XVI. Tage der Seltenen Erden / Workshop on Rare Earth Chemistry

im Rahmen des Graduiertenkollegs 352

Berlin, 4.-6. Dezember 2003

For financial support we thank:

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Preface

Dear participants of the XVI. Workshop on Rare Earth Chemistry,

the “Tage der Seltenen Erden” started in Köthen (Anhalt) in the mid 80ies. Originally the workshop was a pure East German meeting. After the unification of Germany the conference got a national character. Nowadays the workshop is getting more and more international and the number of participants is increasing steadily. In the near future the meeting may change from a national workshop to a European conference. The increasing number of participants of the workshop reflects the rapid growing interest in all fields of rare earth chemistry. Even the character of the conference has changed over the years we tried to keep some traditions. Thus, the topics of the workshop traditionally include all scientific fields of rare earth chemistry, e.g. solid state compounds, clusters, organometallics, and coordination complexes. This year, as a result of the annular meeting of researchers from all fields of rare earth chemistry it was possible to establish a national program on rare earth chemistry sponsored by the DFG (Schwerpunktprogramm 1166).

To encourage a number of young researchers to participate on the meeting, which is part of Graduiertenkolleg 352, the workshop is traditionally free of charge. As result of generous financial support we even are able to offer travel grants for students who present a lecture or a poster. We gratefully acknowledge all sponsors of this meeting, which all are listed on the front page of this book of abstracts.

Finally, we thank Dr. K. Lange and Dr. M. Gamer for skillfully executing most of the actual organizational work.

Berlin, November 2003

Peter Roesky

Prof. Dr. Peter Roesky

Prof. Dr. Herbert Schumann

Vorträge / Oral Contributions

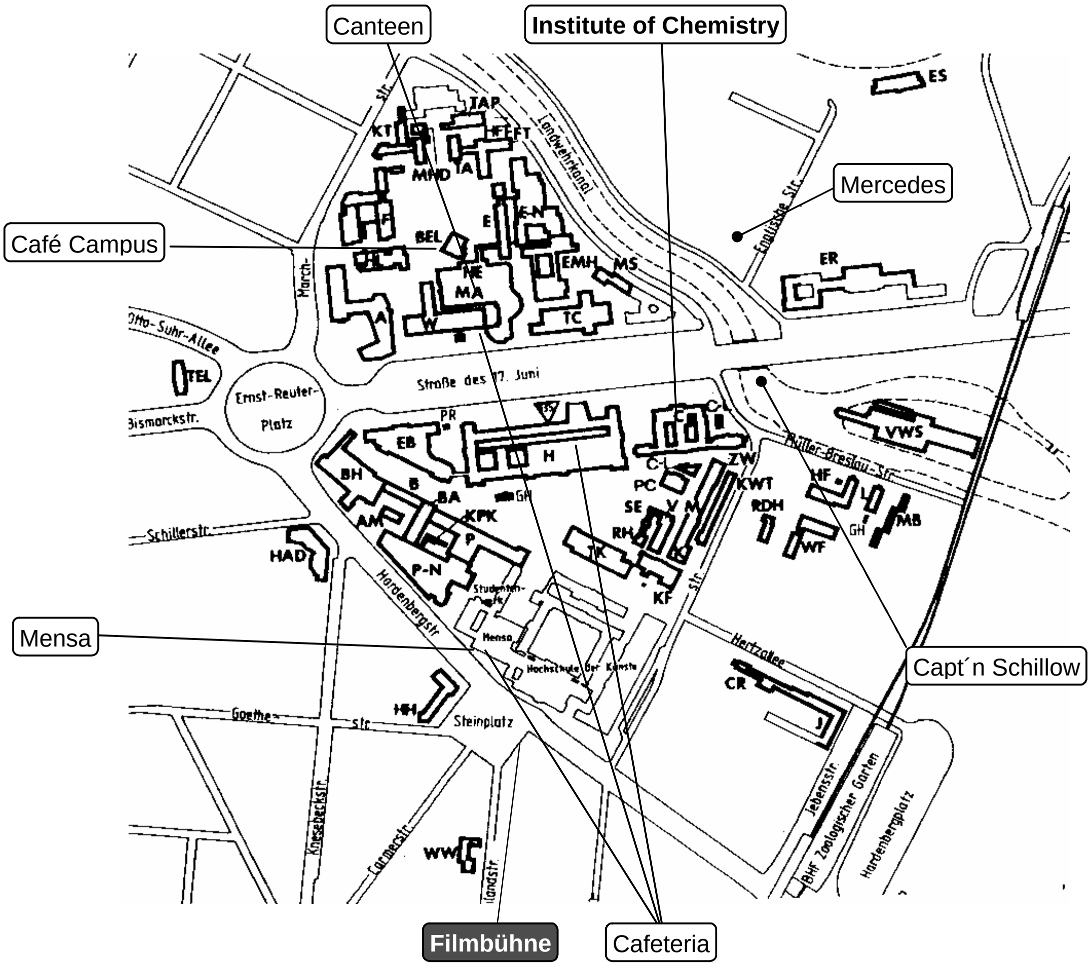
Donnerstag / Thursday 04.12.2003		Chair person	Freitag / Friday 05.12.2003		Chair person	Samstag / Saturday 06.12.2003		Chair person
			09.^{00}	**PL 2** Tobin J. Marks	Glen B. Deacon	09.^{00}	**PL 4** Bart Hessen	Mathias S. Wickleder
			10.^{00}	**OC 1** Gerd Meyer		10.^{00}	**OC 15** Kai C. Hultzsch	
			10.^{20}	**OC 2** Helen C. Aspinall		10.^{20}	**OC 16** H. Martin Dietrich	
			10.^{40}	**OC 3** Gerd W. Rabe / Florian A. Riederer		10.^{40}	**OC 17** Rinaldo Poli	
			11.^{00}	**Coffee break**		11.^{00}	**Coffee break**	
			11.^{20}	**OC 4** Glen B. Deacon	Gerd Meyer	11.^{20}	**OC 18** Claudia Wickleder	Herbert Schumann
			11.^{40}	**OC 5** Peter M. Zeimentz		11.^{40}	**OC 19** Joachim Scholz	
			12.^{00}	**OC 6** Mathias S. Wickleder		12.^{00}	**OC 20** Ana de Bettencourt-Dias	
						12.^{20}	**OC 21** Natalie M. Scott	
			12.^{20}	**Lunch**			**End of Conference**	
			14.^{00}	**PL 3** Gary A. Molander	Kai C. Hultzsch			
			15.^{00}	**OC 7** Koen Binnemans				
			15.^{20}	**OC 8** Peter Junk				
			15.^{40}	**OC 9** Sophie M. Guillaume / Isabelle Palard				
17.^{00}	**Introduction**	Peter W. Roesky	16.^{00}	**Coffee break**				
17.^{10}	**PL 1** Igor L. Feduschkin		16.^{20}	**OC 10** Klaus Müller-Buschbaum	Frank T. Edelmann			
18.^{10}	**Poster Session**		16.^{40}	**OC 11** Philip Mountford				
			17.^{00}	**OC 12** Ingo Hartenbach				
			17.^{20}	**OC 13** Jean-François Carpentier				
			17.^{40}	**OC 14** Marc Visseaux				
19.^{00}	**Conference Buffet**		19.^{00}	**Conference Dinner**				

Poster

P 1	Daniel Imbert	New tetrapodal ligands and their Ln(III) complexes: Synthesis, thermodynamic and photophysical properties.
P 2	Daniel Imbert	A kinetically inert and optically active Cr(III) partner for sensitizing Ln(III) in heterodimetallic non-covalent d-f podates.
P 3	Florian A. Riederer	Donor-Functionalized Terphenyl Lanthanide Complexes
P 4	Mikhail Ryazanov	Large Negative Magnetoresistance in the Large Negative Magnetoresistance in the System Gadolinium-Iodine-Hydrogen
P 5	Mikhail Ryazanov	Preparation of Lanthanum Hydride Diiodides Toward Superconductivity Predicted From Electronic Structure Calculations
P 6	Thomas Werner	Cerium-Catalyzed α-Hydroxylation of β-Dicarbonyl Compounds
P 7	Anja-Verena Mudring	Praseodymium diiodide, PrI_2, revisited by synthesis, structure determination and theory
P 8	Hauke Reddmann	Experimentelle Erfassung und Simulation der Elektronenstrukturen von pseudo-trigonal-planaren (substituierten) Cyclopentadienylkomplexen des Neodym(III)
P 9	Matthias Hilder	Optophysical and Structural Properties of Lanthanoid Complexes in the Solid State
P 10	Ulrich Kynast	VIS-, NIR- and Upconverted Luminescence from Rare Earth Sodalites
P 11	Julia Hitzbleck	Calcium, Strontium, and Barium as “pseudo-lanthanides” – Similarities and Differences between Alkaline Earth and Rare Earth Metal Pyrazolates
P 12	Theresa Komm	$Rb_3Pr_3[PS_4]_4$: Das erste Rubidium-Selten-Erd-Thiophosphat
P 13	Thomas Schleid	$M_4N_2Ch_3$: One Composition, but Four Different Structure Types of Lanthanide(III) Nitride Chalcogenides
P 14	Thomas Schleid	$Yb_4O_3Cl_2[SeO_3]_2$: A New Layered Ytterbium(III) Oxychloride Oxoselenate(IV)
P 15	Alexander Jagst	Lanthanoid-Komplexe vielzähniger Hydrazon- und Semicarbazonliganden
P 16	Andreas Fischbach	Peralkylated Rare-Earth Metal Complexes $LnAl_3R_{12}$: Efficient Precursors for Binary and Single-Component Ziegler Catalysts
P 17	Melanie Zimmermann	Postlanthanidocene Complexes Supported by Functionalized Diamide Ligands
P 18	Herfried Richter	Hinweise zur Toxikologie von Seltenen Erden
P 19	Catharina C. Quitmann	Phenylpiperazin als chemische Schere: Von 1-dimensionalen FK-Verbindungen über Dimere zu monomeren Einheiten
P 20	Michael T. Gamer	Mono Bis(diphosphanyl)amide Complexes of Rare Earth Metals
P 21	Tarun K. Panda	Novel Methods for Basic Reagents in Organometallic Chemistry
P 22	Konstantin Rufanov	Towards Lanthanide Alkylidene Complexes. Synthesis, Reactivity and Structure of $Lu(CH_2SiMe_3)_3$ etheral adducts

Lunch & Dinner

- **TU-Mensa (Canteen)**, Hardenbergstraße 34, Mo-Fr 11:00-14:45
- **Canteen in the Mathematics Building MA** (9th floor), Mo-Th 11:00-16:30, Fr 11:00-16:00
- **Cafeterias**:
  - **Cafeteria in the TU-Mensa**, Hardenbergstraße 34, Mo-Fr 8:00-19:00
  - **Cafeteria in the Main Building H** (next to the Audimax (main lecture hall) on the ground floor), Mo-Th 7:30-18 h, Fr 7:30-16:00 h
  - **Cafeteria in the Main Building H** (opposite H 111 on the ground floor), Mo-Fr 8:00-15:00
  - **Cafeteria in the Mathematics Building MA** (ground floor), Mo-Fr 8:00-18:00
- **Café Campus,** in the Villa BEL, Marchstr. 6/8, 11:00-23:00, (Fridays "all you can eat buffet" 6 €)
- **Mercedes-Restaurant Salt'n Pepper**, Salzufer 1, Mo-Fr 7:00-22:00, Sa 8:00-20:00, Su 10:00-20:00 (soup 4.10 €, salads 5.10 €, main menu from 12.10 €)
- **Ship's restaurant "Capt'n Schillow"**, Straße des 17. Juni, Charlottenburger Tor / Landwehrkanal, Mo-Sa 11:00-24:00, Su 10:00-23:00, (soup from 3.60 €, small meals from 6.10 €, salads from 7.50 €, main meals from 8.00 €)
- **Filmbühne → Conference Dinner,** Hardenbergstr. 12, Friday 05.12.2003, ~19:00



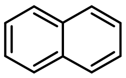
Plenarvorträge /
Plenary Lectures

Rare- and Alkaline-Earth Metal Complexes with Non-Alternated Hydrocarbons and Diimine Ligands

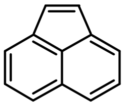
Igor L. Fedushkin

G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences,
Tropininstr. 49, GSP-445, 603950 Nizhny Novgorod; e-mail: igorfed@imoc.sinn.ru

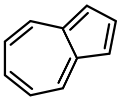
The lanthanide and alkaline earth metal complexes with ligands, which may reversible act as electron reservoir will be discussed. Among these ligands are alternated and non-alternated arenes, hetero- and exo-cyclic diimines:



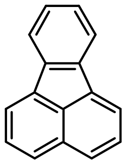
naphthalene



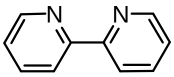
acenaphthylene



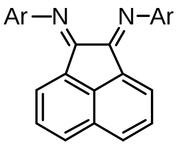
azulene



fluoranthene



bipyridyl



bis(arylimino)-
acenaphthene

Depending on the conditions (metal cation, temperature, etc.) the radical-anions of these ligands may partially or completely disproportionate to the species oxidized and reduced by one electron. Radical-anions of acenaphthylene and guajazulene undergo coupling to form exclusively C_2-symmetric *ansa*-metallocenes. The presence of both, diimine and naphthalene systems in bis(arylimino)acenaphthene allows reduction of the ligand not only to mono- and dianion, but even to tri- and tetra-anions. The ability of this ligand to act as electron and proton reservoir allowed for the first time oxidative addition and reductive elimination on main group metal complexes, e.g. the magnesium complex with bis(arylimino)acenaphthene. The title metal complexes exhibit high reactivity towards different organic, inorganic and organometallic substances due to the strong reduction potential of the ligand anions.

Metal-Ligand Bonding Energetics and the Invention of new Transition Metal- and f-element-mediated Catalytic Processes

Tobin J. Marks

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t-marks@northwestern.edu

The lanthanides, actinides, and related electrophilic transition elements offer many intriguing and instructive characteristics for stoichiometric and catalytic transformations, including large and incrementally tunable ionic radii, high electrophilicity, high kinetic lability, predictable and constrained formal oxidation states, polar metal-ligand bonding, relatively high abundance, and relatively low toxicity. This lecture describes recent exploratory synthetic, mechanistic, and thermochemical research aimed at developing unusual new transformations mediated by these elements. Thus, using experimental metal-ligand bond enthalpies as a guide, two characteristic reactivity patterns, i) insertion of unsaturated functionalities into metal-ligand s-bonds, ii) s-bond metathesis processes, can be coupled to effect a variety of catalytic single- and multistep bond formation processes. These include regioselective hydroamination, hydrophosphination, hydrosilylation, and olefin polymerization with organometalloid chain transfer. A number of these processes can be effected with high chemo- and stereoselectivity to construct complex natural product skeletons.

Application of SmI_2 Chemistry to the Synthesis of Natural Products

Gary A. Molander

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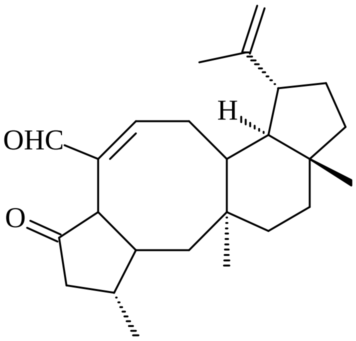
gmolandr@sas.upenn.edu

The development of new strategies for the construction of organic molecules permits more rapid and efficient access to targets of interest. Over the past several years, numerous synthetic methods based upon lanthanide reagents have been developed within our group. Complex molecule synthesis provides opportunities to showcase these methods under demanding conditions. Among the synthetic targets under study, approaches to dibenzylcyclooctadiene ligands and variecolin will be discussed.



