A Rh^I-Centered Cage Compound with Selective Catalytic Properties**

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The development of synthetic catalysts that function according to the principles of enzymatic catalysis is a topic of great current interest. In the last decade examples of such systems—also called synzymes—have been reported.[1] Their number, however, is still limited. Taking nature as a guide, one can design a synzyme by combining a synthetic host molecule with an organic or inorganic catalyst. The objective is to bind a substrate selectively in the host and to achieve catalysis by positioning it in the correct orientation relative to the catalytic center.

In this communication we describe a cage compound with a Rh^I center, which preferentially binds allyldihydroxybenzenes and converts them into the corresponding styrenes and propyl derivatives by isomerization and hydrogenation of the allyl function. The frame of the cage is formed by the cleft molecule **1a**, which can bind catechol and resorcinol.[2] Binding in **1** occurs by π–π stacking and by hydrogen bonding interactions (Fig. 1). The catalytic center of the cage

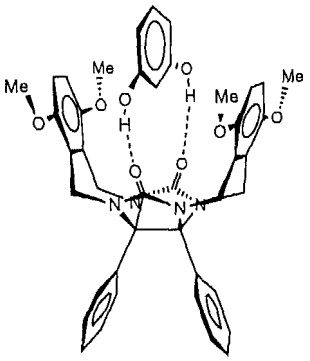
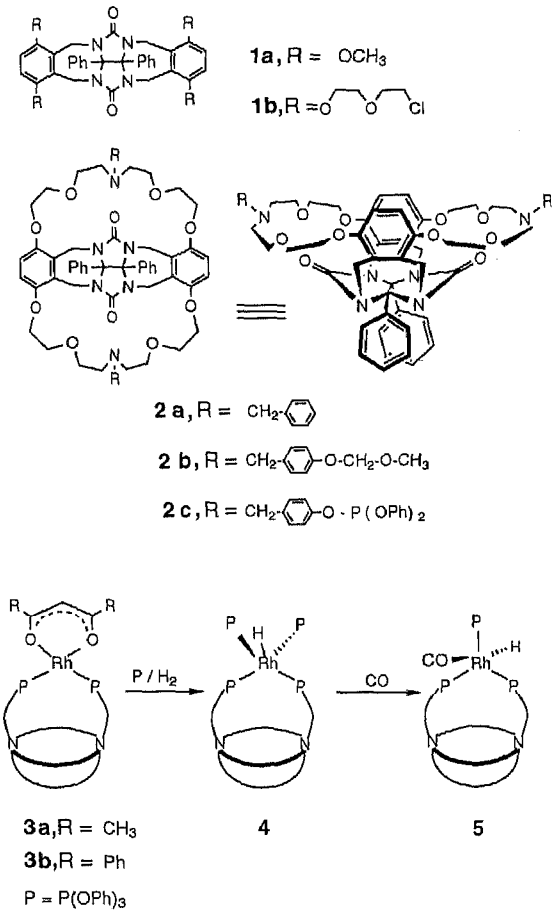


Fig. 1. Structure of the complex of **1a** with resorcinol.

compound is a triphenylphosphite–rhodium complex. The complex $[RhH(CO)\{P(OPh)_3\}_3]$ catalyzes hydroformylation and isomerization reactions.[3] We recently found that $[RhH\{P(OPh)_3\}_4]$ is an isomerization as well as a hydrogenation catalyst. We have succeeded in positioning these complexes above the cavity of compound **1** to form a substrate-selective catalyst.

Synthesis of the cage compound starts from the known diphenylglycoluril derivative **1b**.[4] Double ring-closure of **1b** with two equivalents of *para*-methoxymethyloxybenzylamine[5] in acetonitril resulted in the basket-shaped compound **2b** (71%). Acidic cleavage of the methoxymethyl protecting group in **2b** followed by reaction with $ClP(OPh)_2$ in dichloromethane yielded the bis(triarylphosphite) ligand **2c** in 94% yield. Compound **2c** was fully characterized by elemental analysis and spectroscopic methods (Table 1).

Addition of an equimolar amount of $[Rh(CO)_2(acac)]$ to a solution of **2c** in chloroform resulted in the quantitative exchange of the two carbonyl ligands in the rhodium complex for the phosphites of **2c** and the formation of cage complex **3a**. Cage compound **3b** was prepared in a similar way by using $[Rh(CO)_2(dbm)]$ (Hdbm = dibenzoylmethane)[6]. Space-filling models show that compounds of



type **3** can exist in different conformations, prescribed by the square-planar coordination of the metal in combination with the rigidity of the spacers. In complex **3a** the acetylacetonate

Table 1. Physical properties of the new compounds. Ar = aryl. Correct C,H,N analyses.

