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Highly Active Neutral Nickel(II) Catalysts for Ethylene Polymerization Bearing Modified  $\beta$ -Ketoiminato LigandsDong-Po Song,<sup>†,‡</sup> Wei-Ping Ye,<sup>†</sup> Yong-Xia Wang,<sup>§</sup> Jing-Yao Liu,<sup>§</sup> and Yue-Sheng Li<sup>\*†</sup><sup>†</sup>State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China, <sup>‡</sup>Graduate School of the Chinese Academy of Sciences, Changchun Branch, Changchun 130023, People's Republic of China, and <sup>§</sup>State Key Laboratory of Theoretical & Computational Chemistry, Jilin University, Changchun 130023, People's Republic of China

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A series of novel neutral nickel complexes **4a–e** bearing modified  $\beta$ -ketoiminato ligands [(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=C(R<sub>1</sub>)CHC(2'-R<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O)Ni(Ph)(PPh<sub>3</sub>) (**4a**, R<sub>1</sub> = R<sub>2</sub> = H; **4b**, R<sub>1</sub> = H, R<sub>2</sub> = Ph; **4c**, R<sub>1</sub> = H, R<sub>2</sub> = Naphth; **4d**, R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = Ph; **4e**, R<sub>1</sub> = CF<sub>3</sub>, R<sub>2</sub> = Ph) have been synthesized and characterized. Molecular structures of **4b** and **4e** were further confirmed by X-ray crystallographic analysis. Activated with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, all the complexes are active for the polymerization of ethylene to branched polyethylenes. Ligand structure, i.e., substituents R<sub>1</sub> and R<sub>2</sub>, greatly influences not only catalytic activity but also the molecular weight and branch content of the polyethylene produced. The phenyl-substituted complex **4b** exhibits the highest activity of up to 145 kg PE/mol<sub>Ni</sub>·h·atm under optimized conditions, which is about 10 times more than unsubstituted complex **4a** (14.0 kg PE/mol<sub>Ni</sub>·h·atm). Highly branched polyethylene with 103 branches per 1000 carbon atoms has been prepared using catalyst **4e**.

## Introduction

In the past decade, interest in late transition metal catalysts for olefin polymerization has been on the rise with a major advance that came with the discovery of cationic nickel(II) and palladium(II) catalysts.<sup>1</sup> They were found to have attractive characteristics compared with early transition metal

counterparts.<sup>2–17</sup> Using some late transition metal catalysts, the microstructure of polyethylene can be controlled from essentially linear to highly branched by changing polymerization temperature and ethylene pressure.<sup>2,4,5</sup> Recently, Grubbs and his co-workers reported that the single-component salicylaldiminato neutral nickel(II) catalysts bearing a bulky substituent at the *ortho* position of the phenoxy group not only show high activities toward ethylene polymerization but also can copolymerize ethylene with some functional monomers,<sup>18b,18c</sup> which greatly stimulated this area. As a result, a

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(1) (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (b) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479. (c) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (d) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (e) Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 534. (f) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325.

(2) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

(3) (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (c) Li, W.; Zhang, X.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 12246. (d) Chen, G.; Guan, Z. *J. Am. Chem. Soc.* **2004**, *126*, 2662. (e) Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *128*, 12072. (f) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744.

(4) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664.

(5) Gates, D. P.; Svejda, S. A.; Onate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320.

(6) Leatherman, M. D.; Brookhart, M. *Macromolecules* **2001**, *34*, 2748.

(7) Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules* **2000**, *33*, 6945.

(8) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. *J. Science* **1999**, *283*, 2059.

(9) Mecking, S.; Held, A.; Bauers, F. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 545.

(10) (a) Tempel, D. J.; Brookhart, M. *Organometallics* **1998**, *17*, 2290.

(b) Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 10634. (c) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. (d) Shultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539. (e) Leatherman, M. D.; Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 3068.

(11) (a) Camacho, D. H.; Guan, Z. B. *Organometallics* **2005**, *24*, 4933. (b) Leung, D. H.; Guan, Z. B. *J. Am. Chem. Soc.* **2008**, *130*, 7538.

(12) (a) Speiser, F.; Braunstein, P. *Inorg. Chem.* **2004**, *43*, 1649. (b) Kermagoret, A.; Braunstein, P. *Organometallics* **2008**, *27*, 88. (c) Chavez, P.; Braunstein, P. *Organometallics* **2009**, *28*, 1776.

(13) (a) Rose, G. M.; Coates, G. W. *J. Am. Chem. Soc.* **2006**, *128*, 4186. (b) Rose, G. M.; Coates, G. W. *Macromolecules* **2008**, *41*, 9548.

(14) (a) Huang, Y. B.; Jin, G. X. *Organometallics* **2008**, *27*, 259. (b) Han, F. B.; Sun, X. L.; Tang, Y. *Organometallics* **2008**, *27*, 1924. (c) Dorcier, A.; Basset, J. M. *Organometallics* **2009**, *28*, 2173. (d) Brasse, M.; Campora, J. *Organometallics* **2008**, *27*, 4711. (e) Gao, R.; Sun, W. H. *Organometallics* **2008**, *27*, 5641. (f) Long, J. M.; Gao, H. Y.; Wu, Q. *Eur. J. Inorg. Chem.* **2008**, 4296. (g) Noda, S.; Nozaki, K. *Organometallics* **2009**, *28*, 656.

(15) Chan, M. S. W.; Deng, L.; Ziegler, T. *Organometallics* **2000**, *19*, 2741.

(16) Deng, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 1094.

(17) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 6177.

large number of neutral nickel catalysts have been explored.<sup>19–28</sup> For example, Brookhart and his co-workers demonstrated that neutral nickel catalysts containing a five-membered nickel chelate exhibited high activities toward ethylene polymerization.<sup>19</sup>

(18) (a) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149. (b) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460. (c) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Hwang, S.; Grubbs, R. H.; Roberts, W. P.; Litzau, J. J. *J. Polym. Sci., Polym. Chem. Ed.* **2002**, *40*, 2842. (d) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Waltman, A. W.; Grubbs, R. H. *Chem. Commun.* **2003**, 2272. (e) Waltman, A. W.; Younkin, T. R.; Grubbs, R. H. *Organometallics* **2004**, *23*, 5121.

(19) (a) Hicks, F. A.; Brookhart, M. *Organometallics* **2001**, *20*, 3217. (b) Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 250. (c) Hicks, F. A.; Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 3533. (d) Jenkins, J. C.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 5827.

(20) (a) Soula, R.; Broyer, J. P.; Llauro, M. F.; Tomov, A.; Spitz, R.; Claverie, J.; Drujon, X.; Malinge, J.; Saudemont, T. *Macromolecules* **2001**, *34*, 2438. (b) Gibson, V. C.; Tomov, A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 719. (c) Tian, G. L.; Boone, H. W.; Novak, B. M. *Macromolecules* **2001**, *34*, 7656. (d) Li, X. F.; Li, Y. S. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2680. (e) Li, Y. S.; Li, Y. R.; Li, X. F. *J. Organomet. Chem.* **2003**, 667. (f) Zhang, D.; Jing, G. X. *Organometallics* **2003**, *22*, 2851. (g) Liang, H.; Liu, J. Y.; Li, X. F.; Li, Y. S. *Polyhedron* **2004**, *23*, 1619. (h) Hu, T.; Tang, L. M.; Li, X. F.; Li, Y. S.; Hu, N. H. *Organometallics* **2005**, *24*, 2628. (i) Zhang, D.; Jin, G. X. *Organometallics* **2003**, *22*, 2851. (j) Zhang, D.; Jin, G. X. *Inorg. Chem. Commun.* **2006**, *9*, 1322.

(21) (a) Na, S. J.; Lee, B. Y. *J. Organomet. Chem.* **2006**, *691*, 611. (b) Zeller, A.; Strassner, T. *J. Organomet. Chem.* **2006**, *691*, 4379. (c) Okada, M.; Shiono, T. *J. Organomet. Chem.* **2007**, *692*, 5183. (d) Chen, Q.; Yu, J.; Huang, J. *Organometallics* **2007**, *26*, 617. (e) Wei, W. P.; Huang, B. T. *Inorg. Chem. Commun.* **2008**, *11*, 487. (f) Shen, M.; Sun, W. H. *J. Organomet. Chem.* **2008**, *693*, 1683. (g) Li, W. F.; Sun, H. M.; Shen, Q. *J. Organomet. Chem.* **2008**, *693*, 2047. (h) Chandran, D.; Kim, I. *J. Organomet. Chem.* **2009**, *694*, 1254. (i) Rodriguez, B. A.; Delferro, M.; Marks, T. J. *Organometallics* **2008**, *27*, 2166. (j) Rodriguez, B. A.; Delferro, M.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5902.

