

# Synthesis of Branched Ultrahigh-Molecular-Weight Polyethylene Using Highly Active Neutral, Single-Component Ni(II) Catalysts

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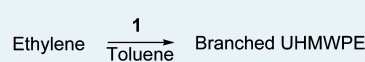
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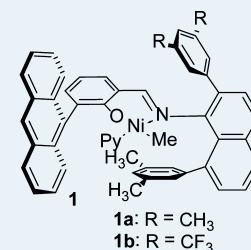
## Supporting Information

**ABSTRACT:** Neutral nickel methyl complexes incorporating 2,8-diarylnaphthyl groups have been synthesized and characterized. Salicylaldiminato nickel systems **1a,b** are exceptionally active neutral nickel single component catalysts for the polymerization of ethylene capable of producing lightly branched ultrahigh-molecular-weight polyethylene (UHMWPE). In addition, complex **1a** shows a “quasi-living” polymerization behavior.

**KEYWORDS:** nickel catalysts, polymerization, UHMWPE, salicylaldimine, branched polyethylene



1. High activity, TOF up to  $1.7 \times 10^5 \text{ h}^{-1}$ ;
2. UHMWPEs,  $M_w$  up to  $3.0 \times 10^6 \text{ g mol}^{-1}$ , 4–31 branches per 1000 carbon atoms;
3. “Quasi-living” polymerization.

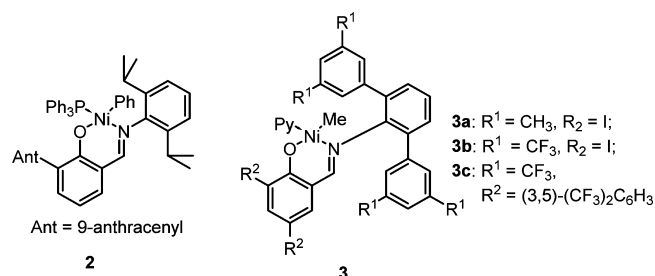


## INTRODUCTION

The development of late transition metal catalysts for olefin polymerization has advanced substantially<sup>1</sup> since the pioneering discovery of cationic Ni(II) and Pd(II) aryl-substituted diimine catalysts in 1995.<sup>2</sup> The key to generating high-molecular-weight polymers using these catalysts is the presence of bulky ortho-alkyl substituents on the aryl rings which provide steric bulk in the two axial sites of the square coordination plane. The positioning of these groups retards the rate of chain transfer relative to the rate of propagation.  $\beta$ -Elimination/readdition reactions move the metal down the alkyl chain (“chain-walking”) and can occur without chain transfer. As a result, polyethylenes with microstructures ranging from linear to highly branched can be produced. Hyper-branched structures can also be observed with proper choice of catalyst, temperature, and ethylene pressure.<sup>3</sup> Moreover, these catalysts have proved capable of copolymerizing of ethylene and  $\alpha$ -olefins with polar vinyl monomers such as acrylates, methyl vinyl ketones, and silyl vinyl ethers to yield highly branched copolymers.<sup>2,4</sup>

Typically, cationic nickel catalysts are more sensitive to polar solvents and impurities relative to the neutral analogues. Therefore, there has been strong interest in developing less electrophilic neutral nickel catalysts that polymerize ethylene to high molecular weight polymers. Early examples of neutral nickel catalysts bearing phosphino-enolate ligands normally provided low-molecular-weight polyethylene.<sup>5</sup> A significant advance in development of neutral nickel polymerization catalysts, discovery of the salicylaldiminato-based nickel systems by the groups from DuPont<sup>6</sup> and Caltech<sup>7</sup> was reported in 1998. Neutral Ni(II) complexes based on salicylaldiminato ligands which incorporate a bulky ortho-disubstituted aryl group could produce high-molecular-weight polyethylene. Catalyst **2** bearing a bulky 9-anthracenyl group, believed to

promote phosphine dissociation, was found to be particularly productive and was shown to copolymerize ethylene and functionalized norbornenes.<sup>7b</sup> Mecking's group reported a series of neutral Ni(II) methyl catalysts bearing terphenyl substituted N,O ligands which showed higher activity than the similar isopropyl-substituted complexes.<sup>8</sup> Significant effects of remote substituents (R, Figure 1) on polymer branching and



