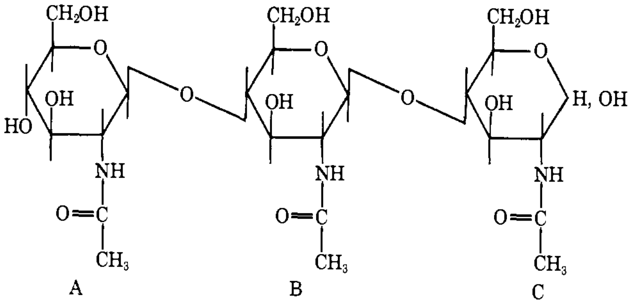

in site C forms a strong hydrogen bond with the carbonyl group of alanine 107.

Our exchange results are consistent with the X-ray structure. The amide hydrogen which exchanges too rapidly for measurement in the presence of lysozyme can be associated with site B. The other two amide hydrogens exchange much more slowly since they cannot exchange with water while hydrogen is bonded to the enzyme. The more slowly exchanging hydrogen can be associated with site C since the lack of linearity of the exchange curve in this region can be explained by the presence of the α and β anomers of chitotriose. If we assume that mutarotation cannot occur while chitotriose is bound we would expect that the extent of opening of the hydrogen bond in site C would be different depending upon whether the α or β anomer were bound. This difference would be reflected in a difference in exchange rate. By elimination the more rapidly exchanging hydrogen can therefore be associated with site A.

The equilibrium between lysozyme, P, and chitotriose, M, can be represented as $PM \rightleftarrows P + M$, where $K = (P)(M)/(PM)$. The dissociation constant for the complex has been measured by a number of methods[3] and has a value of about 0.5×10^{-5} at pH 5. The kinetics of the above reaction have been measured by temperature-jump and stopped-flow techniques.[4-6] Association and dissociation rates are much faster than the exchange rates observed here.

From the total concentrations of lysozyme and chitotriose present and the above value of K, it is possible to calculate $(M)/[(PM) + (M)]$ for each kinetic experiment. For experiments at the higher lysozyme concentration used, the ratio has a value of 0.0088. At the lower lysozyme concentration the value is 0.16. Reference to Figure 1 shows that there is approximate agreement between the exchange curves at these two lysozyme concentrations. Consequently, we can infer that exchange may occur mainly through PM rather than through M. More specifically, exchange apparently occurs through states in which the chitotriose is bound to the enzyme but the amide hydrogen bonds at sites A or C are broken. However, this conclusion must be preliminary until the unpleasant scatter of these points can be eliminated.

We can offer the following tentative explanations for the scatter of exchange points when lysozyme is present. This molecule is known to bind strongly about nine molecules of water during freeze-drying.[7] This water could be bound in the active cleft. Incomplete removal of this water from clefts in which chitotriose is present could give exchange points which are too high. An alternative possibility would be that water in a cleft could still slowly exchange with chitotriose after freezing. Removal of this water during drying could give points which are too low. More work is being carried out to settle the question.

It is clear that the "tritium exchange probe" method should be useful in gaining new understanding of interactions between protein active sites and the molecules which bind to them. The method will be most useful in situations where binding is strong since under such conditions, differences in exchange behavior in the presence and absence of the protein will be most marked.

Acknowledgments. We should like to thank Professor David Chipman for a generous gift of chitotriose. The work was supported in part by NSF Grant No. GB19559.

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Catalytic Reduction of Olefins with a Polymer-Supported Rhodium(I) Catalyst

Sir:

Many biological systems are capable of selecting substrates for reaction from solution on the basis of bulk molecular properties. These same systems, which are generally catalytic, also allow a large turnover of substrates without loss of the catalytic site. This is accomplished in most cases by attaching the reagent to the inside of large, semiordered, insoluble polymer. Solvent channels in the polymer allow soluble substrates to enter and leave the stationary reagent site. In this way, the substrates are easily separated from reagents and the overall geometric and polar properties of the solvent channels determine the substrates that are able to enter into the catalytic center.

We now wish to report that this rather simple principle has been used to develop a new class of olefin hydrogenation catalysts which demonstrates many of the best properties of homogeneous and heterogeneous catalysts.[1] In addition they are capable of selecting olefins from solution on the basis of overall molecular size.

Polystyrene beads (200–400 mesh) with 1.8% cross-linking of divinylbenzene were chloromethylated on 10% of the aromatic rings by the procedure of Pepper, Paisley, and Young.[2] The chloromethylated polymer was treated with a 1 *M* tetrahydrofuran solution of lithiodiphenylphosphine[3] for 1 day to replace 80% of the chlorines with diphenylphosphine groups.[4] These beads were then equilibrated with a twofold excess

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[1] P. Legzdins, G. L. Rempel, and G. Wilkinson, *Chem. Commun.*, 825 (1969); and Mobil Oil, Patent, U. S. No. 1,800,371 (1969).

[2] K. W. Pepper, H. M. Paisley, and M. A. Young, *J. Chem. Soc.*, 4097 (1953).

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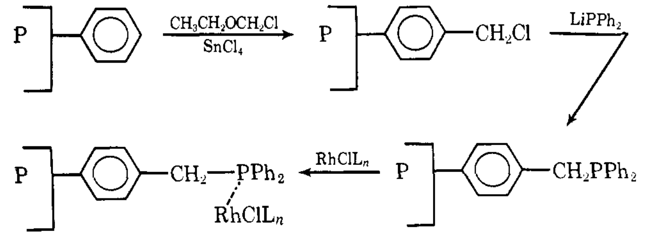
[4] Determined by microanalysis.

of tris(triphenylphosphine)chlororhodium(I)[5] for 2–4 weeks.



