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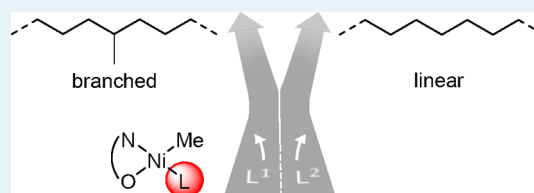
Ancillary Ligands Impact Branching Microstructure in Late-Transition-Metal Polymerization Catalysis

Philip Kenyon,[†] Laura Falivene,[§] Lucia Caporaso,^{*,‡} and Stefan Mecking^{*,†}[†]Chair of Chemical Materials Science, Department of Chemistry, University of Konstanz, 78457 Konstanz, Germany[§]Physical Sciences and Engineering Division, Kaust Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia[‡]Dipartimento di Chimica e Biologia, Università di Salerno, Via Papa Paolo Giovanni II, I-84084 Fisciano, Italy

Supporting Information

ABSTRACT: The influence of the labile ligand on the rate of β -hydride elimination (BHE) for salicylaldiminato Ni(II) complexes is shown using a series of precatalysts which differ only in the labile ligand but produce polyethylenes with a range of molecular weights ($M_n = 466$ to 100 kg mol^{-1}), degrees of branching (1.7 to 7.3 branches/1000 C), and melting temperatures (from 132 to 123°C) under the same conditions. The use of a weakly coordinating solvent (diethyl ether) was able to suppress this increase in BHE. DFT studies on a related salicylaldiminato Ni(II) complex show that BHE can feasibly occur following recombination of the labile ligand with the catalyst.

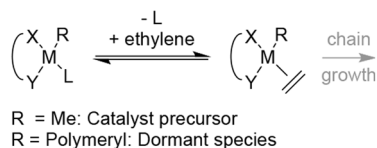
KEYWORDS: homogeneous nickel(II) catalysts, ethylene insertion polymerization, mechanism, density functional theory, polyethylene



Catalysts for olefin polymerization based on late transition metals typically comprise a bidentate or multidentate ligand bound to the active site. This controls fundamental steps of polymer formation, namely insertion into the growing chain and β -hydride elimination (BHE). A control of BHE is essential, as it is a key to chain transfer and branch formation by “chain walking” and thus ultimately determines polymer molecular weights and degrees of branching.^{1–6}

Other coordinating species present are generally considered to not impact these pathways and the balance between them. Thus, in single-component catalyst precursors, the “ancillary” ligand L (Scheme 1) which stabilizes the complex is thought to

Scheme 1. Activation of Catalyst Precursors by Displacement of an Ancillary Ligand L and Possible Reversible Formation of Dormant Species during Polymerization



R = Me: Catalyst precursor
R = Polymeryl: Dormant species

impact productivities via its ease of displacement by the monomer substrate but not to otherwise affect the product microstructure in terms of branching or molecular weight.

We now show for the exemplary case of a neutral Ni(II) catalyst that this ancillary ligands can clearly impact branching microstructures and polymer properties. This is related to the mechanism of chain growth and BHE in catalysts with an

unsymmetrical environment, that is with two different donors in the bidentate ligand ($X \neq Y$).

Salicylaldiminato Ni(II) catalysts stand out for their functional group tolerance,^{4,7} enabling aqueous polymerizations.⁸ Also, they allow for an unprecedented control of microstructure^{9,10} particularly via substituents on their bidentate N[^]O-ligand,^{11–13} giving access to both hyperbranched oligomers¹⁴ and moderately branched¹⁵ or linear ultrahigh-molecular-weight polyethylene.¹⁶ By contrast, the ancillary ligand is presumed to only modulate the activity; this is the case in both computational investigations and practical experiments where the use of cocatalysts such as Lewis acids¹⁷ and phosphine scavengers⁷ or phase-transfer activation is widespread.^{18,19}

For this study, the salicylaldiminato catalyst structure 1-L (Figure 1) was chosen, with the rationale that the pyridine

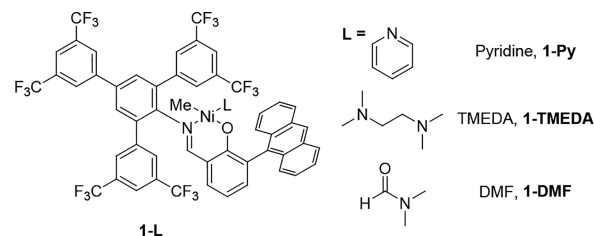


Figure 1. General catalyst structure of 1-L and labile ligands investigated.

