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A Highly Active Anilinoperinaphthenone-Based Neutral Nickel(II) Catalyst for Ethylene Polymerization

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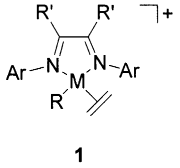
A general synthetic route for the preparation of 2-anilinoperinaphthenones is reported. 2-(2,6-Dimethylanilino)perinaphthenone (**4a**) and 2-(2,6-diisopropylanilino)perinaphthenone (**4b**) are used as ligands for the corresponding neutral nickel(II) complexes [[(2,6-$Me_2C_6H_3$)-$NC_{13}H_7O$]Ni(Ph)(PPh_3)] (**5a**) and [[(2,6-$^iPr_2C_6H_3$)$NC_{13}H_7O$]Ni(Ph)(PPh_3)] (**5b**). The key features of these nickel complexes are a hindered N-aryl ring, a five-membered-ring nickel chelate, and an anionic N-donor moiety. Complexes **5a**,**b** are active, but short-lived, ethylene polymerization catalysts with turnover numbers in excess of 60 000 mol ethylene/mol catalyst. Polymer branching is controlled by variation of temperature and pressure. A correlation between ethylene pressure and polymer molecular weight suggests that chain transfer occurs by a β-hydride elimination pathway. Finally, decomposition of **5b** to free ligand is observed under the polymerization conditions employed.

Introduction

Interest in late transition metal complexes as olefin polymerization catalysts has been on the rise in the past several years,[1−23] stimulated in part by the discovery of α-diimine-based cationic nickel and palladium catalysts, **1**.[2−8,11−14] These catalysts were found to have quite different properties compared to their early metal counterparts.[2−8,11−14] The microstructue of polyethylenes produced with the α-diimine nickel catalysts may be varied from essentially linear to highly branched simply by changing the polymerization temperature and ethylene pressure.[2,3,5,6,8] The palladium version of the α-diimine catalysts produces highly branched polyethylene regardless of polymerization conditions. [2,3,12,13] These catalysts are also known to "chain straighten" poly-α-olefins, producing polymers with fewer branches than expected.[2,5,6] An attractive feature of late metal olefin polymerization catalysts is an increased functional group tolerance both for comonomers and polymerization solvents.[14,15] For example, emulsion polymerizations with late metal catalysts have been successfully carried out in water,[14,15,18,24] and both the nickel and palladium α-diimine catalysts have been reported to successfully copolymerize ethylene with alkyl acrylates.[4,7,25] The nickel catalysts require temperatures above 120 °C, whereas the palladium analogues are active under milder conditions.



1
M = Ni, Pd

Typically, the cationic nickel systems are more electrophilic and thus more sensitive to protic solvents and comonomer functional groups relative to the cationic palladium analogues. Therefore there has been sub-

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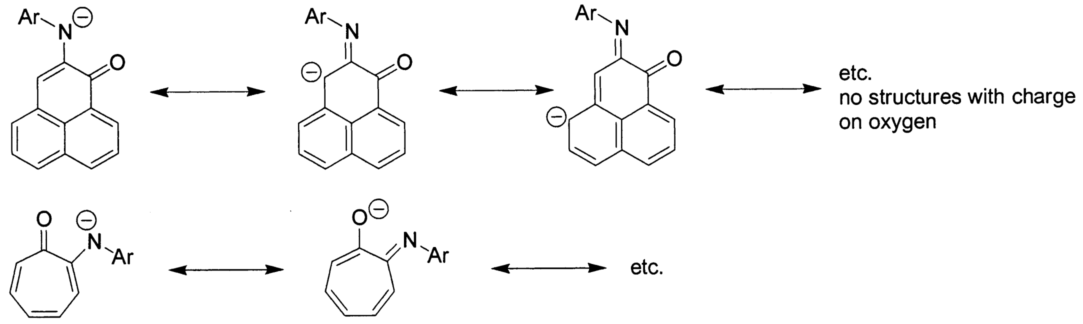
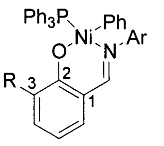
Scheme 1



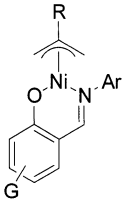
stantial interest in developing neutral nickel analogues to overcome these limitations. The most industrially relevant neutral nickel catalysts are the SHOP-type catalysts developed for the conversion of ethylene to linear α-olefins.[16−18] Modified SHOP catalysts convert ethylene to high molecular weight polymers, but only under special conditions.[16,17,23] Recently, neutral nickel catalysts that incorporate at least one bulky N-aryl ring were reported. Salicylaldimine catalysts, **2**, were described by DuPont[26] and by Grubbs.[27,28] The most active systems contain either electron-withdrawing nitro substituents in the aromatic ring or bulky substituents at C-3, with a 9-anthracenyl group being most effective. In the latter case, activities of 1.3 × 10^5 mol ethylene(mol Ni·h)$^{-1}$ and lifetimes in excess of 6 h were observed at 45−50 °C.



