroanthracene[g] Mixture of hydrogenated anthracenes | (D) | 76 14 |
| Furan | 15 | 1:100 | Tetrahydrofuran[d] | | 5[a] |
| Benzofuran | 96 | 1:100 | Perhydrobenzofuran $C_8H_8O$ $C_8H_{12}O$ | (K) | 19 12 1.5 |
| Anisole | 10 | 1:100 | Cyclohexyl methyl ether[b] | | 5[a] |
| N,N-Dimethylaniline | 48 | 1:100 | Cyclohexyldimethylamine | (L) | 2 |
| Coumarin (diethyl ether) | 144 | 1:10[h] | Dihydrocou | (H) | |

| | 96 | 1:100 | | (H) | 26 |
| (diethyl ether) | | | 8 unidentified compounds | | 10 |
| Methyl vinyl ketone | 24 | 1:58 | Polymer Methyl ethyl ketone | | ~99 Trace |
| Ethyl benzoate | 24 | 1:13 | Ethyl cyclohexanecarboxylate Ethyl cyclohex-1-enecarboxylate | (E) | 2 13 |
| N,N-Dimethylbenzamide) (diethyl ether) | 68 | 1:10 | N,N-Dimethylcyclohexanecarboxamide Benzyl alcohol | (H) | 54 4 |
| Acetophenone | 24 | 1:40 | Cyclohexyl methyl ketone | (B, E) | ≤1 |
| 2-Cyclohexen-1-one | 42 | 1:47 | Cyclohexanone Cyclohexanol | (F) | 3 Trace |
| Styrene | 24 | 1:41 | Vinylcyclohexane Ethylbenzene Cyclohexenylethane | (B) | 5[e] 6 4 |
| 1-Phenylpropyne | 43 | 1:23 | Propenylcyclohexane Propylbenzene Allylbenzene cis-Propenylbenzene trans-Propenylbenzene | (B) | 2 3 1 1 2 |
| Propylbenzene | 25 | 1:34 | Propylcyclohexane | (B) | 15 |
| Allylbenzene | 30 | 1:36 | Allylcyclohexane Propylcyclohexane Propylcyclohexene Propylbenzene | (B) | 2 3 5 4 |
| 1-Hexene | 5 | 1:0 | n-Hexane 2-Hexenes | (A) | 4 10 |
| 2-Hexene (cis- and trans-) | 5 | 1:50 | n-Hexane 1-Hexene 3-Hexenes | (A) | 1.4 1 0.5 |
| 3-Hexene (trans-) | 5 | 1:50 | n-Hexane 2-Hexenes | (A) | 1 0.5 |
| 3-Hexene (trans-) | 24 | 1:50 | n-Hexane 2-Hexenes | (A) | 6 <1 |
| 1,3-Hexadiene | 27 | 1:50 | n-Hexane 1-Hexene 2-Hexenes 3-Hexene (trans-) | (A) | 3 29 9 1 |
| 1,5-Hexadiene | 27 | 1:50 | n-Hexane 1-Hexene 2-Hexenes 3-Hexene (trans-) 2,4-Hexadienes 1,4-Hexadienes | (A) | 7 20 45 3 2 10 |

**Table II** (*Continued*)

| Reactant (solvent) | Reaction duration, h | Catalyst/ reactant ratio | Product(s) | (GC column) | % conversion |
|---|---|---|---|---|---|
| 1,4-Hexadiene | 27 | 1:50 | n-Hexane | (A) | 5 |
| | | | 1-Hexene | | 8 |
| | | | 2-Hexenes | | 11 |
| | | | 3-Hexene (*trans*-) | | 0.5 |
| | | | 2,4-Hexadienes | | 12 |
| 2,4-Hexadiene | 27 | 1:50 | n-Hexane | (A) | 15 |
| | | | 1-Hexene | | 11 |
| | | | 2-Hexenes | | 15 |
| | | | 3-Hexene (*trans*-) | | 0.5 |
| Cyclohexene | 15 | 1:100 | Cyclohexane | (F) | 1 [a] |
| Cyclohexene + D$_2$ | 15 | 1:100 | C$_6$H$_{10}$D$_2$[d] | | 1 [a] |
| 1,5-Cyclooctadiene | 37 | 1:32 | Cyclooctene | (B, E, F) | 50 |
| | | | Cyclooctane | | 26 |
| Cyclooctatetraene | 72 | 1:21 | Cyclooctene | (E) | 60 |
| | | | Cyclooctane | | 28 |

[a] Unpurified catalyst. [b] Analyzed by NMR. [c] E. L. Muetterties, M. C. Rakowski, F. J.Hirsekorn, W. D. Larson, V. J. Basus, and F. A. L. Anet, *J. Am. Chem. Soc.*, **97**, 1266 (1975). [d] Analyzed by mass spectroscopy. [e] Percent of volatiles. Significant polymer formation was noted. [f] Additional catalyst equal to initial amount added after 24 and 72 h. [g] Collected by preparative GC (column I) and identified by melting point and infrared spectrum (R. L. Clarke, *J. Am. Chem. Soc.*, **83**, 965 (1961)) as well as by GC/MS. [h] Additional catalyst equal to initial amount added after 100 h.

more methyl groups in sequence suffice to seriously depress the hydrogenation rate in these arenes. Electronically, the expected order would be reversed; hence, the steric feature seems unequivocally documented.

