Organometallics **2001,** *20,* 3217−3219

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

Frederick A. Hicks and Maurice Brookhart*

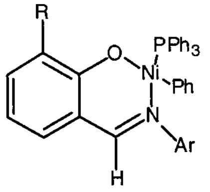
Department of Chemistry, University of North Carolina at Chapel Hill,
Chapel Hill, North Carolina 27599

Received March 16, 2001

Summary: The synthesis of a neutral nickel(II) complex of 2-(2,6-diisopropylanilino)tropone is described. The important attributes of this ligand include a hindered N-aryl ring, a five-membered-ring chelate, and an anionic N-donor. The complex has been characterized in the solid state by X-ray crystallography, and relevant features are discussed. The nickel complex is capable of polymerizing ethylene with a turnover frequency of up to 8.8×10^6 g of PE (mol of catalyst)$^{-1}$ h^{-1} and of producing polyethylenes with a wide range of branching numbers by changes in pressure and temperature. The catalyst shows an excellent tolerance for polar additives in ethylene polymerization experiments and is quite insensitive to added PPh_3.[1]

There is a growing interest in exploring late-transition-metal catalysts as alternatives to the ubiquitous early-transition-metal Ziegler−Natta type olefin polymerization catalysts.[1,2] The impetus behind this movement is the belief that the decreased electrophilicity of late transition metals will allow the synthesis of a wide array of ethylene/α-olefin copolymers with functionalized olefins presently unavailable with Ziegler−Natta type catalysts.[3] In line with this notion are recent reports of a new family of Ni- and Pd-based α-diimine catalysts which effect not only the rapid polymerization of ethylene and α-olefins to high molar mass materials[4,5] but also the first transition-metal-catalyzed copolymerization of ethylene and α-olefins with acrylate monomers.[6,7] The key to the behavior of these catalysts was found to be the use of sufficiently hindered aryl groups such as 2,6-$(C_6H_3)iPr_2$ on the α-diimine nitrogens to block the axial coordination sites and prevent rapid chain transfer.

In the hope of developing single-component catalysts which do not require the addition of cocatalysts, there has been a renewed effort toward the development of neutral nickel-based polymerization catalysts, which are less electrophilic than the cationic Ni and Pd systems. This decreased electrophilicity could also lead to catalysts which are better able to produce functionalized copolymers. While there is an extensive body of literature on neutral nickel catalysts for olefin oligomerization and polymerization, most notably the family of SHOP-type catalysts,[1,8] the recent report of aryl-substituted α-diimine cationic Ni and Pd catalysts has led to the synthesis of a new generation of neutral nickel catalysts which incorporate the element of a hindered N-aryl moiety. While Ni complexes which incorporate two N-aryl groups have been found to be relatively poor catalysts[9] and catalysts containing one N-aryl group and a phosphine are active for the formation of branched oligoethylenes,[10] a new class of complexes reported by DuPont[9] and the Grubbs group[11] based upon the salicylaldiminato ligand are moderately active ethylene polymerization catalysts in the presence of an activator. More recently, the Grubbs group has shown that by placing bulky groups *ortho* to the phenoxy group, **2** vs **1**, catalysts which require no added activator are produced which can polymerize ethylene with a turnover frequency (TOF) of 3.7×10^6 g of PE (mol of Ni)$^{-1}$ h^{-1} over a 6 h period.[12] Computational work by Ziegler and co-workers supports the proposal that the bulky *ortho* substituent is primarily responsible for the high levels of catalyst activity by promoting PPh_3 dissociation.[13] Additionally, these catalysts can effect the copolymerization of ethylene with CO, functionalized norbornenes, and functionalized α,ω-olefins; however, no reports of the incorporation of acrylates or other conjugated functionalized monomers have appeared yet,



1, R = H
2, R = 9-Anthracenyl

---

[1] Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

[2] Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

[3] Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.

[4] Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

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

[6] Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

[7] Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

[8] Vogt, D., Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996; pp 245−258.

[9] Johnson, L. K.; Bennett, A. M. A.; Ittel, S. D.; Wang, L.; Parthasarathy, A.; Hauptman, E.; Simpson, R. D.; Feldman, J.; Coughlin, E. B. WO 9830609, 1997.

[10] Rachita, M. J.; Huff, R. L.; Bennett, J. L.; Brookhart, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4627.