R = H, **2a**

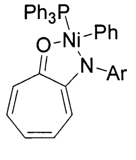
R = 9-anthracenyl, **2b**

Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$



2c

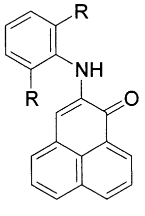
G = Functional group(s)



3, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

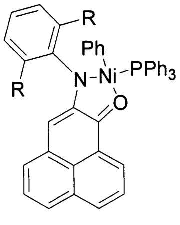
We reported catalysts of type **3** based on anilinotropone ligands.[29] High activities were observed for the unsubstituted catalyst (6 × 10^4 mol ethylene mol Ni^{-1} h^{-1}), and compared with the unsubstituted salicylaldimine catalyst **2a** (3400 mol ethylene mol Ni^{-1} h^{-1}), the anilinotropone catalyst appears to be more reactive. Clearly a major difference between these two systems is that the salicylaldimine catalysts possess a six-membered nickel chelate while the anilinotropone catalyst contains a five-membered nickel chelate. It is not clear if chelate size is responsible for the difference in activities, but Keim showed with SHOP-type systems that an increase in activity is observed with contraction of chelate size.[30]

This work examines other neutral nickel catalyst analogues containing five-membered chelates with potentially different electronic properties. We report the synthesis and polymerization activity of **5a**,**b** prepared from the anilinoperinaphthenone ligands **4a**,**b**. A unique feature of the deprotonated anilinoperinaphthenone ligand compared to the salicylaldimine and anilinotropone ligands is that the negative charge cannot be delocalized by resonance onto oxygen, and thus charge density at oxygen should be substantially less in **5** than in **2** or **3** (Scheme 1).



R = Me, **4a**

R = ^{i}Pr, **4b**



R = Me, **5a**

R = ^{i}Pr, **5b**

Results and Discussion

Ligand Synthesis. The anilinoperinaphthenone ligands, **4a** and **4b**, were prepared by the palladium-catalyzed coupling of 2-bromoperinaphthenone with 2,6-dimethyl and 2,6-diisopropylaniline, respectively, using the methodology developed by Buchwald and Hartwig.[31−34] Racemic 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), 1,1′-bis(diphenylphosphino)ferrocene (DPPF), 2-di-*tert*-butylphosphino-1,1′-biphenyl, and 2-dicyclohexylphosphino-1,1′-biphenyl were screened as possible ligands for the palladium-catalyzed coupling. 2-Dicyclohexylphosphino-1,1′-biphenyl was determined to give the best yield and the fewest side products. Both coupling reactions were carried out with 1 equiv of bromoperinaphthenone, 1.2 equiv of aniline, 1.4 equiv of sodium *tert*-butoxide, and a 10 mol % catalyst loading

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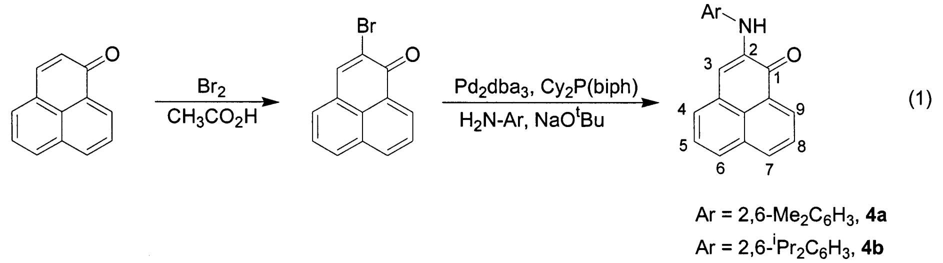
Scheme 2



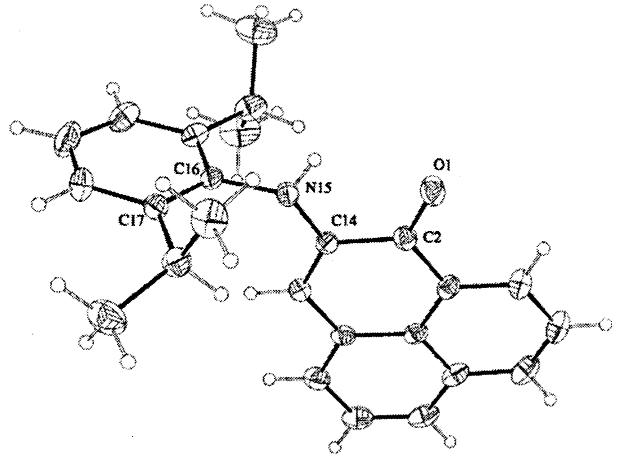
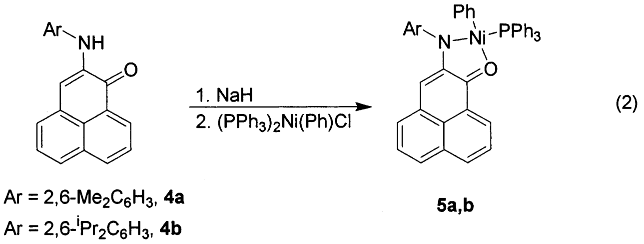


