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 Poulenic.

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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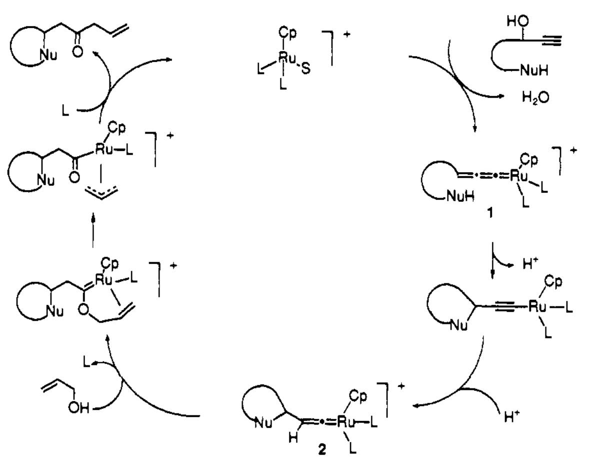
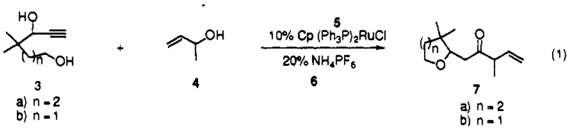
In spite of the known ability of many transition metals to form allenylidene complexes,[1,2] their chemistry remains largely unexplored.[3,4] Their ease of formation from ruthenium complexes[2] and their interesting structure wherein three carbons are potentially activated attracted our attention toward 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.

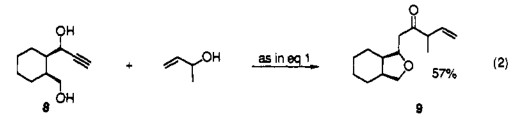
Scheme I. A Proposed Cyclization-Reconstitutive Addition Involving Allenylidene Metal Complexes as Reactive Intermediates

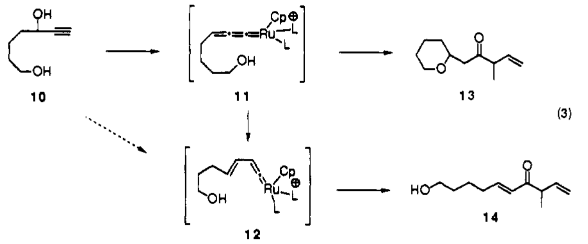


To test the feasibility of this concept, a neat mixture of propargyl alcohol **3a** and 3-buten-2-ol (**4**) containing 10 mol % Cp$(Ph_3P)_2RuCl$ (**5**) and 20 mol % NH_4PF_6 (**6**) was heated at 100 °C for 8 h (eq 1). Direct flash chromatography gave a 61% yield of the tetrahydropyranyl ketone **7a**[6] 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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[5] For reactions of terminal acetylenes and allyl alcohols, see: Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809. Trost, B. M.; Kulawiec, R. J. Unpublished work in these laboratories.

[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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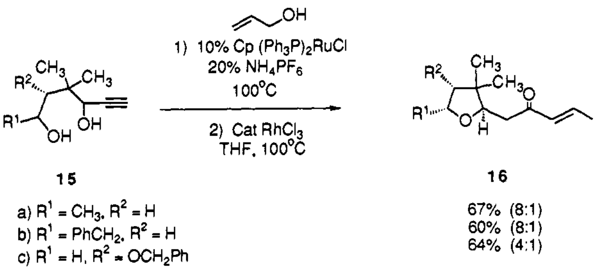


(4)

15

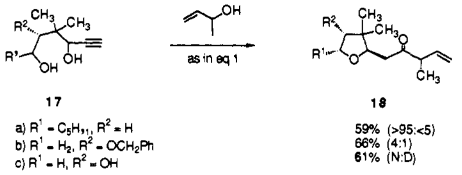
a) $R^1 = CH_3$, $R^2 = H$
b) $R^1 = PhCH_2$, $R^2 = H$
c) $R^1 = H$, $R^2 = OCH_2Ph$

16

67% (8:1)
60% (8:1)
64% (4:1)

to the formed ring was observed in all cases. Using the ^{13}C NMR correlations of Bartlett,[9] the major diastereomer was assigned as *E*. With allyl alcohol as the reaction partner, the initial adducts were directly equilibrated to the thermodynamically more stable (E)-α,β-unsaturated isomers.

Creation of a third stereogenic center in the β,γ-unsaturated chain by using 3-buten-2-ol occurs with little selectivity (eq 5). Since the α,β-unsaturated ketones derived by simple isomerization are synthetically more useful, the lack of stereocontrol in the side chain is less consequential. Ring stereochemistry, however, continues to be high. It is interesting to note that the presence of additional free alcohol as in **17c** did not interfere.



