Synthesis and Ethylene Polymerization Activity of a Series of 2-Anilinotropone-Based Neutral Nickel(II) Catalysts

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A method for the synthesis of bulky 2-anilinotropones has been developed, utilizing palladium-catalyzed cross-coupling techniques. Deprotonation of these anilinotropones followed by reaction with $(PPh_3)_2Ni(Ph)Cl$ produces ethylene polymerization catalysts of the general formula $[[(2\text{-R-6-R}'C_6H_3)NC_7H_5O]Ni(Ph)(PPh_3)]$ (**3a**−**j**: R, R′ = Me, Me (**a**), ^{i}Pr, ^{i}Pr (**b**), ^{t}Bu, H (**c**), ^{t}Bu, Me (**d**), Ph, Ph (**e**), Cl, Cl (**f**), Br, Br (**g**), 2,3,4,5,6-F_5 (**h**), Me, H (**j**), Me, CF_3 (**k**)). Ethylene polymerizations with **3a**−**j** have been explored under a variety of reaction conditions. The complex $[[(2,6\text{-}^iPr_2C_6H_3)NC_7H_4O(7\text{-aryl})]Ni(Ph)(PPh_3)]$ (**14**: aryl = phenyl (**a**), 1-naphthyl (**b**)), possessing steric bulk at the 7-position, have been prepared and are both long-lived and active ethylene polymerization catalysts. At low temperatures **14a**,**b** produce polyethylene with narrow molecular weight distributions (MWD ca. 1.2). The polymerization results suggest that chain transfer occurs via a β-hydride elimination pathway and that catalyst decomposition proceeds through reductive elimination of the free ligand from a nickel−hydride intermediate.

Introduction

Olefin polymerization catalysts based on early-metal metallocene complexes were introduced nearly two decades ago and are seeing increasing commercial utilization.[1−3] Their single-site nature makes them attractive for ligand tailoring, and as a result these catalysts have been modified in innumerable ways to enhance polymerization activity, improve catalyst lifetime, increase the α-olefin/ethylene reactivity ratio in copolymerizations, and control microstructures of polypropylene and other poly-α-olefins.[1−3] A drawback of metallocene and classical Ziegler catalysts is the extreme oxophilicity of the early-metal center. This oxophilicity renders metallocenes inactive toward most functionalized monomers and highly sensitive to polar solvents and impurities. The sensitivity of metallocenes to polar substituents is largely responsible for an increase in interest in late-transition-metal complexes as olefin polymerization catalysts over the past several years.[4−7] Late-metal catalysts complement early-metal catalysts in several ways. (1) Polymers exhibiting quite different microstructures are frequently obtained.[5,8−11] This arises from the ability of the metal to walk along the growing polymer chain via a series of β-elimination and reinsertion reactions which can occur at rates competitive with or faster than olefin insertion. This process results in formation of branched polymers from ethylene and "chain-straightened" polymers from α-olefins.[5,9] (2) Certain monomers such as *trans*-2-butene, which cannot be polymerized by early-metal systems, can be successfully polymerized with late-metal systems.[12] (3) Many late-metal catalysts are compatible with protic solvents and nucleophilic impurities. Water compatibility has led to successful emulsion polymerization of ethylene.[13−16] (4) Expanded functional group tolerance has permitted the copolymerization of alkyl acrylates (polar monomers) with ethylene and α-olefins (nonpolar monomers).[17−20]

Much of our effort has focused on cationic systems of the general type **1** based on α-diimine ligands as well as catalysts incorporating closely related neutral

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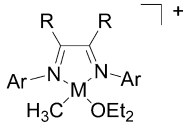
ligands.[8,9,11,12,17,18,21,22] The α-diimine Ni complexes are



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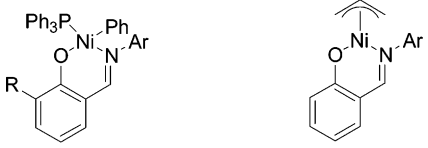
M = Ni, Pd

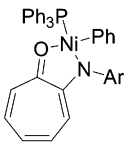
very reactive toward ethylene and α-olefins and, as noted above, produce polymers with unique microstructures. The cationic Ni catalysts are electrophilic and sensitive to protic solvents. Functional group compatibility is diminished relative to Pd analogues; however, it should be noted that copolymerization of ethylene and alkyl acrylates has been achieved at high ethylene pressures (>500 psig) and temperatures above 80 °C.[20,23]

In view of the high sensitivity of the cationic Ni and Pd catalysts, there has been substantial interest in developing neutral Ni catalysts to overcome these limitations. Several early examples of neutral Ni catalysts based on SHOP-type ligands have been reported, although productivities and molecular weights are often low.[16,19,24,25] More recently, neutral Ni catalysts modeled after **1,** containing a bulky ortho-disubstituted aryl imine functionality, have been reported. Catalysts of type **2**, based on salicylaldimines, have been described



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

2c



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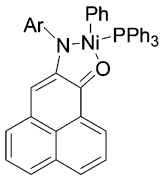

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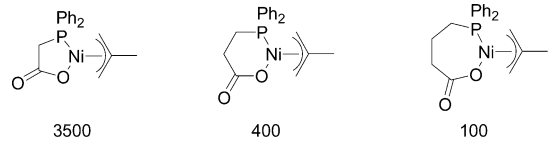
by both the DuPont[26] and the Grubbs groups.[27,28] The most active systems contain either electron-withdrawing nitro substituents in the aromatic ring[26] or bulky substituents at C-3, with a 9-anthracenyl group being most effective.[27,28] In the latter case, activities of 1.3 × 10^5 mol of PE ((mol of Ni) h)$^{-1}$ and lifetimes in excess of 6 h have been observed at 45−50 °C.[28]



TON = 3500 400 100

Figure 1. Ethylene oligomerization with SHOP-type catalysts.

We have recently reported catalysts of type **3** and **4** based on anilinotropone and anilinoperinaphthenone ligands, respectively.[29,30] High activities have been observed for the unsubstituted anilinotropone catalyst (6 × 10^4 mol of PE ((mol of Ni) h)$^{-1}$), and in a direct comparison with the parent, unsubstituted salicylaldimine catalyst, **2a** (3400 mol of PE ((mol of Ni) h^{-1}), the anilinotropone systems appear to be more reactive.[27,29] Clearly a major difference between these two systems is that the salicylaldimine catalysts contain a six-membered chelate, while the anilinotropone catalysts contain a five-membered chelate. It is not clear if chelate size is responsible for the difference in activities, but Keim has shown with SHOP-type catalysts that a decrease in activity is observed with expansion of chelate size (Figure 1).[31]

The goal of this work was to fully explore the ethylene polymerization properties of the anilinotropone-based system. Reported herein is the synthesis of several 2-anilinotropone ligands and the corresponding Ni(II) complexes as well as extensive ethylene polymerization results using these catalysts. Also reported are catalysts derived from hindered 2-anilino-7-aryltropone ligands and their activity toward ethylene. Preliminary reports of parts of this work have appeared in the literature.[29,32]

Results and Discussion

Ligand Synthesis. Initial attempts to prepare anilinotropones were based on literature reports of nucleophilic substitution of 2-(tosyloxy)tropone by isopropylamine.[33−35] However, nucleophilic substitution with a variety of anilines was unsuccessful. In addition to trace amounts of the desired product **5b**, the predominant product obtained was the benzenoid rearrangement product, **6**, derived from attack of the aniline at the 3-position (Scheme 1).[36] On the basis of the work of Buchwald and Hartwig on the palladium-catalyzed cross-coupling of amines with aryl halides and triflates, the possibility of a palladium-catalyzed cross-coupling of aniline with a 2-halo- or 2-triflatotropone was considered.[37−40] Buchwald has demonstrated the utility

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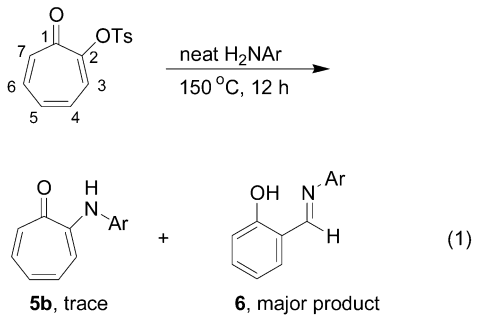
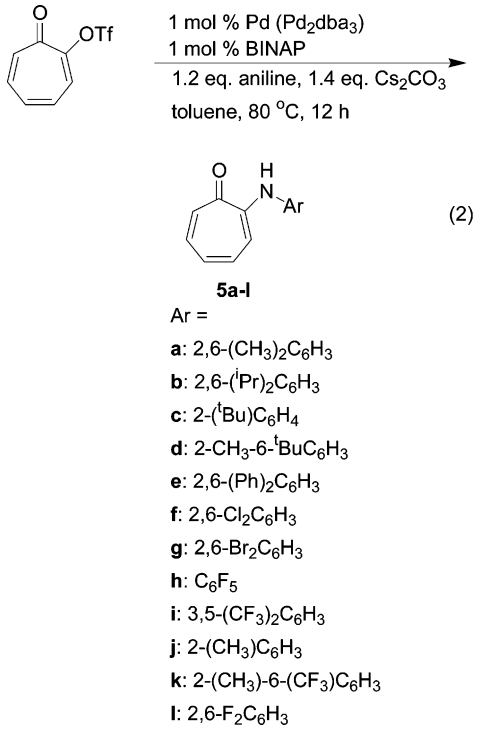
Scheme 1[a]



[a] H_2NAr = 2,6-diisopropylaniline.

Scheme 2



of this methodology for coupling two sterically hindered substrates.[37]

Initial attempts at aniline−tropolone cross-coupling were carried out with the commercially available 2-(tosyloxy)tropone. The results were a significant improvement over the nucleophilic route employed previously, but even with catalyst loadings of 5 mol %, yields were only ca. 30%. Upon switching to 2-triflatotropone, cross-coupling yields were significantly higher, even with 1 mol % catalyst loading (Scheme 2).[32] Yields of **5a**−**i** were previously reported[32] and range from 36 to 90%. Low yields are obtained for highly sterically encumbered anilines (36% for **5d** and 37% for **5e**), but remarkably, coupling products from electron-deficient anilines are formed in good to excellent yields (**5f**, 75%; **5i**, 89%). Anilinotropones **5j**−**l**, reported here for the first time, are produced in yields of 88−89%.

Crystals of 2-(2,6-diisopropylanilino)tropone (**5b**) suitable for X-ray diffraction were prepared by slow diffusion of hexamethylsiloxane into a concentrated solution of **5b** in toluene at room temperature. Crystallographic data for **5b** are summarized in Table 1, and an ORTEP diagram is shown in Figure 2. The C−O and C−N bond lengths (1.2519(24) and 1.3546(24) Å, respectively) are

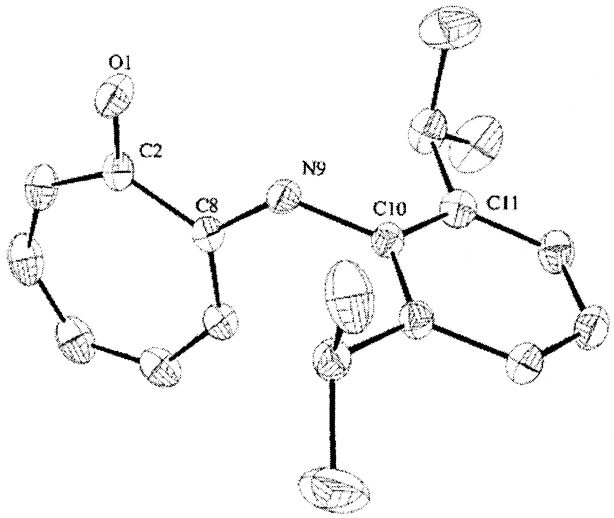


Figure 2. ORTEP view of **5b** showing important atom labels. Selected interatomic distances (Å): C(2)−O(1) = 1.2519(24), C(8)−N(9) = 1.3546(24). Torsion angle (deg): C(8)−N(9)−C(10)−C(11) = 88.4(3).