Variecolin

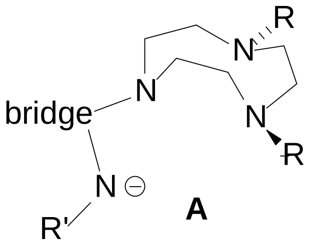
Neutral and Cationic Group 3 and Lanthanide Metal Hydrocarbyl Complexes with Anionic Polydentate Nitrogen Ligands

B. Hessen, S. Bambirra, C. G. J. Tazelaar, and A. Meetsma

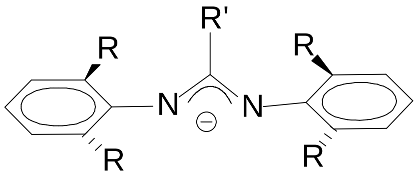
Stratingh Institute for Chemistry and Chemical Engineering, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

The chemistry of cationic hydrocarbyl complexes of the transition metals has been the subject of intensive study over the last 15 years. This has largely been spurred by their often spectacular reactivity in olefin polymerization catalysis. In contrast, the chemistry of cationic hydrocarbyl complexes of the group 3 metals and lanthanides was practically unexplored, until a couple of years ago. Recent results from the groups of Piers, Okuda and from our laboratory have shown that these species can be a source of both interesting organometallic chemistry and of interesting catalysis.

In this presentation, the chemistry of neutral and cationic group 3 and lanthanide metal hydrocarbyl complexes with monoanionic polydentate nitrogen-based ligands will be discussed. Two ligand systems have allowed us full access to such species over the whole range spectrum of these metals. One is the tetradentate 1,4,7-trizazcyclononane-amide ligand system (**A**), the other the amidinate ligand with sterically demanding substituents (**B**).



A



B

Synthetic, structural and stability aspects of these compounds will be presented, as well as their catalytic activity in e.g. the living polymerization of ethene at unusually high temperatures, and the rapid and selective dimerisation of terminal alkynes to unusual *Z*-buta-1-ene-3-ynes.

Vorträge /
Oral Contributions

Rare Earth Diiodides and Derivatives

Gerd Meyer, Niels Gerlitzki, and Stefanie Hammerich

Institut für Anorganische Chemie, Universität zu Köln,
Greinstrasse 6, D-50939 Köln, Germany

The rare earth diiodides, MI_2, may be synthesized from the corresponding triiodides, MI_3, by reduction with their metals at elevated temperatures or, alternatively, through so-called metallothermic reduction reactions with alkaline or alkaline-earth metals. In these cases ternary iodides may be obtained that may be derived from the binary diiodides by either formal addition or substitution. Prominent formula types that are thus obtained are $A^{I}MI_3$, or the mixed-valent $A^{I}_{5}M^{II}_{2}M^{III}I_{12}$ and $A^{II}MI_4$ with A^{I} and A^{II} representing alkaline or alkaline-earth elements (and their analogues), respectively. Further iodides that are relevant in these systems are, for example, Pr_2I_5, $Ba_6Pr_3I_{19}$ and interstitially stabilized phases such as $\{Er_{14}(N_2)(C_2)_2\}I_{24}$, $La_9O_4I_{16}$ and $Ba\{Ce_4N_2\}I_8$.

Lanthanide Oxides and Silicates for Microelectronics: Precursors and MOCVD

Helen C. Aspinall, Jeffrey Gaskell, and Anthony C. Jones

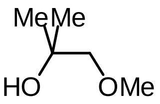
Department of Chemistry, Donnan and Robert Robinson Laboratories, University of Liverpool,
Crown Street, Liverpool, L69 7ZD, U.K:

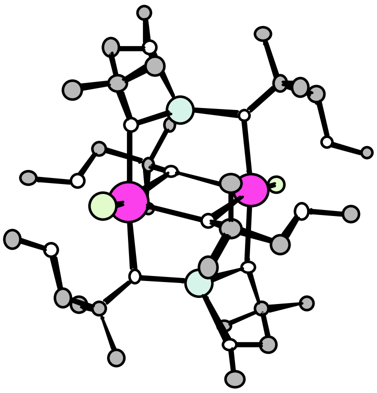
Lanthanide oxides and silicates have recently been identified as ideal materials for high-κ dielectric applications.[1] Such materials are essential if the size of Si-based microelectronics is to continue to be reduced. Metal-organic chemical vapour deposition (MOCVD) is an attractive technique for the deposition of metal oxides,[2] having a number of advantages over other deposition techniques. However, there have been very few reports of the successful MOCVD of rare-earth oxides or silicates, mainly due to a lack of suitable precursors with appropriate physical properties and decomposition characteristics.

In this contribution we present some applications of the relatively new technique of liquid injection MOCVD in the synthesis of thin films of lanthanide silicates[3] and oxides.[4]

Our preliminary work has used the well-known lanthanide tris(silylamides) for deposition of lanthanide silicates. For synthesis of oxides we have used the MMP ligand (below) developed by Anwander and Herrmann.[5] In the course of this work we have begun to unravel some of the fascinating coordination chemistry of MMP with the early lanthanides.

HMMP





$[Pr(MMP)_3LiCl]_2$

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[1] G. D. Wilk, R. M. Wallace, J. M. Anthony, *J. Appl. Phys.* **2001**, *89*, 5243-5275.

[2] A.C. Jones, *J. Mater. Chem.,* **2002**, *12*, 2576.

[3] H. C. Aspinall, P. A. Williams, J. Gaskell, A. C. Jones, J. L. Roberts, L. M. Smith, P. R. Chalker, G. W. Critchlow, *Chem. Vap. Deposition* **2003**, *9*, 7-10.

[4] H. C. Aspinall, J. Gaskell, P. A. Williams, A. C. Jones, P. R. Chalker, P. A. Marshall, J. F. Bickley, L. M. Smith, G. W. Critchlow, *Chem. Vap. Deposition*, **2003**, in press.

[5] R. Anwander, F. C. Munck, T. Priermeier, W. Scherer, O. Runte, W. A. Herrmann, *Inorg. Chem.* **1997**, *36*, 3545.

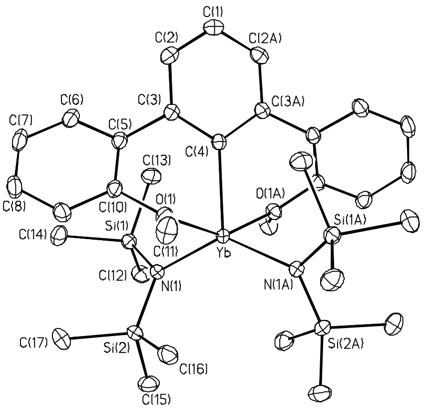
Recent Developments in Terphenyl Lanthanide Chemistry

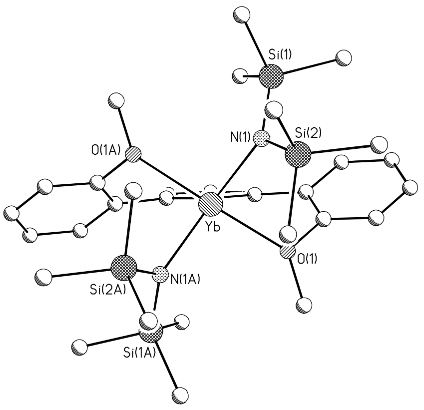
Gerd W. Rabe and Florian A. Riederer

TU München, Lichtenbergstr. 4, 85747 Garching

The vast majority of known terphenyl element compounds is based on *p* block elements, followed by a number of such compounds of *s* block elements and some representatives of the late transition metals. The interest in sterically encumbering σ bonded terphenyl element compounds arises from previously made observations that such ligand systems were found to be suitable for the stabilization of main group element compounds in unusual coordination geometries and unprecedented bonding situations. Two recent review articles[1,2] summarize the current knowledge about terphenyl element compounds. Interestingly, there is no mention in these two articles on terphenyl based compounds of the *f* elements and early transition metals.

In recent years we were able to demonstrate that the use of sterically demanding terphenyl groups as the only supporting ligand allows for the kinetic stabilization of novel low-coordinate complexes of the lanthanides and group 3 elements scandium and yttrium.[3-7] Our work is part of an effort to develop the chemistry of lanthanide and group 3 elements with terphenyl ligands, and to explore the coordination chemistry as well as the reactivity of such compounds. Shown are two views of the molecular structure of a novel lanthanide bis(amide) compound that is based on a chiral (racemic) donor-functionalized terphenyl ligand.





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[1] B. Twamley, S. T. Haubrich, P. P. Power, *Adv. Organomet. Chem* **1999**, *44*, 1.
[2] J. A. C. Clyburne, N. McMullen, *Coord. Chem. Rev.* **2000**, *210*, 73.
[3] G. W. Rabe, C. S. Strissel, L. M. Liable-Sands, T. E. Concolino, A. L. Rheingold, *Inorg. Chem.* **1999**, *38*, 3446.
[4] G. W. Rabe, C. D. Bérubé, G. P. A. Yap, *Inorg. Chem.* **2001**, *40*, 2682.
[5] G. W. Rabe, C. D. Bérubé, G. P. A. Yap, *Inorg. Chem.* **2001**, *40*, 4780.
[6] G. W. Rabe, C. D. Bérubé, G. P. A. Yap, K.-C. Lam, T. E. Concolino, A. L. Rheingold, *Inorg. Chem.* **2002**, *41*, 1446.
[7] G. W. Rabe, M. Zhang-Presse, F. A. Riederer, G. P. A. Yap, *Inorg. Chem.* **2003**, *42*, 3527.

Structurally Characterised Fluorocarbon Lanthanoid Complexes – at Last!

Glen B. Deacon and Craig M. Forsyth

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glen.deacon@sci.monash.edu.au

Lanthanoid polyfluoroaryls were amongst the earliest σ-bonded organometallics to be prepared,[1,2] with the further novelty that most were divalent. However, they were only characterized analytically and spectroscopically, e.g. [$YbR_2(THF)_4$] (R = C_6F_5, *p*-HC_6F_4), $Eu(C_6F_5)_2$ and the last was not even solidified. Numerous attempts to obtain a structure of [$Yb(C_6F_5)_2(THF)_4$] failed despite apparently excellent crystals. This situation has now been transformed. Thus [$Eu(C_6F_5)_2(THF)_5$] prepared by redox transmetallation

$$Eu + Hg(C_6F_5)_2 \text{ ? } Eu(C_6F_5)_2 + Hg?$$

has a seven coordinate pentagonal bipyramidal structure with *trans* C_6F_5 groups and very long Eu–C bonds.[3] The Yb analogue, fortuitously isolated as adequate single crystals from decomposition of "$YbPh(C_6F_5)$" is six-coordinate octahedral with *trans* C_6F_5 groups. The mixed complex can be effectively trapped by redox transmetallation / ligand exchange revealing the possibility of acidity based selectivity.

$$Yb + HgPh(C_6F_5) + C_5Me_5H \text{ ? } Yb(C_5Me_5)(C_6F_5) + Hg? + PhH$$

The Yb half sandwich is eight coordinate pseudo-octahedral with the site trans to C_5Me_5 occupied by an agostic Yb···F interaction.[4] Relatively stable $[Ln(C_6F_5)(THF)_n]^+$ (Ln = Eu, n = 6; Ln = Yb, n = 5), initially detected in the remarkable $[Yb^{II}(C_6F_5)(THF)_5]$ $[Yb^{III}(C_6F_5)_2\{N(SiMe_3)_2\}_2]$ have been deliberately synthesized

$$Ln + HgPh(C_6F_5) + HNMe_3BPh_4 \text{ ? } [Ln(C_6F_5)]^+[BPh_4]^- + Hg? + NMe_3 + PhH$$

and characterised by X-ray crystallography. Low temperature ^{171}Yb NMR spectroscopy has enabled Yb–F coupling to be observed for the first time.

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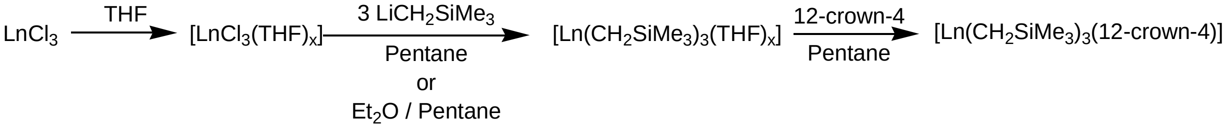
[1] G. B. Deacon *et al*, *J. Organomet. Chem.* **1977**, *135*, 103-114.
[2] *J. Organomet. Chem.* **1979**, *182*, 121-141.
[3] C. M. Forsyth, G. B. Deacon, *Organometallics 2000*, *19*, 1205-1207; G. B. Deacon, C. M. Forsyth, *Organometallics*, **2003**, *22*, 1349-1352.

Alkyl Complexes of the Rare Earth Elements supported by a Crown Ether

<u>Peter M. Zeimentz</u>, Thomas P. Spaniol and Jun Okuda*

Institut für Anorganische Chemie,RWTH Aachen, Professor-Pirlet-Str. 1, 52074 Aachen

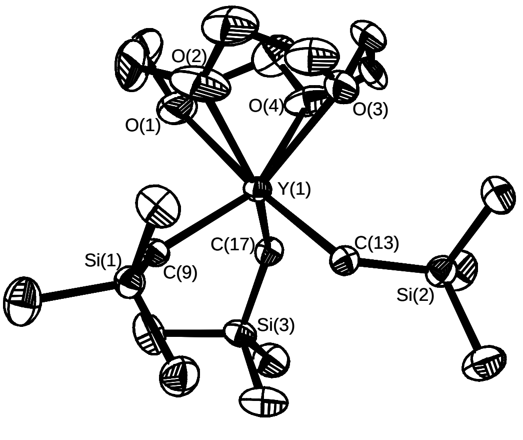
Trimethylsilylmethyl complexes of the lanthanoids are known since 30 years ago.[1] In the recent past these complexes were used as reagents for the syntheses of organometallic complexes of the lanthanoids via alkane elimination.[2] Due to the thermal instability especially of the complexes of the larger lanthanoids their isolation was rather difficult. Some years ago crown ethers could be shown to stabilise organometallic complexes of the rare earth elements.[3]



$$\mathrm{LnCl_3} \xrightarrow{\text{THF}} [\mathrm{LnCl_3(THF)}_x] \xrightarrow[\text{Pentane or } \mathrm{Et_2O} \text{ / Pentane}]{3\ \mathrm{LiCH_2SiMe_3}} [\mathrm{Ln(CH_2SiMe_3)_3(THF)}_x] \xrightarrow[\text{Pentane}]{\text{12-crown-4}} [\mathrm{Ln(CH_2SiMe_3)_3(12\text{-}crown\text{-}4)}]$$

Ln = Sc, Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

By reaction of the instable trisalkyl complexes with 12-crown-4 in a practically simple one-pot procedure some new thermally stable alkyl complexes even for the early lanthanoids could be prepared and characterized.[4]



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[2] K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228.