Earlier we demonstrated that in competitive hydrogenation experiments with 1-hexene-benzene mixtures and the $\eta^3$-C$_3$H$_5$Co[P(O-$i$-C$_3$H$_7$)$_3$]$_3$ catalyst the ratio of hydrogenated arene to hexane was about 7:10 as compared to a ratio of about 3:10 with the $\eta^3$-C$_3$H$_5$Co[P(OCH$_3$)$_3$]$_3$ catalyst.[8] Thus terminal olefins compete more effectively than benzene for the latter catalyst. Substantial amounts of cyclohexene were formed in addition to cyclohexane whereas in the absence of the terminal olefins only cyclohexane was formed. Accordingly, it was of interest to examine the behavior of alkenyl and alkynyl derivatives of benzene in our hydrogenation system. Styrene gave vinylcyclohexane and ethylbenzene in nearly equivalent amounts under conditions of low conversion. Also produced in equivalent amounts was cyclohexenylethane. The latter could have arisen from the styrene displacement of the substituted cyclohexene by analogy to the above cited 1-hexene-benzene system. Alternatively the cyclohexenylethane might have arisen by the following sequence. Steric factors should favor initial binding of the styrene at sites removed from the vinyl group, e.g., as in **1**. Addition of four hydrogen atoms could then yield an intermediate like **2** which could on two additional



1                              2
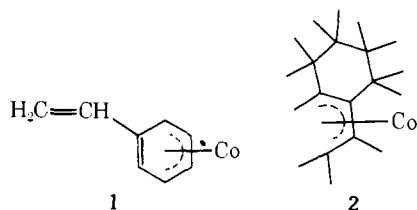
hydrogen atom additions yield either vinylcyclohexane or cyclohexenylethane. In any case, the aromatic portion of the styrene molecule competed effectively with the vinyl group for the catalyst in this hydrogenation reaction. A similar result was obtained with the conjugated alkenylbenzene, propenylbenzene, where nearly equivalent quantities of propenylcyclohexane, propylcyclohexane, propylcyclohexene, and propylbenzene were produced. An acetylenic function appears to compete for catalyst more effectively than the aromatic ring. 1-Phenylpropyne produced about a 2:7 ratio of propenylcy-

**Table III.** Arenes Not Hydrogenated by $\eta^3$-C$_3$H$_5$Co[P(OCH$_3$)$_3$]$_3$

| Arene (solvent) | Reaction time, h | Catalyst/ Reactant ratio |
|---|---|---|
| 1,2,3,4-Tetramethylbenzene | 72 | 1:10 |
| Hexamethylbenzene | 24 | 1:100 |
| Fluorobenzene | 48 | 1:100 |
| Chlorobenzene | (Reacts with oxidation to destroy catalyst) | |
| Benzonitrile | 42 | 1:46 |
| Phenylacetonitrile | 71 | 1:41 |
| Triphenylphosphine (diethyl ether) | 336 | 1:24 |
| Thioanisole | 22 | 1:40 |
| Na$^+$C$_5$H$_5$ | 49 | 1:10 |
| Phenol | (Protonation of catalyst) | |
| Benzoic acid | (Protonation of catalyst) | |
| Nitrobenzene | 24 | 1:100 |
| Charcoal (pentane) | 168 | |
| (C$_3$H$_7$)$_4$NC$_6$H$_5$CO$_2$ (acetonitrile) | 96 | 1:20 |

clohexane to substituted benzenes (allyl, propyl, and *cis*- and *trans*-propenyl). However, formation of allylbenzene would have a deleterious effect on the arene ring hydrogenation as discussed below.

Allylbenzene produced a small amount of allylcyclohexane and large amounts of propyl- and propenylbenzenes. The allyl functionality interacts quite selectively with the catalyst and totally blocks the hydrogenation of propylbenzene. Thus, although propylbenzene alone gave about a 15% conversion to propylcyclohexane in 25 h, a mixture of equivalent amounts of propylbenzene and allylbenzene yielded no propylcyclohexane in 30 h; only the above cited hydrogenation products of allylbenzene were detected for this reactant mixture. In a competitive experiment with a 1:1 allylbenzene-benzene mixture, there was no hydrogenation of the benzene. This effect was not observed for propenylbenzene and for propenylbenzene-benzene mixtures until significant quantities of allylbenzene were formed in the hydrogenation system.