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Table 1. Ethylene Polymerization Results with Precatalysts 1-L in Toluene and Diethyl Ether^a

entry	precatalyst	T (°C)	yield (g)	TOF ^b	M _n (× 10 ³ g mol ⁻¹) ^c	M _w /M _n ^c	T _m (°C) ^d	crystallinity (%) ^d	branches (/1000 C) ^e
1	1-Py	10	0.4	0.38	216	1.5	140/134	75/64	0.6
2	1-Py	20	2.6	2.81	505	1.2	141/135	74/58	1.2
3	1-Py	30	4.1	4.35	466	1.6	140/132	73/52	1.7
4 ^f	1-TMEDA	10	0.6	3.40	557	1.4	143/136	75/60	1.1
5 ^f	1-TMEDA	20	1.5	8.15	237	2.5	141/130	70/54	3.3
6 ^f	1-TMEDA	30	2.1	11.50	100	1.9	127/123	67/54	7.3
7 ^g	1-DMF	10	0.5	1.45	505	1.9	144/135	62/46	1.0
8 ^g	1-DMF	20	1.2	3.24	232	2.7	145/134	58/47	2.1
9 ^g	1-DMF	30	4.2	11.28	133	3.1	127/126	59/45	5.8
10 ^h	1-TMEDA	10	2.6	5.66	749	1.6	144/136	65/49	0.9
11 ^h	1-TMEDA	20	4.6	9.86	579	1.8	144/135	63/46	0.8
12 ^h	1-TMEDA	30	7.6	16.32	505	1.9	143/134	61/49	1.0

^aPolymerization conditions: 5 μmol of precatalyst, 100 mL of toluene, 40 bar of C₂H₄, 40 min. ^b10⁴ × mol [C₂H₄] × mol⁻¹ [Ni] × h⁻¹. ^cDetermined by GPC at 160 °C. ^dDetermined by DSC, 1st/2nd heating, 10 K min⁻¹. ^eDetermined by ¹³C NMR spectroscopy. ^fCarried out with 1 μmol of precatalyst. ^gCarried out with 2 μmol of precatalyst. ^hCarried out with 2 μmol of precatalyst in 100 mL of diethyl ether.

complex (1-Py) shows minimal branching at low temperatures so any deviations from the virtually linear microstructure will be clearly observable.

The labile ligands *N,N,N',N'*-tetramethylethylenediamine (TMEDA), dimethylformamide (DMF) and pyridine were chosen as anticipated isolable species with ligands, L, with very different binding strengths.

On the basis of exchange experiments (discussed in the SI) and polymerization experiments (see Table 1 and Figure 2),

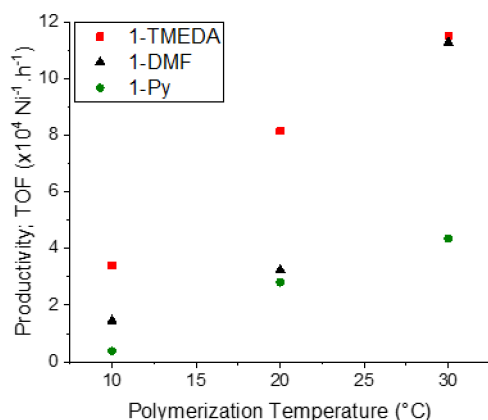


Figure 2. Productivity of 1-L showing clearly the influence of the labile ligand on catalyst activity.

the strength of binding was determined to be pyridine (1-Py) > DMF (1-DMF) > TMEDA (1-TMEDA). This differing coordination strength is reflected in the polymerization activities at a low temperature of 10 °C where binding of pyridine significantly hinders polymerization.

Polymerization was carried out with an appropriately efficient cooling and heating system, such that the polymerization temperature was carefully controlled (<0.5 °C above the stated temperature throughout the reaction) ensuring that the heat generated by polymerization did not influence the rate of BHE.