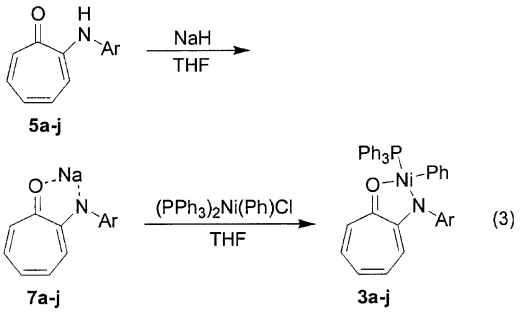
Table 1. Crystallographic Data for 5b

formula	$C_{19}H_{23}NO$
mol wt	327.46
color	yellow
cryst syst	monoclinic
space group	*C*2/*c*
a (Å)	15.5935(6)
b (Å)	14.1245(5)
c (Å)	19.3648(7)
α (deg)	90
β (deg)	113.759(1)
γ (deg)	90
V (Å^3)	3903.63(25)
D_{calcd} (Mg/m^3)	1.114
wavelength (Å)	0.710 73
μ (mm^{-1})	0.07
cryst dimens (mm)	0.35 × 0.20 × 0.25
temp (°C)	−100
mode	*ω*
2*θ* range (deg)	4.00−50.00
no. of rflns	18 103
no. of indep rflns	3325
R(*F*)	0.073
R_w(F)	0.079
hkl range	−18 to +16, 0−16, 0−23
type of diffractometer	Bruker SMART
abs cor method	SADABS
radiation for intensity measmts	Mo Kα
monochromator	graphite
Z	8

of intermediate value for single and double bonds, indicating some degree of delocalization on the order of an amide group. Also of note is the near 90° angle at which the N-aryl ring sits relative to the plane of the seven-membered tropone ring. Finally, the N−H hydrogen was found and determined to be hydrogen-bonded to the carbonyl oxygen, O1.

Catalyst Synthesis. Deprotonation of 2-anilinotropones proceeds readily in THF with a slight excess of sodium hydride. The sodium salts of the anilinotropones were isolated as THF adducts, usually with 1 equiv of THF coordinated. In all cases the salt was isolated prior to reaction with the nickel precursor. An X-ray crystal structure of the sodium salt of 2-(2,6-diisopropylanilino)tropone was obtained (see the Supporting Information). As with the free ligand the N-aryl ring is perpendicular to the plane of the tropone ring.

Scheme 3



The C−N and C−O bond lengths are 1.292(8) and 1.298(9) Å, respectively: thus, relative to the neutral ligand the C−N bond has contracted and the C−O bond has lengthened. Note also that the sodium ion has taken the place of the hydrogen-bonded N−H proton.

Neutral nickel complexes of **5** were first synthesized by combining the sodium salt of the appropriate anilinotropone with bis(triphenylphosphine)nickel phenyl chloride in toluene for ca. 18 h. Sodium chloride was separated by filtration, and the product was isolated by recrystallization from toluene/pentane. While effective for some of the more bulky anilinotropones, this method was inefficient for the less sterically hindered ones. Due to the low to moderate solubility of $(PPh_3)_2Ni(Ph)Cl$ in toluene, a significant amount of bis(anilinotropone)-nickel(II) complex (see below) was formed during the course of the reaction. Removal of this impurity required multiple recrystallizations. To eliminate formation of this bis-ligand complex, the reaction was run in THF at room temperature for 1 h (Scheme 3). THF was chosen because of its ability to dissolve $(PPh_3)_2Ni(Ph)$-Cl. Upon filtration and standard workup (see the Experimental Section for details) the desired (anilinotropone)nickel(II) complex was obtained free of bis-ligand complex. A previously reported X-ray structure of **3b**[29] confirms the geometry depicted in Scheme 3 with PPh_3 trans to nitrogen and the phenyl group trans to oxygen. Also of note is the lack of change of the C−N and C−O bond lengths from those in **5b**, indicating that the negative charge lies predominantly on the nitrogen atom.

Ethylene Polymerization Studies: Polymerizations Employing 3b. Catalyst **3b** is a highly active ethylene polymerization catalyst. Table 2 summarizes polymerizations conducted in toluene. To accurately compare activities and lifetimes under various reaction conditions, it is critical to avoid reaction exotherms which are common with such highly active catalysts. For example, even with temperature control via water-cooled coils in a 1 L autoclave, a concentration of 74 μM of **3b** in 200 mL of toluene under 400 psig of ethylene leads to an uncontrollable exotherm from a starting reaction temperature of 60 °C to a peak temperature of 103 °C (entry 1). Various catalyst loadings were investigated to determine the optimal range for both temperature control and high activity. A concentration of ca. 25−40 μM was determined to be optimal under the chosen conditions for obtaining reliable temperature control and maximum catalyst turnover numbers.[41]

The ethylene polymerization activity of catalyst **3b** was screened under a wide variety of conditions. The first variable investigated was reaction temperature (entries 2−5, Table 2). Ethylene pressure was held constant at 400 psig. With the exception of the run at 40 °C, the M_n value of the resultant polymers decreases with increasing temperature. The degree of branching, determined by ^{1}H NMR spectroscopy, steadily increases from 40 to 100 °C (8−67 branches per 1000 carbon atoms). The molecular weight distributions for entries 2−5 are clearly monomodal with all polydispersities ca. 2.0, indicating that the number-average molecular weights are the chain-transfer-limited values. This implies that the lower molecular weights obtained at higher temperatures are the result of an increase in the ratio of the chain transfer rate relative to the chain propagation rate, a normal feature of such polymerizations. The catalyst TON is at a maximum at 80 °C.

Table 2. Ethylene Polymerization with 3b, $[(2,6\text{-}^iPr_2C_6H_3)NC_7H_5O]Ni(Ph)(PPh_3)$[a]

entry	cat. (10^{-6} mol)	T (°C)	ethylene (psig)	yield (g)	TON	$10^{-3}M_n$	PDI	branches/ 1000 C
1	14.8	60[b]	400	13.7	33 000	57	2.8	64
2	7.6	40	400	1.2	8 200	204	2.8	8
3	7.6	60	400	6.8	31 900	292	2.0	27
4	7.6	80	400	11.4	53 600	119	1.8	49
5	7.6	100	400	4.0	19 000	61	1.9	67
6	5.2	80	1 atm	0.15	980	6.7	2.0	113
7	5.2	80	50	4.0	27 000	50	1.7	90
8	5.2	80	100	6.3	42 500	63	1.9	76
9	5.2	80	200	9.2	62 100	90	1.8	61
10[c]	5.2	80	200	7.6	52 400	92	1.8	61
11	5.2	80	400	7.1	47 800	104	2.0	45
12	5.2	80	600	2.6	17 500	120	2.0	41
13[c,d]	5.2	80	200	7.5	51 500	78	1.9	66
14[c,d]	5.2	80	400	10.9	74 500	108	1.9	48
15[c,d]	5.2	80	600	8.8	60 400	111	2.0	43

[a] Reactions run in 200 mL of toluene for 1 h unless otherwise noted. [b] Exotherm from 60 to 103 °C. [c] Reaction time 10 min. [d] Research Plus grade ethylene.

The effects of ethylene pressure variation on the polymerization activity of **3b** were also studied (entries 6−12, Table 2) with several trends evident. As seen in entries 6−12 (80 °C data), polymer molecular weights steadily increase and branching numbers decrease from 113 to 41 branches per 1000 carbon atoms as pressure increases from 1 atm to 600 psig of ethylene. A ^{13}C NMR spectrum of the polymer of entry 7 (90 branches/1000 C), run using a protocol reported by Cotts,[42] indicated the presence of methyl, ethyl, propyl, and higher branches in a ratio of ca. 14:2:1:1. No signals were observed that corresponded to hyperbranched material (branches on branches). All of the resultant polymers have molecular weight distributions at or near 2.0, again indicating that the number-average molecular weights are the chain-transfer-limited values. Maximum turnover numbers were obtained at 200 psig of ethylene. Comparison of entries 11 (60 min run) and 12 (10 min run) shows that only ca. 20% more polymer is generated after 10 min, indicating that the catalyst lifetime at 80 °C and 200 psig is relatively short. Using the 10 min data, an initial turnover frequency is calculated to be 3.1×10^5 mol of ethylene ((mol of Ni) h)$^{-1}$. The actual initial TOF will be higher, since a

(41) At concentrations of 15 μM and lower, turnover numbers are significantly reduced likely due to quenching of some catalyst by trace impurities.

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Table 3. Ethylene Polymerization with 3b plus Phosphine Scavengers[a]

entry	initiator	yield (g)	TON	$10^{-3}M_n$	PDI	branches/ 1000 C
1	none	7.6	51 300	91	1.8	61
2	$B(C_6F_5)_3$	6.7	45 300	84	1.9	58
3	$B(C_6H_5)_3$	8.5	57 000	79	2.0	60
4	$Ni(COD)_2$	7.9	53 300	87	1.8	61

[a] Reactions run in 200 mL of toluene at 80 °C and 200 psig of ethylene for 10 min with 5.2 μmol of catalyst.

Table 4. Polymerization with 3b plus PPh_3[a]

entry	PPh_3 (equiv)	time (min)	tield (g)	TON
1	0	10	7.5	51 500
2	5	10	6.3	43 400
3	0	30	8.8	60 400
4	5	30	8.7	60 000
5	50	15	1.2	5 600
6	50	60	3.4	16 400

[a] Reactions run at 200 psi Research Plus grade ethylene, 80 °C, in 200 mL of toluene with 5.2 μmol of catalyst.

significant amount of catalyst decays during the 10 min run. When salicylaldimine catalyst **2a** was subjected to the same reaction conditions, it was found to be more than an order of magnitude less reactive with a TOF of 0.24×10^5 mol of ethylene ((mol of Ni) h)$^{-1}$. Additionally, **3b** produces polyethylene with a substantially higher M_n value when compared with **2b** (89 600 vs 2800).

Catalyst **3b** has an initial activity comparable to that of the anthracenyl-substituted salicylaldimine catalyst (reported TON = 1.32×10^5 mol of ethylene ((mol of Ni) h)$^{-1}$);[28] however, **2b** is reported to have a significantly longer lifetime relative to **3b**. This remarkable aryl effect prompted us to investigate the analogous 7-aryl-substituted versions of the anilinotropone-based catalyst. These studies are reported in a subsequent section.