(22) (a) Zuideveld, M.; Wehrmann, P.; Röhr, C.; Mecking, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 869. (b) Kuhn, P.; Sémeril, D.; Jeunesse, C.; Matt, D.; Neuburger, M.; Mota, A. *Chem.–Eur. J.* **2006**, *12*, 5210. (c) Göttker-Schnetmann, I.; Wehrmann, P.; Röhr, C.; Mecking, S. *Organometallics* **2007**, *26*, 2348. (d) Yu, S. M.; Berkefeld, A.; Göttker-Schnetmann, I.; Müller, G.; Mecking, S. *Macromolecules* **2007**, *40*, 421. (e) Bastero, A.; Göttker-Schnetmann, I.; Röhr, C.; Mecking, S. *Adv. Synth. Catal.* **2007**, *349*, 2307. (f) Guironnet, D.; Mecking, S. *Chem. Commun.* **2008**, 4965. (g) Berkefeld, A.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 1565.

(23) (a) Komon, Z. J. A.; Diamond, G. M.; Leclerc, M. K.; Murphy, V.; Okazaki, M.; Bazan, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 15280. (b) Chen, Y.; Wu, G.; Bazan, G. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 1108. (c) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369.

(24) (a) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 1830. (b) Komon, Z. J. A.; Bazan, G. C. *Macromol. Rapid Commun.* **2001**, *22*, 467. (c) Wasilke, J. C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001. (d) Boardman, B. M.; Bazan, G. C. *Organometallics* **2008**, *27*, 1671.

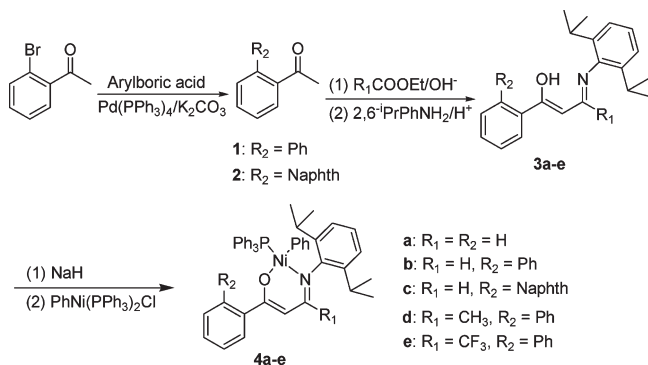
(25) (a) Held, A.; Bauers, F. M.; Mecking, S. *Chem. Commun.* **2000**, 301. (b) Bauers, F. M.; Mecking, S. *Macromolecules* **2001**, *34*, 1165. (c) Bauers, F. M.; Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3020. (d) Bauers, F. M.; Chowdhry, M. M.; Mecking, S. *Macromolecules* **2003**, *36*, 6711. (e) Bauers, F. M.; Thomann, R.; Mecking, S. *J. Am. Chem. Soc.* **2003**, *125*, 8838. (f) Kolb, L.; Monteil, V.; Thomann, R.; Mecking, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 429–432. (g) Wehrmann, P.; Mecking, S. *Macromolecules* **2006**, *39*, 5963. (h) Wehrmann, P.; Zuideveld, M. A.; Thomann, R.; Mecking, S. *Macromolecules* **2006**, *39*, 5995. (i) Göttker-Schnetmann, I.; Korthals, B.; Mecking, S. *J. Am. Chem. Soc.* **2006**, *128*, 7708. (j) Weber, C. H. M.; Chiche, A.; Krausch, G.; Rosenfeldt, S.; Ballauf, M.; Harnau, L.; Göttker-Schnetmann, I.; Tong, Q.; Mecking, S. *Nano Lett.* **2007**, *7*, 2024.

(26) (a) Tomov, A.; Broyer, J.-P.; Spitz, R. *Macromol. Symp.* **2000**, *150*, 53. (b) Soula, R.; Novat, C.; Tomov, A.; Spitz, R.; Claverie, J.; Drujon, X.; Malinge, J.; Saudemont, T. *Macromolecules* **2001**, *34*, 2022. (c) Soula, R.; Saillard, B.; Spitz, R.; Claverie, J.; Llauro, M. F.; Monnet, C. *Macromolecules* **2002**, *35*, 1513.

(27) (a) Zhang, L.; Brookhart, M.; White, P. S. *Organometallics* **2006**, *25*, 1868. (b) Yu, S. M.; Mecking, S.; et al. *Macromolecules* **2007**, *40*, 421.

(28) Li, X. F.; Li, Y. G.; Li, Y. S.; Chen, Y. X.; Hu, N. H. *Organometallics* **2005**, *24*, 2502.

### Scheme 1. General Synthetic Route of the Neutral Nickel Complexes Used in This Study



The mechanistic investigation has also been conducted on ethylene polymerizations catalyzed by the neutral nickel catalysts derived from bulky anilinothiopyran ligands.<sup>19d</sup> The salicylaldiminato nickel-methyl pyridine catalysts reported by Mecking's group, bearing substituted aryls at the 2,6-position of the N-aryl moiety, displayed high efficiency for ethylene (co)polymerization even when the polymerization was carried out in water.<sup>22,25</sup> Bazan's group investigated various  $\alpha$ -imino-carboxamide nickel catalysts, which exhibited excellent performance in promoting olefin polymerization.<sup>23,24</sup> By comparison to their cationic nickel counterparts, the neutral nickel catalysts are more tolerant toward polar reagents. Thus, polymerization in aqueous emulsion can be carried out successfully to afford stable polyolefin dispersions.<sup>25,26</sup>

To date, the majority of investigations on neutral nickel catalysts have focused on salicylaldiminato ligand-based ones, since Grubbs' discovery of single-component neutral nickel systems.<sup>18b</sup> The neutral catalysts based on  $\beta$ -ketoiminato ligands attract little attention, but are expected to have great potential for olefin polymerization. Recently, for example, Brookhart and Mecking reported that electron-poor enolatoimine neutral nickel catalysts are highly active for ethylene polymerization under nonaqueous or aqueous conditions.<sup>27</sup> We also reported the synthesis and structural characterization of a series of  $\beta$ -ketoiminato neutral nickel catalysts, which revealed favorable performance in the copolymerization of ethylene with methyl methacrylate.<sup>28</sup> However, in contrast to neutral salicylaldiminato nickel ones, these catalysts showed only low activities toward ethylene polymerization, probably due to the lack of enough steric hindrance to decrease the rate of catalyst deactivation and enhance the activity.<sup>28</sup> The fact that variation of the ligand structure may lead to profound changes in the catalytic activity and the property of the polymer prompts us to investigate modified  $\beta$ -ketoiminato neutral nickel catalysts. Herein we report a series of novel neutral nickel catalysts **4a–e** based on modified  $\beta$ -ketoiminato ligands and the influence of substituted R<sub>1</sub> and R<sub>2</sub> groups on their ethylene polymerization behaviors. Compared with unsubstituted catalyst **4a**, aryl-substituted catalysts **4b** and **4c** showed significantly increased activities for ethylene polymerization.

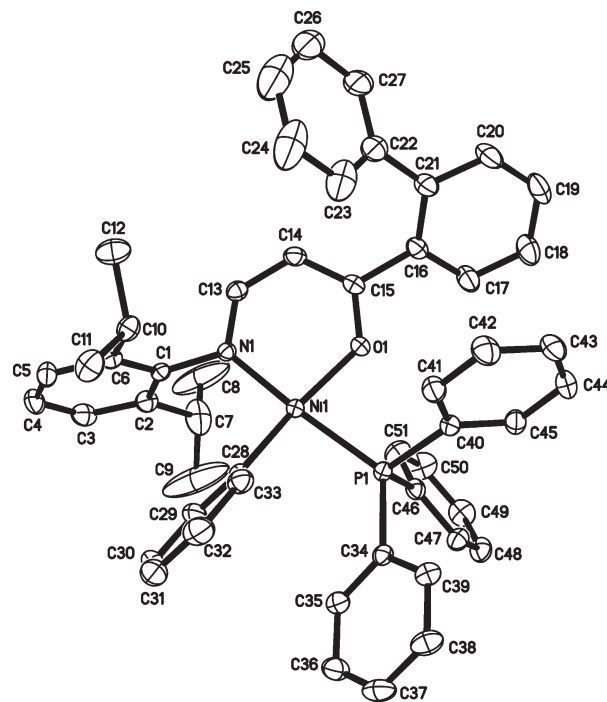
### Results and Discussion

**Synthesis and Characterization of the Neutral Nickel Complexes.** A general synthetic route for neutral nickel complexes **4a–e** bearing  $\beta$ -ketoiminato chelate ligands used in this study is shown in Scheme 1. Suzuki coupling reaction provides a convenient synthetic method for 2'-phenylacetophenone and



2'-naphthylacetophenone.<sup>29</sup> The  $\beta$ -diketones were first prepared via reaction between the corresponding substituted (or unsubstituted) acetophenone and an ester with the help of a strong base, such as potassium *tert*-butoxide, in anhydrous diethyl ether.  $\beta$ -Ketoimines **3a–d** were prepared in good yields by the condensation of the  $\beta$ -diketones with 2,6-diisopropylaniline in ethanol containing a little formic acid as a catalyst. The synthesis of ligand **3e** seemed to be more difficult relative to the others, and Schiff base condensation was carried out in boiling toluene with *p*-toluenesulfonic acid as a catalyst. The deprotonation of free ligands **3a–e** readily proceeded with excess sodium hydride in anhydrous THF for 4 h at room temperature, and the isolated sodium salts then reacted with an equivalent amount of *trans*-PhNi(PPh<sub>3</sub>)<sub>2</sub>Cl for 12 h in toluene to afford neutral nickel catalysts **4a–e**.