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Perchlorates and Perrhenates of Rare Earth Elements: Syntheses, Crystal Structures, and Thermal Behaviour

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Perchlorates of the rare earth elements are obtained from aqueous solution in form of their hexahydrates. According to the formulation $[M(H_2O)_6](ClO_4)_3$ the ClO_4^- groups do not coordinate to the M^{3+} ions so that the structure is *0-dimensional* with respect to the linkage of M^{3+} and ClO_4^- ions. If the hexahydrates are carefully heated in an argon stream, dehydration takes place forcing the perchlorate ions to enter the inner coordination sphere of the cations. Depending on the dehydration state and the M^{3+} size, *1-dimensional chain structures* as found for $M(ClO_4)_3{\cdot}3H_2O$ (M = Tb, Lu) and $Yb(ClO_4)_3{\cdot}2H_2O$, *2-dimensional layer structures* as observed in $M(ClO_4)_3{\cdot}H_2O$ (M = La, Pr) or *3-dimensional networks* as described for $M(ClO_4)_3{\cdot}H_2O$ (M = Er, Yb) can be obtained. Even the anhydrous species $M(ClO_4)_3$ (M = La-Lu, Y) can be prepared in single crystalline form by careful dehydration.[1]

In contrast to the perchlorates, the perrhenates are obtained as tetra- or trihydrates from the respective solutions and show the ReO_4^- ions directly coordinated to the M^{3+} ions. For the tetrahydrates $M(ReO_4)_3{\cdot}4H_2O$ four different structure types have been found, which can be either *3-dimensional* (M = La, Pr) or *1-dimensional* (M = Nd-Lu). The trihydrates contain double chains for M = La, Ce while the unique structure of $Sc(ReO_4)_3{\cdot}3H_2O$ shows the Sc^{3+} ions linked to *zig-zag* chains with a remarkable sevenfold coordination of the cations.[2]

The thermal decomposition of rare earth perchlorates (around 250°C) leads to the respective oxide-chlorides. According to mass spectroscopic investigations, elemental chlorine and oxygen are the only released species during the reaction. Rare earth perrhenates are thermally much more stable. They decompose above 800°C under evolvation of Re_2O_7. In a first step the oxide perrhenates $M_3(ReO_6)O_2$ are formed which contain ReO_6^{5-} octahedra and O^{2-} centered tetrahedra of metal ions.

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Lanthanide Complexes forming Columnar Mesophases

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Bertrand Donnio[b], **and Daniel Guillon**[b]

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Lanthanide complexes with a disklike shape (discotic complexes) can form liquid-crystalline phases upon heating. In these liquid-crystalline phases or mesophases the molecular order is between that of an ordered solid and a disordered liquid. The mesophase is an anisotropic fluid. In columnar mesophases, the molecules are stacked into columns. Depending on the type of 2D lattice formed by the columns, one can make a distinction between a hexagonal columnar phase (Col_h), a tetragonal columnar phase (Col_t) or a rectangular columnar phase (Col_r). To stabilize the mesophase and to reduce the transition temperatures, long alkyl chain are attached to the disklike core of these complexes. At the melting point, the alkyl chains obtain a disordered liquid-like conformation, but the columns remain intact. At the clearing point (second melting point), the columnar supramolecular organization is lost. A powerful experimental tool to study these complexes is high-temperature X-ray diffraction, but also hot-stage polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) can provide valuable information.

In this presentation, an overview is given of the different types of discotic liquid-crystalline lanthanide complexes described in the literature.[1] Special attention will be paid to the substituted bis(phthalocyaninato)lanthanide(III) complexes in which the lanthanide ion is sandwiched between two phthalocyanine rings. The lutetium compounds can be considered as one-dimensional molecular semiconductors, and most of these complexes show electrochromism. Another type of interesting compounds are metal-containing liquid crystals (metallomesogens) which contain both a lanthanide ion and a transition metal ion. Different types of liquid-crystalline f-d complexes will be discussed.

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Some recent Lanthanoid Chemistry involving ß-dinitrogen ligands

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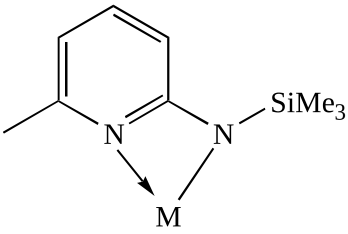
email: peter.junk@sci.monash.edu.au

Organometallic complexes of the lanthanoid elements have attracted great interest due to their potential application in hydrogenation, polymerisation, hydroboration and oligomerisation catalytic processes. More recently, organoamido- and alk/aryloxo-lanthanoid complexes have been studied for their uses in similar roles as well as potential MOCVD and ceramics precursors. These compounds have scope for considerable chemistry using Cp^- compounds as comparisons.

The use of sterically hindered amido ligands, such as the ubiquitous $[N(SiMe_3)_2]^-$, generates low nuclearity and low coordination number (< 8) lanthanoid species. Our recent work on the smaller bite angle of similarly sterically hindered 2-(trimethylsilylamido)-6-methylpyridine, 1, and bis(2,6-diisopropylphenyl)-formamidinate , 2, will be presented including the synthesis of alkali metal reagents suitable as precursors to lanthanoid complexes. The synthesis of several *homo*- and *heteroleptic* lanthanoid complexes incorporating 1 and 2 will be presented.



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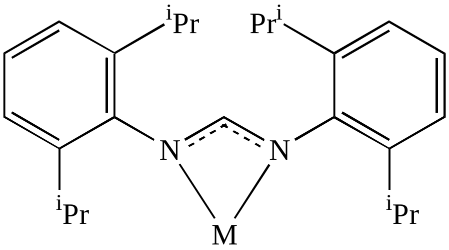

2

Unpretended Reactivity of Borohydride Lanthanide Complexes in Cyclic Esters Polymerization

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Rare earth borohydride complexes have been recently used as versatile precursors in organolanthanide chemistry. We have shown that the trivalent homoleptic rare earth complexes, $Ln(BH_4)_3(THF)_3$ (Ln = La, Nd, Sm) are extremely valuable reagents for the controlled polymerization of cyclic esters.[1-2] Our interests in polymers derived from such monomers lie in their potential applications as bioresorbable and biocompatible products. a,? -dihydroxytelechelic poly(e-caprolactone) have been prepared in a short period of time (5 min), with high molar masses (40 000) and low polydispersity indexes (1.1). The monosite initiator $(?\text{-}C_5Me_5)_2Sm(BH_4)(THF)$ polymerizes e-caprolactone and lactide more slowly (30 min) and leads to polymers with similar characteristics. Use of this organometallic derivative allowed a better control of and deeper insights into the polymerization mechanism. This convenient approach to dihydroxypoly(e-caprolactone) opens up the route to copolymers, especially amphiphilic ones of major interest in the medical field.[3]

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Neue ungewöhnliche Stickstoff-Koordinationen der Selten-Erd-Elemente

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Institut für Anorganische Chemie der Universität zu Köln

Stickstoff-koordinierte Selten-Erd-Metallzentren stehen seit einiger Zeit im Mittelpunkt unseres Interesses. Da insbesondere vollständige Stickstoff-Koordinationen in homoleptischen Verbindungen in Lösung nur mit wenigen, stark chelatisierenden Liganden zu erhalten sind, haben wir uns besonders auf solvens-freie Synthesewege spezialisiert. Der Ausschluß von Solventien ermöglicht dabei, auf festkörper-chemischen Synthesewegen nicht nur zu homoleptischen Produkten zu kommen,[1,2] sondern darüber hinaus auch einfache Heterozyklen mit Selten-Erd-Elementen zur Reaktion zu bringen, von denen es zuvor keine Selten-Erd-Verbindungen gab.[3,4] Diese weisen zum Teil außergewöhnliche Stickstoff-Koordinationen auf, die zuvor in der Selten-Erd-Chemie unbekannt waren (Abb.1, $[La(dpa)_3]_2$, H-dpa=2,2‘-Dipyridylamin). Vorgestellt werden Produkte, die auf Synthesewegen von Tief- bis Hochtemperatur, bezogen auf den Stabilitätsbereich von Liganden und Produkten, erhalten wurden.

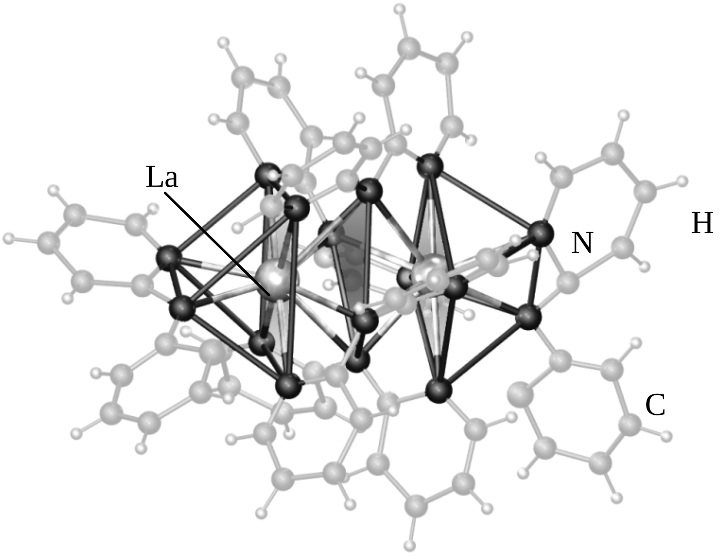

Abb.1: Die Molekülstruktur von $[La(dpa)_3]_2$. Neben zwei einfach 1,3-chelatisierenden dpa-Liganden wird Lanthan im Dimer von einem Gürtel doppelt 1,3-chelatisierender dpa-Liganden umgeben, so daß sich ein doppelt quadratisches Antiprisma aus Stickstoff um La ergibt, das zusätzlich beidseitig zweifach überkappt ist. La weist eine C.N. von zehn auf.[4]

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New Group 3 and related compounds with polydentate N- and N,O- donor ligands

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Email: philip.mountford@chem.ox.ac.uk; http://users.ox.ac.uk/~chem0072/PMount.html

Up to the early to mid 1990s the organometallic chemistry of scandium was dominated by cyclopentadienyl derivatives. Recently there have been significant advances in the synthesis and reactivity of non-cyclopentadienyl organometallic and related compounds of scandium.[1] These include: compounds containing arene and other $?^{x}$-C_xR_x ligands; compounds with macrocyclic and *fac*-L3 ligands; compounds with polydentate ligands that incorporate amide donors; compounds with bidentate, monoanionic N,N' donor ligands; and compounds with iminophenolate, bis(phenoxide) and some other anionic O-donor ligands.[2]

This lecture will highlight our recent efforts in the synthesis of new organo-scandium and organo-yttrium compounds with polydentate N- and N,O-donor ligands. Preliminary results in the polymerisation of ethylene by cationic organo-Group 3 derivatives will be presented. Some of the compounds studied to date are illustrated in the Figure below. In addition, connections between the structures of Group 3 complexes of bis(phenoxide)diamine ligands and possible active species in Group 4 a-olefin living polymerisation systems will be discussed.

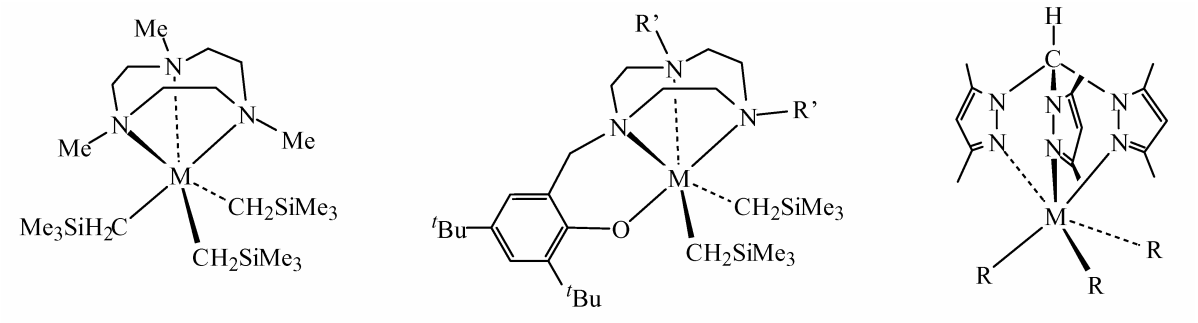

Figure (M = Sc, Y)

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[1] For recent reviews see: (a) P. Mountford, B. D. Ward, *Chem. Commun.* **2003**, 1797-1803; (b) F.T. Edelmann, D. M. M. Freckmann, H. Schumann, *Chem. Rev.* **2002**, *102*, 1851; (c) W. E. Piers, D. J. H. Emslie, *Coord. Chem. Revs.* **2002**, *233*, 131.

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Oxodisilicates $M_2Si_2O_7$ of the Rare-Earth Elements

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Considering rare-earth oxodisilicates of the composition $M_2Si_2O_7$ (M = Sc, Y, La; Ce – Lu) at least *ten* structure types (A – I, K) are already known to literature.[1-4] Not all of them contain pyroanionic disilicate units, so the B- and I-type consist of one *ortho*- and one *catena*-trisilicate or two *ortho*- and one *catena*-tetrasilicate anion, respectively. The other types exhibit pyroanionic $[Si_2O_7]^{6-}$ groups in three different conformations. First, the C- and D-type structures contain centrosymmetric double-tetrahedra with a linear Si–O–Si-bridging angle, thus a staggered conformation results. With a non-linear bridging angle only eclipsed conformations are realized within the rare-earth oxodisilicates. The two different possibilities are shown in the figures below. Fig. 1 represents a conformation with a common three-oxygen-membered *backbone* and four oxygen *feet*. The disilicate conformation of Fig. 2 consists of two pairs of oxygen *horns* at each silicon atom and only two oxygen *feet*. The rare-earth oxodisilicates of the A-, F-, G-, H- and K-type follow the conformation of Fig. 1, the E-type's $[Si_2O_7]^{6-}$ units are built like in Fig. 2.

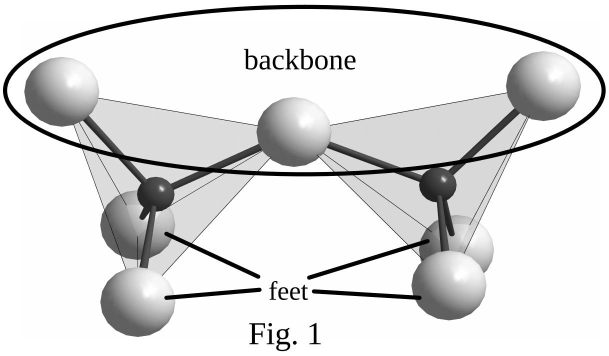

Fig. 1

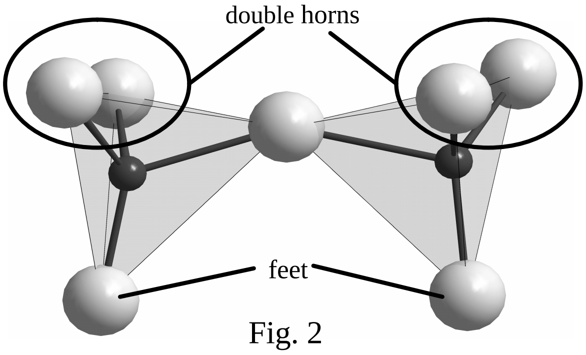

Fig. 2

A completely different nomenclature is implemented in literature for the yttrium disilicates. α-$Y_2Si_2O_7$ [5] is structurally not yet characterized, but adopts the cell dimensions of the B-type disilicates. β- , γ- and δ-type $Y_2[Si_2O_7]$[5] are equally to the C-, D- and E-type of the other rare-earth homologues. The y-type[6] $Y_2[Si_2O_7]$ has so far no analogon among the rare-earth prototypes. Neither has the new ε-type $Y_2[Si_2O_7]$, but this structure can be considered as a stacking variant of the E-type $M_2[Si_2O_7]$ arrangement.

