transitional temperature range. In the smectic phase increasing temperature leads to the disappearance of long-range order, and hence the susceptibility decreases. The behavior of the magnetic susceptibility on cooling in a magnetic field of 1.5 T, with a change from the isotropic to liquid-crystalline phase (Figure 5) may be explained by magnetic anisotropy

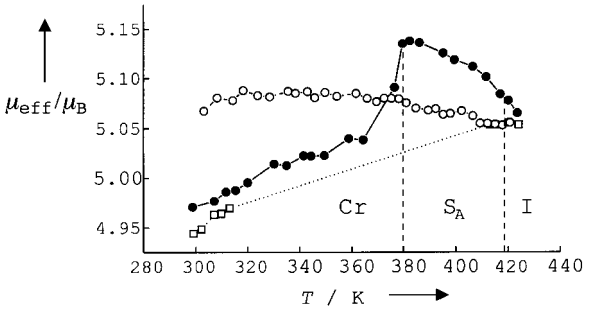

Figure 5. Effective magnetic moment μ_{eff} versus temperature for the Fe^{3+} complex in an applied magnetic field of 1.5 T. ● heating run; ○ cooling run at 1.5 T; □ cooling run at zero magnetic filed. Cr: crystal, S_A: smectic A, I: isotropic phases.

caused by magnetic field induced orientation of the molecules. During the alignment of the molecules, the axis of maximum magnetic anisotropy orients itself parallel to the director in the smectic phase, and a macroscopic orientation of the sample appears. One cannot exclude the possibility that this process is accompanied by a change of the HS/LS ratio because of possible changes of elastic properties of the compound that occur during the rearrangement of the molecular packing.

In conclusion, the possibility of coexistence of spin crossover and liquid-crystalline properties in a single compound has been demonstrated. Our efforts are directed towards enhancing the synergy between SC and LC phenomena. To achieve this we intend to chemically modify the system to increase the SC transition temperature and simultaneously decrease the transition temperature to the liquid-crystalline state. Furthermore, SC compounds containing thermochromic Fe^{2+} will be studied. Due to the presence of paramagnetic ions, the material reported here exhibits enhanced magnetic anisotropy and can be aligned by a magnetic field in the mesophase of a liquid crystal.

Experimental Section

N-ethylethylenediamine, $Fe(NO_3)_3 \cdot 9H_20$, and KPF_6 were used as received from Aldrich. Aldehyde **1** was prepared according to the literature procedure.[3]

2: *N*-Ethylethylenediamine (0.046 g, 0.52 mmol) was added in small portions to **1** (0.208 g, 0.52 mmol) in EtOH (30 mL). The mixture was heated for 20 min at 100 °C, and NaOH (0.021 g, 0.52 mmol) in H_2O (1 mL) was added. $Fe(NO_3)_3 \cdot 9H_20$(0.1 g, 0.53 mmol) in EtOH (5 mL) was added to the resulting orange solution with stirring. A twofold excess of KPF_6 in methanol was added to the resulting suspension of the complex, which was then heated to reflux for 15 min. The product was filtered from the hot mixture. The brown precipitate was washed with methanol and dried in vacuo. Yield: 0.25 g (42 %). Elemental analysis (%) calcd for $C_{56}H_{78}N_4O_8PF_6Fe$: C 59.21, H 6.87, N 4.93; found: C 59.02, H 6.94, N 5.11.

The temperatures and textures of phase transitions were determined with a polarization microscope, equipped with a hot stage and with temperature control of better than ± 0.05 K. Differential scanning calorimetry measurements were carried out on a Perkin-Elmer DSC-2M differential scanning calorimeter (scan rate of 5 K min^{-1}).