Figure 1. ORTEP view of **4b**. Selected interatomic distances (Å) and angles (deg): C(14)−N(15) = 1.367(2), C(2)−O(1) = 1.234(2), C(14)−N(15)−C(16)−C(17) = 104.01(21).

Scheme 3



of Pd_2dba_3 and 2-dicyclohexylphosphino-1,1′-biphenyl at 80 °C in toluene for 18 h (Scheme 2). The required catalyst loading was significantly higher than typically reported for most couplings of this type, but was necessary to produce anilinoperinaphthenones in yields of 60−70%.[31−34] Use of 5% catalyst loading led to yields in the 40−50% range. Similar problems were not observed with 2-triflatotropone.[35]

The ^1H NMR spectrum of **4b** is typical of both ligands and is described here. Characteristic resonances include a broad singlet at 6.60 ppm assigned to the N−H proton and a sharp singlet at 6.12 ppm assigned to H_3. A doublet at 1.20 ppm, which integrates to 12 protons, is assigned to four equivalent methyl groups of the two isopropyl substituents and indicates that rotation about the N-aryl bond is fast on the NMR time scale.

An X-ray quality crystal of 2-(2,6-diisopropylanilino)-perinaphthenone (**4b**) was prepared by slow diffusion of hexamethylsiloxane into a concentrated solution of **4b** in toluene at room temperature. As expected, the sterically bulky isopropyl groups hold the N-aryl ring nearly perpendicular to the plane of the perinaphthenone ring. The torsion angle for the C−N (C14−N15−C16−C17) bond was determined to be 104.01(21)°. The C−N bond length of 1.367(2) Å is shorter than the 1.435(2) Å C−N bond of 2-(2,6-diisopropyl)anilinotropone, while the C−O bond lengths are similar at 1.234(2) and 1.252(2) Å, respectively.[29]

Catalyst Synthesis. We expected precatalysts (**5a**,**b**) to be available from reaction of the sodium salts of **4a**,**b** with $(PPh_3)_2Ni(Ph)Cl$.[27,29] Isolation of the sodium salts formed from **4a**,**b** upon deprotonation with sodium hydride proved to be extremely difficult. The sodium salts produced from reaction of NaH with salicylaldimine and anilinotropone, precursors of **2** and **3**, were reported to be relatively stable compounds under an inert atmosphere.[27,29] Deprotonation of **4a**,**b** with NaH was indicated by a distinct color change from bright red to bright green. However, upon attempted isolation using techniques successful for **2** and **3**, protonation of the salt was apparent from the color change back to the original bright red color characteristic of **4a**,**b**. The sodium salts could be isolated using rigorously dried glassware and cannulae, but partial protonation occurred over the course of several days' storage in the solid state under argon. Therefore, attempts to use the isolated sodium salts for catalyst preparation were abandoned in favor of an in situ technique (see below). The extreme sensitivity of the ligand salt to adventitious water is likely due to the higher basicity of the anion as a result of the lack of resonance stabilization of negative charge by the carbonyl moiety (Scheme 1).

Catalysts **5a**,**b** were readily synthesized by in situ deprotonation of the anilinoperinaphthenone ligand with excess sodium hydride in THF followed by addition of $(PPh_3)_2Ni(Ph)(Cl)$ as a solid (Scheme 3). The excess sodium hydride in the reaction mixture does not react with either the nickel precursor or the final product and can be filtered away prior to product isolation. Catalysts **5a**,**b** were obtained as purple crystals in yields of 65% and 70%, respectively, upon recrystallization and were fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis.

