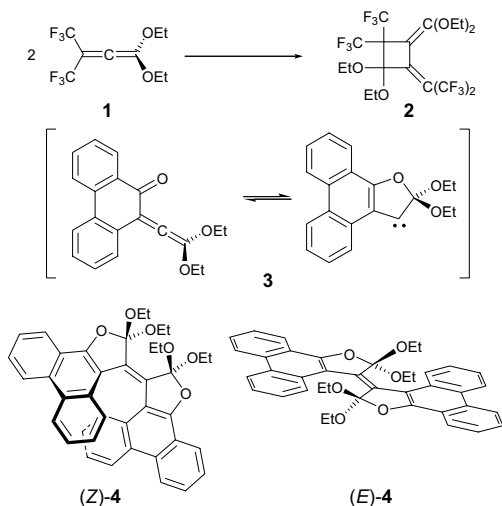


From Allenes to Oligonuclear Complexes

A well-balanced integration of carefully planned strategies, combined with a straightforward evaluation of developing new points of view, has spontaneously uncovered a variety of topics, through which runs a common thread, and which are discussed below.

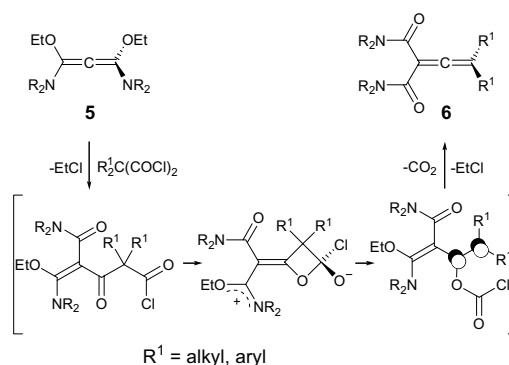
Die ausgewogene Abstimmung sorgfältig geplanter Strategien in Kombination mit einer unmittelbar anschließenden Auswertung sich neu entwickelnder Perspektiven ließ spontan eine Reihe von Themen sichtbar werden, durch die sich ein roter Faden zieht, und die im Folgenden diskutiert werden.

Recognizing the similarities in different areas of chemistry allows the prediction of potential results in related fields. For instance, during our investigations on carbenes, we became interested in push-pull substituted allenes. Due to the ambiphilicity (carbene character) of their central carbon atom, they readily dimerize. Examples for this are the dimerization of 1,1-bis(trifluoromethyl)-3,3-bis(diethoxy)allene **1** to give 1,2-bis(methylene)cyclobutane **2** or the dimerization of allene **3** to give the olefins (*Z*)-**4** and (*E*)-**4** (Scheme 1).^[1]



Scheme 1. Dimerization of **1** and **2**.

Stimulated by our investigations on push-pull substituted allene **1**, we focused on tetradonor-substituted allenes, and as a result, we employed tetraethoxyallene as a synthetic equivalent to the fictitious malonic ester 1,1/1,3- dianion synthon. This concept led to the synthesis of heterocumulenes and, even more importantly, starting from 1,3-bis(dialkylamino)-1,3-diethoxyallenes (**5**) to the synthesis of allene-1,1-dicarboxanilides (**6**) via *transallenation* (Scheme 2).^[1]

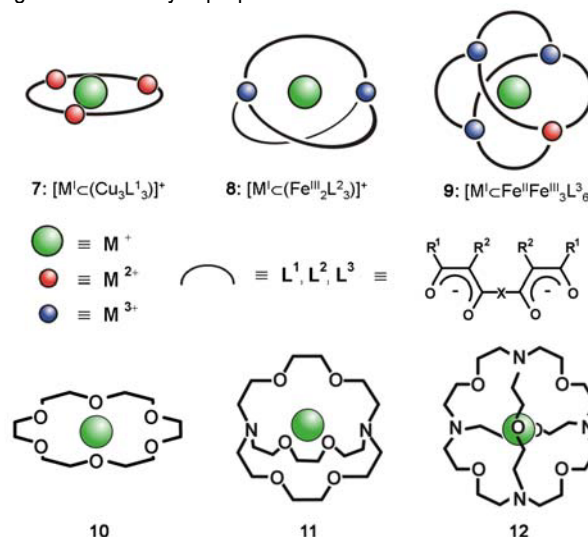


Scheme 2. Mechanism of the *transallenation*.