**Figure 1.** Salicylaldiminato nickel catalysts.

molecular weights were observed. Complex **3a** bearing methyl groups at the terphenyl 3,5-positions produced hyperbranched oligomers which could be further functionalized.<sup>8mm</sup> However, the complex **3b** bearing CF<sub>3</sub> groups at the terphenyl 3,5-positions produced high-molecular-weight ( $M_n$  ca.  $10^4 \text{ g/mol}$ ) semicrystalline PE. Moreover, complex **3c** could produce strictly linear polyethylene with high molecular weight ( $M_n$  up to  $5.8 \times 10^5 \text{ g/mol}$ ) in supercritical CO<sub>2</sub>.<sup>9</sup>

In addition to the salicylaldiminato systems, complexes based on other ligand backbones have been reported by several groups.<sup>10–13</sup> Bazan's group investigated various  $\alpha$ -iminocarbox-

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amide nickel complexes which exhibited excellent performance in promoting ethylene polymerization and showed “quasi-living” behavior when combined with Ni(COD)<sub>2</sub>.<sup>10</sup> Brookhart and co-workers reported a series of neutral nickel catalysts containing five-membered nickel chelates that showed high activities toward ethylene polymerization.<sup>11</sup> Li’s group reported a series of highly active  $\beta$ -ketiminato neutral nickel(II) catalysts.<sup>12</sup>

Most of these systems produce PEs with  $M_n$  values on the order of  $10^5$  g/mol or less. Polyethylenes with molecular weights on the order of  $10^6$  g/mol are difficult to obtain even for the early metal catalyst systems.<sup>14</sup> PEs with  $M_n$  values in the range of  $10^6$ – $10^7$  g/mol are termed ultrahigh-molecular-weight polyethylenes (UHMWPEs). Catalysts which produce UHMWPEs must exhibit rate ratios of chain propagation/chain transfer (or chain termination) of greater than ca.  $3.5 \times 10^4$ . The synthesis of UHMWPEs from late transition metal catalysts is rare.<sup>15,16a</sup> Rieger reported that aryl-substituted  $\alpha$ -diimine nickel complexes bearing bulky 2,6-diphenyl substituents could produce linear ultrahigh-molecular-weight polyethylenes.<sup>15b</sup>

Recently, we reported that “sandwich” nickel(II)  $\alpha$ -diimine complexes incorporating the 8-tolynaphthylimino group yield highly branched PE (Figure 2).<sup>16a</sup> The 8-tolyl groups are

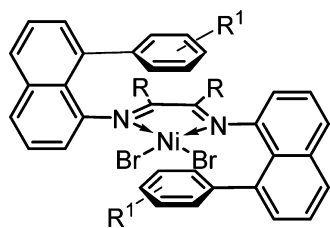


Figure 2. “Sandwich” nickel diimine catalysts.

positioned over the axial sites and greatly retard chain transfer. The nickel system was shown to yield highly branched PE with  $M_n$  values up to  $1.8 \times 10^6$  g/mol.<sup>16a</sup> Coates and Daugulis reported that such “sandwich” nickel(II)  $\alpha$ -diimine complexes polymerize  $\alpha$ -olefins to produce “chain-straightened” polymers (via 2,1 insertion and chain-walking) to produce polymers which resemble semicrystalline PE.<sup>17</sup>

