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Titanium (IV) and Nickel (II) Catalysts Based on Anilinetropone Ligands

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/46096>

1. Introduction

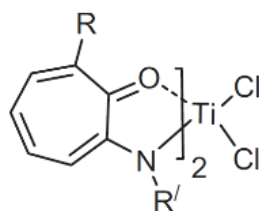
Historically, the development of highly active olefin polymerization catalysts has been a trigger for creating new polymers which impact on our daily lives in countless beneficial ways [1-5]. A recent instance is the development of group 4 metallocene catalysts that exhibit very high ethylene polymerization activities [2,3]. Based on the highly active group 4 metallocene catalysts, high performance linear low-density polyethylene (LLDPE), isotactic poly-(propylene) (iPP) and syndiotactic polystyrene (sPS) etc., have been developed [6]. Therefore, much effort has been directed towards the development of highly active catalysts, following the group 4 metallocene catalysts. In consequence, quite a few highly active catalysts based on both early and late transition metal complexes have been developed [7-14]. There are, however, only a few examples of titanium complexes displaying high ethylene polymerization activities [15-19], though titanium metal is the major player in highly active heterogeneous Ziegler-Natta catalysts. Accordingly, further researches have been conducted on titanium catalysts with the intention of developing the highly active titanium catalysts and applying them to the polymerization of ethylene.

As a result of ligand-oriented catalyst design research, Sandaroos and coworkers [19-21] described the catalytic performance of new titanium complexes 1-9 containing aminotropone chelate ligands for ethylene polymerization (Scheme 1). The following subsections detail the results observed in these works.

2. Search for acquiring the fundamentally active ligand

Among the typical catalyst components, ligands play a predominate role in the polymerization process. During electron exchange between metal and monomer, ligands help the metal to balance its electron density with receiving electrons from the coordinated

ethylene through the metal and releasing electrons whenever required to facilitate the ethylene insertion process (Figure 1). Accordingly, to obtain a highly active catalyst, the existence of ligands with a notable balance between their electron donating and withdrawing, evidenced by calculation of energy gap between the HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) of them, is a predominate requirement [22]. For comparison, the energy gap between the HOMO and LUMO of three well-known ligands, namely phenoxy-imine [15,23-29], pyrrolide-imine [15,27-29], indolide-imine [30] and the new aminotropone chelate ligand [19] was studied using density-functional theory (DFT). Because of the reasonable energy gap between the HOMO and LUMO of aminotropone (2.6 eV), it was theoretically offered as a fundamentally active ligand (Scheme 2).



Catalyst	R'	R	Reference(s)
1	phenyl	H	19-21
2	2,6-dimethylphenyl	H	19
3	cyclohexyl	H	19
4	4-(t-Buyl)cyclohexyl	H	19
5	cyclooctyl	H	19
6	Ethyl	H	19
7	isopropyl	H	19
8	phenyl	methyl	19,20
9	phenyl	t-Butyl	19,20

Scheme 1. Titanium (IV) complexes based on anilinetropone ligands 1–9.

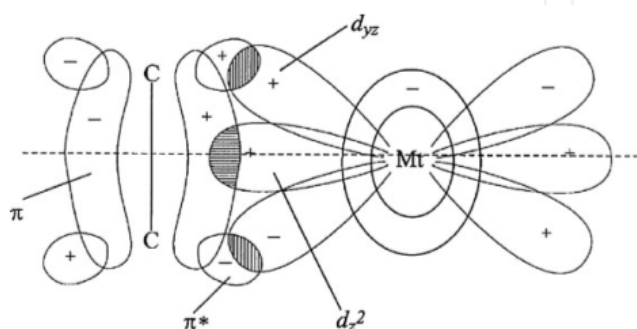
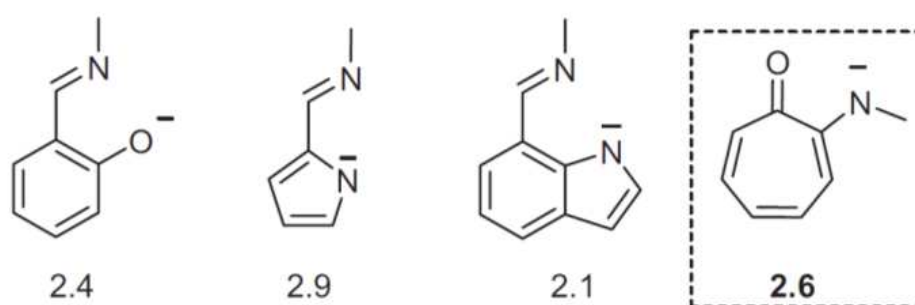


Figure 1. Presentation of the olefin coordination on the transition metal [19].



Scheme 2. Energy gap (eV) between HOMO and LUMO of aminotropone compared to those related to phenoxyimine, pyrrolide-imine and indolideimine [16,19].

3. Substituent effects

This section concentrates on the steric features of bis(aminotropone)Ti complexes compared with those of bis(phenoxyimine) Ti complexes (Ti-FI catalysts). Unlike Ti-FI catalysts, which require sterically demanding substituents in ortho position to the phenoxy oxygen atom in order to exhibit high ethylene polymerization activity [23-26], the activity of bis(pyrrolide-imine) Ti catalysts (Ti-PI) decreases with more congestion adjacent to the anionic N of the PI ligand because there is not enough space for monomer insertion [16]. The steric bulk in Ti-FI catalysts is thought to afford effective ion separation between the cationic active species and an anionic co-catalyst, resulting in enhancement of the catalytic activity. Accordingly, bis(aminotropone) Ti complexes 1, 8 and 9 with a series of substituents (H, methyl and *t*-Butyl) adjacent to the carbonyl were prepared and examined as ethylene polymerization catalysts (Figure 2; Table 1, entries 1, 37 and 40) [19]. The polymerization results provided information on the potential of bis(aminotropone) Ti complexes for ethylene polymerization, and additional information about the effect of the substituent adjacent to the carbonyl on catalytic performance.

