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Ethylene (co) oligomerization using iminopyridyl Ni(II) and Pd(II) complexes bearing benzocycloalkyl moieties to access hyperbranched ethylene oligomers and ethylene-MA co-oligomers

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Hyperbranched ethylene oligomers and polar functionalized co-oligomers synthesized *via* ethylene chain walking (co) oligomerization is a very attractive strategy. In this study, a series of dibenzhydryl iminopyridyl ligands with benzocycloalkyl and naphthyl moieties and the corresponding Ni(II) and Pd(II) complexes were synthesized and characterized. The Ni(II) complexes were highly effective in ethylene oligomerization and ethylene oligomers with hyperbranched microstructures were generated from this system. The corresponding Pd(II) complexes showed moderate oligomerization activities in ethylene oligomerization and hyperbranched ethylene oligomers were also yielded from the system. More significantly, the Pd(II) complexes can also effectively promote the co-oligomerization of ethylene with methyl acrylate (MA) to obtain hyperbranched polar functionalized ethylene-MA co-oligomers. The reaction temperature, catalyst ligand structure and metal type all have significant effects on ethylene (co) oligomerization with respect to catalytic activity, molecular weight and topology of the oligomers.

KEYWORDS

Ni(II) and Pd(II) complexes, ethylene oligomerization, hyperbranched, benzocycloalkyl, ethylene-MA co-oligomers

Introduction

The ethylene chain walking (co) oligomerization is a very attractive strategy for the direct synthesis of hyperbranched ethylene oligomers and polar functionalized co-oligomers (Stephenson et al., 2014; Wiedemann et al., 2014; Falivene et al., 2018; Mecking and Schmitte, 2020). Over the years, an impressive research effort has been conducted to rationally design ligands that enable a better control of the ethylene oligomerization and on the resulting oligomer microstructure (Tomov et al., 2006; Junges et al., 2007; Mukherjee et al., 2009; Albahily et al., 2011; Alzamy et al., 2013; Yang et al., 2014; Hameury et al., 2015; Luo et al., 2016; Liu et al., 2017; Nifant'ev et al., 2018; Sydora, 2019; Olivier-Bourbigou et al., 2020; Yeh et al., 2021). In particular, a few late-transition metal catalysts have made important advances in the preparation of branched ethylene oligomers *via* the chain walking mechanism. For example, a few N,N-iminopyrrolyl and N,O-salicylaldiminato neutral Ni(II) catalysts with specially designed ligands (Stephenson et al., 2014; Wiedemann et al., 2014; Falivene et al., 2018; Mecking and Schmitte, 2020; Cruz et al., 2021) and cationic Ni(II)- and Pd(II)- α -diimine catalysts with minor steric hindrance (Xiang et al., 2011; Meduri et al., 2013; Guo et al., 2019a) were used in the synthesis of hyperbranched ethylene oligomers and hyperbranched ethylene-based polar functionalized co-oligomers. Lately, a series of novel iminopyridyl Ni(II) and Pd(II) catalysts have also been developed to yield hyperbranched ethylene oligomers and ethylene-based co-oligomers (D'Auria et al., 2017; Saki et al., 2020; Li et al., 2021; Yan et al., 2021). Compared to the widely used α -diimine systems, which are typically used to prepare polyethylene or ethylene-based copolymers of high molecular weights, these iminopyridyl catalysts possessing a unilateral steric hindrance are known for the synthesis of low molecular weight polyethylene (Chart 1A). (Laine et al., 1999; Meneghetti et al., 1999; Laine et al., 2000; Bianchini et al., 2010) Many improvements in terms of catalytic activity, thermal stability and properties of the resulting polymer have been made *via* the introduction of bulky ortho-aryl substituents, modification of the pyridine backbone and electronic tuning (Chart 1) (Yue et al., 2014; Huang et al., 2015; Chen et al., 2016; Dai et al., 2016; Huang et al., 2016; Chen et al., 2018; Guo et al., 2019b; Dai and Li, 2020; Ge et al., 2021; Li and Dai, 2021; Peng et al., 2021; Fan et al., 2022a; Fan et al., 2022b; Yan et al., 2022a). Among all the modified catalysts, a series of half "sandwich" iminopyridyl Ni(II) and Pd(II) complexes bearing an 8-aryl-naphthyl substituent (Chart 1B) and rotation-restricted iminopyridyl Ni(II) and Pd(II) complexes with dibenzosuberyl groups (Chart 1C) can effectively suppress chain transfer in ethylene polymerization to yield high-molecular-weight polyethylene and ethylene-based copolymers (Chen et al., 2016; Dai et al., 2016; Dai and Li, 2020; Ge et al., 2021; Li and Dai, 2021; Peng et al., 2021). In contrast, N-teraryl iminopyridyl Ni(II) and Pd(II)

