

Subproject C1.06

**Generation and Applications of new Nano-Structured Materials
Novel Chiral Lanthanides-C₆₀ Buckminster Fullerene Clusters**

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Introduction

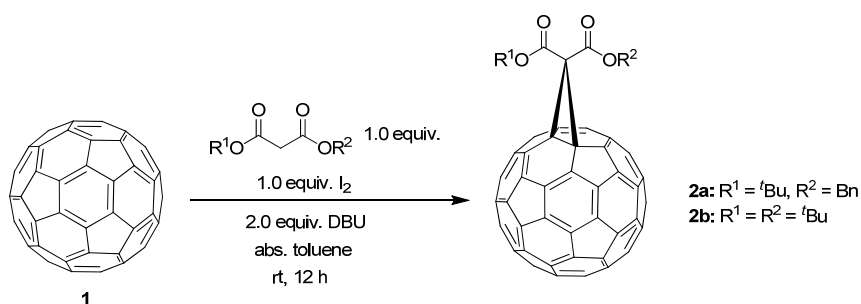
The subproject C1.06 conducted as a co-operation between the research groups of Prof. P. W. Roesky and Prof. S. Bräse deals with the synthesis and the application of novel nano-structured coordination compounds comprising lanthanides–C₆₀ Buckminster fullerene clusters.

These novel nano-structured clusters shall disclose intriguing properties because lanthanide complexes exhibit fundamentally different optical and magnetic properties compared to transition metal clusters. Besides, C₆₀ fullerenes offer very flexible addition types. This offers several coordination possibilities engendering manifold structural motives. Moreover, the fullerene core features remarkable opto-electronic properties. Its capacity of accepting up to six electrons leads to widespread scopes of application as Organic Light Emitting Diodes (OLEDs) and Organic Photovoltaics (OPs). Bearing these considerations in mind, attaching lanthanides to fullerenes should facilitate the formation of versatile coordination compounds with exciting new properties.

Synthesis of the Methanofullerene Ligands

As mentioned above the aim of our project is the synthesis of lanthanide complexes, which are ligated by various functionalized C₆₀ derivatives. In order to prepare these coordination compounds, fullerene mono-adducts bearing one functional group as binding site for the lanthanide were studied in the beginning of the project. We first focused on easily accessible mono-adducts of C₆₀ to understand the complexation behavior of these compounds in lanthanide chemistry.

As the conversion of C₆₀ (**1**) with malonates via the Bingel reaction^[1] is a well understood and reliable method to get diversely functionalized fullerenes and as malonic acid derivatives were considered to be promising ligands, we decided to synthesize C₆₀–malonate adducts first, to understand their coordination behavior. Former studies carried out by the Bräse group showed that a variation of the Bingel-Hirsch reaction protocol using iodine and DBU as reagents, (Scheme 1) afforded best yields and purities for C₆₀–mono-adducts.



Scheme 1: Synthesis of malonate–Buckminster fullerene mono-adducts.

The malonates **2a**, **2b**, obtained by this synthetic route, were treated with trifluoro acetic acid to yield the corresponding acids **3a**, **3b** (Figure 1). Compound **3a** is expected to complex only one lanthanide atom, whereas monoadduct **3b** offers the possibility to generate a bimetallic complex.

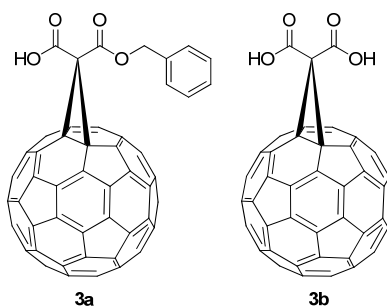


Figure 1: Malonic acid–Buckminster fullerene mono-adducts.

Moreover, we were also interested in enantiomerically pure chiral complexes, because of their high synthetic potential. These kinds of compounds could be used for example in asymmetric organic reactions or for the construction of enantiopure metal clusters. Therefore we also synthesized fullerenes, functionalized by bisoxazoline (Box) ligands (Figure 2, **4a–4e**). Bisoxazolines are known to undergo addition reactions to C_{60} under Bingel reaction conditions because they can be regarded as masked malonates. As found by the Bräse group in this case also the iodine-modified Bingel-reaction (Scheme 1) afforded the best yields of mono-adducts **4**.

