varying the steric demands of substituents around the periphery of our hydrogen-bonded components, we expect to be able to select from among alternative geometrical isomers of hydrogen-bonded assemblies in the solid state.

Supplementary Material Available: Brief synthetic outline, details of X-ray data collection, tables of crystal data and atomic positional parameters, and ORTEP drawings for both complexes (23 pages). Ordering information is given on any current masthead page.

β-Cyclodextrin/Pyridine Gel Systems. The Crystal Structure of a First β-Cyclodextrin–Pyridine–Water Compound

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General models for gel structure involve a dynamic interlocking three-dimensional network of solvent and "gelant" held together by ordered regions.[1-3] We report here the crystal structure of a compound in the β-cyclodextrin–pyridine–water gel system, which evidences such an interlocking network of β-cyclodextrin (β-CD) and solvent.

Isotropic physical gels are obtained from solutions of rigorously anhydrous β-CD in dry pyridine. For concentrations up to 2.5 × 10^{-1} M, melting points vary linearily with temperature; at higher concentrations the gels become sensitive to rapid temperature increases, with formation of a microcrystalline solid and free pyridine. Slow syneresis with formation of anhydrous needles[4] within the gel has been observed, although samples may be stable for several years. Ternary gels exist with toluene, chloroform, or tetrahydrofuran, with the cosolvent in the isotropic phase.

The ^{2}H NMR signals of pyridine-d_5 have line widths (10–15 Hz), in the melt and gel, typical for solution samples, implying the pyridine is in an isotropic fluid state. Solution technique ^{13}C NMR spectra of molten and gel samples show narrow line widths, requiring some β-CD molecules to be in an isotropic state. On going from liquid to gel, the intensity of the β-CD ^{13}C signals decreases considerably with respect to the signals of pyridine, due to a percentage of molecules becoming fixed in ordered junction zones as observed for agarose gels.[5] Addition of water by slow diffusion through the gel from $CuSO_4 \cdot 5H_2O$ yields a crystalline form, corresponding to the title compound.[6]

The structure is a novel packing of β-CD monomers that is less compact (2300 Å^3 per β-CD) than known monomeric (~1500–1750 Å^3) or dimeric (~1800 Å^3) structures. Monomers have been described either as the "herringbone" packing for hydrates[7] and inclusion[8] and cationic insertion[9] compounds or as arranged in sheets in the "brick" packing model.[10] Dimeric layers of inclusion compounds form C-centered layers in four classes of molecular packing.[11] In contrast to all of these compounds formed in aqueous solutions, in our pyridine medium, water was introduced under strict control.

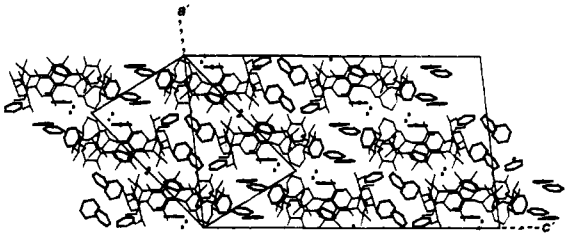

Figure 1. Projection of the structure along the *b* axis showing the packing of cyclodextrin layers in the triple unit cell: $a' = a + c = 23.641$, $b' = -b = 14.742$, $c' = 2a - c = 40.03$ Å, $\beta = 96.57°$ (similarly transformed anhydrous form: $a' = 22.135$, $b' = 15.224$, $c' = 39.94$ Å, $\beta = 95.83°$).

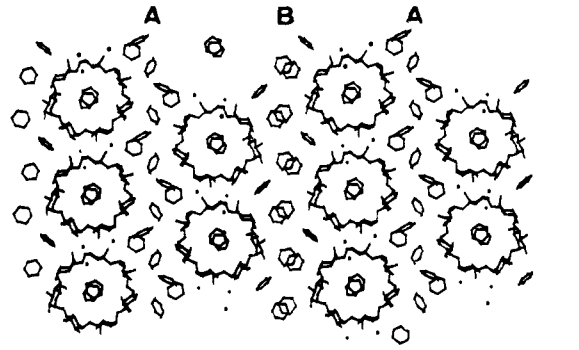

Figure 2. Section of the structure in the (1, 0, 2) plane, isolating a monomeric layer.

