

Developing Neutral Bidentate (N,O) Nickel(II) Catalysts for Ethylene Homo- and Copolymerization

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ABSTRACT

LEI ZHANG: Developing Neutral Bidentate (N,O) Nickel(II) Catalysts for Ethylene Homo- and Copolymerization
(Under the direction of Professor Maurice Brookhart)

Research on polymerizations catalyzed by late metal complexes has been rejuvenated since our lab reported cationic α -diimine Ni/Pd catalysts which are active to polymerize ethylene into high molecular weight polymers with unique branched microstructures. Compared with early metals, the reduced oxophilicity of late metals has also enabled these catalysts to copolymerize ethylene with polar olefins. Neutral coordinated bidentate Ni(II) catalysts are expected to exhibit enhanced polar group tolerance compared with their cationic counterparts, due to the weakened metal-oxygen bond. New neutral (N,O)Ni(II) catalysts, each of which has a bulky N-aryl group have been reported and studied for ethylene homo- and copolymerization.

Chapter 2 describes the synthesis, characterization and polymerization studies of new neutral anilinoenone-based (N,O)Ni(II) catalysts having a strong electron-withdrawing trifluoromethyl group. These catalysts are active for ethylene polymerization to form branched polymer in the presence of an activator. Changes in the substitution pattern affect the catalytic activities and polymer properties. Polymerization results are compared and discussed.

Chapter 3 presents mechanistic investigations of ethylene insertion and coordination with neutral anilinoenone (N,O)Ni(II) catalysts. An ethylene insertion barrier is derived by

bulk ethylene polymerizations at various pressures at 60 °C. Preliminary results of copolymerization of ethylene with polar and nonpolar olefins indicate a reduced catalytic activity compared to ethylene homopolymerization.

Chapter 4 details a study to enhance the catalytic activity of anilinetropone (N,O)Ni(II) catalysts by adding strong electron-withdrawing nitro groups to the ligand backbone. These modified catalysts display dramatically enhanced activity for ethylene polymerization. The results are compared with the unnitrated parent catalysts. Copolymerization of ethylene and polar or nonpolar olefins and oligomerization of α -olefins using these catalysts are also performed and presented.

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LIST OF ABBREVIATIONS AND SYMBOLS

‡	denotes transition state
°C	degree Celsius
δ	chemical shift
η	hapticity
ΔG	change in Gibbs' free energy
Ar	aryl
atm	atmosphere
COD	cyclooctadiene
d	doublet
DFT	density functional theory
DSC	differential scanning calorimetry
eq	equation
equiv	equivalent
Et	ethyl
GC	gas chromatography
GPC	gel permeation chromatography
g	grams
h	hours
HDPE	high density polyethylene
Hz	hertz
ⁱ Pr	isopropyl

J	scalar coupling constant, in Hz
k	rate constant
kcal	kilocalorie
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
Lu	2,4-lutidine
M	molar (moles solute/liter solution)
m	multiplet
<i>m</i>	meta
Me	methyl, CH ₃
mL	milliliter
M _n	number average molecular weight
mol	moles
M _w	weight average molecular weight
MWD	molecular weight distribution
NMR	nuclear magnetic resonance
<i>o</i>	ortho
<i>p</i>	para
Ph	phenyl
ppm	parts per million
py	pyridine
q	quartet
RT	room temperature

s	seconds
s	singlet (used in NMR data)
sep	septet
SHOP	Shell higher olefins process
soln	solution
t	triplet
^t Bu	tertiary butyl, -C(CH ₃) ₃
THF	tetrahydrofuran
T _m	melt transition temperature
TMSCl	trimethylsilyl chloride
TOF	turnover frequency
TON	turnover number
VTMoS	vinyltrimethoxysilane

CHAPTER ONE

Group 10 Transition Metal Catalyzed Polymerization:

Background and Research Goals

Products made from polyethylene (PE) are encountered daily, from shampoo bottles to plastic bags. PE consists of a family of important commodity polymers. High density PE (HDPE) can be made with Ziegler-Natta or metallocene catalysts and linear low density PE (LLDPE) can be synthesized by copolymerizing ethylene with α -olefins in the presence of early transition metal catalysts. Industrially, low density PE (LDPE) and functionalized PE derived from the copolymerization of ethylene and polar monomers are produced by free radical processes that give little control over polymer structures.

Advancements in insertion polymerization catalysts have drawn increased attention for the copolymerization of polar monomers with ethylene. The development of catalysts operating by coordination/insertion for copolymerization is desirable since it not only provides an alternate route to polymers produced by radical processes, but it also potentially allows access to specialty polymeric materials with controlled structures previously unattainable. However, early transition metals are generally inadequate because of their high oxophilicity, which causes the formation of strong bonds between metal centers and polar atoms and shuts down propagation. Despite this disadvantage, there are examples of

copolymerization of ethylene and certain polar comonomers catalyzed by early metal complexes.¹⁻³ In most cases, the functional groups (e.g. amines and alcohols) are masked by Al-, B- or Si-based protective groups (e.g. Et₂AlCl and TMSCl), and deprotected after copolymerizations, which increases the number of steps and also make the processes inefficient in forms of atom economy. In contrast, late transition metals are relatively functional group tolerant due to population of the *d*-orbitals and reduced oxophilicity. There are numerous examples of late metal catalysts, such as Grubbs' ruthenium metathesis catalysts, utilized for organic synthesis where polar functionalities, such as esters and amines, are present in the substrates.⁴ Examples of copolymerizations of polar monomers with ethylene and α -olefins by late metal catalysts, e.g. Ni(II) and Pd(II), have been performed and will be described in more detail below.

Early Studies of Late Metal-Catalyzed Olefin Polymerizations

Unlike early transition metals, late transition metal alkyl complexes tend to undergo facile β -hydride elimination as a result of increased population of *d*-orbitals. This phenomenon was previously observed by Ziegler when trying to polymerize ethylene in the presence of nickel complexes. Instead of PE, 1-butene was formed rapidly and the “nickel effect”⁵ was coined. In the 1970s, Keim and coworkers⁶ utilized this characteristic feature of late transition metals to develop the Shell Higher Olefin Process (SHOP) where the neutral Ni(II) complex, (Ph₂PCH₂COO)Ni(Ph)(L), was employed to oligomerize ethylene into mostly value-added linear, α -olefins of C_{4~20+} range. These oligomers can then be applied as comonomers for LLDPE products, or used in the synthesis of plasticizers and detergents. Further efforts to enhance these catalysts' performance have afforded not only new types of

bidentate ligands including (O,O)⁷, (N,N)⁸ and (N,O),⁹ but also active neutral nickel catalysts that polymerize ethylene^{8,10-13}. For example, in modified SHOP catalysts **1** (Figure 1.1), when a strong electron-withdrawing CF₃ group is present at R₁, turnover frequencies (TOFs) as high as 4.2x10⁶ mol C₂H₄/(molNi•h) can be reached.¹³ The PEs obtained are essentially linear with less than 2 methyl-ended branches per 1000 methylene groups (2 branches/1000C).

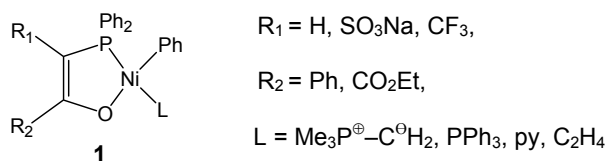


Figure 1.1 Modified SHOP catalysts **1**.

These modified SHOP catalysts have also been studied for their compatibility with polar additives during polymerization, and more importantly, their ability to incorporate polar comonomers into the polymeric backbones. As a matter of fact, the SHOP was operated in 1,4-butanediol under high ethylene pressure (1500 psi) and high temperature (80 ~ 120 °C) for the ease of product separation and catalyst recycling. Modified SHOP catalysts are also compatible with polar additives, such as acetone and THF.^{12,14,15} This high compatibility with polar additives is advantageous because 1) it avoids extensive purification of solvents and olefin feedstocks, and 2) it allows the polymerization to be conducted in diverse solvents. For example, emulsion polymerizations of ethylene have been successfully carried out with neutral (P,O)Ni(II) complexes.^{14,16-18} Polyketones with alternating CO and olefin units can also be synthesized using these catalysts.¹² However, copolymerizations of ethylene with polar comonomers only proceed well when the olefinic group and polar functionalities are

separated by more than 2 methylene spacers.¹² One exception was reported by Gibson¹⁹ where bulky (P,O) ligands were used for neutral Ni(II) catalysts to incorporate methyl methacrylate at the polymer chain-end. Another drawback of modified SHOP catalysts is that the PE produced has low molecular weight, generally $\sim 10^4$ g/mol.

Cationic α -Diimine Ni/Pd Catalyzed Polymerizations

A breakthrough occurred when cationic α -diimine Ni/Pd complexes, **2** (Figure 1.2),²⁰⁻²³ were discovered to be extremely active ethylene polymerization catalysts which resulted in high molecular weight PE with unique branched microstructures. The activities of some of these Ni(II) catalysts reach those of typical metallocenes (TOF $\sim 10^6$ /h). These diimine catalysts are also the first late transition metal systems able to polymerize α -olefins,^{20,24} 1,2-disubstituted olefins^{25,26} and cyclic olefins²⁷ into high molar mass polymers. Low temperature NMR studies of ethylene enchainment have revealed a chain-walking mechanism for the branch formation (Scheme 1.1).²⁸⁻³¹ During the chain growth, (N,N)M(alkyl)(C₂H₄)⁺ is the catalyst resting state. After migratory insertion, the agostic interaction between β -H and M facilitates elimination to form (N,N)M(olefin)(H)⁺ intermediates. Without loss of olefin by chain transfer, which occurs in oligomerization catalysts, hydride reinsertion leads to formation of another (N,N)M(alkyl) species. This complex can either undergo more β -hydride eliminations/reinsertions or simply insert another ethylene for continuous chain growth. This propagation pathway also accounts for the lower number of branches observed in α -olefin polymerization where migration of the metal along the chain results in a net outcome of 2, ω -insertion.^{20,27,32}

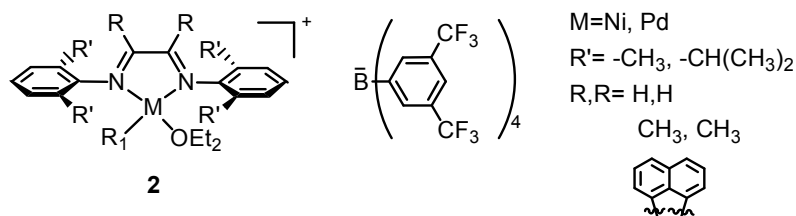
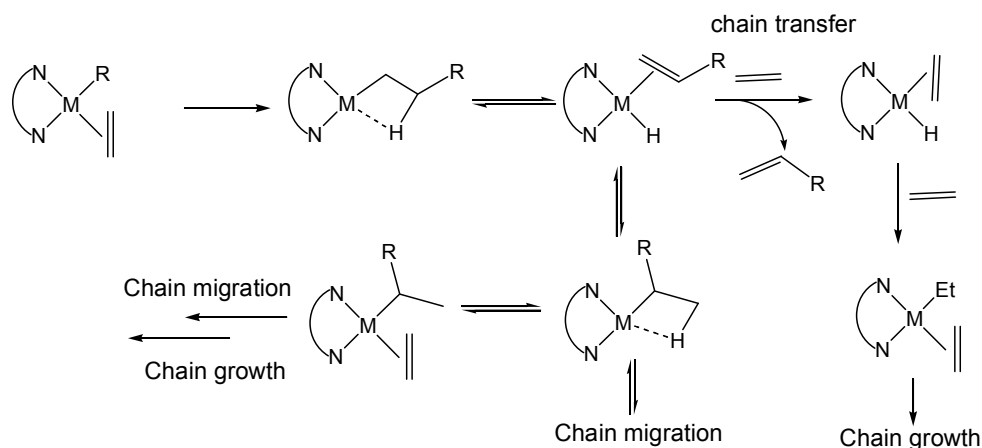


Figure 1.2 Cationic α -diimine Ni/Pd catalysts **2**.

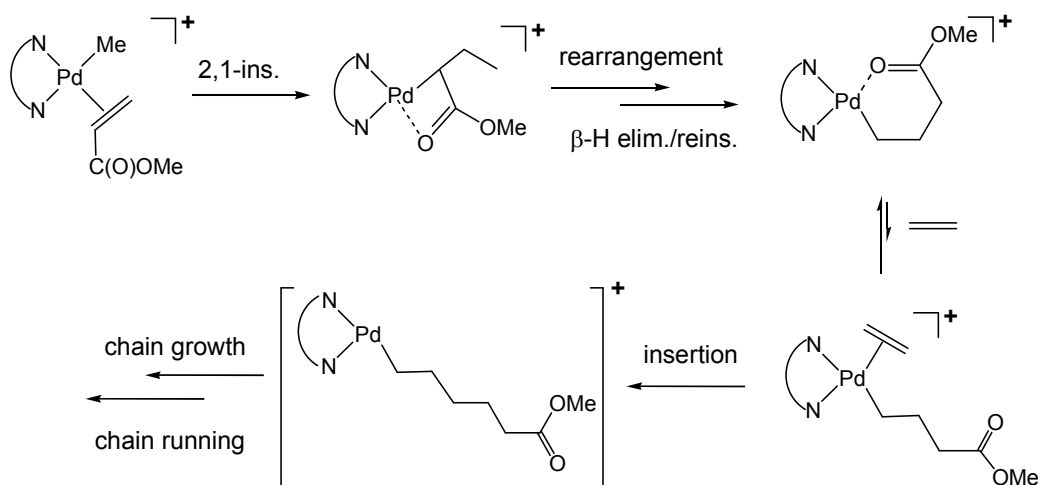


Scheme 1.1. Mechanism of cationic α -diimine Ni/Pd-catalyzed ethylene polymerization.

The most notable feature that allows this reaction to occur is the obvious steric bulk posed by the *ortho*-substituents on the imine aryl groups of the catalysts. The perpendicular aryl ring forces the alkyl group to occupy the axial sites of the metal square plane, thereby retarding chain transfer after β -H elimination, increasing the polymer molecular weight and giving products possessing unique branching. Diimine Ni(II) and Pd(II) catalysts exhibit different polymerization behaviors. For the Ni(II) system, PE branching is dependent on polymerization conditions, i.e. temperature, ethylene pressure and catalyst. As a consequence, the PE structure varies from linear to 120 branches/1000C. However, the degree of branching is almost the same under all conditions for PE produced by Pd(II) catalysts, ~100 branches/1000C, while the structure can vary from hyperbranched to short-chain branched³³.

Copolymerizations of ethylene and α -olefins with polar comonomers can be carried out with diimine Ni/Pd catalysts.²⁴ Various functionalized vinyl monomers, such as acrylates and vinyl ketones, are readily incorporated into high molecular weight polymers using diimine Pd(II) catalysts, though at a reduced insertion rate compared with olefin homopolymerization.^{24,34} Diimine Ni(II) catalysts are also able to copolymerize acrylates and ethylene, but need high temperature (120 °C) and pressure (1000 psi). Recently DuPont has reported the successful copolymerization of vinylsilanes and olefins using diimine Ni(II) catalysts with high activities.³⁵

Mechanistic aspects of the Pd(II)-catalyzed copolymerization of olefins with methyl acrylate have been studied (Scheme 1.2.).^{24,34} After 2,1-insertion of acrylate, the Pd complex undergoes facile rearrangement to form a stable six-membered chelate where the cationic metal center coordinates strongly to the carbonyl oxygen and impedes subsequent monomer coordination and insertion.



Scheme 1.2. Mechanism of cationic α -diimine Pd(II)-catalyzed copolymerization of ethylene with methyl acrylate.

Recent Studies with Neutral Bidentate (N,O)Ni(II) Catalysts for Polymerizations

Neutral Ni(II) catalysts are suitable candidates for ethylene copolymerization with polar comonomers because their reduced electrophilicity (neutral vs. cationic) should weaken the chelation between O and the metal center and thus these species should readily coordinate and insert olefinic monomers. The main concept used to design new generation neutral Ni(II) complexes is to adopt the success of Brookhart's cationic α -diimine Ni/Pd catalysts with bulky substituents installed to hinder the chain transfer and to produce high molecular weight, branched polymer. Bidentate (N,O) ligands have attracted great attention because the monoanionic ligand structures are easy to access, and the N-containing chelate arm can be modeled after the diimine by adding steric bulk on the N-phenyl *ortho*-positions.

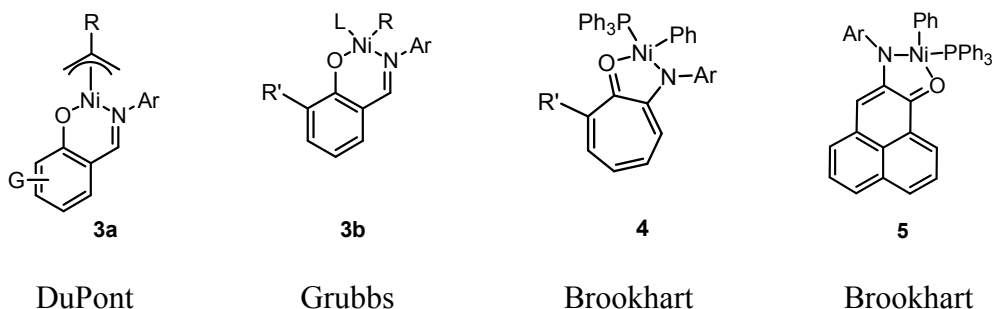
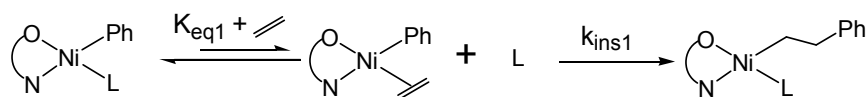


Figure 1.3 New generation neutral bidentate (N,O)Ni(II) catalysts **3a**, **3b**, **4** and **5**.