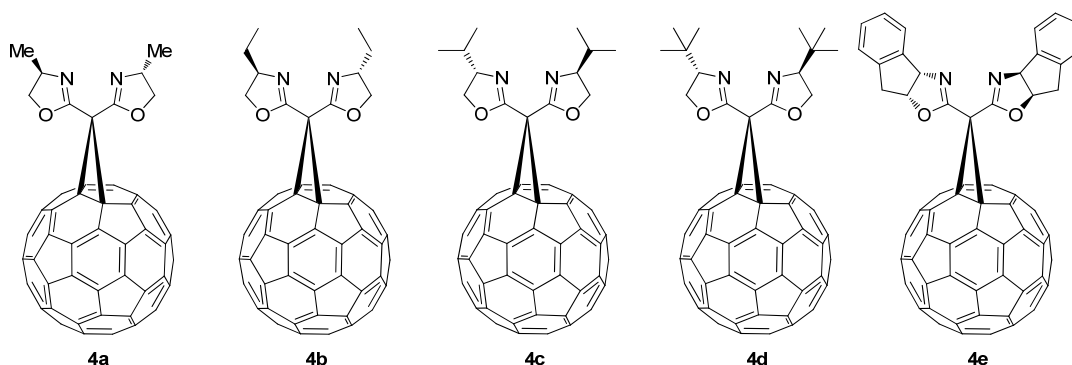


Figure 2: Bisoxazoline–Buckminster fullerene mono-adducts.

Having successfully synthesized malonic acid and bisoxazoline fullerene mono-adducts we decided to obtain C_{60} derivatives with other functional groups which potentially can coordinate to lanthanide metals. Our first choice were β -diketones since a number of lanthanide derivatives are known. Up to now, there are only few examples of Bingel reactions with β -diketones^[2]. Therefore we decided to make more of these compounds accessible. We were able to isolate two C_{60} - β -diketone derivatives with promising complexation properties (Figure 3; **5a**, **5b**) by just using the same protocol as for the mono adducts mentioned above. Especially the pyridyl derivative **5b** should be a very potent ligand, as, due to the N-atom in close neighborhood of the carbonyl group, it is able to coordinate to two metal centers.

Besides the above mentioned mono-adducts we also synthesized fullerene derivatives bearing macrocyclic malonate functionalities (**6**) that give rise to crownether complexes.

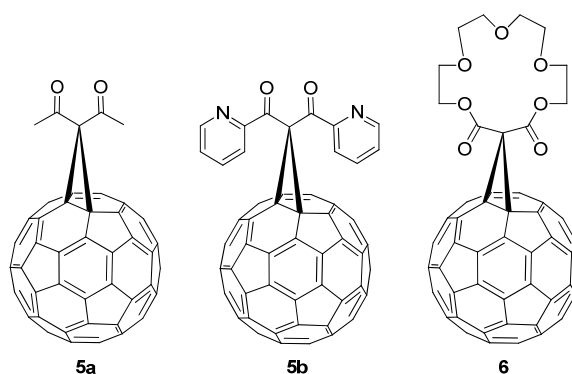
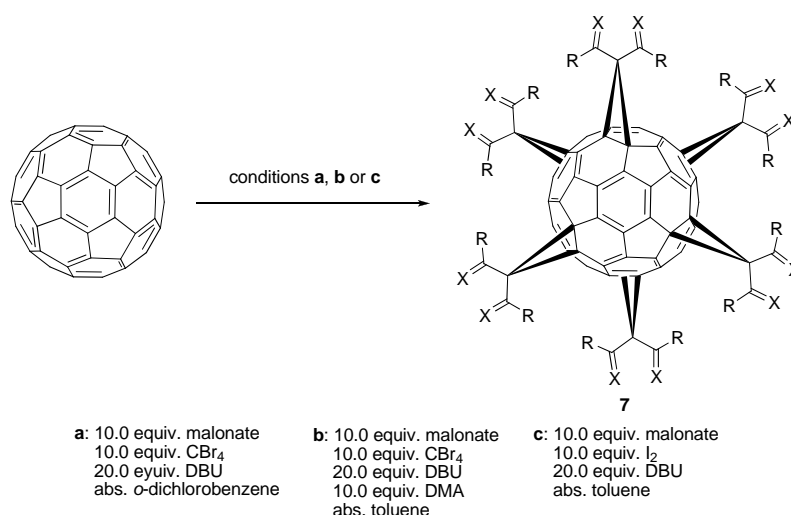


Figure 3: C_{60} - β -diketone **5a**, **5b** and crownether-derivatives **6**.

