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Transition metal catalysis in confined spaces

Leenders, S.H.A.M.

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Abstract:
Selective co-encapsulation of metal complexes and aromatic compounds in a capsule was achieved. A charge transfer complex is observed with the formation of the ternary complex and can be fine-tuned according to the oxidation potentials of the metal complexes which act as donors in this system. Therefore different charge transfer bands can be observed, based on the electronic properties of the electron donor.
6.1 Introduction

In the previous chapters a ligand template approach was demonstrated as a way to form a confined space around a metal center. This approach consists of using a functionalized ditopic building block for the assembly. One part of the building block can bind the metal center (i.e. phosphine or carbene moiety) while the other part (pyridine functionality) of the building block is used in the formation of the assembly. In this chapter we describe the exploration of the host-guest approach wherein the host is pre-assembled and after assembly the guests are embedded through weaker interactions. Hence, the hosts have well-defined and rigid confined spaces, which makes them interesting objects for exploring chemistry with specific organic and organometallic compounds that are enclosed inside.\textsuperscript{1-4} Forming a micro-environment around the guests by the hosts has shown to be a feasible approach to induce new selectivity in organic reactions and catalysis.\textsuperscript{5-7} Furthermore, when metal catalysts are captured inside a capsule the cages resemble to some extend the second coordination sphere in enzymes, and as such new reactivity and selectivity may be displayed by the catalysts.\textsuperscript{8-11} Also in the photosynthetic apparatus in nature the second coordination sphere is of importance, and in analogy chromophoric guests have been encapsulated and subjected to detailed studies. As such, induced charge transfer (CT) complexes or exciplexes have been enforced by the close proximity of different guests that have been co-encapsulated. It has been demonstrated that selective encapsulation of guests in a preformed host like cyclodextrins,\textsuperscript{12} cucurbit[8]urils,\textsuperscript{13,14} pillar[5]arenes,\textsuperscript{15} porous coordination polymers\textsuperscript{16,17} and metallocages\textsuperscript{18} can be used to obtain new charge transfer complexes. Additionally, the formation of charge transfer complexes can be used as driving force to form new supramolecular assemblies.\textsuperscript{19,20} In this chapter, we investigate the formation of ternary complexes and how the redox properties of the guest that is the electron donor influences the obtained charge transfer complexes. Via this way ternary complexes can be obtained in which a metal complex is in close proximity to an aromatic guest inside a metallocage. Understanding and achieving selective co-encapsulation can form a stepping stone in bringing a metal complex and substrate together in the confined space, which is important for future studies on catalysis in these confined spaces.
6.2 Characterization of the selective co-encapsulation

A self-assembled nanosphere, already reported in literature (Figure 1) has recently been demonstrated to facilitate exciplex formation with different guests\textsuperscript{21-23} and also metal complexes could be enclosed, after which a charge transfer band was observed.\textsuperscript{24} While the charge transfer complex is only considered as a weak interaction between the donor and acceptor, they can often be easily observed and characterized due their intense colors.

![Diagram of octahedral nanosphere and guests for co-encapsulation](image)

**Figure 1:** Octahedral shaped nanospheres 1 and guests for co-encapsulation.

The water soluble octahedral nanosphere 1 (Figure 1) has been studied in detail and it has been demonstrated to bind a large variety of guests, mostly on the basis of hydrophobic effects and interactions with the electron poor sidewalls of the cavity. The broad array of guests that have been accommodated in this molecular container include metal complexes,\textsuperscript{24-26} substrates for organic reactions,\textsuperscript{27,28} halogens\textsuperscript{29,30} and a variety of molecules with interesting spectroscopic properties.\textsuperscript{31,21-23} Generally, the procedure for encapsulation in this metalloca ge is easy and the host-guest complexes are formed by mixing the components. We investigated whether (CpMe)Rh(cod) 3 (Cp = cyclopentadiene, cod = 1,5-cyclooctadiene) could be encapsulated. Upon stirring a suspension of 3 and 1a in D$_2$O at 100 °C for prolonged reaction times, no encapsulation of 3 was indicated by NMR spectroscopy under these conditions.
Previously, it has been reported that cage 1 only binds some guests in the presence of an appropriate second molecule that is co-encapsulated. As such, we investigated the binding of the metal complex in presence of triphenylene (6) as co-guest. Heating a suspension of 1a, 3 and 6 in D$_2$O at 100 °C for one hour resulted in a suspension with a colored solution. Interestingly, after cooling down and filtration of the excess of guests a purple colored solution was obtained indicating that the ternary complex 1a•3•6 was formed (Scheme 1).

![Scheme 1: Co-encapsulation of complexes 3 and 6 in the cavity of 1.](image)

Both the rhodium complex and the triphenylene have a solubility in water that is too low to be detected by $^1$H NMR spectroscopy, but in the presence of the cage their signals are clearly visible. The binding was confirmed by the clear upfield shifts displayed by the guest molecules in the $^1$H NMR spectrum, depicted in Figure 2. The shielding caused by the aromatic rings of the cage resulted in a typical shift of the triphenylene signals of 1.7 and 1.4 ppm, whereas the signals of the metal complex shifted in the range of 2.4-3.3 ppm. Another sign of guest encapsulation is the change of symmetry of the metallocage from T$_d$ to effectively C$_3$ (on the NMR timescale), as is clear from $^1$H NMR spectroscopy. The loss of symmetry of the capsule occurs because each guest occupies one half of the capsule. The guests are closely packed against the triazine panel and on the NMR timescale the cage loses its T$_d$ symmetry (See Figure 2c). For the empty cage, all pyridine rings are equivalent (because of the T$_d$ symmetry), and only two signals for the pyridine protons are expected. However, for the cage with the two guests inside, eight sets of pyridine protons are observed. Importantly, the symmetry of the guest molecules is not affected by the encapsulation, indicating that these can still freely rotate inside the void of the capsule. Additional support for guest encapsulation is provided by diffusion ordered NMR (DOSY) showing that the diffusion of the guests matches that of the capsule. Due to the enforced close proximity of the two different guests, also NOE signals can be observed between the two guests in the 2D NOESY spectrum. In addition, the guests also display NOE contacts with the capsule 1a, suggesting a tight fit of the compounds in the metallocage.
Figure 2: Clear upfield shifts observed in the $^1$H NMR spectra of guests 3 and 6: spectrum of a mixture of guests in CDCl$_3$ (a, top) and inside molecular container 1 in D$_2$O (b, bottom). c) On the right a modeled structure is displayed showing the loss of symmetry of the metallocage. Annotation of the proton signals is done with help of COSY experiments.

