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Bimetallic Coordination Insertion Polymerization of Unprotected Polar Monomers: Copolymerization of Amino Olefins and Ethylene by Dinickel Bisphenoxyiminato Catalysts

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S *Supporting Information*

ABSTRACT: Dinickel bisphenoxyiminato complexes based on highly substituted *p*- and *m*-terphenyl backbones were synthesized, and the corresponding atropisomers were isolated. In the presence of a phosphine scavenger, $Ni(COD)_2$, the phosphine-ligated *syn*-dinickel complexes copolymerized α-olefins and ethylene in the presence of amines to afford 0.2−1.3% α-olefin incorporation and copolymerized amino olefins and ethylene with a similar range of incorporation (0.1−0.8%). The present rigid catalysts provide a bimetallic strategy for insertion polymerization of polar monomers without masking of the heteroatom group. The effects of the catalyst structure on the reactivity were studied by comparisons of the syn and anti atropisomers and the *p*- and *m*-terphenyl systems.

Functionalized polyolefins have desirable physical properties, including improved adhesion to substrates, response to stimuli, and increased compatibility with other materials for use in polymer blends and composites.[1] While numerous functionalized polymers have been synthesized, even on industrial scales, their synthesis is primarily achieved through radical polymerization or postpolymerization modification, which often provide only limited control over the polymer microstructure (e.g., tacticity, branching, functionality incorporation).[1d,f,2] Polymers generated by coordination polymerization and having polar groups, including ester,[3] amine,[3c,i,4] alcohol,[2e,3c,f,i,4a,b,d,f,5a,b] and acid[3c,f] functionalities, have been reported. For insertion polymerization (IP) of amino olefins (AOs), protection of the amine or masking with a Lewis acid is common.[3c,i,4f,5c] IP of α-olefins functionalized with tertiary amines catalyzed by zirconocene complexes favors bulky subtituents on the amine to discourage base coordination to Zr and afford olefin coordination.[4d,e,l,m] Herein we present a strategy for AO copolymerization employing an alternate mechanism in which inhibitory binding of base to the metal is disfavored by the proximity of two catalytic sites.

Multinuclear late-transition-metal catalysts have recently been used to incorporate polar olefins by coordination IP.[6] Such catalysts are generally more tolerant of polar groups because of their reduced oxophilicity.[3b,f−h,7] In addition, their multinuclear nature has been proposed to disfavor the formation of stable chelates that can slow polymerization after polar olefin insertion.[6a] Bimetallic Ni complexes have thus been studied for the polymerization of olefins, including polar monomers.[6b]

We recently reported dinickel bisphenoxyiminato catalysts with pyridine (Py) auxiliary ligands for the copolymerization of ethylene and α-olefins.[8a] Permethylation of the central arene of the *p*-terphenyl (*p*-TPh) backbone allowed for the isolation of syn and anti atropisomers.[8a] The syn atropisomer **1-s-Py** (Figure 1) successfully polymerized ethylene in the presence of up to 500 equiv of tertiary amine per Ni center.[8b] This is notable in view of reports that related neutral Ni catalysts are more inhibited by tertiary amines than by water, alcohols, and ethers.[9] We attribute the increased tolerance to a steric effect wherein the binding of an amine to one Ni center of the syn atropisomer disfavors the binding of an amine to the other Ni, allowing the polymerization to continue.[8b] We expected this effect to allow for the incorporation of polar monomers, but the inherently low turnover and low levels of α-olefin incorporation of these catalysts precluded AO polymerization.

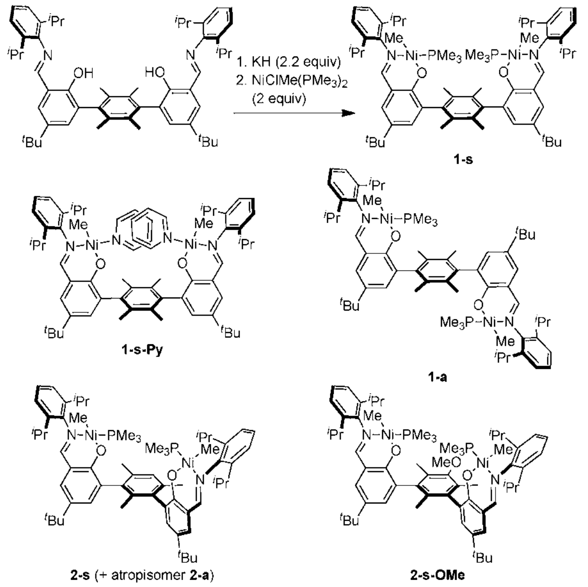

Figure 1. Dinickel bisphenoxyiminato complexes used in this study.

