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Expedient Synthetic Identification of a Novel P-stereogenic Ligand Motif for the Palladium-Catalyzed Preparation of Isotactic Polar Polypropylenes

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Abstract: The *iso*-specific statistical copolymerization of unprotected polar monomers with propylene still stands a as grand challenge in the field of polymer chemistry. Current research in the field is hampered as to date only a single natural product derived dimenthylphosphine-motif is known to allow for the preparation of moderately isotactic polypropylene copolymers. To overcome this structural limitation, we developed time-efficient synthetic protocols that minimize the tediousness associated with P-donor ligand development. The strength of these protocols was exemplified by the preparation of twenty-five new P-stereogenic Phosphine/Sulfonate and Bisphosphine Monoxide type palladium catalysts, which could typically be developed in parallel within a standard workday. This work has led to identification of a novel structural lead candidate for the *iso*-specific propylene polymerization. The best performing catalysts utilizing this P-stereogenic donor motif achieved triad isotacticities of up to *mm* = 0.75, the highest value within the reported ones with group 10 metal catalysts, for the homo- and copolymerization of propylene with unprotected polar monomers at an industrially relevant temperature of 50°C.

Introduction

The tacticity of polypropylenes (PPs) greatly determines the properties of one of the world's most applied plastics.[1] While atactic PP lacks in general the hardness and rigidity of the crystalline iso- and syndiotactic forms, isotactic PP (iPP) prevails as industries most desirable form of the latter.[2] The statistical incorporation of functional polar monomers into stereoregular PP-chains could deliver a new generation of highly desirable engineering plastics due to, for example, their improved interfacial properties, wettability and enhanced degradability. Still the Ziegler-Natta[3] or *ansa*-metallocene[4] catalysts currently employed by industry for the preparation of iso- or syndiotactic PP are not generally tolerant to unmasked polar monomers, whose direct copolymerization with propylene presents the most efficient way to prepare these unique specialty plastics.[5] Nickel or palladium polymerization catalysts can overcome their predecessors' limitations and allow direct copolymerization of polar monomers with olefins. Still to date design and development of catalysts that allow the preparation of highly isotactic functionalized polypropylenes (We call this isotactic Polar PP (iPPP) from now on) poses as a grand challenge. So far in the literature only one ligand motif based on a dimenthylphosphine afforded moderately isotactic PPP with *mm*s between 0.55 and 0.61 at an industrially relevant temperature regime of 50°C by both Ni and Pd catalysts (Figure 1, top).[6, 7] Importantly suitable modification of this privileged menthyl scaffold is a considerable synthetic challenge in itself, and therefore the lack of alternative structural motifs is a current major roadblock for further development of the field. In order to overcome this current limitation, we were interested in identifying other classes of superior structural motifs that can be both easily prepared and diversified. While predictive catalyst exploration by computational methods is nowadays widespread, the design of catalysts capable of inducing high isotacticity in propylene polymerization is severely hampered by the large number of close lying, energetically accessible isomeric structures that are responsible for the observed polymer tacticities (Figure 1, middle). Namely, all permutations of (i) conformers of the chelate ring and additional $R^{1/2}$ conformations of the ligand, (ii) four orientations of the

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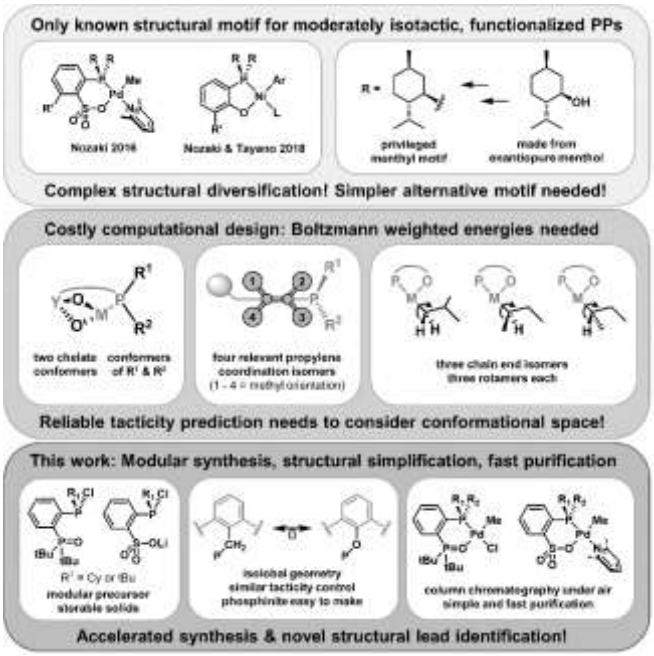

Figure 1. Comparison of design strategies for catalysts allowing the *iso*-selective (co)polymerization of propylene with polar monomers.

propylene methyl-group, and (iii) three model chain-end structures with three rotamer conformations for each, have to be considered. Therefore, it is still an extremely time-intensive task to obtain reliable predictive results by computational methods, even when compared to experimental lab work. As stereoregularity was previously transferred during polymerization from the C-stereogenic menthyl groups to the polymer via enantiomorphic site control,[6] we wondered if P-stereogenic phosphines could serve as a viable alternative. It should be noted that while a chiral structural motif is needed for this task, the catalysts themselves can be racemic since transfer of the propagating chain from one metal center to another is less likely.[8] Nevertheless, to date the development of phosphine ligands often suffers from tedious syntheses and purification steps under inert conditions. We herein present our successful three-component solution to these synthetic problems: we were able to prepare several novel P-stereogenic Phosphine/Sulfonate (P/S) and Bisphosphine Monoxide (BPMO) type[9] ligands and their respective palladium-based polymerization catalysts in parallel within a regular workday (Figure 1, bottom). Using storable modular building blocks bearing P-Cl moieties, we quickly diversified our ligand library by simple substitution of the third substituent on the phosphorus atom; especially phenol derived phosphinites in place of phosphines greatly sped up ligand syntheses. With their palladium complexes separable by column chromatography in air, homo- and copolymerization of propylene with polar monomers were accomplished to give crystalline i(P)PPs with unprecedented *mm*s of up to 0.75.

Results and Discussion

An overview of the two synthetic routes for the preparation of P/S type complexes **1b-m** and BPMO type complexes **2a-n** is outlined in Scheme 1. For detailed information on the syntheses and crystallographic characterization of twenty-three compounds, refer to the SI.