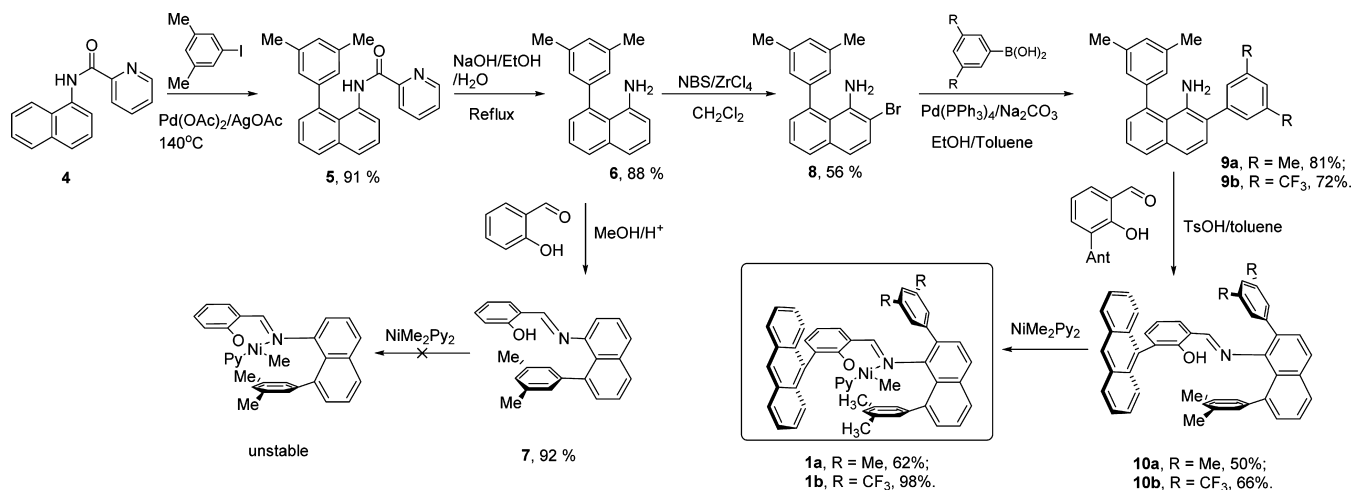
Herein, we report the synthesis of neutral nickel complexes containing 8-arylnaphthylimino groups and their remarkable behavior as catalysts for ethylene polymerization.

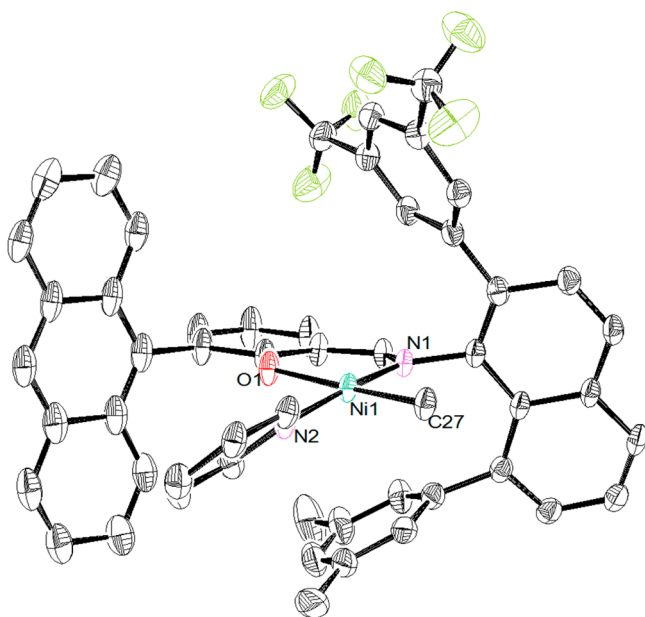
## RESULTS AND DISCUSSION

**Synthesis of Catalysts.** 8-(3,5-Dimethylphenyl)naphthalen-1-amine **6** was synthesized using a known procedure (Scheme 1).<sup>16</sup> Yields for each step are high and the amine **6** is readily purified. Condensation of amine **6** with salicylaldehyde gives the desired salicylaldimine **7** in 92% yield. Unfortunately, the corresponding nickel complex derived from the salicylaldimine **7** could not be obtained. Attempts to prepare salicylaldiminato nickel complexes derived from less sterically hindered amines afford the bis-ligated complexes.<sup>7c</sup> The 2,8-(diaryl)naphthalen-1-amines **9a,b** derived from **6** were synthesized in a two-step procedure. Selective bromination of amine **6** with *N*-bromosuccinimide (NBS) gave 2-bromo-8-(3,5-dimethylphenyl)naphthalen-1-amine **8** in moderate yield.<sup>18</sup> We then employed Suzuki coupling to synthesize 2,8-(diaryl)naphthalen-1-amines **9a,b** in good yields by treating bromo amine **8** with aryl boronic acids in the presence of a Pd(0) catalyst. Finally, the amines **9a,b** were used in the preparation of salicylaldimines **10a,b** by the acid-catalyzed condensation with 3-(9-anthryl)salicylaldehyde. Salicylaldiminato Ni(II)-Me complexes **1a,b** were prepared in good yields by adding (pyridine)<sub>2</sub>NiMe<sub>2</sub><sup>19</sup> to toluene solutions of ligands **10a,b**.<sup>8g</sup> Notably, no decomposition of the nickel methyl complex **1a** was observed over 2 weeks in C<sub>6</sub>D<sub>6</sub>. Single crystals of complex **1b** were grown by slowly evaporation of a hexane solution under argon. In the solid state, Ni in **1b** adopts a nearly square planar coordination geometry; the methyl group is trans to oxygen as expected on electronic grounds (Figure 3).<sup>8b</sup> As can be seen in Figure 3, the aryl rings effectively shield the axial sites above and below the square coordination plane.

