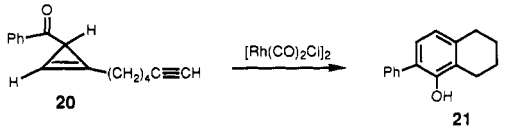
Our mechanistic rationale to account for the Rh(I)-catalyzed transformation is shown in Scheme I. Electrophilic attack of $[ClRh(CO)_2]_2$ on the more substituted carbon of the cyclopropene π-bond[8b] is followed by ring opening to give the rhodium-carbene complex **10**.[11,13] This carbenoid undergoes a subsequent [2 + 2]-cycloaddition reaction with the terminal alkyne in a manner analogous to that encountered with its Fischer carbene counterpart. Two cycloaddition pathways are possible. The major route is favored due to a minimization of steric interactions between the alkyl group on the carbenoid center and the substituent on the alkyne carbon. The resulting rhodacycle **11** rearranges to **12** either by a direct 1,5-sigmatropic shift or via a sequence involving a retro [2 + 2] ring opening followed by an 8π electrocyclization. The transient species **12** undergoes reductive elimination of rhodium to produce the observed oxepin **7**. A related sequence of reactions nicely rationalizes the formation of the minor phenol **8**, which is derived by an NIH shift[14] of the nonisolable oxepin **17** (i.e., **17** → **18** → **19** → **8**). Apparently, the presence of substituent groups on the 2- and 7-positions of oxepin **7** enhances its stability, thereby allowing for its isolation and characterization.[15] Oxepin **7** is in ready equilibrium with arene oxide **13**, and this transient undergoes a 1,2-phenyl shift upon treatment with acid to produce phenol **9** (via **15**) in excellent yield.[16]

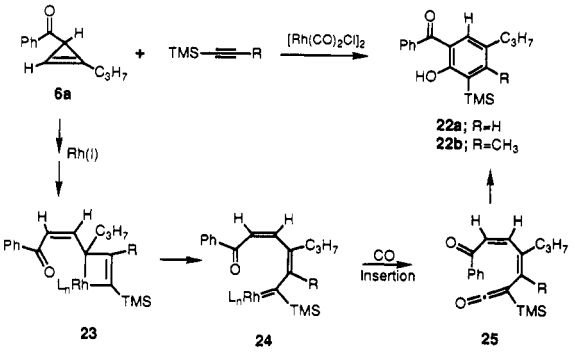
Encouraged by the bimolecular trapping results, we decided to investigate the intramolecular annulation reaction of cyclopropene **20** with the Rh(I) catalyst. The annulated phenol **21** was isolated in 45% yield and is presumably formed by a mechanism related to that described in Scheme I.



20 **21**

The above phenol synthesis has several attractive features worth noting. Mechanistically, cycloaddition of the carbenoid with a terminal alkyne (**10** → **11**) is a highly selective process which proceeds in a manner similar to that involved in the Fischer carbene benzannulation process. Instead of introducing the "CO" by insertion, the CO unit is already built into the backbone and is well set up for cyclization to the oxepin ring. The readily available acylcyclopropene ring serves as a 4-carbon synthon. Easy access to a variety of α-diazo ketones and terminal alkynes provides additional leverage to introduce a diverse array of substituents onto the phenol backbone. Finally, rather than using stoichiometric amounts of metal, an efficient catalytic cycle is involved.

One final point has to do with the reaction of cyclopropene **6** with trimethylsilyl-substituted alkynes. Introduction of the silyl group on the alkyne caused a significant change in the character of the reaction. Thus, when cyclopropene **6** was treated with (trimethylsilyl)acetylene in the presence of $[Rh(CO)_2Cl]_2$, none of the expected product was observed. Instead, a low yield of phenol **22a** was isolated. Carrying out the reaction under a CO atmosphere, however, afforded phenol **22a** in 47% yield. A related reaction also occurred using (trimethylsilyl)-1-propyne (i.e., **22b**). We suspect that the reaction proceeds via rhodacycle **23**, which ring opens to give **24**. This transient species prefers to undergo CO insertion, and this is followed by 6π electrocyclization and tautomerization to produce **22**.[17] The dramatic difference which results from changing the alkyne substituent to a silyl group is



not totally understood. Perhaps the steric bulk of the trimethylsilyl group present in **24** prevents this transient from achieving the proper geometry necessary for cyclization to the 8-membered rhodacycle. Alternatively, the ability of a silicon atom to stabilize the ketene backbone may promote the insertion reaction.[18] It should be noted that the CO insertion encountered here is significantly different from that reported by Liebeskind and Cho which provided α-pyrones.[13]

In conclusion, we have demonstrated that the Rh(I)-catalyzed reaction of acylcyclopropenes represents a new and novel approach toward substituted phenols. Further studies on the mechanism and synthetic potential of this method are in progress.

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Supplementary Material Available: Listing of spectroscopic data for new compounds (5 pages). Ordering information is given on any current masthead page.

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Very Fast Ester Hydrolysis by a Cyclodextrin Dimer with a Catalytic Linking Group

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Many artificial enzymes have been constructed with catalytic groups added to substrate binders such as cyclodextrins or synthetic cavities.[1] However, multiple binding interactions are needed to fix the geometry of a reactive substrate center relative to the catalytic groups. This approach was employed in the remote functionalizations of flexible substrates.[2,3]

Very high binding constants can result when two cyclodextrins are linked in ditopic hosts for substrates that have two hydrophobic ends,[4] particularly if *two* linking chains are used.[5] We have now prepared a cyclodextrin dimer with a metal-binding group in the linker. With substrate esters that doubly bind so as to put the ester group next to the metal ion, catalytic hydrolysis occurs with good turnover and very high rate accelerations. The mechanism apparently involves attack by a metal hydroxide species, as in many metalloenzymes.