For catalyst **5b**, coordination of the anilinoperinaphthenone ligand to the nickel center causes rotation about the N-aryl bond to become slow on the NMR time scale and thus renders the individual methyl groups of an isopropyl unit inequivalent in the ^1H NMR spectrum. Two doublets, each of which integrate to six protons, are observed at 1.14 and 1.04 ppm, while in **4b** one 12H doublet is observed (see above). As expected, the broad singlet seen for **4b** at 6.60 ppm, attributed to the N-H proton, is absent. Other minor changes in the ^1H NMR spectrum of **5b** relative to **4b** are observed and noted

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Table 1. Ethylene Polymerizations Catalyzed by 5a,b[c]

entry	catalyst	loading (μmol)	time (min)	temp (°C)	pressure (psig)	TON[a]	yield PE (g)	M_n	MWD	branches/ 1000 C[b]
1	**5a**	10.0	30	80	200	8000	2.24	25k	3.5	51
2	**5a**	10.0	30	80	400	3900	1.08	23k	3.2	43
3	**5b**	10.6	30	40	200	5600	1.66	171k	1.5	17
4	**5b**	10.6	30	60	200	7300	2.17	142k	2.1	34
5	**5b**	10.6	30	80	200	47 200	14.00	99k	1.9	43
6	**5b**	10.6	30	100	200	10 700	3.18	31k	2.4	66
7	**5b**	12.0	30	80	50	13 200	4.44	37k	2.2	72
8	**5b**	10.6	30	80	100	19 200	6.02	54k	2.5	70
9	**5b**	10.6	30	80	400	24 500	7.28	142k	2.2	27
10	**5b**	10.6	10	80	200	23 700	7.02	62k	2.7	46
11	**5b**	10.6	60	80	200	62 500	18.54	90k	1.6	44
12	**5b**	5.3	60	80	200	63 300	9.40	112k	1.9	34
13	**5b** + 5PPh_3	10.6	30	80	200	17 900	5.31	80k	1.8	36
14	**5b** + 50PPh_3	10.6	30	80	200	3400	1.01	19k	2.4	43

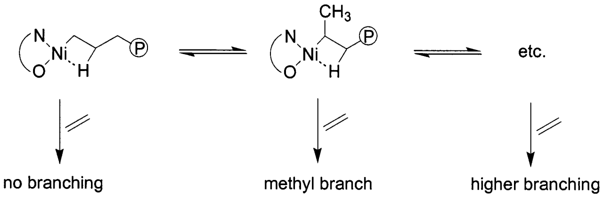
[a] In units of mol ethylene/mol cat. [b] Branching numbers were determined by ^{1}H NMR spectroscopy. [c] All polymerizations run in 200 mL of toluene with a maximum exotherm of 2 °C.

in the Experimental Section. Repeated attempts to grow an X-ray quality crystal of **5b** were unsuccessful; however, on the basis of closely related structures of **2** and **3**, it is very likely that the bulky triphenylphosphine ligand is trans to the better donating and more bulky N-aryl ligand.[27,29]

Ethylene Polymerization. The anilinoperinaphthenone nickel complexes **5a**,**b** are active ethylene polymerization catalysts. When toluene solutions of complexes **5a**,**b** are exposed to ethylene under a variety of conditions, polyethylenes of various molecular weights and branching densities are produced. Results are summarized in Table 1. Several trends are evident. First, **5b** is significantly more reactive than **5a** with turnover numbers of 47 000 and 8000, respectively, under identical reaction conditions (200 psig ethylene, 80 °C, entries 1 and 5). The added steric bulk of the isopropyl-substituted aryl ring greatly enhances catalyst activity. In view of the high reactivity of **5b**, the effects of changes in ethylene pressure, reaction temperature, and reaction time as well as polymerization in the presence of PPh_3 were investigated using this catalyst.

The reactivity of **5b** was at a maximum at 80 °C and 200 psig ethylene. Catalyst turnover numbers ranged from 5600 at 40 °C and 200 psig ethylene (entry 3) to 63 300 at 80 °C and 200 psig ethylene (entry 12). Catalyst turnover number increased from 50 to 200 psig ethylene, but doubling the ethylene pressure to 400 psig resulted in a decrease in turnover number to 24 500 (entry 9). As temperature was increased from 40 °C to 100 °C, with pressure held constant at 200 psig ethylene, the number average molecular weight of the polymer decreased from 171 000 to 31 000 and the branching number increased from 17 to 66 branches per 1000 carbon atoms (Table 1, entries 3−6). A ^{13}C NMR spectrum of the polymer of entry 5, run using a protocol reported by Cotts,[12] indicated that methyl and ethyl branches are present in an approximate ratio of 6.7:1. Propyl branches were observed, but the signal was too weak to integrate accurately. Analysis of the more highly branched polymer of entry 7 revealed methyl, ethyl, and propyl branches in an approximate ratio of 14:2:1. The methyl resonance corresponding to C_4 and longer branches integrated to approximately the same intensity as the methyl resonance for the propyl branch. As pressure was increased incrementally from 50 to 400 psig, with temperature held constant at 80 °C, the number average molecular weight of the polymer increased from 37 000 to 142 000 and the branching decreased from 72 to 27 branches per 1000 carbon atoms (Table 1, entries 5, 7−9). With the exception of the low-temperature 40 °C run (entry 3) all of the M_w/M_n values are ca. 2.0, which implies that the M_n values are at the chain transfer limited maximum.