**Ethylene Polymerization.** Neutral nickel complex **1a** was investigated as a single component catalyst for ethylene polymerization in toluene. The results are summarized in Table 1. The catalyst is quite stable at 50 °C. Complex **1a** exhibits constant polymerization activities over 1 h (TOF:  $4.5 \times 10^4$  h<sup>-1</sup> for 60 min and  $4.7 \times 10^4$  h<sup>-1</sup> for 30 min; entries 1 and 2). Polymerization activities are strongly dependent on ethylene pressure and reaction temperature. As seen in entries 2–4, activities increase nearly linearly with ethylene pressure

### Scheme 1. Synthesis of Complexes 1





**Figure 3.** Solid-state molecular structure of complex **1b** (ORTEP view, 30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg). Ni1–O1 1.908 (2), Ni1–N1 1.905 (3), Ni1–N2 1.922 (3), Ni1–C27 1.931 (3), N2–Ni1–C27 89.1 (1).

with a TOF of up to  $1.2 \times 10^5 \text{ h}^{-1}$  at 600 psig ethylene pressure. From these observations, it appears that the (major or exclusive) resting state is either the nickel alkylpyridine species or a nickel  $\beta$ -agostic alkyl complex.<sup>20</sup> The activity decreases as the temperature is increased to 60 °C, perhaps due to catalyst degradation. At 40 °C the activity is reduced, but no evidence of catalyst decomposition was found.<sup>21</sup> When the polymerization is carried out in the presence of 5 equiv of pyridine, a decrease in TOF is observed under the same reaction conditions (entries 7 vs 4). Suppression by added pyridine suggests under these conditions a fraction of the catalyst rests as the pyridine adduct.

The most notable feature of this catalyst system is the production of lightly branched ultrahigh-molecular-weight polyethylene. The molecular weight  $M_n$  is  $5.5 \times 10^5 \text{ g/mol}$  in a 30 min run at 200 psig ethylene and increases to  $9.4 \times 10^5 \text{ g/mol}$  in a 60 min run. The PE produced exhibits ca. 30 branches per 1000 carbon atoms and a  $T_m$  of 99 °C. In an ideal coordination/insertion polymerization where chain transfer via  $\beta$ -hydride elimination limits the  $M_n$ , the maximum value of  $M_n$  is attained when the  $M_w/M_n$  reaches 2. The fact that  $M_n$  nearly doubles when the polymerization time doubles from 30 to 60

min (see entries 1 and 2, Table 1) yet the  $M_w/M_n$  is 2.5–2.8, implies that the  $M_n$  under these conditions is not chain-transfer limited. This aspect will be discussed in more detail below.

The degree of branching of the polyethylene produced is sensitive to ethylene pressure and reaction temperature. For example, catalyst **1a** at 50 °C produces PE with a branching density of 28 at 200 psig, 20 at 400 psig and 17 branches per 1000 carbon atoms at 600 psig. The number of branches increases from 10 to 24 branches per 1000 carbon atoms upon raising the reaction temperature from 40 to 60 °C. The molecular weight  $M_w$  reaches  $3.0 \times 10^6 \text{ g/mol}$  ( $M_n = 1.3 \times 10^6 \text{ g/mol}$ ) with 17 branches per 1000 carbon atoms at 600 psig ethylene over 30 min (entry 4). <sup>13</sup>C NMR spectroscopy indicates that mainly methyl branches are present in the polymer. Similar molecular weights and branching numbers are observed with and without added pyridine (entries 4 vs 8). The presence of the branches in the polymer backbone is reflected by the melting temperatures determined by DSC. Compared with typical UHMWPE ( $T_m = 130\text{--}136 \text{ °C}$ ),<sup>14</sup> lower melting points (e.g., 99 °C, entry 1; 118 °C, entry 4) of the UHMWPE produced by **1a** were observed.