Preparation of P-stereogenic Phosphine/Sulfonate (P/S) type complexes: The sulfonate-directed *ortho*-lithiation of anhydrous benzenesulfonic acid with two equivalents of *n*-butyl lithium followed by selective mono-addition to stoichiometric amounts of either cyclohexyl- or *tert*-butyldichlorophosphine at -78 °C was successfully applied to generate P/S precursors **3a/b** bearing one P-Cl bond (Scheme 1a). Whereas purification of both P/S precursors **3a/b** was not possible due to inseparable lithium salts, the crude compounds were of sufficient purity for further syntheses. After determination of their respective formula weights by ^{1}H-NMR analysis, the precursors were stored as solids at room temperature in a glovebox before further use. The isolation of **3a/b** as storable solids means that the addition of a second nucleophile is the only step required for the synthesis of **4b-m.** Isolation and purification of the ligands **4b-m** were unnecessary, and we directly added the crude ligand mixtures to chloro(1,5-cyclooctadiene) methylpalladium(II). Addition of 2,6-lutidine or pyridine[10] to these crude complex mixtures furnished catalysts **1b-m**, which then were purified using standard chromatographic techniques under air. By utilizing this streamlined procedure, several new ligands and complexes could be prepared in parallel during a workday, which greatly accelerates the screening of new ligands for polymerization. Importantly, purification by flash column chromatography rapidly gave high purity compounds in higher yields as compared to traditional methods of separate ligand/complex preparation due to circumventing loses during intermediate purification steps, while avoiding the purification of oxygen sensitive intermediates altogether.

Preparation of P-stereogenic Bisphosphine Monoxide Complexes: The same first two steps described for the preparation of the P/S type complexes were followed by utilizing *ortho*-lithiation of a phosphine oxide instead of sulfonate to furnish the BPMO type precursors **5a/b** (Scheme 1b). In contrast to the P/S precursors, **5a/b** can be purified by recrystallization (For scXRD structures of **5a/b** see SI).[11] Addition of either Li or Na based nucleophiles to **5a/b** gave ligands **6a-n**. After direct complexation of the crude ligand mixtures to chloro(1,5-cyclooctadiene)methylpalladium(II) to provide intermediate complexes **7a-k**, the BPMO complexes were conveniently purified under air by flash column chromatography. This procedure works well even for cases such as **2a/b** for which formation of insoluble Li-salt adducts hampered the isolation of the free ligands.[12] Subsequent chloride abstraction from **7a-n** in the presence of 2,6-luthidine or pyridine[10] yields the target complexes **2a-n** after purification by recrystallization

On safety issues concerning the synthesis of 9a: Due to their special far-reaching steric profile and strongly donating nature we became interested in utilizing imidazolin-2-ylidenaminophosphine donors in our complexes **1l**, **1m**, **2l**, **2m** and **2n**.[13] During the preparation of the free N-heterocyclic carbene (NHC) **9a** which was required for the preparation of the precursor **10a**, we noticed

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that the only reported route in the literature for this widely used compound *posed significant safety concerns on larger scales* (Scheme 2a).[14] To overcome these hazards we adapted and modified a synthetic method for imidazolium salts by Glorius and coworkers towards their tetrafluoroborate salts.[15] This allowed us the safe and column-free preparation of colorless, crystalline imidazolium tetrafluoroborate salts **8a/b** on 42.4 and 66.1 g scales respectively (Scheme 2b). Subsequent deprotonation of **8a/b** under inert conditions gave the important free NHCs **9a/b** as colorless solids.[16] *Overall this procedure does not require the use copious amounts of elemental potassium in THF under reflux conditions. Moreover, it circumvented the formation of large amounts of finely powdered potassium sulfide. The later can be difficult to handle under inert conditions on larger scales and turns out to be quite pyrophoric due to contamination with residual potassium metal.*

Homopolymerization of propylene with P/S complexes 1a-m: The pre-catalysts **1a** and **1b** were screened in the homopolymerization of propylene at 50 °C. While achiral **1a** yielded atactic polymeric material with an *mm* value of

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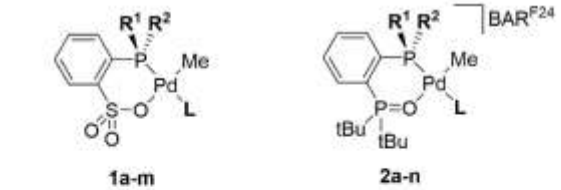
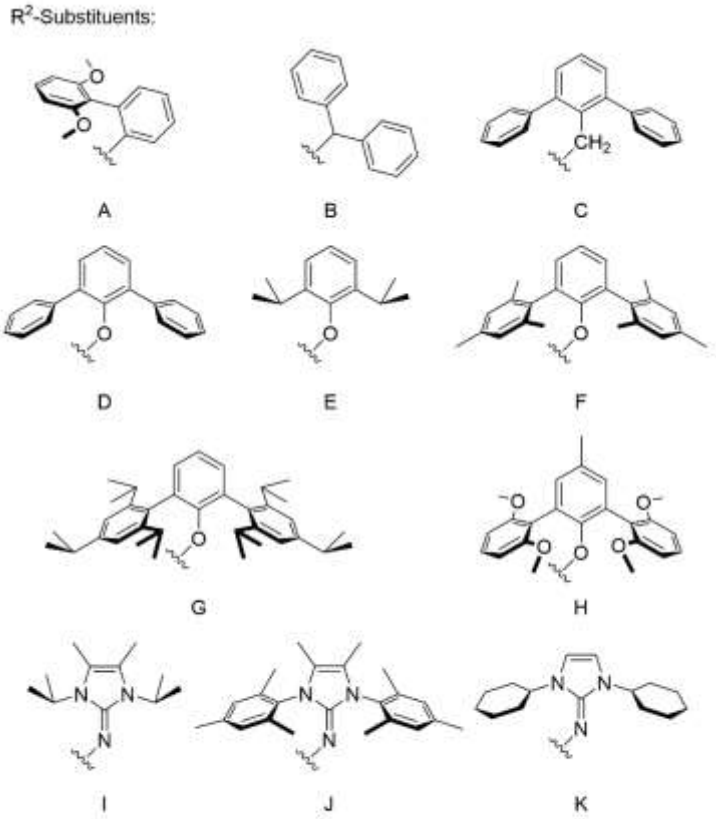


