

# 博士論文（要約）

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

### 1-1. Background and motivation

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, for example, suppress unwanted side reactions that can occur during catalysis as well as promote advantageous reaction channels thus leading to e.g. higher catalytic activity or selectivities.<sup>1-2</sup> This means overall that, by careful electronic design of bidentate ligands, reactions catalysed by their respective organometallic complexes can be greatly steered in a favourable manner. Therefore, the further development of these specialized different kinds of unsymmetric bidentate ligands is of great interest.

Boryl ligands have shown to provide a dominating  $\sigma$ -donating ability which is e.g. manifested in their strong *trans*-influencing properties.<sup>3-4</sup> While boryl ligands are historically known for a while,<sup>5-6</sup> 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.<sup>7-11</sup> 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 even surpassing the donating ability of carbene ligands.<sup>12-13</sup> The imidazolin-2-ylidenamino residues are strong  $\pi$ -donors owing to the stabilization of a charge separated Lewis structure stabilized by aromatization of the imidazolium ring and their strong electron releasing ability can efficiently relayed to connected phosphorus donors. Besides their donating ability their special sterical properties are of great interest in the field of late transition metal catalysed olefin (co)polymerization.<sup>14</sup> Furthermore as they are synthetically derived from N-heterocyclic carbenes (NHCs), their preparation in principle greatly benefits from their established parent field.<sup>15-17</sup> The second part of this thesis will start with the synthesis of new N-heterocyclic guanidyl substituted bisphosphine monoxide (BPMO) ligands.<sup>18</sup> A focus will be put on racemic, P-stereogenic donors as they are of interest for the stereoselective (co)polymerization of propylene.<sup>19-20</sup> 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.

### 1-2. General underlying design principles for the ligands used in this work based on the background of late transition metal catalysed olefin (co)polymerizations

Our group recently reported the application of a rigid carbene/phenolate ligand (abbreviated as IzQO) in the Ni and Pd catalysed (co)polymerization of olefins such as ethylene and propylene with polar olefinic substrates.<sup>21-22</sup> Some key features of the specific ligand design in the context of square-planar  $d^8$  Ni and Pd complexes which are responsible for its success are briefly described in the following. One of the key roles of for the electronically unsymmetric choice of donors lies in the acceleration of the migratory insertion steps of the propagating polymer chain into the coordinated olefins. Strong *trans*-influencing donors such as N-heterocyclic carbenes (NHCs) or phosphines destabilize the propagating alkyl species in this step to allow an overall lower barrier of insertion.<sup>23</sup> Additionally, unlike early transition metal catalysts which excel in the polymerization of non-polar olefinic substrates, late transition metal catalysts also tolerate unprotected polar substrates.<sup>24</sup> While they in principle tolerate polar substrates, they still suffer from catalyst poisoning due to strong unproductive coordination of the polar substrates to the metal centers. Here another strong point of strong  $\sigma$ -donating ligands comes to play: Their pronounced *trans*-influence allows faster ligand exchange reactions and thus a substrate poisoned catalyst can potentially re-enter a productive polymerization cycle faster. A special aspect for ligands with a NHC functionality in polymerization reactions is the potential reductive elimination of the propagating alkyl chain and the carbene donor, which poses as their main irreversible catalyst decomposition pathway. The main prerequisite for this reaction is constructive overlap of the empty carbene  $\pi^*$ -orbital with filled  $\sigma$ -orbital of the propagating chain.<sup>25</sup>

As this constructive overlap effectively requires the NHC to be out of coplanarity in the square planar complex, it can be efficiently suppressed by enforcing a coplanar coordination environment as provided by the rigid IzQO system.

Another important aspect in the design of a ligand for a polymerization catalyst is the steric bulk it can provide around a metal center. The coordination of e.g. an alkene ligand to a  $\beta$ -agostic resting species is suspected to accelerate an otherwise suppressed  $\beta$ -hydrogen elimination pathway. As the possibility of a ligand to approach the metal in an axial position is required for this to occur, steric shielding of axial positions by the ligand is to be expected to suppress this undesired pathway.<sup>23, 26</sup> In case of prochiral olefinic substrates, the respective orientation of the monomers to each other in the chain significantly impacts their mechanical properties. Highly stereoregular polymers such as isotactic polypropylene can be crystalline and solid, and therefore show an inherent higher hardness in comparison to stereoirregular polymers who are usually not solid anymore. Therefore, to be in principle able to employ such materials as solids for application purposes it is necessary to control the stereoregularity during the polymerization process. Control can here be achieved by energetically biasing different isomers of the olefin adducts of the polymerization catalysts prior to the chain propagating migratory insertion event. Two types of stereocontrol can here be achieved by firstly tuning the head-to-tail selectivity by biasing olefin coordination modes (Figure 1a) before successive insertion events. Secondly enantiomorphic site control via a bias of the relative orientation of prochiral olefins before chain propagation (Figure 1b) translates into the stereoregularity of the polymer chain.