2c: Yield: 94%; ^{31}P NMR (80 MHz, $CDCl_3$, 25 °C, $(MeO)_3PO$): $\delta = 125.9$; ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.37-7.07$ (m, 38H; ArH), 6.70 (s; 4H), 5.66 (d, $^2J(H,H) = 16$ Hz, 4H; Ar-C*H*H-N), 4.23–4.06 (*m*, 4H; N-CH_2-Ar), 3.94–3.67 (m, 28H; -CH_2O, Ar-C*H*H-N), 2.88 (t, $^2J(H,H) = 5.6$ Hz, 8H; -CH_2-N); IR (CsI): $\tilde{\nu}$ [cm^{-1}] = 1712 (N-C(O)-N), 1197 (P-O-Ph), 504 ($P(OR)_3$); MS (FAB, *m*-nitrobenzyl alcohol): *m/z* 1522 ($M^+ + H$).

3a: Yield after isolation: 85%; ^{31}P NMR (80 MHz, $CDCl_3$, 25 °C, $(MeO)_3PO$): $\delta = 121.4$, 121.3, 121.2, 120.2 (d, $^1J(Rh,P) = 304$ Hz); ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.33-7.00$ (m br, 38H; ArH), 6.67–6.63 (m br, 4H; ArH), 5.65 (d, $^2J(H,H) = 16$ Hz, 4H; Ar-C*H*H-N), 5.07 (s, 1H; Me-C-C*H*-C-Me), 4.11–3.50 (m br, 32H; N-CH_2-Ar, -CH_2-O, Ar-C*H*H-N), 2.88–2.75 (m br, 8H; -CH_2N), 1.51–1.50 (m, 6H; -CH_3); IR(CsI): $\tilde{\nu}$ [cm^{-1}] = 1715 (N-C(*O*)-N), 1580 (C-C, diketone), 1197 (P-O-Ph), 596 (diketone).

3b: Yield after isolation: 85%; ^{31}P NMR (80 MHz, $CDCl_3$, 25 °C, $(MeO)_3PO$): $\delta = 120.7$, 120.5, 119.1 (d, $^1J(Rh,P) = 304$ Hz); ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.56-6.92$ (*m* br, 48H; ArH), 6.64–6.49 (m br, 5H; ArH, Ar-C-C*H*-C-Ar), 5.64 (d, $^2J(H,H) = 16$ Hz, 4H; Ar-CH*H*-N), 4.07–3.62 (m br, 32H; N-CH_2Ar, -CH_2-O, Ar-C*H*H-N), 2.95–2.63 (m br, 8H; -CH_2-N); IR (CsI): $\tilde{\nu}$ [cm^{-1}] = 1712 (N-C(O)-N), 1542 (C-O, diketone), 1194 (P-O-Ph), 592 (diketone).

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ligand can be *above*, *in*, *partially in*, or *next to* the cavity. In line with this, the ^{31}P NMR spectrum of **3a** shows four doublets at 120.2, 121.2, 121.3, and 121.4 ($J_{Rh,P} = 304$ Hz); the intensity ratio varies with conditions. With more bulky substituents R the diketonate ligand does not fit *inside* the cavity. Therefore, in the ^{31}P NMR spectrum of **3b** only three doublets at $\delta = 119.1$, 120.5, and 120.7 ($J_{Rh,P} = 304$ Hz) are observed. Compounds **3a** and **b** can be isolated by precipitation in hexane (Table 1).

The binding properties of cage complex **3b** were evaluated by monitoring the shift of various cage and guest signals in ^1H NMR titrations.[7] A titration with resorcinol gave an association constant of $K_a = 2850 \pm 300\,M^{-1}$, in good agreement with the value measured for the reference compounds **1a** ($K_a = 2600 \pm 400\,M^{-1}$)[2] and **2a** ($K_a = 2900 \pm 300\,M^{-1}$)[8]. In the case of catechol it was not possible to observe a shift directly because of serious overlap of signals. The association constant for this guest was therefore determined in a competition experiment with resorcinol. The value found, $K_a = 200 \pm 100\,M^{-1}$, is also comparable with that of the binding of catechol in **1a** ($K_a = 60 \pm 10\,M^{-1}$)[2] and in **2a** ($K_a = 70 \pm 30\,M^{-1}$).[8]

Addition of a small excess of $P(OPh)_3$ to **3** in chloroform in the presence of H_2 afforded the hydrido complex **4**. The phosphites in this compound surround the Rh center tetrahedrally, and the hydride is positioned along one of the trigonal axes.[3c, 9] The two P atoms of the $P(OPh)_3$ ligands on the one hand and those of ligand **2c** on the other have almost the same δ and $J_{Rh,P}$ values. Therefore, the $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits one doublet at δ=127.6 with some second order features ($J_{Rh,P} = 229$ Hz) (Fig. 2, left). Because of this nonequivalence combined with the fact that two pairs of faces of the tetrahedron are unequal, the doublet of quintets of the hydride signal in the high-field ^1H NMR spectrum ($\delta = -11.0$, $J_{P,H} = 44$ Hz) is broadened (Fig. 2, right). Even when a large excess of free $P(OPh)_3$ is present, no phosphorus signal of uncoordinated phosphite groups of **2c** was observed. This demonstrates the strong chelate effect of **2c**.[10]