The DuPont group³⁶ and Grubbs³⁷⁻⁴⁰ have independently reported a series of neutral (N,O)Ni(R)(L) complexes, **3a** and **3b**, based on substituted salicylaldimines, that are active for ethylene polymerization into high molecular weight branched PE in the presence of activators. Anilinetropone (N,O)Ni(Ph)(PPh₃) **4**⁴¹⁻⁴³ and anilinonaphthenone (N,O)Ni(Ph)(PPh₃) **5**⁴⁴ developed by our group polymerize ethylene into high molecular weight, branched PE with excellent activities without need of activators. Like modified

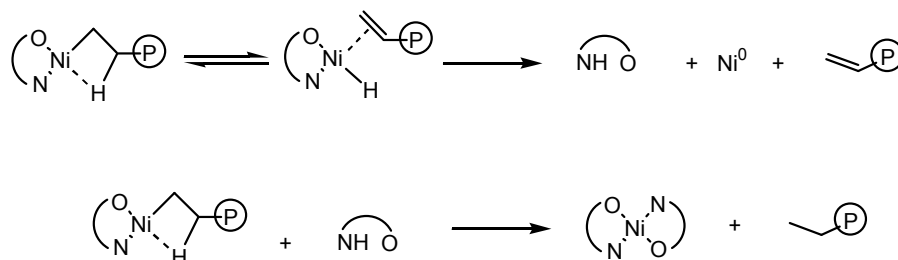
SHOP catalysts, catalysts **3-5** tolerate polar functionalities. Emulsion polymerization with **3b** gives semicrystalline PEs of $M_n < 10^5$ g/mol with a relatively narrow molecular weight distribution of 2~4.⁴⁵

Increasing steric bulk in the *ortho*-position of the coordinating oxygen on the aromatic rings (aryl of **3b**, tropone of **4**) also has great influence on the performance of the catalysts. For example in **3b**, when $R' = \text{Ph}$ and $L = \text{PPh}_3$, the catalyst polymerizes ethylene in absence of an activator such as $\text{Ni}(\text{COD})_2$ or a Lewis acidic borane compound, though with lower productivity than polymerization using an activator. These activators are typically needed to sequester PPh_3 and push the equilibrium to the $(\text{N},\text{O})\text{Ni}(\text{R})(\text{C}_2\text{H}_4)$ side (Scheme 1.3). Activity in the absence of activators indicates the presence of sufficient bulk around the Ni coordination sphere to drive phosphine dissociation.



Scheme 1.3. Mechanism of neutral $(\text{N},\text{O})\text{Ni}(\text{II})$ -catalyzed ethylene polymerization.

Increasing steric hindrance around nickel proves to be an effective strategy not only to block the chain transfer, but also to prolong the catalyst lifetime. A recent study shows that when H is replaced with naphthyl at R' in **4**, the catalyst productivity increases linearly with time at 40 °C for at least 3 h, and generates PE of molecular weight too high for GPC analysis.⁴² The longer lifetime of the catalyst is associated with lack of active species deactivation to the bis-ligand complex $(\text{N},\text{O})_2\text{Ni}$, which is also the proposed decomposition pathway for $(\text{P},\text{O})\text{Ni}(\text{Ph})(\text{L})$ (Scheme 1.4).^{40,46} The bulky bidentate (N,O) ligand disfavors the formation of the unstable bis-ligand $\text{Ni}(\text{II})$ complex.



Scheme 1.4. Proposed deactivation pathways of neutral (N,O)Ni catalysts.

Besides the steric effect, electronic effects caused by the substitutions on the ligand backbones have also been screened.^{37,42} The addition of strong electron-withdrawing groups on the monoanionic (N,O) bidentate ligand has led to a dramatic enhancement in catalytic productivity. For example, substituting H with NO₂ on the *para*-position of salicylaldimine in **3b** has increased TON by 10-fold under otherwise identical polymerization conditions.³⁷

Unlike cationic α -diimine Ni/Pd complexes, no neutral catalysts currently polymerize α -olefins. Oligomerization of 1-hexene with **4** has given oligomers with branching density of 147-152 branches/1000C. The lower than expected amount of branching (166 branches/1000C) implies minor chain walking after 2,1-insertion of monomer.⁴²

Catalysts **3b** have also been applied to the copolymerization of ethylene and polar functionalized norbornenes and α -olefins. Mechanistic investigations of ethylene polymerization, including insertion barriers and coordination properties, with **4**⁴³ and of acrylate insertion with **3b** have been performed.^{43,47}

Research Goals and Achievements

In recognition of the many advantages, such as functional group tolerance and easy modification of ligand backbones, and the significant potential for application of neutral

nickel polymerization catalysts, the research described in this dissertation has continued the development and study of the neutral bidentate (N,O)Ni(R)(L) systems for polymerization. Through design and synthesis of a series of new ligand structures, new complexes **6a-f** (Figure 1.4) of six-membered Ni(II) chelates have been developed and are described in Chapter 2. Complexes **6a-d** are active for ethylene polymerization into branched structure in the presence of activators, e.g. Ni(COD)₂ or B(C₆F₅)₃. Substitutions at R₁, R₂ and R₃ positions have greatly affected catalyst productivities and polymer properties. Ethylene polymerization results of **6a-d** are compared and discussed in this chapter.

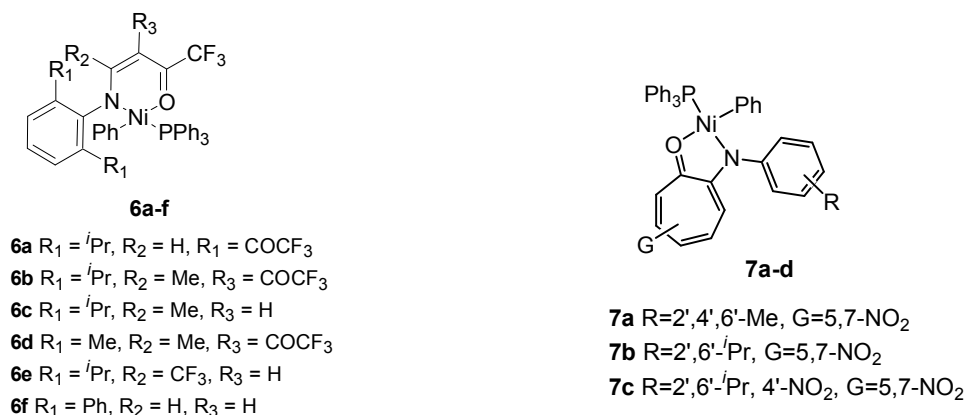


Figure 1.4. Neutral anilinoenone-based (N,O)Ni(II) complexes **6a-f** and anilinetropone-based (N,O)Ni(II) complexes **7a-c**.

By replacing H with NO₂ groups, new neutral anilinetropone Ni(II) catalysts **7a-c** (Figure 1.4) have been developed (Chapter 4). Catalysts **7a-c** have exhibited dramatically enhanced activities for ethylene polymerization compared with their unsubstituted parent catalysts. **7b** has especially high productivity with a TOF exceeding 2 million and is the most active neutral Ni(II) ethylene polymerization catalyst discovered to date. PEs produced by **7a-c** are lightly branched and of high molecular weights. Copolymerization of ethylene and vinyltrimethoxysilane is possible using catalyst **7a** though at a reduced rate.

Chapter 3 presents mechanistic investigations conducted with trifluoroacetyl-substituted anilino-enone (N,O)Ni(Ph)(L) catalysts (L=PPh₃ or 2,4-lutidine) of ethylene coordination, insertion and catalyst decomposition. (N,O)Ni(Ph)(2,4-Lu) complex polymerizes ethylene without the need of a phosphine scavenger and is used for high temperature bulk ethylene polymerizations where an ethylene insertion barrier of $\Delta G^\ddagger=15.6$ kcal/mol was obtained and is comparable to the value reported for neutral anilinetropone-based Ni(II) catalysts. Copolymerizations of ethylene with polar monomers were also performed and will be presented in this chapter together with the results from 1-hexene oligomerization using catalyst **6a**.

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CHAPTER TWO

Synthesis, Characterization, and Ethylene Polymerization Activities of Neutral Nickel(II) Complexes Derived from Anilino-substituted Enone Ligands Bearing Trifluoroacetyl and Trifluoromethyl Substituents

This chapter is reproduced from an *Organometallics* paper (2006, 25, 1868) with permission from L. Zhang, M. Brookhart and P. S. White. Two new neutral anilinoenone-based (N,O)Ni(Ph)(PPh₃) complexes **3e** and **3f** are added. The synthesis, characterization and polymerization activities of **3e** and **3f** are included.

Introduction

In 1995, cationic Ni(II) and Pd(II) catalysts derived from bulky aryl-substituted α -diimines were reported to convert ethylene and α -olefins to high molecular weight polyolefins.¹ These materials exhibited unique microstructures due primarily to the now well-established ability of the metal to migrate along the polymer chain via β -hydride elimination/reinsertion reactions without undergoing chain transfer.²⁻⁷ This discovery was followed by intense collaborative activities between the UNC and DuPont Versipol groups, and later by other groups, in developing the catalytic chemistry and related mechanistic understanding of the diimine systems and related catalysts.⁸⁻²¹

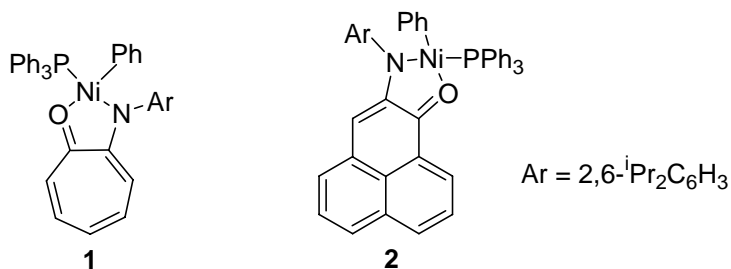
A particular appeal of examining late metal catalysts was the potential to copolymerize ethylene and polar monomers such as alkyl acrylates.²²⁻²⁴ While a limited set of polar monomers were successful in copolymerizations using the diimine systems, even the successful polar monomers exhibited reduced rates due to the substantial electrophilicity of the cationic metal center and the propensity to form stable chelate structures following polar monomer incorporation.^{8,11,25} In addition, these cationic catalysts were sensitive to polar additives such as water and alcohols. For these reasons, considerable attention turned to developing neutral catalysts based on Ni(II) which should have reduced electrophilicity and thus reduced sensitivity to polar groups.

The first neutral Ni(II) catalysts for ethylene polymerizations were reported in the 1980s.^{22,26-28} These catalysts were primarily based on modifications of the SHOP systems and incorporated anionic phosphino-enolate ligands. Such systems normally provided low molecular weight linear polyethylene at modest rates. Incorporation of bulky substituents²⁹ or perfluoroalkyl groups³⁰ in the backbone of the P,O chelates greatly accelerated the polymerization rates but molecular weights of the linear PE were modest. Claverie³¹ and Mecking^{32,33} have shown that neutral P,O chelate Ni complexes bearing perfluoroalkyl or hydrophilic groups can be used for emulsion polymerizations of ethylene in water. Other interesting SHOP-type derivatives, though mainly used for oligomerization, are zwitterionic Ni(II) complexes developed recently by the Bazan group.³⁴

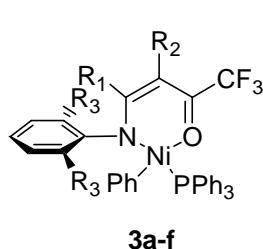
Neutral ligands based on bidentate anionic N,O ligands have received considerable recent attention since incorporation of a bulky *ortho*-substituted aryl-N functionality, modeled after the diimine systems, results in substantial increases in polymer molecular weights as well as incorporation of branching due to chain-walking.³⁵⁻⁴⁰ Early prominent

examples were based on salicylaldimines formed from *ortho*-disubstituted anilines and first reported by the DuPont³⁹ and Grubbs groups.⁴⁰ These systems were shown to copolymerize ethylene and norbornene derivatives containing polar functionalities;⁴⁰ Mecking demonstrated that related Ni(II) catalysts were effective for aqueous emulsion polymerization of ethylene.³²

This laboratory has reported the synthesis of anionic five-membered N,O chelates derived from bulky anilinetropones³⁵⁻³⁷ and anilinoperinapthenone⁴¹ for preparation of Ni(II) catalysts of types **1** and **2** shown below. These systems proved to be compatible with polar solvents and highly active for formation of branched PEs. Mechanistic studies established the nature of the catalyst resting state(s), and the mechanisms of chain transfer and decomposition.³⁷ DFT studies of both the salicylaldimine and the anilinetropone systems have been reported.^{17,42}



We report here our efforts to further enhance the activity of neutral Ni(II) catalysts through synthesis and screening of a series of catalysts **3a-f**, which incorporate the strongly electron-withdrawing -CF_3 and/or -C(O)CF_3 groups in the ligand backbone. Complex **3a** shows especially high activity and long lifetime when activated with $\text{B(C}_6\text{F}_5)_3$ or Ni(COD)_2 .

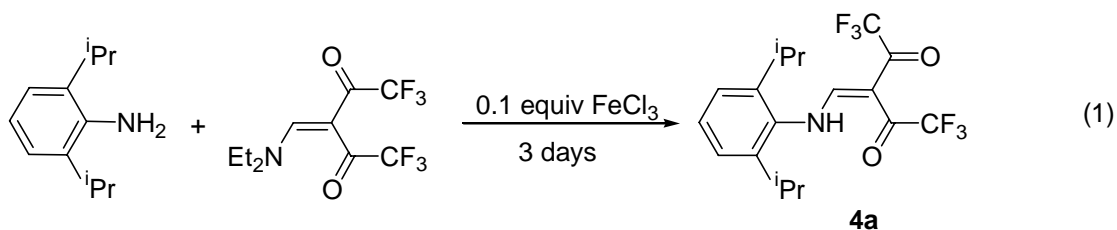


- 3a** $R_1 = \text{H}$, $R_2 = \text{COCF}_3$, $R_3 = i\text{Pr}$
3b $R_1 = \text{Me}$, $R_2 = \text{COCF}_3$, $R_3 = i\text{Pr}$
3c $R_1 = \text{Me}$, $R_2 = \text{H}$, $R_3 = i\text{Pr}$
3d $R_1 = \text{Me}$, $R_2 = \text{COCF}_3$, $R_3 = \text{Me}$
3e $R_1 = \text{CF}_3$, $R_2 = \text{H}$, $R_3 = i\text{Pr}$
3f $R_1 = \text{H}$, $R_2 = \text{H}$, $R_3 = \text{Ph}$

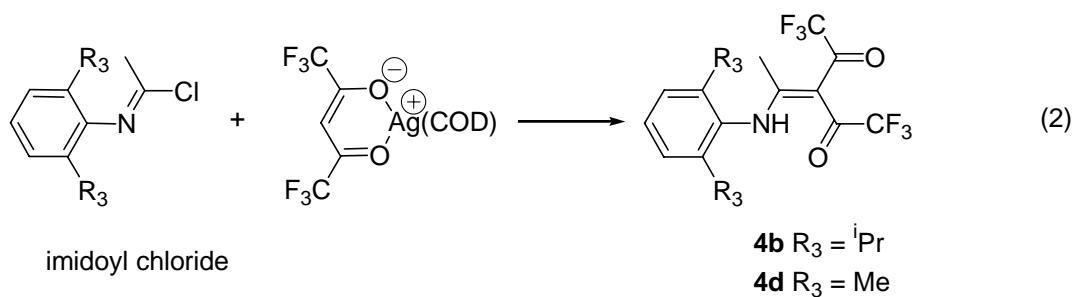
Results and Discussion

Ligand Syntheses. Complexes **3a-f** all share a common five-membered N,O chelate backbone and differ only in the substitution patterns along the backbone. As noted in the Introduction, the rationale for preparing these complexes with highly electron-withdrawing fluoroalkyl substituents was the expectation, based on analogy to P,O chelates, that such complexes may exhibit significantly enhanced activities in ethylene polymerization. All of the complexes **3a-f** are prepared from the corresponding acyl-substituted enamine ligands, **4a-f**. But despite the similarities in structure, different synthetic routes must be employed to access these ligands.

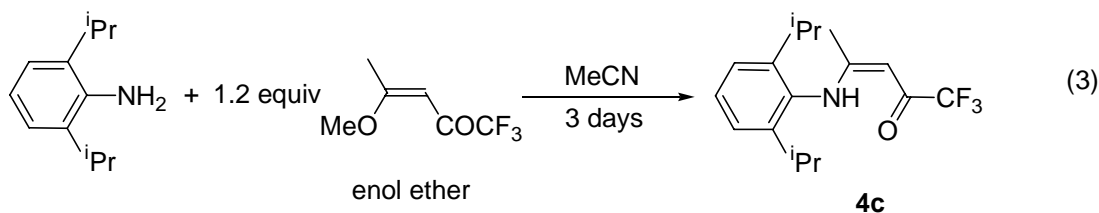
Ligand **4a** is prepared by displacement of the Et_2N - group in N,N-diethylaminomethylene-1,1,1,5,5,5-hexafluoroacetylacetone (DAMFA) by 2,6-diisopropylaniline catalyzed by the Lewis acid FeCl_3 (eq 1), in analogy with known chemistry of DAMFA. Following chromatographic purification, **4a** was isolated in good yields and high purity.



Ligands **4b** and **4d** were prepared by the reaction of the corresponding imidoyl chloride with silver cyclooctadiene hexafluoroacetylacetonate in toluene at 25 °C (eq 2). Crystallizations from CH₂Cl₂/hexane at lower temperature afford the pure ligands in excellent yields. Use of the silver enolate is required since the lithium enolate results in substantial imidoylation at oxygen.

