Encapsulation of Cationic Ruthenium Complexes into a Chiral Self-Assembled Cage

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A chiral supramolecular assembly encapsulates the two cationic ruthenium sandwich complexes [CpRu(η⁵-C₆H₅)]⁺ and [CpRu(η⁶-cymene)]⁺. The host–guest complexes K₁₁[CpRu(η⁵-C₆H₅)]⁺⊂Ga₄L₆ (2) and K₁₁[CpRu(η⁶-cymene)]⁺⊂Ga₄L₆ (3) were characterized by one- and two-dimensional NMR techniques as well as by electrospray mass spectrometry. Encapsulation of the prochiral complex [CpRu(η⁶-cymene)]⁺ by the chiral host renders enantiotopic protons diastereotopic as evidenced by ¹H NMR spectroscopy.

The control of reactivity at a catalytic metal center is often achieved by tailoring the ligands coordinated to the metal. Sophisticated chiral ligands or chiral additives can be utilized to achieve stereoselectivity in metal-catalyzed transformations. However, another way to achieve stereoselectivity is to regulate the secondary coordination sphere by using the well-defined environment of a chiral supramolecular host. Thus the encapsulation of transition metal catalysts can lead to a new class of molecular reactors with catalytic properties determined by both catalyst and host. For example, enantioselective reactions could be envisioned to proceed with an achiral catalyst inside a chiral cavity. The use of supramolecular structures as molecular reaction vessels for organic transformations has been reported, and only recently a few papers on encapsulation of organometallic complexes into preformed cavities have been published.

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Figure 1. View down the 3-fold axis of the Ga₄L₆ tetrahedral assembly, encapsulating [CpRu(η⁵-C₆H₅)]⁺. Six bis-bidentate catechol amide ligands span the edges of the tetrahedron, and the Ga³⁺ atoms are located on the vertices (red spheres). Left: CAChe model, energy minimized (MM3) with one ligand highlighted in black. Right: Schematic; five of the six ligands are drawn as lines for clarity.

In pursuing encapsulated organometallic chemistry it is necessary to identify suitable substrates whose reactivity, size, and shape are compatible with the supramolecular assembly. Cationic ruthenium catalysts are used for a wide variety of C–C bond formation reactions. Examples of such reactions include alkene–alkyne coupling and formation of 1,3-diienes from allenes. Since Cp₂Fe⁺ and Cp₂Co⁺ were found to encapsulate in the M₄L₆ assembly, we turned our attention to similarly hydrophobic cationic ruthenium complexes. Here we report the encapsulation of the organometallic complexes [CpRu(η⁶-C₆H₅)]⁺ (Figure 1) and [CpRu(η⁶-cymene)]⁺ into a chiral host, constructed from achiral components.

The host–guest chemistry of tetrahedral M₄L₆ assemblies (M = Ga³⁺, Al³⁺, Fe³⁺; L = 1,5-bis(2',3'-dihydroxybenzamido)naphthalene), composed of simple metal and ligand components, has been investigated. The hosts are water soluble but have hydrophobic cavities into which they can
bind a variety of cationic guest molecules. The strength of guest binding strongly depends on the size of the guest; NMe4+ for example has a low binding constant and is easily replaced by other alkylammonium cations. The weak binding is reflected in the 1H NMR spectrum of K6(NMe4)5[NMe4Ga4L6] (1; indicates that 1 equiv of NMe4+ is encapsulated in the cavity). Due to fast chemical exchange two very broad signals for the NMe4+ protons at 2.21 ppm and 0.70 ppm for exterior and interior NMe4+ are displayed, respectively (Figure 2, left). When 1 equiv of [CpRu(η6-C6H6)]Cl was added to an aqueous solution of 1, an exchange reaction took place within minutes which was readily apparent in the 1H NMR spectrum. The signal of the interior NMe4+ disappeared, while two new signals for the encapsulated ruthenium complex were observed at 2.60 ppm (η6-C6H6) and 1.89 ppm (Cp-H) (Figure 2, right). These signals are shifted significantly to higher field compared to the unencapsulated complex, for which the corresponding signals are displayed at 6.04 and 5.29 ppm.

This upfield shift is indicative of encapsulation and can be attributed to shielding of the naphthalene moiety of the host assembly, illustrating that the guest molecule is in close contact with the host. Further addition of [CpRu(η6-C6H6)]Cl does not lead to an increase of the signals assigned to the encapsulated guest. Instead, two new signals are observed at higher field (4.93 and 4.58 ppm), corresponding to [CpRu(η6-C6H6)]2+, which is presumably ion paired to the exterior of the assembly.

Rather than exchanging NMe4+ for the ruthenium sandwich complexes, the host assembly can also be synthesized in the presence of these cationic organometallic complexes. Combining 6 equiv of the ligand, 4 equiv of Ga(acac)3, and 1 equiv of sandwich complex in the presence of KOH resulted in the formation of the desired products (K11[CpRu(η6-C6H6)Ga4L6], 2; K11[CpRu(p-cymene)Ga4L6], 3) as yellow powders in very good yields (93% and 87% respectively).

Figure 2. Guest exchange reaction of NMe4+ for [CpRu(η6-C6H6)]+. Left: K6(NMe4)5[NMe4Ga4L6] before the addition of [CpRu(η6-C6H6)]+. Right: 5 minutes after the addition of [CpRu(η6-C6H6)]2+; the guest exchange is complete. 16

Additional evidence for encapsulation is shown in the 2D-NOESY spectrum of 2 illustrating the close proximity of the guest molecule to the naphthalene portion of the ligand backbone (HDO cross-peak deleted for clarity).

To probe the effect of the chiral environment on an encapsulated organometallic species, a [CpRu(p-cymene)]2+ complex was employed. A significant feature of the corresponding host–guest complex (3) is revealed in the 1H NMR spectrum (Figure 4). The M4L6 assemblies contain four metal centers, each of which can adapt either a Λ or Δ configuration. It has been established that only homochiral isomers of the assemblies form, i.e., each assembly is either Λ,Λ,Λ,Λ- or Δ,Δ,Δ,Δ-configured and does not racemize. Each individual cluster is therefore chiral and the Λ,Λ,Λ,Λ- and Δ,Δ,Δ,Δ-assemblies are enantiomers. The isopropyl sub-

Figure 3. 2D-Gradient NOESY spectrum of 2 illustrating the close proximity of the guest molecule to the naphthalene portion of the ligand backbone (HDO cross-peak deleted for clarity).
The achiral [CpRu(p-cymene)]^+ assemblies described here, the high affinity of the sandwich complexes discussed above for the cavity encouraged us to explore the catalytically active and similarly hydrophobic compounds of the general formula CpRu(diene)Cl. Current investigations in our laboratories with these complexes are underway.

In summary, progress has been made toward the development of organometallic catalysis encapsulated within supramolecular structures. Two organometallic ruthenium complexes, [CpRu(p-cymene)]^+ and [CpRu(p-cymene)]^+, were encapsulated and their reactivity is altered by encapsulation. Due to incorporation of the achiral [CpRu(p-cymene)]^+ into a chiral host, the enantiotopic methyl protons become diastereotopic. Future challenges will include identification of a system in which encapsulation does not lead to reduced guest reactivity, but allows for stoichiometric and catalytic reactions to take place inside the chiral vessel. Further, a chiral host might mediate asymmetric transformations with an achiral encapsulated catalyst.

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Supporting Information Available: Experimental procedures and characterization for 2, 3, 4, and 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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