Attempts to crystallize the ternary product using metallocage 1a did not yield suitable crystalline material for X-ray diffraction. However, when we changed the nanosphere to its palladium analogue with a 2,2'-bipyridine cis-capping ligand (metallocage 1b), and guest 3 for its iridium analogue complex 5, suitable crystals for X-ray diffraction were obtained. It can be observed from the crystal structure that the guests occupy the void of the sphere together (Figure 3) showing a tight fit of both guests inside the cage. The guest pair (5·6) was disordered in three positions, hence only the 33.3% occupancy is displayed, to clearly show the host-guest structure. Although the solid state structure cannot be directly compared with the structure in solution, the disorder in three positions corresponds with the effective C$_3$-symmetry of the host-guest assembly on the NMR timescale, as derived from the NMR spectra in solution at room temperature.
Figure 3: Solid state structure of ternary complex 1b-5-6 (33.3% occupancy). The metal complex 5 is shown in green and triphenylene 6 is shown in purple. Solvent molecules and nitrate anions have been omitted for clarity.

The crystal structure shows that the triphenylene guest (6) is close to the triazine panel. However, it is not stacked completely parallel to the panel. The distance of 6 (central ring) to the central ring of the triazine panel is 3.48 Å and that from triphenylene to the iridium atom is 4.84 Å. Furthermore, we observe that the angles between the pyridines that are connected to the palladium have an average of 86.4°. This is similar to an average of 86.6°, which has been reported for the crystal structure of the cage when an adamantoid cluster of water is inside.36b

6.3 Scope of the co-encapsulation by changing the steric on the guests

With the observation that the two guests are only together embedded inside the cavity of the metallocage and no individual encapsulation occurs, the scope of the metal complexes and aromatic moieties that can be co-encapsulated was explored. The 1H NMR spectrum of 1c-3-6 shows that no full encapsulation takes place as empty cage 1c is still present. Integration of the pyridine proton signals and comparison of these to the aromatic signals allows the determination of the efficiency of the formation of
the ternary complex, expressed in a percentage of occupied cage, which is 78% for \textbf{1c·3·6}. The metal complex was changed to the sterically similar, but electronically different iridium complex \textbf{5}, which resulted in a similar amount of ternary complex (see Table \textbf{1}). Studies of the steric influences on the amount of co-encapsulation were done with complex \textbf{2} and \textbf{4}. A minimal increase in the formation of ternary complex \textbf{1c·2·6} was observed when no methyl groups are present on the cyclopentadiene ligand, however a large decrease in co-encapsulation is observed when four methyl groups are present, resulting in 28% of complex \textbf{1c·4·6} (Table \textbf{1}).

\textbf{Table 1:} Formation of the of the ternary complexes in metallocage \textbf{1c}, all encapsulation studies were done with the same equivalents of guests for 1 hour at 100 °C. Percentages are based on integration of the pyridine signals in 'H NMR spectroscopy.

<table>
<thead>
<tr>
<th>Aromatic Guest</th>
<th>Triphenylene (6)</th>
<th>Pyrene (7)</th>
<th>Perylene (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal donor</td>
<td>Co-encapsulation (%)</td>
<td>Co-encapsulation (%)</td>
<td>Co-encapsulation (%)</td>
</tr>
<tr>
<td>(CpMe₄)Rh (4)</td>
<td>28</td>
<td>81</td>
<td>14</td>
</tr>
<tr>
<td>(CpMe)Rh (3)</td>
<td>78</td>
<td>98</td>
<td>37</td>
</tr>
<tr>
<td>(Cp)Rh (2)</td>
<td>84</td>
<td>97</td>
<td>43</td>
</tr>
<tr>
<td>(CpMe)Ir (5)</td>
<td>75</td>
<td>98</td>
<td>32</td>
</tr>
</tbody>
</table>

Interested by this difference in the formation of the co-encapsulated species the aromatic guest was changed to pyrene (7) or perylene (8). The ternary complexes formed with pyrene all result in a higher amount of co-encapsulation. For this guest (7) also a high formation of ternary complex with the sterically hindered (CpMe₄)Rh(cod) is observed (81%). Opposite to this, co-encapsulation with perylene results in less of the ternary complexes of which \textbf{1c·4·6} is the lowest, forming a mere 14% of ternary complex.

The higher formation of ternary complexes with pyrene, compared to triphenylene, made us investigate if there is a preference for ternary complexes with pyrene instead of triphenylene. A solution of the triphenylene ternary complex \textbf{1c·2·6} was therefore mixed with 10 equivalents of pyrene at 100 °C for 1 hour (depicted in Scheme 2, top). After cooling down and filtration of the excess guest, this resulted in an exchange of aromatic guest and the ratio of \textbf{1c·2·6} to \textbf{1c·2·7} was determined to be 1:6.3. In a similar way, a solution of \textbf{1c·2·7} was mixed with triphenylene (6) at 100 °C for 1 hour. In this case the ratio of \textbf{1c·2·6} to \textbf{1c·2·7} is 1:36.0, indicating that pyrene easily displaces triphenylene and has a higher affinity for the cavity of the metallocage.
Scheme 2: Exchange studies of preformed ternary complexes with pyrene (top) or triphenylene (bottom). Observed from these experiments is that the metallocage has a preference for binding pyrene.