The crystal structure was solved using a new molecular replacement package.[12,13] Eight pyridine molecules per β-CD are located in inter- and intramolecular channels (Figure 1), and three water molecules are outside the cavity. One pyridine is included within the β-CD cavity, and a second is located at the primary hydroxyl level. Six others are present within two channels (A and B), both along the crystallographic 2-fold screw axis.

Sheets of β-CD molecules stacked nearly parallel to the *b* axis (inclination ≈ 10°) form an open arrangement of nonoverlapping β-CD monomers. The overall packing consists of layers, formed of pyridine and β-CD units, appearing with a 3-fold translational periodicity along $a' = a + c$; water molecules are located interlayer.

The interlayer distance (7.88 Å) is within the previously observed range; in the layers, β-CD molecules are packed more openly in a pseudo-C-centered arrangement (unit area 620 Å^2) than in dimer structures (unit area 460 Å^2). Each layer (Figure 2) contains two alternative symmetry-related rows of β-CD, each

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intermolecularly hydrogen bonded along the *b* axis via two primary hydroxyls in the sole intralayer hydroxyl–hydroxyl interaction; all other hydroxyl interactions are interlayer. These β-CD rows are separated by the A and B independent pyridine channels containing differently oriented pyridine molecules. In the layer, each β-CD is surrounded by six others: two at 14.74 Å and four at about 22 Å.

The layer stacking reveals the presence of a third channel interconnecting the A and B channels along the *a'* axis centered on each β-CD cavity, forming the three-dimensional pyridine network independent of, and interlocking with, the β-CD network.

This novel structure of a compound containing 40% weight of pyridine in a very low density β-CD packing shows a long-range ordering of solvent in a β-CD network, which may constitute a structural approach to the ordered zones of the gels. The gels may be considered to be in a metastable state of isotropic and ordered zones, with slow diffusion of discrete β-CD molecules giving crystallogenesis and expulsion of free pyridine.

Acknowledgment. This research was partly supported by MRT and Rhône Poulenc.

Supplementary Material Available: Tables of bond distances and angles, atomic coordinates, and isotropic thermal parameters for β-cyclodextrin–pyridine–water (9 pages); table of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

A Novel Ru-Catalyzed Tandem Cyclization–Reconstitutive Addition of Propargyl Alcohols with Allyl Alcohols

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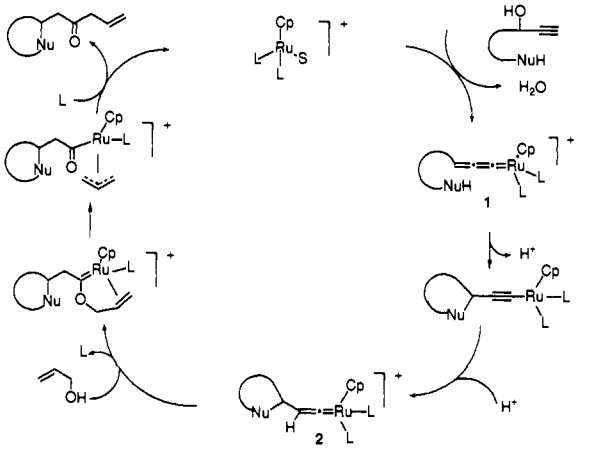
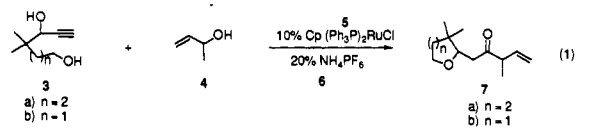
In spite of the known ability of many transition metals to form allenylidene complexes,[1,2] their chemistry remains largely unexplored.[3,4] Their ease of formation from ruthenium complexes[2] and their interesting structure wherein three carbons are potentially activated attracted our attention toward their potential for involvement in a catalytic cycle as outlined in Scheme I.[5] The success of this concept requires (1) more rapid formation and reaction of the allenylidene intermediate **1** toward the nucleophile than reaction of the vinylidene complex corresponding to the starting acetylene (which should form rapidly under the reaction conditions) with allyl alcohol, (2) lack of reactivity of the allenylidene complex toward allyl alcohols, (3) the ability of the substituted vinylidene complex **2** to participate in a catalytic cycle involving allyl alcohol, and (4) compatibility of the nucleophile with the mildly acidic conditions required for the addition of allyl alcohol.