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Group 3 Metal and Lanthanide Complexes Incorporating Fluorenyl-based Ligands: Unusual Bonding Modes

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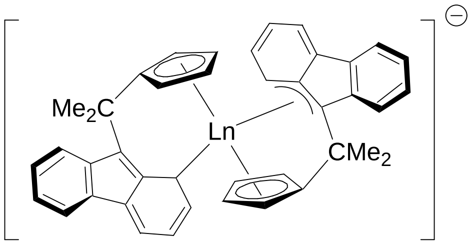
Fluorenyl-based ligands have played a unique role in the organometallic chemistry of group 4 metals in recent years, mostly due to their outstanding performances in the stereospecific polymerization of α-olefins. Their use with group 3 metals, and in particular the lanthanides, remains however largely unexplored. We will discuss here the synthetic and structural chemistry of new series of organolanthanide complexes based on two families of chelating fluorenyl ligands. The first series is concerned with metallocene complexes based on the single-carbon-bridged cyclopentadienyl/fluorenyl ligand system $[\text{Cp-CMe}_2\text{-Flu}]^{2-}$. It includes neutral and ionic complexes that contain, respectively, one and two $[\text{Cp-CMe}_2\text{-Flu}]^{2-}$ units per metal center (e.g. **1**).[1,2] The second series deals with the first fluorenyl "Constrained Geometry" group 3 metal complexes, which are derived from the $[(3,6\text{-}^t\text{Bu}_2\text{Flu})\text{SiR}_2\text{N}^t\text{Bu}]^{2-}$ (R = Me, Ph) ligand system (e.g. **2**).[3] The appropriateness of the different synthetic routes (amine and alkane eliminations, salt elimination) to reach such new *ansa*-lanthanidocenes, and =the original bonding features of the fluorenyl moieties onto the metal center that these neutral and anionic complexes adopt in the solid state (dissymmetric bonding delocalized over the phenyl rings with reduced hapticity, **D**-**E**) will be presented.



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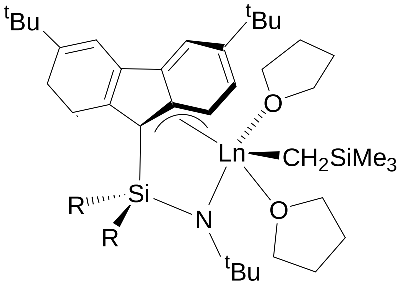

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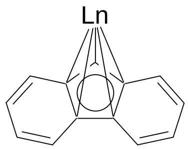
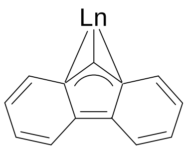


A



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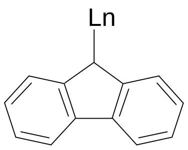

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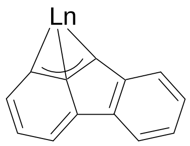

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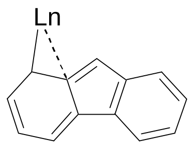

E

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Borohydrido Complexes of Early Lanthanides: New Highly Specific Catalysts for the Polymerization of Isoprene

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The trisborohydride $Nd(BH_4)_3(THF)_3$ has been used for the ROMP of ε-caprolactone. It was shown that the BH_4 group behaves like an hydride: after reduction of the monomer, propagation occurs via an alkoxyde moiety.[1]

The BH_4 ligand can also be seen as a pseudohalide ligand, it can be displaced with a nucleophilic group. We used this strategy to activate lanthanide borohydrides: in the presence of an alkylating reagent, we obtained new lanthanide catalysts, efficient for the controlled polymerization of isoprene. Some results are presented in table 1.

Table 1. Polymerization of isoprene using Ln/alkyl reagent catalysts

Catalyst	Time (h)	Yield (%)	1,4-*trans* (%)	1,4-*cis* (%)	3,4 (%)	M_nx10^{-3}	PDI
$Nd(BH_4)_3(THF)_3/AlEt_3$	20	89	34.1	61.5	4.4	9.3	1.67
$Nd(BH_4)_3(THF)_3/MgBu_2$	2h45	69	95.1	3.2	1.7	27.6	1.57
$LL'Nd(BH_4)/MgBu_2$	22	79	98.1	-	1.9	24.4	1.50

Associated to $Al(Et)_3$, the catalytic system is moderatly active, giving a mixture of *cis* and *trans* polymer. In the presence of $Mg(Bu)_2$, the resulting dual component Nd/Mg catalyst is highly stereospecific, giving *trans*-1,4-polyisoprene more than 95 % regular.[2]

The role played by the spectator ligands of the lanthanide compound was also investigated. A catalytic system made of an organometallic borohydride associated to $Mg(Bu)_2$ allows a better control of the process, and the rate of *trans*-specifity is enhanced to more than 98 %.

An overview of these unprecedented catalytic Nd/Mg systems will be presented, including mechanistic aspects.

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New Rare Earth Metal Catalysts for the Hydroamination of Aminoalkenes

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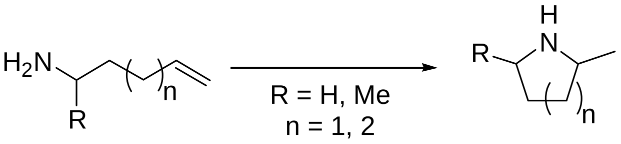
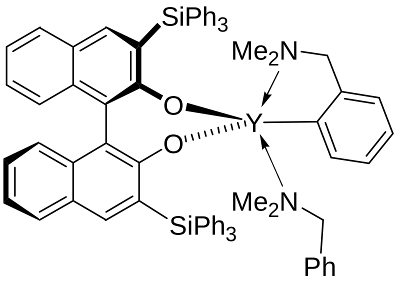
Henkestraße 42, D-91054 Erlangen, Germany



The hydroamination reaction has become a fast growing topic in organometallic catalysis.[1] Significant research interest originates from potential applications in the synthesis of pharmaceuticals and industrial relevant basic and fine chemicals. While cyclopentadienyl based rare earth metal catalysts have been known for more than a decade,1a non-metallocene catalyst systems have evolved only recently.[2] The advantages of the latter complexes are convenient and easy synthesis as well as facile tunable ligands. Furthermore, chiral cyclopentadienyl-free catalyst systems[2e,g] could also become useful in asymmetric hydroamination reactions,[1d] as chiral lanthanocenes are known to epimerize readily under the catalytic conditions.[3] In this talk we will present the synthesis of new non-metallocene catalyst systems, e.g. binaphtolate **1**. Catalytic activity, diastereoselectivity and enantioselectivity in hydroamination/ cyclization reactions of aminoalkenes will be addressed.



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New Synthetic Pathways to Half-Sandwich Complexes of the Rare Earth Metals

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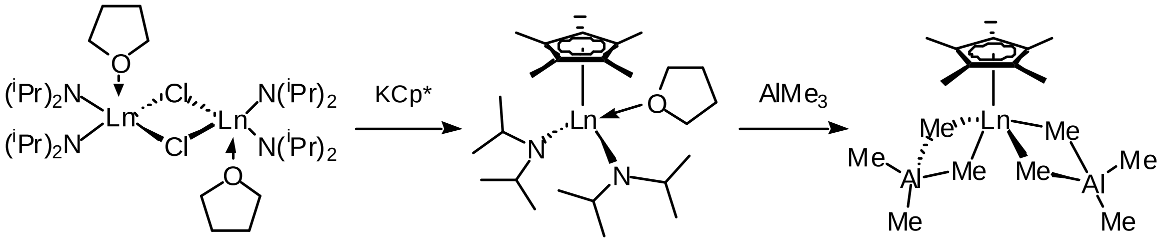
Organolanthanide complexes supported by only one cyclopentadienyl-type ancillary ligand is ascribed a high potential in homogeneously catalyzed reactions, e.g., in the polymerization of styrene or acrylonitrile.[1] Moreover, an intrinsic stereoelectronic unsaturation is anticipated to impart unprecedented structural chemistry.[2] A very limited number of catalytically relevant bis(amido) and bis(hydrocarbyl) half-sandwich complexes has been structurally examined disclosing pertinent synthetic imponderabilities such as *(i)* Lewis base (solvent) complexation, *(ii) ate* complexation, and *(iii)* metal-size-dependent ligand redistribution reactions.[3,4] Recently, we described the synthesis of mono(tetramethylcyclopentadienyl) bis(silylamide) complexes according to our previously established *extended silylamide route* and a trialkylaluminum mediated silylamide→alkyl transformation affording unsolvated half-sandwich complexes of type $CpLn[(\mu\text{-}R)_2AlR_2]_2$.[5]



Meanwhile we have developed additional synthetic routes to mono(cyclopentadienyl) complexes addressing the issues *(i)* high solubility, *(ii)* mononuclearity, *(iii)* accessiblity of derivatives of the entire lanthanide series, and *(iv)* stereoelectronic variation of the Cp ring. A comprehensive account on synthetic and structural aspects will be given.

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Multiple Bonding Between Lanthanide Atoms and Main Group Elements: Experiment and Theory

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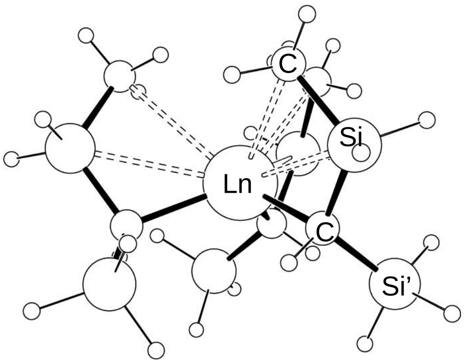
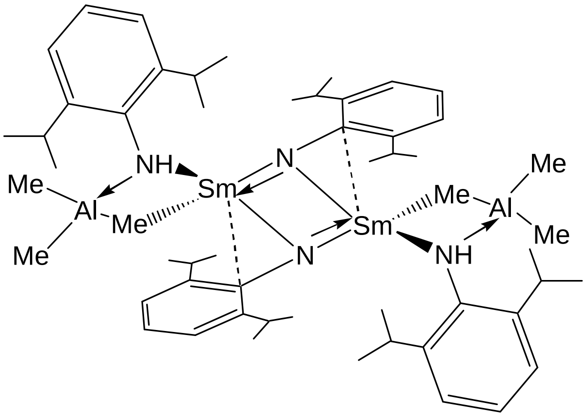
Lanthanide ions form a variety of coordination and organometallic complexes that are perceived as containing purely ionic metal-ligand interactions, with little or no involvement of the metal *d* orbitals in covalent bonding of σ type. Even more controversial is the possibility for these centers to establish covalent interactions of π type. Nevertheless, a number of experimental observations do not seem to be understandable without invoking such interactions. This presentation will highlight experimental results and computational studies aimed at understanding the role of the metal *d* (and even *f*) orbitals in metal-ligand bonding for these compounds. Three classes of compounds will be illustrated: (i) the pair of isoelectronic and isostructural $Ln[Y(SiMe_3)_2]_3$ (Y = CH, Ln = La, Sm;[1] Y = N, Ln = Sm[2]); (ii) the remarkable $[(\mu\text{-ArN})Sm(\mu\text{-NHAr})(\mu\text{-Me})AlMe_2]_2$ compound with very short Sm-N interactions[3]; and (iii) the putative Cp_2CeX system (X = F^+, O, NH, CH^-, CH_2).[4] The presentation will also highlight the involvement of *d* orbitals in the establishment of agostic interactions.





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Luminescence of Eu2$^+$ in Thiocyanates

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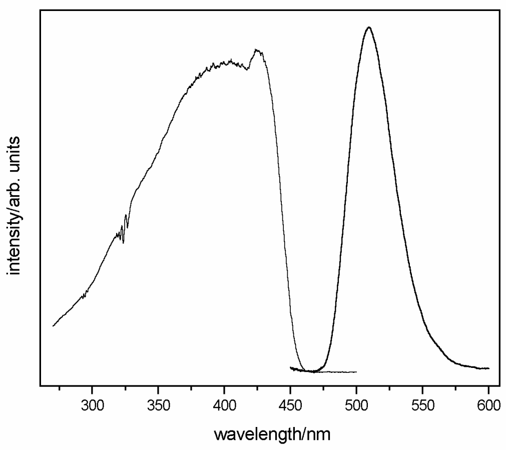
The luminescence of Eu^{2+} ions depends strongly on the crystalline environment. While sulfides and nitrides are used as phosphors for new bright LEDs the luminescence of Eu^{2+} doped in thiocyanates was not investigated yet. On the other hand, it seems to be of interest to compare these host lattices to get some information on the influence of the decreasing covalency of the thiocyanates. This forced us to prepare the alkaline earth thiocyanates $Sr(SCN)_2$ and $Ba(SCN)_2$ and solve their crystal structures. Both compounds are isotypic and the cations are fourfold coordinated by sulfure as well as fourfold coordinated by nitrogen atoms.[1]



Exitation and emission spectra of $Sr(SCN)_2:Eu^{2+}$ at

In both host lattices Eu^{2+} shows a strong bright green luminescence at low temperatures.[2,3] This shows that the influence of the covalency is very large. While the emission of Eu^{2+} doped in $Sr(SCN)_2$ is strongly quenched with increasing temperatures and could not be detected above 220 K[2] the quenching temperature of Eu^{2+} doped in $Ba(SCN)_2$ is much higher.[3] Furthermore, the decay time of $Sr(SCN)_2:Eu^{2+}$ (τ = 453 nsec at 12 K) is very small. Because the Stokes shift is comparable to other host lattices in this case these behaviour can be explained by the assumption that the position of the lowest excited state is very close to the conduction band, and the energy difference is estimated to be about 1100 cm^{-1}. After excitation an excitonic state is thermally populated followed by a nonradiative decay to the ground state. This is also shown due to the decreasing intensity at higher excitation energies. This process is similar to that in the imaging plate phosphor, $BaFBr:Eu^{2+}$, and may serve for a better understanding of these phenomena. Furthermore, some Fano antiresonances could be detected in the case of $Sr(SCN)_2:Eu^{2+}$.