As the Bräse group has got expert knowledge in the synthesis of Buckminster Fullerene hexakis-adducts we also planned to use appropriate sixfold functionalized C_{60} -derivatives for the construction of lanthanide complexes.

There are three different protocols that allow access to fullerene hexakis adducts (Scheme 2, **7**). The one using iodine instead of carbon tetrabromide (conditions **c**) was established by the Bräse group and is to date the first example of a sixfold Bingel reaction with iodine as halogenating reagent.



Scheme 2: Synthesis protocols for the sixfold Bingel reaction by Sun (**a**)^[3], Hirsch (**b**)^[4] and Bräse (**c**).

Applying these three protocols we synthesized a couple of new hexakis adducts suitable for complexation experiments with lanthanides (figure 4).

Due to their comparatively bulky chiral rests complexes of the Box-derivatives **8c** and **8d** (Figure 4) come into consideration to act as chiral Lewis acid catalysts in asymmetric reactions. Indeed the corresponding copper chloride complex (Figure 5, **9**) showed acceptable asymmetric inductions in Diels-Alder reactions as preliminary results show. In the literature there are few examples of catalytically active chiral pyridine-Box-lanthanide-complexes.^[5] That is why we consider Fullerene derivatives of simple Box to be very potent catalysts, too.

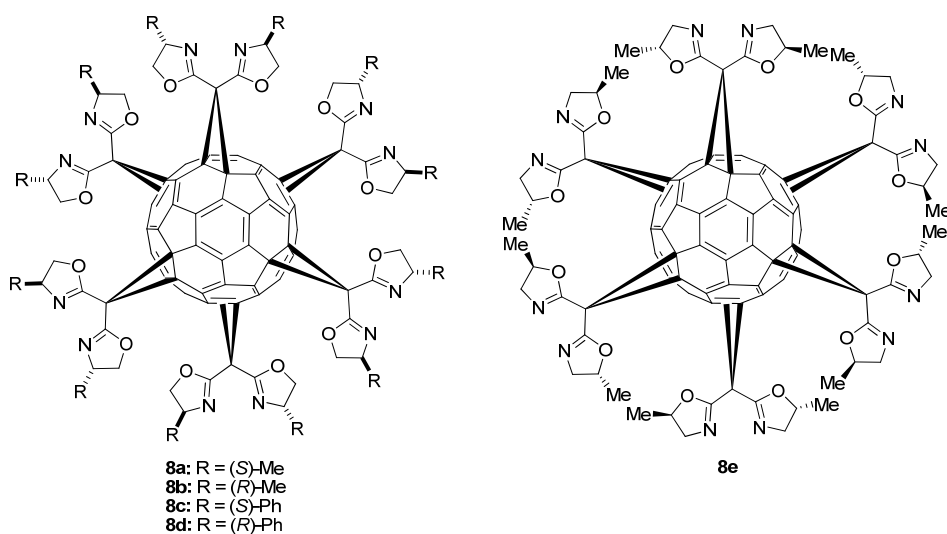


Figure 4: Hexakis-Box Buckminster fullerene adducts.

The compounds bearing less bulky chiral rests might be suitable to form complexes of the formula $M(\text{Box})_2$ (**10**) and thus yield chiral lanthanide clusters (Figure 5).