A variant of our bimetallic complex with a different auxiliary ligand was targeted because the stability of the Py-ligated complexes causes lower activity.[10] A variety of mono- and

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dinickel alkyl phenoxyiminato complexes with Py, amine, nitrile, and phosphine auxiliary ligands have been employed as catalyst precursors.[6c,9a,10] No activator or scavenger is needed for Py, amine, or nitrile auxiliary ligands, and the precursor behaves as a single-component catalyst.[8a,9a,10,11] For phosphine-ligated complexes, $Ni(COD)_2$ and $B(C_6F_5)_3$ were used as phosphine scavengers.[6c,9a,12] The PMe_3-ligated complexes **1-s** and **1-a** (Figure 1) were synthesized by deprotonation of the syn and anti *p*-terphenyl bisphenoxyimines, respectively, and subsequent metalation with $NiClMe(PMe_3)_2$. In ethylene/1-hexene copolymerization, **1-s** displayed a significant increase in activity (>2 orders of magnitude) relative to **1-s-Py** (Table 1, entries 1–3).

Table 1. Ethylene/1-Hexene Copolymerizations[a]

	complex	additive	yield (g)	*a*[b]	*R*[c]	%I[d]
1	**1-s-Py**	none[e]	0.003	1		–
2	**1-s-Py**	none[f]	0.033	1		1.0
3	**1-s**	none[e]	1.266	317		1.2
4	**1-a**	none[e]	1.590	397		1.1
5	**2-s**	none[e]	1.444	361		1.1
6	**2-a**	none[e]	1.469	367		1.0
7	**2-s-OMe**	none[e]	1.095	274		0.9
8	**1-s**	$NMeEt_2$	0.187	23	13	0.8
9	**1-a**	$NMeEt_2$	0.106	13	30	0.5
10	**2-s**	$NMeEt_2$	0.199	25	15	0.3
11	**2-a**	$NMeEt_2$	0.087	11	34	0.9
12	**2-s-OMe**	$NMeEt_2$	0.142	18	17	0.7
13	**1-s**	NEt_3	0.073	9	33	1.0
14	**1-a**	NEt_3	0.011	1	290	1.3
15	**2-s**	NEt_3	0.447	56	7	0.3
16	**2-a**	NEt_3	0.006	1	515	–
17	**2-s-OMe**	NEt_3	0.457	57	5	0.7
18	**1-s**	NMe^nPr_2	0.094	12	26	0.9
19	**1-a**	NMe^nPr_2	0.005	1	639	1.2
20	**2-s**	NMe^nPr_2	0.783	98	4	0.2
21	**2-a**	NMe^nPr_2	–[g]	–	–	–
22	**2-s-OMe**	NMe^nPr_2	0.165	21	14	0.7
23	**1-s**	N^nPr_3	–[g]	–	–	–
24	**1-a**	N^nPr_3	–[g]	–	–	–
25	**2-s**	N^nPr_3	0.447	56	6	0.2
26	**2-a**	N^nPr_3	–[g]	–	–	–
27	**2-s-OMe**	N^nPr_3	0.390	49	6	0.5

[a] Polymerizations were run for 1 h at 25 °C under ethylene (100 psig) in toluene with 4 μmol of dinickel complex, 4 equiv of $Ni(COD)_2$, and 500 equiv of 1-hexene and additive per Ni. Solution volume = 5 mL. [b] Activity, defined as mass of polymer (in g) per mmol of Ni per hour. [c] *R* = (activity without additive)/(activity with additive). [d] Mole percent incorporation of 1-hexene as determined from ^1H and ^{13}C NMR spectroscopy. [e] Polymerization was run for 0.5 h. [f] Polymerization was run for 3 h to get enough polymer for ^1H and ^{13}C NMR spectra. [g] Insufficient product for accurate mass determination (<1 mg).