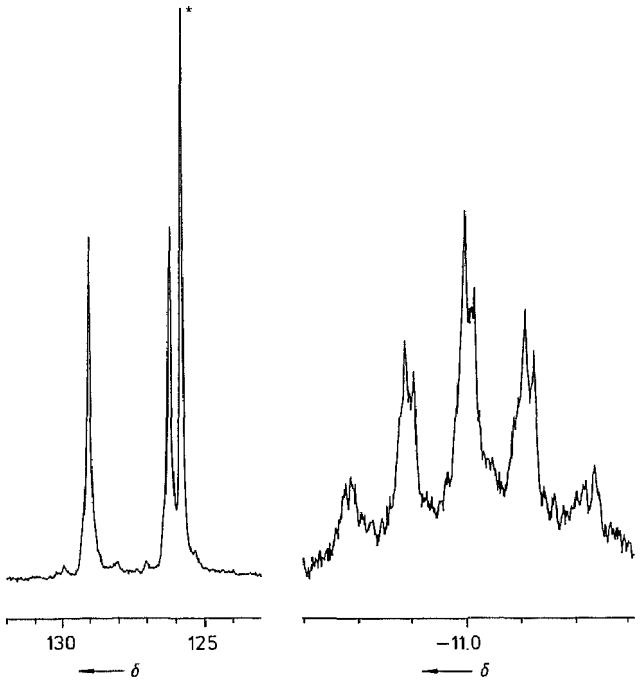


Fig. 2. Left: The $^{31}P\{^1H\}$ NMR spectrum of **4**. The signal marked with an asterisk is due to free $P(OPh)_3$. Right: The hydride region of the ^1H NMR spectrum of **4**.

Bubbling CO through a solution of **4** in chloroform gave the carbonyl hydride cage complex **5**. Compound **5** could also be obtained directly by treating **3a** or **3b** with a mixture of CO and H_2 in the presence of a small excess of $P(OPh)_3$. The model compound $[RhH(CO)\{P(OPh)_3\}_3]$ has a trigonal bipyramidal structure and exhibits only one doublet in its ^{31}P NMR spectrum, because of the equivalence of the P atoms and the very small *cis* P–H coupling.[3c] In the case of cage complex **5**, the $^{31}P\{^1H\}$ NMR spectrum showed a complex doublet at $\delta = 138.6$ ($J_{Rh,P} = 239$ Hz). We attribute this complexity to the nonequivalence of the P atoms in **5**.

Under Ar (1 atm) and in the presence of a small excess of $P(OPh)_3$ a solution of **5** in $CHCl_3$ is able to isomerize an equimolar amount of 4-allylcatechol (**6**)[11] to the corresponding *cis*- and *trans*-methylstyrenes in a ratio of about 1:3. Allylbenzene showed a much lower reactivity under the same conditions (monitored by ^1H NMR spectroscopy; Fig. 3). In two hours 68% of the allylcatechol had been

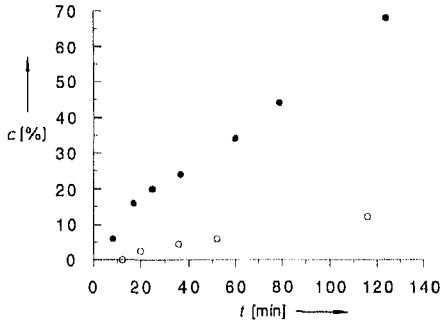
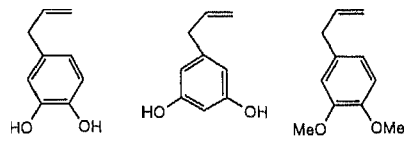


Fig. 3. The isomerization of 4-allylcatechol (•) and allylbenzene (○) in separate experiments by **5**.

converted, while in the same period only 12% of the allylbenzene had reacted. The conversion of 4-allylcatechol starts immediately, whereas for allylbenzene an induction period of about 10 min is observed. In accordance with the literature,[3e] we assume that the actual catalyst is the hydride **4**. This catalyst is probably generated by the substrate itself: in the first step the propylenic substituent displaces the CO ligand. This explains the induction time of the reaction with the nonbinding substrate. From these results we conclude that the isomerization preferentially takes place *inside* the cavity of **5**.