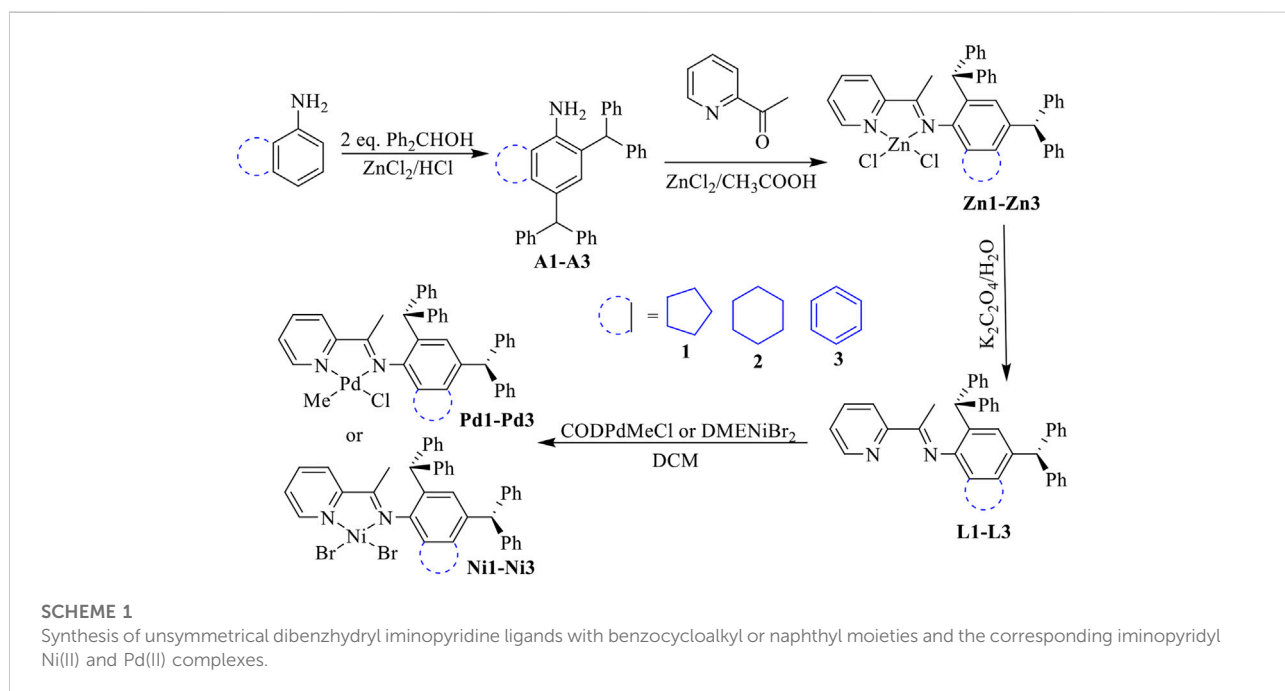
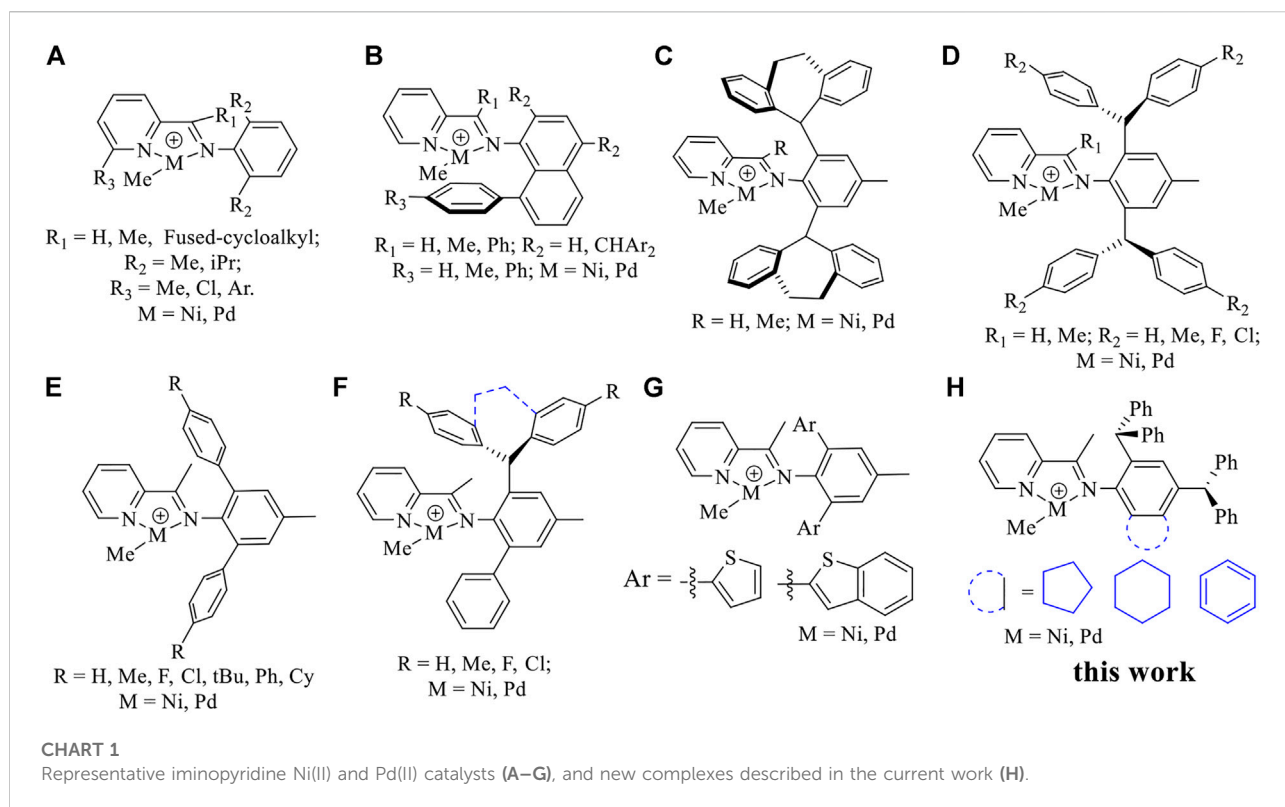
catalysts with weak neighboring group interactions were prone to simultaneous chain walking and chain transfer reactions, thus facilitating the synthesis of hyperbranched ethylene oligomers and ethylene-MA co-oligomers (Charts 1E,G) (Fan et al., 2022a; Fan et al., 2022b; Yan et al., 2022a). More interestingly, the hybridized form of the mentioned above two types (Charts 1C,E) was also highly effective in suppressing chain transfer in ethylene polymerization to yield high-molecular-weight polyethylene (Chart 1F) (Ge et al., 2021).