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Reduced 1-Aza-1,3-dienes: New Ligands in Organolanthanide Chemistry

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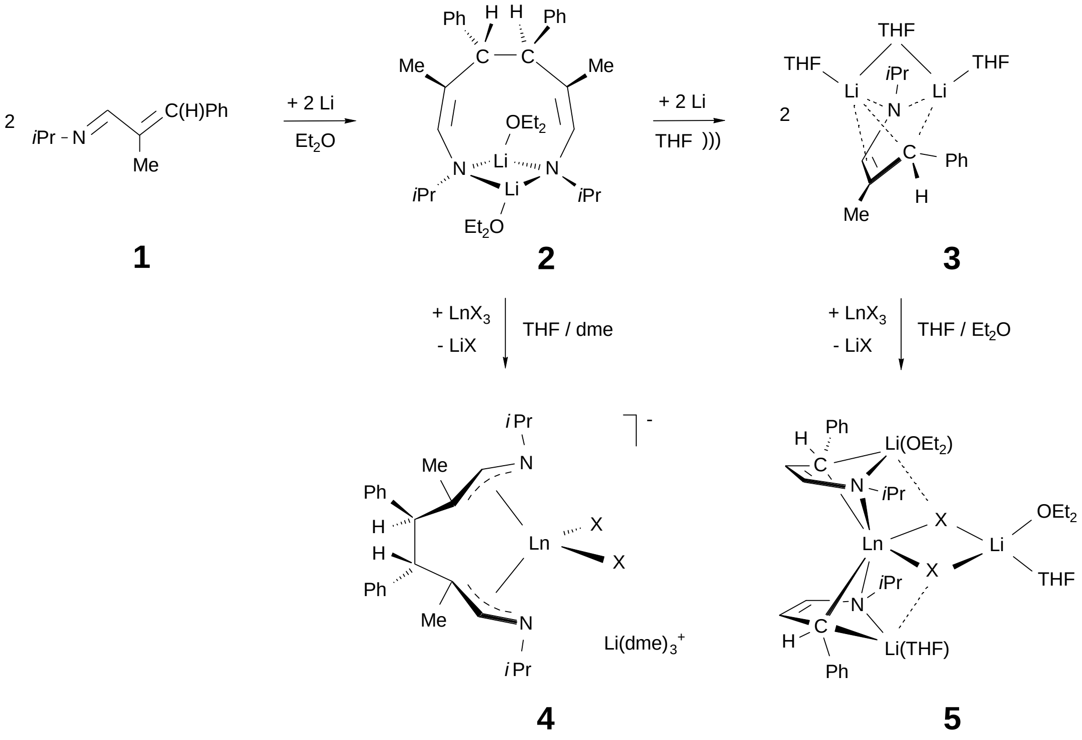
Recently we reported on the reduction of the 1-aza-1,3-diene **1** to the 1-azabut-2-ene-1,4-diyl-dianion **3**, where - initially unexpected but almost quantitatively - the hexa-1,5-diene-1,6-diamide **2** was generated as an intermediate during the reaction course.[1] However, it is rather the two-fold enamide structure than the extraordinary preparative approach that makes compound **2** such an interesting novel ligand system to the chemistry of lanthanides.



The structures of these lanthanide complexes **4** indicate that the coordination mode of the hexa-1,5-dien-1,6-diamide ligand is very flexible and sensitively depends on the ligand environment at the metal center. Treatment of **3** with different lanthanide halogenides lead to novel 1-aza-1,3-diene lanthanide complexes **5**.

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Neue thiophenhaltige Lanthanoid-Komplexe als Precursoren für Polymer-Leuchtdioden

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In unserer Arbeitsgruppe sind wir daran interessiert, Lanthanoid-Komplexe zu synthetisieren, die polymerisiert werden können, und gleichzeitig Lanthanoid-Lumineszenz anregen. Zu diesem Zweck haben wir eine Reihe von organischen Liganden hergestellt, die über eine oder mehrere Thiophengruppen verfügen. An diese sind dann aromatische funktionelle Gruppen mit Carboxylsäure-Resten angebracht, zur Komplexierung der metallischen Ionen. In unserem Vortrag werden wir über die neuen Liganden berichten, deren Eigenschaften und die der aus ihnen hergestellten Polymere, sowie über die metallischen Komplexe, die wir isoliert und charakterisiert haben.

A New, Very Bulky Aminopyridinato Ligand for Lanthanoids: Steric Management of Amidolanthanoid Catalysts

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The high coordination flexibility of the aminopyridinato ligand class (Figure 1) has led to an exciting area of chemistry including the stabilisation of a number of heterodinuclear complexes with unusual lanthanoid-transition-metal combinations as well as highly selective polymerisation catalysts.[1-3]

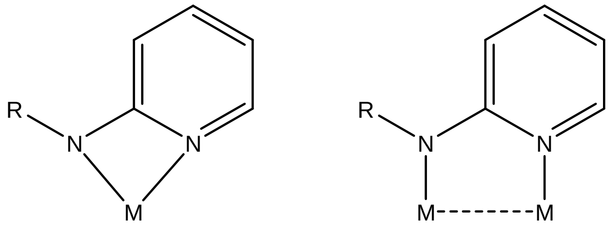

Figure 1

The ligand periphery can be readily modified and we have recently synthesised new types of aminopyridinato ligands that incorporate a number of *i*-Pr substituents on the ligand backbone. These very bulky systems can be utilised in probing key issues in amidolanthanoid catalysts such as deleterious ligand redistribution reactions (as have commonly thwarted lanthanoid amide chemistry in the past) and active site monomer-dimer pre-equilibria. Several synthetic approaches have led to a variety of unique amidolanthanoid complexes for example the heteroleptic mono-amide [La(Ap*)Br$_2$(thf)$_3$] (Figure 2) which shows a remarkably high stability toward ligand redistribution. The reactivity of such lanthanoid complexes will be discussed.

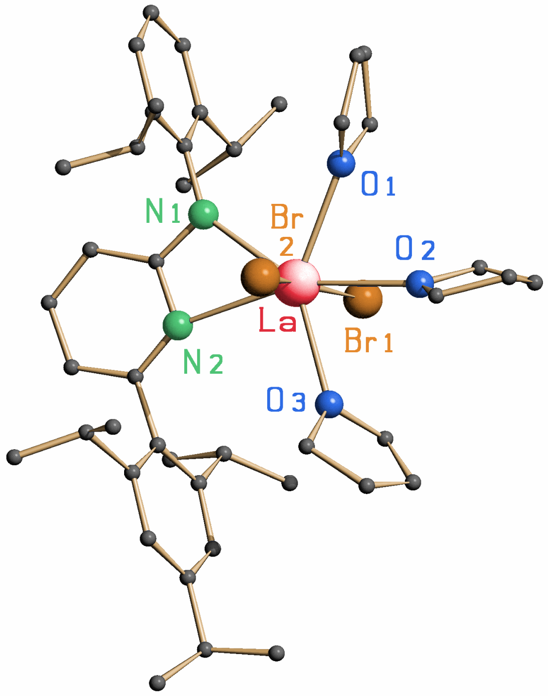

Figure 2

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Poster

New tetrapodal ligands and their Ln(III) complexes: Synthesis, thermodynamic and photophysical properties.

Steve Comby, Anne-Sophie Chauvin, Daniel Imbert, and Jean-Claude G. Bünzli

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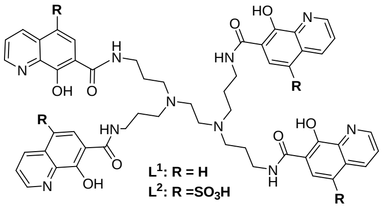
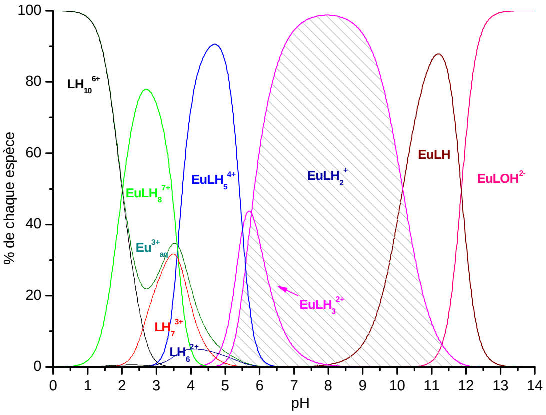


We present new lanthanide-containing chelates which are water soluble at physiological pH. The ligands have been designed to take advantage of the chelating effect of bidentate subunits connected to a *N*,*N*,*N*',*N*'-tetrakis(3-aminopropyl)-1,2-ethanediamine framework. They form stable complexes with Ln(III) ions, the four chromophoric units being coordinated to the metal centre, exploiting the entropic effect generated by the anchor. In the case of $\mathbf{L^2}$ the presence of sulfonate groups allows a high solvatation of the ligand and its chelates in aqueous media, which enlarges the range of possible applications. Furthermore, both ligand $\mathbf{L^1}$ and its complexes are soluble in organic media such as methanol or dichloromethane. We describe here the synthesis of $\mathbf{L^1}$ and $\mathbf{L^2}$, and their complexation reactions in organic and aqueous media, respectively. We focus on the thermodynamic properties of $\mathbf{L^2}$ in water (pK_as of the ligand, stability constants of the complexes), which have been investigated by the use of UV-vis spectrophotometric and potentiometric methods, revealing that $\mathbf{L^2}$ forms only a mono-metallic complex at pH = 7.4 with Ln(III) ions. Luminescence measurements carried out both on the ligands and their complexes reveal the influence of the sulfonate group on the photophysical properties.



Formation curves of the Eu(III) complexes of L^2 in water

A kinetically inert and optically active Cr(III) partner for sensitizing Ln(III) in heterodimetallic non-covalent d-f podates.

Daniel Imbert, Martine Cantuel, Gérald Bernardinelli, Jean-Claude G. Bünzli, Gérard Hopfgartner, and Claude Piguet

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Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 quai E. Ansermet, 1211 Geneva 4, Switzerland

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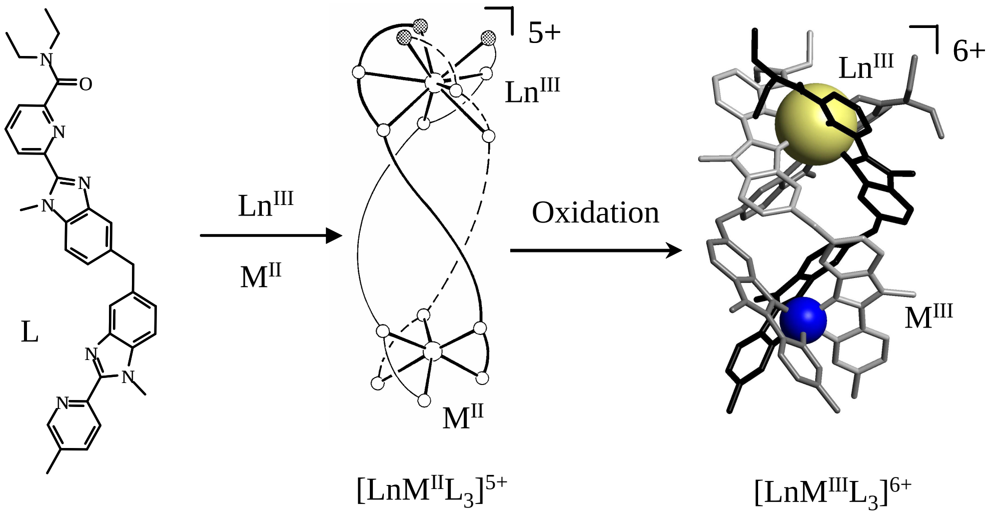
The segmental ligand L is used to specifically coordinate lanthanide (Ln^{III}) and 3d block (M^{II}) ions. Triple helicates $[LnML_3]^{5+}$ (M=Zn, Fe, Co), obtained when reacting together L, Ln^{III} and M^{II} in a 3:1:1 ratio, present tunable physical and magnetic properties.[1] For M = Cr^{III}, subsequent oxidation yields the inert organized supramolecular triple-helical heterodimetallic d-f complexes $[LnCrL_3]^{6+}$,[2] whose structural and physical properties are presented in this contribution. Particular attention will be focused the intramolecular energy transfer $Cr^{III} \rightarrow Ln^{III}$ (Ln = Eu, Tb) and $Ln^{III} \rightarrow Cr^{III}$ (Ln = Nd, Yb), occurring along the threefold axis, responsible of a directional light-conversion.



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Donor-Functionalized Terphenyl Lanthanide Complexes

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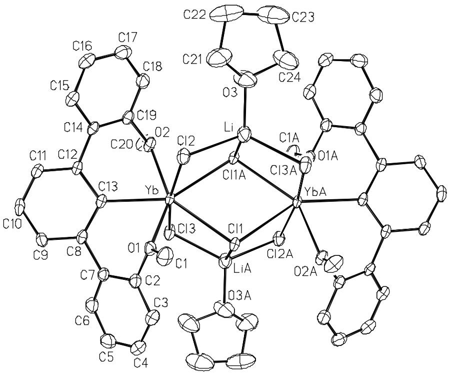
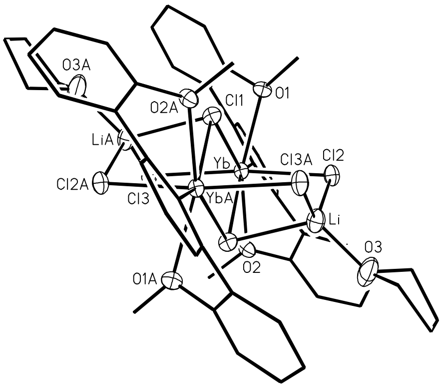
Although much work on organolanthanide chemisty has been published in recent years, the chemistry of low-coordinate complexes of the relatively large and strongly electropositive lanthanide cations free from stabilizing π-ligands remains poorly developed. The search for stable lanthanide complexes containing novel ancillary ligand systems capable of facilitating different catalytic processes is one of the challenging problems in organolanthanide chemistry. We wanted to explore the usability of sterically encumbering terphenyl ligand systems for the synthesis of kinetically stablized compounds of the lanthanide elements. We recently introduced a number of such compounds bearing σ-bonded terphenyl ligand systems as the only ancillary organic ligand at the lanthanide atom. However, all of the complexes were found to be of only limited stability *in solution*, particularly in tetrahydrofuran solution at ambient temperature, thereby limiting the usability of such species for further reactions. Therefore, we were interested in probing the use of *donor-functionalized* terphenyl groups as ligand systems for the lanthanides, and decided to employ terphenyl systems with a stabilizing methoxy-function attached to the ortho-position of the aryl substituents in the 2,6-positons. Shown are two views of the molecular structure of a novel lanthanide compound that is based on the chiral (racemic) donor-functionalized terphenyl ligand Danip [= 2,6-di(o-anisol)phenyl].





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Large Negative Magnetoresistance in the System Gadolinium-Iodine-Hydrogen

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GdI_2 is a layered metallic d^1 compound, which orders ferromagnetically at 276(3) K and displays large negative magnetoresistance (MR) ~ 70 % at 7T close to room temperature. The spin-polarized band structure calculations, performed to establish relations between the electronic structure and specific properties of materials, revealed a Van Hove singularity near the Fermi surface of GdI_2 (approx. 0.2 eV below E_F).[1] Based on these results it could be assumed, that, moving the Fermi level closer to the saddle points via hole doping of GdI_2, a more pronounced MR effect can be achieved. Here, we report on magnetic measurements and magnetoresistivity studies of hole-doped GdI_2H_x as well as related $GdIH_x$ compounds.

Hydride halides $GdIH_x$ ($0.67 < x < 1.0$) form another family of compounds in the system Gd-I-H. They are metallic layered compounds, which crystallize with the ZrX (X = Cl, Br) structure type. The heavy atom substructure consists of close-packed metal atom bilayers sandwiched between layers of halogen atoms. The H atoms occupy tetragonal voids in the metal atom bilayers. The magnetization data of $GdIH_x$ show an antiferromagnetic transition at $T_N = 26 – 40$ K, depending on the H concentration x.

A colossal negative magnetoresistance (≈ 99 %) at low temperatures (< 25 K) has been found for the $GdIH_x$ with the hydrogen concentration approaching its lower limits of 0.67 as demonstrated for the deuteride.[2] These compounds show metallic conductivity above 25 K. Upon cooling below 25 K the zero-field resistivity increases dramatically by several orders of magnitude. On the other hand, the magnetoresistivity measurements reveal that resistivityincrease can be completely suppressed by magnetic fields up to 5 T.