To further prove that perylene is thermodynamically the least favored in the void of metallocage 1, an excess of all three the aromatic guests were stirred at the same time in the presence of 2 and 1c. After 1 hour at 100 °C, this resulted in a ratio of 1c•2•6 : 1c•2•7 of 1:9.1 (see Scheme 3) and no perylene was encapsulated.

Scheme 3: Competition experiments of three aromatic compounds with metal complex 2 showing that the metallocage 1c has a strong preference to bind pyrene.

Heating the suspension with the guests for a longer time (6 hours) slightly influenced the ratio (1:10.3) and still didn’t result in the encapsulation of 8. This demonstrates that the metallocage has different affinities for the aromatic guests and that this is represented in the amount of the ternary complex that is formed.
6.4 Tuning of the charge-transfer band through co-encapsulation

Intrigued by the different colors that were observed with the different ternary complexes, the co-encapsulated species were studied by UV-Vis spectroscopy. Upon co-encapsulation of rhodium complex 3 and triphenylene, the pale yellow solution of empty cage 1c turned to purple and a new absorption band at 555 nm (2.23 eV) was observed. This new band is indicative for the formation of a charge transfer complex (see Figure 4). To confirm that the cage facilitates the new absorption band we combined the compounds in chloroform. The absence of a charge transfer band in UV-Vis for this solution demonstrates that the metallocage is responsible for the exciplex formation.

![Figure 4: a) UV-Vis absorption spectra indicating the charge transfer complexes in capsule 1c with triphenylene (250 μM). b) Photo of the different colored solutions of the ternary complexes demonstrating that the metal complex changes the color of the solution (in metallocage 1a).](image)

The formation of charge transfer complexes of soluble molecules in supramolecular complexes based on cucurbit[8]uril have been previously reported.13-15,37 In the current system, the formation of the host-guest system is based on extraction of the guests which are insoluble in water. The metal complexes that are encapsulated by this metallocage makes it possible to investigate the effect of the redox potential on the charge transfer complex. As such, other pairs of guests for the formation of ternary complexes were investigated. The donor in the charge transfer complex is expected to be the metal complex, hence various complexes with different steric and electronic properties were studied. The same steric structure was retained and only the electronic properties were changed by utilizing (CpMe)Ir(cod) (5) for the encapsulation studies. When 5 was co-encapsulated with triphenylene, the charge transfer band was shifted to higher energy (513 nm, 2.42 eV, see Table 2) compared to that obtained with the rhodium complex (3). This blue shift of the charge transfer
band by 0.19 eV was anticipated as the oxidation potential of 5 (0.02 V vs. Fe\(^{0/+}\)) is higher than that of 3 (0.12 V vs. Fe\(^{0/+}\)), as indicated by the redox potentials of the complexes in chloroform, that were established by cyclic voltammetry measurements (see Table 2 and experimental section 6.7.4).

**Table 2:** Charge transfer energies (ΔE\(_{CT}\)) of the ternary complexes facilitated by metallocage 1c. Energies are based on fitting of the charge transfer peaks in UV-Vis spectroscopy (λ\(_{CT}\)). The charge transfer energies are in line with the redox properties of the metal complex (E\(_{ox}\)) which were determined with cyclic voltammetry.

<table>
<thead>
<tr>
<th></th>
<th>Pyrene (7)</th>
<th>Triphenylene (6)</th>
<th>Perylene (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(_{ox}) (V)(^{[a]})</td>
<td>ΔE(_{CT}) (eV)</td>
<td>ΔE(_{CT}) (eV)</td>
<td>ΔE(_{CT}) (eV)</td>
</tr>
<tr>
<td>(CpMe(_4))Rh (4)</td>
<td>-0.28</td>
<td>1.88</td>
<td>2.22</td>
</tr>
<tr>
<td>(CpMe)Rh (3)</td>
<td>0.02</td>
<td>2.03</td>
<td>2.40</td>
</tr>
<tr>
<td>(Cp)Rh (2)</td>
<td>0.07</td>
<td>2.01</td>
<td>2.50</td>
</tr>
<tr>
<td>(CpMe)Ir (5)</td>
<td>0.12</td>
<td>2.04</td>
<td>2.38</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Oxidation potentials are referenced to ferrocene (Fc\(^{0/+}\)).

The same trend was observed when changing the electronic properties of the rhodium complex by substituting it with four methyl groups. Complex (CpMe\(_4\))Rh(cod) 4 has a lower oxidation potential (−0.28 V vs. Fe\(^{0/+}\), a difference of 0.3 V, compared to 3) and therefore gave a charge transfer band at lower energy (586 nm, 2.13 eV). When the smallest complex with no substituents on the Cp ring was encapsulated, it was expected to give a charge transfer band slightly higher in energy than 1c•3•6, based on the slightly higher oxidation potential of 2 (0.07 V vs. Fe\(^{0/+}\), a difference of 0.05 V compared to 3). Indeed, for this smaller complex the location of the CT band at 530 nm (2.34 eV) corresponds with these expectations. Based on the charge transfer energies and the oxidation potentials of the metal complexes, a trend is visible that shows that metal complexes with a higher oxidation potential yield a charge transfer band with triphenylene at lower wavelength. To the best of our knowledge this is the first time that metal complexes have been used to fine tune the charge transfer bands via the formation of ternary complexes, based on their redox potentials. We were therefore interested if similar trends would be observed if other aromatic guests were co-encapsulated. For this purpose pyrene (7) and perylene (8) were used to form the ternary complexes. Pyrene resulted in almost quantitative formation of the ternary complexes (see Table 2), including the sterically demanding 4. However, the location of the charge transfer band was difficult to exactly determine as it partially overlaps with the absorption of pyrene (see Figure 5).
Figure 5: UV-Vis absorption spectra of the charge transfer complexes in capsule 1c with pyrene (7, left) and perylene (8, right).