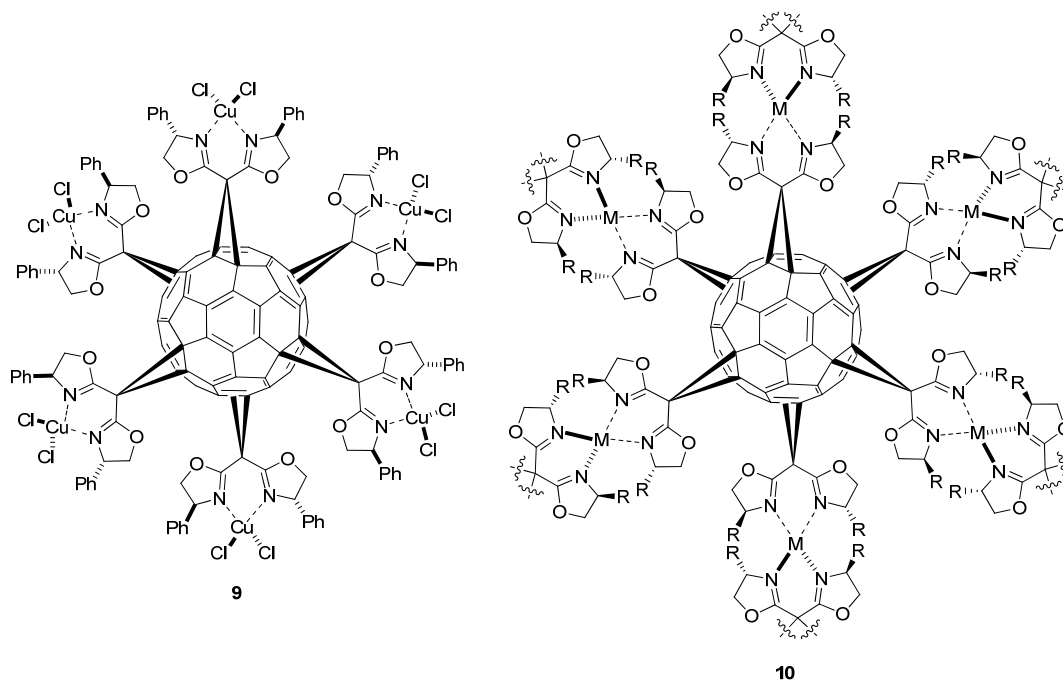
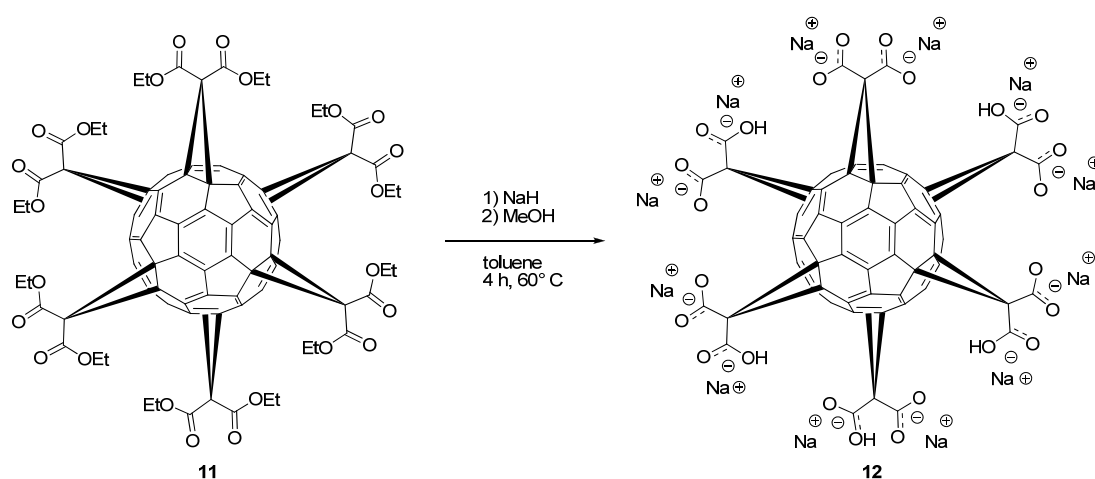


Figure 5: Complexes of the stoichiometries $M(\text{Box})X_2$ (**9**) and $M(\text{Box})_2$ (**10**).