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Preparation of Lanthanum Hydride Diiodides Toward Superconductivity Predicted From Electronic Structure Calculations

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LaI_2 is a d^1 metallic layered compound, which crystallizes with the tetragonal Ti_2Cu structure. The structural similarity of the LaI_2 layer with square planar coordination of La and CuO_2 layer in high-T_c cuprates initiated band structure calculations,[1] which revealed strong nesting characteristics at the Fermi surface of LaI_2. A more detailed study of electronic structure, reported in,[2] has shown the presence of Van Hove singularity approx. 0.5 eV below the Fermi level. All experiments to achieve superconductivity by moving the Fermi level closer to the saddle points via hole doping of LaI_2 failed. Substitution of La by Ba as well as H insertion into the structure proved impossible.[3]

The renewed investigation of the reaction of LaI_2 with hydrogen showed that the iodide absorbs considerable amount of H, however, associated with significant changes to the structure. The square planar nets rearrange into nets with a trigonal coordination of the La atoms. Based on early work of Hughbanks[4] this transition can be rationalized in terms of 3-center metal-metal bonding. Heating LaI_2 up to 650 ^{o}C under 1 atm hydrogen led to $LaI_2H_{0.95}$, which was characterized by powder X-ray diffraction and magnetic measurements. $LaI_2H_{0.95}$ crystallizes in the hexagonal space group $P6_3/mmc$ with lattice constants a = 4.2158(7) Å and c = 15.508(3) Å. The magnetic susceptibility of LaI_2, $LaI_2H_{0.75}$ and $LaI_2H_{0.95}$ was measured in the temperature range 2-350 K. No superconductivy was found for these compounds down to 2 K. For LaI_2 the Pauli paramagnetism has been determined to be equal to $43(2)\cdot 10^{-6}$ cm^3/mol in good agreement with the value estimated from electronic structure calculations.

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Cerium-Catalyzed α-Hydroxylation of β-Dicarbonyl Compounds

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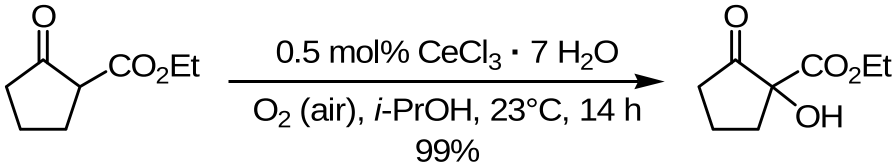
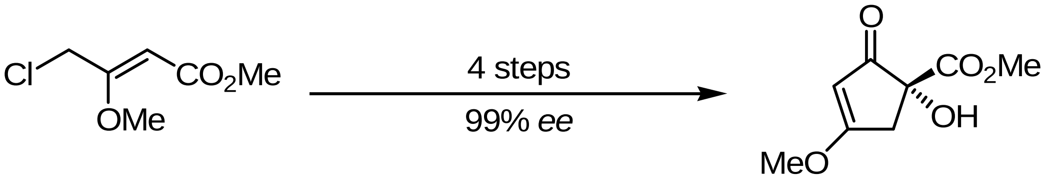
Oxidation is a common strategy for functionalizing organic compounds. In terms of economical and ecological considerations molecular oxygen is the oxidant of choice. We introduce cerium(III)chloride-heptahydrate as a catalyst for the oxidation of β-dicarbonyl compounds with molecular oxygen in isopropanol as the solvent.

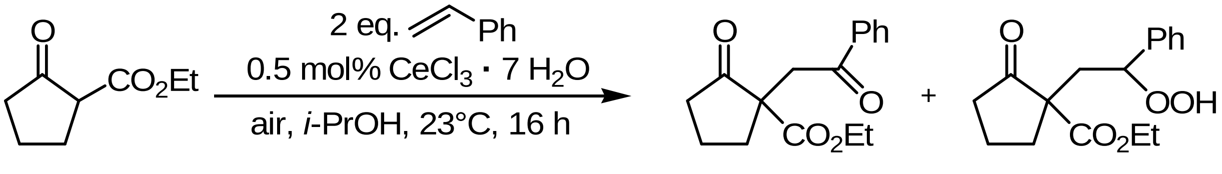


Quantitative conversion is achieved by simply stirring β-dicarbonyl compounds with catalytic amounts of $CeCl_3 \cdot 7\ H_2O$ under an atmosphere of O_2 at ambient temperature. After filtration of the reaction mixture, the α-hydroxylated products are obtained in quantitative yield and with quantitative selectivity.

We have prepared the antibiotic (–)-kjellmanianone in a four step reaction sequence. The key step of the syntheses was a cerium-catalyzed α-hydroxylation, which was followed by resolution of the racemate with candida antarctica lipase B.



We propose a radical mechanism for the α-hydroxylation. This assumption is supported by the fact that, if styrene is present in the reaction mixture, the C–C-coupling product is obtained.



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Praseodymium Diiodide, PrI_2, revisited by Synthesis, Structure Determination and Theory

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To elucidate the electronic properties of the modifications of PrI_2 first principles electronic band structure calculations have been carried out using the tight-binding linear-muffin-tin-orbital method (LMTO) as well as the full potential augmented plane wave method (FP-LAPW). The band structure and the bonding were analysed in terms of projections of the bands onto orthogonal orbitals. It was especially focussed on Pr-Pr interactions by crystal overlap Hamiltonian population (COHP) analysis. The calculations show accordingly that a configurational crossover between a $[Xe]6s^0 5d^0 4f^n$ and a $[Xe]6s^0 5d^1 4f^{n-1}$ configuration can be observed in the case of PrI_2, depending upon the structure adopted. A higher *d* orbital contribution results in stronger Pr- Pr interactions. Thus, the driving force appears to be an optimization of bonding.

Experimentelle Erfassung und Simulation der Elektronenstrukturen von pseudo-trigonal-planaren (substituierten) Cyclopentadienylkomplexen des Neodym(III)

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Während die Kristallfeld(KF)-Aufspaltungsmuster diverser pseudo-trigonal-pyramidal und -trigonal-bipyramidal koordinierter Cyclopentadienylkomplexe des Neodym(III) (Cp_3NdX bzw. Cp_3NdY_2) mittlerweile weitgehend aufgeklärt werden konnten, ist über derartige Aktivitäten auf dem Gebiet der entsprechenden pseudo-trigonal-planaren (substituierten) Grundkörper (Cp'_3Nd) bislang noch nicht berichtet worden.

In den letzten Jahren wurden die trigonal-planaren Molekülstrukturen mehrerer höher alkylierter oder silylierter Cp'_3Nd-Komplexe röntgenographisch belegt, wegen der induktiven Effekte der Alkyl- bzw. Silylgruppen ist dort jedoch der wichtige Absorptionsübergang $^4I_{9/2} \rightarrow {}^2P_{1/2}$ jeweils durch einen energetisch niedrig liegenden Charge transfer-Übergang verdeckt. Aus diesem Grund untersuchen wir hier zweckmäßigerweise die monosubstituierten Komplexe $(C_5H_4tBu)_3Nd$ (**1**) und $(C_5H_4SiMe_3)_3Nd$ (**2**), bei denen dieser Schlüsselübergang gut beobachtbar ist.

Die Molekülstrukturen der Verbindungen **1** und **2** sind zwar nicht bekannt, jedoch weisen deren Absorptionsspektren im Bereich 11000-17500 cm^{-1} eine große Ähnlichkeit mit denen von $(C_5Me_5)_3Nd$ und $(C_5Me_4H)_3Nd$ auf (deren trigonal-planare Strukturen röntgenographisch belegt sind), so daß wir auch für die Verbindungen **1** und **2** eine effektives KF der Symmetrie D_{3h} annehmen.

Auf der Basis der Absorptionsspektren wurden die zugrunde liegenden KF-Aufspaltungsmuster der Verbindungen **1** und **2** abgeleitet und durch Anpassung der offenen Parameter eines phänomenologischen Hamilton-Operators mit reduzierten r.m.s.-Abweichungen von 25.0 bzw. 24.7 cm^{-1} (bei 58 bzw. 63 Zuordnungen) simuliert.

Die verwendeten Parameter gestatten die Abschätzung spektrochemischer und nephelauxetischer Effekte sowie die Aufstellung von experimentorientierten nicht-relativistischen und relativistischen Molekülorbital-Schemata der Verbindungen **1** und **2** (im f-Bereich).

Optophysical and Structural Properties of Lanthanoid Complexes in the Solid State

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Lanthanoids are popular luminescent active centres utilised in various applications due to their unique optoelectronic properties.

For quantum mechanical reasons lanthanoids can not be excited directly by light. However, by attaching strongly absorbing organic chromophores to the lanthanoid it can be excited indirectly from the triplet state of the ligand. The commonly accepted electronic pathway is given in the figure below. It can be seen that this class of substances can be used in any area in which energy rich light is converted into light of lower energy.

One class of compounds presented on this poster are various Eu and Tb complexes of differently substituted benzoic acid derivatives. Their aromatic π electron system absorbs light strongly and furthermore they form kinetically stable lanthanoid benzoate complexes due hard Lewis acid Lewis base interactions. These complexes represent quite promising, efficient luminescent materials. Additionally, some Tb cyclopentadienyl have been synthesised and characterised. This photophysical study of airsensitive organometallic Tb complexes in the solid state unpresented. To connect these two sets of compounds the cyclopentadienyl complexes have been co-coordinated with benzoato ligands.

The poster presents photoelectronic properties of these complexes in the solid state. Furthermore some structures will be presented.

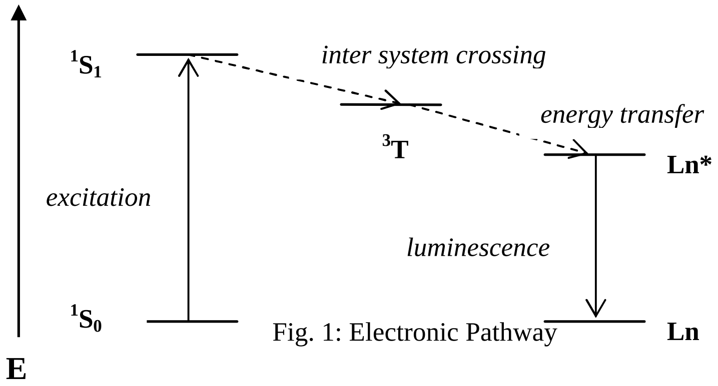

Fig. 1: Electronic Pathway

VIS-, NIR- and Upconverted Luminescence from Rare Earth Sodalites

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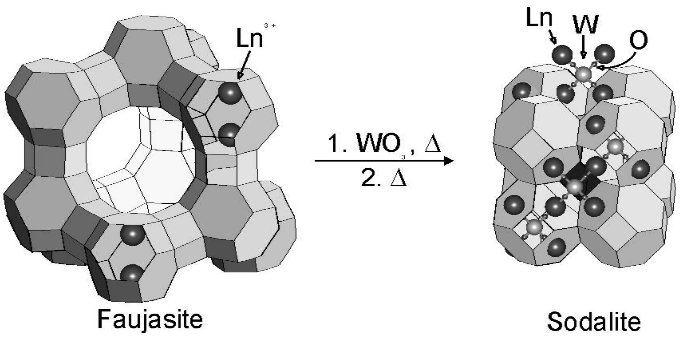
In the recent past, numerous attempts have been untertaken to utilize nano-, meso- and microporous materials as hosts for luminescent guest species.[1] The accessible spectral range now spreads from the Vacuum Ultraviolet (VUV) to the Near Infrared (NIR), if sodalites are included in this scope. Although borderline materials in this context with respect to pore sizes, examples of their versatility in accomodating small, but efficient luminescent entitites are discussed. In particular, optical materials, whose spectral range of operation is allocated in the NIR have recently attracted our attention. NIR emission, or other optical processes involving excited states at energies in the NIR, such as e.g. upconversion, is in nanoporous hosts usually hampered by too strong an electron-phonon coupling. Radiationless deactivation is caused by coupling to the host lattice itself, as in e.g. SiO_2 based materials, or, most disadvantageously, by the presence of occluded water.



We have initially tackled this problem using tungstate loaded faujasites, which can subsequently be converted into the sodalite system[2,3] (see figure), and were, despite phase impurities rewarded with materials emitting efficiently, even in the NIR.

Depending on the rare earth dopands, the sodalite materials obtained can be excited to show both, either NIR emission, or Upconversion in the visible. The Nd-emission at 1064 nm is comparable in intensity to that of commercial Nd-doped glasses[3], while 546 and 657 nm upconverted emission of e.g. the Ho^{3+}/ Yb^{3+} couple could be observed with the bare eye on excitation with a 50 mW / 980 nm diode laser. Phase pure materials were subsequently synthesized directly from individual precursors (SiO_2, WO_3, Al_2O_3, Ln_2O_3) using a high temperature route. However, a multitude of stoichiometric and morphological parameters remains to be optimized in striding for the ultimate goal of a sodalite microlaser in analogy to already known zeolite lasers[5].

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Calcium, Strontium, and Barium as "pseudo-lanthanides" – Similarities and Differences between Alkaline Earth and Rare Earth Metal Pyrazolates

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The close similarity between the more commonly isolated divalent lanthanides and alkaline earth metals (Yb^{2+}/Ca^{2+}; Eu^{2+}, Sm^{2+}/Sr^{2+}) can be explained comparing ionic radii.[1] To chemically prove this relationship only the well established cyclopentadienide chemistry[2] in addition to a few other examples, such as complexes with P-donor systems by Izod et al.,[3] provide a solid basis for comparison. On the other hand, little basis of comparison has been available for the heaviest, stable alkaline earth metal barium, whose ionic radius exceeds those of the divalent rare earths. With the ongoing challenge to prepare and study complexes of the larger divalent lanthanides, the respective barium compound might provide critical insight into the reactivity and structural features of such species.

A series of heavy alkaline earth metal pyrazolates was successfully obtained using metal based synthetic routes originally developed for lanthanides; mirroring similarities in reactivity. In addition, structural characterization revealed striking similarities in both bonding and structural chemistry, as shown by the isomorphous $[Ca(Ph_2pz)_2(dme)_2]$ and $[Yb(Ph_2pz)_2(dme)_2]$ derivatives.[4] This poster will demonstrate that this observation provides a powerful tool in the preparation of a series of analogues compounds presented herein.

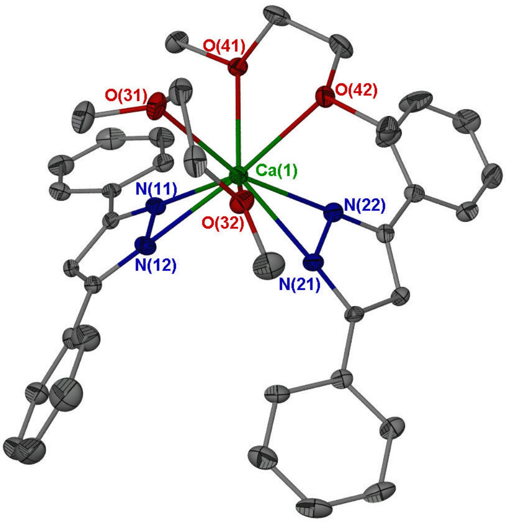

Figure1: Crystal Structure of $[Ca(Ph_2pz)_2(dme)_2]$

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$Rb_3Pr_3[PS_4]_4$: Das erste Rubidium-Selten-Erd-Thiophosphat

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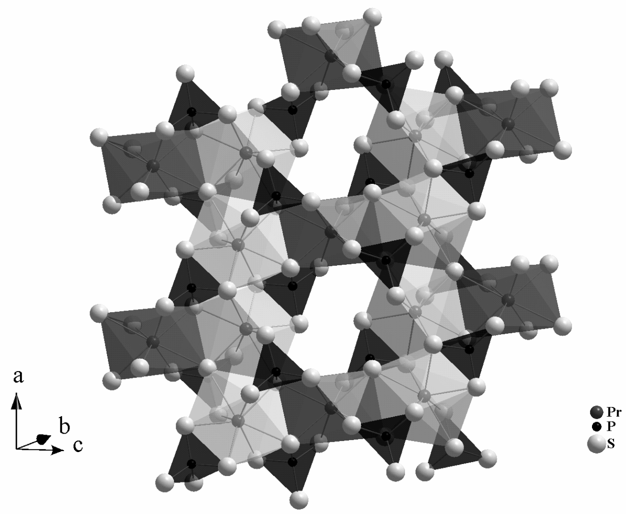
Thiophosphate der Selten-Erd-Elemente sind sowohl mit Beteiligung von Kalium-Kationen (z. B. $K_3La[PS_4]_2$[1] und $K_4Nd_2[PS_4]_2[P_2S_6]$[2]) als auch unter Beteiligung von Caesium-Kationen ($Cs_4Pr_2[PS_4]_2[P_2S_6]$[3]) bereits länger bekannt. Es sollte nun untersucht werden, ob auch mit anderen Alkalimetall-Kationen, insbesondere jenen des Rubidiums, analoge Verbindungen gebildet werden. Dargestellt wurde $Rb_3Pr_3[PS_4]_4$ durch Reaktion von Praseodym-Metall, Schwefel und rotem Phosphor mit Rubidium-Bromid (RbBr) als Flußmittel und Rubidium-Quelle in evakuierten Kieselgasampullen bei 950°C. Es kristallisiert triklin in der Raumgruppe $P\bar{1}$ ($a = 926{,}79(6)$, $b = 1050{,}83(7)$, $c = 1453{,}28(9)$ pm, $\alpha = 84{,}329(5)$, $\beta = 88{,}008(5)$, $\gamma = 80{,}704(5)°$, $Z = 2$) in Form flaschengrüner Plättchen.