Scheme 4



Catalyst lifetime was also investigated. Polymerizations at 80 °C and 200 psig were run for 10, 30, and 60 min (Table 1, entries 5, 10, 11). From 10 to 30 min the turnover number doubled from 23 700 to 47 200, while from 30 to 60 min the turnover number increased from 47 200 to 62 500, a 32% increase. These data indicate that the catalyst half-life is ca. 20−30 min. The lifetimes of these catalysts are slightly longer that the lifetimes reported for catalyst **3**.[29] Entries 11 and 12 indicate that cutting the catalyst loading in half has little effect on the overall polymerization activity. This result implies that mass transport issues do not compromise catalyst turnover number at the current catalyst loadings even though the polymerization solution becomes viscous as polyethylene is produced.

Polymerizations with **5b** were also run in the presence of 5 and 50 equiv of triphenylphosphine. Unlike catalyst **3**, a significant decrease in activity (∼65% reduction) is observed with just 5 equiv of added PPh_3 (entry 13), while 50 equiv of added PPh_3 severely inhibits ethylene polymerization (entry 14, ∼93% reduction). Polymerization with **5b** is not, however, shut down completely, as is reported for catalysts **2a**,**b**.[27,28] Anilinotropone catalyst **3** is not inhibited by 5 equiv of added triphenylphosphine, but 50 equiv causes the activity to drop to one-quarter of the original value.[36]

Catalysts **3** and **5b** have very similar activities under identical reaction conditions (TON = 62 100 and 62 500, respectively). The branching numbers of the polymers

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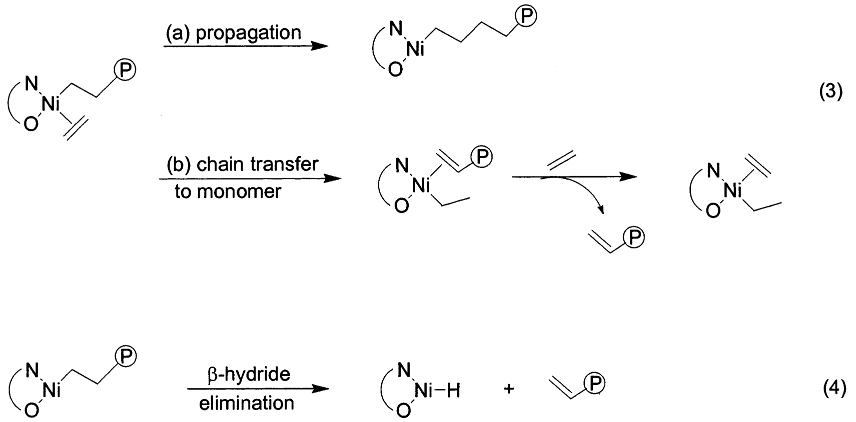
(36) Manuscript in preparation.

Scheme 5



produced with **3** follow the same temperature and pressure trends as **5b**; however, the absolute number of branches is approximately 20 branches per 1000 carbons more for **3**.[29] These numbers compare favorably to **2a** and **2b**, which under similar conditions have turnover numbers of 3400 and 40 700, respectively. Catalyst **2b**, however, has a very long lifetime.[27,28]

The variable-temperature and -pressure experiments suggest the branching mechanism depicted in Scheme 4, which mirrors the mechanism suggested for branching in the diimine catalyst system, **1**.[3] A branch in the polymer is introduced first by β-hydride elimination of a growing polymer chain followed by olefin rotation and reinsertion with opposite regiochemistry. This process may occur more than once prior to ethylene insertion and may therefore lead to methyl as well as higher branches. As ethylene pressure is increased, monomer coordination and insertion become more favorable, and therefore the unimolecular branching pathway is less favored. Similarly, as temperature is increased, the unimolecular branching pathway is favored over the bimolecular ethylene coordination and insertion reaction, and more branching is observed.

The fact that the molecular weight significantly increases with ethylene pressure (e.g., $M_n = 37$k, 50 psi, 80 °C; 54k, 100 psi, 80 °C; entries 7 and 8) suggests that chain transfer to monomer is not the major chain transfer mechanism. The alkyl olefin intermediate in the polymerization may partition as shown in eq 3. Pathway (a) represents insertion and propagation, while pathway (b) represents chain transfer to monomer.[37,38] If chain transfer to monomer is the sole chain transfer mechanism, then the ratio of k_{ct}/k_p should be independent of ethylene concentration, and thus the chain transfer limited molecular weight should be independent of ethylene concentration. The observed dependence of M_n on ethylene pressure implies a chain transfer process that is not significantly dependent on ethylene concentration. This is best rationalized by a conventional β-hydride elimination mechanism shown in eq 4. Given the qualitative M_n values and the substantial error in these determinations, some chain transfer may occur via the chain transfer to monomer pathway.