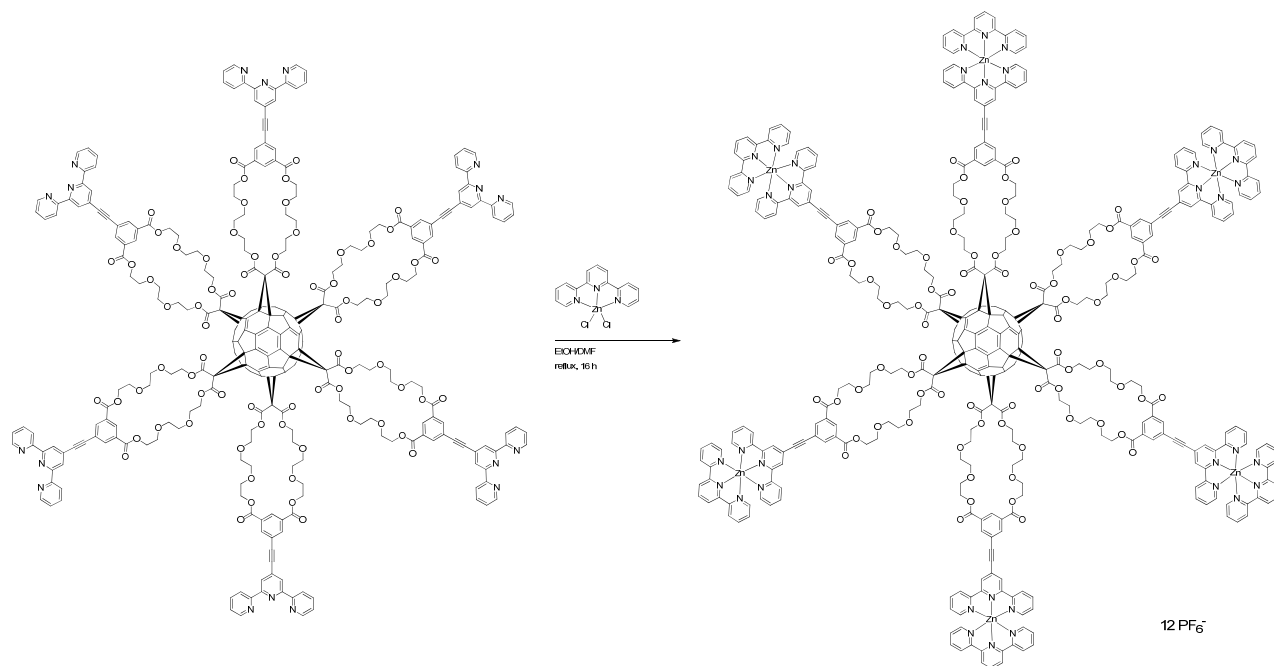
Especially the methyl derivative **8e** (Figure 4) should be predestined for that because, in comparison to the other Box-derivatives, its chiral rests are farer away from the metal coordinating N-Atoms. Thus they will not interfere with those of the second Box-unit in the above mentioned complexes. Following a protocol by A. Hirsch *et al.*^[6] that starts from the hexakis adduct **11** we obtained the dodeca sodium carboxylate **12** (Scheme 3). This compound is likely to coordinate up to twelve lanthanide ions and therefore is a very auspicious complex ligand.



Scheme 3: Synthesis of the C_{60} -dodeca sodium carboxylate **12**.

The coordination behavior of the above mentioned compounds towards lanthanides is now being investigated by the group of P. W. Roesky. This group has already covered the spherical shaped polyphosphide P_8^{4-} with four lanthanide atoms [C1.06:4].

In addition to the box systems, we continued to evaluate crown ether type fullerene hybrids. The complexation with a large set of metals (e.g. iridium (shown), copper, iron) gave nanometer large systems. The complexation of crown ether was examined in collaboration with the Klopfer group.

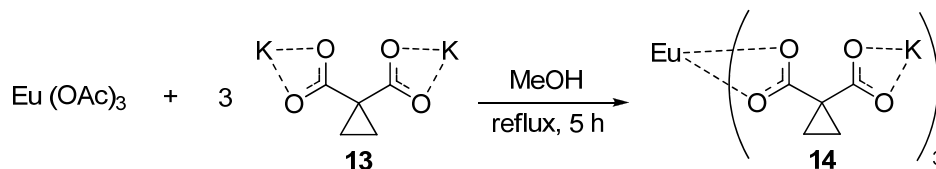


Scheme 4: Example of a synthesis of a crown ether C_{60} metal complex.