The blocking of the benzene hydrogenation sequence by allylbenzene does not occur before the hydrogen addition to the $\eta^3$-C$_3$H$_5$Co[P(OR)$_3$]$_3$ complex because there was no

spectral evidence of interaction between $\eta^3$-$C_3H_5$Co-[P(OCH$_3$)$_3$]$_3$ and allylbenzene (as in the case for benzene and alkylbenzenes) nor did allylbenzene displace the allyl group at any place in the catalytic cycle (the catalyst was recovered unchanged as judged by its NMR). Allylbenzene and propenylbenzene differ in that allylbenzene can act as a quasi-1,4-diene ligand by utilization of the olefinic bond and the 1,2 aromatic bond while propenylbenzene can act as a quasi-1,3-diene ligand. The postulated[13] $C_3H_5$CoH$_2$[P(OR)$_3$] intermediate has a d$^6$ configuration and should[14] interact more favorably with nonconjugated dienes, e.g., allylbenzene, than with conjugated dienes like an $\eta^4$-arene ligand or propenylbenzene. This thesis is supported by our finding that the nonconjugated diene norbornadiene blocks the benzene hydrogenation sequence. After 6 h of hydrogenation of a 1:1 benzene–norbornadiene mixture, no cyclohexane and only trace amounts of cyclohexene were observed.

Aromatic aldehydes and esters[15] behaved differently than aromatic ketones and ethers in the hydrogenation system. Acetophenone and anisole yielded only the fully hydrogenated products cyclohexyl methyl ketone and cyclohexyl methyl ether, respectively. Ethyl benzoate gave ethyl cyclohex-1-enecarboxylate and ethyl cyclohexanecarboxylate in about a 6:1 ratio. The apparent aberrant behavior of the ester with respect to the ketone is inexplicable. Based on electronic factors, specifically a comparison of Hammett substituent constants, both the ketone and ester should have a low reactivity since nitrobenzene, which has somewhat higher Hammett $\sigma$ values (more electron withdrawing), is totally nonreactive. The reactivity (percent conversion) of acetophenone was found to be very low, but the ester was significantly more reactive. These observations raise the possibility that these aromatic compounds interact initially with the catalyst in a different fashion than does benzene or an alkylbenzene. In this mechanistic context, it is notable that coumarin was converted very slowly only to dihydrocoumarin which demands an alternative mode of binding to the catalyst (although a cis form of the conjugated olefin and carbonyl portion is not feasible in this cyclic lactone system). Termination of hydrogenation at dihydrocoumarin has also been observed with metal surface catalysts under mild conditions.[16]

Included in Table II are the results of hydrogenations with the various hexenes and hexadienes. The most notable feature in the hexadiene hydrogenations were the relatively large amount of 1- and 2-hexenes produced from the 1,3-, 1,4-, 2,4-, and 1,5-hexadienes. In all these olefin systems, isomerization was a competing reaction to the hydrogenation sequence.

As expected for the postulated[13] $C_3H_5$CoH$_2$[P(OR)$_3$] intermediate, the linear hexadienes totally blocked the hydrogenation of benzene as specifically established in catalytic experiments of 1:1 mixture of benzene with 1,3-hexadiene and with 1,4-hexadiene. These experiments suggest that a linear diene, either a conjugated or a nonconjugated diene, competes far more effectively for the key intermediate than does benzene which is postulated[13] to complex as a 1,3 or conjugated diene (i.e., as a $\eta^4$-$C_6H_6$ ligand).

All the competitive experiments of benzene with olefins,

dienes, allylbenzene, and propenylbenzene point to an initial cobalt–benzene complex of the form $\eta^1$-$C_3H_5$CoH$_2$-[P(OR)$_3$]($\eta^4$-$C_6H_6$). In our recently discussed ruthenium system,[1] an analogous d$^6$ intermediate is formed in the sequence $\eta^6$-arene-Ru-$\eta^4$-arene $\rightleftharpoons$ Ru($\eta^4$-arene)$_2$ $\rightleftharpoons$ H$_2$Ru($\eta^4$-arene)$_2$. Tetrahapto binding of the arene results in a loss of aromatic ring stabilization and should render the ring system more susceptible to hydrogenation. Such a binding of the arene in a catalyst precursor or in a catalytic intermediate may well be a feature common to all homogeneous catalytic hydrogenations of arenes. We plan similar competitive hydrogenation experiments with metallic solid state catalysts to see if there are any common mechanistic features between the surface and coordination catalysis regimes of arene hydrogenation.

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