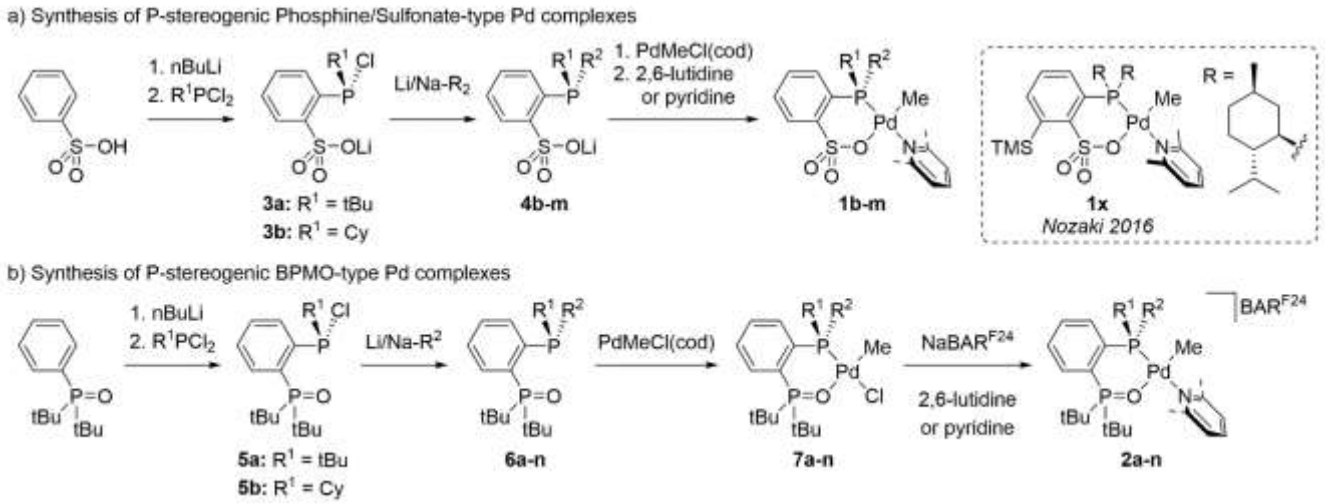
1a-m

2a-n

1	R^1	R^2	L
a	tBu	tBu	lut
b	tBu	Me	lut
c	tBu	A	py
d	tBu	B	lut
e	tBu	C	py
f	tBu	D	py
g	Cy	D	py
h	tBu	E	py
i	tBu	F	py
j	tBu	G	py
k	tBu	H	py
l	tBu	I	lut
m	tBu	J	lut

2	R^1	R^2	L
a	tBu	Me	lut
b	Cy	Me	lut
c	tBu	B	lut
d	Cy	B	lut
e	tBu	D	lut
f	Cy	D	lut
g	tBu	E	lut
h	Cy	E	lut
i	Cy	F	lut
j	tBu	H	py
k	Cy	H	lut
l	tBu	I	lut
m	Cy	I	lut
n	tBu	K	lut





Scheme 1. Overview of synthetic routes utilized for catalyst preparation. **1a** was synthesized following a literature procedure.[18] The reference system **1x** was previously reported.[6a]

0.32 (Table 1, Entry 1), **1b** containing a P-stereogenic methyl/*tert*-butyl phosphine showed slightly improved tacticity control in comparison to **1a** with an *mm* of 0.38.[17] The activity, however, halved while the obtained polymer showed both an increased amount of regiodefects (3.82%) and a lower M_n. The reduced M_n and increased amount of regiodefects could be explained thereby, that the R^2 = methyl substituent was not bulky enough to prevent β-hydrogen elimination processes.[18] Replacement of the small methyl group in **1b** by a larger biphenyl motif in **1c** was unable to impart either significant regio- or stereocontrol, yielding atactic PP (*mm* = 0.18; regiodefects = 17.8%; see figure 2a).[19] XRD analysis of a single crystal of **1c** reveals that the R^2 aryl residue on the phosphorus donor could easily rotate out of the catalytic pocket.[20] This observation is supported by a previous study that

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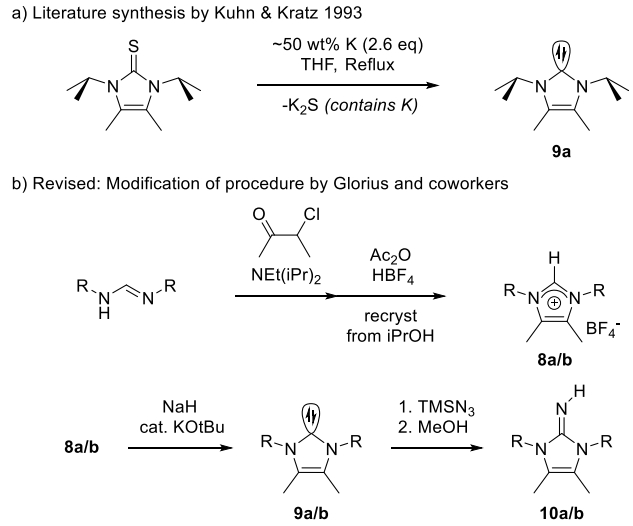

Scheme 2. Comparison of synthetic routes for preparation of **10a/b**.[14, 15] [a] **8/9/10a**: R = iPr; **8/9/10b**: R = Mes. [b] **8a**: 42.4 g, 38%; **8b**: 66.1 g, 66%; **9a**: 27 g; 95%; **9b**: 14 g, 88%. [c] **10a/b** were prepared according to literature procedures.[13, 21]

found the rotational flexibility of P/S type Pd complexes to be important to achieve high selectivity in consecutive stereo- and regioselective acrylate insertions.[22] Thus, we sought to increase the reach and rigidity of the applied steric bulk deeper into the axial pocket of the complex by attaching a diphenylmethane residue to the phosphine donor. Catalyst **1d** displayed similar tacticity control (*mm* = 0.40) compared to the methyl analogue **1b**, but with an activity over 35 times greater. As increased steric bulk in the axial positions of the complex showed benefits, we introduced a tilted and widely spanned terphenylmethyl group into catalyst **1e**. Gratifyingly, the PP prepared with **1e** showed clear improvement on **1b** with for example higher degrees of isotacticity (*mm* = 0.52). The PP prepared with catalyst **1f**, an oxa-analog of **1e** showed similar tacticity (*mm* = 0.45). As the cyclohexyl substituted phosphinite **1g** diminished tacticity control (*mm* = 0.33) we continued to use *tert*-butyl residues for R^1 while screening different phenol-derived R^2 residues in our subsequent P/S catalysts. In **1h** a less widespan residue was introduced which was reflected in both a lower PP M_n (1.07 kg·mol^{-1}) and an increased amount of regiodefects (2.57%) when compared to **1f**. The crystal structure of **1f** shows the proximity of the *ortho*-substituents on the phenyl side arms near both catalytically relevant coordination sites *cis* and *trans* to the phosphine donor (See SI, figure S6). We therefore introduced methyl groups at the *ortho* positions to test their influence on the polymerization. To this end, the mesityl substituted phosphinite catalyst **1i** outperformed **1e** in all aspects but activity. Still further increasing of the bulk in the phenyl *ortho*-positions through the introduction of isopropyl groups (**1j**) did not lead to any improvements and noticeable catalyst decomposition was detected. As an alternative steric middle ground between **1i**and **1j**, we prepared **1k** which

Table 1. Propylene polymerisation with P-sterogenic P/S type catalysts.[a]

