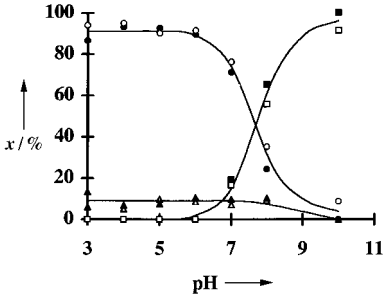

Figure 1. Distribution of water-soluble ruthenium(II) hydrides as a function of pH value based on the integrated intensities of ^{1}H (filled symbols) and ^{31}P NMR signals (empty symbols) of [HRuCl(tppms)$_3$] (●, ○, [H$_2$Ru(tppms)$_4$] (■, □), and [{HRuCl(tppms)$_2$}$_2$] (▲, △). [Ru] = 2.4 × 10^{-2} M, [TPPMS] = 7.2 × 10^{-2} M, 0.2 M KCl, 50 °C, H$_2$, p_{total} = 1 bar.

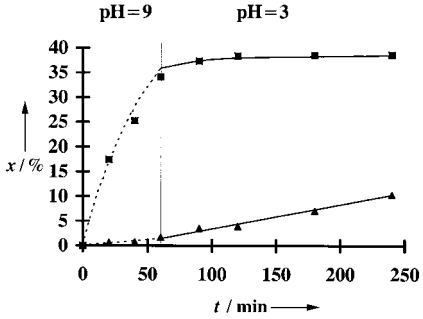

Figure 2. Selectivity of the hydrogenation of cinnamaldehyde to cinnamyl alcohol (■) and dihydrocinnamaldehyde (▲) as a function of pH value. For further details, see the Experimental Section.

Figure 2. The reaction was run for one hour at pH 9, and there was high selectivity towards formation of the unsaturated alcohol. Afterwards the pH value was lowered with HCl to 3, which halted the reduction of the aldehyde. Instead, hydrogenation of the C=C bond was observed. There was a complete inversion of selectivity.

Our results clearly show the effect that the pH value has on the rate and selectivity of the catalyzed reactions. Providing static-pH conditions is a must for performing meaningful mechanistic studies and for obtaining selective reactions.

Experimental Section

The pH of a solution of 0.2 M KCl (10 mL) kept at 60 °C was adjusted to the desired value (2–12) with HCl or KOH. Complex **3a** (40 mg) and **1** (50 mg) were dissolved in this solution under Ar. After equilibration, the Ar atmosphere was replaced by a H_2 atmosphere. During the dissolution and the hydrogenation of the complex the pH value was kept constant by delivering 0.2 M KOH with a Radiometer ABU 91 autoburette, and the extent of proton production in reaction (a) and (b) was calculated from the volume of added base. For recording the ^{1}H and ^{31}P NMR spectra of the final solutions (Bruker WP 360 SY, 50 °C), the solvent contained 20 % D_2O.

In a three-necked flask equipped with a reflux condenser a mixture of chlorobenzene (5 mL) and 0.2 M KCl (3 mL) buffered with Na_2HPO_4/NaH_2PO_4/HCl was purged for 15 min with H_2 at room temperature. Complex **3a** (10 mg) and **1** (12 mg) were added, and the mixture was heated to 80 °C under H_2. Following the appearance of the characteristic purple (**4a**) or yellow color (**5a**), cinnamaldehyde (50 μL) was added, and the mixture stirred vigorously. Samples of the organic phase were analyzed by gas chromatography (Chrom 5, Carbowax 20 M, 2-m packed column, 200 °C).

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[8] [{HRuCl(tppms)$_2$}$_2$]: ^{1}H NMR: $\delta = -8.9$ (td, J(P,H) = 36 Hz, J(H,H) = 8 Hz); ^{31}P NMR: $\delta = 51.6$ (br s). **4a**: ^{1}H NMR: $\delta = -18.0$ (q, J(P,H) = 21 Hz); ^{31}P NMR: $\delta = 59.0$ (br s). **5a**: ^{1}H NMR: $\delta = -10.3$ (pseudo q, J(P,H) = 34 Hz); ^{31}P NMR: $\delta = 42.5$ (s), 53.2 (s). These data are in agreement with those in ref. [3a] and with those for analogous tppts complexes.[5, 9] The ^{1}H and ^{31}P NMR chemical shifts did not show a systematic change within pH 3 and 10.