In the present study, we designed and synthesized a series of iminopyridyl Ni(II) and Pd(II) complexes (Chart 1H) with benzocycloalkyl and dibenzhydryl moieties. These new iminopyridyl complexes exhibited superior performance in ethylene (co)oligomerization.

Results and discussion

Synthesis and characterization of iminopyridine nickel and palladium complexes

Unsymmetrical bulky dibenzhydryl anilines **A1-A3** containing benzocycloalkyl or naphthyl moieties were synthesized *via* condensation with 2 eq. of benzhydrol in the presence of zinc chloride and hydrochloric acid (Scheme 1). The anilines were obtained in high yields (83–90%) with no need for chromatographic purification and were characterized by using ^1H and ^{13}C NMR (Supplementary Figures S1–S4) and mass spectrometries (Supplementary Figures S15,S16). Further condensation with 2-acetylpyridine using the template-type method afforded the iminopyridine ligands **L1-L3** (Scheme 1). (Rosa et al., 2008; Guo et al., 2018) The ligands were also prepared in high yields (69–83%) with no chromatography involved and were characterized by using ^1H and ^{13}C NMR (Supplementary Figures S5–S8) and mass spectrometries (Supplementary Figures S17,S18). Ni(II) complexes **Ni1-Ni3** were obtained in excellent yields (88–96%) by reaction with one equivalent of $[\text{NiBr}_2(\text{DME})]$ (DME = dimethoxyethane) (Scheme 1). The purity and identity of complexes **Ni1-Ni3** were examined by elemental analyses and MALDI-TOF MS. Similarly, the corresponding Pd(II) complexes **Pd1-Pd3** were synthesized in outstanding yields (90–92%) by exposing the ligands **L1-L3** to PdCIME(COD) (COD = 1,5-cyclooctadiene) (Scheme 1). The purity of the obtained Pd(II) complexes was verified by ^1H and ^{13}C NMR spectrometry (Supplementary Figures S9–S14), elemental analyses and MALDI-TOF MS. The coordination of the palladium precursor shifts the positions of the characteristic peaks in the ^1H and ^{13}C NMR spectra of the corresponding ligands. Due to the electron-absorbing nature of the palladium metal, most of these characteristic peaks are