Entry	Cat.	Yield[b] [mg]	Activity[c] [kg mol^{-1}·h^{-1}] ([mol mol^{-1}·h^{-1}])	M_n[d] [kg mol^{-1}]	PDI [d]	[*mm*][e]	[*mr*][e]	[*rr*][e]	4[*mm*][*rr*] /[*mr*]^2 [f]	2[*rr*] /[*mr*] [g]	Regio-defects[e] [%]	1,3-enchain-ment[e] [mol%]	T_g/T_c/T_m[i] [°C]	$\Delta H_{c/m}$[i] [J·g^{-1}]
1	**1a**	974.9	4.1 (96.5)	1.1	2.2	0.32	0.46	0.22	1.33	0.96	0.58	-	nd	nd
2	**1b**	48.0	0.2 (4.75)	0.46	1.2	0.38	0.37	0.25	2.78	1.35	3.82	-	nd	nd
3	**1c**	173.7	0.72 (17.2)	0.29	1.4	0.18	0.50	0.32	0.92	1.28	17.8	7.96	nd	nd
4	**1d**	1745	7.3 (173)	0.86	2.1	0.40	0.41	0.19	1.81	0.93	1.46	-	nd	nd
5	**1e**	1041	4.3 (103)	1.7	2.3	0.52	0.33	0.15	2.87	0.91	2.42	0.93	-23.4/-/ 57.8	-/4.30
6	**1f**	204.7	0.85 (20.3)	1.8	2.1	0.45	0.39	0.16	1.89	0.82	1.75	0.86	nd	nd
7	**1g**	32.3	0.13 (3.20)	0.88	1.7	0.33	0.48	0.19	1.09	0.79	1.05	-	nd	nd
8	**1h**	390.8	1.6 (38.7)	1.1	2.4	0.49	0.36	0.15	2.27	0.83	2.57	0.25	nd	nd
9	**1i**	784.9	3.3 (77.7)	3.2	2.3	0.52	0.34	0.14	2.52	0.82	0.45	-	-17.6/-/-	-
10	**1j**	23.2	0.10 (2.30)	2.4	2.8	0.52	0.33	0.15	2.87	0.91	0.60	-	nd	nd
11	**1k**	983.2	4.1 (97.4)	2.9	2.3	0.67	0.23	0.10	5.07	0.87	1.09	0.22	-20.8/3.0/ 80.9	-13.0/ 40.8

[a] A mixture of the respective catalysts (20 µmol) and propylene (6.0 g) in toluene (10 mL) was stirred for 12 h at 50 °C in a stainless-steel autoclave (50 mL) containing a glass-tube. [b] Isolated yields after quenching the reactions with methanol and passing through a silica-plug. [c] Activities are defined as mass of the polymer or moles of monomer in the polymer (in parentheses by a suggestion of a reviewer) per mol of catalyst per hour. [d] Molecular weights determined by size-exclusion chromatography with narrow polystyrene standards and corrected by universal calibration. [e] Triad ratios, regiodefects and 1,3-enchainment determined by quantitative ^{13}C-NMR. [f] A value of 1 statistically resembles a chain-end controlled tacticity, large derivations from 1 indicate a poor resemblance of a chain end controlled mechanism, see reference for details.[23] [g] A value of 1 statistically resembles a enantiomorphic site controlled tacticity, large derivations from 1 indicate a poor resemblance of a enantiomorphic site controlled mechanism, see reference for details.[4a] [h] Catalysts **1l/m** only produced trace amounts of polymer under conditions [a]. [i] Glass transition- and crystallization temperatures, melting points, crystallization enthalpies and heats of fusions determined by DSC analysis. [j] nd: not determined.

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Figure 2. ^{13}C-NMR –(CH(*C*H$_3$)CH$_2$)$_n$- regions of polypropylenes obtained by different P-stereogenic catalysts at 50 °C: a) **1c** (Table 1, entry 3; *mm* = 0.18), b) **1k** (Table 1, entry 11; *mm* = 0.67) , c) **2j** (Table 2, entry 4; *mm* = 0.75).

contains methoxy substituents on R^2. Catalyst **1k** produced crystalline PP with an unprecedented *mm* of 0.67 for palladium-based catalysts, exceeding **1i** and even our previous best-performing system with menthyl substituents in terms of tacticity control. The activity of **1k** (4.01 kg·mol^{-1}·h^{-1}) was a clear improvement on **1i** (3.3 kg·mol^{-1}·h^{-1}) and the produced polymer showed noticeably less regiodefects (1.09%) and higher M_n values (2.89 kg·mol^{-1}). Differential Scanning Calorimetry (DSC) analysis of the PP produced by **1k** showed a distinct exothermic T_c peak at 3.0°C with an enthalpy of crystallization of -13.0 J·g^{-1} as well as a single melting endotherm at 80.9°C with a respective heat of fusion of 40.8 J·g^{-1} (Figure 4a). This was a clear improvement over the PPs prepared with our previous menthyl derived Pd P/S and Ni-SHOP catalysts which showed in all cases no T_c but bimodal T_m.[6] In contrast to catalysts **1a-k**, the imidazolin-2-ylidenaminophosphine substituted catalysts **1l/m** only gave trace amounts of polymers. In both cases the catalysts were stable under polymerization conditions but showed extremely poor activity for both ethylene and propylene polymerization.

Homopolymerization of propylene with BPMO complexes 2a-n: Inspired by the success of the Pd P/S catalyst **1k**, we sought out to modify the ligand backbone and test the analogous BPMO-type systems for propylene polymerization (Table 2). The PP produced by catalyst **2c** containing R^1 = *tert*-butyl and R^2 = diphenylmethyl substituents showed some degree of isotacticity (*mm* = 0.50) while the cyclohexyl analogue **2d** only produced completely atactic material (*mm* = 0.21). Screening of various phosphinite BPMO catalysts revealed that only catalysts **2f/j/k** were active for propylene polymerization. **2f** produced highly isotactic, crystalline PP (*mm* = 0.65), albeit with 11.7% regiodefect structures (5.44% assignable to 1,3-enchainment). Overall, the highest *mm* value of 0.75 was achieved by catalyst **2j** (Figure 2c). This was accompanied by a reduction of regiodefects (3.82%) which stemmed mostly from 1,3-enchainment (2.84%). Its cyclohexyl derivative **2k** induced comparable degrees of isotacticity (*mm* = 0.66) as **2f**. Importantly, **2k** showed a five times higher activity of 2.66 kg·mol^{-1}·h^{-1} than **2j** and thus we employed **2k** for copolymerization studies. As for the P/S systems, the imidazolin-2-ylidenaminophosphine containing catalysts **2l/m/n** did not show appreciable activity for either ethylene or propylene polymerization.