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Hemicarceplexes That Release Guests upon Irradiation**

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In the last decade methodology has been developed primarily by Cram and Sherman to trap ("incarcerate") organic molecules within closed-shell organic molecules.[1, 2] The general term hemicarceplex was coined to describe a host for which it is possible to exchange encapsulated guests. When the kinetic barrier for guest entrance and egress is sufficiently high, hemicarceplexes are created which are stable indefinitely at room temperature, and extreme conditions are required to free the encapsulated guest.[3] However, useful systems for the delivery of chemical reagents or therapeutic agents should bind neutral species tightly, be chemically inactive with respect to the bound species, and release the

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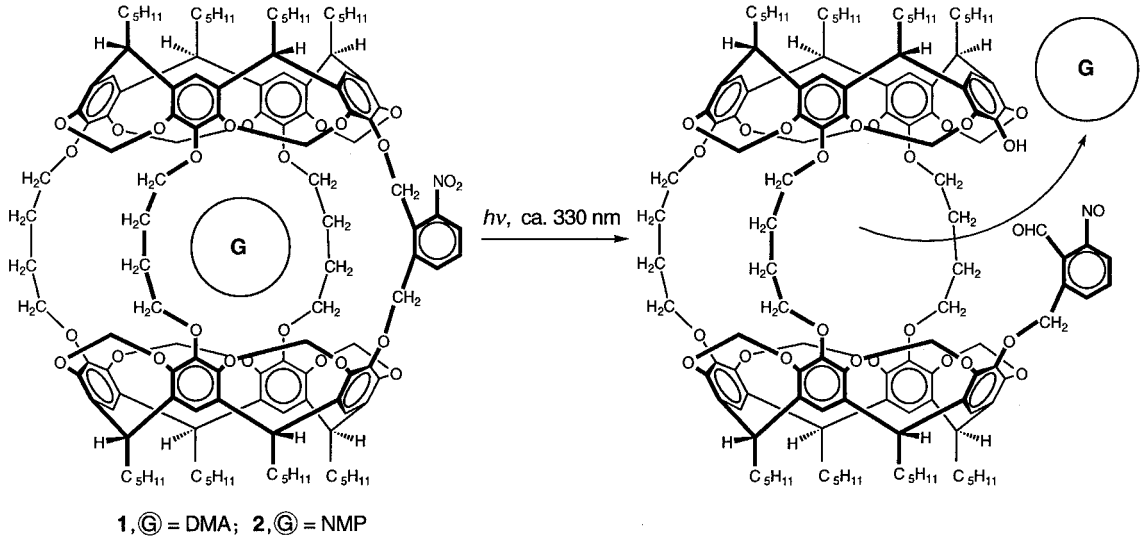

Scheme 1. Schematic representation of the photoinduced release of a guest molecule Ⓖ from a photoactive hemicarceplex.

bound species under definite, easily controlled conditions. We report here new photoactive complexes which are indefinitely stable at room temperature in the dark, but release guests upon irradiation.

Many examples are known where the hydrogen-abstraction reaction of the 2-nitrobenzyl group initiates bond cleavage that releases the substituent attached at the benzyl position.[4] Important applications of this chemistry range from photochemical release of adenosine triphosphate (ATP)[5] to the work of Grell and Warmuth,[6] in which a cryptand incorporating a 2-nitrobenzyl group releases alkali and alkaline earth cations upon irradiation. The concept of a photoactive carcerand is illustrated in Scheme 1. Irradiation leads to cleavage of one phenol ether bond with formation of a large gap in the host shell, through which the incarcerated guest can egress.[7]

The methodology of Cram[8] for creating hosts with mixed bridging units was used to synthesize complexes **1**, which contains a dimethyl acetamide (DMA) guest, and **2**, which contains a *N*-methyl-2-pyrrolidinone (NMP) guest. The position of the guest can easily be monitored by ^{1}H NMR spectroscopy: Upon encapsulation, the signals for the guest's protons (Table 1) are shifted upfield by over 2 ppm compared to the spectrum in chloroform solution. Although hemicarceplexes **1** and **2** are stable indefinitely at ambient temperature, the precursor, which contains only three butylene bridging units, does not retain a detectable amount of either DMA or NMP within its interior. It was believed that the photocleavage products of **1** and **2** would behave similarly.