The observed drop in catalyst activity above 200 psig of ethylene may in part be due to impurities in the monomer feed. To test this possibility, several polymerization reactions were conducted with a significantly more pure ethylene feed (99.9996%, see Experimental Section). Polymerization with more pure ethylene affects the productivity of **3b** at higher ethylene pressures (Table 2, entries 13−15). Polymerization at 400 psig of ethylene (entry 14) with the high-purity ethylene is more active than polymerization at 200 psig with either ethylene source (entries 10 and 13). The activity at 600 psig of ethylene (entry 15) drops off only slightly from the observed activity at 400 psig (entry 14) with the hyperpure ethylene, but in comparison with standard grade ethylene polymerization at 600 psig (entry 12), the TON value increases by almost 400%. These data suggest that impurities in the ethylene feed can inhibit polymerization at higher ethylene pressures, conditions where greater quantities of impurity will be present. It is unclear which impurities in the monomer feed are responsible for the observed drop in catalyst turnover number. Experiments are ongoing to determine the specific nature of the impurity.

Catalyst **3b** was also screened in the presence of both phosphine scavenging cocatalysts (Table 3) and added triphenylphosphine (Table 4). The activity of salicylaldimine catalyst **2b** is reported to increase in the presence of added scavengers and greatly decrease in the presence of added PPh_3.[27,28] In contrast, for **3b** at 80 °C and 200 psig of ethylene no significant changes in TON, M_n, PDI, or branching numbers are observed with 2.4 equiv of added $B(C_6F_5)_3$, BPh_3, or $Ni(COD)_2$. (Similar results were obtained at 40 °C; see the Supporting Information.)

Data in Table 4 show that when the polymerization is carried out in the presence of 5 equiv of PPh_3 (80 °C, 200 psig), a small decrease in TON is observed after a polymerization time of 10 min, while virtually no change in TON is noted after a polymerization of 30 min. These results suggest that added PPh_3 might slightly inhibit the turnover frequency but at the same time increase catalyst lifetime. Entries 5 and 6 demonstrate that at a significantly higher PPh_3 loading (50 equiv) activity is inhibited while catalyst lifetime is substantially increased.

The observation that scavengers do not increase turnover numbers suggests that under the reaction conditions PPh_3 is essentially fully dissociated from the active nickel catalyst. Furthermore, addition of 5 equiv of PPh_3 appears insufficient to shift the equilibrium significantly back toward a PPh_3 complex. In contrast, 50 equiv of PPh_3 substantially retards the TOF and suggests that a large fraction of the catalyst rests as a PPh_3 complex.

Table 5. Ethylene Polymerization with 3b plus Polar Additives

entry	solvent	additive (amt (mL))	yield (g)	TON	$10^{-3}M_n$	PDI	branches/ 1000 C
1	toluene	none	2.8	19 000	189	1.8	37
2	THF	none	3.3	22 500	146	1.8	39
3	hexane	none	2.6	17 400	163	1.8	35
4	PhCl	none	4.8	32 200	182	1.9	46
5	EtOAc	none	0.34	2 290	66	4.0	33
6	toluene	EtOAc (1)	2.3	15 700	192	1.8	36
7	toluene	H_2O (1)	1.4	9 600	128	1.9	38
8	hexane	H_2O (1)	1.5	10 200	135	1.9	39
9	toluene	EtOH (1)	1.1	7 700	131	1.9	37
10	toluene	NEt_3 (1)	2.7	18 800	146	2.0	38
11	toluene	EtOAc (20)	3.8	26 200	163	1.9	43
12	toluene	H_2O (20)	0.85	5 800	86	2.3	41
13	toluene	EtOH (20)	0.16	1 100	21	2.4	48
14	toluene	NEt_3 (20)	0.72	5 000	87	1.5	37

Solvent effects on ethylene polymerization using **3b** (60 °C, 200 psig) were also investigated (Table 5, entries 1−6). THF, hexane, chlorobenzene, and ethyl acetate were all investigated in addition to toluene. Polymerization in ethyl acetate leads to a significant drop in TON and broadening of the molecular weight distribution. With the exception of ethyl acetate, however, activities in all other solvents are comparable to or somewhat greater than the activity in toluene. A significant increase in TON and polymer branching is observed in chlorobenzene at 60 °C.

Neutral, late-metal catalysts are attractive due to their purported polar group tolerance.[4] To test the limits of this tolerance, several polymerizations were carried out in the presence of polar additives (Table 5, entries 7−15). When run in neat THF or with added ethyl acetate (~10 vol % in toluene) polymerizations with **3b** proceed with a small increase in catalyst turnover number. Reactions run with added H_2O or NEt_3 led to 3.5- and 4-fold decreases in activity, respectively. The use of ethanol proved more problematic, leading to a 20-fold decrease in TON. The increased solubility of ethanol in toluene, in comparison with water, is likely

Table 6. 1-Hexene Oligomerization[a]

entry	*T* (°C)	yield (mg)	TON	DP	branches/1000 C
1	40	84	130	21	147
2	60	127	200	16	152

[a] Conditions: 50 vol % 1-hexene in toluene, 3 h, total volume 2 mL.

Table 7. Ethylene Polymerization with 3a−h,j,k

entry	Ar	*t* (min)	yield (g)	TON	$10^{-3}M_n$	PDI	branches/1000 C
1	2,6-Me_2	10	4.7	32 600	43	1.7	61
2	2,6-Me_2	30	6.3	43 100			
3	2,6-$^iPr_2$	10	7.6	52 400	92	1.8	61
4	2,6-$^iPr_2$	30	8.8	60 400			
5	2,6-Ph_2	10	8.7	59 800	95	1.8	53
6	2-^{t}Bu-6-CH_3	10	0.88	6 000	115	2.0	73
7	2-^{t}Bu-6-CH_3	30	0.88	6 000			
8	2,6-Cl_2	10	3.4	23 400	10	2.0	53
9	2,6-Cl_2	30	3.5	24200			
10	2,6-Br_2	10	3.6	23800	22	1.9	56
11	2,6-Br_2	30	3.8	26400			
12	2-Me-6-CF_3	10	6.0	41200	88	1.9	59
13	2-Me-6-CF_3	30	6.8	46700			
14	F_5	10	1.0	7000	1.6[b]	3.03	49
15	2-Me	10	0.81	5600	4.7[b]	2.4	57
16	2-^{t}Bu	10	Trace		18	2.1	72

[a] Reactions run in 200 mL of toluene, 80 °C, 200 psig of ethylene with ~5.2 μmol of catalyst. [b] Determined by ^{1}H NMR.

partially responsible for the more dramatic decrease in TON. Branching numbers vary relatively little with solvent or additive, and under these conditions all are in the range of 35−45 branches per 1000 carbon atoms. Polar solvents and additives appear to slightly increase branching, but no clear trend is evident.

Several neutral nickel ethylene polymerization catalysts have been reported to oligomerize α-olefins.[16,43] To date, none have been reported to be active α-olefin polymerization catalysts. Similar results are observed with **3b** (Table 6). Oligomerization of 1-hexene at 40 and 60 °C leads to low yields of oligomers with degrees of polymerization of 21 and 16, respectively. Branching numbers are 147 and 152 branches per 1000 carbon atoms (slightly less than the expected 166 branches per 1000 carbons atoms), indicating a very minor amount of chain straightening via a 2,1-insertion and chain-walking.[10]

Aryl Substituent Effects on Ethylene Polymerization. A series of anilinotropone ligands and corresponding nickel complexes (**3a**−**h,j,k**) were synthesized in an effort to determine the effects of varying the *o*-aryl substituents on ethylene polymerization. The results are summarized in Table 7. All catalysts were screened at 80 °C and 200 psig of ethylene. Catalyst **3e**, with a 2,6-diphenyl-substituted aryl ring, has a slightly higher polymerization activity than the standard 2,6-diisopropyl-substituted catalyst **3b** (entries 3 and 5). Similar results were observed with analogues of the α-diimine nickel system.[44] With the exception of the 2,6-diphenyl-substituted catalyst, all polymerization catalysts are less active than the standard 2,6-diisopropyl-substituted catalyst. Entries 1−7 show that, as the steric bulk is increased, the M_n values of the polymers produced increase from 42 K with the 2,6-dimethyl-substituted catalyst **3a** to 115 K with the 2-methyl-6-*tert*-butyl-substituted catalyst **3d**. There is not, however, a correlation between steric bulk and catalyst activity. Catalyst **3a** is less reactive than catalyst **3b**, as expected, but further addition of steric bulk, i.e., the 2-methyl-6-*tert*-butyl-substituted catalyst **3d**, causes a decrease in catalyst activity. The monosubstituted catalysts **3c** (2-*tert*-butyl) and **3j** (2-methyl) are both very poor catalysts (entries 15 and 16). Substitution of a trifluoromethyl group for a methyl group in the 2-trifluoromethyl-6-methyl-substituted catalyst (**3k**, entries 12 and 13) causes a slight increase in catalyst turnover number when compared with the dimethyl-substituted catalyst **3a** (41 200 and 32 600, respectively) and a substantial increase in polymer molecular weight (88 000 and 42 000, respectively). While electronic differences are certainly evident, steric factors cannot be ignored, as a trifluoromethyl group is larger than a methyl group. The dichloro- and dibromo-substituted catalysts **3f,g** exhibit comparable turnover numbers and are somewhat less reactive than the dimethyl-substituted catalyst **3a** (entries 8−11). These trends are consistent with steric effects, as judged by *A* values for these groups. The *A* values for −Cl and −Br substituents are quite similar, as the larger size of −Br relative to −Cl is offset by a longer C−Br bond. The *A* value of $-CH_3$ is significantly larger than those of −Cl or −Br. Finally, the pentafluoro-substituted catalyst **3h** produces low-molecular-weight polymer with low activity (entry 14). With the exception of catalyst **3h**, all polymer molecular weight distributions are monomodal and near the chain-transfer-limited value of 2. Polymer branching numbers are between 49 and 73 branches per 1000 carbon atoms for all polymerizations. Finally, none of the modifications to the aryl ring lead to an increase in catalyst lifetime (Table 7, entries 1−13).

The melt transition temperatures of several of the polymers were measured. Branching numbers ranged from 8 branches per 1000 carbon atoms (entry 2, Table 2) to 73 branches per 1000 carbon atoms (entry 6, Table 7). Generally, as expected, the more branched polymers have lower T_m's than those with fewer branches. Polymers with 73, 53, 27, and 8 branches per 1000 carbon atoms (entries 6 and 5, Table 7, and entries 3 and 2, Table 2, respectively) have T_m's of 51, 73, 104, and 122 °C, respectively.