To gain further insight into the increase in  $M_n$  with the reaction time, Ni(COD)<sub>2</sub> was used as a cocatalyst<sup>10a</sup> to sequester pyridine. At low temperature (28 °C) and low ethylene pressure (100 psig), constant turnover frequencies were found over 2 h (Table 2). The molecular weight,  $M_n$ ,

**Table 2.** Polymerization Reactions Using **1a**/Ni(COD)<sub>2</sub>

entry <sup>a</sup>	time (min)	yield (g)	TOF ( $\times 10^{-4} \text{ h}^{-1}$ )	$M_n^b$ ( $\times 10^{-4} \text{ g/mol}$ )	$M_w/M_n^b$
1	10	0.75	3.2	22.7	1.36
2	20	1.61	3.5	49.1	1.38
3	30	2.26	3.2	77.7	1.31
4	60	4.21	3.0	122.8	1.47
5	120	9.69	3.5	160.0	2.11
6 <sup>c</sup>	30	0.64	0.9	26.2	1.64

<sup>a</sup>Conditions: **1a** = 5  $\mu\text{mol}$ ,  $V$  (toluene) = 200 mL, 10 equiv of Ni(COD)<sub>2</sub>, 28 °C, 100 psig ethylene; ethylene: Matheson purity. <sup>b</sup>Molecular weight was determined by GPC in trichlorobenzene at 150 °C. <sup>c</sup>Without Ni(COD)<sub>2</sub>.

increased nearly linearly as a function of reaction time over 60 min (e.g.,  $M_n = 2.3 \times 10^5 \text{ g/mol}$ , 10 min;  $4.9 \times 10^5 \text{ g/mol}$ , 20 min;  $7.8 \times 10^5 \text{ g/mol}$ , 30 min;  $1.2 \times 10^6 \text{ g/mol}$ , 60 min). This feature is a characteristic of living polymerization, yet the  $M_w/M_n$  values (1.3–1.4) are considerably greater than expected for a living polymerization. This behavior is likely due to rapid precipitation of the high-molecular-weight polymer resulting in inhomogeneous reaction conditions with a distribution of sites

**Table 1.** Results of Ethylene Polymerization Reactions Using **1a**

entry <sup>a</sup>	$T$ (°C)	ethylene (psig)	time (min)	yield (g)	TOF ( $\times 10^{-4} \text{ h}^{-1}$ )	branches <sup>b</sup>	$M_n^c$ ( $\times 10^{-4} \text{ g/mol}$ )	$M_w/M_n^c$	$T_m$ (°C)
1	50	200	60	6.3	4.5	31	94.3	2.5	99
2	50	200	30	3.3	4.7	28	55.0	2.8	101
3	50	400	30	5.8	8.3	20	100.8	2.8	111
4	50	600	30	8.4	11.9	17	128.7	2.3	118
5	60	600	30	3.0	4.3	24	62.9	2.4	103
6	40	600	30	3.1	4.4	10	31.7	2.3	123
7 <sup>d</sup>	50	600	30	5.5	7.8	16	124.1	2.4	116

<sup>a</sup>Conditions: **1a** = 5  $\mu\text{mol}$ ,  $V$  (toluene) = 200 mL, ethylene: Matheson purity. <sup>b</sup>Branching numbers per 1000 carbons were determined by using <sup>1</sup>H NMR spectroscopy. <sup>c</sup>Molecular weight was determined by GPC in trichlorobenzene at 150 °C. <sup>d</sup>5 equiv of pyridine.