Catalyst Decay. The fate of the catalyst upon deactivation was investigated. Upon completion of a standard polymerization using **5b**, polymer was collected by precipitation in methanol. The filtrate was concentrated and analyzed by ^{1}H NMR spectroscopy to determine the contents of the residue. The sole species detected was the free ligand, **4b**. This observation contrasts with the behavior of **2a**, **3**, and SHOP-type catalysts, where Ni(II) bis-ligand complexes are observed as the decay products.[27−29] Equations 5 and 6 (Scheme 6) illustrate the contrasting behaviors of **3** and **5b**.

Bis-ligand complex formation with catalysts **3** and **5b** was investigated by ^{1}H NMR spectroscopy. For each experiment, an NMR tube was charged with the nickel complex and its corresponding ligand in equimolar ratios (10.6 mM in C_6D_6 in each case). In each case formation of the bis-ligand complex was observed via ^{1}H NMR spectroscopy at 80 °C (Scheme 7). The formation of the bis-ligand complex of anilinotropone, **6**, was significantly faster ($t_{1/2} < 1$ h) than the formation of the bis-ligand complex based on anilinoperinaphthenone ($t_{1/2} = 26$ h). The weaker acidity of the anilinoperinaphthenone N-H proton may help to explain the slow rate of bis-ligand complex formation. Steric effects may also play a role in the overall rate of bis-ligand complex formation.

Formation of the bis-ligand complex of 2-anilinotropone as the decomposition product of the bulk polymerization is best explained by reductive elimination from a nickel-hydride intermediate to form free ligand followed by attack of the free ligand on a Ni(II) species present in the catalytic cycle. The slow formation of the bis-ligand complex from 2-anilinoperinaphthenone and **5b** suggests that attack of free ligand on a propagating nickel species is too slow to be competitive with ligand reductive elimination. Therefore only 2-anilinoperinaphthenone is observed as the decomposition product of **5b** after polymerization.

Conclusions. Active neutral nickel(II) ethylene polymerization catalysts based on anilinoperinaphthenone ligands are reported. These catalysts have an activity that is similar to the previously reported anilinotropone-based neutral nickel(II) ethylene polymerization catalysts. The similarity in overall activity suggests that the lack of delocalization of electron density onto the oxygen atom has little effect on catalyst performance. The

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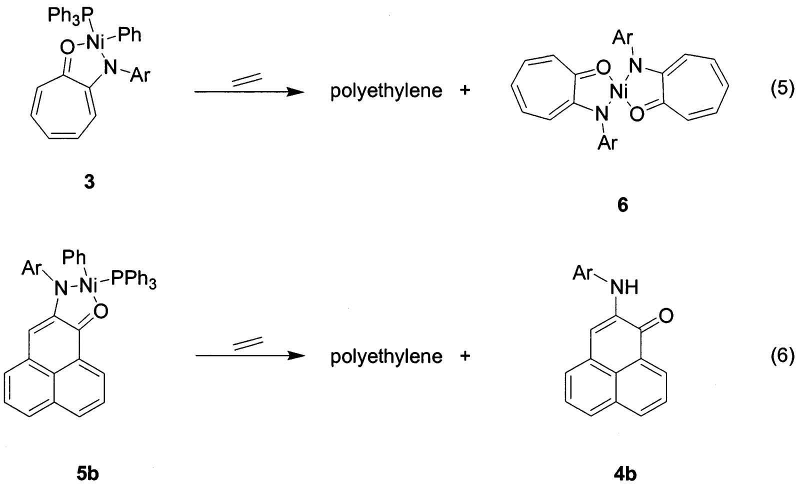
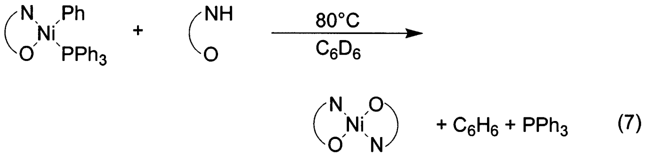
Scheme 6



Scheme 7



polymer branching mechanism is likely similar to the one reported for the diimine system **1**, with branching controlled by the relative rates of Ni migration along the chain and ethylene insertion. A significant correlation between ethylene pressure and polymer molecular weight suggests that chain transfer occurs primarily via a β-hydride elimination pathway with little contribution from chain transfer to monomer. The catalyst decomposes to free ligand, suggesting that reductive elimination of free ligand is a key step in catalyst deactivation. A more detailed mechanistic study of the catalytic propagation cycle and the deactivation pathway is underway.

Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Toluene and pentane were deoxygenated and dried over a column of activated alumina. THF was distilled under a nitrogen atmosphere from sodium benzophenone ketyl prior to use. Polymer grade ethylene was used as received from Matheson. 2-Bromoperinaphthenone,[39] $(PPh_3)_2Ni(Ph)(Cl)$,[40] and complexes **2a**,**b**[27] and **3**[29] were prepared according to literature procedures. Triphenylphosphine was purchased from Aldrich and used without further purification.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 NMR spectrometer. Splitting patterns are designated as follows: s, singlet; bs, broad singlet; d, doublet; dd, doublet of doublets; t, triplet; sept, septet; m, multiplet. All ^1H NMR spectra are reported in δ units, parts per million (ppm) downfield from tetramethylsilane. All ^{13}C NMR spectra are reported in ppm relative to TMS using $CDCl_3$ as an internal standard. ^{31}P NMR are reported in ppm relative to an external 85% H_3PO_4 standard. ^1H NMR spectra of polyethylenes were recorded in C_6D_5Br at 120 °C. The formula used to calculate branching was $(CH_3/3)/[(CH + CH_2 + CH_3)/2] \times 1000$ = branches per 1000 carbons. CH_3, CH_2, and CH refer to the integration obtained for the methyl, methylene, and methine resonances, respectively. ^{13}C NMR spectra of polyethylenes were recorded in a 0.05 M $Cr(acac)_3$ solution in bromobenzene-d_5 with 15 wt % polymer. Peaks were assigned as described by Cotts.[12] High-temperature gel permeation chromatography (GPC) was performed by DuPont (Wilmington, DE) in 1,2,4-trichlorobenzene at 135 °C using a Waters HPLC 150C equipped with Shodex columns. A calibration curve was established with polystyrene standards, and universal calibration was applied using Mark–Houwink constants for polyethylene (κ), 4.34×10^{-4}; (R) 0.724. Elemental analyses were performed by Atlantic Microlabs Inc. of Norcross, GA.

General Procedure for the Conversion of 2-Bromoperinaphthenones to 2-Anilinoperinaphthenones. A flame-dried Schlenk tube was charged with 2-bromoperinaphthenone (200 mg, 0.77 mmol), NaO^tBu (105 mg, 1.08 mmol), Pd_2dba_3 (36 mg, 0.04 mmol), and 2-dicyclohexylphosphine-1,1′-biphenyl (26 mg, 0.08 mmol) under argon. Toluene (3 mL) and 2,6-dimethylaniline (115 μL, 0.93 mmol, **4a**) or 2,6-diisopropylaniline (175 μL, 0.93 mmol, **4b**) were added, and the reaction mixture was heated to 80 °C and stirred for 18 h. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2, and filtered through Celite. The filtrate was concentrated and purified by flash chromatography on silica gel using 15% ethyl acetate in hexanes as the eluent.

2-(2,6-Dimethylanilino)perinaphthenone. Yield: 150 mg, 65%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.8 (d, 1H, $J = 7.4$); 8.2 (d, 1H, $J = 7.9$ Hz); 7.8 (m, 2H); 7.5 (t, 1H, $J = 7.2$ Hz); 7.4 (m, 1H); 7.2 (bs, 3H); 6.6 (bs, 1H); 6.1 (s, 1H); 2.3 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.8, 140.0, 137.2, 136.7, 136.3, 132.3, 131.0, 130.2, 129.0, 128.6, 128.3, 127.8, 127.6, 127.0, 126.9, 124.2, 107.8, 18.7. Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 83.41; H, 6.02; N, 4.30.

2-(2,6-Diisopropylanilino)perinaphthenone. Yield: 160 mg, 58%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.8 (d, 1H, $J = 8$ Hz); 8.2 (d, 1H, $J = 8$ Hz); 7.8 (m, 2H), 7.5 (t, 1H, $J = 4$ Hz); 7.4 (m, 2H); 7.3 (m, 2H); 6.6 (bs, 1H); 6.1 (s, 1H); 3.2 (hept, 2H, $J = 6.8$ Hz); 1.2 (d, 12 H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.6, 147.8, 142.0, 136.3, 134.3, 132.4, 131.1, 130.2, 128.5, 128.1, 128.0, 127.7, 127.6, 127.0, 124.2, 207.8, 28.8, 25.5, 23.8. Anal. Calcd for $C_{25}H_{25}NO$: C, 84.47; H, 7.09; N, 3.94. Found: C, 83.97; H, 7.21; N, 3.73.