2-Anilino-7-Aryltropone-Derived Catalysts. As noted earlier, Grubbs reported that substitution of the salicylaldimine catalyst **2a** in the 6-position with a 9-anthracenyl group greatly increases catalyst performance, leading to much longer lifetimes, higher activities, and higher molecular weight polymers.[27,28] In view of these results, we chose to apply a similar strategy to the anilinotropone system. The synthetic route to 2-anilino-7-aryltropone is relatively straightforward and is depicted in Scheme 4. Tropolone was converted to 2-methoxytropone by reaction with iodomethane in the presence of base. Then 2-methoxytropone, **8**, was brominated using *N*-bromosuccinimide and purified by column chromatography. Both phenylboronic acid and 1-naphthylboronic acid were coupled with 2-methoxy-7-bromotropone using standard Suzuki coupling reaction conditions to yield **10a**,**b**, which were then demethylated with hydrochloric acid to yield 7-aryltropolones **11a**,**b**. Conversion to the triflates was performed using

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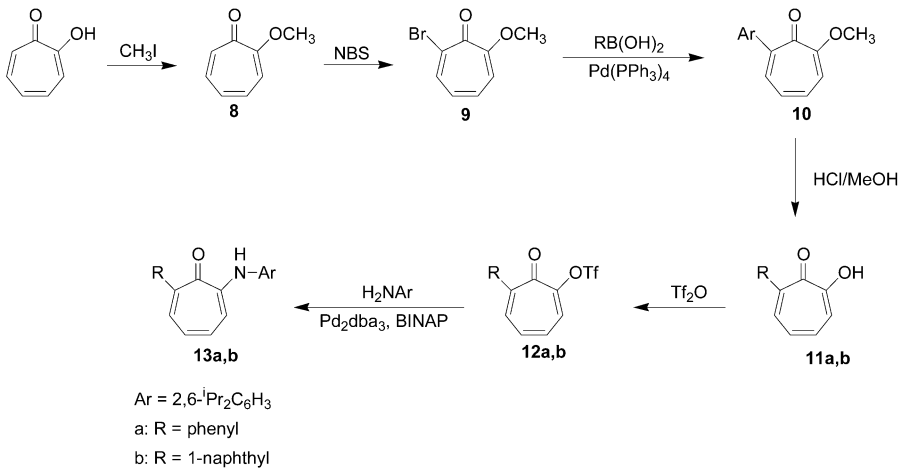
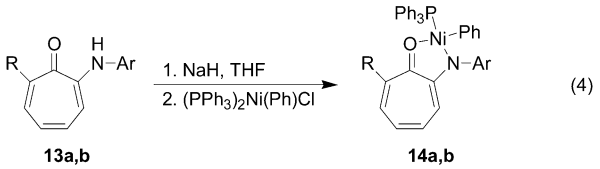
Scheme 4



Scheme 5



(4)

trifluoromethanesulfonic anhydride with pyridine as solvent. The coupling conditions used for the synthesis of the unsubstituted anilinotropone ligands were modified slightly. Catalyst loading was increased from 1.0 to 5.0 mol %, and the reaction temperature was increased from 80 to 90 °C. The more forcing conditions were necessary to compensate for the added steric bulk of the aryl-substituted triflate. In the case of the naphthyl-substituted triflatotropone **12b** the yields of coupled product were significantly reduced (see the Experimental Section).

The synthesis of (2-anilino-7-aryltropone)nickel(II) complexes **14a**,**b** was modified slightly from the procedure described for unhindered anilinotropones **5a**−**j** (Scheme 5). The 2-anilino-7-aryltropones **13a**,**b** were deprotonated in THF in the presence of a 5-fold excess of sodium hydride. One equivalent of $(PPh_3)_2Ni(Ph)Cl$ was added to the reaction mixture in solid form. Sodium hydride and sodium chloride were removed by filtration, and the product was isolated by recrystallization from toluene/pentane.

The polymerization activity of **14a**,**b** was screened at both 40 and 80 °C at 200 psig of ethylene (entries 4−12, Table 8). Polymerization at 80 °C produces polyethylene with 10 min turnover numbers somewhat higher than those with the unsubstituted catalyst (e.g. 64 300 for **14a** vs 52 400 for **3b**). The percentage increase in TON from 10 to 60 min for **14a** (64 300 to 87 700) is somewhat greater than that for **3b** (52 400 to 62 100) but still rather small and indicative of a catalyst half-life on the order of 8−10 min. A substantially different set of results is obtained at 40 °C. Entries 8−10 (Table 8) show that for naphthyl-substituted catalyst **14b** TON increases almost linearly between 10 and 180 min, suggesting a catalyst half-life well in excess of 3 h at 40 °C. Equally significant is the dramatic increase in polymer molecular weight from 10 to 60 min (250 000 to 831 000). The polymer produced in 180 min is too high

Table 8. Ethylene Polymerization with 14a,b[a]

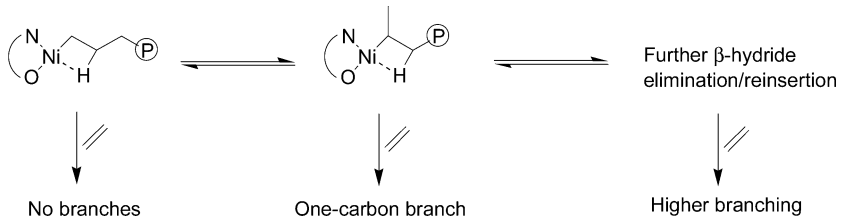
entry	R	T (°C)	t (min)	yield (g)	TON	$10^{-3}\times M_n$	PDI	branches/ 1000 C
1	Ph	25	10	0.47	2 500	74	1.2	10
2	Ph	25	30	1.5	8 100	199	1.4	20
3	Ph	25	60	2.5	13 200	280	1.5	19
4	Ph	40	10	2.0	9 600	251	1.3	34
5	Ph	40	60	8.8	47 400	581	6.4	19
6	Ph	80	10	11.9	64 300			76
7	Ph	80	60	15.2	87 700	88	2.1	63
8	naphthyl	40	10	1.9	11 200	250	1.3	22
9	naphthyl	40	60	8.8	50 600	831	3.8	9
10	naphthyl	40	180	30.7	177 000			11
11	naphthyl	80	10	10.9	51 900	56	2.2	70
12	naphthyl	80	60	16.0	76 200	56	2.7	62

[a] Reactions run in 200 mL of toluene at 200 psig of ethylene with 6.5 μmol of catalyst.

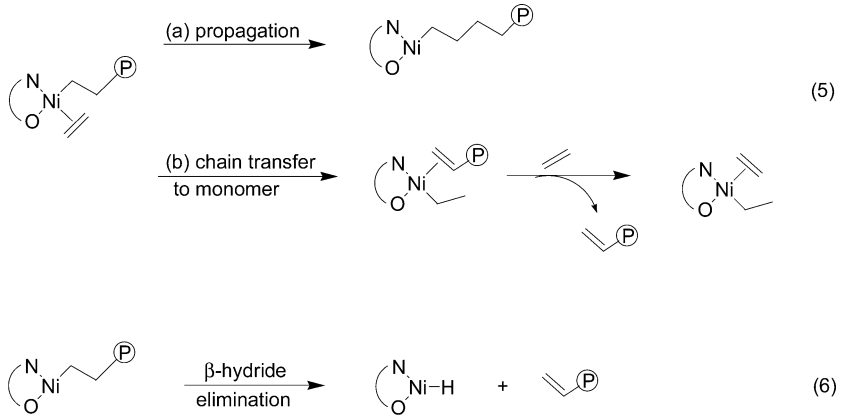
in molecular weight to be analyzed by GPC. The observed increase in molecular weight combined with the low polydispersity observed for entry 8 suggests that very little chain transfer occurs under these conditions. The high polydispersity obtained for entry 9 is likely due to the exceptionally high molecular weight of the polymer and the viscous nature of the sample used for GPC analysis. Similar results were obtained for the phenyl-substituted anilinotropone catalyst (entries 4−7, Table 8). The low polydispersity obtained at 40 °C (10 min) suggests that lowering the reaction temperature further may result in a further decrease in PDI and a living polymerization. Polymerization at 25 °C shows that, while not truly living, the catalyst produces polyethylene with polydispersities well below 2.0 and a continually increasing M_n value with reaction time (entries 1−3).

Catalysts **14a**,**b** exhibit higher turnover numbers relative to the unsubstituted catalyst **3b** at 40 °C. The reason for this increase in activity is not clear. The intrinsic barrier to ethylene insertion may be lowered, or the equilibrium ratio of the PPh_3 complex to the required ethylene complex may be shifted in favor of the ethylene complex. These mechanistic aspects are currently under investigation. The combination of high turnover frequencies and long catalyst lifetime at 40 °C results in high total productivities for these aryl-substituted catalysts, as illustrated by entry 10 where 2×10^5 turnovers are achieved in 3 h. The increased steric bulk of a naphthyl group relative to a phenyl group has little effect on overall catalyst performance

Scheme 6



Scheme 7

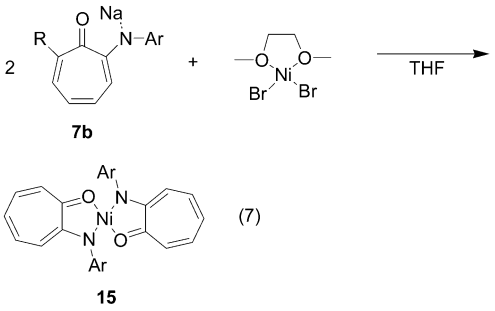


or polymer properties. The branching numbers for both of the aryl-substituted catalysts are similar to those obtained for **3b** under similar reaction conditions. Finally, the initial activity obtained at 80 °C with **14a**,**b** is higher than that obtained at 40 °C with other reaction conditions held constant; however, in terms of productivity the decreased activity at 40 °C is more than compensated for by the dramatically increased catalyst lifetime.

The variable-temperature and -pressure experiments with **3b** suggest the branching mechanism depicted in Scheme 6, which mirrors the mechanism suggested for branching in the diimine catalyst system **2**.[8,9] 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 many times prior to ethylene insertion and therefore lead to methyl as well as higher branches. As the ethylene pressure is increased, monomer coordination and insertion becomes more favorable and therefore the unimolecular branching pathway is less favored. Conversely, as temperature is increased, the unimolecular branching pathway is entropically favored over ethylene coordination and insertion and, therefore, more branching is observed.

The fact that the molecular weight significantly increases with ethylene pressure (e.g. $M_n = 50\,000$, 50 psig, 80 °C; 90 000, 200 psig, 80 °C; entries 9 and 11, Table 2) suggests that chain transfer to monomer is not the major chain transfer mechanism. Theoretical calculations have suggested that for similar systems the alkyl olefin intermediate in the polymerization may partition as shown in eq 5 (Scheme 7).[45−47] Pathway a represents insertion and propagation, while pathway b represents chain transfer to monomer. 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. Since this is not observed, a chain transfer process which is not dependent on ethylene concentration seems more likely. This is best rationalized by the conventional β-hydride elimination mechanism shown in eq 6. Of course, given the qualitative M_n values and the substantial error in these determinations, it is possible that some chain transfer occurs via the chain transfer to monomer pathway.

Scheme 8



Catalyst Deactivation Studies. The fate of the catalyst upon deactivation was investigated. Upon precipitation of the polymer in methanol, the filtrate was separated and the decomposition product was isolated. The decomposition product was determined by ^{1}H NMR spectroscopy to be the bis(anilinotropone)-nickel(II) complex **15**. The identity of this complex was confirmed through independent synthesis by combining (DME)$NiBr_2$ with 2 equiv of the sodium salt **7b** (Scheme 8). Crystals of **15** suitable for an X-ray diffraction study were grown from a concentrated solution of toluene layered with pentane at −30 °C. The crystallographic

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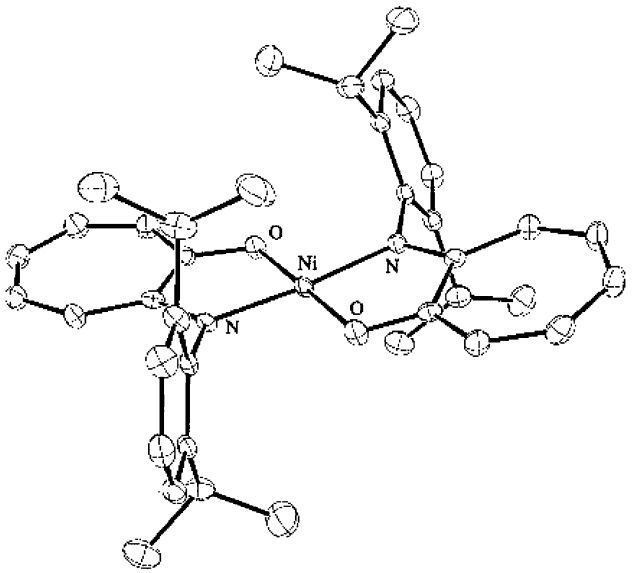

Figure 3. ORTEP view of **15**.