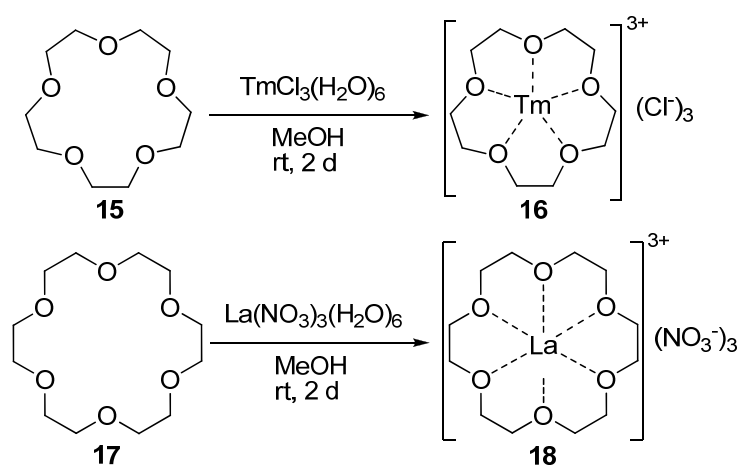
Synthesis of the model-compounds

Parallel to the organic synthesis we evaluated the coordination properties of the above mentioned functional groups before the functionalized fullerenes were made in larger scale. To get this valid information the Roesky group synthesized some model compounds bearing the same functional groups as the corresponding fullerene adducts. By using this strategy we could establish a successful synthetic protocol for lanthanide complexes parallel to the efforts in organic synthesis.

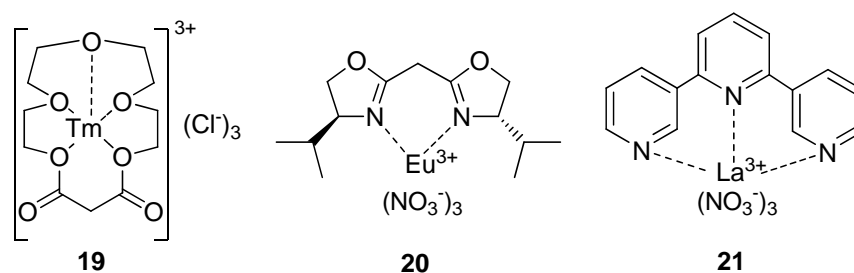
The first class of model compounds used were the cyclopropane dicarboxylates **13** (Scheme 4) being a model for the Fullerene derivatives **3a**, **3b**, **12**. As expected, together with Eu(III) this malonate derivative yielded a complex of the stoichiometry ML_3 (Scheme 4, **14**).



As a benchmark for the complexation properties of the crown-ether-like C_{60} -monoadducts (Figure 3) we synthesized the crown-ether complexes **16** and **18** (Scheme 5).

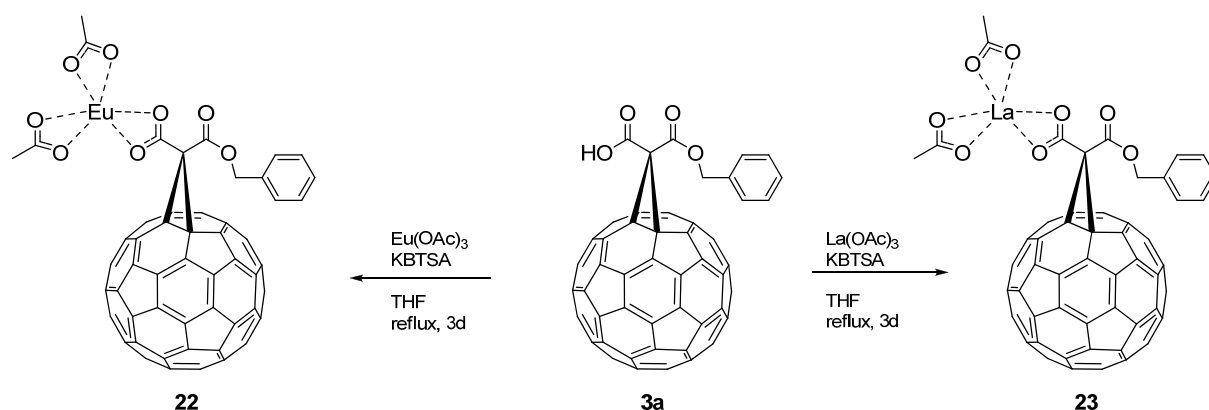


Applying the same reaction conditions we were also able to gain access to Ln-complexes of macrocyclic malonates (**19**), bisoxazolines (**20**) and terpyridines (**21**) (Figure 6).



Synthesis of the fullerene-lanthanide-complexes

After successfully synthesizing many lanthanide model complexes we then started to transfer our knowledge to the fullerene-adducts. Some difficulties occurred, which are the result of the different steric demand and the lower solubility of the fullerenes compared to the model compounds. The first products that could be obtained by using the modified synthetic protocol of the model complexes were the lanthanide carboxylate compounds of the fullerenes (Scheme 6).



Scheme 7: Europium- (**22**) and lanthanum-carboxylate-complex (**23**).