For this reason, catalyst loadings had to be reduced for the more active catalysts (1-DMF and 1-TMEDA). This hampers a very detailed comparison of the productivities as trace impurities may have an increasing influence on polymerization as the loading is decreased. However, it is clear that as the

labile ligand becomes less strongly binding the polymerization activity increases with 1-TMEDA showing the highest productivity.

At 10 °C, the degree of branching is low for all catalysts, and differences between the catalysts are therefore difficult to observe (see Table 1, entries 1, 4, and 7). As temperature increases, the degree of branching increases for all catalysts, reflective of the increased rate of BHE (Figure 3). The catalysts can be distinguished however by the considerable difference in the degree of branching as the temperature is increased. The degree of branching increases very little for 1-Py (compare Table 1, entries 1 and 3) but by comparison for 1-TMEDA there is a large increase of branching from 1.1 (Table 1, entry 4) to 7.3 (Table 1, entry 6) branches per 1000 carbon atoms over the same temperature range. The polyethylene produced by 1-DMF at 30 °C is comparable to 1-TMEDA but slightly more linear (Figure 3).

These differences in the degree of branching also have a significant influence on the melting temperature of the polyethylene produced, with a change of over 10 °C being observed by changing the labile ligand at 30 °C (compare Table 1, entries 3 and 6). The differing rates of BHE were also shown to have an effect on the molecular weight of the polymer produced with the polyethylene produced by 1-Py at 30 °C being more than 4 times higher in molecular weight versus the polymer produced by 1-TMEDA at the same temperature.

In view of this clear impact of the coordination strength of the ancillary ligand on the catalytic properties, an effect of coordinating solvents on the polymer microstructure was also explored. Salicylaldiminato catalysts have been shown to polymerize ethylene even in coordinating solvents such as THF or diethyl ether.¹⁶ While at the low temperatures considered here, polymerization in THF was unsuccessful, 1-TMEDA was found to be highly active for polymerization in diethyl ether, showing productivities comparable to those achieved in toluene, with a linear, high-molecular-weight polymer being obtained even at 30 °C (1.0 branches/1000 C vs 7.3/1000 C in toluene). This underlines the impact of weakly coordinating species on the polymerization behavior.

The mechanistic origin of the experimentally observed impact of the labile ligand introduced with the catalyst precursor or coordinating solvent on polymer microstructure was elucidated by DFT studies. These employed the

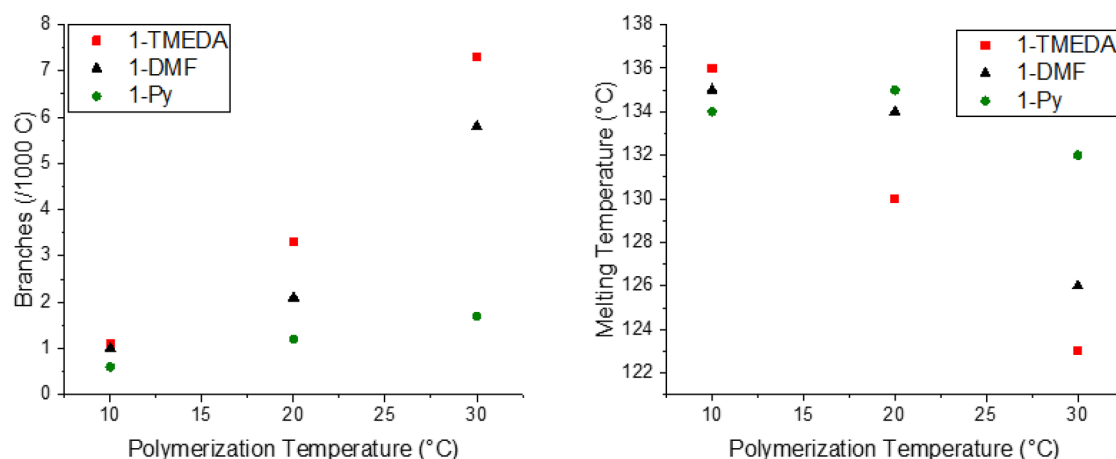


Figure 3. Plots showing the increasing in branching (left) and the decrease in melting temperature (right) for the three precatalysts considered.

salicylaldiminato motif of **2** (Figure 4), as this has been studied extensively with regard to catalytic reaction pathways.¹²

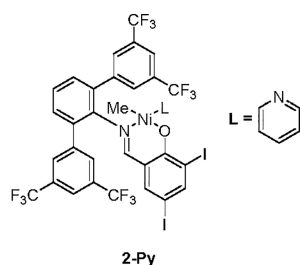


Figure 4. Structure of the complex examined using computational methods.