In der Kristallstruktur betätigen die drei kristallographisch unterschiedlichen Rb^+-Kationen Koordinationszahlen von 10, die drei Pr^{3+}-Kationen weisen jeweils eine Koordinationszahl von 8 auf. Die isolierten $[PS_4]^{3-}$-Tetraeder (d(P–S)= 200 – 209 pm) bilden zusammen mit den praseodymzentrierten Schwefel-Polyedern Schichten der Zusammensetzung $^{2}_{\infty}\{(Pr_3[PS_4]_4)^{3-}\}$.

Die Rubidium-Kationen sind sowohl in den Hohlräumen als auch zwischen den Schichten zu finden, die senkrecht [100] gestapelt werden. Dabei sind diese Schichten so gegeneinander verschoben, daß sich *keine* durchgehenden Kanäle bilden können. Die Orientierung der Schichten wiederholt sich mit einer Repetitionsperiode von drei.



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$M_4N_2Ch_3$: One Composition, but Four Different Structure Types of Lanthanide(III) Nitride Chalcogenides

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The *non*-isotypical nitride chalcogenides $M_4N_2Ch_3$ (M = La - Nd, Sm, Gd, Tb; Ch = S, Se, Te) of the lanthanides are formed by the reaction of the respective metal (M) with sodium azide (NaN_3), chalcogen and the corresponding lanthanide trichloride or bromide (MX_3) at 850 - 900°C in evacuated silica ampoules after seven days according to:

$$34\ \mathrm{M} + 27\ \mathrm{Ch} + 6\ \mathrm{NaN_3} + 2\ \mathrm{MX_3} \longrightarrow 9\ \mathrm{M_4N_2Ch_3} + 6\ \mathrm{NaX}.$$

While the sulfides are stable against water and so can be obtained as pure samples by rinsing off NaCl or NaBr (by-product and fluxing agent), respectively, the analogous selenides and tellurides become more and more sensitive to moist air. The crystal structures differ fundamentally in the linkage of the structure dominating N^{3-} centred $(M^{3+})_4$ tetrahedra.[1] **$Sm_4N_2S_3$**[2] and **$Tb_4N_2Se_3$**[3] crystallize in the monoclinic space group C2/m and consist of two crystallographically different cations showing coordination numbers of *six* relative to the anions. The $[NM_4]$ tetrahedra share *cis*-oriented edges to form strands $^{1}_{\infty}[\mathrm{N(M1)}^{k}_{3/3}(\mathrm{M2})^{t}_{1/1}]^{3+}$. In contrast, the linkage of *trans*-oriented edges of $[NM_4]$ tetrahedra builds up the orthorhombic crystal structure of the telluride **$La_4N_2Te_3$** (space group: Pnma).[4] Due to a slight distortion of the chain $^{1}_{\infty}[\mathrm{N(M1)}^{k}_{2/2}(\mathrm{M2,3})^{k}_{2/2}]^{3+}$, three crystallographically different M^{3+} with coordination numbers of *six* (twice) and *seven* occur. In the nitride selenide **$Nd_4N_2Se_3$**[3] for the first time an arrangement of interconnected $[NM_4]$ tetrahedra to layers is observed. In the monoclinic crystal structure (space group: C2/c) the $[NM_4]$ units are first edge-linked to bitetrahedra $[N_2M_6]^{12+}$ which then become cross-connected to $^{2}_{\infty}[\mathrm{N(M1)}^{k}_{2/2}(\mathrm{M2})^{e}_{2/2}]^{3+}$ layers via their remaining four vertices. Coordination numbers once again are *six* and *seven* relative to the anions (N^{3-} and Se^{2-}). Finally another layered arrangement is found in the monoclinic crystal structure of **$Pr_4N_2S_3$**[4] (space group: C2/c). There are four different Pr^{3+} cations present which show coordination numbers of *six* (twice) and *seven* (twice). The $[NM_4]$ tetrahedra are edge-linked to bitetrahedra just like in $Nd_4N_2Se_3$, but then connected via two vertices to quadruples $[N_4M_{10}]^{18+}$ which again build up layers $^{2}_{\infty}\{([\mathrm{N(M1,2)}^{k}_{2/2}(\mathrm{M3,4})^{e}_{2/2}]_2)^{6+}\}$ via their remaining four free corners.

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$Yb_4O_3Cl_2[SeO_3]_2$: A New Layered Ytterbium(III) Oxychloride Oxoselenate(IV)

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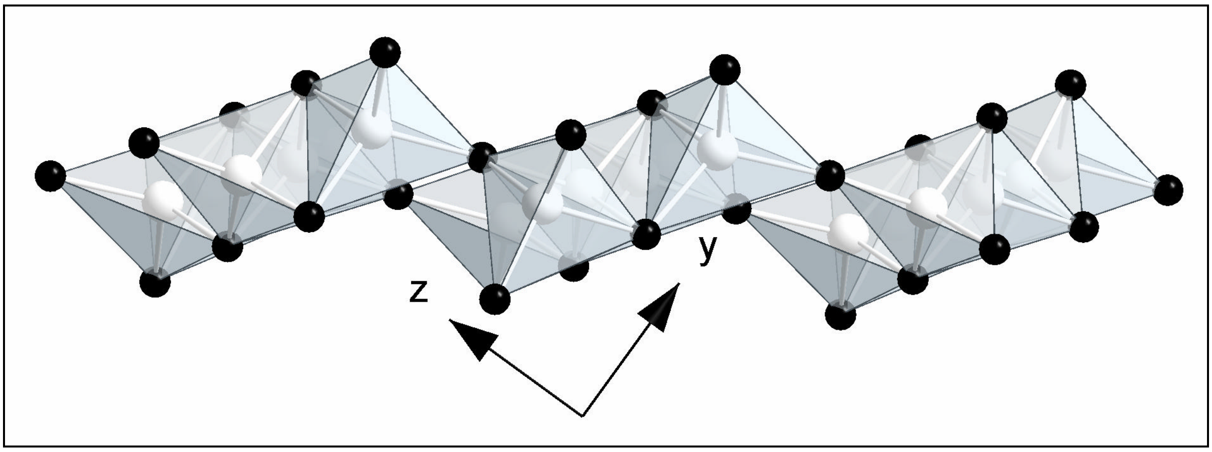
Colourless single crystals of $Yb_4O_3Cl_2[SeO_3]_2$ are obtained as platelets by heating stoichiometric mixtures of Yb_2O_3, YbOCl, $YbCl_3$ and SeO_2 (molar ratio 3:1:1:4) in evacuated sealed silica tubes at 850°C for seven days. Appropriate amounts of CsCl were used as flux. The new compound crystallizes in the triclinic system ($P\bar{1}$; a = 853.87(6), b = 1145.92(8), c = 1195.46(9) pm, α = 68.132(7), β = 78.113(7), γ = 85.748(7)°; Z = 4). Its structure contains eight crystallographically independent Yb^{3+} cations: Yb1 and Yb2 are coordinated as distorted square prism or antiprism by one chloride and seven oxygen ligands, whereas Yb3, Yb4 and Yb5 are monocapped trigonal prismatically surrounded by five oxygen atoms and two chloride anions. Finally eight oxygen atoms build up distorted square prisms around Yb6, Yb7 and Yb8. The Se^{4+} coordination is best described as ψ^1 tetrahedral ($[SeO_3E]^{2-}$; E: *non*-binding electron pair, "*lone pair*") with four sets of Se–O distances from 168 to 175 pm. One can observe six *non*-selenium bonded O^{2-} anions in tetrahedral coordination of four Yb^{3+} cations each (d(O–Yb) = 217 – 230 pm). Those oxocentred tetrahedra $[OYb_4]^{10+}$ form $[O_6Yb_{12}]^{24+}$ blocks by edge-sharing which are further condensed via two edges (Yb1 – Yb3) and four vertices (two Yb6 and two Yb8) to $^2_\infty\{([O_3Yb_4]^{6+})_2\}$ layers spreading parallel (011) (see Figure). These layers are sandwiched by $[SeO_3]^{2-}$ and Cl^- anions as already observed in $Tb_5O_4Cl_3[SeO_3]_2$[1] and $Gd_9O_8Cl_3[SeO_3]_4$[2] with comparable $^2_\infty\{[O_4Tb_5]^{7+}\}$ and $^2_\infty\{[O_8Gd_9]^{11+}\}$ sheets, respectively, of fused $[OM_4]^{10+}$ tetrahedra.



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Lanthanoid-Komplexe vielzähniger Hydrazon- und Semicarbazonliganden

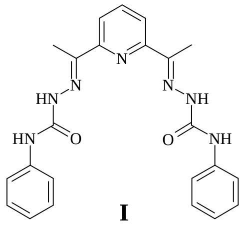
Alexander Jagst[a], Agustín Sanchez Díaz[b], Ezequiel Vazquez Lopez[c], and Ulrich Abram[a]

[a] FU-Berlin,[b] Universität Santiago de Compostela, Spanien,[c] Universität Vigo, Spanien

Radioaktive Isotope von Lanthanoiden und verwandten Elementen (^{153}Sm, ^{166}Ho, ^{177}Lu, ^{90}Y) besitzen ein beträchtliches Potential in der Radioimmunotherapie. Da eine direkte Koordination der Metall-Ionen an Donoratome nativer Biomoleküle meist zu entscheidenden Funktionsbeeinträchtigungen führt, besteht Interesse an Ligandsystemen, die Ln^{3+}-Ionen effektiv chelatisieren, deren Ladung kompensieren und zur Kopplung an Proteine geeignet sind.

Vor diesem Hintergrund synthetisierten wir durch Derivatisierung mit Semicarbaziden und Benzoylhydrazin eine Reihe von Liganden, die sich alle von 2,6-Diacetylpyridin ableiten (**I** – **IV**) und untersuchten deren Komplexbildung mit La^{3+}, Ce^{3+}, Pr^{3+},Sm^{3+} und Eu^{3+}.

Die potentiell fünfzähnigen Liganden **I** – **III** bilden mit diesen Ionen Bis-Komplexe, deren Nettoladung sich aus dem Anteil von Benzoylhydrazon-Einheiten ergibt, die im Gegensatz zu Semicarbazon-Seitenarmen bei der Komplexbildung deprotoniert werden. Während mit bis-substituierten Semicarbazonen ausschließlich dreifach positiv geladene Komplexe vom Typ **V** entstehen, gelingt die Synthese von einfach kationische Lanthanoid-Komplexen (**VI**) mit unsymmetrischen Liganden, die sowohl Benzoylhydrazon-, als auch Semicarbazon-Seitenketten tragen. Die Bis-Chelate besitzen meist die Koordinationszahl 10 und die Koordinationspolyeder lassen sich als zweifach überkappte Würfel bzw. Antiprismen beschreiben. Die Koordination eines zusätzlichen H_2O-Liganden wird lediglich beim Lanthan-Komplex beobachtet.



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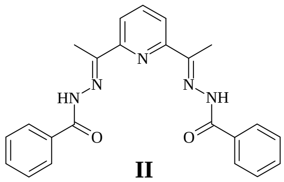

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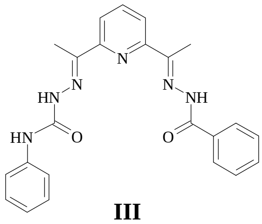

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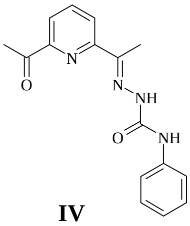

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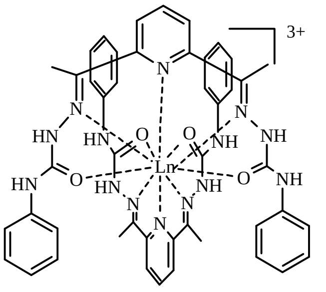
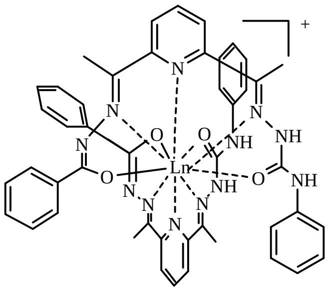


V

Ln^{3+} = La, Pr, Sm



VI

Ln^{3+} = Ce, Eu

Peralkylated Rare-Earth Metal Complexes $LnAl_3R_{12}$: Efficient Precursors for Binary and Single-Component Ziegler Catalysts

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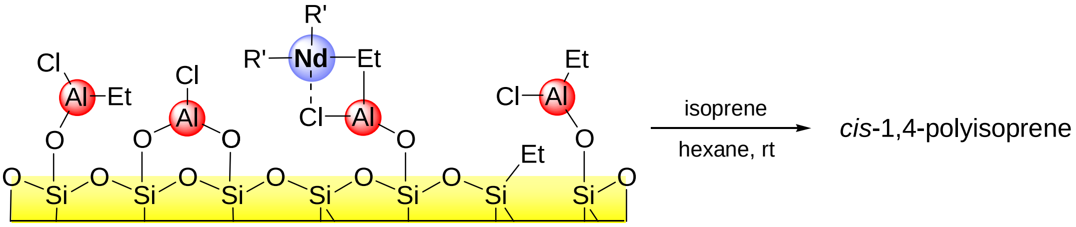
The interaction of low-agglomerated rare-earth metal ("neodymium") complexes such as alkoxide or carboxylate derivatives with various organoaluminum reagents is successfully exploited to generate high-performance catalysts for industrial 1,3-diene polymerization.[1,2] Solubility in aliphatic solvents, low Al:Ln ratios, *cis*-stereospecificity, and *medium* polydispersity are first order criteria to be met by such *ternary Ziegler Mischkatalysatoren*. Although homoleptic tetraalkylaluminate complexes $Ln(AlR_4)_3$ feature a unique preorganized set of heterobimetallic bridging moieties, their application in olefin transformations has not been reported so far.[3] Moreover, compounds $Ln(AlR_4)_3$ are exceptional for that they display an alkyl-only ligated monomeric system obtainable *ate*-complex free for the entire lanthanide series. Herein we describe the use of a $Ln(AlR_4)_3/Et_2AlCl$ *binary* precatalyst system in highly (*cis*)stereoregular isoprene polymerization. Additionally, the applicability of grafted variants such as $Nd(AlMe_3)_4@Et_2AlCl@MCM\text{-}48$ as storable *single-component* heterogeneous catalysts is investigated by employing periodic mesoporous silica MCM-48 as a structured support material.