The high-temperature X-ray measurements where obtained with a STOE STADI 2 diffractometer, equipped with a linear position-sensitive detector (STOE mini PSD). Monochromatic $Cu_{K\alpha}$ radiation was obtained by using a curved germanium detector (111 plane). The temperature-dependent susceptibilities in the range 4.2 – 450 K of the powdered metallomesogen were recorded by using a Faraday-type magnetometer, equipped with an enhanced heating device operating in the range 300 – 450 K and an applied field of 1.5 T.[8]

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Assembly of Encapsulated Transition Metal Catalysts**

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There is considerable interest in the encapsulation of guest molecules in the hollow framework of spherical host molecules. The first examples of containerlike molecules were obtained by performing the synthesis in the presence of the guest molecule.[1] More recent strategies involve the construction of spherical hosts consisting of two self-complementary units held together by hydrogen bonds[2–4] and multicomponent assembly of capsules by using metal – ligand interactions.[5, 6] Initially, only small guest molecules were

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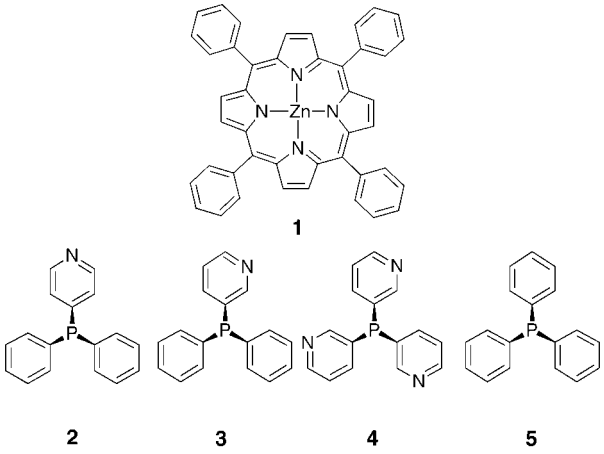
encapsulated, but systems based on functionalized calixarenes serve as self-assembled hosts for large guests such as adamantane and fullerenes.[4] The templated assembly of molecular capsules based on structurally self-complementary bis-porphyrins was recently reported.[7]

An intriguing challenge is to use these supramolecular structures as molecular reaction vessels by performing a reaction inside the capsule. For example, Diels–Alder reactions are accelerated when they take place in self-assembled capsules or metallocages.[8, 9] Many reactions of interest require a transition metal catalyst, but so far the encapsulation of transition metal catalysts in molecular capsules has not been reported. The formation of encapsulated transition metal catalysts would lead to a new class of functional assemblies with catalytic properties that depend on the catalyst site and the structure of the molecular reactor created by encapsulation. Here we report on such a strategy using simple building blocks such as porphyrins[10,11] and pyridylphosphanes.[12] These novel catalyst assemblies show enhanced activity in the palladium-catalyzed Heck reaction[13] and rhodium-catalyzed hydroformylation.[14]

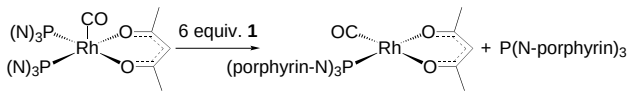
First, the coordination behavior of the pyridylphosphane ligands **2**–**5** towards zinc(II) tetraphenylporphyrin (**1**; Scheme 1) was investigated by NMR and UV/Vis spectroscopy.[15, 16] Job-plot analysis proved the formation of 1:1 complexes between monopyridylphosphanes **2** and **3** and **1**, with binding constants of $K_{1\text{-}2} = 6.1 \times 10^3\,\text{M}^{-1}$ and $K_{1\text{-}3} = 2.3 \times 10^3\,\text{M}^{-1}$. Building block **4** has three nitrogen donor atoms that enable the formation of larger assemblies. Job-plot analysis indicated that indeed three zinc(II) porphyrin units were coordinated to the pyridyl units of **4** (see Supporting Information). This implies that a hemispherical assembly was formed that encapsulates the phosphane ligand in its center.



Scheme 1. Zinc(II) tetraphenylporphyrin and phosphane ligands for catalyst assemblies.

The binding of these building blocks through the nitrogen donor atom is very selective. Triphenylphosphane (**5**) did not coordinate to **1** ($K < 50\,\text{M}^{-1}$). This implicates that the P atom is available for coordination to catalytically active transition metals. After mixing of two equivalents of **1** and $[PdCl_2(\mathbf{2})_2]$ an assembly was formed in which the transition metal is sandwiched between the two porphyrin building blocks. The associated porphyrin units do not have a large impact on the ligand coordination in $[PdCl_2(\mathbf{2})_2]$. The influence of the complexation of three porphyrin units **1** on the coordination behavior of the phosphane moiety of **4** was expected to be much larger, due to the enormous increase in steric bulk and the encapsulation of the phosphane. Indeed, after addition of six equivalents of **1** to a solution of preformed $[PdCl_2(\mathbf{4})_2]$ the ^{1}H and ^{31}P NMR spectra showed the formation of a monophosphane palladium complex due to steric crowding. In addition one equivalent of dissociated $\mathbf{4}(\mathbf{1})_3$ was formed (enforced ligand dissociation).