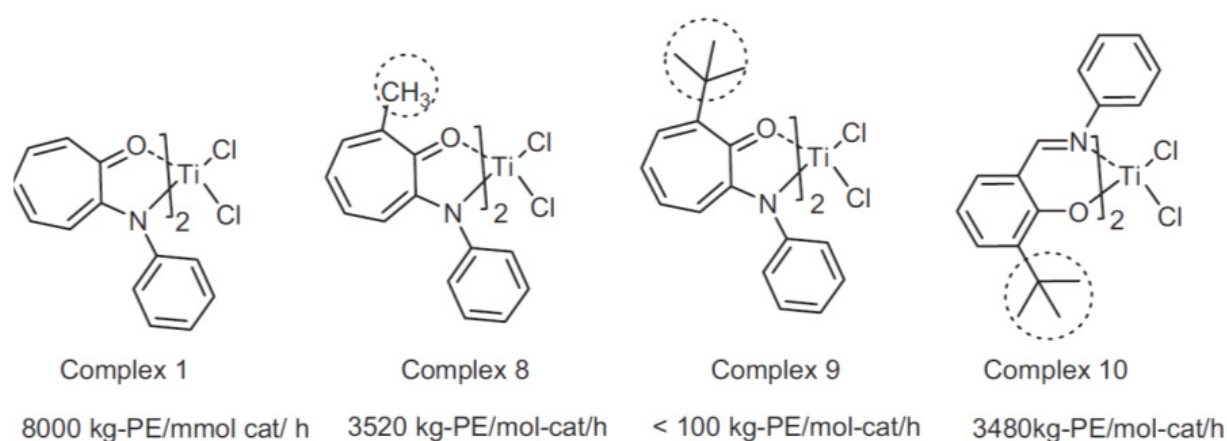


Figure 2. Investigation of substituent effects in bis(aminotropone) Ti complexes in comparison with a typical Ti-FI catalyst 10 [19].

The bis(aminotropone) Ti complex 9, which possesses the *t*-Butyl group, proved to be a poor catalyst for ethylene polymerization under the conditions employed (activity < 100 Kg PE mol cat⁻¹ h⁻¹). Instead, the bis(aminotropone)Ti complex 1 with an H atom adjacent to the

carbonyl formed polyethylene (PE) with M_w 98000 and a high activity of 8000 Kg PE mol cat⁻¹ h⁻¹. Additionally, catalyst 8, which possesses the methyl group, exhibited almost moderate activity (activity 3520 kg PE mol cat⁻¹ h⁻¹). These facts show that, for bis(aminotropone) Ti complexes 8 and 9, the methyl and t-Butyl groups in close proximity to the carbonyl evidently provide unfavorable steric hindrance to ethylene polymerization. This is in sharp contrast to Ti-FI catalysts, which require steric congestion near the polymerization center in order to display high activity. The activity obtained with complex 1 (8000 Kg PE mol cat⁻¹ h⁻¹) is extremely high for a Ti complex with no cyclopentadienyl (Cp) or PI ligand(s) [16,23-26]. In fact, the activity exceeds that displayed by Ti-FI catalyst 10 under analogous conditions (3480 Kg PE mol cat⁻¹ h⁻¹) (Figure 2) [22]. Since the substituent on the amine-N is situated near the active site, the bis(aminotropone)Ti complexes 1-7, containing three types of substituents, aromatic ring (catalyst 1-2), aliphatic ring (catalyst 3-5) and alkyl groups (catalyst 6-7) on amine-N were prepared and evaluated, with methylaluminoxane (MAO) activation, for the polymerization of ethylene to find a correlation between the N-aryl substituent and ethylene polymerization behavior. The polymerization results are presented in Table 1 which also includes the results for Ti-FI catalyst 10, Cp₂TiCl₂ and Cp₂ZrCl₂ as references (compare entries 1, 7, 12, 17, 35-36 and 40-43). The basic trend observed is that an increase in the steric bulk of the substituent in each of the three types of catalyst enhances catalytic activity. A reasonable hypothesis is that the sterically more encumbered substituent on the amine-N part of bis(aminotropone) Ti complexes induces more effective ion separation between the cationic active species and an anionic cocatalyst. In addition, it gives better steric protection to the anionic N from Lewis acidic compounds present in a polymerization medium, leading to increased catalytic activity.

Comparison of catalysts 1-2 with 3-5 revealed dramatically increased activities for 3-5, which is thought to be due to a good match between electronic and steric effects of them. Therefore, it can be concluded that the catalytic activity is influenced by both electronic and steric effects. In other words, a good integration between the steric and electronic properties of the catalyst is needed to reach the highest activities. It should be noted that catalyst 5, which includes a cyclooctyl group on the amine-N, gives an activity of 27200 Kg PE mol cat⁻¹ h⁻¹, which compares favorably with Cp₂TiCl₂ or Cp₂ZrCl₂ combined with MAO. Additionally, in each of catalysts presented in Table 1, sterically more encumbered substituents on the amine-Ns generally afford higher-molecular-weight PEs (compare entries 1, 7, 12, 17 and 35-36). The steric congestion provided by the substituent, which probably reduces the rate of chain transfer more significantly than that of chain propagation, is responsible for the enhancement of the product molecular weight [30].

4. Effects of polymerization conditions

Ethylene polymerization behavior using catalysts 3, 4 and 5 were studied under different reaction times (Table 1, entries 20-34) and temperatures (entries 5-19). The highest activity of catalyst 5 was obtained at 10 °C (31200 Kg PE mol cat⁻¹ h⁻¹). However, the highest activity of catalysts 4 and 3 occurred at about 35 °C (24500 and 18200 Kg PE mol cat⁻¹ h⁻¹, respectively). The reduction in catalyst activity in the polymerization performed at the lower and upper

temperature than the optimum value could be attributed to a low propagation rate and catalyst irreversible deactivation respectively. Ethylene polymerization carried out at different reaction times showed catalyst 5 had a shorter lifetime, but catalysts 3 and 4 showed more stable activities during the polymerization.

Additionally, the activity of the catalysts 1 and 8 and M_w values of resultant polymers increased with increasing the monomer pressure (entries 1-3 and 37-39). This behavior is mainly due to the high concentration of the monomer close to the catalyst active centers.

As could be predicted, as molar ratio of $[Al]/[Ti]$ increased, activity of catalysts increased, but M_w values of resultant polymers decreased [19-21].

The large amount of hydrogen concentration could slightly increase the activity of the catalyst 1, 8 and 9 (Figure 3) [20]. A reasonable explanation for this effect might be increase of homogeneity of polymerization system and return of catalytically less reactive species, such as those resulting from 2,1-insertions, to the catalytic cycle through their fast hydrogenation [20].

Moreover, as it can be seen in Figure 4 [20], polydispersity and M_n of the polymer obtained using the catalyst 1 increases with time.