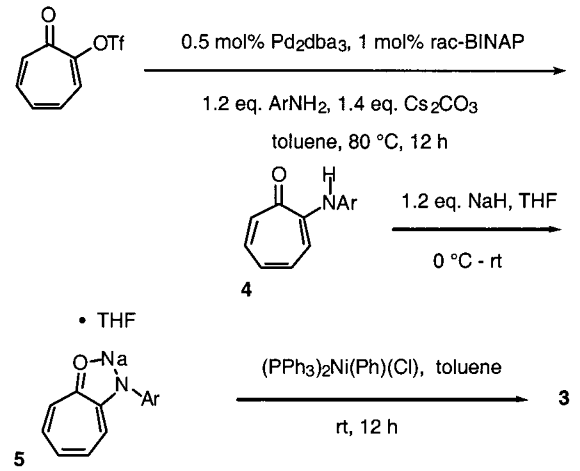
[11] Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149.

[12] Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.

[13] Chan, M. S. W.; Deng, L.; Ziegler, T. *Organometallics* **2000**, *19*, 2741.

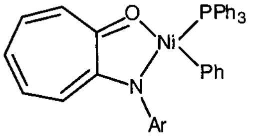
10.1021/om010211s CCC: $20.00
Publication on Web 06/28/2001

Scheme 1



prompting the continued search for new catalysts and a better understanding of the fundamental properties which contribute to catalyst activity.

On the basis of a report by Keim and co-workers that homologation of a five-membered chelate SHOP-type catalyst to a six-membered one leads to an order of magnitude loss of polymerization activity,[14] we sought to design a ligand which incorporated the key elements of the six-membered chelate salicylaldimine ligand but which would lead instead to a five-membered chelate. The 2-anilinotropone moiety was chosen for this purpose because it contained the desired anionic N,O chelate, a hindered N-aryl group, and complete conjugation between the N and O. Using this ligand we describe here the synthesis of a highly active neutral nickel ethylene polymerization catalyst, **3**, which does not require an activator.



3

Ar = $C_6H_3(iPr)_2$

We have recently reported the synthesis of 2-(2,6-diisopropylanilino)tropone (**4**) via the Pd-catalyzed amination of 2-triflatotropone with the requisite aniline.[15] The sodium salt of the ligand, **5**, was obtained via NaH deprotonation and isolated as its THF adduct. The combination of **5** with $(Ph_3P)_2Ni(Ph)(Cl)$ in toluene yields the corresponding Ni complex **3** (Scheme 1).

A single-crystal X-ray analysis confirmed the structure of **3**[16] (Figure 1) and its similarity to the structure of **2**.[11] The triphenylphosphine group is *trans* to the arylamine group, just as in the case of **2**. In fact, all of the Ni–X bond distances are almost identical in the two structures. One significant difference between the two structures is the substantial decrease in the O–Ni–N angle (82.6 vs 94.5°) due to the smaller chelate size of **3**. This decrease is compensated for in large part by a concomitant increase in the O–Ni–P angle (95.5 vs 87.5).

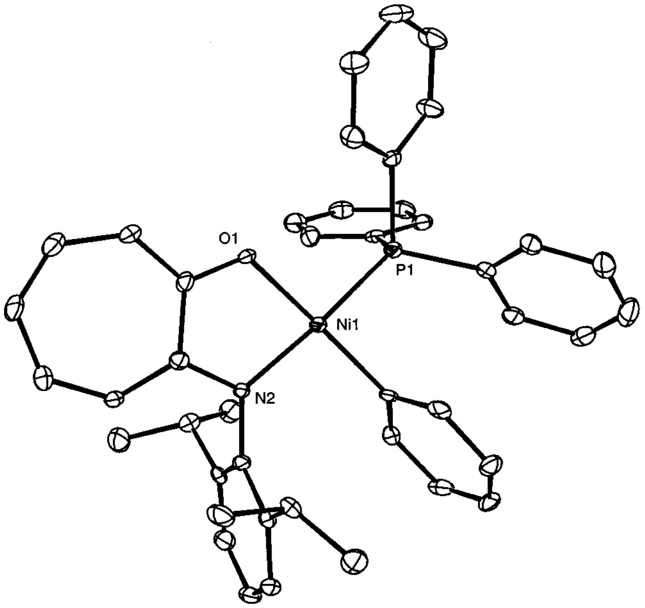


Figure 1. ORTEP view of **3** showing important atom labels. Selected interatomic distances (Å) and angles (deg): Ni(1)–O(1) = 1.906(4), Ni(1)–N(2) = 1.921(4), Ni(1)–P(1) = 2.1838(17), Ni(1)–C(aryl) = 1.911(6), O(1)–C = 1.295(7), N(2)–C = 1.345(8); O(1)–Ni(1)–N(2) = 82.61(18), O(1)–Ni(1)–P(1) = 95.54 (13).

