# 論文の内容の要旨

論文題目　Studies on Electronically Unsymmetric Bidentate Ligands Based on Boron and/or Phosphorus Moieties
（ホウ素とリンに着目した電子的非対称2座配位子に関する研究）

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## Chapter 1. Introduction

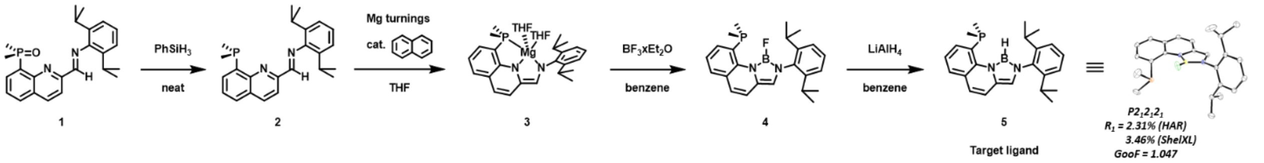
Due to their unique properties, bidentate ligands take up a pivot role in the development of the fields of organometallic chemistry and catalysis. A special subclass of these types of ligands contains two different kinds of donor motives allows the stereoelectronic control over the stability of different isomers of organometallic species. This bias can be exploited to e.g. suppress unwanted side reactions as well as promote advantageous reaction channels progress in their development plays a principal role in organometallic chemistry.

Boryl ligands have shown to provide a dominating σ-donating ability which is e.g. manifested in their strong trans influencing properties.[1-2] While boryl ligands are historically known for a while,[3-4] their application as donor functions in bidentate ligands has only recently drawn attention and still only a very limited number of closely related bidentate ligands have been reported so far.[5-9] To further advance their field, the first subject of this thesis will be the development of a novel rigid bidentate boryl/phosphine ligand, its complex chemistry and application in catalysis.

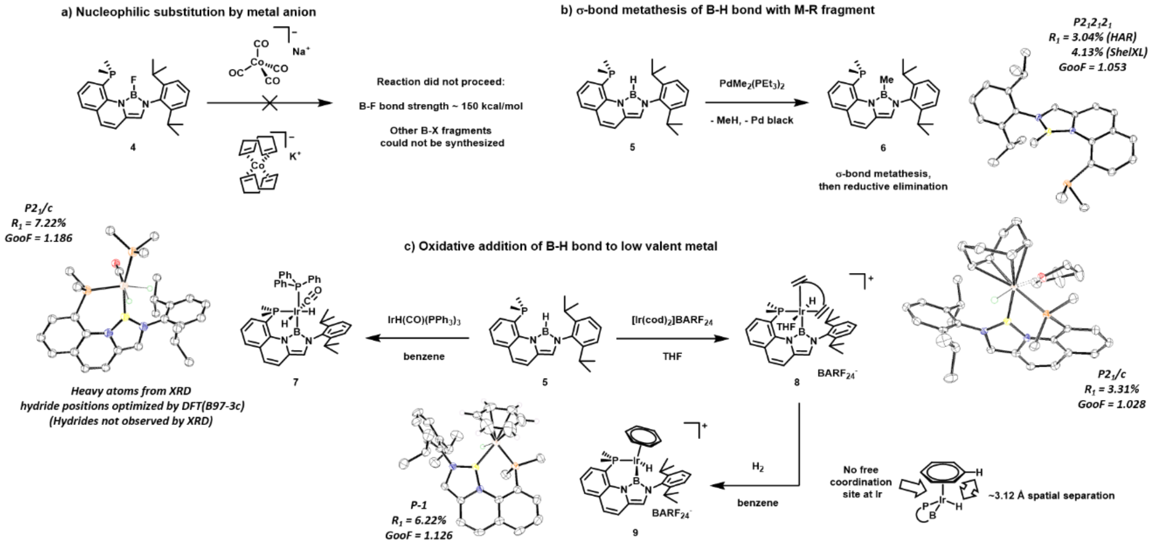
More recently imidazolin-2-ylidenamino substituted phosphines were identified as extremely electron donating ligands.[10-11] Besides their donating ability their special sterical properties are of great interest in the field of late transition metal catalysed olefin (co)polymerization.[12] The second part of this thesis will start with the synthesis of new N-heterocyclic guanidyl substituted bisphosphine monoxide (BPMO) ligands.[13] A focus will be put on racemic, P-stereogenic donors as they are of interest for the stereoselective (co)polymerization of propylene.[14-15] Besides guanidyl phosphines, phosphinites will be explored due to their similar synthesis and related electronic and geometrical structure. Based on the conclusions drawn from their successful application in Pd catalysed (co)polymerization of ethylene and propylene, further modifications of the general ligand design are elucidated.