According to the <sup>1</sup>H and <sup>13</sup>C NMR spectra, neutral nickel complexes **4a–e** bearing  $\beta$ -ketoiminato ligands, similar to those bearing salicylaldiminato ligands, are diamagnetic.<sup>18</sup> To further confirm the structures of these complexes, crystals of **4b** and **4e** suitable for X-ray crystallographic analysis were grown from a benzene–hexane solution. The data collection and refinement data of the analysis are summarized in Table S1 (see Supporting Information), and the ORTEP diagrams together with selected bond lengths and angles for **4b** and **4e** are shown in Figures 1 and 2, respectively. In the solid state, both complexes adopt a near square-planar coordination geometry, and the triphenylphosphine group is *trans* to the N-aryl group, just as those reported previously,<sup>28</sup> because of the steric effect of N-aryl and triphenylphosphine groups. It is noteworthy that complex **4e** exhibited much longer Ni–N and Ni–O bond distances (1.952(6) and 1.914(5) Å, respectively) than complex **4b** (1.917(2) and 1.892(2) Å, respectively), although they displayed similar Ni–C(28) bond distances (1.908(3) and 1.905(7) Å, respectively) and close Ni–P bond distances (2.1878(8) and 2.186(2) Å, respectively). This may be explained by the fact that the electron density at N, O, and subsequently Ni atoms is largely influenced by the strong inductive effect of the trifluoromethyl group. In addition, the decrease of Ni–N–C(1) angles from 124.3° (**4b**) to 117.2° (**4e**) ensures that the steric hindrance brought by the trifluoromethyl group makes a great contribution to the variety of the Ni–N and Ni–O bond distances. Interestingly, it is seen from Figures 1 and 2 that complexes **4b** and **4e** display quite different O–Ni–C(28), N–Ni–P, C(28)–Ni–P, O–Ni–P, O–Ni–N, and C(28)–Ni–N angles. Complex **4b** showed much wider O–Ni–C(28), N–Ni–P, and C(28)–Ni–P angles (166.10(12)°, 169.04(7)°, and 91.58(9)°, respectively) compared with complex **4e** (156.4(3)°, 161.05(18)°, and 86.8(2)°, respectively). In contrast, O–Ni–P (81.41(7)°, O–Ni–N (92.33(9)°), and C(28)–Ni–N (96.35(11)°) angles of **4b** are much narrower than those of **4e** (86.92(15)°, 94.2(2)°, and 99.1(3)°, respectively). As a result, the torsion angles of the planes (C(28), Ni, P) and (N, Ni, O) of complex **4e** (28.5°) are much larger than those of **4b** (13.9°). All of these differences, which may have close relationships to the performances of the catalysts, may be ascribed to the coaction of steric and electronic effects of the trifluoromethyl group. In addition, complexes **4b** and **4e** adopt the same torsion angle (43.2°) of the planes (C(16)–C(21)) and (N, C(13)–(15), O).



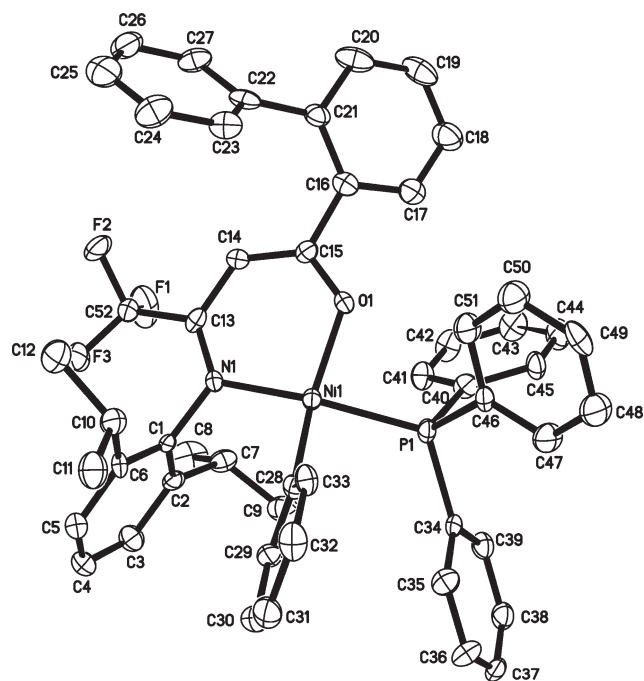
**Figure 1.** Molecular structure of complex **4b**. Thermal ellipsoids are drawn at the 30% probability level, and H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni–C(28) = 1.908(3), Ni–N = 1.917(2), Ni–O = 1.892(2), Ni–P = 2.1878(8), O–C(15) = 1.290(3), N–C(13) = 1.319(4), N–C(1) = 1.440(3), C(13)–C(14) = 1.399(4), C(14)–C(15) = 1.371(4), P–C(34) = 1.822(3), N–Ni–P = 169.04(7), O–Ni–C(28) = 166.10(12), O–Ni–P = 81.41(7), O–Ni–N = 92.33(9), C(28)–Ni–N = 96.35(11), C(28)–Ni–P = 91.58(9).

**Ethylene Polymerization with Neutral Nickel(II) Complexes 4a–e.** It was reported that neutral salicylaldiminato nickel complex **A** (Scheme 2) is inactive toward ethylene polymerization because its deactivation easily occurs by ligand disproportionation and dimerization.<sup>30</sup> Grubbs and his co-workers found that introducing a bulky substituent at the *ortho* position of the phenoxy group not only blocks the axial faces of the nickel center and retards the rate of chain termination but also enhances the catalytic activity by accelerating triphenylphosphine dissociation and decreases the rate of catalyst deactivation.<sup>18,30</sup> For example, catalyst **B**, with a bulky 9-anthracenyl at the *ortho* position of the phenoxy group, displays a high activity of up to 134 kg PE/mol<sub>Ni</sub>·h·atm under optimized conditions.<sup>31</sup> We found that binuclear complex **C**, in which each nickel unit acts as the *ortho* bulky hindrance of the other, also exhibited high catalytic activity and produced high molecular weight polyethylene.<sup>20h</sup> Thus, the neutral  $\beta$ -ketoiminato nickel complexes **4b–e** were designed and synthesized, bearing a bulky substituent at the R<sub>2</sub> position of the ligand, and were expected to be highly active toward ethylene polymerization. However, X-ray crystallographic analysis of complexes **4b** and **4e** showed that they adopt the same torsion angle (43.2°)

(29) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.

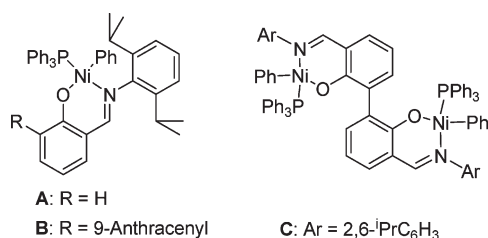
(30) Bansleben, D. A.; Grubbs, R. H.; Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T. *New Late Transition Metal Catalysts for the Polymerization of Ethylene*; *Proceedings of MetCon'98: "Polymers in Transition"*; June 10–11, 1998, Houston, TX; Paper II.3.