Table 9. Crystallographic Data for 15

formula	$NiC_{38}H_{44}N_2O_2$
mol wt	619.46
color	orange
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	18.4952(3)
b (Å)	11.5835(4)
c (Å)	34.7657(13)
α (deg)	82.197(1)
β (deg)	87.842(1)
γ (deg)	83.726(1)
V (Å^3)	3368.21(21)
D_{calcd} (Mg/m^3)	1.222
wavelength (Å)	0.71073
μ (mm^{-1})	0.61
cryst dimens (mm)	0.30 × 0.10 × 0.10
temp (°C)	−100
mode	ω
2θ range (deg)	5.00−55.00
no. of rflns	37 225
no. of indep rflns	14 719
$R(F)$	0.057
$R_w(F)$	0.060
hkl range	−10 to +11, 0−15, −44 to +45
type of diffractometer	Bruker SMART
abs cor method	SADABS
radiation for intensity measmts	Mo Kα
monochromator	graphite
Z	4

data are summarized in Table 9, and an ORTEP diagram of **15** is shown in Figure 3. The structure confirmed that the N atoms are trans to each other in the bis-ligand complex, thereby minimizing steric repulsion of the two bulky N-aryl rings. These results are similar to those reported for the salicylaldimine catalysts and SHOP catalysts.[28,48,49] Formation of the bis-ligand complex 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.

Summary

The utility of palladium cross-coupling as an effective method for the synthesis of a variety of 2-anilinotropones has been demonstrated. Reaction of the sodium salts of the anilinotropones with $(PPh_3)_2Ni(Ph)(Cl)$ provides a convenient route to catalysts of the type [[(2-R-6-R′C_6H_3)NC_7H_5O]Ni(Ph)(PPh_3)], active for ethylene polymerization. Catalysts incorporating alkyl substituents at the 2- and 6-positions of the N-aryl ring generate high-molecular-weight polyethylenes with monomodal molecular weight distributions of ca. 2 (or less at low temperatures). Total turnover numbers of ca. 60 000 are observed in 10 min at 80 °C, but catalyst lifetimes are short at this temperature. Branching increases with increasing temperature and decreasing pressure, consistent with earlier observations using aryl-substituted diimine catalysts. Replacement of the standard 2,6-diisopropyl substituents on the aryl group with 2,6-dimethyl, 2,6-dichloro, 2,6-dibromo, and 2-methyl-6-trifluoromethyl substituents has little effect on productivity. A slight increase in TON is observed for the 2,6-diphenyl-substituted catalyst. Significant reduction in TON is observed for the 2-methyl-6-*tert*-butyl-, 2-methyl-, 2-*tert*-butyl-, and 2,3,4,5,6-pentafluoro-substituted catalysts. Molecular weights generally increase with increasing steric bulk of the ortho substituents. As expected, these neutral catalysts have a high tolerance for polar additives.

Substitution of the 2-(2,6-diisopropylanilino)tropone ligand in the 7-position with either phenyl or naphthyl groups results in a small increase in productivities and lifetimes at 80 °C and 200 psig. However, at 40 °C these catalysts exhibit much longer lifetimes ($t_{1/2}$ > 1 h) and higher total turnover numbers can be achieved relative to 80 °C polymerizations.

Molecular weights of the polyethylenes increase with pressure, which suggest chain transfer at least in part occurs through classical β-hydride elimination rather than chain transfer to monomer. The catalyst decay product is the Ni(II) bis-ligand complex, whose formation must be initiated by reductive elimination of the ligand from a Ni(II) species. Utilization of these catalysts in copolymerizations and mechanistic studies of chain propagation and catalyst decay are in progress.

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. Ethyl acetate, triethylamine, and ethanol were degassed, dried over 4 Å molecular sieves, and stored under argon. Water was degassed and stored under argon. CP grade ethylene was used as received from National Welders Supply. Some studies were conducted utilizing Research Plus grade ethylene obtained from Matheson; the purity level is 99.9996%. The anilinotropones,[32] $(PPh_3)_2Ni(Ph)(Cl)$,[50] salicylaldiminato Ni complex **2**,[27] 2-methoxytropone,[51] 2-methoxy-7-bromotropone,[52] 2-methoxy-7-phenyltropone,[53] 2-methoxy-7-naphthyltropone,[53] 7-phenyltropolone,[53] 7-naphthyltropolone,[53] and $(DME)NiBr_2$[54] were prepared according to literature procedures.

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Yields refer to isolated yields of compounds of greater than 95% purity, as estimated by ^{1}H NMR analysis and elemental analysis. All ^{1}H NMR spectra are reported in δ units in parts per million (ppm) downfield from tetramethylsilane. All ^{13}C NMR spectra are reported in ppm relative to residual ^{13}C in solvent. All ^{31}P NMR data are reported relative to H_3PO_4 external standard. ^{1}H 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.[42] 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 ($k = 4.34 \times 10^{-4}$; $R = 0.724$). M_n for low-molecular-weight polymer samples was determined by ^{1}H NMR end group analysis. Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA.

General Procedure for the Preparation of Anilinotropones. A flame-dried Schlenk tube was charged with 2-triflatotropone (1.0 equiv), Cs_2CO_3 (1.4 equiv), Pd_2dba_3 (0.5 mol %), and racemic 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (1 mol %) under argon. Toluene (5 mL) and the appropriate aniline (1.2 equiv) were added, and the reaction mixture was heated to 80 °C and stirred for the duration noted below. The reaction mixture was cooled to room temperature, diluted with diethyl ether, 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.

Synthesis of 2-(2-Methylanilino)tropone (5j). Following the general procedure, 762 mg (3.0 mmol) of triflatotropone and 384 μL (3,6 mmol) of 2-methylaniline were converted to the anilinotropone in 14.5 h (561 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (bs, 1 H), 7.40−7.30 (m, 3 H), 7.30−7.21 (m, 3 H), 7.12 (dd, J = 10, 10.4 Hz, 1 H), 6.77 (m, 1 H), 6.71 (d, J = 10.4 Hz, 1 H), 2.21 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 154.5, 137.5, 136.5, 136.2, 134.6, 131.4, 130.2, 127.1, 126.1, 124.2, 110.6, 17.8. Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.62; H, 6.17; N, 6.62.

Synthesis of 2-(2-Methyl-6-trifluoromethylanilino)-tropone (5k). Following the general procedure, 762 mg (3.0 mmol) of triflatotropone and 630 mg (3,6 mmol) of 2-methyl-6-(trifluoromethyl)aniline were converted to the anilinotropone in 14.5 h (781 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (bs, 1 H), 7.64 (d, J = 7.8 Hz, 1 H), 7.55 (d, J = 7.6 Hz, 1 H), 7.41 (at, J = 7.8 Hz, 1 H), 7.33 (m, 2 H), 7.07 (at, J = 10.2 Hz, 1 H), 6.77 (m, 1 H), 6.14 (d, J = 10.1 Hz, 1 H), 2.17 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 154.2, 138.6, 137.4, 135.8, 134.9, 134.5, 131.1, 128.4 (q, J = 29.6 Hz), 127.6, 124.8 (q, J = 5.2 Hz), 124.4, 123.3 (q, J = 272 Hz), 110.5, 17.7. ^{19}F NMR (377 MHz, C_6D_6): δ −62.2. Anal. Calcd for $C_{15}H_{12}NOF_3$: C, 64.51; H, 4.33; N, 5.02. Found: C, 64.23; H, 4.24; N, 4.87.

Synthesis of 2-(2,6-Difluoroanilino)tropone (5l). Following the general procedure, 254 mg (1.0 mmol) of triflatotropone and 129 μL (1.2 mmol) of 2,6-difluoroaniline were converted to the anilinotropone in 16 h (219 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (bs, 1H), 7.35 (m, 2H), 7.25 (m, 1H), 7.16 (t, J = 10.2 Hz), 1H), 7.05 (m, 2H), 6.55 (dt, J = 2.5, 10.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 159.0 (d, J = 4.6 Hz, 1C), 156.5 (d, J = 4.6, 1C). 137.3, 135.5, 131.6, 127.3 (t, J = 9.6 Hz, 1C), 125.2, 115.5, (t, J = 15.6 Hz, 1C), 112.1, 111.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −116.6 (s). Anal. Calcd for $C_{13}H_8NOF_2$: C, 66.93; H, 3.89; N, 6.01. Found: C, 66.66; H, 3.90; N, 5.97.

General Procedure for the Synthesis of Na Salts of 2-Anilinotropones. To a sidearm flask in a glovebox was added NaH (1.2 equiv). The flask was removed from the glovebox and placed on a vacuum line under argon. THF (5−10 mL) was added to the flask, and the flask was cooled with an ice−water bath. Slow addition of 2-anilinotropone (1 equiv) as a solution in THF (3 mL) resulted in vigorous evolution of hydrogen. When gas evolution ceased, the flask was removed from the ice−water bath and warmed to room temperature. After 2 h, the solution was cannula-filtered away from the remaining NaH, and the residual NaH was washed with THF (3 mL). The THF was removed in vacuo to produce essentially a quantitative yield of the desired salt as its THF adduct. The amount of THF incorporated varied with different salts and was determined by ^{1}H NMR.

Na Salt of 2-(2,6-Dimethylanilino)tropone (7a). The general procedure was employed with 405 mg (1.8 mmol) of anilinotropone and 50 mg (2 mmol) of NaH. The salt was isolated with 2.18 equiv of THF. ^{1}H NMR (400 MHz, C_6D_6): δ 7.05 (m, 2 H), 6.92 (m, 1 H), 6.58−6.33 (m, 4 H), 6.05 (m, 1 H), 3.40 (THF), 1.94 (s, 6 H), 1.31 (THF).

Na Salt of 2-(2,6-Diisopropylanilino)tropone (7b). The general procedure was employed with 1.28 g (4.5 mmol) of anilinotropone and 120 mg (5 mmol) of NaH. The salt was isolated with 1 equiv of THF. ^{1}H NMR (250 MHz, C_6D_6): δ 7.18−7.04 (m, 3 H), 6.6−6.4 (m, 3 H), 6.32 (dd, J = 8.0, 12.2 Hz, 1 H), 6.02 (dt, J = 3.2, 7.8 Hz, 1 H), 3.36 (THF), 2.94 (m, 2 H), 1.26 (THF), 1.14 (d, j = 7.0 Hz, 6 H), 1.00 (d, J = 7 Hz, 1 H). ^{13}C NMR (100 MHz, C_6D_6): δ 177.6, 165.8, 148.7, 139.0, 134.4, 133.5, 124.2, 123.5, 121.2, 118.4, 117.9, 68.0, 28.2, 25.6, 24.9, 23.9.