These DFT studies suggest that insertion occurs exclusively from species with the alkyl chain arranged in the *cis*-position with respect to oxygen, leading to the alkyl chain being found *trans*- to oxygen immediately after insertion.^{12,20,21} This *trans*-polymeryl species (stabilized by a β -agostic interaction) does not undergo BHE for kinetic and thermodynamic reasons. For BHE to occur, the alkyl chain must be *cis*- to oxygen; however, direct isomerization is prohibited by the high energy of the transition state ($\Delta G^\ddagger = 30$ kcal mol⁻¹ approximately).^{12,21} Rather, BHE occurs after coordination of ethylene, isomerization, and dissociation of ethylene to give the (β -agostic) *cis*-alkyl species.¹²

This mechanistic scenario did not comprise an ancillary ligand introduced with the catalyst precursor. In principle, the role of ethylene in such *cis*/*trans*-isomerizations could be

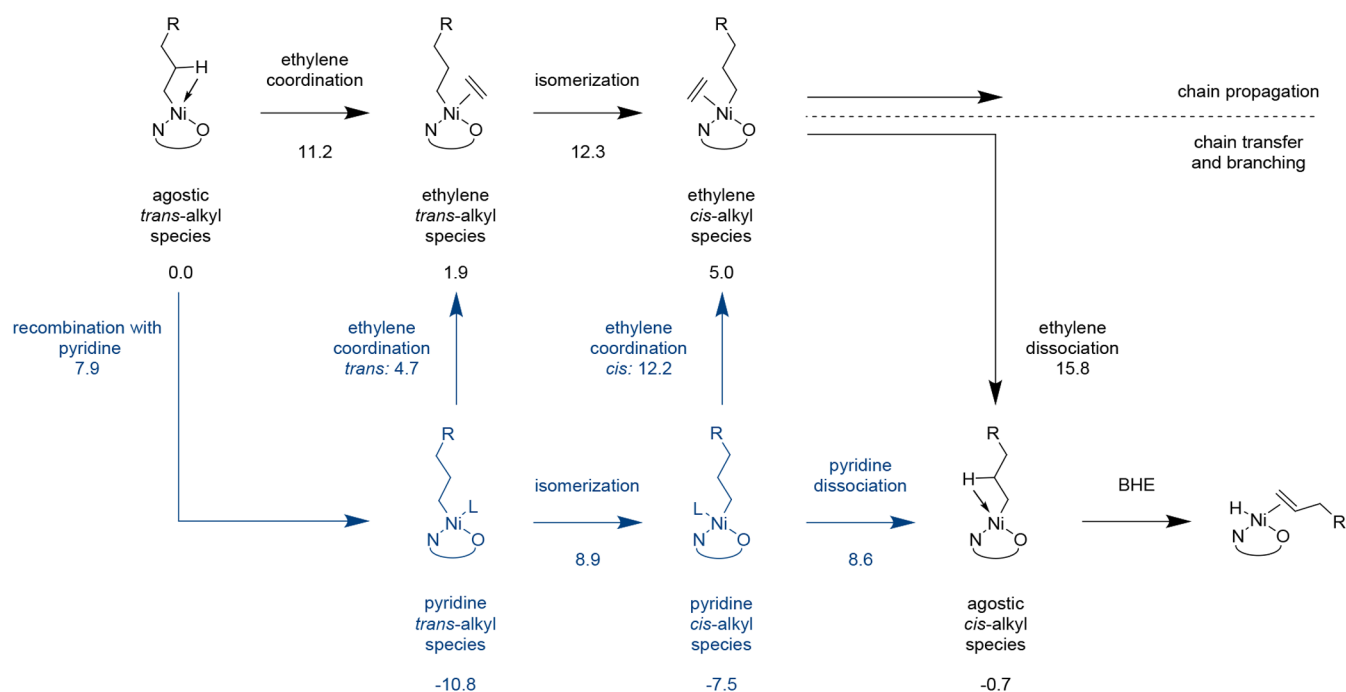


Figure 5. DFT pathways comparing the energy barriers of two pathways to form the agostic *cis*-alkyl species required for BHE. The pathway involving the recombination of pyridine ("pyridine pathway") is shown in blue and the previously determined pathway involving ethylene ("ethylene pathway") is shown in black. Gibbs free energies of all intermediates and transition-states are given in toluene in kcal mol⁻¹.

amended by other coordinating species such as the labile ligand or coordinating solvents. This was investigated here for the case of pyridine as an exemplary ligand (2-Py, see Figure 4).

Starting from the agostic *trans*-alkyl species formed after insertion, binding of pyridine is highly favorable (almost 10 kcal mol⁻¹), in agreement with NMR observations on related salicylaldiminato complexes.¹⁵ From the pyridine *trans*-alkyl species, the barrier for the isomerization to the less favorable pyridine *cis*-alkyl species and for the subsequent dissociation of pyridine to form the agostic *cis*-alkyl species which undergoes BHE (see “pyridine pathway” in blue in Figure 5) is approximately 20 kcal mol⁻¹. Although the competing displacement of pyridine by ethylene is favored by almost 4 kcal mol⁻¹, the determining barrier to the agostic *cis*-alkyl species via the “ethylene pathway” (shown in black in Figure 5) is overall more than 6 kcal mol⁻¹ higher than via the “pyridine pathway”. Interestingly, experimental data for the *cis*-/ *trans*-isomerization of a corresponding Ni-ethyl complex with DMSO as a ligand yielded an estimated barrier of 16.3–17.0 kcal mol⁻¹,²² in good agreement with the aforementioned calculated value.