(31) At 58 °C and 400 psig of ethylene, **B** can produce PE with the highest activity of 134 kg PE/mol<sub>Ni</sub>·h·atm, but the *M<sub>w</sub>* value is only 85.9 kg/mol.<sup>18a</sup>



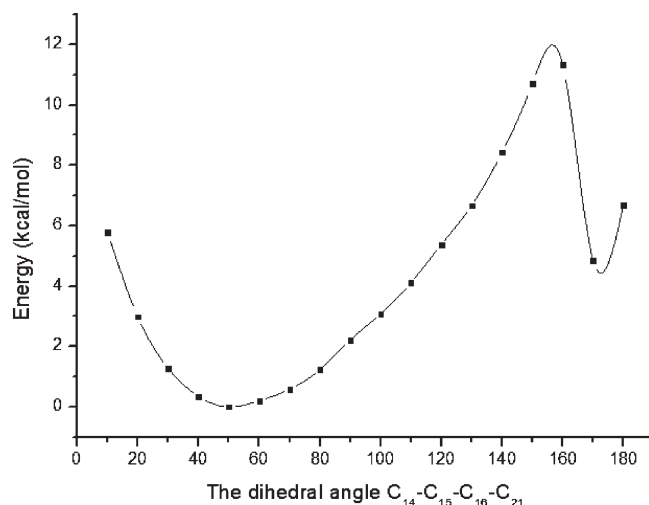
**Figure 2.** Molecular structure of complex **4e**. Thermal ellipsoids are drawn at the 30% probability level, and H atoms as well as a solvent molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni–C(28) = 1.905(7), Ni–N = 1.952(6), Ni–O = 1.914(5), Ni–P = 2.186(2), O–C(15) = 1.282(8), N–C(13) = 1.321(9), N–C(1) = 1.458(8), C(13)–C(14) = 1.400(10), C(14)–C(15) = 1.367(10), P–C(34) = 1.828(7), N–Ni–P = 161.05(18), O–Ni–C(28) = 156.4(3), O–Ni–P = 86.92(15), O–Ni–N = 94.2(2), C(28)–Ni–N = 99.1(3), C(28)–Ni–P = 86.8(2).

**Scheme 2. Neutral Salicylaldiminato Nickel Complexes Reported Previously**

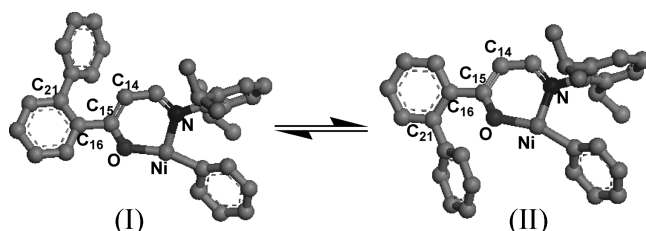


of the planes (C(16)–(21)) and (N, C(13)–(15), O) in the solid state. This observation means that the phenyl group in the R<sub>2</sub> position occupies a position remote from the nickel center, which seems useless for the introduced aryl group to protect catalyst species from the formation of bis-ligated analogue (inactive for ethylene polymerization).

In order to comprehend the actual state of the active species of neutral  $\beta$ -ketoiminato nickel catalysts in solution, the barrier for the rotating of C15–C16 bond was calculated by DFT. On the basis of the structure of **4b** without PPh<sub>3</sub>, we performed a linear transit calculation for the twist angle C14–C15–C16–C21 from 10° to 180°. The calculated energy profile is plotted in Figure 3. As can be seen from Figure 3, two stable structures, **4b-I** and **4b-II** (Figure 4), are found along the energy profile with C14–C15–C16–C21 dihedral angles of about 50° and 170°, respectively. The former configuration is very similar to the crystal structure of **4b** (C14–C15–C16–C21 = 44°). The energy barrier for



**Figure 3.** Rotating barrier of the C15–C16 bond.



**Figure 4.** Optimized structures according to DFT calculations. The torsion angles of C14–C15–C16–C21 are about 50° (I) and 170° (II), respectively.

this isomerization process is estimated to be about 12 kcal/mol, which is lower than for ethylene insertion (more than 15 kcal/mol) for salicylaldiminato neutral nickel catalysts evaluated by Ziegler and co-workers.<sup>15</sup> As a result, the rotation of the biphenyl group around the C15–C16 bond in **4b** is facilitated, which can retard the bis-ligated deactivation of the catalyst in the process of ethylene polymerization. This proved to be rational by subsequent experimental results.

Neutral nickel complexes **4a–e** were investigated as the catalysts for ethylene polymerization in toluene. Typical results summarized in Table 1 indicate that ligand structure significantly affects catalytic activity and polymer microstructure along with properties. Catalyst **4a** (R<sub>1</sub> = R<sub>2</sub> = H) was synthesized for comparison and showed an activity of 14.0 kg PE/mol<sub>Ni</sub>·h·atm (entry 2) under typical conditions using B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as a phosphine scavenger (60 °C, ethylene pressure of 25 atm, and B/Ni molar ratio = 1). It is noteworthy that catalyst **4b** (R<sub>1</sub> = H, R<sub>2</sub> = Ph) showed a much higher activity of up to 137 kg PE/mol<sub>Ni</sub>·h·atm (entry 5) under the same conditions, which is about 10 times more than the unsubstituted catalyst **4a**. Under the same conditions, a comparable catalytic activity of 106 kg PE/mol<sub>Ni</sub>·h·atm (entry 10) of catalyst **4c** (R<sub>1</sub> = H, R<sub>2</sub> = Naphth) was observed. These results have confirmed that an aryl group in the R<sub>2</sub> position will greatly enhance the catalytic activity of the  $\beta$ -ketoiminato neutral nickel catalyst toward ethylene polymerization. Just like salicylaldiminato neutral nickel catalysts, the aryl in the R<sub>2</sub> position may also play a leading role in protecting the active nickel species from the formation of bis-ligated analogues, which has been proven to be inactive toward ethylene polymerization. Complex **4b** was

Table 1. Results of Ethylene Polymerization Reactions<sup>a</sup>

entry	complex ( $\mu\text{mol}$ )	temp ( $^{\circ}\text{C}$ )	pressure (atm)	polymer (g)	activity <sup>b</sup>	$T_m$ ( $^{\circ}\text{C}$ )	$M_w^c$ (kg/mol)	$M_w/M_n^c$	branches <sup>d</sup> /1000 C
1	<b>4a</b> (20)	50	25	0.30	2.00	104	32.6	2.2	n.d.
2	<b>4a</b> (20)	60	25	2.30	14.0	101	27.3	2.2	25
3	<b>4b</b> (10)	40	25	0.30	3.60	99	19.6	2.2	18
4	<b>4b</b> (10)	50	25	12.1	145	97	26.5	1.9	20
5	<b>4b</b> (10)	60	25	11.4	137	91	17.0	1.8	22
6	<b>4b</b> (10)	60	35	6.20	53.1	98	28.9	2.2	24
7 <sup>e</sup>	<b>4b</b> (10)	60	25	0.60	7.20	91	14.7	1.7	30
8 <sup>e</sup>	<b>4b</b> (10)	80	35	0.50	4.29	92	12.9	2.2	n.d.
9	<b>4c</b> (20)	50	25	8.30	50.0	95	14.2	2.0	n.d.
10	<b>4c</b> (20)	60	25	17.5	106	88	9.00	2.0	39
11	<b>4d</b> (20)	50	25	0.90	5.60	n.d.	9.50	2.0	44
12	<b>4e</b> (10)	50	25	1.80	21.6	$\mathcal{J}$	2.54	1.9	103

<sup>a</sup> Reaction conditions: 100 mL of toluene, 1 equiv of  $\text{B}(\text{C}_6\text{F}_5)_3$  ( $\text{B}/\text{Ni}$  molar ratio = 1), polymerization for 20 min. <sup>b</sup> In units of  $\text{kg PE/mol}_{\text{Ni}} \cdot \text{h} \cdot \text{atm}$ . <sup>c</sup> Determined by GPC vs polystyrene standards. <sup>d</sup> Calculated from  $^{13}\text{C}$  NMR. <sup>e</sup> No  $\text{B}(\text{C}_6\text{F}_5)_3$  added. <sup>f</sup> The polymer is ceraceous at room temperature.

also employed as a single-component catalyst for ethylene polymerization (entries 7 and 8), but the activities were low, even though the reaction conditions were enhanced.

The synthesis and  $^1\text{H}$  NMR data of bis-ligand complexes of **3a** and **3b** are shown in the Supporting Information. Bis-ligand complex formation with catalysts **4a** and **4b** was investigated by  $^1\text{H}$  NMR spectroscopy. For each experiment, an NMR tube was charged with the neutral nickel complex (or single-ligand complex) and the corresponding ligand as well as  $\text{B}(\text{C}_6\text{F}_5)_3$  in equimolar ratios (20 mM in 0.5 mL of  $\text{C}_6\text{D}_6$ ). Then the NMR tube was heated to  $60\text{ }^{\circ}\text{C}$  for 20 min and then used for  $^1\text{H}$  NMR data collection. The formation of the bis-ligand complex of **3a** was observed by NMR spectroscopy, and about 8% of catalyst **4a** was transformed into the bis-ligated complex. Compared with **4a**, catalyst **4b** showed a much slower bis-ligated deactivation rate, and about 5% transformed into the bis-ligated complex under the same conditions. The result indicates again that the aryl in the  $\text{R}_2$  position can protect the active nickel species from the formation of bis-ligated analogues.