Although the exact energies are therefore less accurate, still a similar trend can be observed as with triphenylene, but now all shifted to lower energies as a consequence of the lower lying LUMO of pyrene. Similar with triphenylene, co-encapsulation of pyrene with the most electron rich complex, 4, gave the lowest charge transfer band (658 nm, 1.88 eV). Changing the donor to 2, 3 or 5 gave small changes in charge transfer energy (see Figure 5 and Table 2).

The aromatic co-guest was next changed to perylene (8), and again we observe a recurring trend of the charge transfer energy, corresponding with the redox potential of the metal complex (see Figure 5 and Table 2). In general, the charge transfer bands are at higher energy with perylene. Only one exception on the trend based on the redox potentials is observed which is with iridium complex 5. In this case the charge transfer energy of 1c•5•8 is difficult to determine due to the overlap with the UV band of perylene and is therefore not accurate.

While it could be argued that the exciplex could be formed from the electron donor with the triazine panels of the cage 1c we would like to note that different CT bands were observed with the different aromatic compounds, thus indicating that the encapsulated aromatic guest surely plays a role in the exciplex formation. We propose that the metal complex can act as electron donor for the LUMO of the aromatic compound and that the interaction is facilitated by placing the components in confined space. The thus formed charge transfer complex is stabilized due the electron poor cavity of the molecular container. The ability to fine tune the charge transfer band with different donors and acceptors also exclude the role of intramolecular charge transfer complexes and indicates that this is a pure intermolecular process, facilitated by the octahedral cage 1. Based on these finding we constructed a schematic energy diagram for the charge transfer interactions, which is depicted in Figure 6.
Figure 6: Schematic energy diagram of the charge transfer energies facilitated by cage 1c. The ordering of the donor and acceptor species is based on measured charge transfer energies.

6.5 Conclusions

In summary, we have demonstrated the formation of ternary complexes in metallocage 1, in which one metal complex and one flat aromatic guest are co-encapsulated. The amount of the co-encapsulation is depending on the guests and changes with different steric properties. In the UV-Vis spectra of these complexes, clear charge transfer bands are observed of which the energy is controlled by the electronic properties of the donor (metal complex) and the acceptor (aromatic guest). The electronic properties can be fine-tuned through the metal complex which is a new and interesting way to rationalize and form different kind of charge transfer complexes. The void of the metallocage makes it possible to study these very subtle interactions. Understanding these interactions makes it possible to take them into account in the future design of novel host-guest complexes and catalytic systems.

6.6 Acknowledgements

René Becker is acknowledged for help with the cyclic voltammetry measurements and helpful discussions. Tatu Kumpulainen is acknowledged for his help with the UV-Vis studies, helpful discussion and fitting of the UV-Vis spectra. Tomohisa Sawada, Taito Kato and Makoto Fujita are kindly acknowledged for the determination of the crystal structure.
Selective Co-encapsulation Inside a M₆L₄ Cage Using Tunable Charge Transfer Complexes

6.7 Experimental Section

See Chapter 2 for the general experimental section and experimental setup for the DOSY experiments.

6.7.1 Synthesis of building blocks, cages and guests

Pt(en)Cl₂³⁸

K₂PtCl₄ (2 g, 4.818 mmol, 1 equiv.) was dissolved in water (20 mL) and acidified to a pH of 3 with 1M HCl. Then a solution of ethylenediamine (320 µL, 288 mg, 4.787 mmol, 0.99 equiv.) in water (20 mL) was added. After stirring for 2 hours at room temperature a yellow suspension was formed which was filtered. Further washing with water, ethanol and diethyl ether yielded pure product as a yellow solid (1297 mg, 3.978 mmol, 83%). Spectral data in correspondence with literature³⁸: ¹H NMR (300 MHz, DMSO-d₆) δ 5.33 (s, 4H), 2.22 (s, 4H).

Pt(en)(NO₃)₂

Pt(en)Cl₂ (1100 mg, 3.373 mmol, 1 equiv.) was suspended in water (200 mL) and AgNO₃ (1146 mg, 6.746 mmol, 2 equiv.) was added. The suspension was stirred with exclusion from light at room temperature for overnight. The resulting white suspension was formed (or centrifuged: 4000 rpm, 30 min) and concentrated in vacuo. This gave 1206 mg of a pale yellow solid (3.180 mmol, 94%). Spectral data in correspondence with literature³⁹: ¹H NMR (400 MHz, D₂O) δ 5.73 (s br, 4H), 2.51 (s, 4H).

Pd(tmeda)Cl₂⁴⁰

PdCl₂ (2g, 11.28 mmol, 1 equiv.) was suspended in acetone (50 mL) and 1681 µL tetramethylethylenediamine, tmeda (11.28 mmol, 1 equiv.) was added. The suspension was stirred at room temperature for 24 hours, filtered and washed with water, acetone and diethyl ether to yield 2992 mg of yellow solid (90% yield, 10.19 mmol). Spectral data are in correspondence with literature⁴⁰: ¹H NMR (300 MHz, DMSO-d₆) δ 2.72 (s, 1H), 2.64 (s, 3H).