Similar reactions with $[Rh(acac)(CO)(\mathbf{4})_2]$ (**6**; acac = acetylacetonato) resulted in ligand dissociation and formation of the mono-phosphane rhodium complex **7** (Scheme 2). Addition of a solution of ligand **4** to $[Rh(acac)(CO)_2]$ gives the expected rhodium complex with two coordinated phosphane ligands, whereas in the presence of **1** only mono-phosphane rhodium complex **7** was observed. Molecular modeling studies on the rhodium complexes indicated that the rhodium center is completely encapsulated by the porphyrin assembly (Figure 1). The formation of a bis-phosphane complex is prohibited by steric interactions between the assembled porphyrin units. This implicates that the catalytically active species located at the center of the assembly differs from that of the nonencapsulated complex.



Scheme 2. The assembly of porphyrins on the pyridylphosphane ligands enforces mono-phosphane coordination on the rhodium atom. $P(N)_3$ = tris(*m*-pyridyl)phosphane (**4**), porphyrin = zinc(II) tetraphenylporphyrin (**1**), $P(N\text{-porphyrin})_3$ = three zinc(II) porphyrins assembled on tris(*m*-pyridyl)phosphane $[\mathbf{4}(\mathbf{1})_3]$.

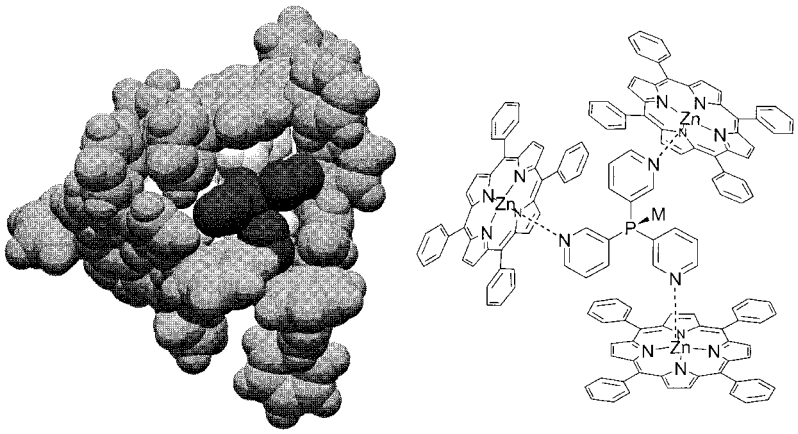


Figure 1. Modeled structure of an encapsulated transition metal catalyst consisting of porphyrin **1** (gray), tris(*m*-pyridyl)phosphane (**4**) (white) and M = [RhH(CO)$_3$] (dark gray).

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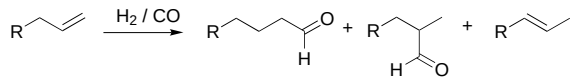
The encapsulated palladium catalysts were studied in the Heck reaction[13] of iodobenzene and styrene. Three palladium tetrakis-phosphane complexes were prepared as catalyst precursors: [Pd(**4**)$_4$], [Pd(**5**)$_4$], and [Pd(**2**)$_4$].[17] Figure 2 plots the formation of the product as a function of time for the catalyst precursors in the presence and absence of **1**. The identical results of the catalytic reaction with [Pd(**5**)$_4$] in the presence and absence of **1** show that the porphyrin does not disturb the reaction. The presence of **1** when [Pd(**2**)$_4$] was used as precursor also did not change the reaction rate significantly. This sandwich complex does not introduce much steric hindrance, and the catalytically active species remains unchanged. In contrast, the impact of **1** on [Pd(**4**)$_4$] is enormous. In the absence of **1** almost no activity was observed, whereas in presence of **1** the product was rapidly formed. The assembly of **1** on the pyridyl units of the phosphanes leads to the formation of a mono-phosphane complex, and this results in fast oxidative addition of iodobenzene and subsequent reaction with styrene.