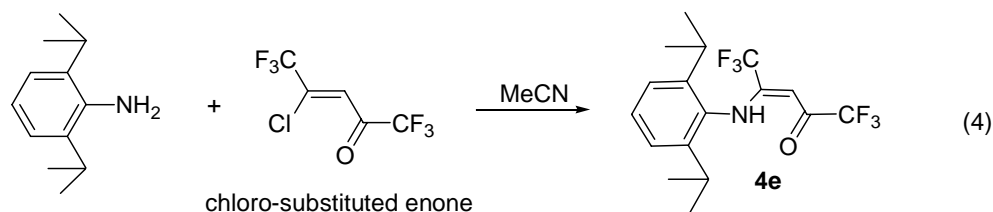


In analogy with the preparation of ligand **4a**, ligand **4c** was prepared by displacement of the methoxy group from the enol ether (4-methoxy-1,1,1-trifluoro-3-penten-2-one) by 2,6-diisopropylaniline (eq 3). High yields of pure product were obtained in acetonitrile after 3 days at 25 °C.

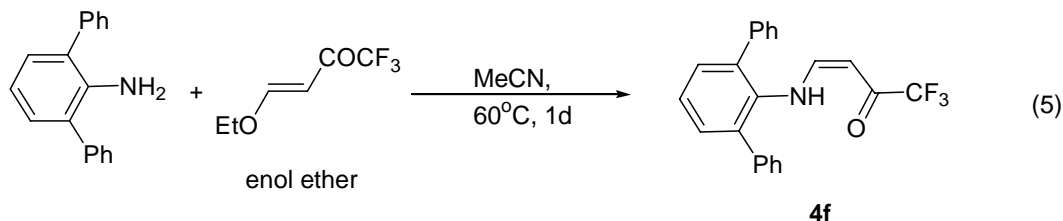


Ligand electronic properties can also be tuned by replacing the vinylic methyl group of ligand **4c** with CF₃ which gives the structure of ligand **4e**. Ligand **4e** was synthesized by nucleophilic substitution of chloride in chloro-substituted enone, 4-chloro-1,1,1,5,5,5-

hexafluoro-pent-3-en-2-one by 2,6-diisopropylaniline in acetonitrile (eq 4). The pure product was isolated after crystallization from CH₂Cl₂/hexane.



Ligand **4f** has phenyl substituents at the *ortho*-position of the aryl ring. Phenyl groups are introduced to enhance the stability, and consequently the performance, of the corresponding Ni(II) complex. Ligand **4f** was synthesized in a manner similar to **4a**, **4c** and **4e** by the reaction between 2,6-diisopropylaniline and enol ether, 4-ethoxy-1,1,1-trifluoro-but-3-en-2-one in acetonitrile, but at an elevated temperature (eq 5).



Ligands **4a-f** were fully characterized by ¹H, ¹³C, and ¹⁹F NMR spectroscopy. All exist in the enamine form rather than the imine form and exhibit a broad N-H signal at ca. 12 ppm. This down field shift suggests that the preferred geometries are U-shaped to accommodate H-bonding between N-H and the carbonyl oxygen. Consistent with the enamine structure, ligands **4a**, **4c** and **4e** display vinylic H resonances at 7.93 ppm, 5.55 ppm and 6.04 ppm, respectively; ligand **4f** shows a vinylic H adjacent to N at 6.68 ppm and a vinylic H adjacent to COCF₃ group at 5.10 ppm.

The solid state structures of ligands **4b** and **4d** have been determined by single crystal X-ray diffraction (Figures 2.1 and 2.2). As anticipated from ^1H NMR data, both ligands exist in the U form appropriate for intramolecular hydrogen bonding, and the five atoms of the chelate backbones of both ligands are within a couple of degrees in the same plane. The aryl rings lie roughly perpendicular to the plane of these chelate backbones. The slight difference between the dihedral angle C(1)-C(6)-N(13)-C(14) of **4b**, 86.9° , and the C(5)-C(6)-N(7)-C(8) of **4d**, 81.5° , can be attributed to the steric effect of the bulkier isopropyl groups in **4b**. The isopropyl methyl groups of **4b** (and **4c**) exhibit two sets of resonances indicating that rotation of the aryl ring is slow on the NMR timescale. Ligand **4a**, which lacks a vinylic methyl group, shows a single resonance for the isopropyl methyl group indicating rapid rotation of the aryl group on the NMR timescale.

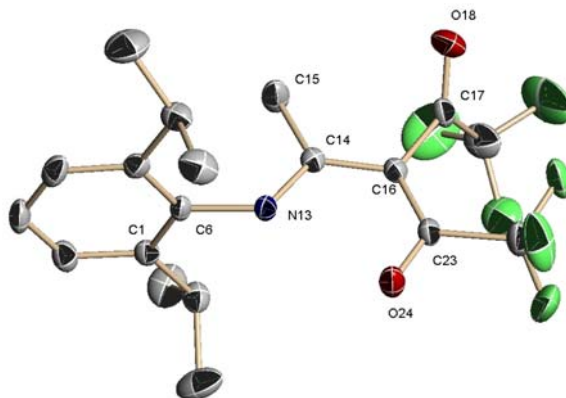


Figure 2.1. ORTEP view of **4b**. Selected interatomic distances (Å) and angles (deg): C(6)–N(13)=1.4475(17), N(13)–C(14)=1.3241(6), C(14)–C(16)=1.4167(18), C(16)–C(23)=1.4170(19), C(16)–C(17)=1.4957(18), C(23)–O(24)=1.2415(16), C(17)–O(18)=1.2014(19), C(1)–C(6)–N(13)–C(14)= $86.86(16)$, N(13)–C(14)–C(16)–C(23)= $-0.62(10)$, C(14)–C(16)–C(23)–O(24)= $1.51(9)$, C(6)–N(13)–C(14)–C(15)= $5.99(11)$.

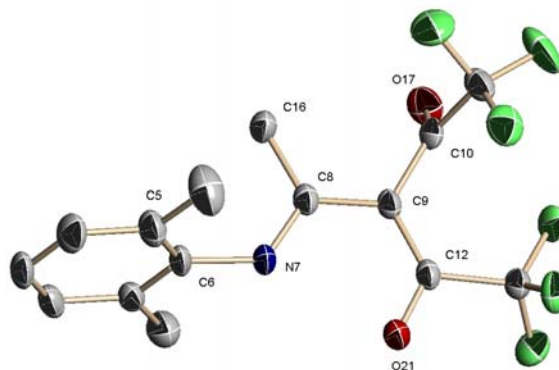
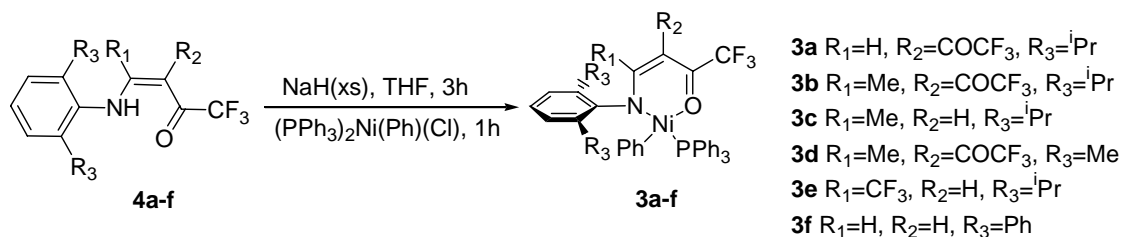


Figure 2.2. ORTEP view of **4d**. Selected interatomic distances (Å) and angles (deg): C(6)-N(7)=1.4497(19), N(7)-C(8)=1.3200(19), C(8)-C(9)=1.4231(20), C(9)-C(12)=1.4160(21), C(12)-O(21)= 1.2373(18), C(9)-C(10)=1.4862(20), C(5)-C(6)-N(7)-C(8)=-81.5(3), C(6)-N(7)-C(8)-C(16)=-6.60(19), N(7)-C(8)-C(9)-C(12)=2.50(18), C(8)-C(9)-C(12)-O(21)=-2.88(17).

Synthesis of Nickel Complexes, 3a-f. Complexes **3a-f** were synthesized as shown in Scheme 2.1. The enamines, **4a-f**, were readily deprotonated with excess sodium hydride in THF to yield the corresponding sodium salts. *In situ* reactions of these sodium salts with $(PPh_3)_2Ni(Ph)(Cl)$ at 25 °C generated the desired Ni(II) complexes. Following filtration and removal of THF, crystallization of the resulting crude mixtures from toluene/pentane at -30 °C gave crystalline complexes suitable for X-ray diffraction in 33-68% yield.



Scheme 2.1. Synthesis of complexes **3a-f**.

These complexes were fully characterized by ^1H , ^{13}C , ^{19}F , and ^{31}P NMR spectroscopy (see Experimental Section). For complex **3a**, the coordination of the ligand to the Ni(II) center slows the rotation around the N-aryl bond and results in the observation of two magnetically inequivalent isopropyl methyl doublets in the ^1H NMR spectrum. The methine signals in **3a-c** and **3e** shift to lower fields by ca. 0.6 ppm (3.60 ppm for **3a**; 3.34 ppm for **3b**; 3.36 ppm for **3c** and 3.20 ppm for **3e**) compared with the corresponding free ligands **4a-c** and **4e**. The ^{13}C resonances of the coordinated carbonyl groups shift to higher fields upon complexation; e.g., the ^{13}C signal in **4b** appears at 176.6 ppm and shifts to 161.4 ppm in **3b**.

Complex **3b** was characterized by single crystal X-ray diffraction (Figure 3.3). The complex is square planar with all L-Ni-L bond angles very close to 90° . As expected based on electronic considerations, the PPh_3 ligand is *trans* to the better donor amido nitrogen. The diisopropyl-substituted aryl ring is nearly perpendicular to the coordination square plane as shown by the Ni(1)-N(6)-C(18)-C(19) dihedral angle of -90.1° . There is a slight twist in the ligand backbone to accommodate the square planar coordination as illustrated by the C(3)-C(4)-C(5)-N(6) dihedral angle of -28.2° . (The N(13)-C(14)-C(16)-C(23) dihedral angle is -0.62° in the ligand **4b**.)

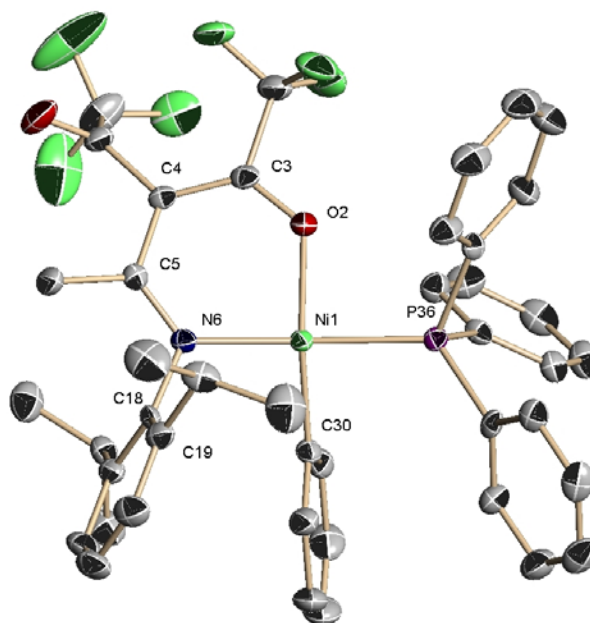


Figure 2.3. ORTEP view of **3b**. Selected interatomic distances (Å) and angles(deg): Ni(1)-N(6)= 1.953(3), Ni(1)-O(2)=1.907(2), Ni(1)-C(30)=1.900(3), Ni(1)-P(36)=2.1884(9), C(3)-O(2)=1.269(4), C(3)-C(4)=1.388(5), C(4)-C(5)=1.460(5), C(5)-N(6)=1.308(4), N(6)-Ni(1)-O(2)=90.42(11), C(30)-Ni(1)-P(36)=86.97(10), Ni(1)-N(6)-C(18)-C(19)=-90.1, C(3)-C(4)-C(5)-N(6)=-28.2, Ni(1)-O(2)-C(3)-C(4)=23.9.

The differing substitution pattern along the ligand backbone significantly affects the steric and electronic properties of the Ni(II) center and their behavior as catalysts for ethylene polymerizations, the results of which are summarized below.

Ethylene Polymerizations Catalyzed by 3a-d. To initiate polymerization, ethylene must replace PPh_3 to yield a Ni(phenyl)(ethylene) complex which then undergoes migratory insertion to yield a Ni-alkyl species which propagates through a series of migratory insertion reactions. The propagating nickel alkyl species can “rest” as a $\text{Ni}(\text{PPh}_3)(\text{alkyl})$ complex, a $\text{Ni}(\text{ethylene})(\text{alkyl})$ complex or a $\text{Ni}(\text{alkyl})$ complex which would most likely exist as a β -agostic structure.^{37,43} For catalysts of type **1** there exists an equilibrium between the $(\text{N},\text{O})\text{Ni}(\text{PPh}_3)\text{alkyl}$ and the $(\text{N},\text{O})\text{Ni}(\text{ethylene})\text{alkyl}$ complexes. At high pressures the

ethylene complex is the major species and the turnover frequency becomes independent of ethylene pressure.

Polymerizations of ethylene catalyzed by **3a-f** were generally carried out in 80 mL of toluene in a 300 mL reactor except for catalyst **3a**, for which ethylene polymerizations, when using $\text{B}(\text{C}_6\text{F}_5)_3$ as activator, were conducted in 200 mL of toluene in a 1 L reactor due to mass transport problems with ethylene (*vide infra*). Ethylene pressures varied between 100 and 400 psig; temperatures varied between 25 °C and 80 °C. Low catalyst loadings were employed so that reaction exotherms could be controlled. Internal temperatures of the autoclaves did not vary more than ca ± 2 °C. Despite the similarities in ligand structures, complexes **3e** and **3f** were not active for ethylene polymerization even in the presence of an activator. Therefore the following discussion is focused on catalysts **3a-d**. Results for ethylene polymerization studies are summarized in Table 2.1 (for complex **3a**) and Table 2.2 (for complexes **3b-d**). Turnover numbers as a function of time and temperature are given in the tables and relate to productivities. Since catalyst decay often occurs during polymerization runs, the intrinsic activities are best judged by calculating turnover frequencies at early times.

Without the addition of an activator to sequester PPh_3 and drive the equilibrium toward the $\text{Ni}(\text{ethylene})(\text{alkyl})$ complex, low productivities are observed for complexes **3a** and **3b** (see Table 2.1, entry 1 and Table 2.2, entry 1) and no polymer is obtained for **3c** and **3d**, even at 200 psig ethylene. In contrast to catalysts of type **1**, this implies that the equilibria lie in favor of the PPh_3 complexes even at high ethylene pressures. Subsequent ethylene polymerizations were conducted using 2~4 equiv of phosphine scavengers to activate these complexes.

For the most active catalyst studied, **3a**, the productivity is greatly enhanced from a TON of only ca. 4700 after 1 h, 100 psig at 70°C without an activator to 1.23×10^5 at 200 psig with 2.5 equiv of $\text{Ni}(\text{COD})_2$ and 3.84×10^5 with 4 equiv $\text{B}(\text{C}_6\text{F}_5)_3$ (compare entries 1, 2 and 6). The optimal productivity for ethylene polymerization is reached at 60 °C (compare entry 3 with entries 2 and 5; and entry 7 with 6 and 8); the catalyst productivity increases as ethylene pressure increases (compare entries 3 and 4). BPh_3 and $\text{Rh}(\text{acac})_2(\text{C}_2\text{H}_4)_2$ were also studied as activators. BPh_3 appears to be nearly as effective as $\text{B}(\text{C}_6\text{F}_5)_3$ (compare entries 11 and 7; 4.37×10^5 TON versus 5.06×10^5 TON), but $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ is clearly much less effective (see entries 11 and 12 vs. 7). At 60 °C, complex **3a** activated by $\text{Ni}(\text{COD})_2$ or $\text{B}(\text{C}_6\text{F}_5)_3$ forms a catalyst system with a short lifetime, $t_{1/2} \sim 20$ min. However, experiments at 35 °C have shown the catalyst is remarkably long-lived (entries 8-10). Between 1.7 and 5.0 h the TON increases linearly with time and shows a calculated TOF of 2.0×10^5 at each time. The TON number at 9 h is less than the extrapolated value (1.35×10^6 vs 1.8×10^6), but at that time the reactor is completely filled with solvent swollen-polyethylene and ethylene uptake is clearly limited by mass transfer. Based on these observations, conservatively the catalyst half-life must be greater than 15 h and likely is much more.