shifted to lower fields. More interestingly, due to the asymmetry of the palladium precursors, the resulting complexes have two isomers with different ratios (cf. ESI).

Single crystals of complex **Pd2** were obtained by layering its CH_2Cl_2 solution with hexanes at room temperature. As shown in **Figure 1**, the **Pd2** complex adopts an approximate square-

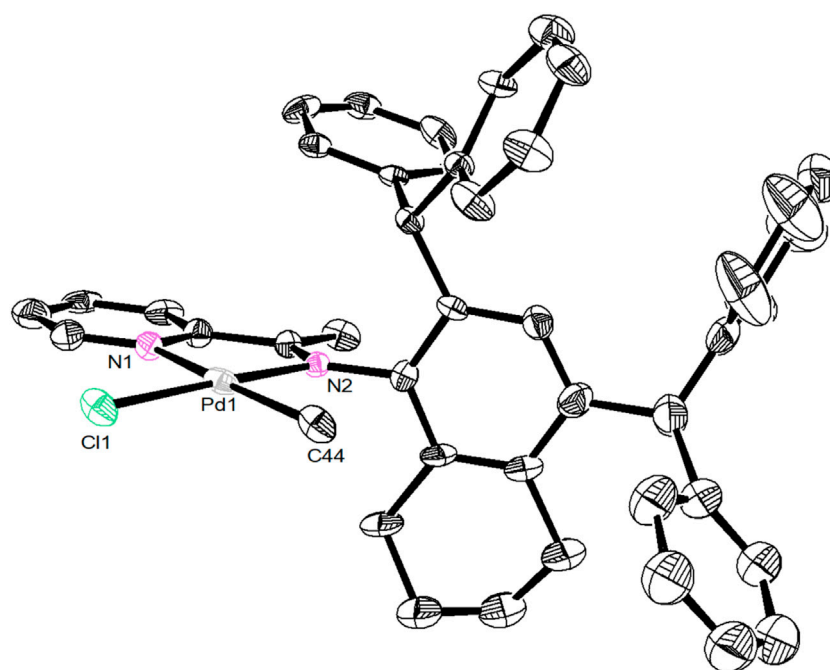


FIGURE 1

A view of the solid-state molecular structure of Pd2 (2164023). Ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity.

TABLE 1 Ni(II) catalysts for ethylene oligomerization^a.

Entry	Precatalyst	T/°C	Yield/g	Activity ^b	M _n (NMR) ^c	B ^d
1	Ni1	30	2.31	13.86	726	95
2	Ni1	50	1.53	9.18	543	105
3	Ni1	70	0.85	5.10	493	117
4	Ni2	30	1.59	9.54	1802	86
5	Ni2	50	1.58	9.48	1072	100
6	Ni2	70	1.08	6.48	792	102
7	Ni3	30	2.07	12.42	737	86
8	Ni3	50	1.46	8.76	645	99
9	Ni3	70	0.96	5.76	591	104

^aConditions: 1 μmol Ni(II) complexes, 200 eq. Et₂AlCl, 20 ml toluene, 1 ml CH₂Cl₂, 10 min polymerization time, 6 atm.

^bActivity = 10⁶ g/(mol Ni·h).

^cM_n (g mol⁻¹) estimated from ¹H NMR, peak intensities.

^dB is the number of branches per 1000 carbons, B = 1000 × 2(I_{CH3})/3(I_{CH2+CH} + I_{CH3}), including saturated end groups.

planar geometry around the palladium center and the phenyl groups in the dibenzhydryl substituent deviate from the axial position of the palladium center. This is responsible for the facile chain transfer reaction observed during the polymerization. In addition, the benzocyclohexyl group exhibits a sterically distorted conformation to provide a more favorable steric environment.