5. DFT studies of catalyst

Since a bis(aminotropone) Ti catalyst contains a pair of non-symmetric bidentate ligands, it potentially displays five isomers (A–E) arising from the coordination modes of the two ligands in an octahedral geometry (Scheme 3) [19]. DFT studies suggested that bis(aminotropone)Ti catalyst 1 assumed isomer A, with a trans-carbonyl-Os, cis-amine-Ns and cis-ClIs disposition. Additionally, DFT calculations were performed on a methyl cationic complex (an initial active species generated from bis(aminotropone) Ti catalyst 1 with MAO) in the presence of ethylene, to obtain information about the structure of the catalytically active species (Figure 5) [19]. The calculations revealed that an ethylene-coordinated cationic species assumed an octahedral geometry with a trans-carbonyl-Os, cis-amine-Ns and cis-Me/coordinated ethylene disposition, which fulfills the pivotal requirement for a high efficient catalyst, i.e., a growing polymer chain and a coordinated-ethylene group in the cis-position. An inspection of the calculated structure indicated that the phenyl group on the amine-N was located in close proximity to the active site, suggesting the substituent on the amine-N is the strategic substituent vis-a-vis catalyst design.

As discussed, unlike catalyst 1, catalysts 8 and 9, with the methyl and t-Butyl groups adjacent to the carbonyl-Os, display very low productivity in the polymerization of ethylene. The calculated structure of methyl cationic complexes originating from 1 and 9 is displayed in Figure 6 [19]. The t-Butyl group of complex 9 seems to provide steric congestion near the polymerization center, which diminishes the rate of chain propagation. This is probably because it obstructs ethylene from gaining access to the active site and subsequent insertion into the Ti-carbon bond. On the other hand, DFT studies show that the active species derived from bis(aminotropone) Ti catalyst 1 possesses higher electrophilicity

Entry	Cat.	Cat. (μ mol)	MAO (mmol)	Time (min)	T ($^{\circ}$ C)	P (bar)	TOF ^a	M _v ($\times 10^3$) ^b	Refs.
1	1	1	1.25	15	25	1	8000	260	19-21
2	1	1	1.25	15	25	3	9100	450	20
3	1	1	1.25	15	25	5	9800	630	20
4	2	1	1.25	15	25	1	9650	530	19
5	3	1	1.25	15	0	1	10450	2600	19
6	3	1	1.25	15	10	1	11800	2580	19
7	3	1	1.25	15	25	1	15200	2300	19
8	3	1	1.25	15	35	1	18200	1860	19
9	3	1	1.25	15	45	1	18000	1740	19
10	4	1	1.25	15	0	1	14650	3500	19
11	4	1	1.25	15	10	1	18000	3120	19
12	4	1	1.25	15	25	1	22600	2950	19
13	4	1	1.25	15	35	1	24500	2560	19
14	4	1	1.25	15	45	1	14650	2240	19
15	5	1	1.25	15	0	1	26400	5620	19
16	5	1	1.25	15	10	1	31260	4950	19
17	5	1	1.25	15	25	1	27200	3540	19
18	5	1	1.25	15	35	1	21100	3140	19
19	5	1	1.25	15	45	1	14560	2800	19
20	3	1	1.25	5	25	1	5800	-	19
21	3	1	1.25	10	25	1	10400	-	19
22	3	1	1.25	15	25	1	15200	2300	19
23	3	1	1.25	25	25	1	22500	-	19
24	3	1	1.25	40	25	1	19500	-	19
25	4	1	1.25	5	25	1	7200	-	19
26	4	1	1.25	10	25	1	13600	-	19
27	4	1	1.25	15	25	1	22600	2950	19
28	4	1	1.25	25	25	1	26500	-	19
29	4	1	1.25	40	25	1	17300	-	19
30	5	1	1.25	5	25	1	8200	-	19
31	5	1	1.25	10	25	1	15240	-	19
32	5	1	1.25	15	25	1	27200	3540	19
33	5	1	1.25	25	25	1	21550	-	19
34	5	1	1.25	40	25	1	10500	-	19
35	6	1	1.25	15	25	1	410	285	19
36	7	1	1.25	15	25	1	680	340	19
37	8	1	1.25	15	25	1	3520	271	19,20
38	8	1	1.25	15	25	3	3750	320	20
39	8	1	1.25	15	25	5	4500	390	20
40	9	1	1.25	15	25	1	<100	352	19,20
41	10	1	1.25	15	25	1	3480	368	18
42	Cp ₂ TiCl ₂	1	1.25	15	25	1	16700	1253	18
43	Cp ₂ ZrCl ₂	1	1.25	15	25	1	20000	1000	18

kg PE mol cat⁻¹ h⁻¹, ^b) Calculated from intrinsic viscosity

Table 1. Ethylene polymerization results with catalysts 1–9, Ti–FI catalyst 10, Cp₂TiCl₂ and Cp₂ZrCl₂