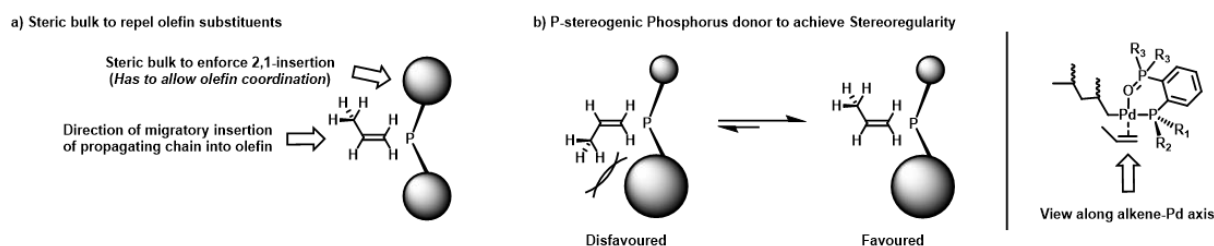
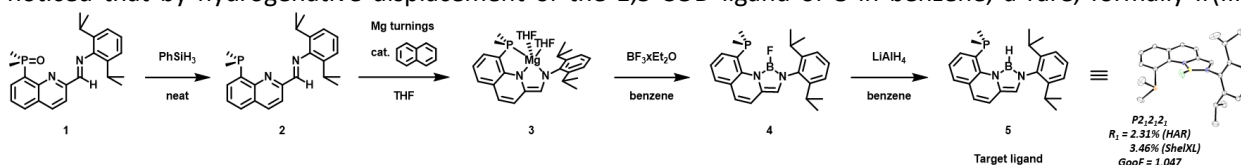


Figure 1. Influence of steric bulk on the olefin coordination mode prior to a migratory insertion event for BPMD-Type Palladium Catalysts exemplary for propylene

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

Based on our previous report of the rigid NHC/phenolate IzQO ligand, we were interested in developing an analogous more strongly donating boryl version of the ligand. The rigidity of the ligand frame was again deemed to be important to also suppress a potential reductive elimination of the donor moiety with appropriate species bound to the same metal. Moreover, we choose to replace the anionic phenol donor of IzQO by a small phosphine to keep an overall monoanionic charge of the ligand as well as to ensure a rigid coordination of the ligand to a metal center. It was also deemed necessary to incorporate a more strongly donating donor than the phenolate as we wanted to make sure that beneficial cis/trans isomerization reactions of a square planar complex were not suppressed by a too large mismatch of the dominating boryl donor with its second weaker one. An important point here is also the inherent functional group incompatibility of free hydroxy groups with the boryl moiety, which due to the high oxophilicity of boron was deemed synthetically difficult to solve. The boryl functionality is furthermore protected from nucleophiles by a bulky residue, while a small dimethylphosphine was chosen to ensure enough space around the activated position *trans* to the boryl functionality in a metal complex. In this work a 13-step synthetic protocol was established that allowed the synthesis of the proposed pure 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.<sup>27</sup> 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.<sup>28-29</sup> It was discovered that the phosphine oxide could be selectively reduced while leaving the imine moiety untouched by heating **1** in neat  $\text{PhSiH}_3$  to give **2** after recrystallization in an excellent 94% isolated yield.