In addition to the decrease in chelate size, another key difference between these two complexes arises from the potential for the negative charge to reside predominantly on the N atom of the anilinotropone ligand of **3** rather than primarily on the O atom as in **2**. No metal complexes of 2-aminotropones have been reported with which this structure could be compared, but comparisons with the single-crystal X-ray structure of the free ligand **4** are instructive (see the Supporting Information). The C–O and C–N bond lengths (1.252 and 1.3546 Å, respectively) of the free ligand are of intermediate value for single and double bonds, indicating some degree of delocalization on the order of an amide group. The ligand can be considered formally as a vinylogous amide. That these bond lengths do not change in a substantial fashion in **2** (C–O = 1.295 Å and C–N = 1.345 Å) indicates that the negative charge resides predominantly on the N atom, and the major contributing resonance structure is the one pictured here.

The change from a six-membered chelate ligand with neutral imine nitrogen to five-membered chelate ligand with an anionic amide nitrogen has a dramatic effect on the reactivity of **3** as compared to **1**. Under optimized conditions,[17] **3** can produce PE without the addition of a cocatalyst with a TOF of 8.8 × 10^6 g of PE (mol of catalyst)$^{-1}$ h^{-1} in a 10 min run.[18] When **1** was subjected

---

[14] Keim, W.; Schulz, R. P. *J. Mol. Catal.* **1994**, *92*, 21.

[15] Hicks, F. A.; Brookhart, M. *Org. Lett.* **2000**, *2*, 219.

[16] Crystal data for **3**: monoclinic, $P2_1/c$, $a = 11.4191(5)$ Å, $b = 15.3128(7)$ Å, $c = 20.2682(10)$ Å, $\beta = 100.509(1)°$, $V = 3484.6(3)$ Å^3, $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares procedures: R1 = 0.066 and R_w = 0.086 for 4550 reflections.

[17] The optimized conditions involve 5.3 μmol of catalyst in 200 mL of toluene under 200 psig of ethylene at 80 °C.

[18] The possibility of mass transfer limited TOF's was raised by one reviewer. Experiments run under identical conditions with 3.0 and 7.6 μmol of **3** produced essentially identical TOF's, indicating mass transfer is not an issue with this system.

Table 1. Ethylene Polymerization Results for 3[a]

entry	temp (°C)	press (psig)	10^{-6} TOF[b]	yield (g)	M_n	PDI	branches per 1000 C[c]
1	40	400	0.23	1.20	204 000	2.81	8
2	60	400	0.89	6.78	292 000	1.97	27
3	80	400	1.50	11.41	119 000	1.75	49
4	100	400	0.53	4.04	60 700	1.85	67
5	80	14	0.027	.145	6 700	2.03	113
6	80	50	0.76	4.0	50 000	1.68	90
7	80	100	1.20	6.3	62 500	1.89	76
8	80	200	1.74	9.2	89 600	1.84	61
9	80	400	1.34	7.1	104 000	1.95	45
10	80	600	0.49	2.6	120 000	1.97	41

[a] Entries 1−4 were conducted with 7.6 μmol of **3**, while entries 5−10 were conducted with 5.2 μmol of **3**. All polymerizations were run in 200 mL of toluene for 1 h. The reaction temperature was controlled within ±2 °C. [b] In units of g of PE (mol of cat)$^{-1}$ h^{-1}. [c] Branching numbers were determined by ^{1}H NMR.[4,5]

to the same reaction conditions, it was found to be more than an order of magnitude less reactive, with a TOF of 0.68×10^6 g of PE (mol of catalyst)$^{-1}$ h^{-1}. Additionally, **3** produced PE with a substantially higher M_n when compared with **1** (89 600 vs 2800).[19] Both of these trends may indicate PPh_3 dissociation is significantly more difficult for the parent salicylaldiminato catalyst. Even when **3** is compared to the sterically modified Grubbs catalyst **2**, it displays a higher TOF than the 3.7×10^6 g of PE (mol of catalyst)$^{-1}$ h^{-1} reported.[20] One limitation of **3** as compared to **2** is its short lifetime, demonstrated by comparing the above-mentioned TOF with the value in Table 1 (entry 8) for a 1 h run.