The variation of the  $\text{R}_1$  group also resulted in a remarkable influence on the catalytic activity. Among the five catalysts, **4b** ( $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{Ph}$ ) displayed the highest activity, up to  $145\text{ kg PE/mol}_{\text{Ni}} \cdot \text{h} \cdot \text{atm}$  (entry 4) under optimized condition, which is comparable with the case of salicylaldiminato neutral nickel systems ( $134\text{ kg PE/mol}_{\text{Ni}} \cdot \text{h} \cdot \text{atm}$ ).<sup>18a</sup> Compared with **4b**, surprisingly, catalyst **4d** ( $\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{Ph}$ ) exhibited a much lower activity of  $5.60\text{ kg PE/mol}_{\text{Ni}} \cdot \text{h} \cdot \text{atm}$  under the same conditions. As shown in Figure 5, the low activity of  $12.0\text{ kg PE/mol}_{\text{Ni}} \cdot \text{h} \cdot \text{atm}$  was still observed in a short period of 5 min, which indicates that **4d** is a catalyst with intrinsically low activity toward ethylene polymerization. Nevertheless, catalyst **4e** ( $\text{R}_1 = \text{CF}_3$ ,  $\text{R}_2 = \text{Ph}$ ) showed a higher activity of  $21.6\text{ kg PE/mol}_{\text{Ni}} \cdot \text{h} \cdot \text{atm}$  relative to catalyst **4d**, but the activity is still much lower than that of **4b**. In a word, introducing a substituent to the  $\text{R}_1$  position tends to have a negative effect on activity, and this observation is consistent with the electron-poor enolatoimine neutral nickel catalysts reported by Brookhart.<sup>27a</sup>

Reaction conditions, such as reaction temperature, also dramatically influence the catalytic activity. For catalyst **4b** ( $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{Ph}$ ), the productivity was greatly enhanced by increasing the temperature from  $40$  to  $50\text{ }^{\circ}\text{C}$  (entries 3 and 4). Compared with **4b**, catalyst **4a** ( $\text{R}_1 = \text{R}_2 = \text{H}$ ) tends to need a higher temperature (entries 2 vs 4) to attain a higher activity maybe due to the lack of steric hindrance.

The data listed in Table 1 indicate that substituent  $\text{R}_2$  considerably affects the molecular weight and the

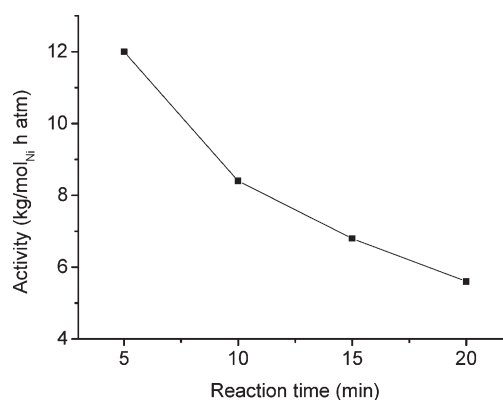
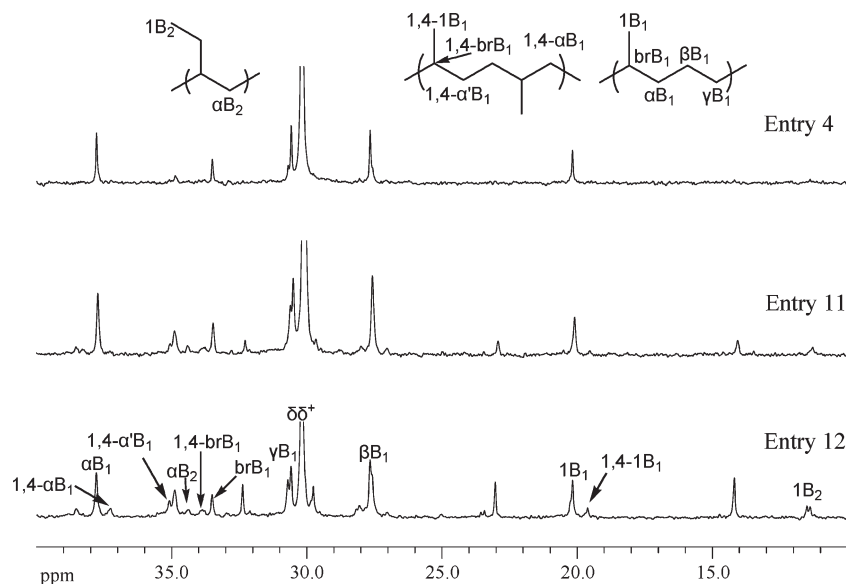


Figure 5. Catalytic activity vs reaction time for catalyst **4d**. Conditions: 100 mL of toluene at  $50\text{ }^{\circ}\text{C}$ , 1 equiv of  $\text{B}(\text{C}_6\text{F}_5)_3$  ( $\text{B}/\text{Ni}$  molar ratio = 1), ethylene pressure 25 atm,  $20\text{ }\mu\text{mol}$  of catalyst.

microstructure of the polyethylene produced. Under the typical conditions, the weight-average molecular weights ( $M_w$ ) of the polymers produced by **4a**, **4b**, and **4c** decreased from  $27.3$  to  $9.00\text{ kg/mol}$  with substituent  $\text{R}_2$  changing from hydrogen to phenyl to naphthyl, while the branching numbers increased from about 22 to 39 branches per 1000 carbon atoms (entries 2, 5, and 10). Furthermore, few ethyl and longer branches besides methyl ones were observed in the PE produced by catalyst **4a** (entry 2), while not only methyl but also ethyl and propyl branches in an approximate ratio of 31:5:3 were found for those produced by catalyst **4c** (entry 10), according to the analyses of  $^{13}\text{C}$  NMR spectra (see Figures S1 and S2 in the Supporting Information). This result implies that the  $\text{R}_2$  group probably accelerates chain migration and chain termination reactions, leading to more branched and lower  $M_w$  polyethylene, which is different from the case of salicylaldiminato neutral nickel systems.<sup>18a,18b</sup>

The variation of the  $\text{R}_1$  group also had a remarkable influence on the branch content and microstructure of the polymer produced, allowing access to the polyethylene whose structure varies from a relatively linear semicrystalline material (entry 4) to a highly branched (entry 12) and completely amorphous material. As shown in Figure 6, methyl branches are the only type of branches in the polymer chain produced by **4b** (entry 4), and the branching numbers is ca. 20 branches per 1000 carbon atoms. Compared with **4b**, interestingly, the branches of the polyethylene prepared by **4d** are not only methyls but also ethyls in an approximate ratio of 17:5 (Figure 6). Surprisingly, the more highly



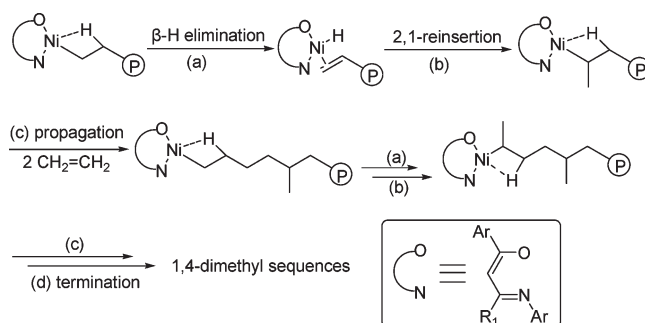


**Figure 6.**  $^{13}\text{C}$  NMR of polyethylene with different branching numbers produced by **4b** (entry 4), **4d** (entry 11), and **4e** (entry 12). The spectra were assigned according to the literature.<sup>33</sup>

branched polyethylene (103 branches per 1000 carbon atoms) can be prepared using trifluoromethyl-substituted **4c**, and the branches are mainly methyl and ethyl in an approximate ratio of 6:4.3 (Figure 6). Here, the branching number is comparable with that of polyethylene prepared using cationic  $\alpha$ -diimine nickel catalysts.<sup>2</sup> In addition, polymer molecular weights decreased from 26.5 to 2.54 kg/mol with the variation of the  $\text{R}_1$  group from hydrogen to methyl to trifluoromethyl (compare entries 4, 11, and 12). These results indicate that increasing the steric hindrance of  $\text{R}_1$  can greatly enhance the branch content of the polymers produced, and an electron-withdrawing group seems to increase the branching number and decrease the molecular weight. This may be best explained by the significant difference between structures **4b** and **4e** (Figures 1 and 2). The greatly distorted coordination square plane of **4e**, caused by the steric and electronic effects of the trifluoromethyl group, may remarkably influence the coordination and insertion of ethylene monomers in the process of polymerization, which is the critical factor in influencing the catalytic activity and polymer properties.