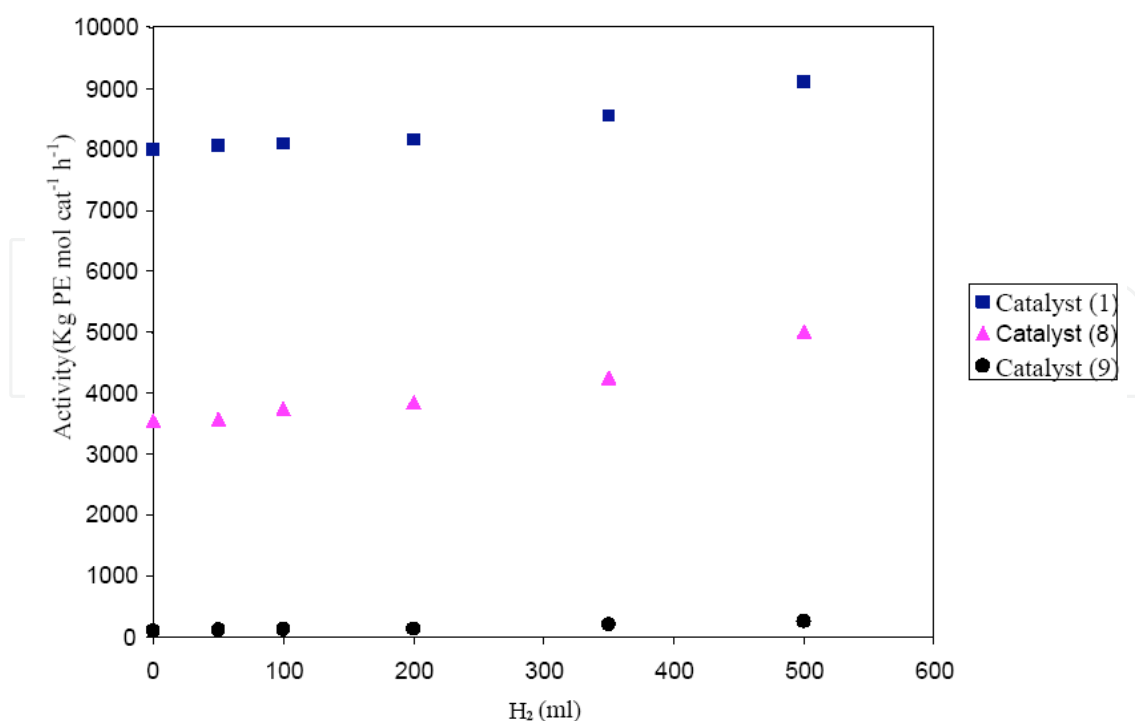


Figure 3. Influence of H₂ concentrations on the catalyst activity. Polymerization conditions: [Al]/[Ti] = 1250, polymerization time = 15 min, temperature = 25 °C, monomer pressure = 1 bar, [Ti] = 1 mmol, toluene = 250 mL [20].

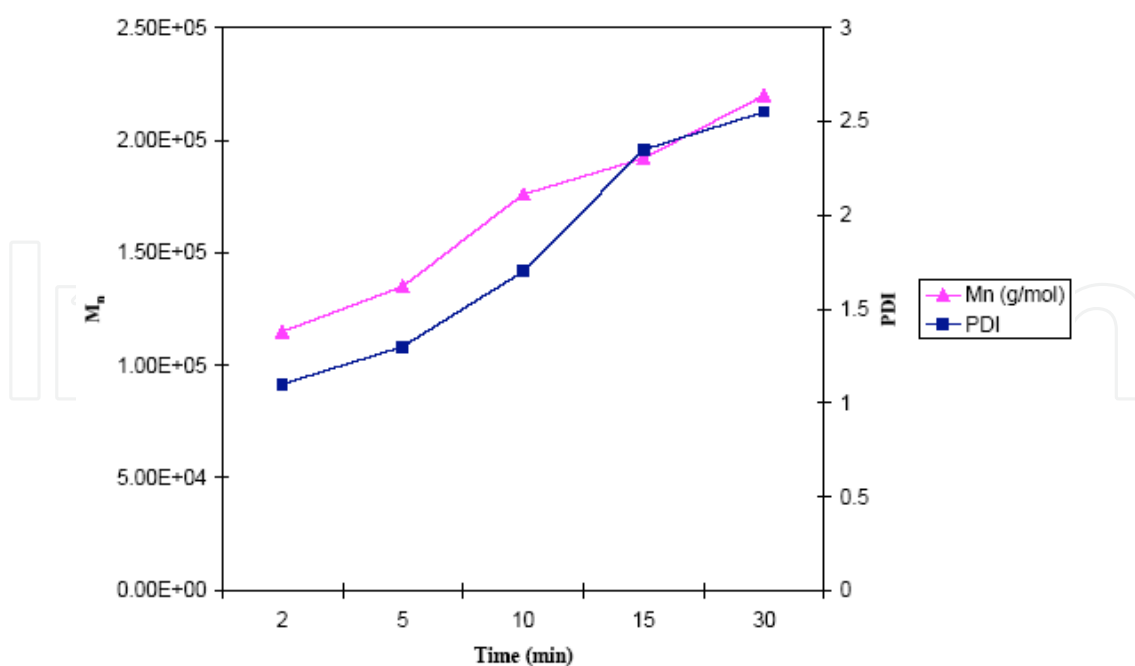
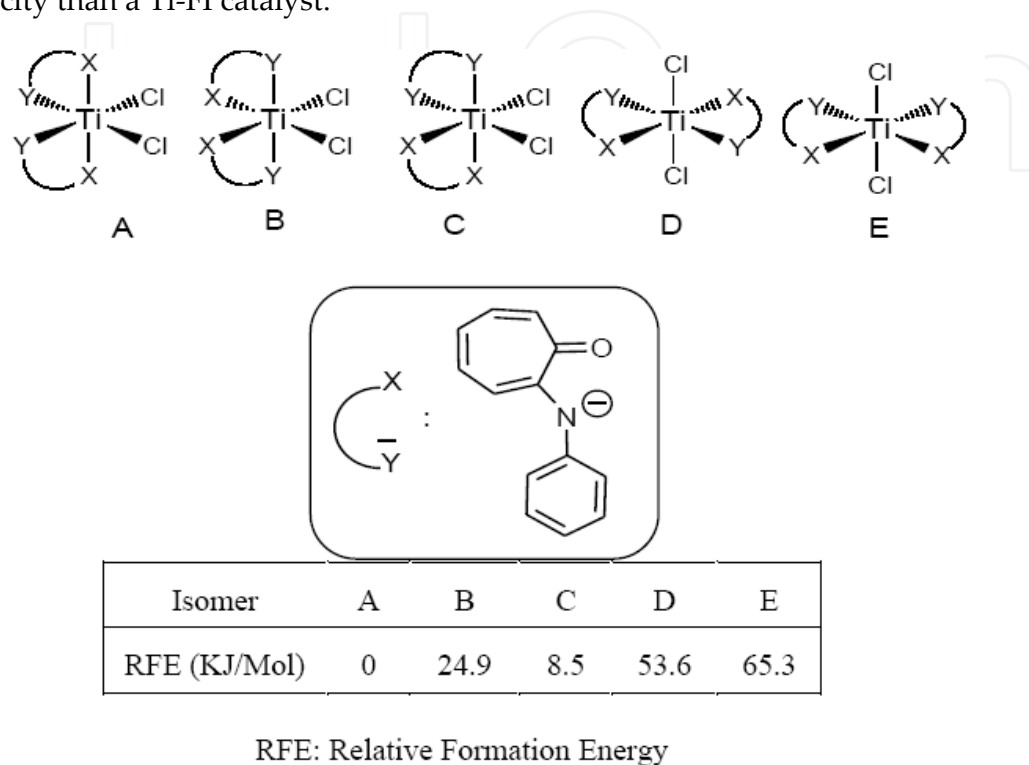


Figure 4. PDI and Mn versus time for the polymer obtained by catalyst 1. Polymerization conditions: [Al]/[Ti] = 1250, temperature = 25 °C, monomer pressure = 1 bar, [Ti] = 1 μmol, toluene = 250 mL. M_n and PDI were obtained from GPC [20].

at the Ti center compared with that of Ti-FI catalyst 10 (Mulliken charge of the Ti in atomic unit, catalyst 1=2.212 [19], catalyst 10=2.005 [16]). Considering that the active species derived from a typical metallocene (Cp_2TiCl_2) has a Mulliken charge (Ti) of 1.308 [16], bis(aminotropone) Ti catalyst 1 exhibits particularly high electrophilicity. Therefore, a bis(aminotropone) Ti catalyst generates a catalytically active species that has higher electrophilicity than a Ti-FI catalyst.