General Procedure for the Conversion of (N,O)Ni(Ph)(PPh$_3$). A flame-dried Schlenk tube was charged with the appropriate anilinoperinaphthenone (150 mg, 0.50 mmol **4a**; 200 mg, 0.56 mmol **4b**), and sodium hydride (40 mg, 1.7 mmol for **4a**; 75 mg, 3.1 mmol for **4b**) under argon. THF (25 mL) was added, and the reaction mixture was stirred for 18 h. A color change from dark red to bright green was observed on

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both cases. Solid $(PPh_3)_2Ni(Ph)(Cl)$ (348 mg, 0.50 mmol for **4a**, 391 mg, 0.56 mmol for **4b**) was added under positive argon flow, and the reaction mixture was stirred for 1 h. The reaction mixture was filtered through Celite, and the solvent was removed in vacuo. The residue was recrystallized from toluene/pentane and isolated by cannula filtration.

Complex 5a. Yield: 225 mg, 65%. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.2 (d, 1H, $J = 7.4$ Hz); 7.8 (d, 1H, $J = 7.4$ Hz); 7.6−7.5 (m, 8H); 7.4 (m, 3H); 7.3 (m, 8H); 6.8 (d, 2H, $J = 6.9$ Hz); 6.7 (d, 2H, $J = 7.4$ Hz); 6.6 (m, 1H); 6.3 (t, 1H, $J = 7.0$ Hz); 6.2 (t, 2H, $J = 7.5$ Hz); 5.7 (s, 1H); 2.3 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 190.0, 189.9, 153.5, 149.2, 148.2, 137.9, 136.9, 136.8, 134.9, 134.6, 134.5, 13.2, 130.1, 128.4, 128.3, 128.2, 127.9, 127.4, 126.6, 125.7, 125.0, 124.9, 123.2, 121.2, 105.4, 18.7. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.7 (s). Anal. Calcd for $C_{45}H_{36}NiNPO$: C, 77.61; H, 5.21; N, 2.01. Found: C, 77.60; H, 5.17; N, 1.98.

Complex 5b. Yield: 290 mg, 70%. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.2 (d, 1H, $J = 8$ Hz); 7.8 (d, 1H, $J = 8$ Hz); 7.5 (m, 7H); 7.4 (m, 3H); 7.3−7.2 (m, 9H); 6.9 (m, 3H); 6.8 (d, 2H, $J = 7$ Hz); 6.3 (t, 1H, $J = 6.8$ Hz); 6.2 (t, 2H, $J = 6.4$ Hz); 5.7 (s, 1H); 3.9 (hept, 2H, $J = 6.8$ Hz); 1.1 (d, 6H, $J = 6.8$ Hz); 1.0 (d, 6H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 189.6, 155.6, 148.2, 147.7, 145.9, 145.5, 137.8, 134.5, 131.9, 131.8, 131.7, 131.4, 130.2, 128.4, 128.5, 128.3, 127.8, 126.6, 125.8, 125.2, 125.2, 124.1, 122.8, 121.2, 108.7, 28.5, 26.2, 23.9. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.3 (s). Anal. Calcd for $C_{49}H_{44}NiNPO$: C, 78.20; H, 5.89; N, 1.86. Found: C, 77.77; H, 6.25; N, 1.85.

General Procedure for High-Pressure Ethylene Polymerization. A 1000 mL Parr autoclave was heated under vacuum to 125 °C and then was cooled to the desired reaction temperature and backfilled with ethylene (3 × 100 psig). The autoclave was charged with toluene (185 mL) and degassed with ethylene (3 × 100 psig) with stirring. In a glovebox a sidearm flask was charged with the catalyst. The flask was removed from the glovebox and placed on a vacuum line under Ar. The catalyst was dissolved in toluene (15 mL) and cannula transferred into the vented autoclave with the stirring motor off. The autoclave was sealed and pressurized to the desired level, and the stirring motor was reengaged. Temperature control was maintained by internal cooling coils with exotherms less than 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 methanol and dried in a vacuum oven. This procedure was employed with modifications in time, temperature, and ethylene pressure. Results are summarized in Table 1.

NMR Scale Bis-ligand Complex Formation Reactions. A J-Young tube was charged with 7.4 μmol of both the appropriate nickel complex and corresponding ligand. Benzene-d_6 (700 μL) was added, and bis-ligand formation was observed by ^1H NMR spectroscopy at 80 °C. Anilinotropone: $t_{1/2} < 1$ h. Anilinoperinaphthenone: $t_{1/2} = 26$ h.

Anilinoperinaphthenone Bis-ligand Complex. ^1H NMR (400 MHz, C_6D_6): δ 7.8 (d, 1H, $J = 8$ Hz), 7.7 (m, 1H), 7.5 (d, 2H, $J = 8$ Hz), 7.0 (t, 1H, $J = 8$ Hz), 6.0 (d, 1H, $J = 8$ Hz), 5.6 (d, 1H, $J = 7$ Hz), 5.0 (sept, 2H, $J = 7$ Hz), 2.0 (d, 6H, $J = 7$ Hz), 1.55 (d, 6H, $J = 7$ Hz).

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