From NMR spectroscopic studies, it is clear that the amount of released guest increases linearly with time until approximately 60 % of **1** or **2** are emptied. The results for **2** are shown in Figure 1. Once irradiation is stopped, guest release and photocleavage terminate in all cases. The cleavage reaction is independently monitored by the appearance of the proton signal for the photoproduct aldehyde at $\delta = 11.5$; the rate of appearance of the photoproduct corresponds to the rate of guest release. The rates of guest release for both hemicarceplexes show a linear dependence on light intensity, indicating that decomplexation is a single-photon process. This evidence supports a model in which excitation of the nitroxylyl group leads to bond cleavage, which removes the kinetic barrier to guest egress. The rate of DMA and NMP release are the same within experimental error, indicating that the portal formed is too large to retain guests containing six or seven heavy atoms.

A second class of photoactive hemicarceplexes with analogous thermal stability was constructed[9] in which all

Table 1. Selected data for compounds **1**–**3**.

1: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.69$ (d, 1H; CH (nitroxylyl group)), 7.52 (d, 1H; CH (nitroxylyl group)), 7.40 (t, 1H; CH (nitroxylyl group)), 6.80 (m, 8H; CH (cage)), 5.74 (2d, 4H; H_{outer}), 5.68 (d, 2H; H_{outer}), 5.58 (d, 2H; H_{outer}), 5.28 (s, 2H; CH_2 (nitroxylyl group)), 5.14 (s, 2H; CH_2 (nitroxylyl group)), 4.66 (m, 8H; CH (methine)), 4.29 (d, 2H; H_{inner}), 4.22 (d, 2H; H_{inner}), 4.11 (d, 4H; H_{inner}), 3.85 (brs, 12H; α-CH_2 (tetrymethylene bridge)), 2.17 (brs, 16H; CH_2 (pentyl) and CH_3 (DMA)), 1.92 (m, 12H; β-CH_2 (tetrymethylene bridge)), 1.39 (m, 48H; $(CH_2)_3$ (pentyl)), 0.93 (q, 24H; CH_3 (pentyl)), −0.79 (s, 3H; CH_3 (DMA)), −1.89 (s, 3H; CH_3 (DMA)); FAB$^+$-MS for $[M^+]$: calcd 2157.121, found 2157.122; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 276$ (5500)

2: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.73$ (t, 2H; CH (nitroxylyl group)), 7.45 (t, 1H; CH (nitroxylyl group)), 6.80 (4s, 8H; CH (cage)), 5.74 (d, 4H; H_{outer}), 5,72 (d, 2H; H_{outer}), 5.50 (d, 2H; H_{outer}), 5.30 (s, 2H; CH_2 (nitroxylyl group)), 5.18 (s, 2H; CH_2 (nitroxylyl group)), 4.65 (m, 8H; CH (methine)), 4.26 (d, 2H; H_{inner}), 4.22 (2d, 4H; H_{inner}), 4.09 (d, 2H; H_{inner}), 3.85 (m, 12H; α-CH_2 (tetrymethylene bridge)), 2.16 (brs, 16H; CH_2 (pentyl)), 1.95 (brs, 12H; β-CH_2 (tetrymethylene bridge)), 1.80 (t, 2H; CH_2 (NMP)), 1.38 (m, 48H; 3CH_2 (pentyl)), 0.93 (q, 24H; CH_3 (pentyl)), −0.87 (t, 2H; CH_2 (NMP)), −1.10 (m, 5H; CH_2 and CH_3 (NMP)); FAB$^+$-MS for $[M^+]$: calcd 2169.121, found 2169.123; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 276$ (5500)

3: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.76$ (brd, 4H; CH (nitroxylyl group)), 7.50 (m, 8H; CH (nitroxylyl group)), 6.80 (2s, 8H; CH (cage)), 5.46 (d, 4H; H_{outer}), 5.30 (m, 14H; CH_2 (nitroxylyl group) and H_{outer}), 5.09 (m, 8H; CH_2 (nitroxylyl group)), 4.59 (m, 8H; CH (methine)), 4.00 (m, 8H; H_{inner}), 2.16 (brs, 16H; CH_2 (pentyl) and CH_3 (DMA)), 1.38 (m, 48H; 3CH_2 (pentyl)), 0.93 (q, 24H; CH_3 (pentyl)), −1.30 (m, 3H; CH_3 (DMA)), −1.26 (m, 3H; CH_3 (DMA)); FAB$^+$-MS for $[M^+ + H]$: calcd 2437.084, found 2437.084; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 276$ (11900)