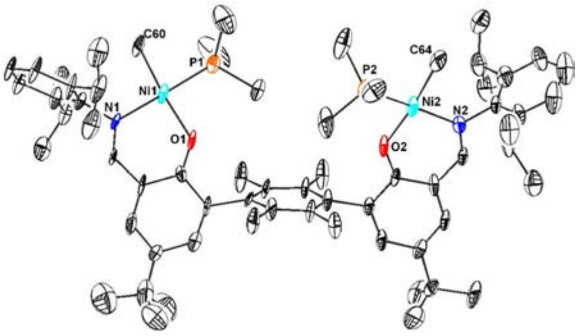


Figure 2. Solid-state structure of **1-s** with thermal ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

Complexes **2** (Figure 1), the *m*-TPh analogues of **1**, were synthesized to examine the effects of changing the Ni–Ni distance and the relative orientation of the Ni coordination planes. The orientation of **2-s-OMe** was verified by nuclear Overhauser effect spectroscopy [Figure S45 in the Supporting Information (SI)]. The solid-state structures of **1-s** and **2-s** confirmed the syn orientation relative to the central ring and the coordination of the PMe_3 groups trans to the imines (Figures 2 and S76).[13] The Ni–Ni distances are >8 Å, and the TPh backbones are bowed (average TPh backbone angle of 171° for **1-s** vs 177° for **1-s-Py**).[8b] The Ni–Ni distance is significantly longer in **1-s** (8.9 Å) than in **1-s-Py** (7.1 Å).[8b] This likely occurs because the PMe_3 ligands have a relatively conical steric profile, whereas the planar Py ligands of **1-s-Py** can avoid steric repulsion. The structural distortion of the ligand framework supports our proposal that the decreased inhibition by amines with the syn isomer versus the anti isomer is due to steric repulsion that hinders binding of amines at both Ni centers.

The five PMe_3-ligated dinickel complexes displayed similar activities and 1-hexene incorporation in ethylene/1-hexene copolymerizations (Table 1, entries 3–7). The generated polymer contains primarily methyl and butyl branches, similar to the Py-ligated analogues, and up to 1.2% incorporation of 1-hexene (as calculated from ^1H and ^{13}C NMR data).[8a] Polymerizations run over different time periods indicated that the catalysts continued to produce polymer over the course of the trial (Tables S3 and S4 in the SI).[14] Ethylene/1-hexene copolymerizations in the presence of tertiary amines revealed distinct inhibition trends. As expected from our previous studies of the Py-ligated catalysts,[8b] the anti atropisomers were much more inhibited than the syn isomers but their incorporation of 1-hexene was not significantly affected (e.g., entries 13–16). **2-s** and **2-s-OMe**, which experienced the least inhibition of activity, produced polymers with the lowest levels of 1-hexene incorporation (e.g., entries 15 and 17). The relative activities can be rationalized by the mechanistic proposal that steric interactions disfavor the binding of amines to both Ni centers in the syn complex.[8b] Thus, a shorter Ni–Ni distance should disfavor the binding of a second amine, as observed for **2-s**.

For **2-s**, where the metal centers are closest, the presence of amines cause the greatest decrease in 1-hexene incorporation (from 1.1 to 0.2–0.3%; Table 1, entries 5, 10, 15, 20, and 25). For **1-s**, the 1-hexene incorporation dropped only from 1.2 to 0.8–1.0% (entries 3, 8, 13, and 18), but there was a greater activity decrease than for **2-s**. The steric considerations for simultaneous binding of two amines also apply to the relative binding of ethylene and 1-hexene when one amine is coordinated. For the closely spaced metal centers in **2-s**, amine coordination more strongly affects binding at the second metal site, resulting in less favorable 1-hexene coordination than for **1-s**. Variation in 1-hexene incorporation is expected to affect the catalyst activity, as previous reports indicated that the overall activity of the catalyst decreased significantly when an α-olefin was copolymerized with ethylene relative to the homopolymerization of ethylene.[8a,11a,15] Ethylene/1-hexene copolymerizations with **2-s** and **2-s-OMe** in the presence of amines resulted in different levels of incorporation of 1-hexene and a divergent trend in the activity (**2-s-OMe** produced more polymer in the presence of N^nPr_3 than in the presence of NMe^nPr_2, opposite to what was seen with **2-s**;

Table 1, entries 20, 22, 25, and 27). These dissimilarities between the two syn complexes with *m*-TPh backbones suggest that subtle differences in the sterics affect the polymerization behavior and that tuning of the ligand framework may allow for optimization of the polymerization.