Pd(tmeda)(NO₃)₂

Pd(tmeda)Cl₂ (1.5g, 5.11 mmol, 1 equiv.) was suspended in 150 mL of water. With exclusion from light AgNO₃ (2 equiv. 1736 mg) was added and stirred at room temperature for overnight. The resulting suspension was then filtered and the filtrate was concentrated in vacuo to yield 1.681 g of yellow solid (4.85 mmol, 95%). ¹H NMR (400 MHz, D₂O) δ 2.89 (s, 1H), 2.68 (s, 3H).

p-tpt (para-trispyridinetriazine)

A flask was charged with 4-cyanopyridine (30 g, 288 mmol, 1 equiv.) and heated to 150 °C. Powdered NaOH (1152 mg, 28.8 mmol, 0.1 equiv.) was added to the resulting liquid and the resulting mixture was stirred at 150 °C for 24 hours. The solid was washed with acetone (3x180 mL) and dissolved in 250 mL 2M HCl, then activated charcoal was added and sonicated for 30 min. The suspension was filtered over Celite and neutralized with 5M NaOH (approx. 150 mL). The product was filtered and washed with water and acetone. After drying this yielded 17 g of white solid (57% yield). Spectral data are in correspondence with literature⁴¹: ¹H NMR (400 MHz, CDCl₃) δ 8.98 – 8.91 (m, 1H), 8.61 – 8.54 (m, 1H).
M₆L₄ cage from Pt(en)(NO₃)₂⁺⁺⁺⁺⁺⁺ (1a)
Pt(en)(NO₃)₂ (600 mg, 1.582 mmol, 6 equiv.) was dissolved in 30 mL of water in a high pressure tube and para-trispyridinetriazine (329 mg, 1.055 mmol, 4 equiv.) was added. The tube was sealed tight and heated to 150 °C for 3 days. The solution was then cooled down, filtered and concentrated in vacuo to yield 782 mg of white solid (84%). Spectral data are in correspondence with literature: ¹H NMR (300 MHz, D₂O) δ 9.10 (d, J = 5.1 Hz, 24H), 8.58 (d, J = 5.4 Hz, 24H), 2.85 (s, 24H).

M₆L₄ cage of Pd(tmeda)(NO₃)₂ (1c)
Following a literature procedure, Pd(tmeda)(NO₃)₂ (1130 mg, 3.26 mmol, 6 equiv.) was dissolved in 54 mL of H₂O and p-tpt (678 mg, 2.17 mmol, 4 equiv.) was added. The resulting suspension was stirred at 80 °C for 1 hour. After filtration and concentration in vacuo a yellow solid was obtained (1.788 g, 99%). Spectral data are in correspondence with literature: ¹H NMR (400 MHz, D₂O) δ 9.36 – 9.28 (m, 24H), 8.82 – 8.77 (m, 24H), 3.20 (s, 24H), 2.80 (s, 72H).

General procedure for the synthesis of rhodium cyclo-octadiene (cod) complexes
A flame dried schlenk was charged [(cod)RhCl]₂ (250 mg, 0.507 mmol, 1 equiv.) and Na₂CO₃ (250 mg, 2.359 mmol, 4.65 equiv.) and flushed with N₂/vacuum for 3 times. Then MeOH was added (25 mL) to the stirring solution followed by consecutive addition of freshly distilled (substituted) cyclopentadiene (9.46 mmol, 18.7 equiv.). The solution was stirred at rt or 60 °C for the indicated time after which it was filtered and concentrated in vacuo a yellow solid was obtained (1.788 g, 99%). The residue was dissolved in Et₂O, filtered and concentrated again. Pure product was obtained by sublimation with a bulb to bulb apparatus at the indicated temperature and under high vacuum (10⁻² bar) to yield yellow crystals of the desired compound.

CpRh(cod) (2)⁻⁴⁵
Synthesized according to general procedure: cyclopentadiene was added (625 mg, 795 µL) and stirred for 5 hours at 60 °C. Sublimed at 100 °C to give 185 mg of product (0.670 mmol, 66% based on Rh). Spectral data in correspondence with literature. ¹H NMR (400 MHz, C₆D₆) δ 4.95 (s, 5H), 3.97 (s, 4H), 2.34 – 2.12 (m, 4H), 1.95 (m, 4H). HRMS (FD⁺) calcd. for C₁₃H₁₇Rh 276.03853 [M]+, found 276.03768 (Δppm = 3.1).

(MeCp)Rh(cod) (3)
Synthesized according to general procedure: methyl-cyclopentadiene was added (760 mg, 808 µL) and stirred for 4 hours at 60 °C and at room temperature for overnight. Distilled at 140 °C to give 267 mg of product (0.920 mmol, 91% based on Rh) as a yellow liquid which solidifies upon cooling down. ¹H NMR (400 MHz, CDCl₃) δ 5.18 (s br, 2H Cp-H), 4.92 (t, J = 1.9 Hz, 2H Cp-H), 3.73 (s, 4H COD-CH), 2.29 – 2.11 (m, 4H COD-CH₂), 1.76 (s, 3H Cp-Me). ¹³C NMR (75 MHz, CDCl₃) δ 100.61 (d, J = 4.0 Hz Cp(C)-Me), 87.81 (d, J = 3.7 Hz Cp), 85.17 (d, J = 4.1 Hz Cp), 64.11 (d, J = 14.3 Hz COD-CH), 32.61 (COD-CH₂), 12.70 (Cp-Me). HRMS (FD⁺) calcd. for C₁₄H₁₉Rh 290.05418 [M]+, found 290.05383 (Δppm = 1.2). Anal.: found (calcd.) for C₁₄H₁₉Rh: C, 57.97 (57.94); H, 6.58 (6.60).
Selective Co-encapsulation Inside a M₆L₄ Cage Using Tunable Charge Transfer Complexes

(Me₄Cp)Rh(cod) (4)

Synthesized according to general procedure: tetramethyl-cyclopentadiene was added (1158 mg, 1433 µL) and stirred for overnight at room temperature. Sublimed at 130 °C to give 178 mg of product (0.536 mmol, 53% based on Rh). ^1H NMR (500 MHz, CDCl₃) δ 5.04 (s, 1H Cp-H), 3.07 (s, 4H COD-CH), 2.27 – 2.12 (m, 4H COD-CH₂), 1.93 (q, J = 9.0, 8.1 Hz, 4H COD-CH₂), 1.85 (s, 6H Cp-Me), 1.62 (s, 6H Cp-Me). ^13C NMR (126 MHz, CDCl₃) δ 99.51 (d, J = 3.8 Hz Cp-C), 95.72 (d, J = 4.3 Hz Cp-C), 84.96 (d, J = 4.3 Hz Cp-C), 69.29 (d, J = 14.2 Hz COD-CH), 32.84 (COD-CH₂), 10.94 (CpMe), 9.78 (CpMe). HRMS (ESI+) calcd. for C₁₇H₂₅Rh 332.10113 [M]+, found 332.10279 (Δppm = 5.00). Anal.: found (calcd.) for C₁₇H₂₅Rh: C, 62.32 (61.45); H, 7.51 (7.58).