The desired europium- and lanthanum-acetate-complexes (**22**, **23**) were obtained in good yields. As a result of the low solubility of the functionalized fullerene in all of the common solvents (e. g. hexane, tetrahydrofuran, toluene, acetonitrile, dimethylsulfoxide, etc.) long reaction times were necessary. The new compounds could be characterized by NMR and MS.

With the functionalized fullerenes **4c** and **6** we already carried out some reactions and there were strong hints pointing to the desired lanthanide-adducts, but the complete characterization is still in progress (Figure 7).

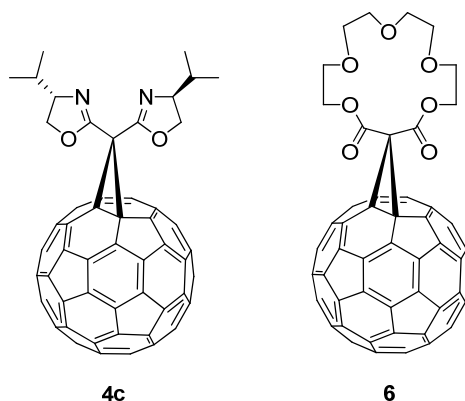


Figure 7: Fullerene adducts that already gave preliminary results.

Summary and Prospects

In the course of the subproject C1.06 plenty of new Buckminster fullerene adducts, to date unknown in literature, with promising complexation properties towards lanthanides, have been synthesized. These are the bisoxazoline-monoadducts (Figure 2, **4a–4e**) as well as the β -diketone monoadducts (Figure 3, **5b**). The hexakis adducts containing bisoxazoline functionalities (Figure 4, **6a–6e**) are altogether unknown in literature.

In addition a new method of the hexakis Bingel reaction, using iodine instead of carbon tetrabromide, could be worked out (Scheme 2, **c**).

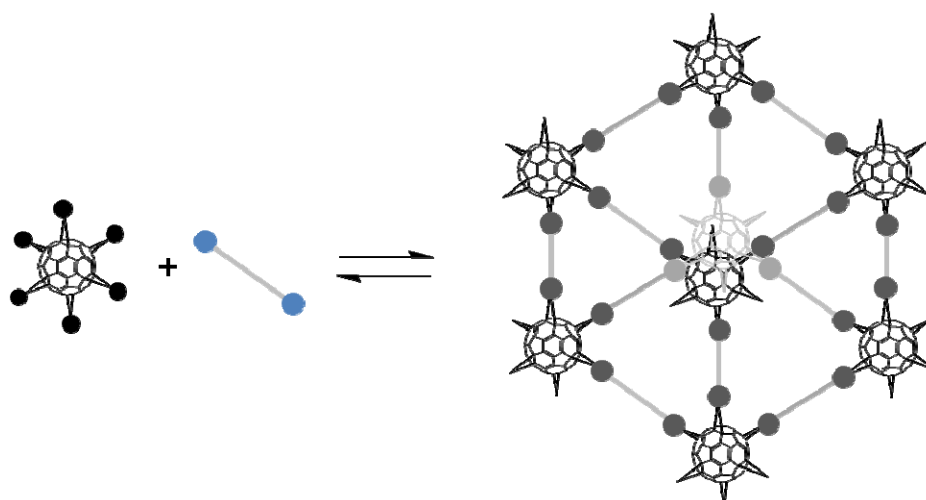
As result of our efforts in the construction of new lanthanide complexes a number of model complexes were already synthesized (Schemes 4, 5; Figure 6). Moreover, the first synthetic procedure for lanthanide based fullerenes is now available (Scheme 6). Based on these results we should now be able to build up more lanthanide complexes, which should have some fascinating magnetic and opto-electronic properties.

Fluorescence measurements of the europium-carboxylate-compound are still in progress. One other major goal is to get the crystal-structures of the desired products and this is coevally difficult,

because the compounds do not crystallize in a spontaneous way. So finding the appropriate crystallization conditions is one of our future challenges.

Furthermore we are also interested in the synthesis of fullerene derivatives that are bearing two different functionalities, e. g. a carboxyl- and an oxazoline-group. These complexes could then be able to coordinate two different metals.

