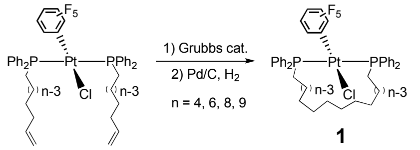
Description of Research Accomplishments

My research interests are in the area of Organic and Organometallic Chemistry. Carbon-containing (organic) molecular fragments that are bonded to metal atoms often have unique geometries and reactivities on account of the metal's electronic properties. Organometallic compounds are important in catalysis, medicine, and the construction of molecular scale devices (nanoscience).

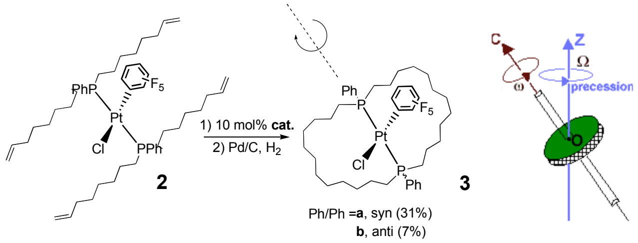
Olefin- and Alkyne-Metathesis in the Coordination Spheres of Transition Metal Complexes

Ring closing metathesis is a powerful tool for the synthesis of small or large ring systems. The application of the ring closing metathesis reaction (applying e.g. Grubb's olefin metathesis catalyst or Schrock's alkyne metathesis catalyst) in the coordination sphere of transition metal complexes provides a novel general route to macrocyclic metal complexes.[1] These metal complexes are interesting classes of compounds that might serve as starting point for molecular scale devices (Scheme 1).

Macrocycles by Ring Closing Metathesis

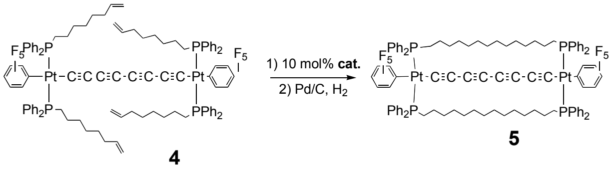


Dimacrocyclic Compounds by Ring Closing Metathesis



Dimacrocyclization: potential precursor to **molecular gyroscopes**

Dimacrocycles by Ring Closing Metathesis: Synthesis of a sp-carbonchain complex protected by a sp^3 carbon chain.



Protected carbon charbonchain complex: Potential precursor to isolated molecular wires

Scheme 1. Ring Closing Metathesis in the Coordination Spheres of Transition Metals: Synthetic Approach to Molecular Machines and Gyroscopes.

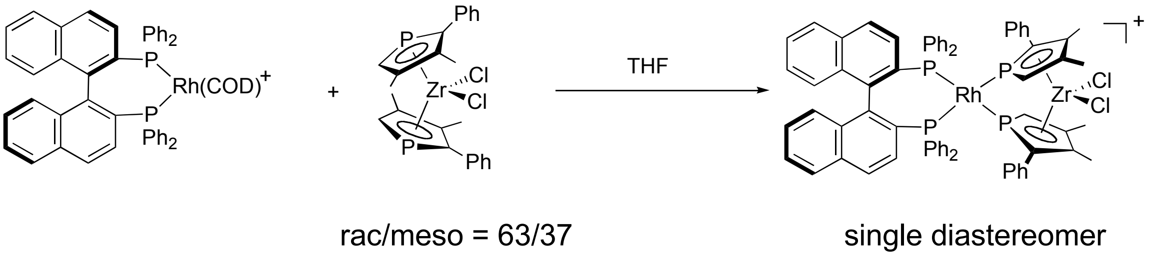
Macrocyclization of appropriate precursor complexes applying the Grubb's metathesis catalyst lead (after hydrogenation of the formed double bond) to saturated macrocyclic metal complexes **1** of different ring size.[2] Metathesis of the precursor complex **2** lead to two isomers of a dimacrocyclic metal complex **3**.[3] These macrocyclization reactions potentially lead to the synthesis of molecular gyroscopes. In the meantime, the methodology described above was successfully applied in trimacrocyclization reactions yielding gyroscope-like compounds.[4]

In the bimetallic platinum complex **4** both platinum centers are connected by a sp-carbon chain $(C{\equiv}C)_4$ ("carbon-chain complex"). Application of a ring closing metathesis / hydrogenation sequence lead to the carbon chain complex **5**. In this complex, the sp-carbonchain is effectively protected by the surrounding sp^3-chain. Compounds like **5** are interesting model compounds for protected molecular wires.[5]

Alkyne metathesis applying Schrocks alkyne metathesis catalyst was successfully applied in macrocyclizations as well.[6]

Diastereoselective Assembly of Phosphametallocenes

Phosphametallocenes are an interesting class of compounds, which have similar properties than metallocenes. In phosphametallocenes, one carbon of the coordinated cyclopentadienyl ligand is replaced by phosphorus, forming a phospholylligand. Due to the phosphorus in the ring system, unsymetrically substituted phospholylligands form two diastereomers (rac and meso).