Ni(II) complexes catalyzed ethylene oligomerization

Upon activation by 200 eq. of Et₂AlCl, the Ni(II) complexes demonstrated extremely high ethylene oligomerization activity (level of 10⁶–10⁷ g mol⁻¹ h⁻¹) and yielded low molecular weight (ca. 0.5–1.8 kg/mol) ethylene waxes with high branching

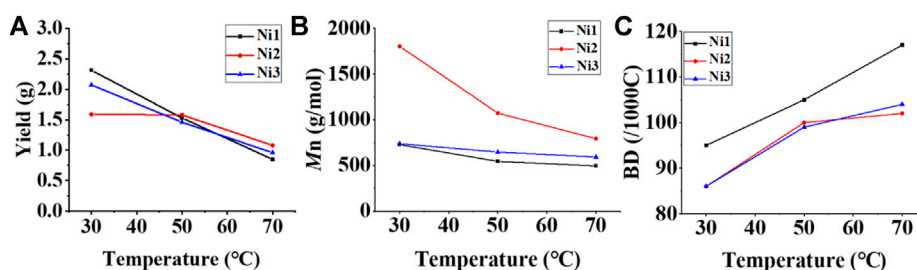


FIGURE 2

Plots of yield (A), molecular weight (B), and branching density (C) of ethylene oligomers produced with Ni1–Ni3 relative to temperature at 30–70°C.

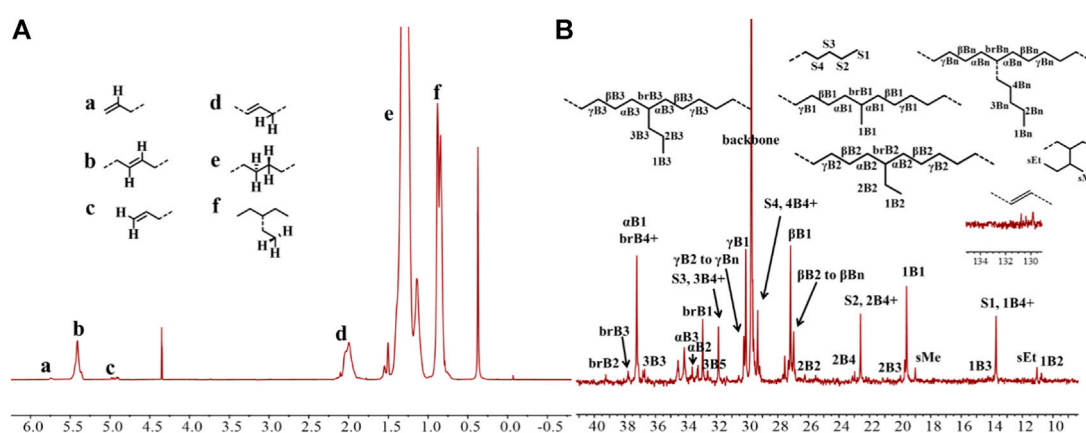


FIGURE 3

The ^1H (A) and ^{13}C (B) NMR spectral analyses of the hyperbranched ethylene oligomer obtained with Ni2 at 70°C. Assignments are numbered based on ref. Cotts et al., 2000; Randall, 1989; Galland et al., 1999. Supplementary Figures S1–S4 are assigned to the chain ends. xBy delineates the branches, where x is the carbon, beginning with 1 at the methyl end and y is the branch length. brBy denotes the methine groups for branches with different lengths.

densities (86–117/1000°C) (Table 1). As the reaction temperature increased, the catalytic activities of all the complexes in this system gradually decreased (Figure 2A). This is probably due to the decrease of ethylene solubility in toluene as the reaction temperature increases. A faster catalyst deactivation at higher temperatures may also play an important role. The molecular weight of the resulting ethylene oligomers reduced (Figure 2B), whereas the branching density elevated (Figure 2C) when the reaction temperatures were increased for all these complexes. Interestingly, compared to the benzocyclopentyl complex Ni1, the benzocyclohexyl complex Ni2 produced higher molecular weight ethylene oligomers with lower branching densities (Figures 2B,C), which is caused by the fact that the cyclohexyl group provides a larger steric hindrance than the cyclopentyl group, since a larger steric hindrance in the α -diimine nickel system helps to obtain higher molecular weight polymers (Gong