The ability of the reported complexes to incorporate 1-hexene in the presence of amines suggested that these complexes might be effective for the polymerization of AOs. AO substrates were selected to have ethyl or propyl substituents on the basis of the ability of the syn catalysts to perform ethylene/1-hexene copolymerizations in the presence of such tertiary amines (Table 1). Indeed, the use of a variety of tertiary AOs (500 equiv) in copolymerizations with ethylene resulted in incorporation levels similar to those for 1-hexene (0.4−0.8 and 0.3−0.4% with **1-s** and **2-s**, respectively; Table 2, entries 3−14). Incorporation of N(allyl)^{n}Pr$_2$ was not successful with **1-s**, but 0.1% incorporation was achieved using **2-s**. The proximity of the large N^{n}Pr$_2$ moiety at the allylic position likely hinders binding of olefin to the metal and insertion. All of the longer-chain olefins were incorporated by both **1-s** and **2-s**. The number of CH$_2$ units between the olefin and amine moieties (beyond allylamine) did not significantly affect the level of polar monomer incorporation. Copolymerizations of ethylene and N(pentenyl)^{n}Pr$_2$ performed with **1-a**, **2-a**, and **2-s-OMe** yielded no polymer, 6 times less polymer than with **2-s** with 0.7% incorporation, and results similar to those for **2-s**, respectively (entries 15−17).

Table 2. Ethylene/Amino Olefin Copolymerizations[a]

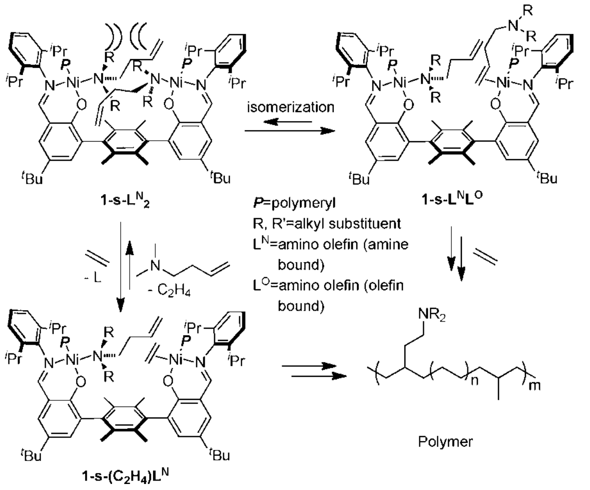
	complex	comonomer	yield (g)	a^{b}	%I^{c}
1	**1-s**	N(allyl)^{n}Pr$_2$	0.034	8	0.0
2	**2-s**	N(allyl)^{n}Pr$_2$	0.083	21	0.1
3	**1-s**	N(butenyl)^{n}Pr$_2$	0.019	5	0.4
4	**2-s**	N(butenyl)^{n}Pr$_2$	0.044	11	0.4
5	**1-s**	N(pentenyl)^{n}Pr$_2$	0.064	16	0.5
6	**2-s**	N(pentenyl)^{n}Pr$_2$	0.178	45	0.3
7	**1-s**	N(hexenyl)^{n}Pr$_2$	0.063	16	0.7
8	**2-s**	N(hexenyl)^{n}Pr$_2$	0.217	54	0.3
9	**1-s**	N(heptenyl)^{n}Pr$_2$	0.059	15	0.8
10	**2-s**	N(heptenyl)^{n}Pr$_2$	0.310	78	0.3
11	**1-s**	N(octenyl)^{n}Pr$_2$	0.050	13	0.7
12	**2-s**	N(octenyl)^{n}Pr$_2$	0.398	100	0.3
13	**1-s**	N(pentenyl)Et$_2$	0.034	8	0.5
14	**2-s**	N(pentenyl)Et$_2$	0.151	38	0.3
15	**1-a**	N(pentenyl)^{n}Pr$_2$	–[d]	–[d]	–[d]
16	**2-a**	N(pentenyl)^{n}Pr$_2$	0.032	8	0.7
17	**2-s-OMe**	N(pentenyl)^{n}Pr$_2$	0.176	44	0.3

[a] Polymerizations were run for 0.5 h at 25 °C under ethylene (100 psig) in toluene with 4 μmol of dinickel complex, 4 equiv of Ni(COD)$_2$, and 500 equiv of comonomer per Ni. Solution volume = 5 mL. [b] Mass of polymer (in g) per mmol of Ni per hour. [c] Mole percent incorporation of comonomer as determined by ^{1}H NMR spectroscopy. [d] Insufficient product for accurate mass determination (<1 mg).

