transverse decay with a single value of x ($\sim$10 μm); however, a quantitative fit would require a distribution of values for x. Consequently, in order to minimize the number of adjustable parameters, we have chosen an alternate approach.

We will assume that the water exists in three sites: (1) the bulk water (site A), (2) the "layered water" around the glass beads (site B) which is in rapid exchange with (3) the surface of the glass beads (site C). If the T_2 for the water in site C is much less than the lifetime at site C which is much less than the T_2 for site B, then sites B and C taken together relax with a single time constant[5] τ_{BC}, the lifetime for a molecule at site B to exchange to site C. Consequently, sites B and C, taken together, form a pseudo-site with relaxation time τ_{BC}. If τ_{BC} is much less than the relaxation time for the bulk water, T_{2A}, then the total magnetization relaxes[6] with two time constants, $1/\tau_B$ and $1/T_{2A} + 1/\tau_A$, where τ_i is the lifetime at site i ($1/\tau_B = 1/\tau_{BC} + 1/\tau_{BA}$).

An analysis of the data in terms of two rate constants, T_2^{-1}(short) and T_2^{-1}(long), is shown in Table I. Figure 1 shows that this analysis adequately describes the gross features of the relaxation; however, a more extensive analysis would probably require a description of the type given in eq 1.

The temperature dependence of T_2(short) shows that it behaves like an exchange time, as it should in terms of the above analysis. The temperature dependence of T_2(long), however, indicates that $\tau_A > T_{2A}$. Assuming a Gaussian distribution[4] for the displacement of the water molecules and a diffusion constant $D = 2.5 \times 10^{-5}$ cm^2/sec, then, after 2.5 sec, 10% of the molecules will have traveled less than 15 μm. In view of the diameter of the glass beads ($\sim$100 μm), then τ_A being larger than T_{2A} does not necessarily imply any restriction of the diffusion of the bulk water to the surface of the glass beads.

As indicated by Glasel and Lee,[1] one would expect effects arising from magnetic susceptibility differences in the two phases to be proportional to at least the first power of the frequency of the measurements. It can be seen from Table I that the line widths are proportional to the frequency. Also in agreement with Glasel and Lee,[1] it was found that spinning the sample reduced the line width by a factor of 2 (for a spinning rate of 50 Hz).

On the other hand, both T_2^{-1}(short) and T_2^{-1}(long) are independent of the frequency in the range studied within the experimental error of 10% for the short time component and considerably more for the long time component (due to the low amplitude of the latter). Consequently, it is clear that the transverse relaxation measured with a CPMG sequence is not dominated by magnetic susceptibility effects.

Irrespective of the analysis of the details of the transverse relaxation, the major conclusion of this work is that the transverse relaxation measured with a CPMG sequence is not dominated by effects resulting from field gradients produced by the difference in the magnetic susceptibilities of the beads and the bulk water. On the other hand, the line widths are dominated by these effects.

References and Notes

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Catalytic Hydrogenation of Arenes. II.[1] Arene Selectivity over Olefin and Reaction Mechanism for the Hydrogenation Reaction

Sir:

Recently, we reported[1] catalysis of arene hydrogenation at 25° by a discrete, soluble coordination complex, η^3-$C_3H_5Co[P(OCH_3)_3]_3$. We have now found that this catalyst exhibits a unique selectivity toward arenes over olefins. This finding of selectivity, buttressed with other new experimental results, provides considerable insight to the reaction mechanism in arene hydrogenations with this catalyst.

Competitive experiments[2] have demonstrated that the allyl-cobalt(I) complex catalyzes hydrogenation of benzene to cyclohexane at a rate three-four times that of cyclohexene to the alkane. Similar experiments with 1-hexene and with 2-hexene show analogous substrate selection with the rate of benzene hydrogenation at least twice that of the hexenes (isomerization of the hexenes does not proceed under these conditions). This remarkable, but not very large, selection for arenes raises the possibility of design of a practical, selective catalyst for arene hydrogenation. Additionally, the selection for the arene resolves unequivocally a mechanistic feature of arene hydrogenation with this cobalt catalyst.

Cyclohexene is not a detectable product in the catalytic hydrogenation of benzene.[3] The ring once partially hydrogenated must only rarely dissociate from the metal center (or separate from a solvent cage) as cyclohexene; cyclohexene cannot be an intermediate in the reaction because $k_{C_6H_6} > k_{C_6H_{10}}$. A similar argument applies to cyclohexadiene dissociation since the rate of cyclohexadiene to cyclohexane conversion by this cobalt catalyst is only about 1.3 times that for benzene hydrogenation (competitive experiments). Thus we can confidently visualize the hydrogenation sequence to proceed with transfer of hydrogen to ring without separation of reduced arene from the metal center until a cyclohexyl form is attained.