The molecular weights of polyethylenes produced by catalysts **4a**, **4b**, and **4c** ( $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{Naphth}$ ) all decreased with increasing the reaction temperature, while the branch content was enhanced at the same time. A similar phenomenon has also been reported concerning cationic  $\alpha$ -diimine nickel catalysts as well as salicylaldiminato neutral nickel systems<sup>2,18</sup> and demonstrates that the rate of chain migration and termination in our systems also increased at elevated temperature, yielding higher branched and lower  $M_w$  polymers. Ethylene pressure also dramatically affects the microstructure of the resultant polymers. It is noteworthy that the polyethylene with molecular weight increasing from 17.0 to 28.9 kg/mol can be obtained by changing the pressure from 25 to 35 atm (entries 5 and 6) at 60 °C using catalyst **4b**, which suggests that  $\beta$ -hydride elimination is the major chain transfer mechanism.<sup>16,17</sup> As shown in Figure 6, the microstructure of 1,4-dimethyl sequences can be observed in the highly branched polyethylenes produced by catalyst **4d** or **4e** (entries 11 and 12), which can be generated via

### Scheme 3. Proposed Mechanism for Generation of 1,4-Dimethyl Sequences



$\beta$ -hydride elimination and a readdition mechanism (chain walking).<sup>2,15,19</sup> These steps (shown in Scheme 3), (a)  $\beta$ -hydride elimination of a growing polymer chain forming a terminal double bond and (b) 2,1-reinsertion of the resultant double bond to “Ni–H” species, will first introduce a methyl branch in the polymer. After (c) chain propagation of two molecules of ethylene, repeat of steps (a) and (b) one time will result in the 1,4-dimethyl sequences in the polymer chain.

### Conclusions

A family of novel neutral nickel complexes based on modified  $\beta$ -ketoiminato ligands  $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{C}(\text{R}_1)\text{CHC}(2'\text{-}\text{R}_2\text{C}_6\text{H}_4)\text{O}]\text{Ni}(\text{Ph})(\text{PPh}_3)$  have been prepared and characterized. These complexes are highly active to ethylene polymerization in the presence of the activator  $\text{B}(\text{C}_6\text{F}_5)_3$ . The electronic and steric effects of substituents  $\text{R}_1$  and  $\text{R}_2$  exhibited a remarkable influence on the molecular weight and branch content of the produced polyethylenes. The aryl substituent in the  $\text{R}_2$  position was found to greatly increase catalytic activity and the number of branches in the resultant polyethylene. The variation of the  $\text{R}_1$  group also had a remarkable influence on the branch content and microstructure of the polymer produced, allowing access to polyethylene whose structure varies from a relatively linear semicrystalline material to a highly branched (more than

100 branches per 1000 carbons) and completely amorphous material. Reaction conditions, such as reaction temperature and ethylene pressure, also dramatically influence catalytic activity and the microstructure of the polymers obtained. Rational design of new ligands to further enhance catalytic activity and control over the molecular weight and the micromolecular structure of the polyethylenes obtained is currently under investigation and will be reported soon.

## Experimental Section

**General Procedures and Materials.** All work involving air- and/or moisture-sensitive compounds was carried out under a dry nitrogen atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents used were purified from an MBraun SPS system. The NMR data of ligands and complexes were obtained on a Bruker 300 MHz spectrometer at ambient temperature with  $\text{CDCl}_3$  or  $\text{C}_6\text{D}_6$  as the solvent. The NMR analyses of polymers were performed on a Varian Unity 400 MHz spectrometer at 135 °C, using  $o\text{-C}_6\text{D}_4\text{Cl}_2$  as the solvent. Elemental analyses were recorded on an elemental Vario EL spectrometer. Mass spectra were obtained using electron impact (EI-MS) and LDI-1700 (Linear Scientific Inc.). The differential scanning calorimetric (DSC) measurements were performed with a PerkinElmer Pyris 1 DSC differential scanning calorimeter at a rate of 10 °C/min. The molecular weights and the polydispersities of the polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three PLgel 10  $\mu\text{m}$  mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd.).

2'-Bromoacetophenone, phenylboric acid, and 1-naphthylboronic acid were purchased from Acros and directly used without purification. 2,6-Diisopropylaniline and NaH were obtained from Acros. Potassium *tert*-butoxide was purchased from Aldrich Chemicals. *trans*- $\text{PhNi}(\text{PPh}_3)_2\text{Cl}$  and  $\text{Pd}(\text{PPh}_3)_4$  were prepared according to the literature.<sup>32</sup> Commercial ethylene was used without further purification.

**Synthesis of 2'-Phenylacetophenone (compound 1).** Under nitrogen, 30.0 g of 2'-bromoacetophenone (150 mmol) and 1.7 g of  $\text{Pd}(\text{PPh}_3)_4$  (1.0 mmol) were put in a 500 mL bottle, followed by 150 mL of anhydrous toluene, and a yellow solution formed. Subsequently, 21.9 g of phenylboric acid (1.2 equiv), 100 mL of alcohol, and then 45.0 g of anhydrous  $\text{K}_2\text{CO}_3$  (4.4 equiv) were added to the solution, and the mixture was refluxed for 4 h under vigorous stirring. The resultant product was cooled to room temperature, and  $\text{K}_2\text{CO}_3$  was removed by filtration. The solvent was also evaporated, and the product was purified via distillation under reduced pressure at 140 °C, affording 27.0 g (93%) of colorless oil at room temperature.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.56–7.49 (m, 2H, Ar-H), 7.47–7.39 (m, 5H, Ar-H), 7.36–7.33 (m, 2H, Ar-H), 2.00 (s, 3H, CO-CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  205.16 (O=C), 141.32, 141.15, 140.93, 131.16, 130.67, 129.27, 129.11, 128.32, 127.88, (Ph), 30.84 (CH<sub>3</sub>).

**Synthesis of 2'-Naphthylacetophenone (compound 2).** Compound 4 was prepared according to the same method as compound 1 and purified by column chromatography on silica gel. The product (23.0 g, 94%) was collected as white solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93–7.89 (m, 2H, Ar-H), 7.77–7.74 (m, 5H, Ar-H), 7.64–7.48 (m, 5H, Ar-H), 7.46–7.41 (m, 2H, Ar-H), 7.36–7.33 (m, 1H, Ar-H), 1.78 (s, 3H, CO-CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.49 (O=C), 141.70, 139.50,

139.15, 134.05, 132.35, 132.08, 131.29, 128.79, 128.25, 127.79, 127.03, 126.55, 126.09, 125.78, (Ar), 30.18 (CH<sub>3</sub>).

**Synthesis of Ligands 3a–e.** To a slurry of 3.3 g of potassium *tert*-butoxide (1.5 equiv) in anhydrous diethyl ether (40 mL) were added 2.4 g of acetophenone (20 mmol) and 2.9 g of ethyl formate (2.0 equiv) at 0 °C. Immediately a large amount of white solid appeared in the reaction bottle, and the mixture was stirred for 30 min at 0 °C. Then the resulting suspension was allowed to warm to room temperature and stirred for about 10 h. The white solid was separated by filtration and dried under reduced pressure. Formic acid in ethanol was added to the solid until the pH was <7, affording the corresponding  $\beta$ -diketone, which was used directly in the preparation of ligand 3a. Subsequently, 3.5 g of 2,6-diisopropylaniline (1.0 equiv) was added to the obtained  $\beta$ -diketone in ethanol, and the condensation reaction was carried out for about 24 h, yielding 3.5 g of ligand 3a (57%). Ligands 3b–d were prepared according to the same method as 3a, except for the preparation of 3e, which was synthesized from boiling toluene with *p*-toluenesulfonic acid as the catalyst.

**(2,6- $\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CHCHC}(\text{C}_6\text{H}_5)\text{OH}$  (3a)).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.67 (d,  $^3J_{\text{HH}} = 12.6$  Hz, 1H, N-H), 7.98–7.95 (m, 2H, Ar-H), 7.52–7.42 (m, 3H, Ar-H), 7.31–7.28 (m, 1H, Ar-H), 7.22–7.18 (m, 2H, Ar-H), 7.00–6.89 (m, N=C-H), 5.96 (d,  $J = 7.5$  Hz, 1H, C=C-H), 3.26 (sept,  $^3J_{\text{HH}} = 6.9$  Hz, 2H,  $^i\text{Pr}$ -CH), 1.23 (d,  $^3J_{\text{HH}} = 6.9$  Hz, 12H,  $^i\text{Pr}$ -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  189.65 (N=C), 152.99, 143.59, 138.40, 135.19, 130.21, 127.29, 127.05, 126.42, 125.34, 122.75, (Ar), 90.42 (=C), 26.99 ( $^i\text{Pr}$ -CH), 22.75 ( $^i\text{Pr}$ -CH<sub>3</sub>). Anal. Calcd for  $\text{C}_{21}\text{H}_{25}\text{NO}$ : C, 82.04; H, 8.20; N, 4.56. Found: C, 81.65; H, 8.15; N, 4.59.