Na Salt of 2-(2-*tert*-Butylanilino)tropone (7c). The general procedure was employed with 462 mg (1.8 mmol) of anilinotropone and 50 mg (5 mmol) of NaH. The salt was isolated with 1.5 equiv of THF. ^{1}H NMR (250 MHz, C_6D_6): δ 7.42 (d, J = 8.0 Hz, 1 H), 6.98 (m, 1 H), 6.66 (m, 2 H), 6.45 (m, 3 H), 6.04 (at, J = 9.0 Hz, 1 H), 3.44 (THF), 1.37 (THF), 1.29 (s, 9 H).

Na Salt of 2-(2-*tert*-Butyl-6-methylanilino)tropone (7d). The general procedure was employed with 303 mg (1.14 mmol) of anilinotropone and 31 mg (1.3 mmol) of NaH. The salt was isolated with 1.16 equiv of THF. ^{1}H NMR (400 MHz, C_6D_6): δ 7.33 (d, J = 7.6 Hz, 1 H), 7.07 (d, J = 7.6 Hz, 1 H), 6.94 (at, J = 7.6 Hz, 1 H), 6.52 (m, 2 H), 6.39 (m, 2 H), 6.04 (m, 1 H), 3.40 (THF), 1.97 (s, 3 H), 1.30 (s, 9 H + THF).

Na Salt of 2-(2,6-Diphenylanilino)tropone (7e). The general procedure was employed with 352 mg (1.0 mmol) of anilinotropone and 28 mg (1.2 mmol) of NaH. The salt was isolated with 0.55 equiv of THF. ^{1}H NMR (400 MHz, C_6D_6): δ 7.28 (d, J = 7.6 Hz, 2 H), 7.19 (d, J = 6.8 Hz, 2 H), 7.04 (t, J = 7.6 Hz, 1 H), 6.81 (m, 6 H), 6.63 (d, J = 11.6 Hz, 1 H), 6.44 (m, 2 H), 6.08 (at, J = 9.0 Hz, 1 H), 6.00 (d, J = 10.4 Hz, 1 H), 3.52 (THF), 1.39 (THF).

Na Salt of 2-(2,6-Dichloroanilino)tropone (7f). The general procedure was employed with 658 mg (2.5 mmol) of anilinotropone and 71 mg (2.95 mmol) of NaH. The salt was isolated with 1.6 equiv of THF. ^{1}H NMR (400 MHz, C_6D_6): δ 7.08 (d, J = 8.0 Hz, 2 H), 6.73 (d, J = 10.4 Hz, 1 H), 6.59 (at, J = 10.2 Hz, 1 H), 6.51 (m, 1 H), 6.39 (m, 2 H), 6.11 (at, J = 9.2 Hz, 1 H), 3.50 (THF), 1.35 (THF).

Na Salt of 2-(2,6-Dibromoanilino)tropone (7g). The general procedure was employed with 721 mg (2.0 mmol) of anilinotropone and 58 mg (2.44 mmol) of NaH. The salt was isolated with 1 equiv of THF. ^{1}H NMR (400 MHz, C_6D_6): δ 7.26 (m, 2 H), 6.74 (m, 1 H), 6.61 (m, 1 H), 6.50 (m, 1 H), 6.35 (d, J = 11.2 Hz, 1 H), 6.23 (m, 1 H), 6.14 (m, 1 H), 3.51 (THF), 1.33 (THF).

Na Salt of 2-(2,3,4,5,6-Pentafluoroanilino)tropone (7h). The general procedure was employed with 581 mg (1.9 mmol) of anilinotropone and 100 mg (4.2 mmol) of NaH. The salt was isolated with no excess THF. ^{1}H NMR (400 MHz, d_6-acetone):

δ 6.85 (at, H = 10.2 Hz, 1 H), 6.73 (d, J = 10 Hz, 1 H), 6.69 (at J = 11.4 Hz, 1 H), 6.19 (d, J = 11.2 Hz, 1 H), 6.14 (at, J = 9.2 Hz, 1 H).

Na Salt of 2-(2-Methylanilino)tropone (7j). The general procedure was employed with 508 mg (2.4 mmol) of anilinotropone and 69 mg (2.9 mmol) of NaH. The salt was isolated with 0.89 equiv of THF. ^{1}H NMR (400 MHz, C_6D_6): δ 7.11 (m, 2 H), 6.93 (m, 1 H), 6.64−6.45 (m, 4 H), 6.41 (dd, J = 8.6, 11.4 Hz, 1 H), 6.08 (at, J = 9.0 Hz, 1 H), 3.46 (THF), 1.89 (s, 3 H), 1.32 (THF).

Na Salt of 2-(2-Methyl-6-(trifluoromethyl)anilino)-tropone (7k). The general procedure was employed with 688 mg (2.5 mmol) of anilinotropone and 71 mg (2.95 mmol) of NaH. The salt was isolated with 1 equiv of THF. ^{1}H NMR (400 MHz, C_6D_6): δ 7.39 (d, J = 7.6 Hz, 1 H), 7.06 (d, J = 7.6 Hz, 1 H), 6.70 (at, J = 7.6 Hz, 1 H), 6.57 (m, 2 H), 6.45 (dd, J = 8.2, 11.6 Hz, 1 H), 6.28 (d, J = 11.6 Hz, 1 H), 6.08 (at, J = 8.8 Hz, 1 H), 3.46 (THF), 1.88 (s, 3 H), 1.33 (THF).

General Procedure for the Synthesis of 2-Anilinotropone Nickel Complexes (3). In a flame-dried Schlenk flask in a glovebox were added the sodium salt of 2-anilinotropone−THF (1.0 equiv) and $(Ph_3P)_2$Ni(Ph)(Cl) (1.0 equiv). The flask was removed from the glovebox, placed on a vacuum line under Ar, and cooled to −30 °C in a dry ice/acetone bath. THF (∼15 mL) was added to the flask, which was warmed to room temperature for 1 h. The reaction mixture was stirred at ambient temperature for 1 h. THF was removed in vacuo, and the crude reaction mixture was dissolved in toluene (∼15 mL). Cannula transfer onto a pad of Celite was followed by filtration under argon. The Celite pad was washed with toluene (3 × 5 mL), and the solvent volume was reduced to 3−5 mL. Pentane (50 mL) was added, and the Schlenk flask was placed in a −30 °C freezer overnight. Solvent was removed from the precipitate via cannula filtration, and the residual solid was washed with pentane (3 × 10 mL). Drying in vacuo produces the desired nickel complex.

2-(2,6-Dimethylanilino)tropone Ni Complex 3a. The general procedure was employed with 172 mg (0.54 mmol) of the sodium salt and 372 mg (0.54 mmol) of $(Ph_3P)_2$Ni(Ph)(Cl) to afford 190 mg (57%) of the desired complex as a yellow-orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.54 (m, 6 H), 7.39 (m, 3 H), 7.28 (m, 6 H), 7.21 (d, J = 8 Hz, 2 H), 7.09 (dd, J = 10, 10.6 Hz, 1 H), 6.99 (m, 2 H), 6.94 (d, J = 10.6 Hz, 1 H), 6.71 (d, J = 10.7 Hz, 1 H), 6.63 (at, J = 9.5 Hz, 1 H), 6.56 (t, J = 8 Hz, 1 H), 6.22 (m, 2 H), 6.14 (m, 2 H), 2.21 (s, 6 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 179.9 (d, J = 7.2 Hz), 167.7, 150.3 (d, J = 44.5 Hz), 146.4, 136.9 (d, J = 1.8 Hz), 134.7, 134.6 (d, J = 10.7 Hz), 134.3, 131.8 (d, J = 1.9 Hz), 131.4, 130.1, 128.2 (d, J = 9.7 Hz), 127.7, 124.8 (d, J = 2.6 Hz), 124.3, 122.0, 121.1, 120.5, 117.7, 18.3.^{31}P NMR (162 MHz, C_6D_6): δ 29.03. Anal. Calcd for $C_{39}H_{34}$NOPNi: C, 75.26; H, 5.51; N, 2.25. Found: C, 75.49; H, 5.57; N, 2.38.

2-(2,6-Diisopropylanilino)tropone Ni Complex 3b. The general procedure was employed with 201 mg (0.54 mmol) of the sodium salt and 372 mg (0.54 mmol) of $(Ph_3P)_2$Ni(Ph)(Cl) to afford 241 mg (67%) of the desired complex as a yellow-orange solid. ^{1}H NMR (400 MHz, C_6D_6): δ 7.63 (m, 6 H), 7.08 (d, J = 7.0 Hz, 2 H), 6.98 (m, 12 H), 6.76 (d, J = 10.4 Hz, 1 H), 6.58 (at, J = 9.9 Hz, 1 H). 6.53 (d, J = 11.5 Hz, 1 H), 6.45−6.33 (m, 4 H), 6.13 (at, J = 9.4 Hz, 1 H), 3.82 (sept, J = 6.8 Hz, 2 H), 1.32 (d, J = 6.8 Hz, 6 H), 1.09 (d, J = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, C_6D_6): δ 180.2 (d, J = 7.6 Hz), 169.6, 148.9 (d, J = 45 Hz), 144.4, 142.3, 138.1 (d, J = 2.2 Hz), 134.6 (d, J = 10.5 Hz), 133.1, 132.0, 131.6, 129.9 (d, J = 1.9 Hz), 125.9, 125.5 (d, J = 2 Hz), 123.7, 122.2, 121.7, 121.3, 121.1, 29.0, 25.9, 23.9. ^{31}P NMR (162 MHz, C_6D_6): δ 28.9. Anal. Calcd for $C_{43}H_{42}$NOPNi: C, 76.12; H, 6.24; N, 2.06. Found: C, 75.83; H, 6.24; N, 1.98.

2-(2-*tert*-Butylanilino)tropone Ni Complex 3c. The general procedure was employed with 201 mg (0.53 mmol) of the sodium salt and 372 mg (0.54 mmol) of $(Ph_3P)_2$Ni(Ph)(Cl) to afford 195 mg (57%) of the desired complex as a yellow-orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47 (m, 6 H), 7.38 (m, 3 H), 7.28 (m, 6 H), 7.18 (dd, J = 1.4, 8 Hz, 1 H), 7.11 (bs, 1 H), 6.95 (at, J = 10.2 Hz, 1 H), 6.81 (m, 2 H), 6.72 (m, 1 H), 6.55 (M, 2 H), 6.46 (d, J = 9.4 Hz, 1 H), 6.42 (dd, J = 1.6, 7.7 Hz, 1 H), 6.23 (m, 2 H), 6.07 (bs, 1 H), 1.51 (s, 9 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 179.9 (d, J = 7.5 Hz), 169.1, 151.3 (d, J = 45 Hz), 146.9, 142.3, 138.4 (broad), 137.8 (broad), 134.8, 134.6 (d, J = 10.5 Hz), 133.7, 131.9, 131.5, 130.1 (d, J = 1.9 Hz), 128.9, 128.8, 128.2 (d, J = 9.7 Hz), 126.3, 125.1 (broad), 124.2, 121.6, 120.9, 120.7, 120.5, 36.4, 32.8..^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.34. Anal. Calcd for $C_{41}H_{38}$NOPNi: C, 75.71; H, 5.89; N, 2.15. Found: C, 75.76; H, 5.92; N, 2.19.