Polymers produced using either $\text{Ni}(\text{COD})_2$ or $\text{B}(\text{C}_6\text{F}_5)_3$ as the activator are quite similar. Monomodal GPC traces are observed with molecular weight distributions generally in the range of 2-4, indicating a single-site catalytic species is involved for ethylene polymerization. (MWD values above 2 occur in cases exhibiting high total TONs. As noted above under these conditions the autoclave is filled with solvent swollen polymer and mass transfer effects likely result in an increase of the MWD value above 2.) M_n values are limited by chain transfer to the monomer as is supported by entries 3 and 4 showing that increase of

ethylene pressure does not result in significant increase of PE molecular weight. M_w values lie in the range of 23,000-100,000 and decrease as expected at higher temperatures. Total branching numbers as measured by ^1H NMR spectroscopy,⁴⁴ fall between 35-45 branches per 1000 carbons. Higher temperatures (60-70 °C) produce polymers with branching numbers in the high end of this range while lower temperatures (35-50 °C) show branching numbers in the low end of the range. (Compare entries 2, 6 with entries 8, 9.) The degree of branching of PE produced by complex **3a** with $\text{Ni}(\text{COD})_2$ or $\text{B}(\text{C}_6\text{F}_5)_3$ as an activator is higher than that from catalysts of type **1** or type **2** where generally 10 branches/1000C are observed for type **1** and 17~34 branches for type **2**. The 9 h run at 35 °C produces PE with an unusually high branching number compared to runs at shorter time (entry 10). We ascribe the high branching to the fact that the reactor was filled with solvent swollen polyethylene, causing slow mass transport of ethylene to the Ni(II) center and thus a reduced polymerization rate vs. the polymer chain β -hydride elimination/reinsertion rate responsible for branching. While standard runs were carried out at 200 psig, a 400 psig experiment (entry 4, Table 2.1) shows branching is decreased at higher pressures. Both the increase in branching with increase in temperature and the decrease in branching at higher pressures is consistent with behavior noted previously for the diimine Ni/Pd catalysts and related systems.^{4,12,36,37} A detailed mechanistic explanation of these effects has been advanced.^{12, 13}

Table 2.1 Ethylene polymerization results using catalyst **3a**^a.

entry	cat.	cocat.	T	psig	t	TON ^b	M _w ^c	MWD	Br ^d
	(μmol)	(μmol)	($^{\circ}\text{C}$)		(h)		(g/mol)		/1000C
1 ^e	3.9	0	70	100	1	4,700	--	--	--
2 ^e	1.5	3.8	70	200	1	123,000	23,000	2.4	42
3 ^e	1.5	3.8	60	200	1	188,000	27,000	2.3	39
4 ^e	1.5	3.8	60	400	1	287,000	29,000	2.2	35
5 ^e	1.5	3.8	50	200	1	142,000	34,000	2.1	35
6 ^f	1.2	4.8	70	200	1	384,000	23,000	3.1	45
7 ^f	1.5	6.0	60	200	1	506,000	25,000	3.7	41
8 ^f	1.2	4.8	35	200	1.7	336,000	115,000	6.0	35
9 ^f	1.2	4.8	35	200	5	990,000	100,000	5.4	34
10 ^f	1.2	4.8	35	200	9	1,349,000	--	--	46
11 ^f	1.2	4.8	60	200	1	437,000	--	--	49
12 ^f	1.2	4.8	60	200	1	164,000	--	--	47

a. All polymerization temperatures are well-controlled with variation less than ± 2 $^{\circ}\text{C}$. b. In units of $\text{molC}_2\text{H}_4 \cdot \text{mol}^{-1}\text{Ni}$. c. M_w , weight average molecular weights were measured by GPC in 1,2,4-trichlorobenzene at 135 $^{\circ}\text{C}$. d. Branching numbers were measured by ^1H NMR spectroscopy in $\text{C}_6\text{D}_5\text{Br}$ at 120 $^{\circ}\text{C}$. e. Polymerization was carried out in 80 mL toluene in a 300 mL reactor with 2.5 equiv $\text{Ni}(\text{COD})_2$. f. Polymerization was carried out in 200 mL toluene in a 1L reactor with 4.0 equiv $\text{B}(\text{C}_6\text{F}_5)_3$.

Complexes **3b-d** are active ethylene polymerization catalysts in the presence of 2.5 equiv $\text{Ni}(\text{COD})_2$ as activator, but all are less productive than **3a** (Table 2.2). Polyethylenes produced by **3b-d** have lower molecular weights and are more highly branched when compared to polymers produced by **3a** under similar conditions (200 psig ethylene, 60 $^{\circ}\text{C}$, compare entries 2, 8, 12 of Table 2. 2 with entry 3 of Table 2.1). As seen from entries 2 and 12, decreasing the steric bulk around Ni(II) by replacing *ortho* isopropyl groups with methyl

groups has dramatically decreased the polymer molecular weight and catalyst productivity from $M_w = 17,000$, TON = 78,000 for **3b** to $M_w = 3,000$, TON = 30,000 for **3d**. Entries 4 and 5 show the lifetime of catalytic species generated from **3b**/Ni(COD)₂ is long with $t_{1/2} > 60$ min at 50 °C. The polymerization results follow the trend observed with complex **3a** (vide supra).

Table 2.2. Ethylene polymerization results using catalyst **3b-d**^a.

entry	cat	cat. (μmol)	T (°C)	psig	t (h)	TON ^b	M_w^c	MWD	Br ^d /1000C
1	3b	8	70	100	3	trace	1500 ^e	--	79
2	3b	5	60	200	1	78,000	17,000	4.9	65
3	3b	2.5	50	100	1	52,000	19,000	3.6	54
4	3b	2.3	50	200	1	106,000	27,000	3.3	58
5	3b	3.9	50	200	0.5	48,000	20,000	3.5	56
6	3b	3.2	50	300	1	87,000	24,000	3.2	53
7	3b	1.7	40	200	1	32,000	21,000	3.0	55
8	3c	5.0	60	200	1	37,000	13,000	3.0	56
9	3c	5.0	50	200	1	32,000	17,000	2.3	41
10	3c	3.5	50	300	1	48,000	18,000	3.7	34
11	3c	11.3	25	200	3	3,000	59,000	2.8	--
12	3d	12.5	60	200	1	30,000	3,000	1.5	--

a. Polymerization was carried out in 80 mL toluene in a 300 mL reactor with 2.5 equiv Ni(COD)₂. The temperature is well-controlled with variation less than ± 2 °C. b. In units of $\text{molC}_2\text{H}_4 \cdot \text{mol}^{-1}\text{Ni}$. c. M_w , weight average molecular weights were measured by GPC in 1,2,4-trichlorobenzene at 135 °C. d. Branching numbers were measured by ¹H NMR spectroscopy in at 100 °C. e. M_n , number average molecular weight was measured by ¹H NMR in C₆D₅Br at 100 °C.

Conclusions.

A series of new neutral (N,O) chelated Ni(II) complexes **3a-f** derived from anilino-substituted enone ligands bearing electron-withdrawing trifluoromethyl and trifluoroacetyl groups have been synthesized and characterized. Complexes **3a-d** are active for ethylene polymerization in the presence of an activator (Ni(COD)₂ or B(C₆F₅)₃) to sequester PPh₃. Moderately branched polyethylenes, generally in the range of 35-55 branches per 1000 carbons, are produced, consistent with expectations based on the presence of *ortho*-disubstituted aryl groups on nitrogen. The productivity ranking under standard conditions (200 psig, 60 °C, Ni(COD)₂ activator) follows the order **3a>3b>3c~3d**. The spread in productivities is modest but significant (188,000 TONs for **3a** to 30,000 TONs for **3d**). The rationale for these productivity differences is not obvious. Variations could result not only from differences in intrinsic turnover frequencies but also variable lifetimes. We do note that **3a**, the most productive catalyst, is the only one which bears no substituent α to nitrogen. A notable feature of **3a**, the catalyst we investigated most thoroughly, is not only the excellent productivity at 60 °C, but the very long lifetime at 35 °C. Judging from entries 8-10, Table 2.1, the half-life must exceed many hours since no decrease in activity after 5 h is seen while the productivity at 9 h was limited by reactor capacity. Further studies of **3a** are underway concerning the detailed mechanism of chain propagation and transfer and the catalyst decay pathway as well as use of **3a** for copolymerizations of ethylene and polar monomers.

Experimental Section

General Considerations. All manipulations of air- and/or water sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Solid organometallic compounds were transferred in an argon-filled drybox and, unless stated otherwise, were stored at room temperature. The ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra were acquired using Bruker 300 or 400 MHz spectrometers. Chemical shifts were reported in δ units, parts per million (ppm) and referenced against residual deuterated solvent peaks (^1H , ^{13}C) or external standards CF_3COOH (^{19}F) and H_3PO_4 (^{31}P). Flash Chromatography was performed using 60 Å silica gel (SAI). High temperature gel permeation chromatography (GPC) was performed by DuPont (Wilmington, DE) in 1,2,4-trichlorobenzene at 135 °C using Waters HPLC 150C equipped with Shodex columns. All calibration curves were established with polystyrene standards and universal calibration was applied using Mark-Houwink constants for polyethylene ($k = 4.34 \times 10^{-4}$; $\alpha = 0.724$). Elemental analyses were performed by Altantic Microlab Inc. of Norcross, GA.

Materials. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through alumina columns under an argon or nitrogen atmosphere. NMR solvents were vacuum-transferred from CaH_2 , degassed by repeated freeze-pump-thaw cycles and stored over 4 Å molecular sieves. 2,6-Diisopropylaniline, FeCl_3 , NaH , $\text{B}(\text{C}_6\text{F}_5)_3$, $\text{Rh}(\text{acac})_2(\text{C}_2\text{H}_4)_2$ and $\text{Ni}(\text{COD})_2$ were used as received. Polymer-grade ethylene was used as received for bulk polymerizations and NMR experiments. The following starting materials were prepared according to literature procedures: $(\text{PPh}_3)_2\text{Ni}(\text{Ph})(\text{Cl})^{45}$, N-2,6-diisopropylphenylacetimidoyl chloride⁴⁶, N-2,6-

dimethylphenylacetimidoyl chloride⁴⁶, Ag(COD)(hfacac)⁴⁷, N,N-diethylaminomethylene-1,1,1,5,5,5-hexafluoroacetylacetone (DAMFA)⁴⁸, 2,6-diphenylaniline⁴⁹, 4-chloro-1,1,1,5,5,5-hexafluoro-pent-3-en-2-one⁵⁰, 4-ethoxy-1,1,1-trifluoro-but-3-en-2-one⁵¹ and 4-methoxy-1,1,1-trifluoro-3-penten-2-one⁵². Yields refer to isolated yields of compounds of greater than 95% purity as estimated by ¹H NMR analysis and elemental analysis.

Analysis of Polymer Branching by ¹H NMR Spectroscopy. ¹H NMR spectra were recorded in either CDCl₃ at room temperature or C₆D₅Br at 120 °C. Assignment of peaks and calculation of polymer branching were carried out following the previously published method.⁵¹

General Polymerization Procedure. Polymerizations were carried out in a mechanically stirred 300 mL Parr[®] reactor equipped with an electric heating mantle controlled by a thermocouple dipping into the reaction mixture. The reactor was heated under vacuum at 120 °C for 1~2 h, and then backfilled with Ar, cooled to the desired reaction temperature. 70 mL toluene was injected, and the reactor was purged with ethylene (3x100 psig). A solution of the catalyst in 10 mL toluene was added to the vented reactor via cannula. The reactor was sealed and pressurized with ethylene to the desired pressure, and the stirring motor was engaged. When the reaction time was reached, ethylene pressure was released, and the reaction was quenched with 120 mL MeOH. Polymer was collected and weighed after removing the volatiles in vacuo and dried in a vacuum oven overnight at 80 °C.

A 1L Parr[®] reactor with external heating and cooling control was also used for polymerizations. A similar procedure as for the 300 mL Parr[®] reactor was used, but 190 mL

toluene was injected before ethylene purging and the reaction was quenched with 250 mL MeOH instead.

For cocatalyst studies, the catalyst solution was prepared by dissolving both catalyst and cocatalyst in 10 mL toluene at RT except for Ni(COD)₂, the catalyst solution was prepared at -20 °C.

3-[(2,6-Diisopropyl-phenylamino)-methylene]-1,1,1,5,5,5-hexafluoro-pentane-2,4-dione, 4a: A Schlenk tube flame-dried under vacuum was charged with diethylaminomethylene-1,1,1,5,5,5-hexafluoroacetylacetone (DAMFA) (3.577 g, 12.3 mmol) and FeCl₃ (0.1982 g, 1.2 mmol) under argon. Dry toluene (10 mL) was added, followed by 2,6-diisopropylaniline (2.8 mL 14.8 mmol). After refluxing for 3 days, the mixture was cooled to RT, quenched with 1 N HCl (10 mL), extracted with ether (3x10 mL) and washed with saturated NaHCO₃ (50 mL), and brine (50 mL). After drying over Mg₂SO₄, volatiles were removed under reduced pressure and pure product was obtained by silica gel chromatography eluting with ethyl acetate and hexane (1:16 vol:vol). Yield: 2.230 g (46%). ¹H NMR (400 MHz, CDCl₃): δ 12.01 (br s, 1H, NH), 7.93 (br s, 1H, vinylic H), 7.41 (t, J=7.6Hz, 1H, Ar-*p*H), 7.26 (d, J=7.6Hz, 2H, Ar-*m*H), 2.97 (septet, J=6.8Hz, 2H, *i*Pr-CH), 1.23 (d, J=6.8Hz, 12H, *i*Pr-CH₃). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 181.4 (q, J=37.6Hz, CO), 175.1 (q, J=34.4Hz, CO), 162.5 (vinylic C=CH), 143.9 (Ar C-N), 133.5, 130.0, 124.6 (Ar-C), 116.8 (q, J=292.4Hz, CF₃), 116.4 (q, J=287.6Hz, CF₃), 101.6 (vinylic C=CH), 28.6 (*i*Pr-CH), 23.6 (*i*Pr-CH₃). ¹⁹F NMR (376 MHz, CDCl₃): δ -72.68, -68.88. Anal. Calcd. (C₁₈H₁₉NO₂F₆): C, 54.7; H, 4.84; N, 3.54. Found: C, 55.8; H, 5.04; N, 3.69.

3-[1-(2,6-Diisopropyl-phenylamino)-ethylidene]-1,1,1,5,5,5-hexafluoro-pentane-2,4-dione, 4b, and 3-[1-(2,6-Dimethyl-phenylamino)-ethylidene]-1,1,1,5,5,5-hexafluoro-pentane-2,4-dione, 4d. General procedure: A toluene solution of Ag(COD)(hfacac) was added to the imidoyl chloride in toluene solution via cannula at RT. AgCl rapidly precipitated from the solution. The mixture was further stirred for 2 h at room temperature, then filtered through a pad of celite and washed 2 times with toluene. After removal of solvent in vacuo, products were recrystallized from toluene or pentane to yield clear crystals.

Synthesis of 4b: Ag(COD)(hfacac) (3.568 g, 8.4 mmol) in 50 mL toluene, N-2,6-diisopropylphenylacetimidoyl chloride (2.000 g, 8.4 mmol) in 30 mL toluene. Yield: 3.310 g (96%). ¹H NMR (400 MHz, CDCl₃): δ 13.07 (br s, 1H, NH), 7.39 (t, J=7.6Hz, 1H, Ar-*pH*), 7.25 (d, J=7.6Hz, 2H, Ar-*mH*), 2.78 (septet, J=6.8Hz, 2H, *iPr-CH*), 1.87 (s, 3H, vinylicCH₃), 1.16(d, J=6.8Hz, 6H, *iPr-CH*₃), 1.21 (d, J=6.8Hz, 6H, *iPr-CH*₃). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 184.8(br s, CO), 176.6(br s, CO), 171.6 (vinylic CCH₃), 144.9 (Ar C-N), 130.9, 130.0, 124.4(Ar-C), 116.5 (br q, J=300Hz, 2CF₃), 100.4 (vinylic C=CCH₃), 28.9 (*iPr-CH*₃), 22.5 (*iPr-CH*₃), 24.3 (*iPr-CH*), 17.8 (vinylic CCH₃). ¹⁹F NMR (376 MHz, CDCl₃): δ -75.38, -71.57. Anal. Calcd. (C₁₉H₂₁F₆NO₂): C, 55.7; H, 5.17; N, 3.42. Found: C, 55.6; H, 5.02; N, 3.38.

Synthesis of 4d: Ag(COD)(hfacac) (2.328 g, 1.1 mmol) in 25 mL toluene, N-2,6-dimethylphenylacetimidoyl chloride (1.000 g, 1.1 mmol) in 25 mL toluene Yield: 1.543 g (79%). ¹H NMR (400 MHz, CD₂Cl₂): δ 12.98 (br s, 1H, NH), 7.26 (t, J=7.6Hz, 1H, Ar-*pH*), 7.20 (d, J=7.6Hz, 2H, Ar-*mH*), 2.20 (s, 6H, 2,6-Ar-*o-CH*₃), 1.89 (s, 3H, vinylic CH₃). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 183.(br s, CO), 177.(br s, 2CO), 171.2 (vinylic CCH₃), 134.6, 133.8, 129.2, 129.(Ar-C), 116.3 (q, J=288Hz, 2CF₃), 100.4 (vinylic C=CCH₃), 18.0

(2,6-Ar-*o*-CH₃), 17.2 (vinylic CH₃). ¹⁹F NMR (376 MHz, CD₂Cl₂): δ -77.2, -73.6. Anal. Calcd. (C₁₉H₂₁F₆NO₂): C, 51.0; H, 3.71; N, 3.96. Found: C, 51.0; H, 3.62; N, 3.75.

4-(2,6-Diisopropyl-phenylamino)-1,1,1-trifluoro-pent-3-en-2-one, 4c. A solution of 2,6-diisopropylaniline (1.63 mL, 8.7 mmol) and 4-methoxy-1,1,1-trifluoro-3-penten-2-one (1.746 g, 10.4 mmol) in MeCN (8 mL) was stirred at room temperature for a prolonged time (monitored by silica TLC, about 3 days). The solvent was removed under reduced pressure after the completion of reaction as judged by TLC. The crude product was redissolved in Et₂O (20 mL) and was washed with 1 N HCl, then saturated aqueous NaHCO₃. After drying over Na₂SO₄, Et₂O was removed to provide pure product 2.537 g (93%). ¹H NMR (400 MHz, CDCl₃): δ 12.17 (br s, 1H, NH), 7.34 (t, J=7.6Hz, 1H, Ar-*pH*), 7.20 (d, J=7.6Hz, 2H, Ar-*mH*), 5.55 (s, 1H, vinylic H), 2.91 (septet, J=6.8Hz, 2H, *i*Pr-CH), 1.80 (s, 3H, vinylic CH₃), 1.21 (d, J=6.8Hz, 6H, *i*Pr-CH₃), 1.14 (d, J=6.8Hz, 6H, *i*Pr-CH₃). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 176.7 (q, J=33Hz, C=O), 170.4 (vinylic CCH₃), 145.5 (Ar-C-N), 132.1, 129.2, 124.0 (Ar-C), 117.6 (q, J=287Hz, CF₃), 89.5 (vinylic CH), 28.6 (*i*Pr-CH₃), 22.6 (*i*Pr-CH₃), 24.5 (*i*Pr-CH), 19.7 (vinylic-CH₃). ¹⁹F NMR (376 MHz, CDCl₃): δ -75.35. Anal. Calcd. (C₁₇H₂₂F₃NO): C, 65.2; H, 7.08; N, 4.47. Found: C, 64.6; H, 6.94; N, 4.27.