In order to decide whether the reaction is truly catalytic and to exclude possible electronic effects of the substituents on the substrate we carried out a competition experiment with **4** and a fourfold excess of substrates **6**–**8** in chloroform.



6 **7** **8**

Substrate **8** is not bound in the cavity of **2**. The association constants for **6** and **7**[12] in **2a** were measured by ^1H NMR titrations to be $K_a = 90 \pm 20\,M^{-1}$ and $K_a = 2200 \pm 200\,M^{-1}$, respectively. Under a hydrogen atmosphere ($p\,H_2 = 1.2$ atm) the substrates were completely converted into products, mainly the propyl derivatives. The conversion and

product formation was followed by gas chromatography. A clear correlation was observed between the rate of conversion and the association constant of the substrate: $t_{1/2}$ of the conversion for **7**, **6**, and **8** amounted to 5, 10, and 38 min, respectively. In individual experiments under the same conditions, substrates **6**–**8** were each converted by $[RhH\{P(OPh)_3\}_4]$ at approximately the same rate ($t_{1/2} = 25$ min). From these results we conclude that the reaction of the bound substrate is accelerated by **4**, whereas that of the nonbound is delayed.

The fact that **4** can still react with **8** suggests that the rhodium center in the cage complex is not completely shielded from the solution. Work is now in progress to functionalize the top part of **4** with a cap, which may further improve the selectivity of the catalyst.

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Scavenger Templates: Synthesis and Electrospray Mass Spectrometry of a Linear Porphyrin Octamer**

By *Sally Anderson, Harry L. Anderson,* and *Jeremy K. M. Sanders**

Recently we described how cyclic porphyrin oligomers can be assembled with amine ligands as templates and demonstrated two complementary roles for a template.[1] A positive template brings together two reactive ends of a single molecule, encouraging intramolecular cyclization, while a negative template holds the ends apart, inhibiting intramolecular cyclization and so encouraging intermolecular reaction (Fig. 1). Here we report a new role for positive templates:

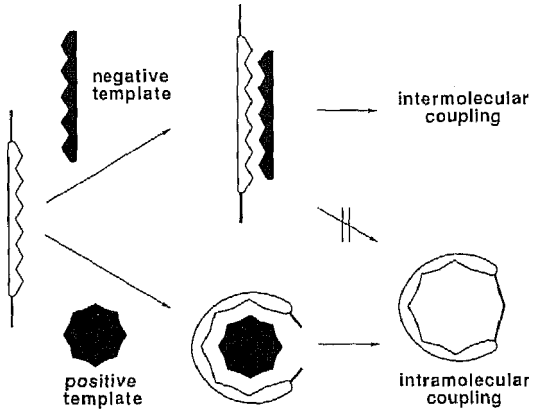
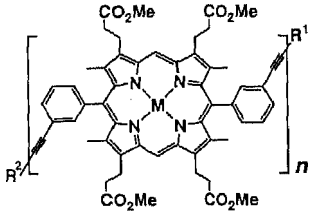
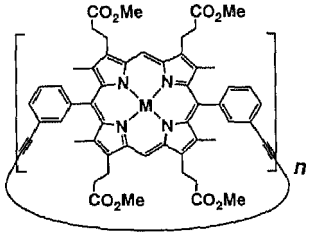


Fig. 1. The use of positive and negative templates to control the outcome of a reaction.

they can scavenge the cyclizable material in a complex mixture and so facilitate the synthesis of linear oligomers.[2] We start by outlining the idea of scavenger templates in general terms and then illustrate its application with the remarkably efficient synthesis of linear porphyrin octamer **1a** from the linear dimer **3a** via linear tetramer **2a**. We also demonstrate



1: $n = 8$ **a**: $R^1 = R^2 = SiMe_3$
2: $n = 4$ **b**: $R^1 = H$, $R^2 = SiMe_3$
3: $n = 2$ **c**: $R^1 = R^2 = H$



4: $n = 2$ $M = Zn, H_2$
5: $n = 4$

the use of electrospray mass spectrometry (ES-MS)[3] to determine the size and the purity of these molecules, which are otherwise rather difficult to characterize.

A common approach to the building-up of linear oligomers is to deprotect one end of a doubly protected oligomer containing n monomer units and couple it to give a fully protected oligomer containing $2n$ units. The cycle can be repeated as required. Partial deprotection gives a statistical mixture of fully protected, monoprotected, and fully deprotected compounds, which creates difficulty in the coupling step: fully protected material is inert, so it does not need to be separated before coupling, but fully deprotected material can couple with monoprotected material, leading to a new reactive oligomer and ultimately to a complex mixture. Conventionally this problem is avoided by separation of doubly deprotected material before coupling, but separation becomes more difficult with longer oligomers and so limits the chain length that can be achieved.

Scavenger templates overcome this problem by preventing fully deprotected molecules from undergoing bimolecular

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