Based on the results obtained from complexation experiments with fullerene mono-adducts fullerene hexakis-adducts bearing six functional groups as binding sites for the lanthanides will be studied in the future. That way we are likely to get new enantiopure chiral lanthanide complexes that exhibit a nearly perfect octahedral topology bearing six lanthanide atoms within their coordination sphere. Those compounds are very likely to show striking luminescence properties and therefore open a wide range of application possibilities in the field of optoelectronics. Beyond that such complexes, not only with lanthanides, but also with other metal ions, might be able to build up network structures, so called metal organic frameworks (MOFs), featuring chiral pores of definite size and shape, and therefore might be utilized as asymmetric catalysts or for chiral chromatography columns, to mention only few examples. In addition to that those structures would be the first so called “inverse MOFs” in which the metal centers act as linkers, whereas the organic ligands, namely the hexakis–methanofullerenes, act as the network knots (Scheme 8).



Scheme 8: Hypothetical inverse MOF consisting of hexakis methanofullerenes.

Topical investigations of the Bräse group tend to broaden the spectrum of hexakis methanofullerenes, especially that of Box-modified derivatives. In that context the compounds bearing isopropyl (**9a**, **9b**) respectively *tert*-butyl groups (**9c**, **9d**, Figure 5) are of great interest, since in complexes their relatively bulky substituents can define more restricted chiral pores than the derivatives synthesized so far. Especially the latter one can presumably be utilized as a new catalyst in asymmetric cyclopropanation reactions, as it is a derivative of the currently most potent catalyst used there, namely the *tert*-butyl-Box (**10**).

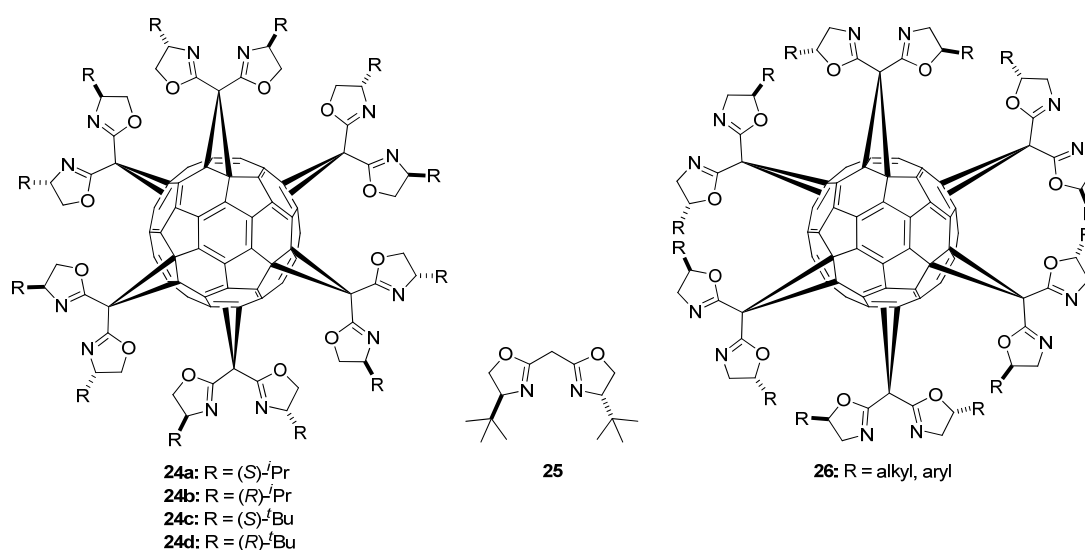


Figure 8: Planned hexakis-Box fullerene adducts (**24**, **26** and *tert*-butyl-Box (**25**)).

For the design of different Box-containing lanthanide clusters and MOFs it would be interesting to synthesize further “iso-Box” derivatives (**26**).

Besides that, another interesting class of compounds would be [5:1]-hexakis-adducts (Figure 9, **27**), bearing five equal addends and one different functionality. In such compounds the single functionality B might act as anchor for the attachment to a surface whereas the other five addends can act as ligands for metal ions. For investigations on this research field a co-operation with Prof. C. Wöll, who is also a member of the CFN, would come into account.

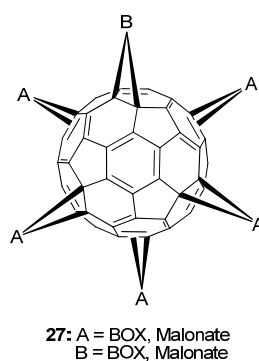


Figure 9: [5:1]-fullerene-hexakis-adducts.

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