4-(2,6-Diisopropyl-phenylamino)-1,1,1,5,5,5-hexafluoro-pent-3-en-2-one, 4e 2,6-Diisopropylaniline (2.4 mL, 12.0 mmol) was added to a 10 mL MeCN solution of 4-chloro-1,1,1,5,5,5-hexafluoro-pent-3-en-2-one (1.37 g, 6.0 mmol) at RT with stirring. As the reaction progressed, the mixture changed color to red-orange and a precipitate formed. The reaction was stopped after 2 days and the red filtrate was collected. The residue after solvent removal was crystallized in CH₂Cl₂: hexane (1:4) and yielded 1.2 g **4e** (55%). ¹H NMR (400 MHz, CDCl₃): δ 11.61 (br s, 1H, NH), 7.36 (t, J=7.6Hz, 1H, Ar-*pH*), 7.19 (d, J=7.6Hz, 2H,

Ar-*mH*), 6.04 (s, 1H, vinylic-*H*), 2.93 (septet, *J*=6.8Hz, 2H, *iPr-CH*), 1.24 (d, *J*=6.8Hz, 6H, *iPr-CH₃*), 1.11 (d, *J*=6.8Hz, 6H, *iPr-CH₃*). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 181.1 (q, *J*=32Hz, CO), 155.3 (q, *J*=32Hz, vinylic CCF₃), 146.7, 131.2, 130.0, 123.9 (Ar-C) 119.1 (q, *J*=278Hz, vinylic CCF₃), 116.9 (q, *J*=286Hz, COCF₃), 87.5 (vinylic C=CF₃), 29.2 (*iPr-CH*), 25.8 (*iPr-CH₃*), 22.0 (*iPr-CH₃*). ¹⁹F NMR (376 MHz, CDCl₃): δ -66.21, -76.80. Anal. Calcd. (C₁₇H₁₉F₆NO): C, 55.6; H, 5.21; N, 3.81. Found: C, 55.0; H, 5.39; N, 3.82.

1,1,1-Trifluoro-4-([1,1';3',1'']terphenyl-2'-ylamino)-but-3-en-2-one, 4f 2,6-Diphenylaniline (0.981 g, 4 mmol) was added to a 10 mL MeCN solution of 4-ethoxy-1,1,1-trifluoro-but-3-en-2-one (0.67 g, 4 mmol) at RT. The reaction proceeded at 60 °C for 20 h. After removal of volatiles, the residue was crystallized in CH₂Cl₂/hexane to give 0.80 g a needle-like clear product (yield 54%). ¹H NMR (400 MHz, CDCl₃): δ 11.30 (br d, *J*=13Hz, 1H, *NH*), 7.48-7.36 (m, 13H, Ar-*H*), 6.68 (dd, *J*=13, 7.6Hz, 1H, vinylic-*H*CN), 5.10 (d, 1H, vinylic-*H*CCO). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 178.4 (q, *J*=33Hz, CO), 155.8 (vinylic-CN), 137.9, 136.0, 134.2, 130.7, 129.1, 128.8, 127.8, 126.6 (Ar-C), 116.6 (q, *J*=287Hz, CF₃), 88.8 (vinylic-CCO). ¹⁹F NMR (376 MHz, CDCl₃): δ -76.70.

Synthesis of complexes 3a-d. General procedure. A Schlenk tube flame-dried under vacuum was charged with ligands **4a-d** and NaH (3 equiv) under argon. THF was added and the mixture was stirred at RT for 3 h. This solution containing deprotonated ligand was transferred via cannula to another flame-dried Schlenk flask containing (PPh₃)₂Ni(Ph)(Cl). After 1h reaction, the mixture was filtered through a pad of dry celite and solvent was removed under vacuum. Crystals suitable for single crystal X-ray diffraction were obtained by slow diffusion of pentane into toluene solution (1:10 vol) in the freezer (~ -30 °C).

Synthesis of 3a. Ligand **4a** (0.218 g, 0.55 mmol) and NaH (39.8 mg, 1.66 mmol) in 10 mL THF. (PPh₃)₂Ni(Ph)(Cl) (0.384 g, 0.56 mmol). Yield: 0.133 g (33%). ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, J=8Hz, 1H, vinylic CH), 7.39~7.23(m, 15H, PPh₃), 6.91 (t, J=7.6Hz, 1H, Ar-*pH*), 6.80 (d, J=7.6Hz, 2H, Ar-*mH*), 6.52 (d, J=7.6Hz, 2H, Ni-Ph-*oH*), 6.25 (t, J=7.6Hz, 1H, Ni-Ph-*pH*), 6.12 (t, J=7.6Hz, 2H, Ni-Ph-*mH*), 3.60 (septet, J=6.8Hz, 2H, *iPr-CH*), 1.13 (d, J=6.8Hz, 6H, *iPr-CH*₃), 1.01 (d, J=6.8Hz, 6H, *iPr-CH*₃). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 177.9 (q, J=34.4Hz, C=O), 161.6 (vinylic CH), 148.4, 142.5, 140.4, 136.6, 133.8, 130.2, 129.5, 128.2, 125.9, 122.7, 121.8 (Ar-C), 118.0 (q, J=300Hz, CF₃), 116.5(q, J=300Hz, CF₃), 105.4 (vinylic C=CH), 28.6 (*iPr-CH*), 25.3 (*iPr-CH*₃), 22.5 (*iPr-CH*₃). ¹⁹F NMR (376 MHz, CDCl₃): δ -71.59, -71.21. ³¹P {¹H} NMR (162 MHz, CDCl₃): δ 27.26. Anal. Calcd. (C₄₂H₃₈NO₂F₆PNi): C, 63.7; H, 4.83; N, 1.77. Found: C, 63.9; H, 4.86; N, 1.79.

Synthesis of 3b. Ligand **4b** (0.300 g, 0.73 mmol) with NaH (52.8 mg, 2.2 mmol) in 60 mL THF. (PPh₃)₂Ni(Ph)(Cl) (0.510 g, 0.73 mmol). Yield: 0.263 g (49%). ¹H NMR (400 MHz, CDCl₃): δ 7.35~7.19 (m, 15H, PPh₃), 6.97 (t, J=7.6Hz, 1H, Ar-*pH*), 6.87 (d, J=7.6Hz, 2H, Ar-*mH*), 6.37 (d, J=7.6Hz, 2H, Ni-Ph-*oH*), 6.29 (t, J=7.6Hz, 1H, Ni-Ph-*pH*), 6.11 (t, J=7.6Hz, 2H, Ni-Ph-*mH*), 3.34 (septet, J=6.8Hz, 2H, *iPr-CH*), 1.68 (s, 3H, vinylic-CH₃) 1.05 (d, J=6.8Hz, 6H, *iPr-CH*₃), 0.99 (d, J=6.8Hz, 12H, *iPr-CH*₃). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 185.8 (q, J=34Hz, C=O), 161.4 (q, J=34Hz, C=O), 166.4 (vinylic CCH₃), 145.2, 141.4, 139.6, 137.0, 133.8, 130.0, 129.5, 127.9, 126.0, 125.3, 123.4, 121.6 (Ar-C), 118.7 (q, J=300Hz, 2CF₃), 105.6 (vinylic C=CCH₃), 28.6 (*iPr-CH*), 24.0 (allylic-CH₃), 24.3 (*iPr-CH*₃), 23.9 (*iPr-CH*₃). ¹⁹F NMR (376 MHz, CDCl₃): δ -76.57, -70.27. ³¹P {¹H} NMR (162 MHz,

CDCl₃): δ 24.11. Anal. Calcd. (C₄₃H₄₀NO₂F₆PNi): C, 64.0; H, 5.00; N, 1.74. Found: C, 63.8; H, 4.70; N, 1.86.

Synthesis of 3c. Ligand **4c** (0.200 g, 0.64 mmol) with NaH (46.0 mg, 1.92 mmol) in 40 mL THF. (PPh₃)₂Ni(Ph)(Cl) (0.444 g, 0.64 mmol). Yield: 0.222 g (50%). ¹H NMR (400 MHz, CDCl₃): δ 7.33~7.16 (m, 15H, PPh₃), 6.92 (t, J=7.6Hz, 1H, Ar-*pH*), 6.80 (d, J=7.6Hz, 2H, Ar-*mH*), 6.43 (d, J=7.6Hz, 2H, Ni-Ph-*oH*), 6.25 (t, J=7.6Hz, 1H, Ni-Ph-*pH*), 6.07 (t, J=7.6Hz, 2H, Ni-Ph-*mH*), 5.49 (s, 1H, vinylic-CH), 3.36 (septet, J=6.8Hz, 2H, *iPr*-CH), 1.67 (s, 3H, vinylic-CH₃), 1.07 (d, J=6.8Hz, 6H, *iPr*-CH₃), 0.99 (d, J=6.8Hz, 6H, *iPr*-CH₃). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 168.5 (vinylic CCH₃), 158.8 (q, J= 30.4Hz, CO), 146.6, 143.0, 140.0, 137.0, 133.9, 130.8, 129.5, 127.6, 125.2, 124.8, 122.9, 121.0 (Ar-C), 119.0 (q, J=286Hz, CF₃) 94.6 (vinylic-CH), 28.3 (*iPr*-CH), 25.8 (vinylic CH₃), 24.38 (*iPr*-CH₃), 23.80 (*iPr*-CH₃). ¹⁹F NMR (376 MHz, CDCl₃): δ -75.01 (CF₃). ³¹P {¹H} NMR (162 MHz, CDCl₃): δ 22.50. Anal. Calcd. (C₄₁H₄₁NOF₃PNi): C, 69.3; H, 5.82; N, 1.97. Found: C, 69.5; H, 5.88; N, 2.13.

Synthesis of 3d. Ligand **4d** (0.300 g, 0.85 mmol) with NaH (61.2 g, 2.55 mmol) in 50 mL THF. (PPh₃)₂Ni(Ph)(Cl) (0.591 g, 0.85 mmol). Yield 0.430 g (68%). ¹H NMR (400 MHz, CDCl₃): δ 7.36~7.20 (m, 15H, PPh₃), 6.62 (br s, 3H, Ar-H), 6.53 (d, J=7.6Hz, 2H, Ni-Ph *oH*), 6.24 (t, J=7.6Hz, 1H, Ni-Ph *pH*), 6.05 (t, J=7.6Hz, 2H, Ni-Ph *mH*), 2.18 (s, 6H, CH₃), 1.54 (s, 3H, vinylic-CH₃). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 185.7 (q, J=35.2Hz, CO), 165.7 (vinylic CCH₃), 161.9 (q, J=34.4Hz, CO), 147.7 (Ar-CN) 144.5, 136.5, 130.0, 129.9, 128.9, 127.9, 127.8, 125.0, 124.9, 121.4 (Ar-C), 118.4 (q, J=283Hz, CF₃), 116.0 (q, J=293Hz, CF₃), 105.6 (vinylic C=CCH₃), 21.8 (vinylic CH₃), 18.9 (Ar-CH₃). ¹⁹F NMR (376

MHz, CDCl₃): δ -76.7, -70.2. ³¹P {¹H} NMR (162 MHz, CDCl₃): δ 27.6. Anal. Calcd. (C₃₉H₃₂NO₂F₆PNi): C, 62.4; H, 4.30; N, 1.87. Found: C, 64.0; H, 4.95; N, 1.76.

Synthesis of 3e. Ligand **4e** (0.200 g, 0.54 mmol) with NaH (52.3 mg, 2.2 mmol) in 20 mL THF. (PPh₃)₂Ni(Ph)(Cl) (0.3789 g, 0.54 mmol). Yield 0.25 g (60%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.27~7.20 (m, 15H, PPh₃), 6.93 (t, J=7.6Hz, 1H, Ar-*oH*), 6.79 (d, J=7.6Hz, 2H, Ar-*mH*), 6.37~6.30 (m, 3H, Ni-Ph *pH* and *oH*), 6.10 (t, J=7.6Hz, 2H, Ni-Ph *mH*), 5.80 (s, 1H, vinylic *CH*) 3.20 (septet, J=6.8Hz, 2H, *i*Pr *CH*), 1.09 (d, J=6.8Hz, 6H, *i*Pr-CH₃) 1.03 (d, J=6.8Hz, 6H, *i*Pr-CH₃). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 163.3 (q, J=35Hz, CO), 155.6 (q, J=32Hz, vinylic CCF₃), 144.7, 140.6, 139.6, 137.0, 134.2, 130.5, 132.3, 128.1, 126.0, 125.5, 122.9, 122.0 (aromatic-C), 120.0 (q, J=286Hz, COCF₃), 119.1 (q, J=281Hz, vinylic-CF₃) 90.1 (vinylic-CCO), 30.0 (*i*Pr-CH), 28.8 (*i*Pr-CH₃), 24.4 (*i*Pr-CH₃). ¹⁹F NMR (376 MHz, CDCl₃): δ -59.8, -74.6. ³¹P {¹H} NMR (162 MHz, CDCl₃): δ 19.4. Anal. Calcd. (C₄₁H₃₈NOF₆PNi): C, 64.4; H, 5.01; N, 1.83. Found: C, 64.2; H, 5.12; N, 1.77.

Synthesis of 3f. Ligand **4f** (0.100 g, 0.27 mmol) with NaH (19.6 mg, 0.82 mmol) in 20 mL THF. (PPh₃)₂Ni(Ph)(Cl) (0.1894 g, 0.27 mmol). Yield 0.10 g (50%). ¹H NMR (400 MHz, CDCl₃): δ 7.56~7.02 (m, 29H, aromatic H and CHCOCF₃), 6.54 (d, J=7Hz, 2H, Ni-Ph *oH*), 6.32 (t, J=7 Hz, 1H, Ni-Ph *pH*), 6.13 (t, 2H, Ni-Ph *mH*). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 164.1 (vinylic-CN), 161.3 (q, J=33Hz, CO), 149.8, 143.3, 140.4, 137.8, 136.3, 134.3, 131.1, 131.0, 130.6, 130.2, 129.8, 128.0, 127.9, 127.0, 125.4, 124.9 (aromatic-C), 121.6 (q, CF₃), 91.2 (vinylic-CCO). ¹⁹F NMR (376 MHz, CDCl₃): δ -74.6. ³¹P {¹H} NMR (162 MHz, CDCl₃): δ 23.5.

X-ray Crystal Structures. Diffraction data were collected on a Bruker SMART 1K diffractometer, at -100°C. Refinement was carried out with the full-matrix least-squares

method based on F (NCRVAX) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Complete details of X-ray data collection for **4a**, **4d** and **3b** are given in Table 2.3.

Table 2.3. Crystallographic Data Collection Parameters for **4b**, **4d**, and **3b**.

	4b	4d	3b
formula	C ₁₉ H ₂₁ F ₆ NO ₂	C ₁₅ H ₁₃ F ₆ NO ₂	C ₄₃ H ₄₀ F ₆ NNiO ₂ P
mol wt	409.37	353.26	806.47
cryst syst	Triclinic	triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
a (Å)	9.5817(4)	7.7190(12)	13.7411(7)
b (Å)	10.9073(5)	9.4574(15)	15.0842(8)
c (Å)	10.9450(5)	11.3047(17)	18.7681(13)
α (deg)	111.170(3)	75.083(6)	90
β (deg)	108.944(3)	78.299(6)	93.375(3)
γ (deg)	97.324(3)	81.459(7)	90
V(Å ³)	969.28	776.82(21)	3883.4(4)
D _{calc} (mg/m ³)	1.403	1.510	1.38
Scan mode	ω - ψ	ω	φ - ω
μ (mm ⁻¹)	0.13	0.15	0.607
cryst dimens (mm)	0.30x0.30x0.25	0.30x0.30x0.25	0.20x0.20x0.10
2 θ range	5.00-56.00	5.00-56.00	3-25
no. of reflns	25391	17608	22578
no. of unique reflns	4647	3371	9345
No. of obsd data (<i>I</i> > 2.5 σ (<i>I</i>))	3773	2833	4530
No. of refined params	338	269	487
hkl range	(-12,12)(0,14)	(-9,10)(0,12)	(-17,18)(-19,16)
	(-14,13)	(-14,14)	(-24,18)
R _F , %	0.043	0.041	0.046
R _w , %	0.051	0.050	0.049
GOF	2.8941	2.3672	1.134
Z	2	2	4

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CHAPTER THREE

Mechanistic Studies of Ethylene Polymerization by Neutral Trifluoroacetyl-substituted Anilinoenone Ni(II) Complexes

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Abstract: Previously, (N,O)Ni(Ph)(PPh₃) **5a** [(N,O)=2,6-*i*PrC₆H₃NCHC(COCF₃)₂] was shown to catalyze ethylene polymerization in the presence of an activator such as B(C₆F₅)₃. In this section, phosphine-free (N,O)Ni(Ph)(2,4-Lu) complex **7** was synthesized and shown to polymerize ethylene without an activator. Ethylene coordination and insertion with both **5a** and **7** were investigated at low temperatures (0~25 °C) and an insertion barrier of $\Delta G^\ddagger=15.6$ kcal/mol was obtained from bulk polymerization studies at 60 °C for catalyst **7**. This value is comparable to other anilinoenone-based neutral Ni(II) catalysts (16~17 kcal/mol) and intermediate between cationic diimine Ni/Pd catalysts. Copolymerizations of ethylene and vinyltrimethoxysilane (VTMoS) were achieved using **5a** and **7** but at reduced rates compared with ethylene homopolymerization.