This barrier only 4 kcal mol⁻¹ higher than that calculated from the agostic *trans*-alkyl species involving ethylene (see “ethylene pathway” in black in Figure 5) confirms that isomerization of complexes [(N[^]O)NiR(L)] (R = polymeryl) at typical polymerization temperatures is feasible. Note that isomerization of the methyl group and the labile ligand was also noted for precatalysts with weakly coordinating ancillary ligands.²³

As both pathways have accessible barriers to the formation of the agostic *cis*-alkyl species (i.e., 15.8 and 19.7 kcal mol⁻¹ for the “ethylene pathway” and “pyridine pathway”, respectively), whether one predominates under reactor conditions or whether they are both operative is not evident a priori and may depend heavily on the conditions of each reaction and the individual catalyst and ancillary ligand, L, combination. However, these DFT studies clearly show that there is no prohibitive barrier to BHE from ligand coordinated “dormant” species.

In summary, additional coordinating ligands introduced with catalyst precursors or otherwise, including solvents, not only impact catalyst productivities but also polyethylene branching microstructures and molecular weights. This is of immediate practical relevance particularly when a very high linearity and very high molecular weights are sought. These properties are strongly reflected in mechanical properties, like strength or abrasion resistance.

Although they do not allow for an a priori prediction of the effect for a given ligand/catalyst, mechanistic considerations supported by DFT studies provide a rationale for the origin of this experimentally observed impact on polymer microstructure. Essentially, ligand or solvent coordinated “dormant” species can provide additional pathways for *cis*-/ *trans*-isomerization and for the formation of the key species undergoing BHE. This alters the competition between chain growth and BHE, the latter being the key step in branch formation and chain transfer. This scenario may apply to many polymerization catalysts with an unsymmetrical coordination environment.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b04028.

Procedures for polymerization of ethylene; synthesis of new complexes; qualitative determination of ligand binding strength; computational details; Cartesian coordinates for pyridine pathway (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for L.C.: lcaporaso@unisa.it.

*E-mail for S.M.: stefan.mecking@uni-konstanz.de.

ORCID

Philip Kenyon: 0000-0003-0244-1347

Laura Falivene: 0000-0003-1509-6191

Stefan Mecking: 0000-0002-6618-6659

Notes

The authors declare no competing financial interest.

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