## Chapter 2. Development of a novel rigid bidentate Boryl/Phosphine ligand

In this work a 13-step synthetic protocol was established that allowed the synthesis of a novel boryl/phosphine ligand on a 1 g scale (Scheme 1). One challenge in this work was the procedural safe introduction of the supporting dimethylphosphine donor into the ligand frame in way that would be synthetically applicable on larger reaction scales. As typical synthetic precursors such as dimethylphosphine and dimethylphosphine halides are difficult to prepare and to handle, they posed as a major safety issue when applied on scale.[16] The problem was circumvented by employing the benign dimethylphosphine oxide in a Ni catalysed C-P cross coupling reaction which safely allowed the introduction of the phosphine motive into the ligand frame to prepare **1** in an 18.5% isolated yield over 9 steps.[17-18] It was discovered that the phosphine oxide could be selectively reduced while leaving the imine moiety untouched by heating **1** in neat $PhSiH_3$ to give **2** after recrystallization in an excellent 94% isolated yield. The realization for $PhSiH_3$ to be able to selectively reduce a phosphine oxide over an imine is an important discovery for phosphorus chemistry and ligand synthesis as it could allow the general preparation of imine-containing ligand motives starting from synthetically and safety-wise highly advantageous phosphine oxide precursors. One pathway for the introduction of the boron-donor atom requires a formally diamide form of the ligand framework. When **2** was reacted with Mg metal, only one single electron reduction event to form a monoanionic radical species was observed in THF in accordance with a previous related report.[19] Nevertheless it was fortuitously discovered that addition of a catalytic amount of naphthalene to Mg metal allows to further reduce this radical intermediate to form a well-defined dianionic Mg complex **3** whose structure could also be determined by scXRD.[20] The use of naphthalene as a catalyst for a formally two-electron reduction with Mg is new and furthermore opens up the question of the role of naphthalene residues present in commonly employed Rieke metals for their reactivity.[21] For the introduction of the boron moiety into the ligand frame the specific choice of electrophilic boron reagent is important. $BF_3xEt_2O$ is known to only form reversibly weak adducts with phosphines and was therefore employed as an electrophile in the reaction with **3**.[22] Optimization of the reaction and workup conditions allowed the isolation of the pure crystalline compound **4** in 41% isolated yield on a 1.47 g scale. The B-F fragment in **4** could afterwards be cleanly converted into the desired B-H fragment by slurrying **4** with an excess of $LiAlH_4$ in benzene to yield the target ligand **5** in 79% isolated yield as colourless blocks on a 1 g scale. With ligand precursors **4** and **5** in hand, three conceptionally different routes were investigated in the preparation of metal complexes (Scheme 2). In the first attempt, the reaction of boryl fluoride **4** with nucleophilic cobaltates $Na[Co(CO)_4]$ and $K[Co(cod)_2]$ was explored (Scheme 2a). Nevertheless, no fluoride displacement or oxidative addition of the B-F bond could be observed, likely due to the inherent strong B-F bond strength of ~150 kcal/mol. The second strategy for complex synthesis employed the σ-bond metathetical exchange of the B-H bond of the target ligand with e.g. metal alkyl and aryl species. In the reaction of hydroborane **5** with $PdMe_2(PEt_3)_2$, the σ-bond metathetical activation of the B-H bond indeed took place as indicated by the formation of $CH_4$ (Scheme 2b). Still, as a consecutive reductive elimination event with the second methylido substituent took place to form methylborane **6** and metallic Pd, no borylmetal complex could be isolated. Compound **6** was identified by multinuclear NMR as well as scXRD analyses and gave insight into interpretation of analogous unsuccessful attempts of complex isolation that were tried out with structurally related Ni and Pd precursors. As the third strategy, the oxidative addition of the B-H bond of **5** was tried out on a variety of low valent metal precursors (Scheme 2c). The reaction of **5** with $[IrH(CO)(PPh_3)_3]$ in benzene and $[Ir(cod)_2]BARF_{24}$ in THF proceeded cleanly to give complexes **7** and **8** in 79% and 84% yield respectively. The octahedral coordination environment was confirmed for both **7** and **8** by scXRD. It was further noticed that by hydrogenative displacement of the 1,5-COD ligand of **8** in benzene, a rare, formally Ir(III) $\eta^6$- benzene complex **9** was formed. The complex could also be obtained preparative in 84% isolated yield and its structure was confirmed by scXRD. In reactivity studies of **8** and **9** with $B_2pin_2$, it was observed that the hydride benzene complex **9** was formed. The complex could also be obtained preparative in 84% isolated yield and its structure was confirmed by scXRD. In reactivity studies of **8** and **9** with $B_2pin_2$, it was observed that the hydride ligand of complexes was replaced by a -Bpin fragment by σ-bond metathesis. Nevertheless, both types of complexes did not show apparent C-H activation reactivity with e.g. $C_6D_6$ as seen by the lack of observed H/D exchange under a $H_2$ atmosphere or absence of C-D borylation products with e.g. HBpin or $B_2pin_2$. Based on the isolation of the arene complex **8**, it is implied that C-H activation in these η$^6$-arene complexes could be hindered by the spatial separation of the reactive Ir fragment with the arene C-H bonds as well as the lack of free coordination sites on the Ir center. A future directive for reactivity studies is therefore the exploration of η$^6$-arene coordination suppression by introduction of other supporting ligands as well as modifications on the arene ligand by e.g. nucleophilic aromatic substitution through an outer-sphere mechanism.