Introduction.

Compared with early transition metals, the increased occupancy of *d*-orbitals of late metals have made late metal complexes tolerant of a wide range of polar functionalities.^{1,2} This allows less rigorous purification of olefin feedstocks and solvents, and enables polymerizations to be carried out under diverse conditions, such as emulsion polymerization.^{3,4} More attractively, late metal catalysts have emerged as candidates to enchain polar monomers into polymeric structures.⁵⁻⁷ However, as a result of increased electron densities, late metal alkyl complexes favor β -hydride elimination to form $L_nM(H)(olefin)$ complexes, some of which have been established as intermediates during polymerization⁸⁻¹⁰. The Shell higher olefin process (SHOP) is based on this feature, using neutral five-membered chelated (P,O)Ni(II) catalysts for ethylene oligomerization into mostly linear α -olefins.^{11,12} Modified SHOP catalysts polymerize ethylene into linear PE of low molecular weight (MW) with low productivities.¹³⁻¹⁵

Active cationic α -diimine Ni/Pd catalysts, **1** (Figure 3.1), discovered by our lab¹⁶ rejuvenated the interest to study late metal complexes for ethylene polymerization into high molecular weight polymer. Some diimine Ni catalysts have activities comparable to traditional metallocenes for ethylene polymerization (TOF $\sim 10^6$). The bulky *ortho*-aryl substituents effectively retard chain transfer and promote formation of high MW PEs with branched microstructures^{16,17}. To date, these diimine Ni/Pd catalysts are the only late metal catalysts that polymerize α -olefins, 1,2-disubstituted olefins as well as cyclic olefins.^{16,18-20} Copolymers of ethylene and acrylates were also synthesized using diimine Ni/Pd catalysts, but at a reduced rate compared with ethylene homopolymerization.^{6,21} Mechanistic investigations of diimine Pd-catalyzed ethylene and methyl acrylate copolymerization

revealed that the rearrangement to a stable Pd-O chelate after polar monomer insertion hindered subsequent monomer coordination and consequently affected overall propagation rates.²²

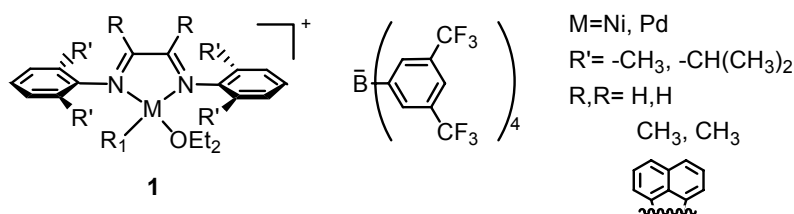


Figure 3.1. Cationic α -diimine Ni/Pd catalysts **1**.

Neutral Ni(II) complexes are expected to have a weaker chelation between Ni-O due to decreased electrophilicity of metal center.^{7,23-27} New generation neutral (N,O)Ni(II) systems such as salicylaldimine-based catalysts **2a**²⁷ and **2b**,^{7,23} anilinetropone-based catalyst **3**,^{25,28} anilinoperinaphthenone-based **4**,²⁶ and anilinoenone-based **5**²⁹ were reported (Figure 3.2). These catalysts are all active for ethylene polymerization into branched structure due to the shared ligand design feature in which their chelate N arms are modeled after the diimine N-aryl groups. Copolymerizations of ethylene and polar monomers, such as norbornenyl acetates, were studied with **2b**,^{7,24} as well as ethylene emulsion polymerizations.^{30,31} To fully understand neutral Ni(II) system and to develop new, more efficient polymerization catalysts, some mechanistic investigations have been performed on neutral (N,O)Ni(II) complexes derived from salicylaldimine³² and anilinetropone^{32,33} ligands. In this chapter, mechanistic studies are continued on anilinoenone-based neutral Ni(II) catalysts by investigating ethylene coordination and insertion, as well as catalyst decomposition. Catalyst **5a**, the most active among **5a-d** for polymerization,²⁹ and its phosphine-free analog **7** are discussed in this

section. Results of copolymerization of ethylene with both polar or nonpolar olefins using catalysts **5a** and **7** will also be presented and discussed at the end of this chapter.

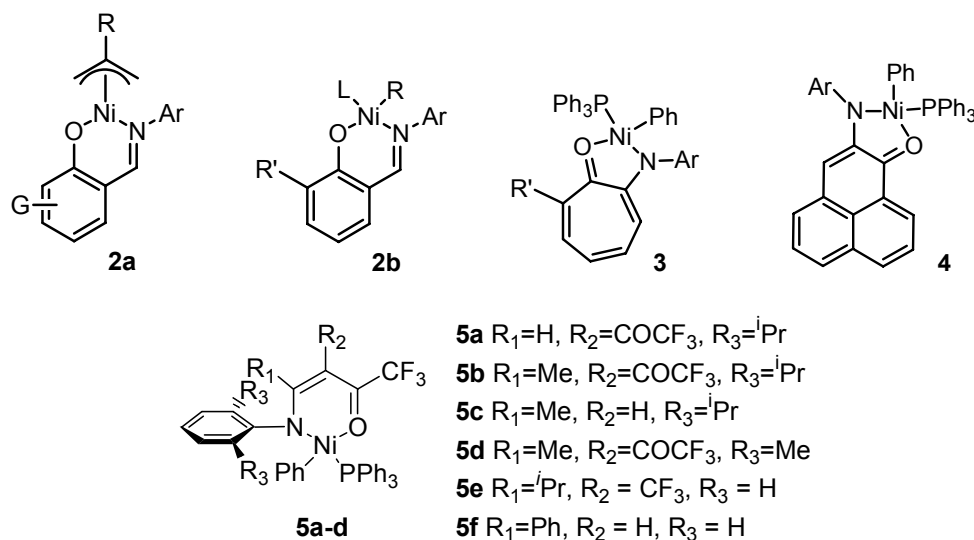
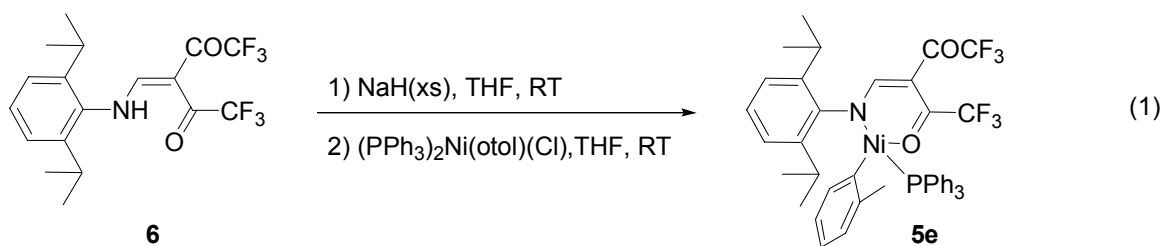


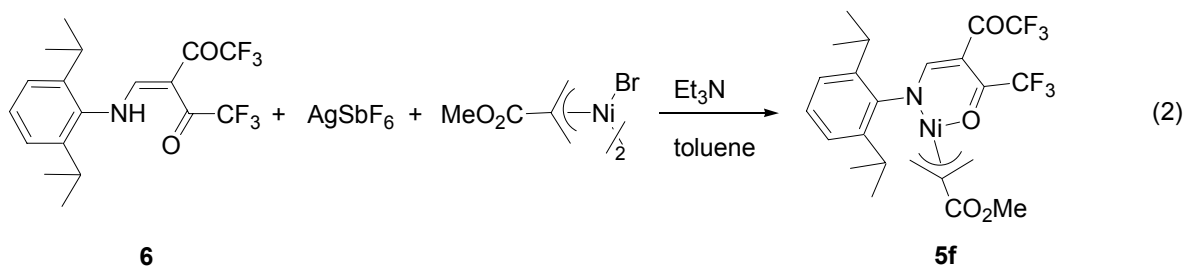
Figure 3.2. New generation bidentate neutral (N,O)Ni(II) catalysts **2-5**.

Results and Discussion

When **5a** was used for polymerization, an activator such as $B(C_6F_5)_3$ was needed to aide PPh_3 displacement by ethylene. It is desirable to use neutral Ni(II) catalysts that do not require activators for ethylene polymerization because activators sometimes restrict the utility of catalysts and deter further mechanistic studies. The first attempt to develop “activation-free” system involved the replacement of PPh_3 by bulky $P(o\text{-tol})_3$ with the expectation that increased steric bulk would facilitate phosphine dissociation. However, the synthesis of intermediate $(P(o\text{-tol})_3)_2Ni(Ph)(Cl)$ was unsuccessful. Instead, (N,O)Ni(*o*-tol)(PPh_3), **5e** was synthesized with the similar idea that the *o*-tolyl group would promote the sluggish first ethylene insertion (eq. 1). When studied for ethylene polymerization, **5e** still required the use of an activator and displayed an activity comparable to **5a** ($TOF \sim 1 \times 10^5$ /h).

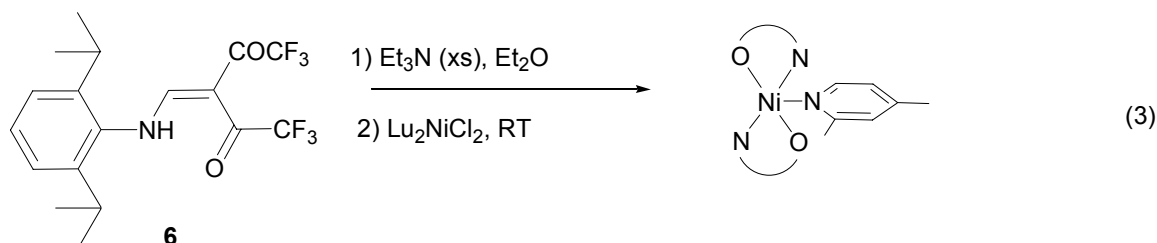


Synthesis of phosphine-free anilinoenone (N,O)Ni(Ph)(Lu) 7. Attention then shifted to the synthesis of phosphine-free anilinoenone based neutral Ni(II) complexes. Anilinoenone-based $\text{Ni}(\eta^2\text{-CH}_2\text{C}(\text{CO}_2\text{Me})\text{CH}_2)$ complex **5f** was synthesized by ligand deprotonation with Et_3N , followed by reaction with $[(\eta^2\text{-CH}_2\text{C}(\text{CO}_2\text{Me})\text{CH}_2)\text{NiBr}]_2$ and AgSbF_6 in toluene (eq 2). However, **5f** showed little activity for ethylene polymerization without an activator.

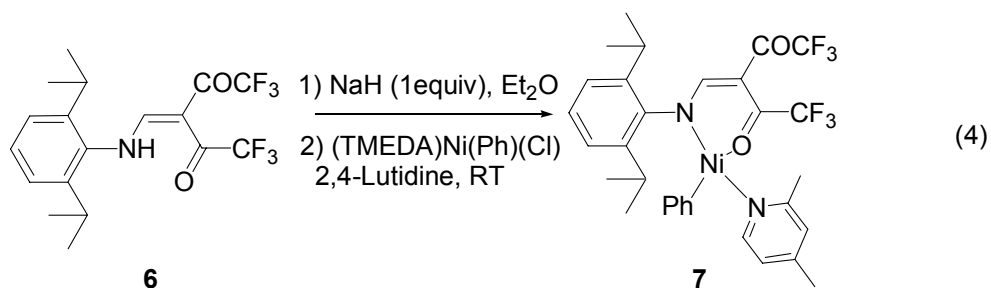


Attempts to synthesize other neutral Ni(II) alkyl complexes with weak donors, following previously reported procedures,^{7,32} yielded only decomposed products. For example, the addition of an Et_2O solution of ligand **6** to $(\text{TMEDA})\text{NiMe}_2$ in the presence of CH_3CN or pyridine gave bis-ligand product $(\text{N,O})_2\text{Ni}$ and unidentified diamagnetic species after workup. Reaction between the salt of deprotonated ligand **6** (using either NaH or Et_3N) and Lu_2NiCl_2 (Lu: 2,4-lutidine) produced paramagnetic $(\text{N,O})_2\text{NiLu}$, **11**, instead of $(\text{N,O})\text{Ni}(\text{Cl})(\text{Lu})$ (eq 3), which may react with an alkylating agent to produce $(\text{N,O})\text{Ni}(\text{R})(\text{Lu})$. $(\text{N,O})_2\text{NiLu}$ has a square pyramidal structure as later confirmed by X-ray diffraction. In this reaction, the Lu_2NiCl_2 starting material is not soluble in THF, while the

desired product (N,O)Ni(Cl)(Lu) is soluble and further reacts with deprotonated ligand **6** to form (N,O)₂NiLu.



A revised phosphine-free complex, (N,O)Ni(Ph)(Lu), **7**, was designed and synthesized by the reaction of deprotonated ligand **6** with (TMEDA)Ni(Ph)(Cl) in the presence of 2 equiv Lu in Et₂O, a less coordinating solvent (eq. 4). A phenyl ligand is used instead of an alkyl ligand to avoid undesired side reactions, such as β -hydride elimination, and to stabilize the complex with a stronger metal-aryl bond. Crystallization by layering the ether solution with pentane and storage in the freezer (-30 °C) for days produced a dark brown crystalline solid suitable for X-ray analysis in 68% yield.



Complex **7** was fully characterized with ¹H, ¹⁹F and ¹³C NMR spectroscopy. ¹H NMR spectroscopy showed that all four methyl groups on the two isopropyl groups are magnetically inequivalent, as shown by four ¹H doublets due to coupling with the methine protons. Fluxional behavior of the coordinated Lu was observed at RT. The two *meta*-¹H

signals of the pyridyl group appear as a very broad singlet at 7.08 ppm due to slow rotation around Ni-N(Lu) bond. The downfield chemical shifts of 2-methyl and 6-H groups of the coordinated Lu at 3.63 ppm and 9.00 ppm indicate the presence of an electrophilic Ni(II) center, compared with uncoordinated Lu at 2.45 ppm and 8.29 ppm, respectively.

The solid structure of **7** was obtained from X-ray diffraction (Figure 3.3). Ni adopts a square planar geometry with C_1 symmetry. The sum of the four angles about Ni is 360.6° . The aromatic rings (two aryl groups and Lu) are perpendicular to the Ni coordination plane to minimize steric interactions. The electron density is delocalized throughout the five-membered chelating ligand, resulting in a longer C(16)-O(15) bond, a shorter C(18)-N(19) bond and a ligand backbone coplanar with the Ni coordination plane.

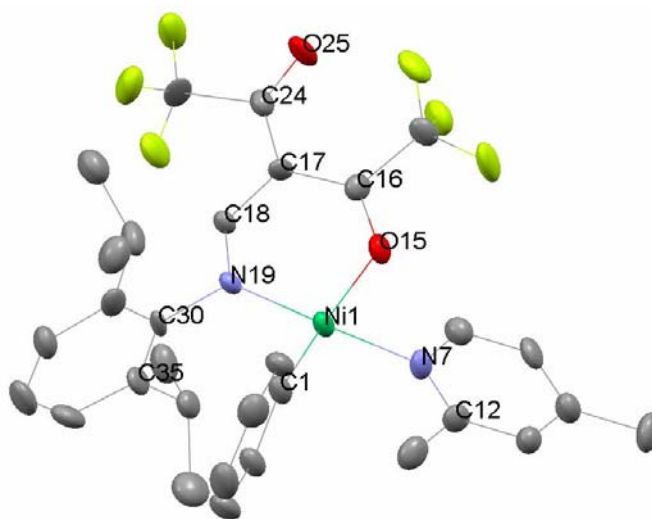
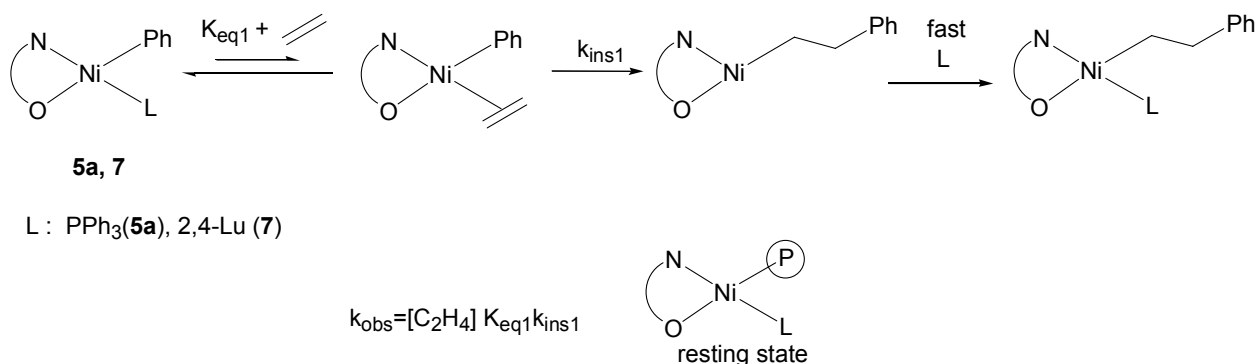


Figure 3.3. Thermal ellipsoid plot of complex **7**, bond distances in Å and angles in degree. Ni(i)-N(7)=1.916(6), Ni(1)-N(19)=1.898(6), Ni(1)-O(15)=1.902(6), Ni(1)-C(1)= 1.879(8), C(16)-O(15)=1.261(10), C(24)-O(25)=1.205(10), C(18)-N(19)=1.301(10), C(30)-N(19)=1.476(10), C(1)-Ni(1)-N(19)=95.6(3), C(1)-Ni(1)-O(15)=167.0(3), N(7)-Ni(1)-C(1)=88.9(3), O(15)-C(16)-C(17)-C(18)=4.0(12), O(15)-Ni(1)-N(7)-C(12)=-93.8(7), C(18)-N(19)-C(30)-C(35)=-82.4(8).