2-(2-*tert*-Butyl-6-methylanilino)tropone Ni Complex 3d. The general procedure was employed with 219 mg (0.59 mmol) of the sodium salt and 409 mg (0.59 mmol) of $(Ph_3P)_2$Ni(Ph)(Cl) to afford 185 mg (47%) of the desired complex as a yellow-orange solid. ^{1}H NMR (400 MHz, C_6D_6): δ 7.63 (m, 6 H), 7.23 (bs, 1 H), 7.15 (m, 1 H), 6.98 (m, 10 H), 6.81 (m, 2 H), 6.75 (d, J = 10.4 Hz, 1 H), 6.58 (at, J = 10 Hz, 1 H), 6.48 (m, 2 H), 6.41 (m, 3 H), 6.11 (at, J = 9.0 Hz, 1 H), 2.46 (s, 3 H), 1.69 (s, 9 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 179.8 (d, J = 7.3 Hz), 168.1, 149.3 (d, J = 45.3 Hz), 145.6, 142.1, 138.3 (broad), 137.2 (broad), 134.7, 134.5 (d, J = 10.5 Hz), 133.9, 133.1, 131.9, 131.4, 130.1, 128.2 (d, J = 9.9 Hz), 128.1, 127.1, 124.9 (broad), 124.4, 121.7, 121.1, 120.4, 119.7, 36.9, 33.3, 19.6..^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.02. Anal. Calcd for $C_{42}H_{40}$NOPNi: C, 75.92; H, 6.07; N, 2.11. Found: C, 75.75; H, 6.11; N, 2.15.

2-(2,6-Diphenylanilino)tropone Ni Complex 3e. The general procedure was employed with 225 mg (0.55 mmol) of the sodium salt and 380 mg (0.55 mmol) of $(Ph_3P)_2$Ni(Ph)(Cl) to afford 220 mg (54%) of the desired complex as a yellow-orange solid. The compound was isolated with 0.33 equiv of toluene. ^{1}H NMR (400 MHz, C_6D_6): δ 7.95 (d, J = 7.6 Hz, 4 H), 7.49 (m, 6 H), 7.20 (m, 6 H), 7.13 (m, 6 H), 6.98 (8 H + toluene), 6.77 (d, J = 11.6 Hz, 1 H), 6.55 (m, 2 H), 6.4 (m, 4 H), 6.02 (m, 1 H), 2.09 (toluene). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 179.6 (d, J = 7.5 Hz), 168.9, 148.0 (d, J = 45.1 Hz), 144.6, 140.8, 138.3 (d, J = 2.7 Hz), 137.0, 134.8, 134.5 (d, J = 10.6 Hz), 133.8, 131.8, 131.3, 130.5, 130.2, 130.0 (d, J = 1.9 Hz), 129.3, 128.5, 128.1 (d, J = 9.8 Hz), 127.7, 127.0, 125.6, 125.2, 124.9 (d, 1.9 Hz), 122.0, 121.2, 121.1, 120.5, 21.5..^{31}P NMR (162 MHz, C_6D_6): δ 29.03. Anal. Calcd for $C_{49}H_{38}$NOPNi·0.33(toluene): C, 79.3; H, 5.27; N, 1.80. Found: C, 79.24; H, 5.37; N, 1.77.

2-(2,6-Dichloroanilino)tropone Ni Complex 3f. The general procedure was employed with 200 mg (0.50 mmol) of the sodium salt and 344 mg (0.50 mmol) of $(Ph_3P)_2$Ni(Ph)(Cl) to afford 250 mg (75%) of the desired complex as a yellow-orange solid. ^{1}H NMR (400 MHz, C_6D_6): δ 7.54 (m, 6 H), 7.39 (m, 3 H), 7.29 (m, 6 H), 7.09 (dt, J = 1.0, 10.2 Hz, 1 H), 6.96 (m, 5 H), 6.72 (d, J = 10.8 Hz, 1 H), 6.70 (d, J = 8.1 Hz, 1 H), 6.63 (at, J = 9.5 Hz, 1 H), 6.23 (at, J = 9.5 Hz, 1 H), 6.23 (m, 2 H), 6.14 (m, 2 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 180.2 (d, J = 6.8 Hz), 167.7, 149.9 (d, J = 45.3 Hz), 144.2, 137.1 (d, J = 1.7 Hz), 135.5, 134.8, 134.7 (d, J = 10.6 Hz), 131.7, 131.3, 130.2 (d, J = 2 Hz), 128.2 (d, J = 9.7 Hz), 128.1, 125.6, 124.9 (d, J = 2.1 Hz), 123.2, 122.9, 121.4, 117.8. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.13. Anal. Calcd for $C_{37}H_{28}NOPNiCl_2$: C, 67.00; H, 4.26; N, 2.11. Found: C, 66.95; H, 4.37; N, 2.15.

2-(2,6-Dibromoanilino)tropone Ni Complex 3g. The general procedure was employed with 220 mg (0.49 mmol) of the sodium salt and 341 mg (0.49 mmol) of $(Ph_3P)_2$Ni(Ph)(Cl) to afford 315 mg (85%) of the desired complex as a yellow-orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.54 (m, 6 H), 7.39 (m, 3 H), 7.28 (m, 6 H), 7.21 (d, J = 8.0 Hz, 2 H), 7.09 (m, 1 H), 7.00 (m, 2 H), 6.94 (d, J = 10.4 Hz, 1 H), 6.72 (d, J = 10.8 Hz, 1 H), 6.63 (at, J = 9.4 Hz, 1 H), 6.56 (t, J = 8.0 Hz, 1 H), 6.22 (m, 2 H), 6.14 (t, J = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 180.2 (d, J = 6.8 Hz), 167.3, 149.6 (d, J = 45.7 Hz), 146.5, 137.4, 135.5, 134.8, 134.7 (d, J = 10.6 Hz),

132.0, 131.7, 131.3, 130.2 (d, J = 1.6 Hz), 128.2 (d, J = 9.8 Hz), 126.4, 124.9 (d, J = 2 Hz), 123.2, 123.0, 122.3, 121.4, 118.0. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.03. Anal. Calcd for $C_{37}H_{28}NOPNiBr_2$: C, 59.08; H, 3.75; N, 1.86. Found: C, 59.35; H, 3.82; N, 1.90.

2-(2,3,4,5,6-Pentafluoroanilino)tropone Ni Complex 3h. The general procedure was employed with 136 mg (0.44 mmol) of the sodium salt and 308 mg (0.44 mmol) of $(Ph_3P)_2$-Ni(Ph)(Cl) to afford 169 mg (57%) of the desired complex as a yellow-orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.52 (m, 6 H), 7.39 (m, 3 H), 7.30 (m, 6 H), 7.18 (dt, J = 0.9, 10.25 Hz, 1 H), 7.06 (m, 1 H), 6.87 (d, J = 7.2 Hz, 2 H), 6.80 (d, J = 10.8 Hz, 1 H), 6.74 (at, J = 9.6 Hz, 1 H), 6.50 (d, J = 11.2 Hz, 1 H), 6.36 (t, J = 7.15 Hz, 1 H), 6.28 (m, 2 H). ^{13}C NMR (100 MHz, CD_2Cl_2; spectrum hard to interpret due to extensive F coupling): δ 180.8 (d, J = 6.5 Hz), 169.1, 152.2 (d, J = 45.5 Hz), 136.8, 136.2, 135.4, 134.6 (d, J = 10.7 Hz), 132.3 (m), 131.4, 131.0, 130.3 (d, J = 1.9 Hz), 128.9 (m), 128.3 (d, J = 9.8 Hz), 125.5 (d, J = 2.5 Hz), 124.5, 124.3, 122.0, 118.0. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.71. ^{19}F NMR (377 MHz, CD_2Cl_2): δ −147.73 (m), −163.75 (t, J = 22.6 Hz), −166.52 (m). Anal. Calcd for $C_{37}H_{25}NOPNiF_5$: C, 64.94; H, 3.68; N, 2.05. Found: C, 64.45; H, 3.90; N, 2.31.

2-(2-Methylanilino)tropone Ni Complex 3j. The general procedure was employed with 100 mg (0.34 mmol) of the sodium salt and 234 mg (0.34 mmol) of $(Ph_3P)_2Ni(Ph)(Cl)$ to afford 105 mg (51%) of the desired complex as a yellow-orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.50 (m, 6 H), 7.39 (m, 3 H), 7.28 (m, 6 H), 6.98 (dt, J = 1.0, 10.2 Hz, 1 H), 6.87−6.67 (m, 6 H), 6.59 (d, J = 10.4 Hz, 1 H), 6.53 (dd, J = 1.3, 7.6 Hz, 1 H), 6.49 (at, J = 9.5 Hz, 1 H), 6.27 (d, J = 11.6 Hz, 1 H), 6.18 (m, 2 H), 6.06 (bs, 1 H), 2.19 (s, 3 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 179.9 (d, J = 7.5 Hz), 168.5, 151.6 (d, J = 44.4 Hz), 147.8, 138.0 (broad), 137.1 (broad), 134.7, 134.6 (d, J = 10.6 Hz), 134.1, 132.1, 131.9, 131.5, 130.1 (d, J = 2.3 Hz), 130.0, 128.2 (d, J = 9.7 Hz), 126.3, 126.2, 125.0 (broad), 124.2, 122.0, 121.0, 120.8, 118.6, 17.9. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.43. Anal. Calcd for $C_{38}H_{32}NOPNi$: C, 75.02; H, 5.30; N, 2.30. Found: C, 74.12; H, 5.33; N, 2.31.

2-(2-Methyl-6-(trifluoromethyl)anilino)tropone Ni Complex 3k. The general procedure was employed with 192 mg (0.51 mmol) of the sodium salt and 357 mg (0.51 mmol) of $(Ph_3P)_2Ni(Ph)(Cl)$ to afford 205 mg (59%) of the desired complex as a yellow-orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.49 (m, 6 H), 7.37 (m, 3 H), 7.27 (m, 7 H), 7.04 (d, J = 9.9 Hz, 1 H), 6.96 (m, 2 H), 6.86 (m, 2 H), 6.63 (d, J = 10.6 Hz, 1 H), 6.55 (m, 2 H), 6.17 (m, 3 H), 6.05 (m, 1 H), 2.17 (s, 3 H). ^{13}C NMR (100 MHz, CD_2Cl_2; spectrum is hard to interpret due to extensive F coupling): δ 180.1 (d, J = 7.3 Hz), 168.0, 149.4 (d, J = 46.0 Hz), 146.4, 138.1, 136.8, 135.2, 134.8, 134.6 (d, J = 10.6 Hz), 134.4, 134.0, 131.8, 131.3, 130.1 (d, J = 2.5 Hz), 128.2 (d, J = 9.7 Hz), 126.2, 125.1 (broad), 124.8, 124.7 (broad), 124.5 (q, J = 5.6 Hz), 124.3, 123.5, 122.4, 121.9, 121.1, 118.9, 18.2. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.37. Anal. Calcd for $C_{39}H_{31}NOPNiF_3$: C, 69.25; H, 4.62; N, 2.07. Found: C, 69.15; H, 4.57; N, 2.10.