**Scheme 1.** Synthetic route employed for the preparation of the novel rigid bidentate Boryl/Phosphine ligand. $^a$**1:** 18.5% yield over 9 steps; **2**: 94% yield; **3**: 89% yield; **4**: 41% yield; 79% yield (isolated yields given in all cases).



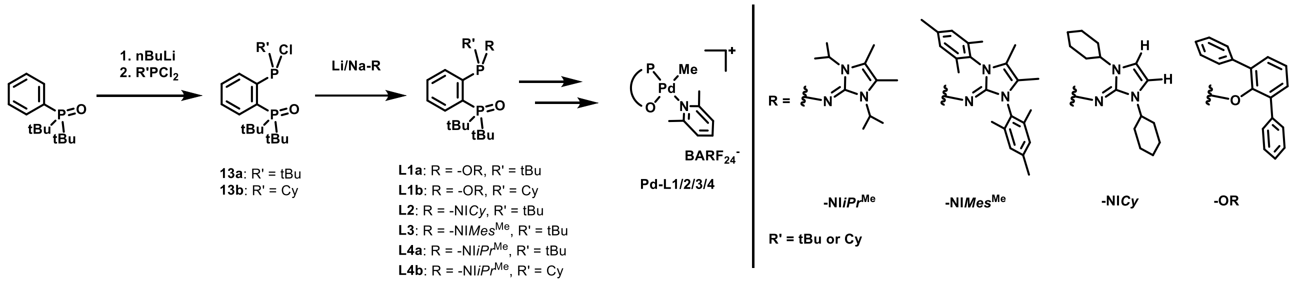
**Scheme 2.** Synthetic routes explored for the preparation of metal complexes of the novel rigid bidentate Boryl/Phosphine ligand.