et al., 2019; Hai et al., 2021; Lu et al., 2021a; Zhao et al., 2021; Wang et al., 2022). Moreover, compared with the rigid planar naphthalene-based complex Ni3, the flexible stereoscopic benzocyclohexyl complex Ni2 yielded higher molecular weight ethylene oligomers with similar branching density (Figures 2B,C). This may also be due to the greater steric hindrance of the cyclohexyl group over the phenyl substituent. In terms of catalytic activity, complex Ni2 is less active than Ni1 and Ni3 at low temperatures while the opposite trend is observed at high temperatures (Figure 2A). This is most likely due to the greater thermal stability of the bulkier nickel complex Ni2 at high temperatures although it is not conducive to the coordination and insertion of ethylene molecules. The above discussion indicates that the introduction of a flexible stereoscopic cyclohexyl group can improve the molecular weight and thermal stability of the catalytic system. The microstructure of

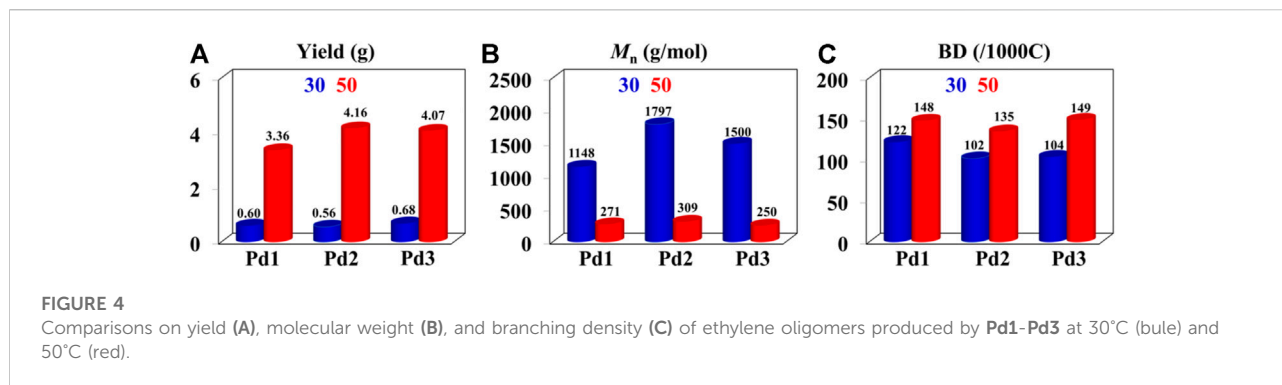


FIGURE 4

Comparisons on yield (A), molecular weight (B), and branching density (C) of ethylene oligomers produced by Pd1-Pd3 at 30°C (blue) and 50°C (red).

TABLE 2 Pd(II) catalysts for ethylene oligomerization^a.

Entry	Precatalyst	T (°C)	Yield (g)	Activity ^b	M_n (NMR) ^c	B ^d
1	Pd1	30	0.60	2.00	1148	122
2	Pd1	50	3.36	11.20	271	148
3	Pd2	30	0.56	1.87	1797	102
4	Pd2	50	4.16	13.87	309	135
5	Pd3	30	0.68	2.27	1500	104
6	Pd3	50	4.07	13.57	250	149

^aReaction conditions: 10 μ mol Pd catalyst, 2.0 equiv. NaBARF, 4 atm Ethylene, 40 ml DCM, 3 h polymerization time.

^bActivity is expressed as 10^4 g mol⁻¹ h⁻¹.

^c M_n (g mol⁻¹) estimated from ¹H NMR, peak intensities.

^dB is the number of branches per 1000 carbons, $B = 1000 \times 2(I_{CH_3})/3(I_{CH_2+CH} + I_{CH_3})$, including saturated end groups.

a representative ethylene oligomer (Table 1, entry 6) was revealed using ¹H and ¹³C NMR analyses (Figure 3). The resonance assignments for ¹H NMR spectrum of the ethylene oligomer reveal the existence of a high amount of terminal methyl groups, a minor quantity of terminal double bonds, a major quantity of internal double bonds and a C=C-CH₂ group (Figure 3A). Furthermore, the ¹³C NMR spectra reveal the existence of a branch-on-branch structure, a double bond and the branches with different chain lengths (ethyl, methyl, *n*-propyl, etc.) (Figure 3B). The chain end groups and methyl branches were the most common among the branches, and the presence of *sec*-butyl groups indicated that the ethylene oligomer possessed hyperbranched structures (Cotts et al., 2000).