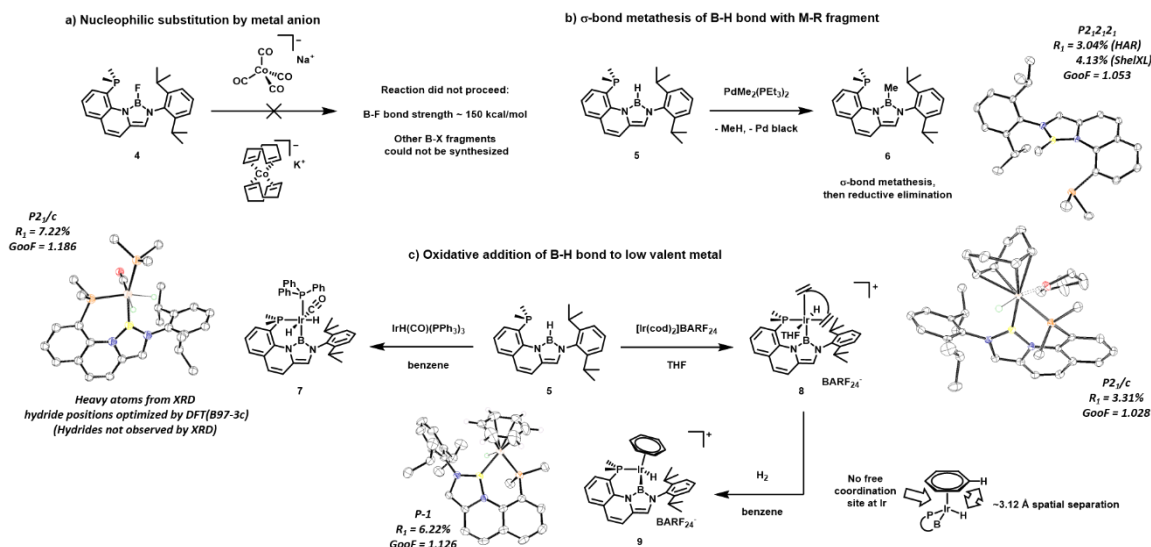
The realization for  $\text{PhSiH}_3$  to be able to selectively reduce a phosphine oxide over an imine is an important discovery for phosphorus chemistry and ligand synthesis as it could allow the general preparation of imine-containing ligand motives starting from synthetically and safety-wise highly advantageous phosphine oxide precursors. One pathway for the introduction of the boron-donor atom requires a formally diamide form of the ligand framework. Alkali metals typically employed for this task are known to reductively cleave aryl phosphorus bonds to form the respective aryl metal and phosphide species.<sup>30</sup> On the other hand for Mg this reductive cleavage of aryl-phosphorus bonds is not known. 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.<sup>31</sup> Nevertheless it was fortuitously discovered by experiments employing Rieke-Mg that the 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.<sup>32</sup> 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.<sup>33</sup> For the introduction of the boron moiety into the ligand frame the specific choice of electrophilic boron reagent is important as boron Lewis acids form usually strong adducts with phosphines. Common methods for deprotection of phosphines with e.g. amines were expected to destroy this specific ligand framework.<sup>34</sup>  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  is known to only form reversibly weak adducts with phosphines and was therefore employed as an electrophile in the reaction with **3**.<sup>35</sup> 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  $\text{LiAlH}_4$  in benzene to yield the target ligand **5** in 79% isolated yield as colourless blocks on a 1 g scale. Both **4** and **5** crystallized in enantiopure form due to a helical chirality in the ligand backbone that was induced by steric repulsion as revealed by scXRD analysis. 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  $\text{Na}[\text{Co}(\text{CO})_4]$  and  $\text{K}[\text{Co}(\text{cod})_2]$  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  $\sim 150$  kcal/mol. The second strategy for complex synthesis employed the  $\sigma$ -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  $\text{PdMe}_2(\text{PET}_3)_2$ , the  $\sigma$ -bond metathetical activation of the B-H bond indeed took place as indicated by the formation of  $\text{CH}_4$  (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  $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$  in benzene and  $[\text{Ir}(\text{cod})_2]\text{BARF}_{24}$  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)  $\eta^6$ -



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

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  $\text{B}_2\text{pin}_2$ , it was observed that the hydride ligand of complexes was replaced by a -Bpin fragment by  $\sigma$ -bond metathesis. Nevertheless, both types of complexes did not show apparent C-H activation reactivity with e.g.  $\text{C}_6\text{D}_6$  as seen by the lack of observed H/D exchange under a  $\text{H}_2$  atmosphere or absence of C-D borylation products with e.g. HBpin or  $\text{B}_2\text{pin}_2$ . Based on the isolation of the arene complex **8**, it is implied that C-H activation in these  $\eta^6$ -arene complexes could be hindered