Diffusion-ordered NMR spectroscopy confirmed that the amines were incorporated into the polymers (see Figures S72 and S73). The diffusion constant for the CH_2 peak of the polymer chain (at 1.4 ppm in C$_2$Cl$_4$D$_2$) matched the diffusion constant for the NCH_2 peaks (at 3.0 ppm). AO incorporation levels were lower and the activities higher with **2-s** than with **1-s** for all of the polar monomers investigated, mirroring the copolymerizations with 1-hexene in the presence of amines (vide supra). The levels of polar monomer incorporation were in the same range as for 1-hexene. The possibility that the incorporation of amines could lead to the formation of chelates that would inhibit polymerization or lead to termination was considered. The AO monomers were examined by 1D total correlation NMR spectroscopy (TOCSY) and compared with the polymers. The TOCSY spectra of the AO precursors showed correlations between the NCH_2 peak and the olefinic peaks that were not observed for the polymers, indicating that the polymers were not terminated by the amine monomers (Figure S74).

The similar levels of incorporation of AO and 1-hexene (in the presence of tertiary amines) and the activity profiles in copolymerizations with various catalysts support a related mechanism of polymerization for the two cases (Scheme 1).

Scheme 1. Mechanism for Ethylene/AO Copolymerization



Coordination of the amine moiety to Ni sterically hinders binding of an amine to the second Ni center for the syn complexes. Ethylene or the olefin moiety of the polar monomer have a lower steric profile than the amine and hence can coordinate to the second Ni and afford chain growth.

The incorporation of AOs with the present catalysts is notable for several reasons. Monometallic neutral Ni catalysts are greatly inhibited by amines, as reported previously[9a] and also observed for **1-a-Py**,[8b] **1-a**, and **2-a** relative to the syn analogues. The proposed mechanism for polymerization and polar olefin incorporation relies on two Ni centers but is distinct from previous proposals.[6] Other dinickel complexes have been claimed to incorporate polar monomers by a mechanism in which insertion of the monomer into the polymer growing at one Ni center is followed by coordination of the polar moiety to the second Ni center, thereby avoiding chelation that would slow the polymerization.[6a] Also, greater incorporation of various monomers was explained by concomitant coordination of a CH bond or polar group to one Ni center and an olefin to the other, thus favoring comonomer coordination and insertion.[6a,c] The mechanism at work with the present catalysts is not consistent with those proposals because the Ni centers are likely too distant for a single monomer to coordinate to both. Moreover, for those proposed mechanisms, varying the number of CH$_2$ groups between the amine and olefin functionalities should have a significant effect on the degree of polar monomer incorporation, which was not observed here (Table 2).

The proposed mechanism (Scheme 1) is expected to extend to other classes of polar monomers. Binding of polar olefins through the heteroatom instead of the olefin typically leads to different steric profiles around the metal center. In the present design, binding of the olefin orients the substituents in the plane perpendicular to the metal−olefin interaction and away from the second metal center. Conversely, coordination of the amine (or other polar) moiety would be expected to direct the steric bulk toward the second metal center. Hence, judicious design of the metal−metal distance and ligand steric properties could be employed for the copolymerization of other polar olefins.

In summary, we have synthesized a series of rigid terphenyl dinickel bisphenoxyiminato complexes with phosphine auxiliary ligands that exhibit activity for copolymerization of ethylene and amino olefins. The syn complexes are more active than the anti analogues because of a bimetallic effect arising from the proximity of the Ni centers. The polar monomers and 1-hexene are incorporated at similar levels. Comparisons between the *m*- and *p*-TPh catalyst systems support a mechanism in which inhibitory coordination of amines at both Ni centers is disfavored because of steric repulsion. Thus, coordination of olefin moieties with smaller steric profiles is favored, allowing for polymer formation and polar monomer incorporation. Future efforts will focus on extending the present approach for polar olefin polymerization to other monomers and catalyst types in order to increase the level of functional group incorporation, catalyst activity, and tolerance of other polar groups.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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