**(2,6- $\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CHCHC}(2'\text{-Ph-C}_6\text{H}_4)\text{OH}$  (3b)).** Yield: 61%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.20 (d,  $^3J_{\text{HH}} = 12.3$  Hz, 1H, N-H), 7.50–7.30 (m, 8H, Ar-H), 7.25–7.22 (m, 1H, Ar-H), 7.15 (m, 8H, Ar-H), 6.53 (dd,  $^3J_{\text{HH}} = 12.3$ , 7.2 Hz, 1H, N=C-H), 5.07 (d,  $^3J_{\text{HH}} = 7.2$  Hz, C=C-H), 3.15 (sept,  $^3J_{\text{HH}} = 6.9$  Hz, 2H,  $^i\text{Pr}$ -CH), 1.19 (d,  $^3J_{\text{HH}} = 6.9$  Hz, 12H,  $^i\text{Pr}$ -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.41 (N=C), 151.48, 143.47, 140.61, 140.39, 138.94, 135.17, 129.09, 128.82, 128.43, 128.11, 127.71, 126.97, 126.49, 126.17, 126.01, 122.69, (Ar), 96.29 (=C), 27.26, 27.03, ( $^i\text{Pr}$ -CH), 22.69 ( $^i\text{Pr}$ -CH<sub>3</sub>). Anal. Calcd for  $\text{C}_{27}\text{H}_{29}\text{NO}$ : C, 84.55; H, 7.62; N, 3.65. Found: C, 84.72; H, 7.66; N, 3.61.

**(2,6- $\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CHCHC}(2'\text{-Naphth-C}_6\text{H}_4)\text{OH}$  (3c)).** Yield: 53%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.09 (d,  $^3J_{\text{HH}} = 12.9$  Hz, 1H, N-H), 7.87–7.81 (m, 3H, Ar-H), 7.75, (d,  $J = 8.1$  Hz, 1H, Ar-H), 7.55–7.38 (m, 7H, Ar-H), 7.20–7.05 (m, 3H, Ar-H), 6.26 (dd,  $^3J_{\text{HH}} = 12.6$ , 7.5 Hz, 1H, N=C-H), 4.91 (d,  $^3J_{\text{HH}} = 7.5$  Hz, C=C-H), 2.82 (sept,  $^3J_{\text{HH}} = 6.9$  Hz, 2H,  $^i\text{Pr}$ -CH), 1.07–1.04 (dd,  $J = 6.9$ , 3.9 Hz, 12H,  $^i\text{Pr}$ -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  193.23 (N=C), 151.38, 143.48, 141.54, 138.60, 137.31, 135.01, 132.41, 131.09, 130.34, 128.43, 127.02, 126.50, 126.29, 124.96, 124.59, 124.13, 122.52, (Ar), 95.28 (=C), 27.03 ( $^i\text{Pr}$ -CH), 22.58 ( $^i\text{Pr}$ -CH<sub>3</sub>). Anal. Calcd for  $\text{C}_{31}\text{H}_{31}\text{NO}$ : C, 85.87; H, 7.21; N, 3.23. Found: C, 85.93; H, 7.17; N, 3.18.

**(2,6- $\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{C}(\text{CH}_3)\text{CHC}(2'\text{-Ph-C}_6\text{H}_4)\text{OH}$  (3d)).** Yield: 55%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.23 (s, 1H, N-H), 7.65 (d,  $J = 6.9$  Hz, 1H, C=C-H), 7.45–7.30 (m, 10H, Ar-H), 7.16 (d,  $J = 7.5$  Hz, 2H, Ar-H), 3.00 (sept,  $^3J_{\text{HH}} = 6.9$  Hz, 2H,  $^i\text{Pr}$ -CH), 1.50 (s, 3H, CO-CH<sub>3</sub>), 1.22–1.15 (dd,  $J = 16.2$ , 6.9 Hz, 12H,  $^i\text{Pr}$ -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  193.00 (N=C), 163.83, 146.15, 142.20, 141.79, 137.29, 133.57, 131.59, 130.68, 130.14, 129.11, 128.35, 128.05, 127.91, 127.41, 127.13, 126.88, 123.77, 123.60, (Ar), 98.03 (=C), 28.54 ( $^i\text{Pr}$ -CH), 24.59, 22.76, ( $^i\text{Pr}$ -CH<sub>3</sub>), 19.22 (CH<sub>3</sub>). Anal. Calcd for  $\text{C}_{31}\text{H}_{31}\text{NO}$ : C, 84.59; H, 7.86; N, 3.52. Found: C, 84.44; H, 7.85; N, 3.57.

**(2,6- $\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{C}(\text{CF}_3)\text{CHC}(2'\text{-Ph-C}_6\text{H}_4)\text{OH}$  (3e)).** Yield: 50%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.54 (s, 1H, N-H), 7.68 (d,  $J = 7.8$  Hz, 1H, Ar-H), 7.55–7.39 (m, 8H, Ar-H), 7.32–7.25 (m, 1H, Ar-H), 7.15 (m, 2H, Ar-H), 5.53 (s, 1H, C=C-H), 3.03 (m,  $^3J_{\text{HH}} = 6.9$  Hz, 2H,  $^i\text{Pr}$ -CH), 1.25–1.11 (m,  $^3J_{\text{HH}} = 6.9$  Hz, 12H,  $^i\text{Pr}$ -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.22 (N=C), 148.93, 140.98, 140.77, 140.62, 137.22, 132.38, 130.52, 129.10,

(32) (a) Hidai, M.; Kashiwagi, T.; Ikeuchi, T.; Uchida, Y. *J. Organomet. Chem.* **1971**, *30*, 279. (b) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(33) Galland, G. B.; Souza, R. F.; Mauler, R. S.; Nunes, F. F. *Macromolecules* **1999**, *32*, 1620.



128.78, 128.25, 127.50, 123.31, 121.49, (Ar, CF<sub>3</sub>), 96.39 (=C), 28.66 (<sup>1</sup>Pr-CH), 25.30, 21.83, (<sup>1</sup>Pr-CH<sub>3</sub>). Anal. Calcd for C<sub>28</sub>H<sub>28</sub>NO: C, 74.48; H, 6.25; N, 3.10. Found: C, 74.36; H, 6.20; N, 3.14.

**Synthesis of Complexes 4a–e.** A solution of ligand **3a** (0.4 g, 1.0 mmol) in THF (15 mL) was added to sodium hydride (48 mg, 2.0 mmol). Immediately a large amount of bubbles were emitted from the mixture and a yellow solution formed. Then the solution was stirred at room temperature for 4 h, filtered, and evaporated. The solid residue was washed with hexane (20 mL) and dried in a vacuum, affording a light yellow sodium salt. The sodium salt was dissolved in toluene at room temperature and transferred to a toluene solution of *trans*-PhNi(PPh<sub>3</sub>)<sub>2</sub>Cl (0.7 g, 1.0 mmol) in a Schlenk flask under stirring at room temperature for 12 h, forming a red solution. Then the reaction mixture was filtered by cannula filtration and the filtrate was concentrated in vacuo to about 4 mL, to which hexane (15 mL) was added. Subsequently, yellow crystals precipitated from the solution, which was isolated via filtration and washed several times by cold hexane to yield 0.58 g (51%) of complex **4a**. The other neutral nickel(II) complexes **4b–e** were prepared by the same procedure with similar yields.

**[(2,6-<sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CHCHC(C<sub>6</sub>H<sub>4</sub>)O]Ni(Ph)(PPh<sub>3</sub>) (**4a**).** <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.67–7.61 (m, 6H, Ar-H), 7.10–6.89 (m, 20H, Ar-H), 6.40–6.29 (m, 3H, Ar-H), 5.92 (d, *J* = 6.3 Hz, 1H, C=C-H), 4.24 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 2H, <sup>1</sup>Pr-CH), 1.36, 1.25 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 12H, <sup>1</sup>Pr-CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 172.00 (N=C), 161.24, 151.45, 147.55, 142.06, 139.40, 138.14, 134.82, 132.45, 131.89, 129.97, 129.55, 127.00, 125.82, 125.55, 122.89, 121.66, (Ar), 92.12 (=C), 29.10 (<sup>1</sup>Pr-CH), 26.25, 23.17, (<sup>1</sup>Pr-CH<sub>3</sub>). Anal. Calcd for C<sub>45</sub>H<sub>44</sub>NNiOP: C, 76.72; H, 6.30; N, 1.99. Found: C, 76.58; H, 6.34; N, 1.94.