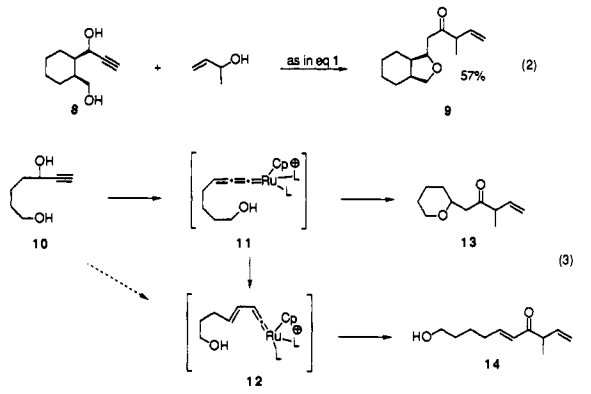
Scheme I. A Proposed Cyclization–Reconstitutive Addition Involving Allenylidene Metal Complexes as Reactive Intermediates



To test the feasibility of this concept, a neat mixture of propargyl alcohol **3a** and 3-buten-2-ol (**4**) containing 10 mol % Cp$(Ph_3P)_2$RuCl (**5**) and 20 mol % NH_4PF_6 (**6**) was heated at 100 °C for 8 h (eq 1). Direct flash chromatography gave a 61% yield of the tetrahydropyranyl ketone **7a**[6] as the exclusive product. Similarly, the tetrahydrofuranyl product **7b**[6] was obtained from the diol **3b** in 71% yield.



The *gem*-dimethyl group is not required (**8** → **9**,[6] eq 2), but it does facilitate cyclization (eq 3). In the latter case, the cyclized (**13**) and noncyclized (**14**) reconstitutive addition products were obtained in a nearly equimolar ratio in 69% yield. Most significantly, *exposure of either product to the reaction conditions does not interconvert it*! Apparently, the slower rate of ring closure in allenylidene complex **11** to give ultimately tetrahydropyran **13** allowed the process of deprotonation–reprotonation to vinylidene complex **12** with subsequent formation of acyclic enone **14** to compete.[7] Further, the vinylvinylidene complex **12** prefers to condense with 3-buten-2-ol rather than reenter the catalytic cycle leading to **13** under the reaction conditions.



Both primary (eqs 1, 2, 4c) and secondary (eq 4a,b) alcohols served as nucleophiles.[8] Good diastereoselectivity with respect

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(6) All new compounds have been fully characterized spectroscopically and their elemental composition established by high-resolution mass spectroscopy and/or combustion analysis. The diastereomers were not separated and were therefore characterized as the isomeric mixtures.

(7) Whether the vinylvinylidene complex forms directly from the propargyl alcohol or via the allenylidene complex is being debated. See ref 2c.

(8) As previously established, reactions with allyl alcohol are accompanied by some isomerization of the β,γ- to the α,β-unsaturated ketone—a process completed by incorporating a Rh-catalyzed isomerization as a step in the workup.

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