## Chapter 3. Development of P-stereogenic bisphosphine monoxide ligands for Group 10 catalysed olefin (co)polymerization

We became interested in imidazolin-2-ylidenamino phosphines as they appeared to be optimal candidates to design ligands for late transition metal catalysed olefin polymerization due to their stron electron donating ability (Scheme 3a). At the start of the project, three different kinds of lithium imidazolin-2-ylidenamido reagents were prepared via their free NHCs.[23-25] For the most promising candidate derived from the NHC **11a** a safe preparative route via the imidazolium salt **10a** was applied which could be prepared on a 42.4 g scale in 38% yield. Subsequent reaction of **10a** with NaH and catalytic KOtBu allowed the isolation of 11a in 95% isolated yield on a 27 g scale (Scheme 3b and c).[26] In analogy, **10b** and **11b** were isolated on a 66.1 and 14 g scale in 66% and 88% yield respectively. In parallel, two P- stereogenic chlorophosphine BPMO precursors **13a/b** were prepared via selective *ortho*-lithiation of **12** by nBuLi and addition of tBu/$CyPCl_2$. The products could be isolated as microcrystalline solids in 78% and 82% yield respectively. Via a combinatorial approach, a small library of P-stereogenic BPMO ligands **L1-4** including two bulky phosphinite derivatives and their Pd based polymerization catalysts were prepared.

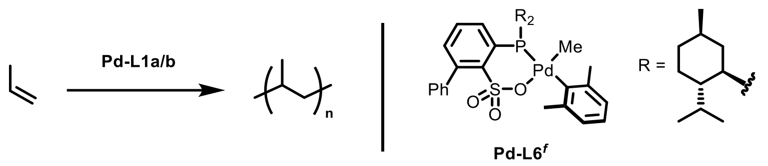
**Scheme 3.** NHC syntheses: a) Strongest donating imidazoline-2-ylidenamino phosphine reported in the literature;[11] b) Literature synthesis of 11a and safety concerns associated with it; c) Revised synthetic strategy for the synthesis of 10/11 a and b

Pd complexes of the phosphinite ligands **L1a/b** exhibited high activities in both ethylene homo and copolymerization with allyl acetate, while the imidazolin-2-ylidenamino derivatives **L2/3/4a/4b** showed no activity. Moreover, **Pd-L1b** allowed the highly desired stereoregular polymerization of propylene with an *mm* = 0.65, which is the highest tacticity control reported so far for a Pd polymerization catalyst (Table 1).[15]



**Scheme 4.** Synthetic Scheme for P-stereogenic BPMO-Type Palladium Catalysts. Isolated yields: 13a: 78%, 13b: 82%, L1a: 95%, L1b: 71%, L2: 88%, L3: 98%, L4a: 38%, L4b: 35%, Pd-L1a: 48%, Pd-L1b: 74%, Pd-L2: 62%, Pd-L3: 83%, Pd-L4a: 83%, Pd-L4b: 78%.

**Table 1.** Propylene polymerization by Palladium Catalysts



| Entry | Catalyst (µmol) | Temp (°C) | Yield$^b$ (mg) | Activity (kg/mol$^{-1}$ h$^{-1}$) | M$_w$$^c$ (10$^3$) | M$_w$/M$_n$$^c$ | [*mm*]$^d$ | [*mr*]$^d$ | [*rr*]$^d$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Pd-L1b (10) | 50 | 65.3 | 0.54 | 2.26 (3.19) | 1.68 | 0.64 | 0.25 | 0.10 |
| 2 | Pd-L1b (10) | 80 | 80.6 | 0.67 | 1.42 (1.95) | 1.75 | 0.56 | 0.29 | 0.15 |
| 3$^f$ | Pd-L6 (20) | 50 | 1410 | 5.9 | 39.9 | 1.9 | 0.59 | 0.29 | 0.12 |

[a] A mixture of catalyst **Pd-L1b** and propylene (6.00 g) in toluene (15 mL) was stirred in a 50-mL autoclave for 12 h at a given temperature [b] Yields of isolated products after evaporation of the solvent [c] Molecular weights determined by size-exclusion chromatography analysis using polystyrene standards and corrected by universal calibration (uncorrected values in parentheses) [d] Triad ratios determined by quantitative $^{13}$C NMR analysis [e] **Pd-L1a/2/3/4a/4b** did not show activity for propylene polymerization [f] Values for **Pd-L6** taken from reference [15].

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