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Postlanthanidocene Complexes Supported by Functionalized Diamide Ligands

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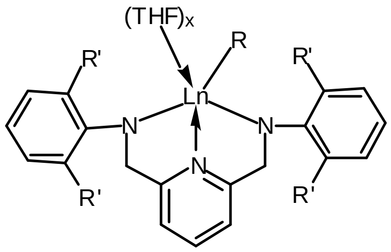
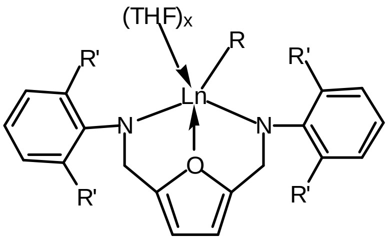
In the past decade „non-metallocene“ or „postmetallocene“ complexes have attracted considerable attention in α-olefin polymerization chemistry.[1-3] Although the rare-earth elements are inevitably connected to this topic, it was only recently that corresponding diamide complexes were described.[4-8] We have previously shown that scandium complexes featuring tridentate diamide ligands as a conformationally rigid ancillary ligand can act as remarkable initiators for acrylate polymerization via terminally bonded alkyl or amide initiating moieties R.[9] Not unexpectedly, the steric bulk of the substituents R’ in ortho position of the anilide units strongly affected the solubility and reactivity of these postlanthanidocene complexes.





Here we wish to report the synthesis, structural characterization, and reactivity of related postlanthanidocene complexes featuring different donor moieties in their chelating backbone. The implications of the stereoelectronic changes for the catalytic performance have been investigated for acrylate polymerization.

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Hinweise zur Toxikologie von Seltenen Erden

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1963 war über die Toxizität der Seltenen Erden arbeitsmedizinisch wenig bekannt, weil die Gefahr von Vergiftungen und Berufskrankheiten wegen der beschränkten Verwendung als gering eingeschätzt wurde.[1] Die Weltproduktion lag damals bei etwa 6.000 t/a REO. In den letzten 40 Jahren wurden die Produktionskapazitäten in einigen Ländern bedeutend ausgebaut. Viele neue Anwendungsgebiete wurden gefunden (Magnete, Supraleiter, Leuchtstoffe, Lichtleiter, Landwirtschaft u. a.). 2002 wurden weltweit 85.000 t REO produziert, wovon 75.000 t REO aus China stammten.[2] Bedingt durch die Ausweitung von Produktion und Anwendung kam ein immer größerer Personenkreis in Kontakt mit Seltene Erden enthaltenden Rohstoffen und Materialien. Die biologische Wirksamkeit von vielen Verbindungen wurde deshalb intensiver untersucht und dokumentiert.[3-5] Produzenten, Handelsunternehmen und Anwender haben entsprechend den gesetzlichen Bestimmungen zahlreiche Vorschriften für den Umgang mit Seltenen Erden erarbeitet, die Angaben über die Toxizität und den Gesundheitsschutz enthalten (Sicherheitsdatenblätter, Betriebsanweisungen u.a.).[6-8]

In dem Beitrag wird auf der Grundlage von Literaturangaben ein Überblick über mögliche Gefährdungen beim Arbeiten mit Seltenen Erden gegeben.

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Phenylpiperazin als chemische Schere: Von 1-dimensionalen FK-Verbindungen über Dimere zu monomeren Einheiten

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Institut für Anorganische Chemie der Universität zu Köln

Das weite Feld von Fk-Reaktionen eröffnete in unserer bisherigen Arbeit schon zahlreiche Möglichkeiten der Synthese von Verbindungen mit bisher nicht bekannten Selten-Erd-Stickstoff Koordinationen.[1,2] Die Umsetzung dieser Produkte, die sämtlich aus lösemittelfreien Reaktionen entstanden, mit anderen Liganden, führte zu neuen heteroleptischen Verbindungen. So gehen $^1_\infty[\mathrm{Sm(Cbz)_5(H\text{-}Cbz)}]$ und $^1_\infty[\mathrm{Yb(Cbz)_2}]$ (eindimensionale Kettenstrukturen) mit Phenylpiperazin (Phpip = $\mathrm{NC_{10}H_{13}(NH)}$) unter Verkleinerung der Struktureinheiten über Dimere bis hin zu Monomeren der Formeln $[\mathrm{Sm^{III}(Cbz)_3(Phpip)_2}]$ und $[\mathrm{Yb^{II}(Cbz)_2(Phpip)_3}]$ über. Der Effekt von Phpip als chemische Schere führt vor Augen, daß die solvensfreie Synthese im Umkehrschluß zu andersartigen und homoleptischen SE-N-Verbindungen führt. Es kann somit gezeigt werden, daß die Wahl des verwendeten Reaktions-Typs und der Synthese-Bedingungen die Koordinationen der Selten-Erd-Zentren stark beeinflußt, wenn nicht sogar vorbestimmt.

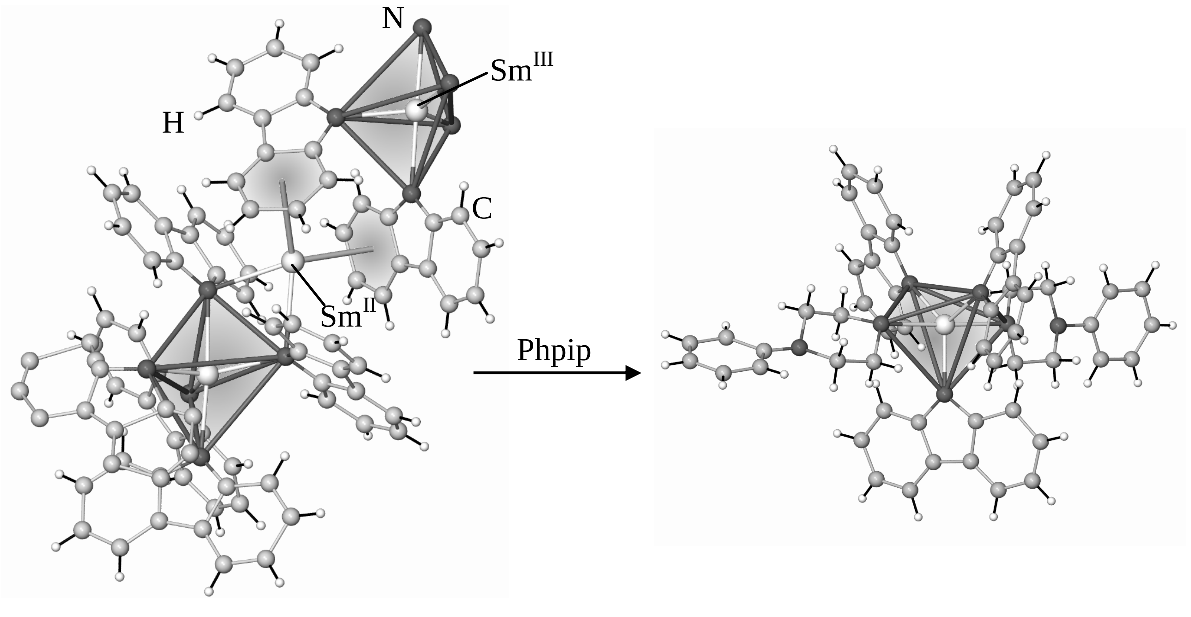

Abb.1: Die 1-dimensionale Kettenstruktur $^1_\infty[\mathrm{Sm(Cbz)_5(H\text{-}Cbz)}]$ über die Umsetzung mit Phpip zum Monomer $[\mathrm{Sm^{III}(Cbz)_3(Phpip)_2}]$.

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Mono Bis(diphosphanyl)amide Complexes of Rare Earth Metals

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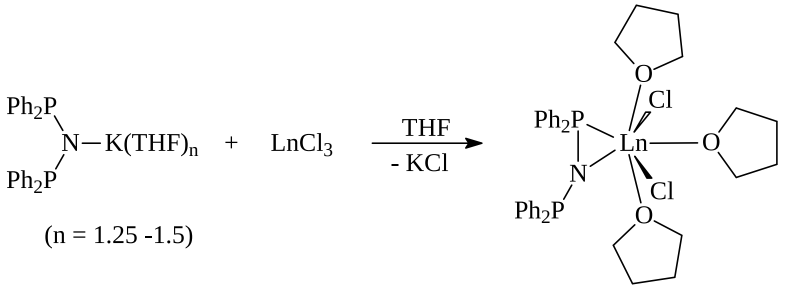
The recently reported potassium salt $[K(THF)_n][N(PPh_2)_2]$ (n = 1.25 - 1.5) (**1**),[1] which can be obtained from $(Ph_2P)_2NH$ and KH in THF, was treated with anhydrous yttrium or lanthanide trichlorides in a 1 : 1.1 molar ratio in THF. This reaction led after crystallization from THF/*n*-pentane (1:2) to the mono substituted bis(diphosphanyl)amide complexes $[\{(Ph_2P)_2N\}LnCl_2(THF)_3]$ (Ln = Y (**2a**), Sm (**2b**), Er (**2c**), Yb (**2d**)) (figure 1).[2]



1

Ln = Y (**2a**), Sm (**2b**), Er (**2c**), Yb (**2d**)

Furthermore the syntheses and characterizations of derivatives as the cyclooctatetraene complexes $[\{(Ph_2P)_2N\}Ln(C_8H_8)(THF)_2]$ (Ln = La (**3a**), Sm (**3b**)), as well as the metallocenes $[(C_5Me_5)_2Sm(m\text{-}Cl)_2K(THF)]_8$ (**4**) and $[\{(Ph_2P)_2N\}Ln(C_5Me_5)_2]$ (**5**) are reported. All new complexes have been characterized by standard analytical/spectroscopic techniques and the solid-state structures were established by single crystal X-ray diffraction.[1-3]

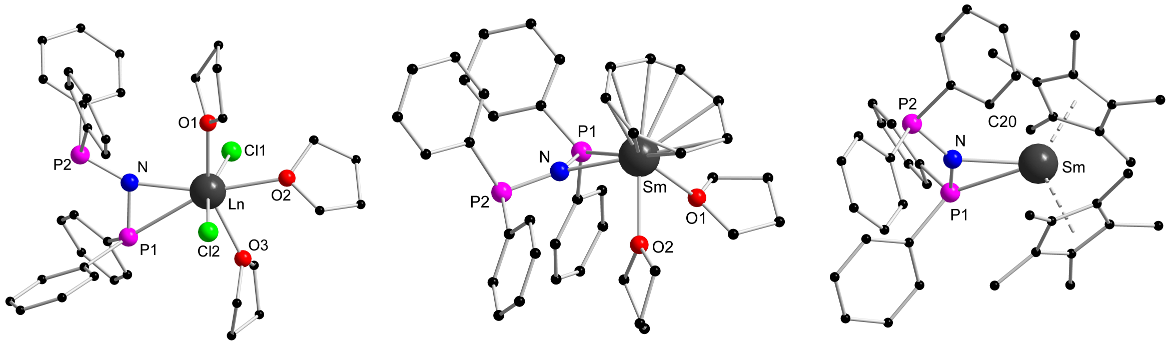


Figure 1-3: Molecular structures of **2d** (left), **3b** (middle), and **5** in the solid state. Hydrogen atoms were omitted for clarity.

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Novel Methods for Basic Reagents in Organometallic Chemistry

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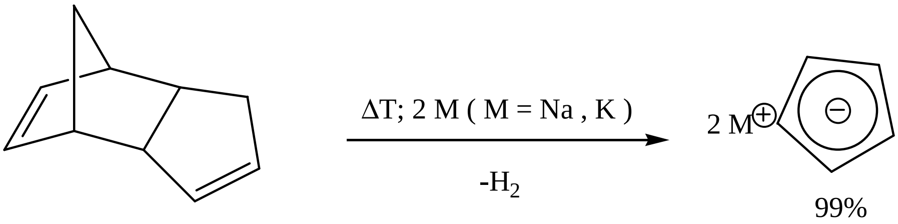
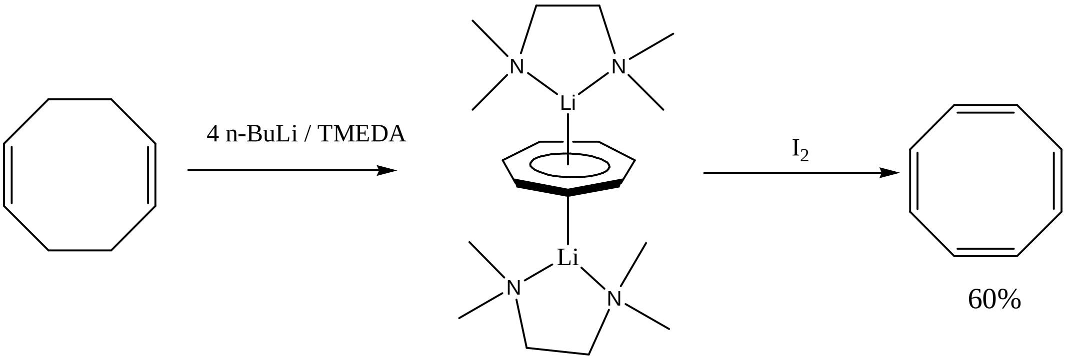
Improved methods for synthesis of alkali metal cyclopentadienide and cyclooctatetraene are reported. Sodium and potassium cyclopentadienide were obtained in one pot synthesis directly by reaction of alkali metals with neat dicyclopentadiene at elevated temperature. The product precipitated as white powders and isolated by filtration. The excess of dicyclopentadiene can be recycled. The new reaction procedure provides a much more convenient access to the products. No dry solvents like THF or decahydronapthalene are needed and no colored impurities are observed.



Another important reagent for organometallic chemistry, cyclooctatetraene (COT) is getting more and more expensive since the production of COT by Reepe synthesis was cancelled by industry. Acetylene under high pressure can be dangerous and expensive equipments are needed to perform the Reepe synthesis in laboratory scale. Therefore a safe and convenient one pot synthesis of COT was developed combining some literature procedure.



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Towards Lanthanide Alkylidene Complexes. Synthesis, Reactivity and Structure of $Lu(CH_2SiMe_3)_3$ etheral adducts

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During our studies on creation of stable lanthanide alkylidene species, syntheses of THF, DME und Diglyme adducts of $Lu(CH_2TMS)_3$ have been succeeded. Termal degradation of THF adduct had believed to resulted in polymeric Lu-alkylidene complex of unkown structure as a product of α-elimination of Me_4Si. Re-investigation of this reaction showed that the most possible pathway of decomposition is, however, γ-elimination. Coordinatively more saturated DME and diglyme adducts are much more stable and don't show similar behavior. Further reactions $Lu(R)_2R'$ THF adducts ($R = C_5H_3(TMS)_3$, R'=Me; $R = R' = CH_2TMS$; $R=R'= N(i\text{-}Pr)_2$) with donor-functionalized phosphor-ylides resulted in formation of different products. Crystal structures of the compounds obtained and reactivity patterns will be discussed.

Acknowledgements: K.R. thanks DFG Graduate College Programme 352 for post-doctoral support.

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