6.7.2 Co-encapsulation studies

Standard procedure for the co-encapsulation of CpRh(cod) analogues with aromatic molecules

A vial equipped with stirring bar was charged with cage (5 µmol, 1 equiv.), Rh complex (15 µmol, 3 equiv.) and aromatic molecule (15 µmol, 3 equiv.). The vial was then purged with N₂/vacuum and D₂O was added. The vial was heated to 100 °C for 1 hour and filtered over a syringe filter. Formation of encapsulation was based on integration of the aromatic guest signals determining how much the full pyridine integration deviates from the expected 48 pyridine protons. The authors would further like to note that due to the low concentration of the guests, no ^13C NMR signals are reported as not all signals could be resolved.

1a•2•6

After encapsulation according to standard procedure, co-encapsulation was observed in 84% according to ^1H NMR. ^1H NMR (300 MHz, D₂O) δ 9.62 (s br, 4H, Py), 9.17 (s br, 29H, Py+empty 1a), 8.59 (s br, 18H, Py+empty 1a), 8.12 (s br, 4H, Py), 6.98 (s, 6H, Ar), 6.35 (s, 6H, Ar), 2.90 (s, 40H, CH₂+empty 1a), 2.09 (s, 5H, Cp), 0.92 (s, 4H, CH-COD), -0.36 (s, 4H, CH₂-COD), -0.94 (s, 4H, CH₂-COD). DOSY (D₂O, 298 K): log D = -9.735 m²/s

1a•3•6

After encapsulation according to standard procedure, co-encapsulation was observed in 74% according to ^1H NMR. ^1H NMR (500 MHz, D₂O) δ 9.50 (s, 6H, Py), 9.16 (s, 6H, Py), 9.05 (s br, 20H, Py+empty 1a), 8.95 (s, 6H, Py), 8.50 (s, 6H, Py), 8.46 (s br, 15H, Py+empty 1a), 8.00 (s, 6H, Py), 6.97 – 6.77 (m, 6H, Ar), 6.18 (s, 6H, Ar), 2.79 (d, J = 25.7 Hz, 32H, CH₂+empty 1a), 1.93 (s, 2H, Cp), 1.86 (s, 2H, Cp), 0.54 (s, 4H, COD), -0.38 (s, 4H, COD), -0.98 (d, J = 7.4 Hz, 4H, COD), -1.52 (s, 3H, CH₃). DOSY (D₂O, 298 K): log D = -9.816 m²/s

1a•4•6

After encapsulation according to standard procedure, co-encapsulation was observed in 21% according to ^1H NMR. ^1H NMR (500 MHz, D₂O) δ 9.65 (s, 6H Py), 9.25 (s, 8H Py), 9.21 (s, 16H Py), 9.14 (s, 11H Py), 8.68 (s, 14H Py+empty 1a), 8.62 (s, 6H Py), 8.02 (s, 6H Py), 7.05 – 6.84 (m, 6H Ar), 6.13 (s, 6H Ar), 2.92 (s, 21H CH₂), 2.88 (s, 17H CH₂), 1.66 (s br, 4H COD-CH), 1.36 (s br, 4H COD-CH₂), 1.10 (s, 1H Cp-H), 0.88 (s, 4H COD-CH₂), -1.70 (s, 6H Cp-Me), -1.72 (s, 6H Cp-Me). DOSY (D₂O, 298 K): log D = -9.731 m²/s
After encapsulation according to standard procedure, co-encapsulation was observed in 75% according to $^1$H NMR. $^1$H NMR (400 MHz, D$_2$O) \( \delta \) 9.46 (s, br, 7H), 9.11 (s, br, 6H, Py), 9.02 (s, br, 6H, Py), 8.92 (s, br, 12H, Py+empty 1a), 8.45 (s, br, 6H, Py), 7.96 (s, br, 6H, Py), 6.82 (s, 6H, Ar), 6.15 (s, 6H, Ar), 2.74 (s, 40H, CH$_2$+empty 1a), 1.97 (s, 2H, Cp), 1.76 (s, 2H, Cp), 0.36 (s, 4H, COD), -0.56 (s, 4H, COD), -1.13 (d, \( J = 7.8 \) Hz, 4H, COD), -1.39 (s, 3H, CH$_3$). DOSY (D$_2$O 298 K): log D = -9.73 m$^2$/s.

After encapsulation according to standard procedure, co-encapsulation was observed in 94% according to $^1$H NMR. $^1$H NMR (400 MHz, D$_2$O) \( \delta \) 9.91 – 7.76 (m, 51H, broad Py peaks), 6.64 (t, \( J = 7.6 \) Hz, 2H, Ar), 6.41 (d, \( J = 7.6 \) Hz, 2H, Ar), 6.16 (s, 2H, Ar), 2.88 (s, 25H, Pt(en)), 1.97 (s, 5H, Cp), 0.76 (s, 4H, COD), -0.58 (s, 4H, COD), -1.11 (d, \( J = 8.8 \) Hz, 2H, COD). DOSY (D$_2$O, 298 K): log D = -9.724 m$^2$/s.