Scheme 3. The relative formation energies of the isomers [19].

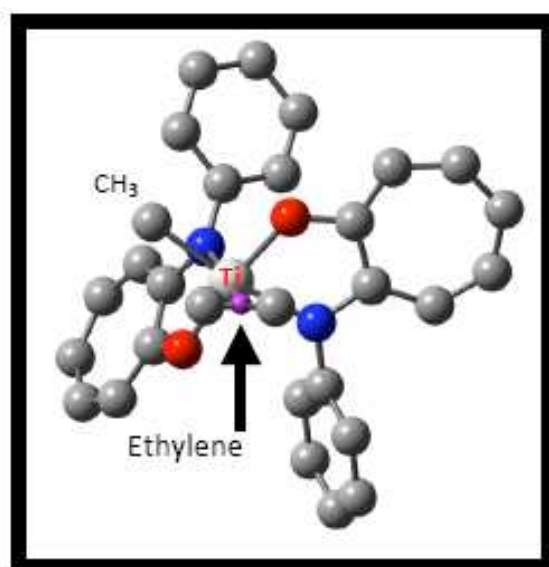


Figure 5. Calculated structure of ethylene-coordinated cationic species derived from bis(aminotropone) Ti catalyst 1. The hydrogen atoms are omitted for clarity [19].

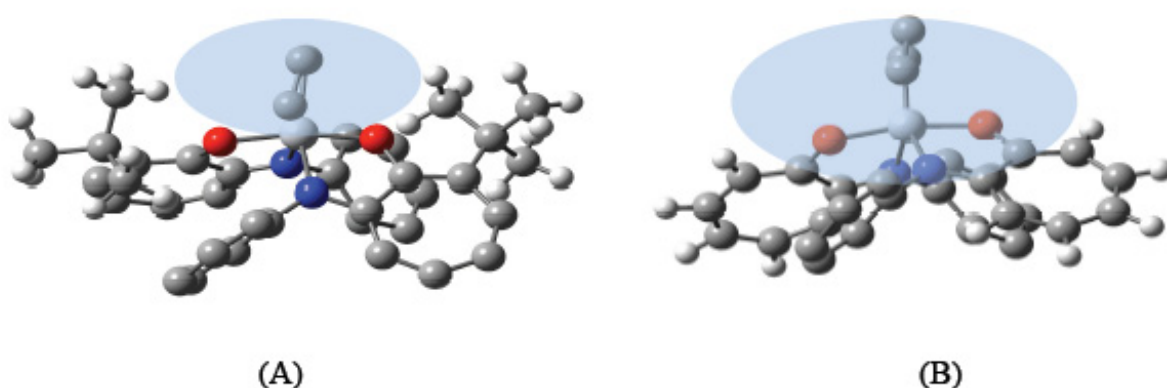


Figure 6. Calculated structures of cationic active species generated from catalyst 1 (A) and catalyst 9 (B). Some of the hydrogen atoms are omitted for clarity [19].

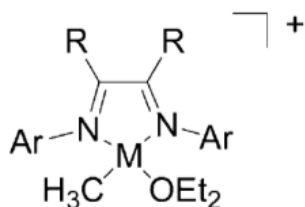
6. Nickel (II) catalysts based on anilinetropone ligands

6.1. Introduction

Olefin polymerization catalysts based on early-metal metallocene complexes were introduced nearly two decades ago and are seeing increasing commercial utilization [31-33]. 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 [31-33]. 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 [34-37]. Late-metal catalysts complement early-metal catalysts in several ways. (1) Polymers exhibiting quite different microstructures are frequently obtained [36,38-41]. 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 information of branched polymers from ethylene and “chain-straightened” polymers from α -olefins [36,38]. (2) Certain monomers such as trans-2-butene, which cannot be polymerized by early-metal systems, can be successfully polymerized with late-metal systems [42]. (3) Many late-metal catalysts are compatible with protic solvents and nucleophilic impurities. Water compatibility has led to successful emulsion polymerization of ethylene [43-46]. (4) Expanded functional group tolerance has permitted the copolymerization of alkyl acrylates (polar monomers) with ethylene and α -olefins (non polar monomers) [47-50].

Much of efforts has focused on cationic systems of α -diimine ligands (Figure 7) as well as catalysts incorporating closely related neutral ligands [38,40-42,48,49,51-53]. The α -diimine

Ni complexes are 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 [47,54].



Catalyst 11; M = Ni and Pd

Figure 7. The α -diimine complexes [38,40-42,48,49,51-53].

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 examples of neutral Ni catalysts based on SHOP-type (Shell Higher Olefin Process) ligands have been reported, although productivities and molecular weights are often low [45,50,55,56]. Neutral Ni catalysts modeled after α -diimine complexes, containing bulky ortho-disubstituted arylimine functionality, have been reported. Catalysts based on salicylaldimines (Figure 8), have been described by both the DuPont [57] and the Grubbs groups [58,59]. The most active systems contain either electron-withdrawing nitro substituents in the aromatic ring [57] or bulky substituents at C-3, with a 9-anthracenyl group being most effective [58,59]. In the latter case, activities of 1.3×10^5 kg PE mol Ni $^{-1}$ h $^{-1}$ and lifetimes in excess of 6 h have been observed at 45 – 50°C [58].