The second reaction studied with an encapsulated catalyst was the rhodium-catalyzed hydroformylation of 1-octene (Table 1).[14] Zinc(II) porphyrin **1** does not interfere with the rhodium-catalyzed hydroformylation, since using triphenylphosphane **5** in the presence and absence of **1** gave the same results. The catalyst formed by ligand **3** hardly showed any change in rate or selectivity when **1** was added. This shows that two porphyrin units can be assembled to form a sandwich-type complex without changing the performance of the active catalyst. In contrast, the assembly of three porphyrin units with ligand **4** significantly altered the performance of the catalyst. At 80 °C the catalyst was almost twice as active, and the selectivity had changed (l:b = 1.5 vs 2.8). At room temperature there was an even larger difference between the porphyrin-encapsulated catalyst and the non-encapsulated analogue; the former gave a tenfold higher activity, and the branched product was now even the favored product (l:b = 0.6). The higher activity and isomerization rate in combination with a higher selectivity for the formation of the branched product indicate that the active catalyst is a mono-phosphane rhodium species.[18, 19] This is in accordance with a high-pressure IR spectroscopic study on the catalytically active species and an NMR spectroscopic study on the [Rh(**4**)$_2$(acac)] precursor, which showed only the presence of mono-phosphane complexes after the addition of **1**. These results clearly show that the performance of the rhodium catalyst can be regulated by the assembly of porphyrin building blocks with the pyridylphosphane rhodium complex.

Table 1. Hydroformylation of 1-octene with various rhodium catalyst assemblies.[a]



Ligand[b]	T [°C]	TOF[c]	l:b[d]	Isomers [%][e]
3	80	2.2×10^3	2.9	0.9
3+**1**	80	2.1×10^3	2.8	1.1
4	80	2.8×10^3	2.8	3.8
4+**1**	80	4.5×10^3	1.5	8.3
5	80	1.7×10^3	2.7	1.5
5+**1**	80	1.7×10^3	2.7	1.2
3	25	6	2.8	3.2
3+**1**	25	6	2.8	0.8
4	25	43	2.8	3.4
4+**1**	25	400	0.6	1.0
5	25	4	3.0	1.5
5+**1**	25	4	3.0	1.2

[a] [Rh(acac)(CO)$_2$] 0.084 mmol L^{-1}, $p = 20$ bar (CO:H$_2$ = 1:1); for detailed conditions, see Supporting Information. [b] P:Rh = 25, porphyrin:P = 3. [c] TOF = turnover frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}; the reaction was stopped after 1 h. [d] l/b = linear/branched. [e] = Percentage isomerization.

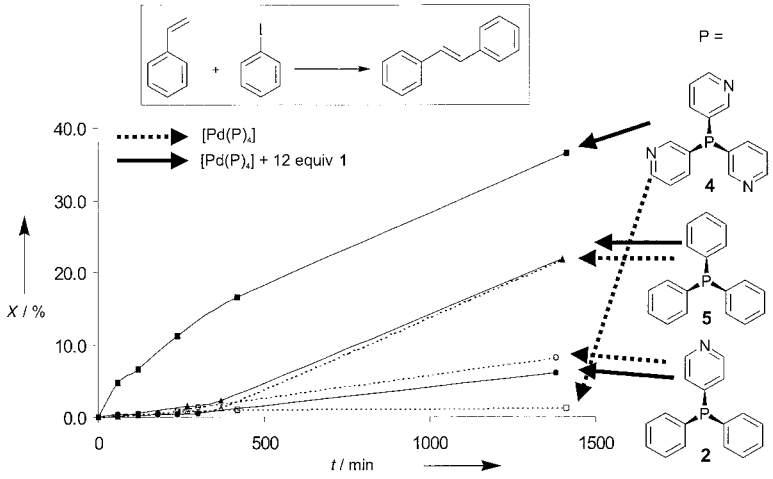


Figure 2. Conversion of styrene in the Heck reaction with various assembled palladium catalysts. The lines through the points are drawn for clarity. X = conversion.