The allene-carboxanilides **6** isomerize via intramolecular Diels-Alder reaction or intermolecular Domino cyclization to give heterocycles. In addition, starting from propargyl alcohols, via [2.3]/[3.3]-sigmatropic rearrangement, we developed a new method for the synthesis of 1,1-functionalized allenes. Butatrienes are accessible via *cumuhomologation*.^[1]

Most of the supramolecular systems which have been generally known in the past, trace back to serendipitous discoveries. However, more recently a concept to rationally design oligonuclear metal complexes was developed.

According to a procedure developed in our laboratories, the metalla-topomers **7-9** of the well known coronates **10** and cryptates **11** and **12** were prepared in one-pot reactions in gram scale (Scheme 3).^[2-4] In comparison with the conventional *N*-linked bi- and tricyclic supramolecular structures **11** and **12**, the new complexes **8** and **9** feature that in their case metal ions function as bridgehead atoms. In contrast to their mere organic counterparts **10-12**, according to the extra metal ions, the complexes **7-9** exhibit additional spectroscopic, electronic, magnetic and catalytic properties.



Scheme 3. Comparison of metalla-topomers with classical supramolecular systems.

The template mediated reaction of diethyl ketipinate (H_2L^1) and copper(II) acetate in the presence of calcium nitrate after crystallization from tetrahydrofuran/diethylether afforded green crystals of complex $[Ca \subset (Cu_3(L^1)_3)(NO_3)_2] \cdot THF \cdot H_2O$ (**13**). In **13**,

the copper ions in the ring are linked by bis-bidentate ketipinate dianions ($L^{1/2-}$, creating a square planar arrangement of oxygen donors around each copper(II) center. Additional coordination of water, tetrahydrofuran and nitrate ions, respectively, results in a square pyramidal environment at all copper ions. The charge of the calcium ion in the center of the metalla-cryptand is compensated by two axially coordinated nitrate ions (Fig. 1, left). Whereas, the encapsulation of the small calcium ion leads to the host-guest system **13** with 1:1 stoichiometry, double deprotonation of bis-tert.-butyl ketipinate (H_2L^2) with 2N potassium hydroxide followed by reaction of the dianion ($L^{2/2-}$ with copper(II) chloride dihydrate, the metalla-crown sandwich complex $\{K\text{-}[Cu_3(L^2)_3]_2OMe\}\cdot 7HOMe$ (**14**) with 2:1 stoichiometry is formed. The molecular structure reveals, **14** being composed of two neutral trimetalla-crown-6-building blocks, rotated by 60° against each others, sandwiching a potassium ion. (Fig. 1, right).^[2]

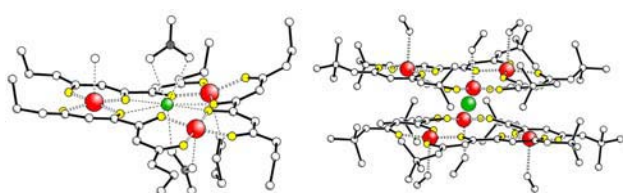


Figure 1. Left: Metalla-coronate **13**. Right: Cation of sandwich **14+**. Counterion MeO^- omitted for clarity.

Deprotonation of 1,1'-(2,6-pyridylene)bis-1,3-(4-dimethyl)pentandione (H_2L^3) with potassium hydride in THF, followed by addition of iron(III) chloride and work up with aqueous potassium hexafluorophosphate accomplishes bicyclic metalla-cryptate $\{K\text{-}[Fe_2(L^3)_3]\}(PF_6)$ (**15**) (Fig. 2).^[3]