At the conclusion of the equilibration period the deep red beads were washed with deoxygenated benzene until the rinses were colorless for 3–5 successive cycles. Fresh oxygen-free benzene was then added and after equilibration of the catalyst under hydrogen at 1 atm for at least 1 hr, an olefin was added. A steady uptake of hydrogen then commenced and the reduced hydrocarbon could be observed by vpc analysis.

As can be seen from Table I, the rate of reduction depended on the molecular size of the olefin. Increasing the ring size of a cyclic olefin or going from an acyclic to a cyclic olefin decreased the rate of reduction. Large rigid olefins such as Δ^2-cholestene showed a dramatic decrease in reduction rate. We attribute this decrease in reduction rate to the restriction of the size of the solvent channels by the random cross-links in the polymer.[6] These observations also demonstrated that the major portion of the reductions was taking place inside of the polymer bead.[7] A surface reduction reaction would have shown a much lower specificity for the larger olefins (see Table I).

Table I

Olefin[a,d]	Beads rel rate[b]	$RhCl(Ph_3P)_3$ rel rate[b,c]
Cyclohexene	1	1.0
1-Hexene	2.55	1.4
Δ^2-Cholestene	1/32	1/1.4 (1/2.3)[e]
Octadecene (isom mix)	1/2.06	1/1.4
Cyclooctene	1/2.54	1.0
Cyclododecene (cis and trans)	1/4.45	1/1.5

[a] Measured by rate of hydrogen uptake at 1 atm. [b] 1 *M* olefin concentrations. [c] $(Ph_3P)_3RhCl$ 2.5 m*M*, in benzene at 25°. [d] The olefins were purified by distillation from sodium under nitrogen. [e] Ratio of H_2 uptake with 10% palladium on carbon.

The catalyst was easily recovered from the reagents by filtration and could be reused many times. The catalyst activity increased slowly to a maximum activity with use[8] and varied by ±5% over ten runs after the activity had maximized. The data given in Table I were obtained with one batch[9] of catalyst which reduced 1 *M* cyclohexene in benzene at a rate of 0.97 ml/min at 1 atm. The relative rates were determined by setting the rate of reduction of cyclohexene before and after the run on each olefin equal to 1.0. Different batches of the catalyst vary in activity.

Work is now in progress to further define the substrate specificity of these catalysts on the basis of substrate size, per cent of cross-linking in the polymer, and substrate polarity.

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[6] A plot of average molecular size, as determined from molecular models, *vs.* corrected relative rates of reduction shows a reasonably linear relationship.

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[9] Obtained by equilibrating 3.2 g of beads with 3.22 g of rhodium complex in 40 ml of benzene for 4 weeks under argon. Analysis showed 0.13 mmol of rhodium/g of beads.

An 11-Atom Polyhedral Metallocarborane Formed from 1,6-*closo*-$B_8C_2H_{10}$ by Polyhedral Expansion

Sir:

Recently the preparation of the $B_6C_2H_8^{2-}$,[1] $B_6C_2H_8^{4-}$,[2] and the $B_{10}C_2H_{12}^{2-}$ [3] ions by reduction of the corresponding *closo*-carboranes with sodium naphthalide and the reaction of these ions with transition metals have been reported. This method of creating polyhedral metallocarboranes may be called "polyhedral expansion" and may eventually prove to be a general reaction of *closo*-carboranes. We now wish to report the further extension of this synthetic method to form an 11-atom polyhedral complex containing formal Co(III) and the $B_8C_2H_{10}^{2-}$ ion, formed from 1,6-dicarba-*closo*-decaborane(10), 1,6-$B_8C_2H_{10}$.

Treatment of 1,6-$B_8C_2H_{10}$ in tetrahydrofuran (THF) at reflux with 2 equiv of sodium naphthalide, followed by addition of a fourfold excess of $Na^+C_5H_5^-$ and an excess of $CoCl_2$, yielded a mixture of products. A purple complex, formulated as $C_5H_5CoB_8C_2H_{10}$ (I), was isolated by column chromatography and recrystallized from hexane–dichloromethane in 38% yield, mp 297–300°. *Anal.* Calcd for $B_8C_2H_{10}CoC_5H_5$: B, 35.36; C, 34.37; H, 6.18; Co, 24.09. Found: B, 36.33; C, 34.03; H, 5.95; Co, 23.20. The mass spectrum exhibited a cutoff at *m/e* 246 corresponding to the $^{59}Co^{12}C_7{}^{11}B_8{}^1H_{15}^+$ ion. The electronic spectrum measured in acetonitrile was [λ_{max}, mμ (ϵ)] 230 (sh) (1100), 277 (3980), 352 (5820), 442 (382), 572 (455). The 32.1-MHz ^{11}B nmr spectrum in acetonitrile-d_3 contained doublets of relative area 1:2:1 at −8.5 (150), +9.5 (153), and +21.7 (139) [chemical shift, ppm, relative to $BF_3 \cdot O(C_2H_5)_2$ (coupling constant, Hz)]. The 60-MHz ^1H nmr spectrum consisted of a sharp singlet of area 5 at τ 4.32 and a broad singlet of area 1 at τ 3.28 which were assigned to the cyclopentadienyl and polyhedral C–H protons, respectively. A structure in which the cobalt completes an 11-member polyhedron with the carborane moiety is consistent with these data (Figure 1). This gross polyhedral geometry is seen in the $B_9C_2H_{11}$ carborane[4,5] and the isoelectronic $B_{11}H_{11}^{2-}$ ion.[6]

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