In conclusion, we have shown that hemispherical assemblies that encapsulate well-defined transition metal catalysts can be prepared by using simple pyridylphosphane and porphyrin building blocks. The self-assembled structures are based on selective coordination of pyridyl groups to zinc porphyrins with a transition metal pyridylphosphane complex as the template. The catalytic performance of the encapsulated transition metal complex was differed significantly in selectivity and activity. So far we have only used porphyrin **1** and template ligands **2**–**4** to form the assemblies, but many other building blocks can be envisaged. This will lead to new nano-objects with interesting catalytic properties.

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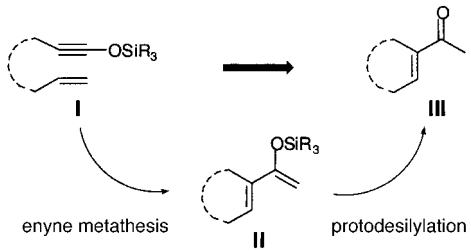
Siloxyalkyne – Alkene Metathesis: Rapid Access to Highly Functionalized Enones**

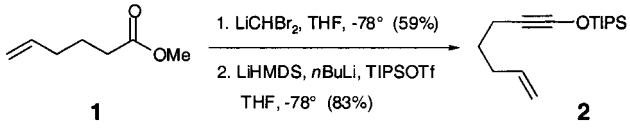
Michael P. Schramm, D. Srinivasa Reddy, and Sergey A. Kozmin*

The advent of structurally defined metal alkylidenes capable of promoting π-bond metathesis under mild conditions, with high efficiency and functional group compatibility, has had a profound effect on modern organic synthesis.[1] Among a range of synthetically useful transformations, the enyne metathesis is particularly noteworthy for the ability to assemble two carbon – carbon bonds in a single step starting from appropriate alkyne and alkene components.[2] However, elaboration of the full synthetic potential of this process has been limited largely to the use of simple, unactivated enyne precursors.[3] We report here a mechanistically intriguing example of the participation of siloxyalkynes in the intramolecular Ru-catalyzed metathesis with terminal alkenes, which resulted in the development of a new method for the synthesis of highly functionalized enones **III** starting from readily accessible acyclic precursors **I** (Scheme 1).[4] Furthermore, this approach represents a novel method for the construction of silyldienol ethers **II** starting directly from enyne **I**, conceptually different from the conventional enol silylation of carbonyl compounds.



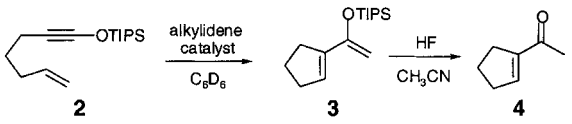
Scheme 1. Projected outcome of the siloxyalkyne – alkene metathesis.

Our studies began with the preparation of a model cyclization substrate **2** (Scheme 2). Construction of siloxyalkyne **2** was accomplished according to a modified Kowalski protocol[5] entailing the initial conversion of ester **1** to the corresponding dibromoketone, followed by generation of the ynolate anion (LHMDS, *n*BuLi) and silylation with TIPSOTf to afford enyne **2**.



Scheme 2. Preparation of siloxyalkyne **2**. LiHMDS = lithium bis(trimethylsilyl)amide, TIPSOTf = triisopropyl trifluoromethanesulfonate.

We next systematically examined several olefin metathesis catalysts in order to achieve the desired conversion of siloxyalkyne **2** to the corresponding diene **3** [Eq. (1)]. Following the unsuccessful attempts to employ either the



(1)

original Grubbs Ru-complex **5**[6] or the Schrock Mo-catalyst **6**[7] (Table 1, entries 1 and 2), we turned our attention to the recently developed Ru-complexes bearing highly nucleophilic imidazolylidene ligands.[8] To our delight, both **7**[9] and **8**[10] were found to promote the desired transformation, nevertheless they displayed a noticeable difference in reactivity.[11] The reaction proceeded to completion in the presence of **8** (5 mol%) over a period of 13 h at 20 °C, and within minutes at 60 °C (entries 4, 5). The cyclization employing complex **7** was

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