Chain propagation studies. Both **5a** and **7** were studied to compare their ethylene coordination and insertion behaviors. Investigations were initially carried out at lower

temperatures with excess ethylene. Because both PPh_3 and Lu (L) are better donors than ethylene, ethylene insertion occurred only after displacement of L ($K_{\text{eq}1}$). After insertion, the intermediate was rapidly trapped by PPh_3 or Lu to give the observed propagating species (Scheme 3.1). As a result, the observed rate constant of ethylene enchainment (k_{obs}) is a product of $[\text{C}_2\text{H}_4]$, $K_{\text{eq}1}$, and the insertion rate constant $k_{\text{ins}1}$. At the studied temperature (Table 3.1), $(\text{N,O})\text{Ni(R)(L)}$ was observed as the catalyst resting state, and no $(\text{N,O})\text{Ni(H)(L)}$ or $(\text{N,O})\text{Ni(R)(C}_2\text{H}_4)$ species were observed throughout the reactions.



Scheme 3.1. Processes of ethylene insertion into Ni-Ph of **5a** or **7**.

In a low temperature experiment, the reaction progress was monitored over time by ^1H and/or ^{19}F NMR spectroscopy by observing the decrease of **5a** or **7**. Therefore, the k_{obs} calculated was the rate constant for the first ethylene enchainment. For example, the rate constant (k_{obs}) of ethylene insertion into Ni-Ph of **5a** at $10\text{ }^\circ\text{C}$ was calculated using the integral of the methine peaks of **5a** (3.63 ppm) and the integral of the propagating species at 3.85 ppm (Figure 3.4.).

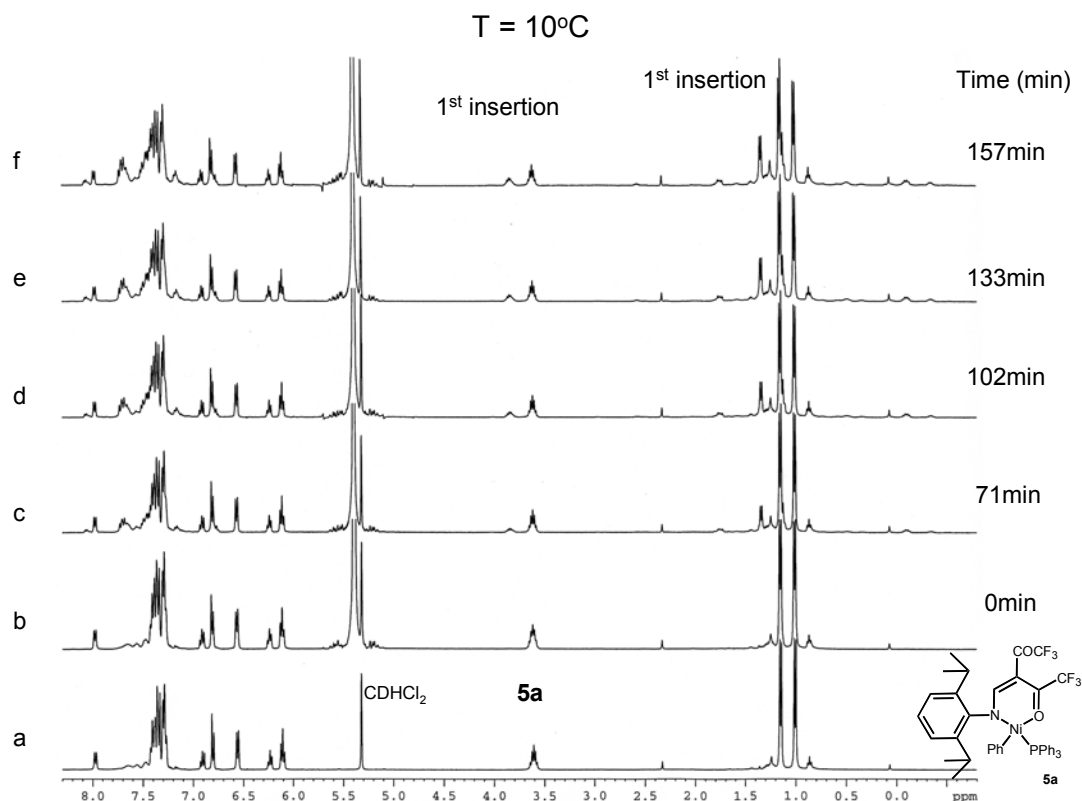


Figure 3. 4. ^1H NMR of ethylene insertion study using **5a** at 10 °C in CD_2Cl_2 . a: Before ethylene injection. b: After ethylene injection. c, d, e, f are spectra taken after 71, 102, 133 and 157 min respectively. The multiplet at 3.63 ppm belongs to methine proton of **5a**, and the multiplet at 3.85 ppm belongs to the propagating species, so does the doublet at 1.3 ppm.

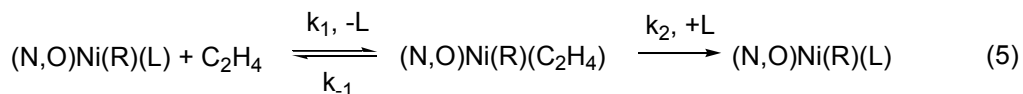
The rate is first order in [**5a**] or [**7**]. The kinetic data for ethylene insertion into Ni-Ph of **5a** or **7** at various temperatures are presented in Table 3.1 (see Experimental section for a typical rate plot). The general trend shows that $k_{\text{obs}}/[\text{C}_2\text{H}_4]$ increases as temperature increases; $k_{\text{obs}}/[\text{C}_2\text{H}_4]$ for ethylene insertion into Ni-Ph of **7** is faster than for **5a** because Lu is a weaker donor than PPh_3 .

Table 3. 1. Kinetic data for ethylene insertion into Ni-Ph of **5a** or **7**.^a

Entry	Cat	T (°C)	[cat] (mM)	C ₂ H ₄ ^b (equiv)	[C ₂ H ₄] (mM)	k _{obs} (x10 ⁵ s ⁻¹)	k _{obs} /[C ₂ H ₄] (x10 ⁴ M ⁻¹ s ⁻¹)
1	5a	7	11.6	23	264	3.3	1.24
2	5a	17	10.1	12	118	11.5	9.75
3	5a	21	12.6	10	124	17.0	13.7
4	7	3	7.8	11	88	1.9	2.2

Ethylene insertion studies were monitored by ¹H and/or ¹⁹F NMR spectroscopy at low temperatures. The amount of injected ethylene was measure by the ¹H NMR spectroscopy.

As stated above, the catalyst resting states are the (N,O)Ni(R)(L) complexes, and no observable (N,O)Ni(R)(C₂H₄) and (N,O)Ni(H)(L) are present in the NMR studies. This makes it impossible to calculate K_{eq1} and k_{ins1} from these low temperature experiments. However by relating the ethylene polymerization to enzyme catalysis, saturation experiments can be conducted at a higher pressure and temperature to extract the intrinsic insertion rate constant k_{ins} (or k₂ in eq 5)



An increase in ethylene pressure results in a shift in the equilibrium toward (N,O)Ni(R)(C₂H₄) (scheme 3.1. and eq 5.). Eventually [Ni(C₂H₄)] reaches saturation at high ethylene pressure and the yield of polymer becomes solely dependent on the rate of ethylene insertion. Saturation experiments were conducted with **7** at 60 °C. Results are summarized in Table 3.2.

Table 3. 2. Saturation study of ethylene polymerization with **7**^a.

Entry	Cat (μmol)	[C ₂ H ₄] psig	t (min)	TON	TOF (/h)	M _n ^b (g/mol)	Br ^c /1000C
1	6.3	100	10	32,000	192,000	23,000	44
2	6.3	200	10	61,000	366,000	24,000	45
3	6.7	400	10	88,000	528,000		
4	7.1	600	10	111,000	666,000		
5	7.5	800	10	124,000	744,000	22,000	45
6	6.3	200	20	100,000	300,000		

a. Polymerizations were conducted in 1 L Parr with 200 mL toluene at 60 °C. Temperature is well-controlled with external cooling water and variation $<\pm 2$ °C. b. M_n, number average molecular weight was measure by ¹H NMR spectroscopy in C₆D₅Br at 100 °C. c. Branching is measured by ¹H NMR at 100 °C in C₆D₅Br.

At 60 °C, **7** exhibits only a small drop in TOF between 10 and 20 min runs (compare entry 2 and 6 of Table 3.2). Therefore at 10 min reaction time TONs reflect true catalyst activity that is not significantly compromised by catalyst decomposition. The small variations in molecular weight at various ethylene pressures imply that chain transfer to monomer controls the polymer MW. An increase in ethylene pressure from 100 psig to 200 psig caused nearly a doubling of the TON. At higher ethylene pressures, i.e. 600 and 800 psig, the rate of increase of the TONs decreases, an indication that the saturation of [Ni(C₂H₄)] was being approached. This trend was analyzed by a Lineweaver-Burk plot of 1/TOF vs. 1/(ethylene pressure) and a straight line was observed (Figure 3.2).

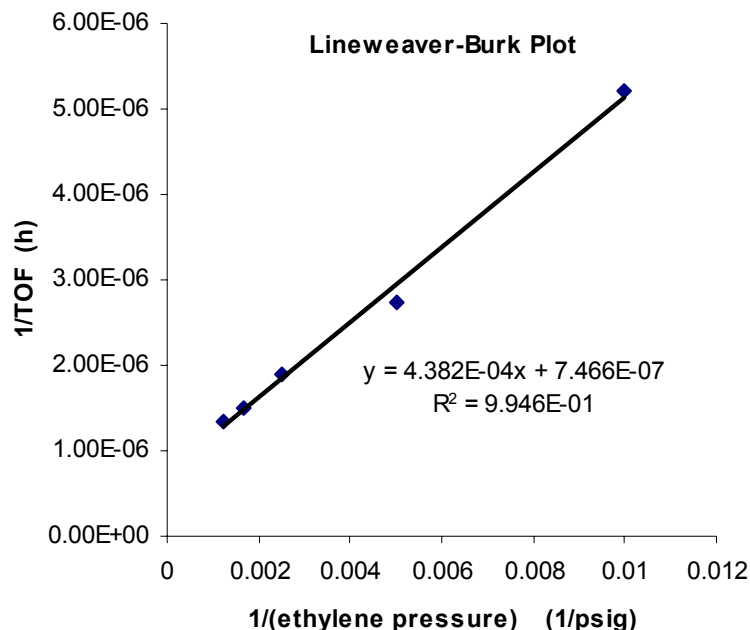


Figure 3. 5. Lineweaver-Burk plot for the saturation study of **7** at various ethylene pressures at 60 °C.

Eq 6 was used for quantitative analysis of this data (K_m is the Michaelis-Menten constant, and the rate constants are related to eq 5). The y intercept of the plot corresponds to $1/TOF_{Max}$, and can be converted into an insertion rate constant of $k_{ins}=372\text{ s}^{-1}$. According to eq 7, the insertion barrier is calculated to be $\Delta G^\ddagger=15.6\text{ kcal/mol}$. This value is comparable to that reported ($\Delta G^\ddagger=16\text{-}17\text{ kcal/mol}$) for the anilinetropone-based neutral Ni(II) system,³² since the experimental errors (sample preparation, polymer collection and temperature control) could lead to a difference as high as 0.5 kcal/mol. The value is also intermediate between cationic diimine Ni(II)^{10,34} ($\Delta G^\ddagger=13.5\sim14.0\text{ kcal/mol}$) and cationic Pd(II)^{9,35} ($\Delta G^\ddagger=18\sim18.5\text{ kcal/mol}$) catalysts. Decreasing the electrophilicity of the metal center from cationic Ni(II) to neutral Ni(II) raises the barrier for ethylene insertion, but insertion still occurs at a faster rate than for cationic Pd(II) catalysts.

$$\frac{1}{TOF} = \frac{K_M}{TOF_{Max}} \times \frac{1}{p_{C_2H_4}} + \frac{1}{TOF_{Max}} \quad K_M = \frac{k_{-1} + k_2}{k_1} \quad (6)$$

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (7)$$

The rate of insertion (k_{ins}) at various temperatures can be also obtained from eq 7. According to Scheme 3.1, both **5a** and **7** should have the same k_{ins} at the same temperature. Therefore K_{eq} at a specific temperature can be derived from $k_{obs} = [C_2H_4]K_{eq}k_{ins}$.

The differences in polymerization productivities and $k_{obs}/[C_2H_4]$ at low temperatures for **5a** and **7** show that PPh_3 is a stronger binding ligand than Lu. To further investigate the difference in binding strength between PPh_3 and Lu, the equilibria shown in eq. 8 were studied using various concentrations of **5a**, **7**, PPh_3 and Lu (Table 3.3). The integrals of **5a**, **7**, free Lu and PPh_3 obtained from 1H , ^{19}F and ^{31}P NMR spectroscopy were used to assess the concentrations of various species. The results implied that the binding affinity for PPh_3 is about 12-16 times stronger than for Lu for anilinoenone based neutral Ni complexes **5a** and **7**. This supports the observation that little polymer was isolated when **5a** was used for polymerization, while **7** gave high productivities at 60 °C.

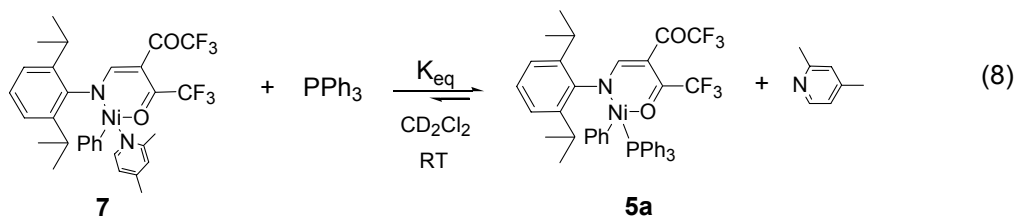
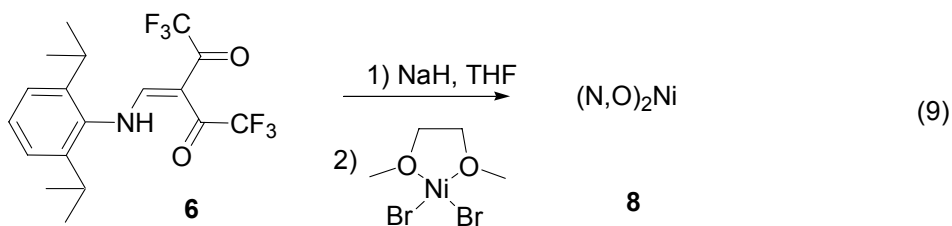


Table 3. 3 The equilibrium between **5a** and **7**.

7 (μmol)	PPh_3 (μmol)	Lu (μmol)	K_{eq}
11.0	14.9	11.0	16
21.5	11.4	0	13
22.6	62.1	0	12

Reactions were carried out in CD_2Cl_2 at 22°C .

Catalyst decomposition study. At later stages of low temperature studies of ethylene insertion with **5a**, a new septet at 4.05 ppm appeared in the ^1H NMR spectrum and corresponded to peaks at -70.3 ppm (br s) and -73.2 ppm in the ^{19}F NMR spectrum. These peaks were later found to belong to $(\text{N},\text{O})_2\text{Ni}$, **8**, which was independently synthesized via reaction of deprotonated ligand **6** with 0.5 equiv $(\text{DME})\text{NiBr}_2$ (eq. 9). $(\text{N},\text{O})_2\text{Ni}$ was characterized by ^1H and ^{19}F NMR and X-ray analysis (Figure 3.6.). In the solid state, Ni has adopted a perfectly square planar coordination. Coordinated oxygens are *trans* to each other, leading to shorter Ni-O bonds (1.8513(8) Å) and elongated Ni-N bonds (1.9145(10) Å) compared to **7** (1.902(6) Å, 1.898(6) Å, respectively) where the oxygen is *trans* to the phenyl group and the nitrogen is *trans* to Lu. The ligand backbone is again coplanar with the Ni coordination plane as a result of delocalized electron density. $(\text{N},\text{O})_2\text{Ni}$ was the only Ni species observed at the end of the reaction when **5a** was completely consumed.