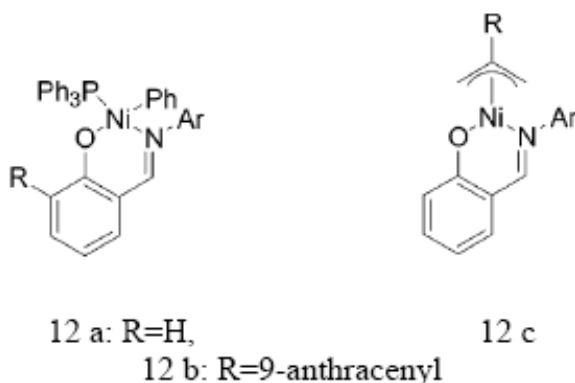


Figure 8. The salicylaldimines catalysts [57-59].

Brookhart [60,61] designed a ligand which incorporated the key elements of the six-membered chelate salicylaldimine ligand but which would lead instead to a five-member chelate. He chose for this purpose the 2-anilino tropone moiety because it contained the desired anionic N,O chelate, a hindered N-aryl group, and complete conjugation between

the N and O. Several variations can be introduced by using hindered or electron-poor N-aryl group and modified tropone skeleton. This family of ligands were synthesized using the palladium catalyzed cross-coupling of aniline with 2-triflatotropone [60-62]. The corresponding highly neutral nickel catalyst is almost high active in ethylene polymerization and it does not require an activator (Figure 9).



Figure 9. Anilinetropone ligands (a) and Ni (II) catalysts based on Anilinetropone (b) [60,61].

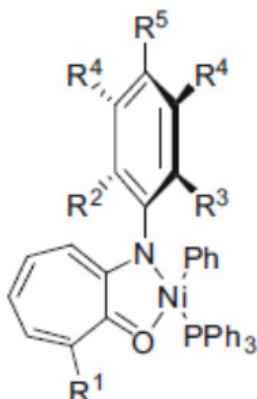
To determine the effects of varying the ortho-aryl substituents on ethylene polymerization, in an effort a series of anilinetropone ligands and corresponding nickel complexes was synthesized (Scheme 4). Among these catalysts, they incorporating alkyl substituents at the 2- and 6-positions of the N-aryl ring generated high-molecular weight polyethylenes with monomodal molecular weight distributions of ca. 2 (or less at low temperatures).

Under optimized conditions (Table 2), catalyst 14 bearing isopropyl substituents at the 2- and 6-positions of the N-aryl ring can produce PE, without the addition of a cocatalyst, with a TOF of 8.8×10^3 kg of PE mol Ni⁻¹ h⁻¹ in a 10 min run. Additionally, 14 produced PE with a substantially higher M_n when compared with the salicylaldimino type bearing the anthryl substituent in the *ortho* position (89.6 vs. 54 kg mol⁻¹). Nevertheless 14 showed a short lifetime when compared to 2-salicylaldimino type bearing the anthryl substituent [62].

As can be seen in Table 3, 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 steadily increases from 40 to 100 °C (8-67 branches per 1000 carbon atoms). 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 TOF is at a maximum at 80 °C. Ethylene pressure has also been shown to have dramatic effects on the resultant PE. Increasing the pressure from 1.01 to 41.34 bar at 80 °C caused a decrease in the branching number from 113 to 41 branches per 1,000 C [62].

Unlike salicylaldimine catalysts whose activates dramatically increase [58,63], no significant changes take placed in TOF, M_n , PDI, or branching numbers for catalyst 14 in the presence of added PPh₃. The observation that scavengers do not increase turnover numbers suggests that under the reaction conditions PPh₃ is essentially fully dissociated from the active nickel

catalyst. Additionally, addition of polar solvent to the polymerization media decreased catalytic activity, but didn't change branching numbers [62].



Catalyst	R ¹ -R ⁵
13	R ¹ = R ⁴ = R ⁵ = H; R ² = R ³ = Me
14	R ¹ = R ⁴ = R ⁵ = H; R ² = R ³ = <i>i</i> Pr
15	R ¹ = R ⁴ = R ⁵ = H; R ² = R ³ = <i>t</i> Bu
16	R ¹ = R ⁴ = R ⁵ = H; R ² = Me; R ³ = <i>t</i> Bu
17	R ¹ = R ⁴ = R ⁵ = H; R ² = R ³ = Ph
18	R ¹ = R ⁴ = R ⁵ = H; R ² = R ³ = Cl
19	R ¹ = R ⁴ = R ⁵ = H; R ² = R ³ = Br
20	R ¹ = H; R ² = R ³ = R ⁴ = R ⁵ = F
21	R ¹ = R ² = R ³ = R ⁵ = H; R ⁴ = CF ₃
22	R ¹ = R ³ = R ⁴ = R ⁵ = H; R ² = Me
23	R ¹ = R ⁴ = R ⁵ = H; R ² = Me; R ³ = CF ₃
24	R ¹ = R ⁴ = R ⁵ = H; R ² = R ³ = F
25	R ¹ = Ph; R ² = R ³ = <i>i</i> Pr; R ⁴ = R ⁵ = H
26	R ¹ = 1-naph; R ² = R ³ = <i>i</i> Pr; R ⁴ = R ⁵ = H

Scheme 4. Ni (II) catalysts based on anilinetropone [62].

Replacement of the standard 2,6-diisopropyl substituents on the aryl group with 2,6-dimethyl (13), 2,6-dichloro (18), 2,6-dibromo (19), and 2-methyl-6-trifluoromethyl(23) substituents had little effect on productivity. A slight increase in TOF was observed for the 2,6-diphenyl-substituted catalyst (17). Significant reduction in TOF was observed for the 2-methyl-6-*t*-Butyl (16), 2-methyl-(22), 2-*t*-Butyl-(15), and 2,3,4,5,6-pentafluoro-substituted (20) catalysts. Molecular weights generally increase with increasing steric bulk of the ortho substituents (Table 2) [62].

Substitution of the 2-(2,6-diisopropylanilino)tropone ligand with either phenyl (25) or naphthyl (26) groups resulted in a small increase in productivities and lifetimes at 80 °C and 13.78 bar. However, at 40 °C these catalysts exhibited much longer lifetimes

($t_{1/2}$ 1 h) and higher total turnover numbers could be achieved relative to 80 °C polymerizations [62].