Table 3. Results of Ethylene Polymerization Reactions Using **1b**

entry <sup>a</sup>	T (°C)	ethylene (psig)	time (min)	yield (g)	TOF ( $\times 10^{-4}$ h <sup>-1</sup> )	branches <sup>b</sup>	$M_n^c$ ( $\times 10^{-4}$ g/mol)	$M_w/M_n^c$	$T_m$ (°C)
1	50	200	60	7.1	5.0	9	113.2	2.5	126
2	50	200	30	4.3	6.2	9	86.5	2.5	125
3	50	400	30	7.8	11.1	7	109.6	2.4	126
4	50	600	30	11.7	16.7	6	125.7	2.4	130
5	60	600	30	6.7	9.6	9	105.3	2.8	122
6	60	200	30	3.1	4.4	11	90.5	2.4	120
7	40	200	30	4.4	6.2	4	91.5	1.9	129

<sup>a</sup>Conditions: **1b** = 5  $\mu$ mol, V (toluene) = 200 mL, ethylene: Matheson purity. <sup>b</sup>Branching numbers per 1000 carbons were determined by using <sup>1</sup>H NMR spectroscopy. <sup>c</sup>Molecular weight was determined by GPC in trichlorobenzene at 150 °C.

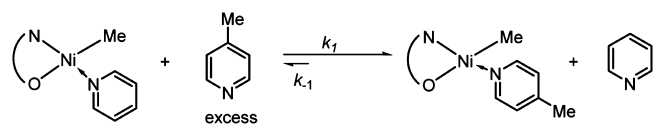
possessing varying activities. This phenomenon has been previously encountered by Bazan who has termed this behavior as “quasi-living” polymerization.<sup>10a</sup> Notably, the molecular weight  $M_w$  reaches  $3.4 \times 10^6$  g/mol ( $M_n = 1.6 \times 10^6$  g/mol) after 2 h accompanied by a broadening molecular weight distribution (entry 5).

Complex **1b** bearing 3,5-CF<sub>3</sub> groups in place of 3,5-CH<sub>3</sub> groups was also studied for ethylene polymerization (Table 3). At 50 °C, catalyst **1b** showed higher activity of  $6.2 \times 10^4$  h<sup>-1</sup> over 30 min (entry 2) compared with that of catalyst **1a** (entry 2, Table 1). However, the TOF for **1b** drops slightly to  $5.0 \times 10^4$  h<sup>-1</sup> over 60 min (entry 1). Similar to catalyst **1a**, the TOF of catalyst **1b** is nearly proportional to ethylene pressure (entries 2–5). The highest TOF was reached at  $1.7 \times 10^5$  h<sup>-1</sup> as ethylene pressure was increased to 600 psig. To the best of our knowledge, this is among the very highest activities reported for salicylaldiminato nickel systems.<sup>8</sup> Similar to catalyst **1a**, a drop in activity was observed at elevated reaction temperatures (entries 2 vs 6, entries 4 vs 5). However, polymerizations at 40 °C exhibited a similar TOF,  $6.2 \times 10^4$  h<sup>-1</sup>, compared with the TOF at 50 °C (entries 2 vs 7).

Similar to catalyst **1a**, ultrahigh-molecular-weight polyethylene was also obtained with catalyst **1b**. For example, polymerization at 50 °C, 200 psig ethylene for 60 min yields PE with  $M_w = 2.8 \times 10^6$  g/mol ( $M_n = 1.1 \times 10^6$  g/mol) (entry 1). In comparison with catalyst **1a**, the polyethylenes produced by **1b** are more linear<sup>22</sup> and exhibit higher melting temperatures (120–130 °C). For example, the branching density was only 6 branches per 1000 carbon atoms at 600 psig (entry 4). The linear ultrahigh-molecular-weight polyethylene demonstrates thermal properties similar to those of UHMWPE produced with early metal systems. In the first heating cycle, high peak melting temperatures (137 °C) and high crystallinity (64%)<sup>23</sup> are observed for the nascent polymer. In the second heating cycle, the crystallinity (45%) is much lower due to entanglement hindering recrystallization from the melt.

The reaction of ethylene (4.0 equiv) with nickel methyl complex **1a** in toluene-d<sub>8</sub> was monitored by in situ NMR spectroscopic studies at 40 °C. The rate of ethylene insertion into the nickel methyl bond of complex **1a** is much slower than subsequent insertions and the only species detected during consumption of ethylene was pyridine complex **1a**. No defined resonances for ethylene complexes,  $\beta$ -agostic species, olefin hydrides, or free pyridine could be observed. This is consistent with results presented earlier suggesting that alkylpyridine complexes are the dominant resting states under polymerization conditions at high ethylene pressures. If we designate the first insertion as initiation and subsequent insertions as propagation, then the rate of initiation is much slower than the rate of propagation.