After encapsulation according to standard procedure, co-encapsulation was observed in 80% according to $^1$H NMR. $^1$H NMR (400 MHz, D$_2$O) \( \delta \) 10.12 – 7.74 (m, 54H), 6.61 (t, \( J = 7.5 \) Hz, 2H, Ar), 6.41 (d, \( J = 7.7 \) Hz, 4H, Ar), 6.13 (s, 4H, Ar), 2.88 (s, 27H, Pt(en)), 2.02 (s, 2H, Cp-H), 1.52 (s, 2H, Cp-H), 0.51 (s, 4H, COD), -0.41 (s, 4H, COD), -0.95 (d, \( J = 8.5 \) Hz, 4H, COD), -1.30 (s, 3H, Cp-CH$_3$). DOSY (D$_2$O, 298 K): log D = -9.749 m$^2$/s.

After encapsulation according to standard procedure, co-encapsulation was observed in 37% according to $^1$H NMR. $^1$H NMR (300 MHz, D$_2$O) \( \delta \) 10.23 – 7.59 (m, 74H, Py+empty 1a), 6.51 (d, \( J = 7.7 \) Hz, 2H, Ar), 6.29 (d, \( J = 7.7 \) Hz, 4H, Ar), 5.95 (s, 4H, Ar), 3.18 – 2.65 (m, 33H, Pt(en)), 1.62 (d, \( J = 8.7 \) Hz, 4H, COD), 1.31 (s, 4H, COD), 0.80 (s, 4H, COD), 0.75 (s, 1H, Cp), -1.57 (s, 6H, CH$_3$), -1.91 (s, 6H, CH$_3$). DOSY (D$_2$O, 298 K): log D = -9.763 m$^2$/s.

After encapsulation according to standard procedure, co-encapsulation was observed in 92% according to $^1$H NMR. $^1$H NMR (400 MHz, D$_2$O) \( \delta \) 10.26 – 7.66 (m, 52H), 6.60 (t, \( J = 7.7 \) Hz, 2H, Ar), 6.42 (d, \( J = 7.7 \) Hz, 4H, Ar), 6.12 (s, 4H, Ar), 2.88 (s, 25H, Pt(en)), 2.09 (s, 2H, Cp-H), 1.42 (s, 2H, Cp-H), 0.37 (s, 4H, COD), -0.53 (s, 4H, COD), -1.05 (d, \( J = 8.5 \) Hz, 4H, COD), -1.13 (s, 3H, Cp-CH$_3$). DOSY (D$_2$O, 298 K): log D = -9.756 m$^2$/s.
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After encapsulation according to standard procedure, co-encapsulation was observed in 40% according to $^1$H NMR. **$^1$H NMR** (400 MHz, D₂O) δ 9.75 – 7.84 (m, 121H), 6.61 (d, $J = 8.1$ Hz, 4H, Ar), 6.12 (d, $J = 7.6$ Hz, 4H, Ar), 5.74 (t, $J = 7.8$ Hz, 4H, Ar), 2.86 (s, 67H, Pt(en)), 2.12 (s, 5H, Cp-H), 1.10 (s, 4H, COD), -0.27 (s, 4H, COD), -0.89 (s, 4H, COD). **DOSY** (D₂O, 298 K): log D = -9.717 m²/s

After encapsulation according to standard procedure, co-encapsulation was observed in 61% according to $^1$H NMR. **$^1$H NMR** (400 MHz, D₂O) δ 9.95 – 7.72 (m, 78H, Py+empty 1a), 6.63 (d, $J = 8.3$ Hz, 4H, Ar), 6.14 (d, $J = 7.7$ Hz, 4H, Ar), 5.77 (s, 4H, Ar), 2.91 (s, 39H, Pt(en)+ empty 1a), 2.23 (s, 2H, Cp), 2.04 (s, 2H, Cp), 0.90 (s, 4H, cod), -0.16 (s, 4H, cod), -0.79 (s, 4H, cod), -1.32 (s, 3H, CH₃). **DOSY** (D₂O, 298 K): log D = -9.717 m²/s

After encapsulation according to standard procedure, co-encapsulation was observed in 36% according to $^1$H NMR. **$^1$H NMR** (400 MHz, D₂O) δ 10.14 – 7.65 (m, 134H, Py+empty 1a), 6.50 (d, $J = 7.9$ Hz, 4H, Ar), 5.95 (d, $J = 6.6$ Hz, 4H, Ar), 5.72 (s, 4H, Ar), 2.91 (s, 69H, Pt(en)+empty 1a), 1.16 (s, 4H, cod), 1.10 (s, 1H, Cp), 0.64 (s, 4H, cod), 0.06 (s, 4H, cod), -0.46 (s, 4H, cod), -1.69 (d, $J = 9.5$ Hz, 12H, CH₃). **DOSY** (D₂O, 298 K): log D = -9.742 m²/s

After encapsulation according to standard procedure, co-encapsulation was observed in 47% according to $^1$H NMR. **$^1$H NMR** (300 MHz, D₂O) δ 9.91 – 7.80 (m, 103H, Py+empty 1a), 6.62 (d, $J = 8.2$ Hz, 4H, Ar), 6.14 (d, $J = 7.7$ Hz, 4H, Ar), 5.77 (t, $J = 7.7$ Hz, 4H, Ar), 2.91 (s, 53H, Pt(en)+empty 1a), 2.29 (s, 2H, Cp), 1.96 (s, 2H, Cp), 0.75 (s, 4H cod), -0.31 (s, 4H, cod), -0.91 (s, 4H, cod), -1.15 (s, 3H, CH₃). **DOSY** (D₂O, 298 K): log D = -9.529 m²/s

6.7.3 Determination of the CT band energies

The charge-transfer band energies were determined by a spectral line-shape analysis of the absorption spectra using Multipeak fitting package in IgorPro v6.36. The absorption spectra were converted from nanometer to wavenumber domain and the different absorption bands were approximated with Gaussian functions. Due to the large overlap of the different absorption bands we had to use up to three Gaussian functions to increase the accuracy of the determination of the CT band energy. The fittings were most reliable in the case of triphenylene (6) where the CT band is well separated from the main absorption band. In the case of pyrene (7), the long wavelength absorption consists of two distinct bands, one located at ~450 nm and a weaker band at ~600 nm. The band at ~450 nm did not exhibit significant changes in the peak position (variation < 15 nm) with the different metal complexes. Therefore the weaker lowest energy band was attributed to the CT absorption band. In the
case of perylene (8), the main absorption of the chromophore overlaps with the CT band especially with RhCp (2), RhCpMe (3), and IrCpMe (5) complexes. Therefore, it was necessary to fit part of the perylene spectrum to increase the accuracy in determination of the peak maxima of the CT band.