Catalyst	P (bar)	T (°C)	TOF ^b	M _w	M _w /M _n	Br/1000 C
13	13.78	80	5424	73.1	1.7	61
14	13.78	80	8800	165.6	1.8	61
16	13.78	80	1014	230.0	2.0	73
17	13.78	80	10038	171.0	1.8	53
18	13.78	80	3924	20.0	2.0	53
19	13.78	80	4152	41.8	1.9	56
20	13.78	80	1152	4.8	3.0	49
21	13.78	80	936	112.8	2.4	57
23	13.78	80	6924	167.2	1.9	59
25	13.78	80	2338	184.8	2.1	63
26	13.78	80	2461	151.2	2.7	62

^a Polymerization time = 10 min , Catalyst = 5.2 μ mol; ^b Kg PE mol cat⁻¹ h⁻¹

Table 2. Selected ethylene polymerization data of the Ni (II) catalysts based on anilinetropone ^a [62]

Molecular weights of the polyethylenes increased with pressure, which suggests that chain transfer at least in part occurs through classical β -H 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 [62].

Similar to other natural nickel ethylene polymerization catalysts which have already been reported for oligomerization of α -olefins [64,65], oligomerization of 1-hexene at 40 and 60 °C by catalyst 14 led to low yields of oligomers with degrees of polymerization of 21 and 16, respectively [62]. Branching numbers are 147 and 152 branches per 1000 carbon atoms, indicating a very minor amount of chain straightening via a 2,1-insertion and chain walking [39].

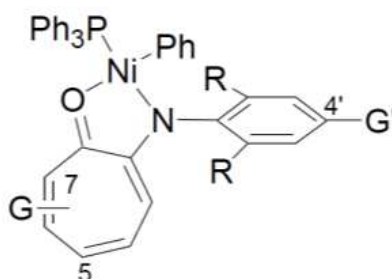
Salicylaldimine-based neutral Ni (II) catalyst bearing electron-withdrawing NO₂ group displayed high activity for polymerization of ethylene and resulted in high M_w polymer with fewer branches than the unnitrated catalysts [63]. Accordingly, Brookhart [66] prepared anilinetropone-based neutral Ni (II) catalysts 27-29 (Scheme 5) to examine the effect on catalyst activity and stability of adding strong electron-withdrawing NO₂ groups to the tropone and N-aryl ring.

As can be seen in Table 4, in comparison with unnitrated catalyst 13, the addition of two NO₂ groups dramatically enhances catalytic activity of 27 at 80 °C (entries 6 vs 4) from a TOF of 5423 to 27428 while the M_w of PE were comparable.

entry	Cat. (μmol)	P (psig)	T ($^{\circ}\text{C}$)	TOF ^b	Mn ($\times 10^3$)	Mw/Mn	Br/1000 C
1	14.8	400	60	5554	57	2.8	64
2	7.6	400	40	947	204	2.8	8
3	7.6	400	60	5368	292	2.0	27
4	7.6	400	80	9000	119	1.8	49
5	7.6	400	100	3157	61	1.9	67
6	5.2	1 atm	80	173	6.7	2.0	113
7	5.2	50	80	4615	50	1.7	90
8	5.2	100	80	7629	63	1.9	76
9	5.2	200	80	10615	90	1.8	61
10	5.2	200	80	8769	92	1.8	61
11	5.2	400	80	8192	104	2.0	45
12	5.2	600	80	3000	120	2.0	41
13	5.2	200	80	8653	78	1.9	66
14	5.2	400	80	12576	108	1.9	48
15	5.2	600	80	10153	111	2.0	43

^a Polymerization time = 10 min, ^b Kg PE mol cat⁻¹ h⁻¹

Table 3. Ethylene polymerization with 14 ^a [62]



Catalyst	G, G' and R	R
27	R = Me, G = 5,7-NO ₂ , G' = Me	H
28	R = ⁱ Pr, G = 5,7-NO ₂ , G' = H	H
29	R = ⁱ Pr, G = 5,7-NO ₂ , G' = NO ₂	H

Scheme 5. Nitrated catalysts based on anilinetropone 27-29 [66]

Moreover, catalyst 27 exhibited higher thermal stability than salicylaldimine-based Ni (II) catalysts [58] as well as higher lifetime than catalyst 13 (entries 3, 4 vs. 5, 6). As the polymerization temperature was increased from 60 $^{\circ}\text{C}$ to 80 $^{\circ}\text{C}$, the polymer Mw decreased while catalytic activity and branching increased for catalyst 27.

Similar to 27, the addition of two or three NO₂ groups led to dramatically enhanced catalytic activities of diisopropyl analog 28 and 29, with a TOF of 80666 for 28 (entry 9) and 39600 for 29 (entry 10) compared with unnitrated parent catalysts 13 and 14.

entry	Cat.	Cat. (μmol)	t (min)	T ($^{\circ}\text{C}$)	ToF ^b	M _w	M _w /M _n	Br/1000 C
1	27	5.5	60	60	800	289000	2.9	10
2	27	6.9	10	60	2260	230000	2.7	8
3	27	2.0	60	80	9650	128000	2.4	18
4	27	2.1	10	80	27428	65000	-	16
5	13	7.6	30	80	1657	-	1.7	-
6	13	5.2	10	80	5423	73000	-	61
7	28	0.9	10	60	4000	-	-	-
8	28	0.45	60	80	6666	-	-	-
9	28	0.9	10	80	80666	-	-	2
10	29	0.5	10	80	39600	-	-	7
11	14	5.2	60	80	1769	162000	1.8	61
12	14	5.2	10	80	8769	165000	1.8	61

^a Ethylene pressure = 13.78 bar. ^b Kg PE mol cat⁻¹ h⁻¹

Table 4. Ethylene polymerizations with 27-29 ^a[66]

All PEs produced by nitro-substituted catalysts 27-29 had monomodal GPC traces (PDIs between 2 and 4) and lower branching densities than those of parent catalysts 13 and 14 (entry 4 vs 6 and entries 9,10 vs. 12).

Catalyst 27 was able to incorporate vinyltrimethoxysilane or 1-hexene into polyethylene, but at a reduced rate compared to ethylene homopolymerization [66]. 1-Hexene or 1-octene oligomerization was also studied with catalysts 27 or 28 [66]. The oligomers were produced with low activities and lower amount of branching than expected (for 1-hexene, the expected number of branches after 2,1-insertion without chain walking is 166 branches/1000C and for 1-octene is 125 branches/1000C), indicating minor chain walking of catalysts during oligomerization.

7. The mechanistic investigation of the polymerization of ethylene

Combined DFT/stochastic studies were undertaken on the mechanism of ethylene polymerization catalyzed by the neutral Ni-anilinetropone catalysts [67]. Chain propagation and isomerization as well as influence of reaction conditions on the branching formation were investigated. Similarly to the case of nickel-salicylaldiminato catalysts the activation barriers for the insertion of ethylene in complexes with the trans alkyl group to the oxygen donor were found higher than those encountered in cis/trans isomerization. Interestingly, stochastic simulation allowed for establishing temperature and pressure dependence of the polymer microstructure. In agreement with experimental evidences the model predicts a decrease with the number of branches with the increase of pressure. Temperature dependence behaves oppositely as a result of an increase in secondary insertions with the temperature.