Because the ethylene complexes could not be detected, the mechanism for ligand exchange at the metal center was examined using pyridine complex **1a**. We investigated displacement of pyridine by 4-picoline at –80 °C in CD<sub>2</sub>Cl<sub>2</sub> under pseudo-first order conditions in which the concentrations of 4-picoline used greatly exceed the concentration of **1a**. The data are summarized in Table 4. The pseudo-first-order rate

Table 4. Kinetics of Displacement of Pyridine by 4-Picoline in **1a** at –80 °C


entry	[Ni] (mM)	[4-picoline] (mM)	$k_1$ [4-picoline] (s <sup>-1</sup> )	$k_1$ (M <sup>-1</sup> s <sup>-1</sup> )
1	7.1	121	$6.19 \times 10^{-4}$	$5.1 \times 10^{-3}$
2	7.1	199	$10.6 \times 10^{-4}$	$5.3 \times 10^{-3}$
3	7.1	355	$18.8 \times 10^{-4}$	$5.3 \times 10^{-3}$

constants are linearly dependent on the concentration of 4-picoline implying the displacement is clearly associative even in this highly hindered system. The second-order rate constant is  $5.3 \times 10^{-3}$  M<sup>-1</sup> s<sup>-1</sup> at –80 °C. It is reasonable to assume that ethylene exchanges with pyridine through an analogous associative mechanism.

## CONCLUSION

Neutral nickel methyl complexes incorporating 2,8-diarylnaphthyl groups have been synthesized and characterized. These single-component catalysts are quite stable and are highly active for ethylene polymerization at 50 °C or below. Turnover frequencies increase linearly with the ethylene pressure, implying that alkyl ethylene complexes are not the resting states. Compared with complex **1a**, the –CF<sub>3</sub>-substituted analogue **1b** has a slightly higher polymerization activity (e.g., a TOF of  $1.7 \times 10^5$  h<sup>-1</sup> vs  $1.2 \times 10^5$  h<sup>-1</sup> at 600 psig C<sub>2</sub>H<sub>4</sub>, 50 °C). For complex **1a**, the molecular weights of polyethylene produced increase nearly linearly as a function of reaction time and conform to a “quasi-living” behavior.<sup>10a</sup>

These single-site catalysts produce ultrahigh-molecular-weight polyethylenes ( $M_w$  up to  $3.0 \times 10^6$  g/mol) with low to moderate branching densities in the range of 4–31 branches per 1000 carbon atoms which can be controlled by variations in temperature and ethylene pressure. Such lightly branched UHMWPEs appear to be unique and bridge the gap between the normal<sup>14,15b</sup> highly linear UHMWPE and the extremely highly branched UHMWPEs reported with nickel diimine catalysts.<sup>16a</sup>

## ■ ASSOCIATED CONTENT

## S Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501948d.

Synthetic procedures for preparation of new ligands and complexes the method used for polymerization of ethylene using **1a** and **1b**,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of new compounds,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of polymers, DSC data of polymers, and a CIF file for **1b** (PDF)

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## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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(20) If the resting state an alkyl ethylene complex, then no pressure dependence of the turnover frequency would be observed; see ref 11d.

(21) TOF is  $4.6 \times 10^4 \text{ h}^{-1}$  in a 60 min run at 40 °C.

(22) Effects on branching through substitution of an aromatic  $-\text{CH}_3$  group by a  $\text{CF}_3$  group has been noted before.<sup>8b</sup> The reasons for the decrease in branching densities of polymers produced by **1a** relative to **1b** are not clear.

(23) Polymer crystallinities were calculated based on a melt enthalpy of 293 J/g for 100% crystalline polyethylene. Please see: Joo, Y. L.; Han, O. H.; Lee, H. K.; Song, J. K. *Polymer* **2000**, *41*, 1355–1368.

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After this paper was published December 24, 2014, author names were corrected in refs 8q, 12a–12e, 13b, and 14g. The corrected version was reposted December 30, 2014.