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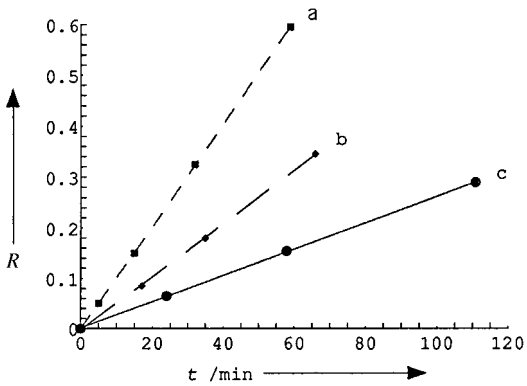
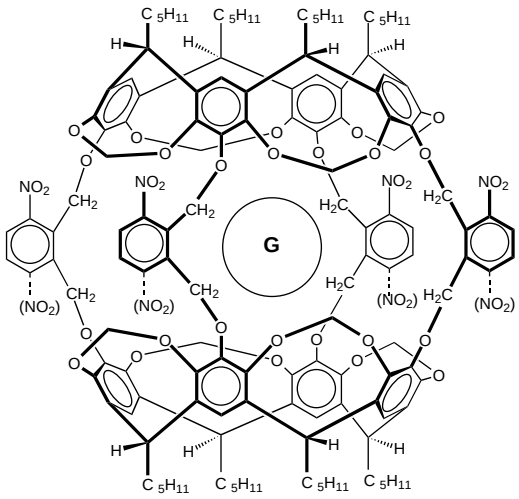


Figure 1. Ratio R of NMP released from **2** to total NMP plotted as a function of irradiation time at various light intensities: a) 2.6, b) 1.3, c) 0.65 W.

four bridging units incorporate the 3-nitro-*ortho*-xylyl functionality. Complex **3** exists as a mixture of inseparable isomers, as indicated by the complexity of the ^{1}H NMR spectrum (Table 1). The isomers differentiate themselves by the relative positions of the nitro groups around the middle of



3, G = DMA

the host (this is symbolized in the drawing by a dashed line between the benzene ring and the NO_2 group in parentheses). The photochemical properties of the four possible isomers are expected to be the same since the number of photoactive groups is equivalent in each case, and each 3-nitro-ortho-xylyl group is believed to react independently.

The absorption of the cage partially masks the absorption of the nitroxylyl groups in the region of the spectrum that was irradiated.[7] However, in the region of maximum light filter transmittance, at approximately 330 nm, the contribution of the nitroxylyl absorption is greater than that of the rest of the host and shows a significant increase when the number of nitroxylyl groups is increased. For example, the extinction coefficient ε in chloroform at 330 nm is $1055\,\text{M}^{-1}\text{cm}^{-1}$ for **1** and **2**, and $2950\,\text{M}^{-1}\text{cm}^{-1}$ for **3**. When solutions with equal concentrations of **1**, **2**, and **3** in chloroform were irradiated, the rate of guest release for **3** is 3.2 times faster than for **1** and **2**. It appears that the introduction of additional nitroxylyl groups increases the probability of a photochemical reaction leading to guest egress. The rate of guest release from **3** also increases linearly with light intensity, showing that guest release is a single-photon process and strongly suggesting that guest release occurs upon a single bond cleavage. In summary, all the photoactive hosts described here release guests into chloroform solution upon irradiation, and the rate of guest release can be controlled by modifying either host absorption or light intensity.

All hemicarceplexes discussed here undergo slow decomplexation when exposed to ambient light over long periods of time, but are stable indefinitely when kept in the dark. Hosts **1**, **2**, and **3** have broad absorption spectra ranging from 240 to 460 nm. A slow photochemical reaction may result from absorption of near-UV and visible light, even if that of the latter is very small. The thermal stability and photoactivity of these hemicarceplexes indicate that incarceration is potentially useful for the controlled delivery of chemical agents. An extension of this work to other hosts, including those which are soluble in aqueous solutions, is currently underway in our laboratory.

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