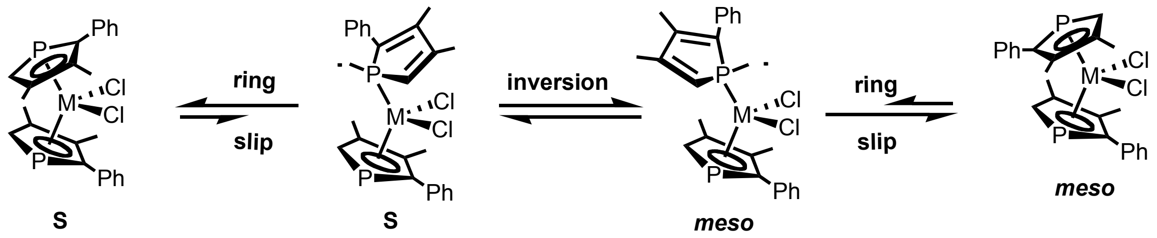


6 **7** **8**

Scheme 2. Bimetallic ansa assembly of chiral phosphametallocenes.

The lone pair of the phosphorus in the coordinated phospholyl-ligand is capable of coordination to a transition metal such as Rhodium (Scheme 2). It turned out that combination of a rac/meso mixture of a phosphazirconocene **7** with a diasteropure Rhodium complex **6** leads to a single diastereomer of a bimetallic Rh-Zr complex **8**. A rac/meso conversion occurs on Zr, either before or after coordination, giving diasteroselectivity.

The rac meso isomerization of chiral phosphametallocenes most likely follows a ring-slip/inversion/ring-slip mechanism (Scheme 3). The phosphoyl ligand of phosphametallocene (S)-**9** undergoes a ring slip from η^5 coordination to η^1 coordination followed by an inversion of the ligand. Ring slip back to a η^5-coordinated phosphyl-ligand affords the meso isomer **10**.[7]



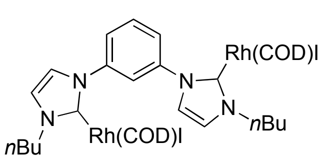
9 **10**

Scheme 3. rac-meso isomerization of phosphametallocenes via a ring-slip /inversion/ring-slip mechanism.

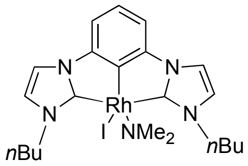
This slip/inversion/slip mechanism takes place either before or after the bimetallic assembly of **6** and **7** to **8**.[8] Diastereopure complexes such as **8** are potential catalysts for polymerization reactions.

Novel Carbene Complexes and their Application as Catalysts in Organic Synthesis

Carbenes are a relatively new class of compounds, which contain divalent carbon atoms and a lone pair. Carbenes can serve as ligands in transition metal complexes and influence their electronic properties. Rh carbene complexes **11** and **12** (Scheme 4) were synthesized by a Metallation-Transmetallation sequence.[9]

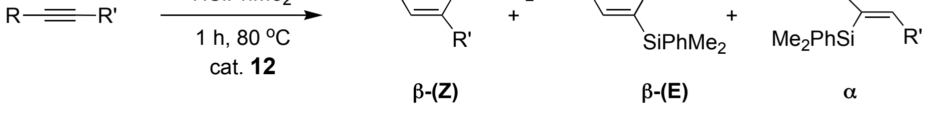


11



12

The Hydrosilylation Reaction



R= Ph, R' = H 95% β-(Z)
R = n-Pr, R' = H 89% β-(Z)
R = R' = Ph 89% β-(E)
R = $CH_2(OH)(CH_2)_3$, R' = H 77% β-(Z)

Scheme 4. Carbene complexes as hydrosilylation catalysts.

Hydrosilylation (addition of silanes to multiple C-C bonds) constitutes an interesting way to silanes. Silanes are important building blocks in organic synthesis. However, typically the addition of silanes to triple bonds provides a mixture of (E), (Z) and α isomers. The novel carbene complexes **11** and **12** are capable of catalyzing hydrosilylation of alkynes (Scheme 4).[10] After 1 h at 80 °C, typically the (Z)-isomer was obtained for terminal alkynes, and the (E)-isomer for internal ones. The catalysts are compatible with alcohols.

Complexes **11** and **12** were successfully applied as hydroamination catalysts as well.[11]

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