Copolymerization of propylene with polar monomers by catalysts 1i/k and 2k: We moved onwards to test the three catalysts **1i/k** and **2k** for the direct copolymerization of polar monomers with propylene to generate iPPPs and the results were summarized in Table 3. Allyl acetate (AAc), allyl chloride (ACl), allyl cyanide (ACN) and methyl acrylate (MA) were chosen as polar monomers. With the P/S catalysts **1i/k**, copolymers were obtained with AAc (entries 1/2), ACN (entry 4), and ACl (entry 6), but no incorporation of the polar comonomer was detected with MA (entry 8). The obtained (co)polymers showed closely related tacticity control as well as low degrees of regiodefect structures in comparison to their respective PP homopolymerization experiments (Table 1, entries 9/11). The ^{13}C NMR analysis of the allyl chloride/propylene copolymer prepared by complex **1k** (entry 6) shows signals of the highly isotactic propylene units and the incorporated polar monomer and signals (Figure 3). This functionalized polymer moreover showed a clear T_C at 3.3°C with a crystallization enthalpy of -1.24 J·g^{-1} and a single T_m at 70.7°C with a heat of fusion of 20.4 J·g^{-1} (Figure 4b). These polymer properties were again a clear improvement over our previous menthyl systems where no T_c but two T_m were observed for all PPs and iPPPs.[6] The occurrence of two T_m is typical for low molecular weight polymers.[24] It should be noted that the M_n = 1.1 kg·mol^{-1} of the polymer prepared by **1k** was lower by a factor of ten when compared to its predecessors (See Table 3, entry 6). Accordingly, the existence of a T_c and a single T_m should be attributed to the higher tacticity control with **1k**. A hint on the influence of steric bulk can be seen by comparison of the incorporation ratios of allyl acetate (AAc) by both catalyst **1i** and **1k** (Table 3, entries 1/2). The less bulky catalyst **1i** shows an activity 2.6 times higher for the copolymerization of ally acetate (AAc) with propylene than **1k**. Under the same conditions the bulkier **1k**, doubled the incorporation ratio of AAc to 1.82%. As for the homopolymerization experiments, the polymers prepared by the BPMO catalysts again showed higher degrees of regio- (4.92 – 6.48%) and 1,3-enchainment defects (3.17 – 3.91%) than their P/S counterparts. Of the polar monomers tested only copolymerization with AAc was successful. Analysis using ^{13}C NMR indicated a low incorporation (0.05%) into the PP chain (Table 3, entry 3). Only unfunctionalized PPs were obtained in the attempted copolymerization experiments with allyl chloride and methyl acrylate (Table 3, entry 7/9). Allyl cyanide completely shut down the polymerization ability of catalyst **1k** (Table 3, entry 5).
The use of BPMO catalysts **2k** resulted in almost negligible incorporation of polar comonomers (Table 3, entries 3/7/9) and the reaction itself was shut down by ACN (entry 5). Intriguingly, however, for all attempted BPMO copolymerization experiments with catalyst **2k**, the isotacticity increased significantly to *mm* = 0.74 - 0.75. This is a compelling improvement when compared to the respective propylene homopolymerization experiments with **2k** (Table 2, entry 5; *mm* = 0.66). With the P-

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Table 2. Propylene polymerisation with P-stereogenic BPMO type catalysts.[a]

Entry	Cat	Yield[b] [mg]	Activity[c] [kg mol^{-1}·h^{-1}] ([mol mol^{-1}·h^{-1}])	Mn[d] [kg mol^{-1}]	PDI[d]	[*mm*] [e]	[*mr*] [e]	[*rr*] [e]	4[*mm*] [*rr*] /[*mr*]^2 [f]	2[*rr*] /[*mr*] [g]	Regio-defects[e] [mol%]	1,3-enchain-ment[e] [mol%]	T_g/T_c/T_m [i] [°C]	$\Delta H_{c/m}$[i] [J·g^{-1}]
1	**2c**	772.7	5.37 (153)	9.4	2.2	0.50	0.32	0.18	3.52	1.13	0.90	-	nd	nd
2	**2d**	252.2	2.1 (49.9)	3.6	2.4	0.21	0.43	0.36	0.70	1.67	2.26	0.06	nd	nd
3	**2f**	65.3	0.54 (12.9)	1.2	1.9	0.65	0.25	0.1	4.16	0.80	11.7	5.44	nd	nd
4	**2j**	91.1	0.76 (18.0)	2.7	2.0	0.75	0.18	0.07	6.48	0.78	3.82	2.84	-28.1/-/84.0	-/24.1
5	**2k**	318.6	2.66 (63.1)	2.8	2.6	0.66	0.24	0.1	4.58	0.83	5.06	3.50	-23.1/-/82.6	-/24.5

[a] A mixture of the respective catalysts (10 µmol) and propylene (6.0 g) in toluene (15 mL) was stirred for 12 h at 50 °C in a stainless-steel autoclave (50 mL) containing a glass-tube. [b] Isolated yields after quenching the reactions with methanol and passing through a silica-plug. [c] Activities are defined as mass of the polymer or moles of monomer in the polymer (in parentheses by a suggestion of a reviewer) per mol of catalyst per hour. [d] Molecular weights determined by size-exclusion chromatography with narrow polystyrene standards and corrected by universal calibration. [e] Triad ratios, regiodefects and 1,3-enchainment determined by quantitative ^{13}C-NMR. [f] A value of 1 statistically resembles a chain-end controlled tacticity, large derivations from 1 indicate a poor resemblance of a chain-end controlled mechanism, see reference for details.[23] [g] A value of 1 statistically resembles a enantiomorphic site controlled tacticity, large derivations from 1 indicate a poor resemblance of a enantiomorphic site controlled mechanism, see reference for details.[4a] [h] Catalysts **2a/b/e/g/h/i/l/m/n** did not show activity for propylene polymerization under conditions [a]. [i] Glass transition- and crystallization temperatures, melting points, crystallization enthalpies and heats of fusions determined by DSC analysis. [j] nd: not determined

stereogenic catalysts here examined, the tacticity so far was significantly improved while activities and molecular weight for propylene homopolymerization are still lower than those with the C-stereogenic **1x**.