Pd(II) complexes catalyzed ethylene (co) oligomerization

The iminopyridine Pd(II) complexes were also used for the ethylene oligomerization process, with activation by 2 equiv. of sodium tetrakis (3,5-bis(trifluoromethyl)phenyl)borate (NaBARF). All the Pd(II) complexes demonstrated moderate catalytic activity and produced colorless oil with low density.

Notably, raising the temperature significantly increased the catalytic activity, whereas the molecular weights of the obtained ethylene oligomers significantly decreased. These results indicate that a high temperature favors chain transfer over chain propagation, and improves the rate of ethylene insertion (Figure 4). The elevated temperatures could lead to ethylene oligomers with significantly higher branching densities, which was not in line with the similarly structured α -diimine Pd(II) system, where the branching density of the obtained polyethylene was generally independent of temperature variations (Lu et al., 2022; Yan et al., 2022b). This may be attributed to the markedly lower molecular weights of the ethylene oligomers obtained at higher temperatures, resulting in a large amount of end groups. Interestingly, compared to the benzocyclopentyl complex Pd1, the benzocyclohexyl complex Pd2 produced ethylene oligomers with higher molecular weights and lower branching densities (Figures 4B,C), similar to the corresponding nickel system. Moreover, compared to the rigid planar naphthalene-based complex Pd3, the flexible stereoscopic benzocyclohexyl complex Pd2 yielded higher molecular weight ethylene oligomers with lower branching density. In terms of catalytic activity, complex Pd2 is less

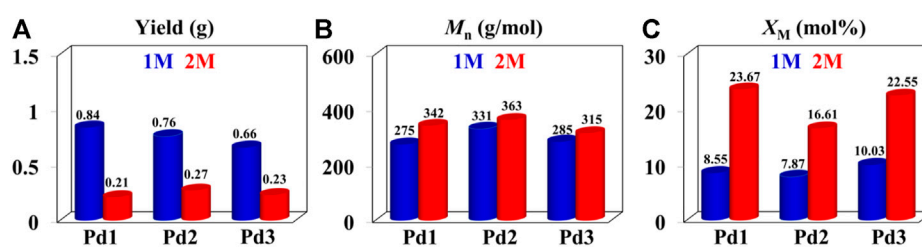


FIGURE 6

Comparisons on yield (A), molecular weight (B) and incorporation ratio (C) of ethylene-MA co-oligomers generated with catalysts Pd1-Pd3 at 1 M (blue) and 2 M (red).

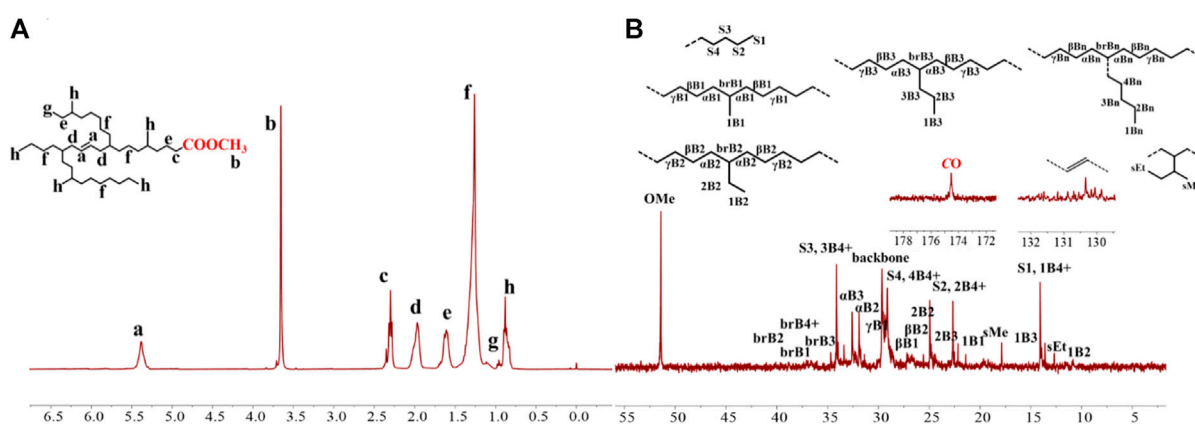


FIGURE 7

The ^1H (A) and ^{13}C (B) NMR spectral analyses of hyperbranched ethylene-MA co-oligomers obtained with Pd1 at 1 M MA. Assignments are numbered based on ref. Cotts et al., 2000; Randall, 1989; Galland et al., 1999. Supplementary Figures S1-S4 are assigned to the chain ends. xBy delineates the branches, where x is the carbon, beginning with 1 at the methyl end and y is the branch length. brBy denotes the methine groups for branches with different lengths.