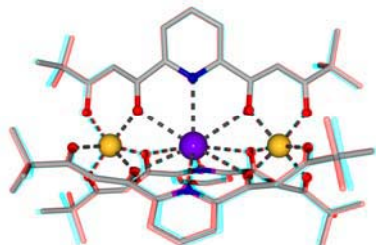
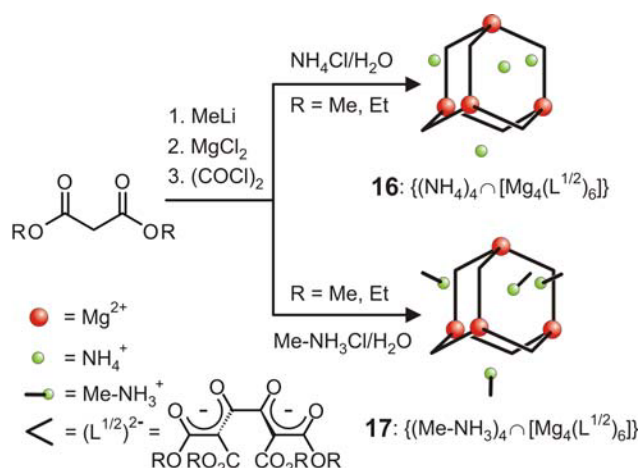


Figure 2. Stereo view of the cation of metalla-cryptate **15**. Counterion $(PF_6)^-$ omitted for clarity.

In the case of **15**, three doubly deprotonated ligands (L^3) together with two iron(III) ions built up the neutral cryptand, which due to the extra electron density derived from the pyridyl spacer is capable to host a cation in the center. Counterion is a hexafluorophosphate anion.

We have previously reported the gram-scale one-pot synthesis of tetrahemispheraplexes **16** and **17** in high yields by deprotonation of dialkyl malonates with methylithium, subsequent addition of magnesium chloride and oxalyl chloride followed by workup with NH_4Cl , $Me-NH_3Cl$, or MOH ($M = K, Cs$) (Scheme 4).^[4]



Scheme 4. Synthesis of the tetrahemispheraplexes **16** and **17**.

Similar complexes are also accessible with Mn^{2+} , Co^{2+} , and Ni^{2+} . In the case of iron(III) we were able to generate all-iron(III) complex $\{H_2O\text{-}[Fe^{III}_4(L^2)_6]\}$ **18** with endohedrally encapsulation of water and four acetonitrile solvent molecules in the pockets of the tetrahedron faces. Minor changes of the reaction conditions led to mixed-valent species like $\{M\text{-}[Fe^I Fe^{III}_3(L^2)_6]\}$ **19** with endohedral encapsulation of a K^+ - oder Cs^+ -ion for charge compensation (Fig. 3).^[4]

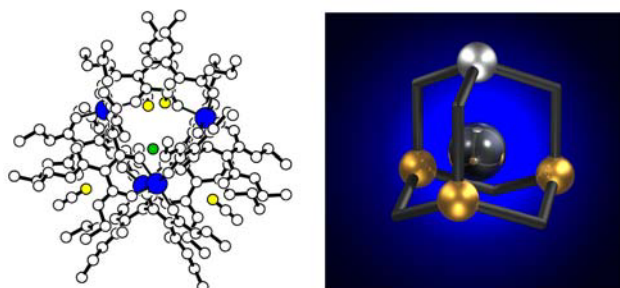


Figure 3. Left: Structure of complex **18**. Right: Cartoon of complex **19**.

In an attempt to generalize the methodology for the construction of three-dimensional complexes with $[M_4L_6]$ stoichiometry, as realized for **18** and **19** with the threefold symmetric tris-bidentate ligands allow the synthesis of clusters of general stoichiometry $[M_4L_4]$.

The construction of a tetrahedral scaffold with $[M_4L_6]$ stoichiometry like **18** and **19** results from the linkage of the four metal ions by six bis-bidentate chelating ligands along the edges. On the other hand, complexes with $[M_4L_4]$ stoichiometry as **20** are accessible with threefold symmetric tris-bidentate ligands. In this case the ligands link three metal ions each across the tetrahedral faces (Fig. 4).^[5]