(5)

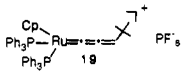
17

a) $R^1 = C_5H_{11}$, $R^2 = H$
b) $R^1 = H_2$, $R^2 = OCH_2Ph$
c) $R^1 = H$, $R^2 = OH$

18

59% (>95:<5)
66% (4:1)
61% (N:D)

A detailed discussion of the mechanism of this reaction is premature. The correctness of the gross scheme as initially outlined is supported by the success of the process and the reaction of propargyl alcohol **10**. That ring closure of **1** (or **11**) precedes addition of allyl alcohol is suggested by the total lack of reactivity of a stoichiometrically formed complex (i.e., **19**) with allyl alcohol.[10] Thus, the allenylidene and vinylidene complexes, while electrophilic, react quite selectively—the allenylidene requires the nucleophile to be internal whereas the vinylidene requires olefin coordination.[5] The sequence illustrates the ability of ruthenium



19

20

to make a propargyl alcohol function as an alternating charge system as in **20**. Use of allyl alcohols bearing substituents other than methyl should allow variation of the side chain substituent.[5] The likely prospects for discovering other reactions involving these novel organometallic intermediates demands more extensive investigation of their chemistry.

This novel construction of tetrahydrofuran and tetrahydropyrans by a tandem cyclization-reconstitutive addition creates four bonds and breaks two bonds in a single operation, thereby building molecular complexity[11] quite rapidly and with reasonable atom economy.[12]

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences, for their generous support of our programs. J.A.F. thanks NIH for a postdoctoral fellowship in partial support of his studies.

Supplementary Material Available: Listing of characterization data for **7a,b**, **9**, **16a–c**, and **18a–c** (3 pages). Ordering information is given on any current masthead page.

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[10] The reactions of terminally unsubstituted allenylidene complexes with heteroatom nucleophiles have been observed (see refs 2d and 3).

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$[Ru_6(Te_2)_7(CO)_{12}]^{2-}$: Hydrothermal Synthesis of a Novel Ru^{2+}/Te_2^{2-} Cluster and Its Relationship to $RuTe_2$

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The synthesis, structure, and chemistry of soluble precursor compounds leading to inorganic solid-state materials currently make up a very active research area.[1-4] However, the mechanism of how discrete molecules transform into ultimate solid-state structures either in solution or in the solid state remains obscure. Recent reports on $Ni_{20}Te_{18}(PEt_3)_{12}$[2a] and $Co_6Te_8(PEt_3)_6$[2e] clusters are concerned with probing the relationships between metal clusters and solid-state structures. The same relationships are being sought in a reverse approach by excising solids into cluster analogues.[5] On any account, clusters can be considered as intermediates between molecules and solids. From this standpoint, the structural resemblance between the intermediates and the ultimate inorganic solid should be discernible if such clusters can be intercepted. Here, we wish to describe a relevant, novel Ru^{2+}/Te_2^{2-} cluster $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ which, we hope, will provide further insight into this issue.

Compound $(Ph_4P)_2[Ru_6(Te_2)_7(CO)_{12}]$ was prepared by heating $Ru_3(CO)_{12}$ with Na_2Te_2 and Ph_4PCl in H_2O at 110 °C in a sealed Pyrex tube.[6] The centrosymmetric cluster $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$, with an idealized S_6 molecular symmetry, contains an octahedral array of six ruthenium atoms upheld by a central ditelluride Te_2^{2-} (Figure 1A). The tellurium atoms in this unit each bind to three ruthenium atoms, forming an Ru_3Te–$TeRu_3$ ethane-like fragment with a staggered conformation. Furthermore, the ruthenium atoms are bridged by six Te_2^{2-} units on the periphery. In the bridging Te_2^{2-} ligands, one Te atom bonds to a ruthenium atom while the other Te atom bridges two ruthenium atoms, acting on the whole as μ_3-type chelating ligands. Finally, the octahedral coordination geometry of each Ru atom is completed by two cis CO groups.

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[5] Lee, S. C.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 840–856 and references therein.

[6] (a) $Ru_3(CO)_{12}$ (64 mg, 0.1 mmol) was mixed with 5 equiv of Na_2Te_2 (150 mg, 0.5 mmol) and 6 equiv of Ph_4PCl (220 mg, 0.6 mmol). The reactants were sealed with 0.5 mL of H_2O in a Pyrex tube (~4 mL volume), and the reaction was run at 110 °C for 65 h. Washing of the reaction mixture with methanol and diethyl ether afforded black needle-like single crystals of $(Ph_4P)_2[Ru_6(Te_2)_7(CO)_{12}]$ (~70 mg) and some dark brown crystalline powder (~60 mg). Crystals suitable for X-ray single-crystal analysis were harvested by mechanical separation. Later, X-ray powder diffraction (XRD) and IR spectroscopic studies showed that the dark brown powder was identical to the black crystals (total yield of 71% based on Ru). The experimentally observed XRD patterns and those calculated from the single-crystal X-ray data are identical. (b) Crystal data for $(Ph_4P)_2[Ru_6(Te_2)_7(CO)_{12}]$: triclinic $P\bar{1}$; $Z = 2$; $a = 13.492$ (3) Å, $b = 13.474$ (4) Å, $c = 14.438$ (3) Å, $\alpha = 114.77$ (2)°, $\beta = 116.50$ (2)°, $\gamma = 90.74$ (2)°, $V = 2067$ (3) Å^3 at −94 °C. $2\theta_{max}$(Mo Kα) = 45.0°. The number of reflections measured 5743. Number of reflections having $F_o^2 > 3\sigma(F_o^2)$: 4368. A DIFABS correction was applied; $\mu = 59.9$ cm^{-1}. The minimum and maximum transmissions were 0.78 and 1.27, respectively. Final $R = 5.2\%$ and $R_w = 5.8\%$.

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