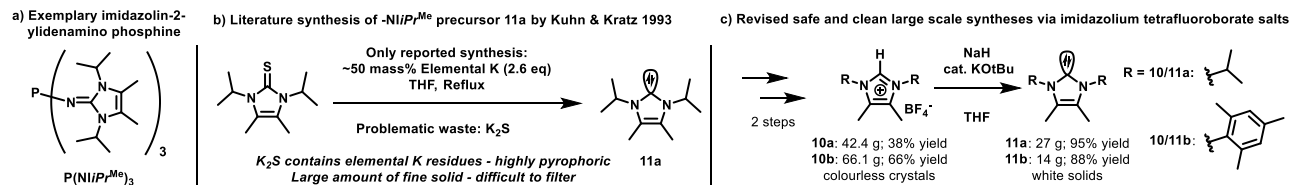
by the spatial separation of the reactive Ir fragment with the arene C-H bonds as well as the lack of free coordination sites on the Ir center. A future directive for reactivity studies is therefore the exploration of  $\eta^6$ -arene coordination suppression by introduction of other supporting ligands as well as modifications on the arene ligand by e.g. nucleophilic aromatic substitution through an outer-sphere mechanism.



Scheme 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

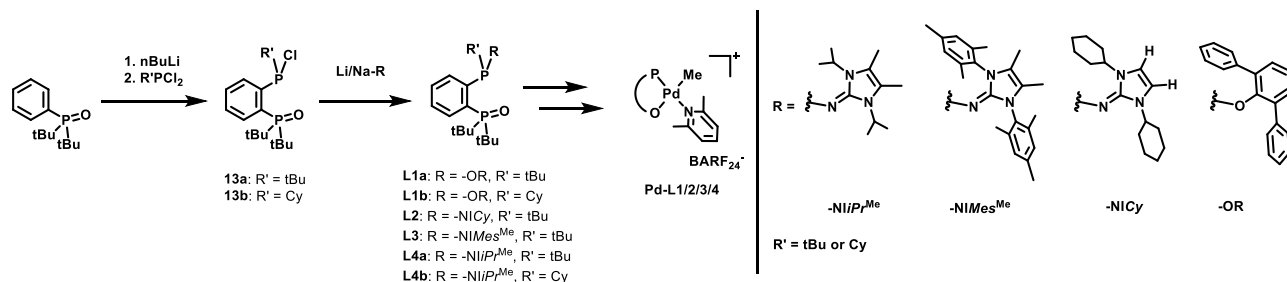
As a classic powerhouse of organometallic chemistry, phosphorus-derived ligands show high versatility as in their widely tuneable  $\sigma$ - and  $\pi$ -donor and -acceptor strength as well as in their high steric flexibility. An intriguing case are imidazolin-2-ylidenamino derived phosphines which show extremely strong  $\sigma$ -donation (Scheme 3a). We became interested in this class of compounds as they appeared to be optimal candidates to design ligands for late transition metal catalysed olefin polymerization. At the start of the project, three different kinds of lithium imidazolin-2-ylidenamido reagents were prepared via their free NHCs.<sup>36-38</sup> For the most promising candidate derived from the NHC **11a** the protocol required the use of large amounts of elemental K which with the nature and amount of the byproduct  $K_2S$  was identified as a major safety risk for reaction upscaling (Scheme 3b).<sup>39</sup> We therefore applied a safer route towards **11a** via the imidazolium salt **10a** which could be prepared on a 42.4 g scale in 38% yield. Subsequent reaction of **10a** with NaH and catalytic KOTu allowed the isolation of **11a** in 95% isolated yield on a 27 g scale (Scheme 3c).<sup>17</sup> In analogy, **10b** and **11b** were isolated on a 66.1 and 14 g scale in 66% and 88% yield respectively. The tetrafluoroborate salts were specifically chosen due to their low hygroscopicity and high crystallinity which allowed purification solely by crystallization in both cases. In parallel, two P-



Scheme 3. NHC syntheses: a) Strongest donating imidazolin-2-ylidenamino phosphine reported in the literature;<sup>13</sup> b) Literature synthesis of **11a** and safety concerns associated with it; c) Revised synthetic strategy for the synthesis of **10/11a** and **b**

stereogenic chlorophosphine BPMO precursors **13a/b** were prepared via selective *ortho*-lithiation of **12** by  $n\text{BuLi}$  and addition of  $t\text{Bu/CyPCl}_2$ . 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. Pd complexes of the weakly donating phosphinite ligands **L1a/b** exhibited high activities in both ethylene homo and copolymerization with allyl acetate (Table 1), 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 2).<sup>20</sup> Based on the discovery of the later catalyst system, currently new iterations of the ligand and complex design are under investigation.