Considerations on the origin of tacticity control: Statistical analysis indicated that the observed tacticity was indeed induced by enantiomorphic site control rather than chain-end control in case of the P-stereogenic P/S and BPMO catalysts: The 2[*rr*]/[*mr*] values obtained of close to 1 were in support of enantiomorphic site control,[4a] while 4[*mm*][*rr*]/[*mr*]^2 values significantly larger than 1 suggest a chain-end controlled mechanism[23] (See columns 10/11 in tables 1/2 and columns 11/12 in table 3). We returned to the crystal structure of **1k** (Figure 5a/c/d) to help us elucidate the role of the P-stereogenic motifs for enantiomorphic site control. The origin of tacticity control for Ni/Pd catalysts containing a P/O type ligand can be considered as follows (Figure 5b): Only when the propagating polymer chain is in a *trans*-position to the P-donor moiety it does become electronically activated for the insert if a *cis*-coordinated olefin (Figure 5b, top left).[8] For the corresponding *cis*-isomer this insertion process is energetically unfavorable (Figure 5b, bottom left). Therefore, the relative coordination mode of the propylene molecule prior to 1,2-insertion in the *cis*-position to the P-donor in the *trans*-isomer dictates the tacticity in the polymer (Figure 5b, top right). Shown in Figure 5c/d are the possible coordination modes of propylene in the *trans*-isomer. We think, the selective coordination in which the methyl group of propylene is always located at the same green position but not at the red ones should provide high regioregularity as well as high isotacticity out of the following scenario. The propylene methyl groups can be repelled by applying steric bulk close to the P-donor so that the insertion takes place selectively via a 1,2-mode. In this complex, the propagating polymer chain located *trans* to the phosphine donor should occupy the largest vacant site, that is

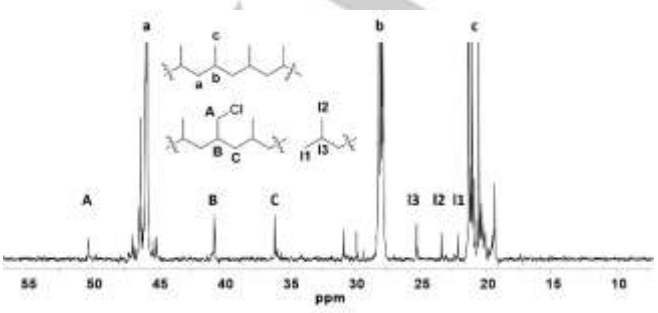

Figure 3. ^{13}C-NMR spectrum of the allyl chloride/propylene copolymer produced by catalyst **1k** (Table 3, entry 6; *mm* = 0.68).

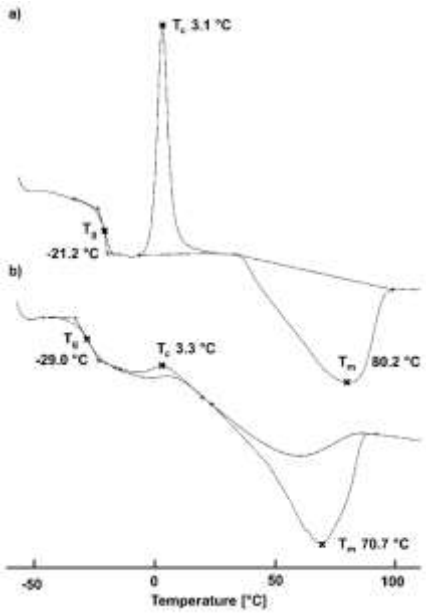

Figure 4. Heating scan regions in the DSC charts after annealing of propylene (co)polymers produced by catalyst **1k** (10 °C / minute heating rate): a) PP homopolymer (See table 1, entry 11); b) ACl / PP copolymer (See table 3, entry 6).

Table 3. Propylene copolymerisation with polar monomers using BPMO and P/S Type catalysts.

Entry	Cat.	Monomer [mL]	Solvent [mL]	Yield[b] [mg]	Activity[e] [kg mol^{-1}·h^{-1}] ([mol mol^{-1}·h^{-1}])	*Mn*[c] [kg mol^{-1}]	PDI [c]	Incorp. [%] [d]	[*mm*] [d]	4[*mm*][*rr*] /[*mr*]^2 [f]	2[*rr*]/ [*mr*][g]	Regio-defects [mol%] [d]	1,3-enchain-ment [mol%] [d]	T_g/T_c/T_m[h] [°C]	$\Delta H_{c/m}$[h] [J·g^{-1}]
1	**1i**	AAc (0.5)	10	117.7	0.49 (11.7)	2.3	2.4	0.85	0.51	2.33	0.8	0.20	-	-20.6/-/-	-/-
2	**1k**	AAc (0.5)	10	49.9	0.19 (4.94)	1.8	2.3	1.82	0.65	4.16	0.80	0.28	-	-20.5/- /73.8	-/24.9
3	**2k**	AAc (0.5)	14.5	161.7	0.34 (8.01)	2.5	1.7	0.05	0.74	5.74	0.74	4.92	3.17	-30.2/- /81.8	-/24.7
4	**1k**	ACN (1.0)	10	38.1	0.16 (3.77)	1.4	2.4	1.50	0.66	4.58	0.83	1.34	0.84	-27.6/- /80.9	-/19.3
5	**2k**	ACN (1)	14	-	-	-	-		-	-	-	-	-	-	-
6	**1k**	ACl (0.25)	10	18.8	0.08 (1.86)	1.1	2.5	1.66	0.68	4.63	0.78	-	-	-29.0/ 3.3/70.7	-1.24/ 20.4
7	**2k**	ACl (0.25)	14.75	121.3	0.25 (6.01)	2.9	1.7	-	0.75	6.48	0.78	5.0	3.42	-27.1/- /89.8	-/22.6
8	**1k**	MA (0.25)	10	65.1	0.27 (6.4)5	2.3	2.2	-	0.67	5.07	0.87	1.08	0.40	nd	nd
9	**2k**	MA (0.25)	14.75	205.5	0.43 (10.2)	2.8	1.7	-	0.74	5.74	0.74	6.28	3.91	-26.3/- /86.1	-/22.4
ref[7a]	**1x**	AAc (0.5)	10	180	0.75 (17.8)	8.9	2.7	1.7	0.55	2.20	0.60	1.0	nd	-11.7/-/ 43.5, 60.4	-/6.7
ref[7a]	**1x**	ACl (0.25)	10	140	0.58 (13.9)	11	2.2	1.7	0.56	2.26	0.60	1.1	nd	-10.0/-/ 42.9, 61.7	-/11.0
ref[7a]	**1x**	MA (0.25)	10	200	0.83 (19.8)	4.6	2.2	1.6	0.56	2.63	0.75	0.9	nd	-14.3/-/ 43.3, 61.8	-/11.4