The above results, and ancillary experiments cited below, delineate some of the steps in the catalytic hydrogenation. The first step (eq 1) is postulated to be a $\pi \rightleftharpoons \sigma$ interconversion[4] for which there is convincing precedent;[5] this postulate is supported by experimental observations in ligand exchange reactions.[1,6] Arenes do not detectably[7] interact with the allyl complex but hydrogen does (eq 2) as shown initially[1] by tensimetric experiments.

$$\eta^3-C_3H_5Co[P(OCH_3)_3]_3 \rightleftharpoons \eta^1-C_3H_5Co[P(OCH_3)_3]_3 \quad (1)$$

$$\eta^1-C_3H_5Co[P(OCH_3)_3]_3 + H_2 \rightleftharpoons \eta^1-C_3H_5CoH_2[P(OCH_3)_3]_3(\alpha) \quad (2)$$

Formation of a hydride (α) has been confirmed through low temperature ^{1}H nmr studies of the allyl complex and hydrogen in cyclohexane. In addition to the ^{1}H resonances for η^3-$C_3H_5Co[P(OCH_3)_3]_3$, there is a weak, complex metal hydride resonance. Three stereoisomers are possible in an octahedral form of (α). There is no evidence of the isomer with the hydrogen ligands at trans positions. Thus, cis hydrogen addition prevails, and one of the two or both cis isomers of the dihydride (α) is present.[8]

Cis elimination of propylene (eq 3) does not occur to any significant extent in the dihydride provided that an arene is

$$\eta^1-C_3H_5CoH_2[P(OCH_3)_3]_3 \rightleftharpoons C_3H_6 + HCo[P(OCH_3)_3]_3 \quad (3)$$

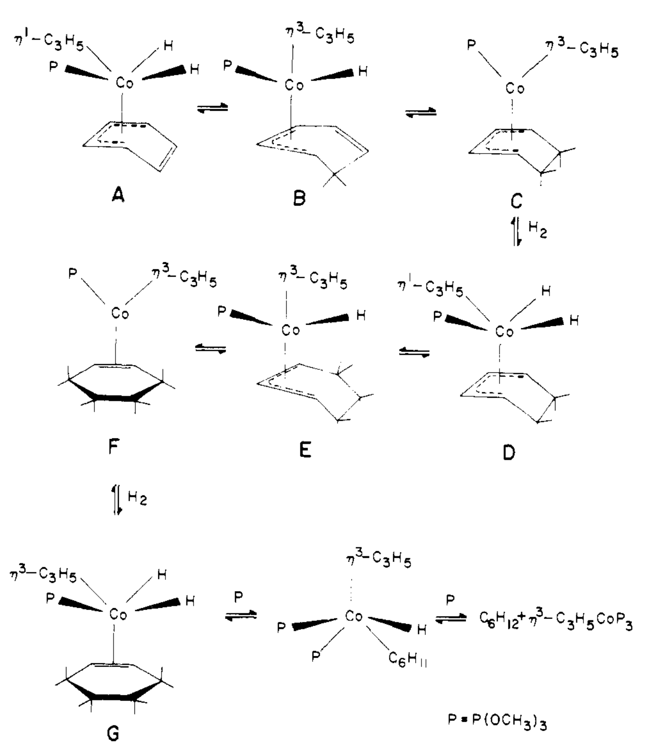

Figure 1. Possible reaction sequence for hydrogen transfer from cobalt to arene in the η^3-$C_3H_5Co[P(OCH_3)_3]_3$ catalyzed hydrogenation of aromatic hydrocarbons. Note the pervasive homofacial character of hydrogen addition to the ring. Sixteen-electron intermediates such as F will be in equilibrium with 18-electron intermediates through reaction with free trimethylphosphite.

present. The allylcobalt complex was recovered in near quantitative yield from the hydrogenation system and propylene (or propane) was not detected, at least in a 24-hr reaction period. In the absence of an arene, the dihydride does slowly evolve propylene (a small amount of which is hydrogenated to propane). This clearly indicates a significant interaction of arene with the dihydride (α), or an intermediate derived from the dihydride (*vide infra*), thereby inhibiting cis elimination. Also, we have shown that the hydride, $HCo[P(OCH_3)_3]_3$, derived from cis elimination is not the active arene hydrogenation catalyst. Closely related to the allylcobalt complex is η^3-$C_6H_5CH_2Co[P(OCH_3)_3]_3$.[9] This π-benzyl complex catalyzes arene hydrogenation but cis elimination of toluene is so rapid even in an arene solution *that hydrogenation ceases* very quickly with the formation of $HCo[P(OCH_3)_3]_3$. This monohydride which possesses a low stability, with decomposition to an intractable solid, appears to be a very active catalyst for HD exchange in H_2-D_2 mixtures[10] but it does not significantly catalyze arene hydrogenation.