inhibiting effects of the COOMe groups. Upon doubling the MA concentrations, the co-oligomerization activities reduced significantly, whereas the incorporation ratios were markedly increased. Compared to the benzocyclopentyl complex Pd1, the benzocyclohexyl complex Pd2 generated higher molecular weight ethylene-MA co-oligomers with lower branching densities and lower incorporation ratios (Figures 6B,C). Moreover, compared with the rigid planar naphthalene-based complex Pd3, the flexible stereoscopic benzocyclohexyl complex Pd2 yielded higher molecular weight ethylene-MA co-oligomers with higher catalytic activities and lower incorporation ratios (Figures 6A-C). This is most likely due to the fact that the larger steric hindrance is not conducive to the coordination insertion of polar monomers, which will result in a higher catalytic activity and a higher molecular weight as well as a lower insertion ratio. The ethylene/MA co-oligomers produced with these Pd(II) catalysts from 2M MA solutions

contain >1 polar functionalized group in each chain. The microstructure of a representative ethylene/MA co-oligomer (entry 1, Table 3) was elucidated by ^1H and ^{13}C NMR analyses (Figure 7). The assignments of the ^1H NMR resonances of ethylene/MA co-oligomer reveal a high amount of terminal methyl groups, a C=C-CH₂-group, a methoxyl group (OCH₃), a CH₂CH₂COOMe, a CH₂COOMe and an internal double bond (Figure 7A). Furthermore, the corresponding ^{13}C NMR spectra reveal the existence of different branches with different chain lengths (ethyl, methyl, n-propyl, etc.), a branch-on-branch structure, an ester carbonyl group, an OCH₃ group and an internal double bond (Figure 7B). The long-chain branches and those carrying chain end ester groups accounted for the majority of all chain branches and the hyperbranching was also detected based on the presence of sec-butyl groups (Cotts et al., 2000). The ester groups in the hyperbranched ethylene-MA co-oligomers are predominately incorporated at the

branching end (Fan et al., 2022a; Fan et al., 2022b; Yan et al., 2022a).

Conclusion

A series of dibenzhydryl iminopyridyl ligands with benzocycloalkyl and naphthyl moieties and the corresponding Ni(II) and Pd(II) complexes were synthesized in excellent yields and characterized by NMR and mass spectrometries and elemental analyses. All the Ni(II) and Pd(II) complexes were employed as catalysts in ethylene oligomerization and ethylene/MA-co-oligomerization. In the Ni(II)-catalyzed ethylene oligomerizations, **Ni1-Ni3** exhibited very high catalytic activities (up to $13.86 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$) and produced highly branched (86-117/1000 C) ethylene oligomers with low molecular weights (493–1802 g/mol). In the Pd(II)-catalyzed ethylene oligomerizations, **Pd1-Pd3** exhibited moderate catalytic activities ($1.87\text{--}13.87 \times 10^4 \text{ g mol}^{-1} \text{ h}^{-1}$) and yielded highly branched (102-149/1000 C) ethylene oligomers with low molecular weights (250–1797 g/mol). For the ethylene-MA co-oligomerizations, polar functionalized ethylene/MA co-oligomers with low molecular weights and very high incorporation ratios (up to 23.67 mol%) were produced using complexes **Pd1-Pd3**. Moreover, the flexible stereoscopic benzocyclohexyl complexes yielded the highest molecular weight ethylene oligomers or E-MA co-oligomers among these complexes. The reaction temperature, catalyst ligand structure and metal type have all significant effects on the ethylene (co) oligomerization with respect to catalytic activity, molecular weight and oligomer topology. Notably, all the produced ethylene oligomers and E-MA co-oligomers were demonstrated to contain hyperbranched microstructures with different topologies.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

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Author contributions

BD: Data curation, Formal analysis, Investigation, Methodology. GC: Investigation, Methodology. ZY: Investigation, Methodology. SD: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Resources, Validation, Supervision, Writing—original draft, Writing—review and editing.

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Conflict of interest

The reviewer LG declared a past co-authorship with the author SD to the handling editor.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2022.961426/full#supplementary-material>

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