[a] A mixture of the respective catalyst (20 µmol for P/S catalysts **1i/k** and in the reference report for **1x**; 40 µmol for BPMO catalyst **2k**), propylene (6.0 g) and polar monomer in toluene was stirred for 12 h at 50 °C in a stainless-steel autoclave (50 mL) containing a glass-tube. [b] Isolated yields after quenching the reactions with methanol and passing through a silica-plug. [c] Molecular weights determined by size-exclusion chromatography with narrow polystyrene standards and corrected by universal calibration. [d] Triad ratios, regiodefects and 1,3-enchainment determined by quantitative ^{13}C-NMR. [e] Activities are defined as mass of the polymer or moles of monomer in the polymer (in parentheses by a suggestion of a reviewer) per mol of catalyst per hour. [f] A value of 1 statistically resembles a chain-end controlled tacticity, large derivations from 1 indicate a poor resemblance of a chain end controlled mechanism, see reference for details.[23] [g] A value of 1 statistically resembles a enantiomorphic site controlled tacticity, large derivations from 1 indicate a poor resemblance of a enantiomorphic site controlled mechanism, see reference for details.[4a] [h] Glass transition- and crystallization temperatures, melting points, crystallization enthalpies and heats of fusions determined by DSC analysis. [i] nd: not determined.

faded purple area. In literature for propylene polymerization by *ansa*-metallocene catalysts, the propylene methyl moiety is proposed to align *anti* in respect to the polymer chain based on previous experimental[25] and computational[26] studies. Similarly, here we propose that the favorable orientation of the propylene-methyl moiety will be *anti* to the polymer chain. Discrimination between the two 1,2-insertion modes requires therefore far reaching steric bulk to repel the polymer chain in one of the axial directions. With this scenario in mind, we return to the crystal structure of **1k**: one of the 2,6-dimethoxyphenyl sidearms in the R^2 residue shows a parallel alignment to the square-planar Pd-coordination plane, effectively protecting one of its faces (See Figure 5d). We think an emphasis should be put here on the far reach of one methoxy group (O3 and C5). In contrast the other side of the coordination plane experiences comparatively less steric pressure due to the tert-butyl group on the phosphine. Another methoxy group (O4 and C6) is seen flanking the coordination site *cis* to the phosphine donor (Figure 5c). Yet this group is located far away enough to not interfere with olefin coordination. Taken together, it is plausible that prior to chain propagation by 1,2-insertion the propylene methyl group is forced to face in the direction of the axial methoxy group (O3 and C5) due to steric repulsion with the polymer chain. At the same time 2,1-insertion will be mainly suppressed by the steric bulk close to the phosphorus donor. This is supported by the SambVca 2.1 plots based on crystal structures of the three best performing catalysts **1k** and **2j/k**, which show that these steric characteristics are shared between both P/S and BPMO catalysts (Figure 5e).[27] In case of the BPMO systems additional steric pressure by the phosphine oxide *tert*-butyl groups is observed mainly in the same north western quadrant as the aforementioned axial methoxy group. In all cases, thus the ligands enforce the growing polymer chain to be in the purple area.

For the insertion of electron rich propylene monomer, not only the steric effect discussed above but also electronic effect favours 1,2-mode over 2,1. This follows a previous report in which the reverse trend towards 2,1-insertion was observed for electron deficient acrylate monomers.[28] An essential and more fundamental understanding of the migratory insertion process for late transition metals was recently reported by Copéret and

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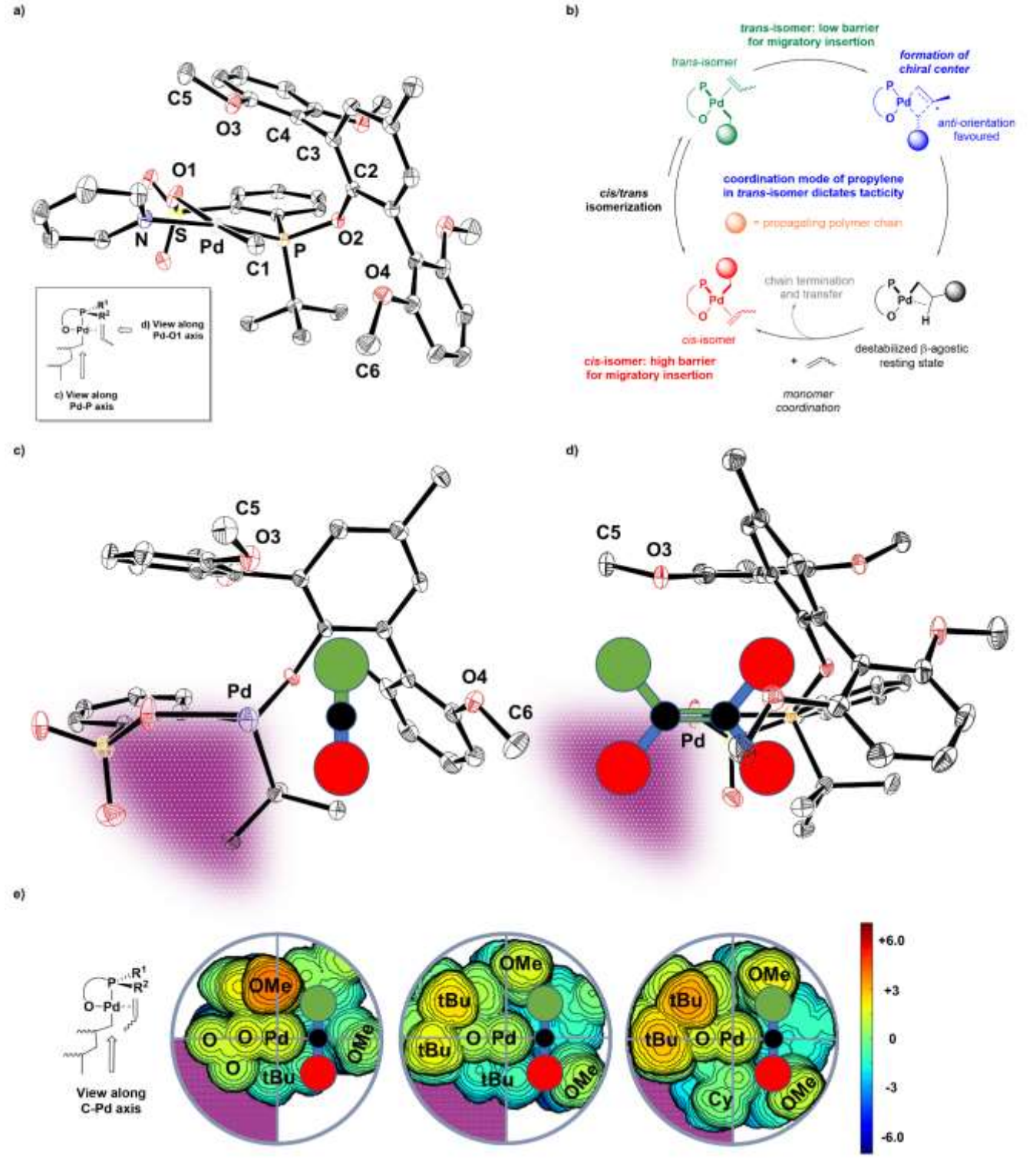