The above studies clearly indicate a significant interaction of arene with the dihydride but we have not succeeded in gaining spectroscopic evidence of the interaction. We suggest that the dihydride (α) interacts with the arene in the manner outlined in eq 4-6. We further suggest that an important intermediate state is η^1-$C_3H_5CoH_2P(OCH_3)_3$-η^4-C_6H_6 since the reactivities of cyclohexadiene and benzene are so similar (*vide supra*); there is precedent for such η^4-arene metal complexes.[11] The compelling evidence for nondissociation of ring after initial reduction suggests the sequence in Figure 1. Note that the last step is irreversible; cyclohexane does not interact with the cobalt complex even in the presence of hydrogen (D_2). The sequence in Figure 1 also neatly accounts for the pervasive all cis stereochemistry[1] of the cyclohexanes derived from xylenes and mesitylene since the sequence requires addition of hydrogen atoms to one face of the arene.

$$\eta^1 - C_3H_5CoH_2[P(OCH_3)_3]_3 \rightleftharpoons \eta^3 - C_3H_5CoH_2[P(OCH_3)_3]_2 + P(OCH_3)_3 \quad (4)$$

$$\eta^3 - C_3H_5CoH_2[P(OCH_3)_3]_2 \rightleftharpoons \eta^3 - C_3H_5CoH_2P(OCH_3)_3 + P(OCH_3)_3 \quad (5)$$

$$\eta^3 - C_3H_5CoH_2P(OCH_3)_3 + C_6H_6 \rightleftharpoons \eta^1 - C_3H_5CoH_2P(OCH_3)_3 - \eta^4 - C_6H_6 \quad (6)$$

Final and conclusive demonstration of this reaction sequence rests on synthesis of the unknown η^3-C_3H_5Co-η^6-C_6H_6 and conversion of this complex to the proposed intermediates in Figure 1 through reaction with $P(OCH_3)_3$ and subsequent hydrogen titration. We are also attempting electronic and steric modification of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ to achieve a very high selectivity for arenes.[12]

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References and Notes

(1) Paper I in this series: E. L. Muetterties and F. J. Hirsekorn, *J. Amer. Chem. Soc.*, **96**, 4063 (1974).

(2) Initial equimolar mixtures of benzene-d_6 and cyclohexene; no inert solvent was employed. Reactions run at 25° and ~760 mm.

(3) This statement applies to all reaction systems in which the hydrogen reactant is not exhausted. Analysis was gc–mass spec.

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(7) Nmr and electronic spectra are not detectably different for the allylcobalt complex in cyclohexane and in benzene.

(8) Alternatively, the observed hydride may be η^3-$C_3H_5CoH_2[P(OCH_3)_3]_2$ (see eq 4) where there would be three stereoisomers with cis hydride ligands (no resonances that could be attributed to the trans stereoisomer were detected).

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(10) Reaction of H_2, D_2, and benzene in the presence of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ yields HD and $C_6H_nD_{12-n}$ molecules with n odd and even numbers. This is tentatively ascribed to catalysis of H–D exchange by trace amounts of $HCo[P(OCH_3)_3]_3$.

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(12) NOTE ADDED IN PROOF. The conjugated, noncyclic olefin, 1,3-hexadiene, was hydrogenated at a rate 2–3 times lower than that of benzene to form only the internal olefin. We have prepared η^3-$C_3H_5Co[P(OCH_3)_3]_2[P(O$-$i$-$C_3H_7)_3]$ and find it is a more active catalyst; the increase in rate over η^3-$C_3H_5Co[P(OCH_3)_3]_3$ is a factor of 3.

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Thermal Stereomutation of Optically Active *trans*-Cyclopropane-*1,2-d₂*[1]

Sir:

Pyrolysis of cyclopropane or its substituted derivatives causes two major reactions:[2] hydrogen shift to an olefin (*e.g.*, cyclopropane → propylene)[3] and stereomutation (*e.g.*, *trans*- → *cis*-cyclopropane-*1,2*-d_2).[4] The trimethylene biradical, first proposed[3] as an intermediate in the olefin-forming reaction, more recently has also been invoked[5] to explain the stereomutation. In the case of cyclopropane itself, thermochemical estimates suggest that rotations about the C–C bonds of trimethylene would be fast relative to cyclization, a relationship that would result in a *stereorandom intermediate*.[5b-d,6]