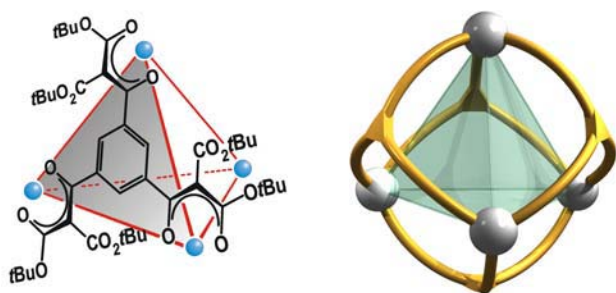
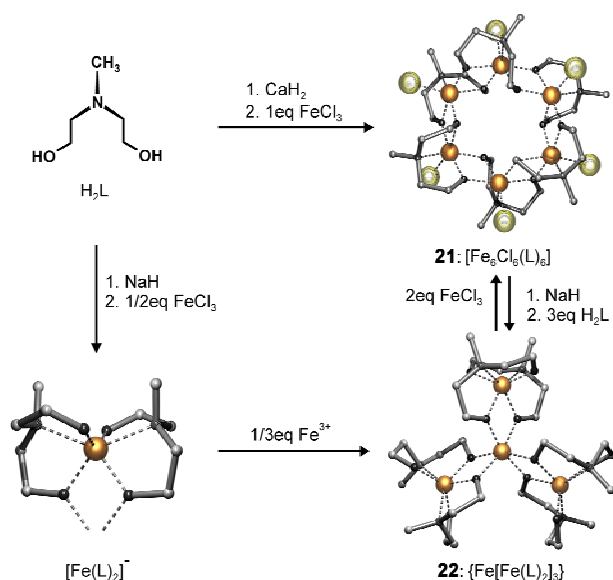


Figure 4. Cartoon presentations of **20**.

In earlier work, we were interested in the template mediated synthesis of six- and eight-membered metalla-coronates $[M\{\text{Fe}_n[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]_n\}]^+$ ($M = \text{Na}, \text{Cs}; n = 6, 8$) so called *ferric wheels* on the basis of triethanolamine. Detailed studies on these systems, initiated the design of many different six-membered iron-coronands like **21** on the basis *N*-substituted diethanolamines. Mechanistic studies on the formation of the *ferric wheels* **21** revealed, that the *ferric stars* **22** are precursors. (Scheme 5).^[6]



Scheme 5. Synthesis of *ferric wheels* **21** and *ferric stars* **22**. Exemplarily demonstrated for *N*-methyldiethanolamine.

Besides for the synthesis of many other metalla-coronands, this method was also used for the convergent synthesis of metalla-dendrimers alike **23** (Fig. 5).

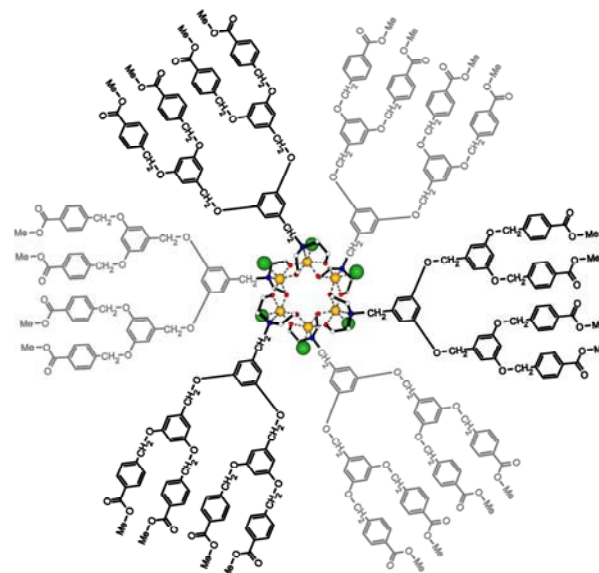


Figure 5. Metalla-dendrimer **23**.

As demonstrated for the diamagnetic indium wheel **24** by variable temperature ^1H NMR spectroscopy (VT ^1H NMR), these systems are not rigid, but rather dynamic, given the fact, the ligands are sufficiently flexible (Fig. 6).^[7]

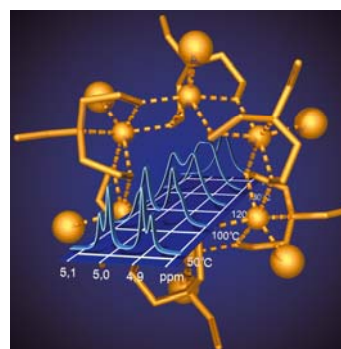


Figure 6. Schematic presentation of indium wheel **24**, together with a detail of its VT ^1H NMR spectrum.