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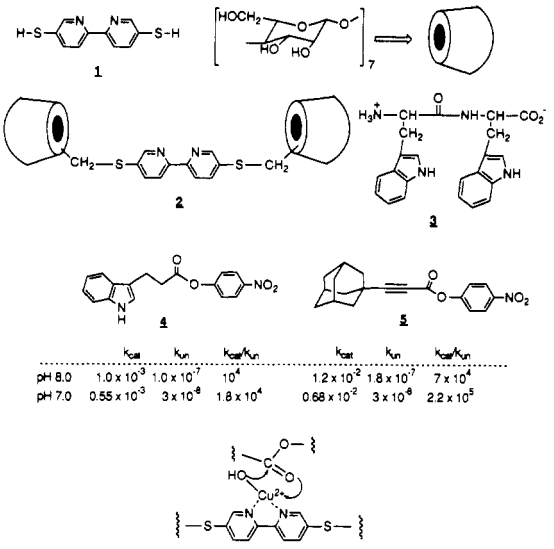

Figure 1.

Dithiol **1** was prepared by coupling of 3-methylpyridine to the bipyridine, conversion of the methyl groups to carboxyl and then amino, double diazotization, and reaction of the diazonium compound with potassium ethylxanthate. The resulting bis-dithiocarbonate was hydrolyzed and converted to the bis-thioacetate, and this was directly deprotected with NH_3 to the dianion of the dithiol **1** and used in the next reaction.

Reaction of the above dithiolate with β-cyclodextrin 6-iodide in DMF at 60–65 °C for 3 h afforded the cyclodextrin dimer **2** in 46% yield; it was isolated by reversed-phase chromatography and characterized by TLC, ^1H NMR, and FAB-MS (M + 1 = 2455). As expected, in water it was able to bind substrates having two appropriate hydrophobic groups. For instance, Trp-Trp **3** binds to **2** with an association constant of $(2.5 \pm 0.5) \times 10^6$ M^{-1}, raised 10-fold when Zn^{2+} is also bound to **2**.

The most striking property of **2** is the ability of some of its metal complexes to catalyze hydrolysis reactions of bound substrates. All reactions were performed in water at pH 7.0 or 8.0 and 37 °C, in contrast to many enzyme model studies that use extreme conditions. The k values (s^{-1}) shown in Figure 1 are the average of at least two runs, with good agreement.[6] Substrate **4** showed a rate enhancement for hydrolysis of over 10^4 (pH 7.0) with the Cu^{2+} complex of dimer **2** and of 80-fold without the Cu^{2+}. With simple β-cyclodextrin, the hydrolysis rate of **4** increased by a factor of only 30-fold, with and without Cu^{2+}.

With Cu^{2+} the data for rate vs pH and vs catalyst concentration fit a mechanism[8] in which the substrate binds to the Cu^{2+}/**2** catalyst, with $K_f = 7.0 \times 10^4$ M^{-1}, and is attacked by hydroxide bound to copper, from a bound water with $pK_a = 7.15$. Thus the observed acceleration relative to the simple hydroxide cleavage rate is at a maximum near pH 7. Ester **5** at 6.0×10^{-5} M shows a rate of hydrolysis with 1.0×10^{-4} M **2** and 2.0×10^{-4} M $CuCl_2$ at pH 7.0 and 37 °C that is 220 000-fold faster than the rate of uncatalyzed hydrolysis. The k_{cat} values are comparable in magnitude to those for the acylation step of one of the best catalytic antibodies by similar nitrophenyl esters.[9]

The nitrophenol and the corresponding carboxylic acid from **5** were both identified in approximately equal amounts by gas chromatography after isolation from the reaction catalyzed by Cu^{2+}/**2**. Furthermore, with an excess of substrate **5**, at least 50 turnovers were seen in the hydrolysis process. In our normal reactions the concentration of **5** is only 60% that needed (1.0×10^{-4} M) for solubility saturation, although in the turnover experiments it was 50 times higher and **5** was partially out of solution until the end of the hydrolysis reaction.

Thus, as hoped, stretching a substrate across a metal catalytic group has led to significant catalysis. We expect that the well-defined geometry in enzyme models using cyclodextrin dimers will lead to other advantages as well.

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(6) The least reliable are the values of k_{un} for pH 7.0, where the rates are extremely slow. However, the k_{un}'s at pH 8.0 are better defined, and those listed for pH 7.0 are if anything a little higher than expected for a reaction first order in OH^-. We have found previously[7] that the hydrolysis of **5** shows catalysis by buffer as well as by OH^-.

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Covalent Modification of Carbon Surfaces by Grafting of Functionalized Aryl Radicals Produced from Electrochemical Reduction of Diazonium Salts

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Modification of carbon surfaces is of interest to several fields of material science and electrochemistry. Probably most important from the industrial point of view is the modification of the surface of carbon fibers to improve the mechanical properties of composites, particularly carbon–epoxy composites.[1] Modification of electrode surfaces for catalytic or analytical purposes and biotechnological applications also currently attracts considerable attention.[2-8] Most of the available methods for modifying carbon surfaces involve their oxidation,[9-14] thus leading to the generation of superficial carboxylic, quinonic, ketonic, or hydroxylic groups[2] that are further reacted with the substance to be attached. The exact nature and number of oxygenated functional groups thus formed are difficult to ascertain and control, and corrosion of the carbon surface is often observed[15-17] leading to large background

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