**Scheme 4.** Synthetic Scheme for P-stereoregic BPMP-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.** Ethylene Homo- and Copolymerization by Palladium Catalysts

Entry	Catalyst ( $\mu\text{mol}$ )	Monomer (mL)	Solvent (mL)	Temp ( $^{\circ}\text{C}$ )	Time (h)	Yield <sup>b</sup> (g)	Activity ( $\text{kg}/\text{mol}^{\text{c}} \text{h}^{-1}$ )	$M_n^{\text{c}}$ ( $10^3$ )	$M_w^{\text{c}}$ ( $10^3$ )	Incorp. <sup>d</sup> (%)	Me br. <sup>e</sup> ( $10^3 \text{ C}$ )
1	Pd-L1a (6)	-	15	80	3	0.40	21.9	42.2 (99.4)	3.48	-	1.3
2	Pd-L1a (6)	-	15	100	3	0.22	12.33	22.8 (53.3)	1.92	-	Nd
3	Pd-L1a (6)	-	15	120	3	0.19	10.55	13.9 (32.2)	2.33	-	Nd
4	Pd-L1b (6)	-	15	60	3	0.83	46.1	28.9 (67.6)	3.18	-	Nd
5	Pd-L1b (6)	-	15	80	3	1.89	105.0	35.5 (83.3)	2.01	-	Nd
6	Pd-L1b (6)	-	15	100	1	0.83	138.1	21.7 (50.6)	1.96	-	Nd
7	Pd-L1b (6)	-	15	120	1	0.77	128.7	14.0 (32.5)	2.59	-	Nd
8	Pd-L1b (0.75)	-	15	80	1	0.29	380.1	Nd	Nd	-	Nd
9	Pd-L1b (0.75)	-	15	100	1	0.32	420.4	Nd	Nd	-	Nd
10	Pd-L1b (0.75)	-	15	120	1	0.33	438.8	Nd	Nd	-	Nd
11	Pd-L1a (10)	AAc (3)	12	80	12	0.20	1.7	18.7 (43.5)	1.75	0.92	1.8
12	Pd-L1b (10)	AAc (3)	12	80	12	0.53	4.42	21.3 (49.7)	2.77	0.077	1.14
13	Pd-L1b (10)	AAc (3)	12	100	12	0.29	2.41	10.7 (24.8)	2.87	0.175	1.59
14 <sup>f</sup>	Pd-L5 (0.75)	-	15	100	1	1.17	1600	9.3	3.1	-	2
15 <sup>f</sup>	Pd-L5 (10)	AAc (3)	12	80	8	3.02	38	5.2	4.0	0.6	-

<sup>a</sup> A mixture of catalyst **Pd-L1-3** and ethylene (3.0 MPa) in toluene was stirred in a 50-mL autoclave for a given time and temperature. <sup>b</sup> Isolated yields after precipitating and washing with MeOH. <sup>c</sup> Molecular weights determined by size-exclusion chromatography analysis using polystyrene standards and corrected by universal calibration (uncorrected values in parentheses) <sup>d</sup> Ratio of monomer incorporation and Me branches per 1000 Carbon atoms determined by <sup>13</sup>C NMR analysis. <sup>e</sup> **Pd-L2/3/4a/4b** did not show activity for ethylene homo and copolymerization with AAC <sup>f</sup> Literature values for **Pd-L5** taken from reference <sup>40</sup> <sup>g</sup> Nd: Not determined.

**Table 2.** Propylene polymerization by Palladium Catalysts

Entry	Catalyst ( $\mu\text{mol}$ )	Temp ( $^{\circ}\text{C}$ )	Yield <sup>b</sup> (mg)	Activity ( $\text{kg}/\text{mol}^{\text{c}} \text{h}^{-1}$ )	$M_w^{\text{c}}$ ( $10^3$ )	$M_w/M_n^{\text{c}}$	$[mm]^{\text{d}}$	$[m]^{\text{d}}$	$[rr]^{\text{d}}$
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 <sup>f</sup>	Pd-L6 (20)	50	1410	5.9	39.9	1.9	0.59	0.29	0.12

<sup>a</sup> 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 <sup>b</sup> Yields of isolated products after evaporation of the solvent <sup>c</sup> Molecular weights determined by size-exclusion chromatography analysis using polystyrene standards and corrected by universal calibration (uncorrected values in parentheses) <sup>d</sup> Triad ratios determined by quantitative <sup>13</sup>C NMR analysis <sup>e</sup> **Pd-L1a/2/3/4a/4b** did not show activity for propylene polymerization <sup>f</sup> Values for **Pd-L6** taken from reference <sup>20</sup>.

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