**[(2,6-<sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CHCHC(2'-phenyl-C<sub>6</sub>H<sub>4</sub>)O]Ni(Ph)(PPh<sub>3</sub>) (**4b**).** Yield: 60%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.56–7.50 (m, 5H, Ar-H), 7.57–7.20 (m, 6H, Ar-H), 7.13–6.82 (m, 19H, Ar-H, N=CH), 6.38–6.28 (m, 3H, Ar-H), 5.13 (d, *J* = 6.3 Hz, 1H, C=C-H), 4.12 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 2H, <sup>1</sup>Pr-CH), 1.35, 1.10 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 12H, <sup>1</sup>Pr-CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 171.00 (N=C), 160.32, 151.40, 147.52, 142.82, 141.27, 140.15, 138.45, 134.81, 132.29, 131.72, 130.28, 129.65, 129.22, 127.00, 125.52, 122.72, 121.64, (Ar), 98.49 (=C), 28.93 (<sup>1</sup>Pr-CH), 26.26, 23.16, (<sup>1</sup>Pr-CH<sub>3</sub>). Anal. Calcd for C<sub>51</sub>H<sub>48</sub>NNiOP: C, 78.47; H, 6.20; N, 1.79. Found: C, 78.29; H, 6.14; N, 1.84.

**[(2,6-<sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CHCHC(2'-naphthyl-C<sub>6</sub>H<sub>4</sub>)O]Ni(Ph)(PPh<sub>3</sub>) (**4c**).** Yield: 65%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.87–7.25 (m, 13H, Ar-H), 7.14–6.59 (m, 19H, Ar-H), 6.33–6.26 (b, 3H, Ar-H), 4.94 (d, *J* = 6.3 Hz, 1H, C=C-H), 4.12, 3.51 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz, 2H, <sup>1</sup>Pr-CH), 1.35, 1.20, 0.97, 0.71 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz, 12H, <sup>1</sup>Pr-CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 174.00 (N=C), 147.43, 142.06, 141.74, 141.21, 138.44, 137.97, 134.84, 134.31, 133.00, 132.63, 132.07, 131.49, 129.87, 129.51, 127.42, 126.86, 126.30, 126.08, 125.80, 125.49, 125.26, 122.56, 121.56, (Ar), 97.79 (=C), 28.79 (<sup>1</sup>Pr-CH), 25.98, 23.12, (<sup>1</sup>Pr-CH<sub>3</sub>). Anal. Calcd for C<sub>45</sub>H<sub>50</sub>NNiOP: C, 79.53; H, 6.07; N, 1.69. Found: C, 79.44; H, 6.04; N, 1.66.

**[(2,6-<sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=C(CH<sub>3</sub>)CHC(2'-phenyl-C<sub>6</sub>H<sub>4</sub>)O]Ni(Ph)(PPh<sub>3</sub>) (**4d**).** Yield: 50%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.64–7.58 (m, 5H, Ar-H), 7.48–7.19 (m, 6H, Ar-H), 7.04–6.91 (m, 18H, Ar-H), 6.40–6.34 (m, 3H, Ar-H), 5.03 (s, 1H, C=C-H), 3.77 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz, 2H, <sup>1</sup>Pr-CH), 1.33 (s, 1H, COCH<sub>3</sub>), 1.30, 1.13 (d, *J* = 6.6 Hz, 12H, <sup>1</sup>Pr-CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 173.08 (N=C), 166.75, 148.27, 143.19, 141.53, 141.17, 140.16, 138.34, 135.26, 134.77, 132.63, 132.06, 130.06, 129.76, 129.50, 127.03, 125.48, 123.36, 121.46, (Ar), 102.98 (=C), 28.85 (<sup>1</sup>Pr-CH), 25.64 (COCH<sub>3</sub>), 24.72 (<sup>1</sup>Pr-CH<sub>3</sub>). Anal. Calcd for C<sub>52</sub>H<sub>50</sub>NNiOP: C, 78.60; H, 6.34; N, 1.76. Found: C, 78.38; H, 6.28; N, 1.72.

**[(2,6-<sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=C(CF<sub>3</sub>)CHC(2'-phenyl-C<sub>6</sub>H<sub>4</sub>)O]Ni(Ph)(PPh<sub>3</sub>) (**4e**).** Yield: 55%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.57–7.52 (m, 5H, Ar-H), 7.42–7.20 (m, 6H, Ar-H), 7.11–6.83 (m, 18H, Ar-H), 6.43–6.28 (m, 3H, Ar-H), 5.50 (s, 1H, C=C-H), 3.65 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz, 2H, <sup>1</sup>Pr-CH), 1.30, 1.27 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz, 12H, <sup>1</sup>Pr-CH<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 177.89 (N=C),

153.82, 146.17, 143.29, 142.50, 140.56, 137.79, 134.66, 132.63, 131.80, 131.31, 130.44, 130.13, 129.57, 129.05, 127.10, 125.74, 123.21, 122.04, (Ar, CF<sub>3</sub>), 98.55 (=C), 29.06 (<sup>1</sup>Pr-CH), 24.80 (<sup>1</sup>Pr-CH<sub>3</sub>). Anal. Calcd for C<sub>52</sub>H<sub>47</sub>NNiOP: C, 73.60; H, 5.58; N, 1.65. Found: C, 73.41; H, 5.54; N, 1.69.

**Ethylene Polymerization.** A 200 mL autoclave was heated under vacuum up to 130 °C for 10 h and then was cooled to the desired reaction temperature in an oil bath at constant temperature. The vessel was purged three times with ethylene and then was charged with toluene (50 mL) under vacuum. A 10 or 20 μmol amount of cocatalyst dissolved in 10 mL of toluene was added into the autoclave by syringe, followed by the same amount of catalyst. The total volume of the reaction medium was fixed at 100 mL. And then the reactor was sealed and pressurized to the desired level, and the stirring motor was engaged. Temperature control was maintained by internal cooling water coils with temperature increases within 2 °C in every case. After the prescribed reaction time, the stirring motor was stopped, the reactor was vented, and the polymer was isolated via precipitation from ethanol. The solid polyethylene was filtered, washed with acetone several times, and dried at 60 °C for more than 10 h under vacuum.

**Crystallographic Studies.** Crystals for X-ray analysis were obtained as described in the preparations. The crystallographic data, collection parameters, and refinement parameters are listed in Table 1. The crystals were manipulated in a glovebox. The intensity data were collected with the ω scan mode (186 K) on a Bruker Smart APEX diffractometer with CCD detector using Mo Kα radiation (λ = 0.71073 Å). Lorentz and polarization factors were applied to the intensity data, and absorption corrections were performed using the SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least-squares. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons.

**DFT Studies.** In order to enhance the understanding of the catalytic structure–reactivity relationship for the neutral β-ketoiminato nickel catalyst, density functional theory (DFT) calculations were carried out using the Amsterdam Density Functional (ADF) program package.<sup>34</sup> The structures and energies are obtained on the basis of the local density approximation augmented with Becke's nonlocal exchange corrections<sup>35</sup> and Perdew's nonlocal correlation correction.<sup>36</sup> A standard double STO basis set with one set of single polarization functions was employed for C, N, and H atoms, while a triple STO basis set with polarization functions was employed for Ni. The 1s electrons of the C, N, and O atoms, as well as the 1s-2p electrons of Ni atom, were treated as frozen core. Finally, first-order scalar relativistic corrections were added to the total energy of the system.

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**Supporting Information Available:** X-ray diffraction data for **4b** and **4e** (as CIF), the data collection and refinement data of the analysis, <sup>13</sup>C NMR spectra for polymers, and the synthesis and <sup>1</sup>H NMR data of bis-ligand complexes of **3a** and **3b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(34) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, 2, 41. (b) Baerends, E. J.; Ros, P. *Chem. Phys.* **1973**, 2, 52. (c) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, 99, 8498. (d) Fonseca, C. G.; Visser, O.; Snijders, J. G.; te Velde, G.; Baerends, E. J. In *Methods and Techniques in Computational Chemistry*, METECC-95; Clementi, E., Corongiu, G., Eds.; STEF: Cagliari, Italy, 1995; p 305.

(35) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098.

(36) Perdew, J. P. *Phys. Rev. B* **1986**, 33, 8822.