Principally, all *ferric wheels* are isostructural, however, they differ fundamentally with respect to their crystal packing. Depending on the nature of their sidearms, the ferric wheels create various substructures. Some create ball shaped discrete molecules, others pile in parallel in cylindrical columns, give rise to compartementation through pronounced van der Waals interaction with incorporated guest molecules or three-dimensional scaffolds by strong π - π interaction as demonstrated for **25** (Fig. 7).^[8]

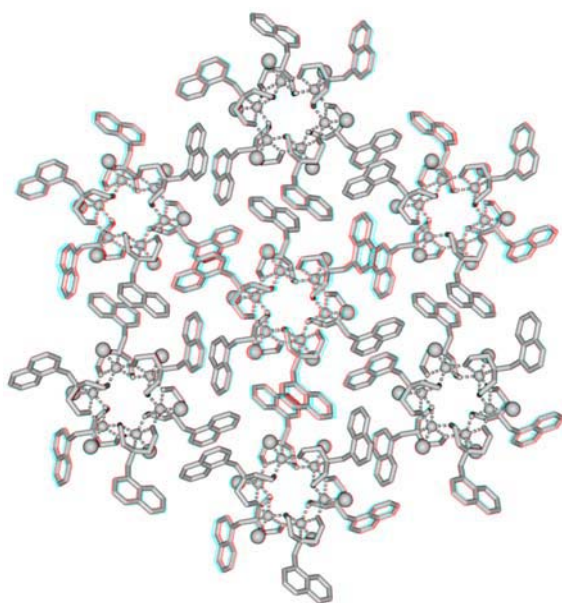


Figure 7. Stereo view of 3D-network of **25**.

As exemplarily shown for **26**, it is possible to determine the exact location of the Mn- and Fe ions in the metal-centered, six-membered, mixed-valent, heterometallic wheel by the combination of FAB-mass spectrometric, X-ray diffractometric, and cyclic voltammetric techniques (Fig. 8).^[9]

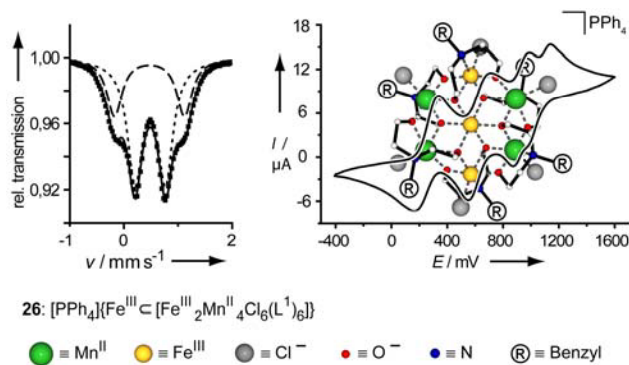


Figure 8. Schematic presentation of complex **26** together with its Mössbauer spectrum and cyclic voltammogram.

The *ferric star* $\{\text{Fe}[\text{Fe}(\text{L})_2]_3\}$ **22** is a single molecule magnet (SMM) and shows hysteresis on magnetization and the *ferric wheel* $[\text{Na}\{\text{Fe}_6[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]_6\}]^+$ **27** reveals cooling by adiabatic increase of magnetization (in cooperation with Prof. Dr. P. Müller, Institute of Physics, Erlangen) (Fig. 9).^[10]

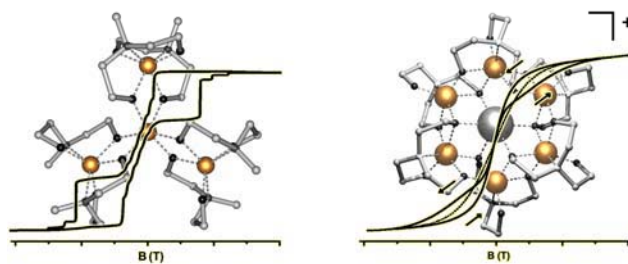


Figure 9. Schematic presentation of the magnetic properties of *ferric star* **22** and *ferric wheel* **27**.

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Prof. Dr. R. W. Saalfrank
 Institut für Organische Chemie
 Universität Erlangen-Nürnberg, 91054 Erlangen
 F.: +49(0)9131-852-2554
 Fax: +49(0)9131-852-1165
 e-mail: saalfrank@chemie.uni-erlangen.de