To get a full mechanistic picture of a typical neutral catalyst system, an elegant and in-depth NMR study of ethylene polymerizations catalyzed by the anilinetropone complexes was

also performed [67]. Detailed information concerning the chain propagation process, the barrier to ethylene insertion, the nature, and dynamics of the intermediate Ni alkyl complexes, and the chain transfer and catalyst decay processes were obtained. The rate of insertion of ethylene into the Ni-phenyl bonds of both unsubstituted and aryl-substituted of anilinetropone nickel (II) complexes (14 and 25) was monitored by low temperature NMR spectroscopy. The ethylene insertion, initially, forms the corresponding $[\text{Ni}(\text{L})(\text{PPh}_3)(\text{CH}_2\text{CH}_2\text{Ph})]$ complexes determined by monitoring the change in concentrations of starting complexes. First-order rate constants were measured as a function of temperature and ethylene concentration.

Even at high ethylene concentrations, only PPh_3 complexes were observed (no ethylene complexes were detected). As expected, rates accelerate with temperature, increasing about an order of magnitude between -10 and 10°C . Insertion is dramatically inhibited by phosphine concentration. Thus, it was concluded that for these systems, the catalyst resting state(s) are an equilibrium mixture of phosphine and ethylene complexes (Figure 10). Nevertheless, at high ethylene pressures, the equilibrium is shifted nearly completely to the side of the ethylene complex and TOF becomes independent of ethylene pressure (saturation conditions).

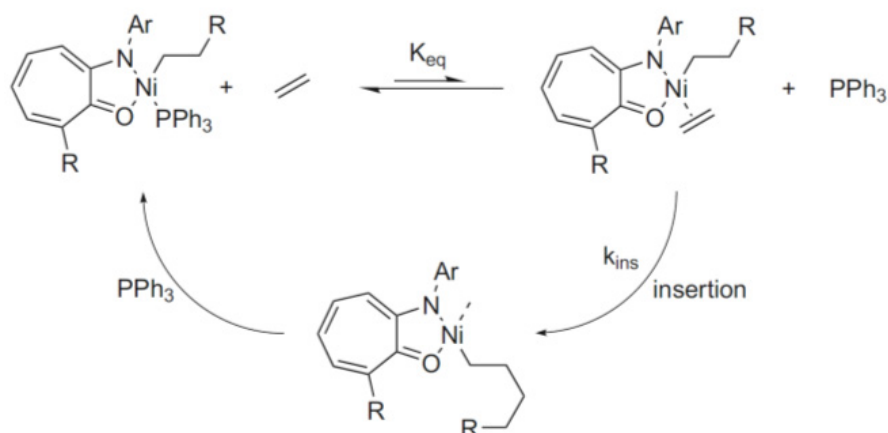


Figure 10. Ethylene polymerization catalyzed by Ni-anilinetropone catalysts [66].

The barriers to migratory insertion in $(\text{N}-\text{O})\text{Ni}(\text{R})-(\text{C}_2\text{H}_4)$ complexes, from measurements of TOFs under saturation conditions, were determined to lie in the range of $16\text{--}17\text{ kcal mol}^{-1}$, that is only about $2\text{--}3\text{ kcal mol}^{-1}$ greater than those observed for cationic diimine complexes.

The intermediate alkyl complexes have α -agostic interactions with dynamic behavior similar to the cationic alkyl diimine complexes. The barrier to β -H elimination and reinsertion is estimated in ca. 17 kcal mol^{-1} . Free energy barrier to nickel-carbon bond rotation in these complexes occurs with a barrier of $11.1\text{ kcal mol}^{-1}$. These isomerization processes account for branched polyethylenes generated from these catalysts and resemble those previously observed with diimine catalysts.

Thermolysis of $(\text{N},\text{O})\text{Ni}(\text{hexyl})(\text{PPh}_3)$ generates the nickel hydride complex and 1-hexene via β -H elimination, through two pathways, one (dominant) independent of phosphine

concentration and one involving reversible loss of phosphine, and thus inhibited by PPh_3 . This process is a model for chain transfer and clearly explains why polymer molecular weights decrease with increasing phosphine concentration. The rate of propagation is retarded by increasing $[\text{PPh}_3]$, while the rate of chain transfer is unchanged, resulting in an increase in $R_{\text{ct}}/R_{\text{prop}}$. Since chain transfer to monomer would exhibit a rate inhibition equal to that for R_{prop} with added PPh_3 it was concluded that the major chain transfer route is a simple β -elimination process, and not chain transfer to monomer.

At much slower rates, reductive elimination of the free ligand occurred from the hydride complex, and is inhibited by added phosphine. Catalyst decay under polymerization conditions was shown to occur by a similar process to generate free ligand and a bis-ligand complex formed by reaction of free ligand with an active catalyst species (Figure 11).

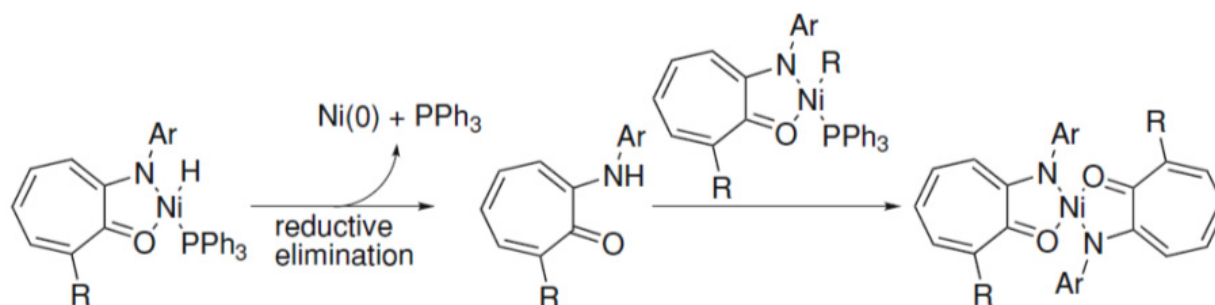


Figure 11. Deactivation of the anilinetropone nickel catalysts [67]

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