Figure 5. a) Molecular structure of catalyst **1k**·2(CH_2Cl_2) in the crystal (ORTEP drawn at 50% probability; all H atoms are omitted for clarity in a/c/d); the pyridine and methylido-ligand for plot c) and d) were truncated for clarity). Selected bond lengths (Å) and angles (deg): Pd-C 2.026(2), Pd-P 2.1989(6), Pd-O1 2.1278(18), Pd-N 2.138(2), P-O2 1.6245(15), P-O2-C2 128.32(14), C1-Pd-P-O2 43.68, P-O2-C2-C3 59.35, C2-C3-C4-O3 121.05, Sum of angles around Pd: 360.72. b) Simplified polymerization mechanism for P/O type catalyst with a focus on showcasing the importance of the propylene coordination mode in the *trans*-isomer for tacticity control. For a variety of chain transfer and termination mechanisms, see reference [8]. For the truncated views c) and d) the proposed steric outline of the four propylene coordination modes prior to chain propagation (propylene coordinated to Pd in *trans*-position to the sulfonate-donor; in green: Favourable propylene methyl group orientation; in red: unfavourable propylene methyl group orientation) and the proposed orientation of the polymer chain (south western quadrants, faded purple area) are indicated: c) Front view along the Pd-P axis. d) Side view along the Pd-O1 axis. e) SambVca 2.1 plots of frontal views on the crystal structures of the three most *iso*-selective catalysts **1k** (left, v_{Buried} = 39.2%) and **2j** (center, v_{Buried} = 41.9%) and **2k** (right, v_{Buried} = 48.3%). 7Å radii plots around the Pd-atoms are shown (See color coded depth scale in Å units on the right). Hydrogen atoms were included in the calculations. The polymer end is proposed to be oriented towards the south western quadrant (indicated with purple shading). The steric outline of the proposed favorable (green; *anti* relative to the propagating polymer chain) and unfavorable (red; *syn* relative to the propagating polymer chain) orientation of the propylene-methyl head prior to 1,2-insertion are indicated in the eastern quadrants.

coworkers: For successful chain propagation an occupied antibonding orbital of π-symmetry induces a nucleophilic character in the M-C carbon.[29] Therefore, the migratory insertion during polymerization can be seen in a simplified picture as a nucleophilic attack of an populated π*-orbital on the π*-orbital of an olefin, which perfectly describes the electronic origin of the observed inverse insertion selectivity for either electron rich or poor olefins.

Evaluation of the P-stereogenic P/S and BPMO catalysts for propylene homo- and copolymerization: In terms of activity, the performance of P/S or BPMO systems are comparable for propylene homopolymerization: While the examined P/S systems mostly showed higher PP-polymerization activities, BPMO type complexes **2a/b/e/g/h/i/l/m/n** all showed no activity. Nevertheless, among the examined BPMO catalysts, **2d/k** achieved comparable activities to their P/S counterparts. As for regio-control, unlike the P/S catalysts, most of the BPMO systems introduced a significant amount of regio- as well as additional 1,3-enchainment defects into the PP chains. The latter originates from the β-hydrogen elimination, chain-walking and reinsertion events, which happens more often with α-diimine catalysts.[30] Regiodefects and 1,3-enchainment in BPMO type catalyst were suppressed by suitable design of the P-donor substituents in **2j/k**. Thus, in principle with careful substituent selection, BPMO catalyst rival P/S systems for the copolymerization of propylene with polar monomers. This was also the case for ethylene / polar monomer copolymerization in a previous study.[31] For copolymerization P/S type catalysts **1i/k** were successfully applied to the propylene/polar monomer copolymerization using AAc, ACN and ACl. BPMO type catalysts were less suitable for copolymerization: **2k** only displayed a very limited ability to incorporate only allyl acetate.

In terms of tacticity control, the BPMO systems clearly exceeded the P/S catalysts: The highest *mm*s for propylene homopolymerization for P/S catalysts was achieved with **1k** (*mm* = 0.67; table 1, entry 11), while the best BPMO catalyst **2j** clearly outperformed the P/S counterpart with an *mm* of 0.75 (Table 2, entry 4). With BPMO catalyst **2k**, an increase of tacticity control was observed in the presence of polar molecules, namely, *mm* changed from 0.66 (Table 2, entry 5) for the homopolymerization experiment to 0.74 – 0.75 for the copolymerization experiments with AAc, ACl and MA (Table 3, entries 2/3/5/7). The P/S catalysts showed in contrast generally closely related tacticity control in both homo- and copolymerization experiments (See entries for catalysts **1i/k** in tables 1 and 3). The use of imidazolin-2-ylidenaminophosphines in both P/S and BPMO complexes led to no polymerization activity, though catalyst decomposition did not seem to take place **1l/m** and **2l/m/n**).

Conclusion

To conclude, we have developed P-stereogenic ligands for the palladium-catalysed copolymerization of propylene with polar monomers at industrially relevant temperatures, with the highest isotacticities reported to date for late transition metal catalysed systems (*mm* = 0.75 for propylene homopolymerization with complex **2j** and *mm* = 0.74 for propylene / AAc copolymerization with **2k**). To overcome the protracted synthetic demands, we developed time-efficient synthetic protocols: The use of modular ligand building blocks and phenol derived phosphinites sped up synthesis while simplified purifications by column chromatography under air minimized time spent on purification. Taking advantage of a rapid screening approach, the effect of the ligand substituents was rationalized empirically. We believe the ligand design concepts we presented here will find further application to other metal catalysts.

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Keywords: Copolymerization • Isolobal relationship • P ligands • Palladium • Synthesis design

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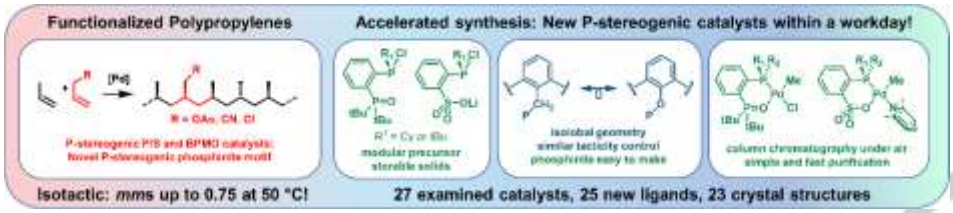

Preparation of functionalized isotactic polypropylenes is hampered by the absence of good tacticity inducing ligand motifs for group 10 catalysts: Only a natural product derived dimenthylphosphine is known. Accelerating ligand and Pd complex syntheses led to a novel P-stereogenic phosphinite motif that allowed propylene copolymerization with unprecedented mms up to 0.75 for group 10 catalysts at an industrially relevant temperature of 50°C.

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