In a series of ethylene polymerization experiments, **3** was shown to produce PE of widely varying properties with changes in temperature and pressure.[21] As can be seen in Table 1 (entries 1−4) PE with branching numbers increasing from 8 to 67 can be obtained by increasing temperatures from 40 to 100 °C. At 40 °C there appears to be an initiation problem, as evidenced by the anomalously low M_n and high PDI with a low M_w tail (entry 1). Catalyst performance is optimal at 80 °C but decreases at higher temperatures.

Ethylene pressure has also been shown to have dramatic effects on the resultant PE. Increasing the pressure from 14 to 600 psig at 80 °C (entries 5−10) causes a decrease in the branching number from 113 to 41 branches per 1000 C. The trends observed for variation of branching number as a function of both temperature and pressure are the same as those previously reported for the cationic Ni diimine systems.[4,5] While M_n is found to increase continuously with increasing pressure, the TON (total number of turnovers) displays a bell curve type dependence on pressure, with the highest productivity coming at 200 psig.[22]

In experiments designed to test the compatability of this catalyst toward functional groups, **3** showed excellent tolerance to the addition of as much as ca. 15 000 equiv (20 mL) of typical additives (see the Supporting Information for experimental details). Reactions run in either neat THF or in the presence of added ethyl acetate actually had higher TOF's than did reaction in toluene alone. Use of H_2O or NEt_3 as an additive lead to only a 3.5- and 4-fold decrease in activity, respectively. The use of EtOH proved more problematic, leading to a 20-fold decrease in TOF. These numbers compare favorably with those obtained with catalyst **2**.[23]

Another intriguing difference in the reactivity of **3** as compared to that of the salicylaldiminato catalysts is the effect of added PPh_3 on polymerization. Addition of 1 equiv of PPh_3 to a typical ethylene polymerization mixture employing **2** decreased the activity by half, and several equivalents totally suppressed polymerization.[12] In contrast, addition of 5 equiv of PPh_3 had essentially no effect on the productivity of catalyst **3** in 10 and 30 min runs. While the reason for this discrepancy is unclear, it serves to highlight the differences in reactivity between the two families of neutral nickel catalysts.

In conclusion, the highly active neutral nickel olefin polymerization catalyst **3**, derived from a 2-anilinotropone ligand, has been introduced. The initial ethylene polymerization activity and M_n are superior to the sterically analogous salicylaldiminato catalyst **1** and comparable to the best catalysts in that series, such as **2**. With respect to neutral nickel systems, catalyst **3** has been shown to produce polyethylenes with an unprecedented range of branching numbers, and hence physical properties, by simple changes in reaction temperature and pressure. It has proven to be exceptionally tolerant of polar additives and surprisingly insensitive to added PPh_3. Future work will focus on mechanistic studies and modification of the ligand framework to produce catalysts with enhanced activities and lifetimes.

Acknowledgment. This work was supported by DuPont and the NSF (Grant No. CHE-9710380). We thank Jason Jenkins for his help in preparing this paper.

Supporting Information Available: Text and tables giving details of the synthesis and of the characterization and crystallographic data for **3** and **5**, experimental procedures for polymerizations, and data for the effects of additives on polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010211S

---

(19) M_n for the polyethylene obtained from catalyst **1** was determined by ^{1}H NMR end group analysis.

(20) The optimized conditions for **2** involve reaction temperatures between 45 and 50 °C and 100 psig of ethylene.[12]

(21) All polymerizations were run with low catalyst loadings to prevent the occurrence of rapid and vigorous exotherms.

(22) Initial experiments employing exceptionally high purity ethylene give increased TON's at 400 psig and above, suggesting that impurities in the ethylene may be contributing to the decrease in activity at higher pressures. The identity of possible interfering impurities is not clear.

(23) Results for the addition of ca. 1500 equiv of the same types of additives to catalyst **2** were reported in ref 12. The addition of ethers was shown to produce a 2−3-fold decrease in activity, ethyl acetate a 12-fold decrease, H_2O a 20-fold decrease, NEt_3 a 100-fold decrease, and EtOH a 50-fold decrease.