2-Triflato-7-Aryltropone. Both triflatotropones were prepared according to literature procedures.[55] 7-Aryltropolone (1 equiv) was dissolved in pyridine (10 mL) and cooled to 0 °C. Triflic anhydride was added dropwise, and the reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was diluted with water (100 mL) and extracted with diethyl ether (4 × 75 mL). The organic phase was washed with water (1 × 50 mL), 1 N HCl (2 × 50 mL), water (1 × 50 mL), and brine (1 × 50 mL) and dried over Na_2SO_4. The solvent was removed to yield the desired product.

2-Triflato-7-phenyltropone (12a). Yield: 1.03 g, 63%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.6 (d, J = 14 Hz, 1H), 7.45 (m, 6H), 7.25 (m, 1H), 7.0 (t, J = 14 Hz, 1H). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −74.9.

2-Triflato-7-naphthyltropone (12b). Yield: 1.09 g, 34%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.9 (m, 1H), 7.65 (m, 2H), 7.5 (m, 7H), 7.15 (m, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −75.0.

General Procedure for the Preparation of 7-Aryl-2-anilinotropones. A flame-dried Schlenk tube was charged with 7-aryl-2-triflatotropone (1.0 equiv), ground cesium carbonate (1.4 equiv), $Pd_2(dba)_3$ (2.5 mol %), and racemic BINAP (5 mol %) under an atmosphere of argon. Toluene (5 mL) and 2,6-diisopropylaniline were added sequentially, and the reaction mixture was stirred at 90 °C under argon. After sufficient reaction time, the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2, and filtered through a pad of Celite. The solution was concentrated, and the residue was chromatographed on silica gel with 15% ethyl acetate in hexanes as the eluent.

7-Phenyl-2-(2,6-diisopropyl)anilinotropone (13a). A 1.03 g (3.12 mmol) portion of 2-triflato-7-phenyltropone and 706 μL (3.74 mmol) of 2,6-diisopropylaniline were converted to anilinotropone in 20 h (550 mg, 49%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.7 (bs, 1H), 7.55 (m, 3H), 7.4 (m, 4H), 7.3 (m, 2H), 7.1 (t, J = 10 Hz, 1H), 6.75 (t, J = 10 Hz, 1H), 6.3 (d, J = 10 Hz, 1H), 2.9 (sept, J = 7 Hz, 2H), 1.16 (d, J = 7 Hz, 6H), 1.14 (d, J = 7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.4, 157.5, 147.2, 143.2, 141.3, 139.3, 135.6, 133.2, 130.1, 129.0, 128.1, 127.5, 124.6, 122.7, 110.5, 28.9, 24.6, 23.4. Anal. Calcd for $C_{25}H_{27}NO$: C, 84.10; H, 7.50; N, 3.92. Found: C, 83.47; H, 7.79; N, 3.62.

7-(1-Naphthyl)-2-(2,6-diisopropyl)anilinotropone (13b). A 350 mg (0.92 mmol) portion of 2-triflato-7-(1-naphthyl)-tropone and 210 μL (1.10 mmol) of 2,6-diisopropylaniline were converted to anilinotropone in 42 h (200 mg, 53%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.7 (bs, 1H), 7.9 (m, 2H), 7.6 (m, 3H), 7.4 (m, 5H), 7.3 (m, 2H), 6.8 (t, J = 9.5 Hz, 1H), 6.4 (d, J = 9.5 Hz, 1H), 3.0 (sept, J = 7 Hz, 1H), 2.9 (sept, J = 7 Hz, 1H), 1.21 (d, J = 7 Hz, 3H), 1.17 (d, J = 7 Hz, 3H), 1.16 (d, J = 7 Hz, 3H), 1.13 (d, J = 7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.8, 156.9, 147.2, 147.1, 141.1, 140.9, 140.3, 136.4, 134.1, 133.0, 132.0, 129.5, 129.4, 129.1, 128.8, 128.3, 127.1, 126.5, 126.1, 126.0, 124.7, 122.9, 111.1, 29.0, 28.9, 25.0, 23.8, 23.7. Anal. Calcd for $C_{29}H_{29}NO$: C, 85.47; H, 7.17; N, 3.44. Found: C, 85.44; H, 7.07; N, 2.72.

Modified Procedure for the Preparation of 2-Anilino-7-aryltropone Ni Complexes. A flame-dried Schlenk tube was charged with the appropriate anilinotropone (1.0 equiv) and sodium hydride (5.0 equiv) under an atmosphere of argon. THF (∼30 mL) was added, and the reaction mixture was stirred for 18 h. Then $(PPh_3)_2Ni(Ph)Cl$ (1.0 equiv) was added as a solid and the reaction mixture was stirred for 1 h and then filtered through a pad of Celite. The solvent was removed in vacuo, and the residue was recrystallized from toluene and pentane.

7-Phenyl-2-(2,6-diisopropyl)anilinotropone Ni Complex 14a. A 65 mg (0.18 mmol) portion of the anilinotropone and 127 mg (0.18 mmol) of $(PPh_3)_2Ni(Ph)Cl$ were converted to the desired product (65 mg, 48%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.3 (m, 9H), 7.1 (m. 7H), 6.95 (m, 8H), 6.8 (m, 3H), 6.5 (t. J = 10 Hz, 1H), 6.35 (d. J = 10 Hz, 1H), 6.25 (m, 1H), 6.15 (m, 2H), 3.55 (sept, J = 7 Hz, 2H), 1.2 (d, J = 7 Hz, 6H), 1.0 (d, J = 7 Hz, 6H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 176.5, 169.8, 149.5, 143.3, 142.4, 137.7, 137.6, 134.4, 134.3, 132.1, 131.7, 129.9, 129.8, 128.2, 128.0, 127.7, 126.2, 125.3, 125.1, 123.5, 121.1, 28.8, 25.7, 23.8. ^{31}P NMR (CD_2Cl_2, 162 MHz): δ 26.5. Anal. Calcd for $C_{49}H_{46}NiNOP$: C, 78.00; H, 6.14; N, 1.86. Found: C, 77.73; H, 6.15, N, 1.81.

7-Naphthyl-2-(2,6-diisopropylanilino)tropone Ni Complex 14b. A 200 mg (0.49 mmol) portion of the anilinotropone and 340 mg (0.49 mmol) of $(PPh_3)_2Ni(Ph)Cl$ were converted to the desired product (90 mg, 23%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.7 (d, J = 8 Hz, 1H), 7.6 (d, J = 8 Hz, 1H), 7.5 (d, J

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= 8 Hz, 1H), 7.4 (m, 3H), 7.2 (td, J = 7.5, 1.3 Hz, 3H), 6.9 (m, 18H), 6.4 (m, 2H), 6.1 (m, 3H), 3.7 (sept, J = 7 Hz, 1H), 3.5 (sept, J = 7 Hz, 1H), 1.3 (d, J = 7 Hz, 3H), 1.1 (d, J = 7 Hz, 3H), 1.05 (t, J = 8 Hz, 6H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 169.6, 169.5, 144.78, 141.3, 138.1, 134.1, 134.0, 133.9, 132.0, 131.8, 131.3, 129.6, 129.5, 127.9, 127.8, 127.1, 126.3, 125.7, 125.3, 123.5, 123.4, 1221.0, 120.7, 28.9, 28.8, 24.9, 23.7, 23.6. ^{31}P NMR (CD_2Cl_2, 162 MHz): δ 26.3. Anal. Calcd for $C_{53}H_{48}$-NiNOP: C, 79.11; H, 6.01; N, 1.74. Found: C, 78.72; H, 6.13, N, 1.70.

L_2Ni from 2-(2,6-Diisopropylanilino)tropone Ni Complex 15. To a flame-dried Schlenk flask in a glovebox were added the sodium salt of a 2-anilinotropone−THF (377 mg, 0.90 mmol)) and (DME)$NiBr_2$ (139 mg, 0.45 mmol). The flask was removed from the glovebox and placed on a vacuum line under Ar. Et_2O (20 mL) was added to the flask, and the reaction mixture was stirred at room temperature for 15 h. The crude reaction mixture was filtered through filter paper and condensed to produce 240 mg (88%) of a red-brown solid. X-ray-quality crystals were grown by slow diffusion of pentane into a concentrated toluene solution of **15** at −30 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.29−7.21 (m, 6 H), 6.26−6.18 (m, 8 H), 5.92 (m, 2 H), 4.18 (sept, J = 6.8 Hz, 4 H), 1.74 (d, J = 6.8 Hz, 12 H), 1.19 (d, J = 6.8 Hz, 12 H). ^{13}C NMR (100 MHz, C_6D_6): δ 180.4, 168.9, 143.6, 141.1, 134.6, 133.8, 126.7, 124.0, 122.8, 120.7, 119.3, 29.2, 24.5, 24.1. Anal. Calcd for $C_{38}H_{42}N_2O_2Ni$: C, 73.67; H, 7.16; N, 4.50. Found: C, 74.10; H, 7.25; N, 4.39.

General Procedure for High-Pressure Ethylene Polymerizations. A 1000 mL Parr autoclave was heated under vacuum to 110 °C and then was cooled to the desired reaction temperature and back-filled with ethylene. The autoclave was charged with toluene (190 mL), degassed with ethylene (2 × 200 psig), and pressurized with ethylene to 200 psig. The stirring motor was engaged, and the reactor was allowed to equilibrate at the desired temperature for approximately 10 min. 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 10 mL of toluene 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. 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, ethylene pressure, and solvent. For the additive studies, 170 mL of toluene and 20 mL of the respective additive were used in place of the 190 mL of toluene mentioned above. For cocatalyst studies, the autoclave was charged with 180 mL of toluene. The catalyst was added in 10 mL of toluene followed by the cocatalyst in 10 mL of toluene. For the studies with excess PPh_3, both the catalyst and PPh_3 were added in the same 10 mL of toluene. Polymerizations run at 60 and 80 °C produced a homogeneous, viscous solution of polymer and solvent (i.e. no precipitate).

Procedure for Ethylene Polymerization at 1 atm. In a glovebox, a sidearm flask was charged with **2** (5 mg, 7.6 μmol). The flask was removed from the glovebox and placed on a vacuum line under argon. Toluene (40 mL) was added to the flask, and the flask was then placed in an 80 °C oil bath. After 10 min, the flask was evacuated and back-filled with ethylene three times and left open to ethylene for the duration of the polymerization. After 2 h, the reaction mixture was cooled to room temperature and poured into 200 mL of stirred MeOH. After the mixture was stirred for 12 h, an oil had separated out on the bottom. The solvent was decanted and the residual oil dissolved in hexane. This solution was filtered through a pad of silica gel with additional hexane, and the solvent was removed in vacuo to yield polymer.

Procedure for 1-Hexene Oligomerization. A flame-dried Schlenk tube was charged with 1 mL of degassed 1-hexene and 0.5 mL of toluene under argon and heated to the desired temperature. A solution of catalyst (7.4 μmol) in toluene (0.5 mL) at the same temperature was added to the 1-hexene/toluene solution via cannula, and the reaction mixture was stirred for 3 h. The product was isolated by rotary evaporation and dried overnight on a vacuum line.

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Supporting Information Available: A table of polymerization data with **3b** at 40 °C in the presence of phosphine-scavenging cocatalysts and tables giving X-ray structure and crystallographic data for the sodium salt **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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