**Table 3:** Wavelengths (nm) and corresponding energies (eV) of the charge transfer (CT) bands obtained from fitting the curves.

<table>
<thead>
<tr>
<th>Aromatic Guest</th>
<th>Pyrene (7)</th>
<th>Triphenylene (6)</th>
<th>Perylene (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{CT}$</td>
<td>$E_{CT}$</td>
<td>$\lambda_{CT}$</td>
</tr>
<tr>
<td>(CpMe)Ir(cod)</td>
<td>0.12</td>
<td>0.030</td>
<td>24000</td>
</tr>
<tr>
<td>(Cp)Rh (cod)</td>
<td>0.07</td>
<td>0.032</td>
<td>28000</td>
</tr>
<tr>
<td>(CpMe)Rh (cod)</td>
<td>0.02</td>
<td>0.035</td>
<td>25000</td>
</tr>
<tr>
<td>(CpMe)Ir (5)</td>
<td>-0.28</td>
<td>0.0051</td>
<td>0.52</td>
</tr>
</tbody>
</table>

6.7.4 Electrochemistry

Cyclic voltammetry was performed on (close to) 1 mM solutions of the analyte in dichloromethane containing 0.1 M nBu$_4$NPF$_6$ as the supporting electrolyte. The voltammograms were recorded using a PGSTAT302N potentiostat (Metrohm/Autolab), a glassy carbon disk (1 mm diameter) as a working electrode, a glassy carbon rod as an auxiliary electrode and a leakless Ag$^{0/+}$ reference electrode (eDAQ ET069). To convert the potential values of the Ag$^{0/+}$ reference to Fe$^{0/+}$ a correction factor of –0.57 V was used as determined by cyclic voltammetry of 1 mM ferrocene in dichloromethane using the same reference electrode. Solution resistance was compensated to 90-95%.

Cyclic voltammetric data was fitted using DigiElch 7 (ElchSoft). For each species, voltammograms from 3 different scan rates (0.1/0.3/1.0 V/s) were fitted simultaneously.

**Redox properties by digital simulation**

The only model that could be properly fitted to all of the voltammograms is a quasi-reversible redox process followed by a reversible chemical transformation:

Redox: $A \leftrightarrow B \quad (E_{ox}; k_s; \alpha)$ with $\alpha = 0.5$  

Chemical: $B \leftrightarrow C \quad (k_f; k_b)$

<table>
<thead>
<tr>
<th></th>
<th>$E_{ox}$ [V] vs Fe$^{0/+}$</th>
<th>$k_s$ [cm/s]</th>
<th>$k_f$</th>
<th>$k_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CpMe)Ir(cod)</td>
<td>0.12</td>
<td>0.030</td>
<td>24000</td>
<td>7.2</td>
</tr>
<tr>
<td>(Cp)Rh (cod)</td>
<td>0.07</td>
<td>0.032</td>
<td>28000</td>
<td>9.2</td>
</tr>
<tr>
<td>(CpMe)Rh (cod)</td>
<td>0.02</td>
<td>0.035</td>
<td>25000</td>
<td>12</td>
</tr>
<tr>
<td>(CpMe)Ir (5)</td>
<td>-0.28</td>
<td>0.0051</td>
<td>0.52</td>
<td>0.055</td>
</tr>
</tbody>
</table>

Since the chemical follow-up reaction is almost non-existent for the CpMe$_4$ species, we ascribe the transformation to a change in Cp coordination, which is in this case most probably slowed down by increased CpMe$_4$ bulk compared to the Cp and CpMe species.

6.7.5 X-ray Crystal Structure of ternary complex 1b•5•6

Crystallographic diffraction data were measured on a Bruker APEX-II/CCD diffractometer equipped with a focusing mirror (Mo Ka radiation $\lambda = 0.71073$ Å) with a cryostat system equipped with a N$_2$ generator (Japan Thermal Eng.). The crystals were removed from the solution, quickly attached to a
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loop of nylon fiber with antifreeze reagent (PVP, Hampton research), and mounted on a goniometer. The data collection was performed at 90 K. The structures were solved by direct methods (SHELXS-2014) and refined by full-matrix least-squares calculations (SHELXL-2014) on $F^2$. Hydrogen atoms were fixed at calculated positions and refined using a riding model.

Single crystals of $\text{1b}•\text{5}•\text{6}$ were obtained by combining $\text{1b}$ (15 µmol, 53 mg), $\text{5}$ (45 µmol, 17 mg) and $\text{6}$ (45 µmol, 11 mg) in a vial with $\text{D}_2\text{O}$ (1 mL). The suspension was then heated for 1 hour at 100 °C, cooled down and filtered over a syringe filter. The clear solution was left to stand in an NMR tube over a week to obtain single crystals.

Various needle crystals were tested, good diffraction data was obtained from a needle crystal of a $(\text{CpMe})\text{Ir(cod)}•\text{triphenylene}$ co-encapsulation complex. Although the Ir complex ($\text{5}$) and triphenylene ($\text{6}$) pair was disordered in three positions, the host-guest structure was clearly observed.

6.8 References