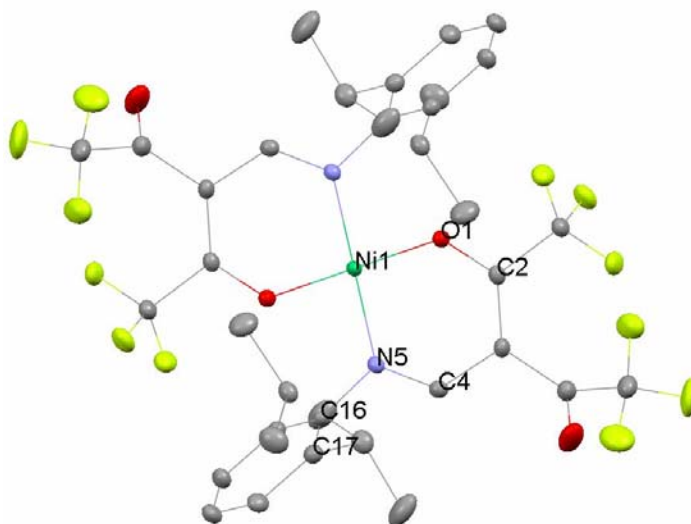


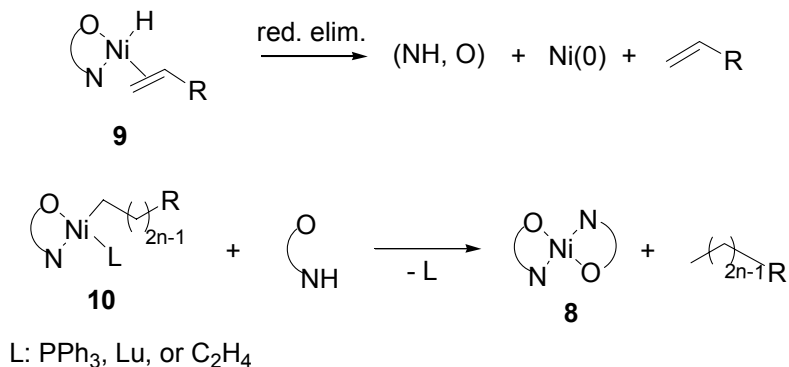
Figure 3. 6. Thermal ellipsoid plot of bis-ligand complex **8**, bond distance in Å and angle in degree. Ni(1)-O(1)=1.8513(8), Ni(1)-N(5)=1.9145(10), O(1)-C(2)=1.2814(14), O(1)-Ni(1)-N(5)=88.21(4), O(1)-Ni(1)-O(1)=180.00(6), C(4)-N(5)-C(16)-C(17)=-83.76(13).

When **7** was investigated for low temperature ethylene insertion studies, a paramagnetic species was formed as seen by ^1H and ^{19}F NMR spectroscopy. Because the reaction between Lu_2NiCl_2 and deprotonated ligand **6** yielded a paramagnetic square pyramidal $(\text{N},\text{O})_2\text{NiLu}$ complex **11**, as mentioned earlier, it seems likely that this same compound was formed in the insertion study with **7**. After quenching a prolonged ethylene insertion run with **7** by MeOH, $(\text{N},\text{O})_2\text{Ni}$ **8** was observed by ^1H and ^{19}F NMR spectroscopy following the removal of volatiles and redissolving the residue in CDCl_3 . This was an indirect confirmation that the initial paramagnetic species was $(\text{N},\text{O})_2\text{NiLu}$. $(\text{N},\text{O})_2\text{Ni}$ **8** is stable in protic solvents at RT. However, the filtrate collected after bulk polymerizations with **7** and **5a** at higher temperature gave only free ligand **6**, implying $(\text{N},\text{O})_2\text{Ni}$ **8** is not stable at elevated temperatures.

Besides the bis-ligand Ni complexes, free ligand **6**, styrene, $\text{PhCH}_2\text{CH}_2\text{R}$ and olefins (both internal and terminal) were seen by ^1H NMR at the end of the insertion reactions with

5a and **7**. These insertion products indicate that the first ethylene insertion into the Ni-Ph bond was slow, while β -H elimination was facile and competed with subsequent ethylene insertion.

Both unimolecular and bimolecular reactions are plausible for the decomposition of **5a** and **7** during polymerization (Scheme 3.2.). After facile β -H elimination, the transient intermediate (N,O)Ni(H)(olefin) **9** can reductively eliminate free ligand **6**. The liberated free ligand can protonate species **10** since the N-H is quite acidic as verified by the highly downfield chemical shift at ~ 12 ppm in the ^1H NMR spectrum.²⁹ Neither **9** nor **10** were observed during the studies due to fast trapping by PPh_3 or Lu.



Scheme 3.2. Proposed catalyst decomposition pathways.

The thermal stability of **5a** was investigated by heating **5a** in toluene- d_8 at elevated temperature (50°C) and monitoring changes via ^1H , ^{19}F , and ^{31}P NMR spectroscopy. **5a** was quite stable at 50°C and spectra remained unchanged for 36 h. However, heating **5a** for 90 h eventually led to the formation of small amounts of free ligand and unknown paramagnetic species, though the major Ni(II) species was still **5a**.

When heating **5a** and free ligand **6** in toluene- d_8 at 80 °C, no immediate reaction was observed. After 18 h unknown paramagnetic species appeared, and though the paramagnetic species grew, the major species in the solution after 30 h were still **5a** and free ligand **6**. These two high temperature experiments indicated that the Ni-Ph bond in **5a** is quite strong and resists protonation by free ligand **6**. Decomposition product **8** should not arise from reaction between **5a** and free ligand **6**, but rather from the reaction of (N,O)Ni(L)(alkyl) **10** with **6** as proposed in Scheme 3.2.

Study of the influence of $B(C_6F_5)_3$ on the polymerization activity of **5a.** In previous bulk polymerizations with catalyst **5a**, an activator such as $Ni(COD)_2$ or $B(C_6F_5)_3$ was used to promote propagation, presumably by sequestering PPh_3 (Scheme 3.1). In a separate NMR experiment, the reaction between $B(C_6F_5)_3$ and PPh_3 produced a white adduct $(C_6F_5)_3B \cdot PPh_3$ that was insoluble in CD_2Cl_2 . However, when 1-4 equiv $B(C_6F_5)_3$ was added to **5a** in CD_2Cl_2 at RT, no white solid was observed but ^{31}P NMR supported the formation of a small amount of $(C_6F_5)_3B \cdot PPh_3$. 1H and ^{19}F NMR suggested that a small amount of $B(C_6F_5)_3$ coordinated to the free carbonyl oxygen of catalyst **5a**. The resonance for the vinylic H of **5a** shifted downfield by 0.11 ppm after the addition of $B(C_6F_5)_3$ (from 8.19 ppm to 8.30 ppm in toluene- d_8) and the fluorine peak assigned to free $COCF_3$ broadened. Increasing the $B(C_6F_5)_3$ loading did not increase the formation of the adduct. The increased electrophilicity of the Ni(II) center due to the coordination between $B(C_6F_5)_3$ and acyl carbonyl group, as well as the phosphine scavenger ability of $B(C_6F_5)_3$ has led the catalyst derived from **5a** and 4 equiv of $B(C_6F_5)_3$ to exhibit higher productivities for ethylene polymerization than **7** at 60 °C (TOF of 506,000,²⁹ and entry 2, Table 3.1, TOF of ~366,000 respectively). Attempts to study ethylene insertion with **5a** plus 4 equiv of $B(C_6F_5)_3$ by 1H

NMR spectroscopy failed because broad peaks and no identifiable propagating species were observed by both ^1H and ^{19}F NMR spectroscopy.

Ethylene copolymerization and 1-hexene oligomerization. As mentioned earlier in the Introduction, one major purpose for studying neutral Ni(II) catalysts is to apply them in copolymerization, especially with polar vinyl comonomers. Copolymerizations of ethylene with 1-hexene and vinyltrimethoxysilane (VTMoS) were carried out with **5a** in the presence of an activator or with **7** alone. The copolymer of ethylene and VTMoS has many commercial applications, such as for insulation and adhesion purposes. Before crosslinking, it is a thermoplastic material and easily processed. Recently, the DuPont group has productively copolymerized ethylene and vinylalkoxysilanes using cationic diimine Ni(II) catalysts.³⁶

Table 3.4 lists results of copolymerizing ethylene and polar or nonpolar olefins using **5a** with an activator. Because $\text{B}(\text{C}_6\text{F}_5)_3$ can coordinate to the polar functionalities and affect the copolymerization, $\text{Ni}(\text{COD})_2$ was used for copolymerization involving VTMoS and norbornenyl (NB) acetate comonomers. $\text{B}(\text{C}_6\text{F}_5)_3$ was only used when 1-hexene was the comonomer. In entries 1-3, an increase in the VTMoS loading led to an increase in the incorporation molar ratio of VTMoS. However, catalyst activities decreased under these conditions and were lower than ethylene homopolymerization. Reduced activities were also observed for copolymerizations of ethylene and 1-hexene or NB acetate. The exact amount of 1-hexene incorporated in the polymer was difficult to estimate due to the complications from chain walking and the similar backbone structures of polyethylene and poly(1-hexene). A broad ^1H NMR resonance at high field for the copolymer of ethylene and NB acetate also deterred further calculations of both the NB incorporation ratio and TON.

Table 3.4. Results of ethylene copolymerization using **5a** with an activator^a.

Entry	Comono.	Cat. (μmol)	Cocat. (μmol)	Comono. ^b mmol/(mL)	Yield (g)	T _m ^c	Comono. (%mol)	M _n ^d	TON	Br /1000C
1	VTMS	6.0	24.0	13.1/(2)	3.75	93/82	1.0		25,000	95
2		6.0	24.0	32.6/(5)	1.65	90/77	1.8		10,000	53
3		6.3	25.3	65.3/(10)	1.07	85/73	2.7		6,000	51
4	1-Hex	1.2	4.8	16.0/(2)	7.10	88/115		11,000	--	58
5		1.2	4.8	40.0/(5)	6.20	87/113		4400	--	53
6		1.2	4.8	80.0/(10)	3.34	84/110		3900	--	64
7	NB	5.9	23.7	20.6/(3)	0.78	78/112	--	--	--	--

a. All copolymerizations were carried out in toluene+comonomer (total vol. 80 mL) with 200 psig ethylene in 300 mL Parr for 1 h at 60 °C. b. Ni(COD)₂ was used as the cocatalyst in all runs except for 1-hexene when B(C₆F₅)₃ was used. c. T_m, the melting temperature was measured by DSC. d. M_n, number average molecular weight was measure by ¹H NMR spectroscopy at 100 °C in C₆D₅Br.

Similar results for the copolymerization of ethylene and VTMoS were observed when **7** was used (Table 3.5). VTMoS was incorporated into the polymer, but catalytic productivities decreased.

Table 3.5. Results for copolymerizations of ethylene and VTMoS using **7**.

Entry	Cat. (μmol)	Comono. mmol/(mL)	Yield (g)	Comonom (%mol)	TON	Br /1000C
1	11.9	13.1/(2)	3.9	0.2	12,000	47

Copolymerizations were carried out in 1 L Parr with 198 mL toluene and 2 mL vinyltrimethoxysilane. Temperature is well-controlled between 59-62 °C. Ethylene pressure is 200 psig.

Oligomerizations of 1-hexene were also studied using catalyst **5a** and B(C₆F₅)₃ (Table 3.6). Again, lower catalytic activities compared to ethylene homopolymerization were observed, and the average number of 1-hexene monomers enchainned (average degree of polymerization, DP) was only 10. The lower than expected branching (166 branches/1000C) indicated minor chain walking of the Ni catalyst. GC results showed that **5a** isomerized 1-hexene into internal 2- or 3-hexenes.

Table 3.6 Results of 1-hexene oligomerization using **5a**.

Entry	Cat. (μmol)	Cocat. (μmol)	1-Hexene mmol/(mL)	t (h)	Yield (g)	Conv %	TOF (/h)	Mn GPC	PDI	Mn NMR	Br /1000C
1	7.6	30.3	1.89/(0.24)	1	0.12	73	180	1200/ 4700	1.1/ 1.0	--	--
2	7.6	30.3	1.89/(0.24)	2	0.14	86	110	800	1.4	--	--
3	7.6	30.3	7.6/(0.95)	3	0.21	33	110	1700	1.3	860	131
4	6.2	24.7	7.6/(0.95)	6	0.28	44	90	1500	1.2	900	114
5	7.6	30.3	7.6/(0.95)	20	0.45	70	40	1000	2.2	830	132

Reactions were carried out in sealed Kontes flask with $\text{B}(\text{C}_6\text{F}_5)_3$ (4equiv), 5 mL toluene and a magnetic stirrer bar at 60 °C. Isomerization of 1-hexene to 2-, 3-hexene is observed by GC.

Conclusions.

Mechanistic investigations of ethylene insertion and coordination and decomposition of catalysts **5a** and **7** were studied. Bis-ligand Ni(II) complexes were formed as decomposition products from ethylene polymerization. The measured ethylene insertion barrier of $\Delta G^\ddagger=15.6$ kcal/mol is comparable to that observed for neutral anilinetropone (N,O)Ni(II) catalysts, and is intermediate between cationic diimine Ni(II) and Pd(II) catalysts. Copolymerizations of ethylene and vinyltrimethoxysilane (VTMoS) were possible with **5a** and **7**, but catalysts displayed lower activities compared with ethylene homopolymerization. $\text{B}(\text{C}_6\text{F}_5)_3$ was found not only to act as a phosphine scavenger, but also to enhance the electrophilicity of Ni(II) by altering the ligand electronic property which led to further increase in the ethylene polymerization productivity.

Experimental Section.

General Considerations. All manipulations of air- and/or water sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Solid organometallic compounds were transferred in an argon-filled drybox and, unless stated otherwise, were stored at room temperature. The ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra were acquired using Bruker 400 or 500 MHz spectrometers. Chemical shifts were reported in δ units, parts per million (ppm) and referenced against residual deuterated solvent peaks (^1H , ^{13}C) or external standards CF_3COOH (^{19}F) and H_3PO_4 (^{31}P). Flash chromatography was performed using 60 Å silica gel (SAI). 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. All calibration curves were established with polystyrene standards and universal calibration was applied using Mark-Houwink constants for polyethylene ($k = 4.34 \times 10^{-4}$; $\alpha = 0.724$). Thermal analysis of polymers was performed on a Seiko Instruments DSC220C differential scanning calorimeter. A Hewlett-Packard 6850 GC with a flame ionization detector on a 25 m x 0.25 μm DB-1 capillary column (J&W scientific) and a HP 3396 Series III integrator were used for gas chromatography analysis. Elemental analyses were performed by Altantic Microlab Inc. of Norcross, GA.

Materials. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through alumina columns under an argon or nitrogen atmosphere. NMR solvents were vacuum-transferred from CaH_2 , degassed by repeated freeze-pump-thaw cycles and stored over 4 Å molecular sieves. $\text{B}(\text{C}_6\text{F}_5)_3$, PhCl , 2,4-lutidine,

NaH, Et₃N and Ni(COD)₂ were used as received. Polymer-grade ethylene was used as received for bulk polymerizations and NMR experiments. The following starting materials were prepared according to literature procedures: Lu₂NiCl₂³⁷, [(η²-CH₂C(CO₂Me)CH₂)NiBr]₂,²⁷ (TMEDA)Ni(Ph)(Cl),³⁸ (TMEDA)NiMe₂,³⁹ and (PPh₃)₂Ni(o-tol)(Cl).⁴⁰ Yields refer to isolated yields of compounds of greater than 95% purity as estimated by ¹H NMR analysis and elemental analysis.

Analysis of Polymer Branching by ¹H NMR Spectroscopy. ¹H NMR spectra were recorded in either CDCl₃ at room temperature or C₆D₅Br at 100 °C. Assignment of peaks and calculation of polymer branching were carried out following the previously published method.⁴¹

Analysis of Vinyltrimethoxysilane Incorporation by ¹H NMR spectroscopy. ¹H NMR spectra were recorded in C₆D₅Br at 100 °C. The integrals of the methoxy signal and all other protons (alkyl and olefinic regions) were used to determine the incorporation ratio by the

following formula:
$$n_{C_2H_4} = \frac{H_{alkyl} + H_{olefinic} - 3 \times \frac{H_{MeO}}{9}}{4} \quad \text{and} \quad VTMoS\% = \frac{\frac{H_{MeO}}{9}}{n_{C_2H_4} + \frac{H_{MeO}}{9}} .$$

(H_{alkyl}: the integral of H in the alkyl region; H_{olefinic}: the integral of H in the olefinic region; H_{MeO}: the integral of H belonging to VTMoS fraction.)

General Polymerization/Oligomerization Procedure. Ethylene polymerizations were carried out in a 1 L Parr reactor equipped with an automatic heating and cooling controller. The reactor was initially heated at 120 °C under vacuum for 1-2 h, then backfilled with argon and cooled to the desired polymerization temperature. After 190 mL toluene was injected, the reactor was purged with ethylene (3x100 psig). A solution of catalyst in 10 mL

toluene was added to the vented reactor via cannula. The reactor was sealed and pressurized to the desired polymerization pressure with the stirring motor engaged. After the desired reaction time was reached, the ethylene pressure was released, and the reaction was quenched with 250 mL MeOH. The polymer was collected by suction filtration and dried in a vacuum oven overnight at 80 °C. Ethylene copolymerization using **7** was carried out in 1L Parr following a similar procedure for homopolymerization, except (190-x) mL toluene and x mL of comonomer were injected into the reactor before purging the reactor.

Ethylene copolymerizations with **5a** were carried out in a 300 mL Parr reactor equipped with a controllable heating mantle. A similar procedure was used as for 1 L Parr polymerizations, except that the pre-injected toluene volume was (70-x) mL and the amount of comonomer used was x mL. The catalyst solution was prepared by dissolving both **5a** and B(C₆F₅)₃ in 10 mL of toluene at RT or **5a** and Ni(COD)₂ in 10 mL of toluene at -20 °C.

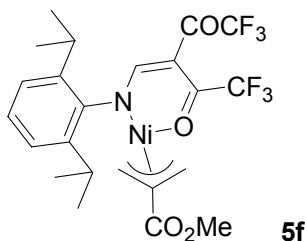
1-Hexene oligomerization was carried out in a Kontes flask fitted with a magnetic stir bar. The flask was charged with **5a** and B(C₆F₅)₃ in the glovebox and the solids were dissolved in toluene (5 mL) at RT. After injection of 1-hexene, the flask was sealed and placed in a pre-heated oil bath at 60 °C with stirring on. When the desired time was reached, the reaction was quenched by MeOH (20 mL). An aliquot was taken for GC analysis. The solution was filtered through a pad of celite. After the removal of volatile, the residue was dried in a vacuum oven at 80 °C overnight and weighed to give the conversion.

Synthesis of Ni complexes.

Synthesis of 5e. A flame-dried Schlenk flask was charged with ligand **6** (56.7 mg, 0.14 mmol) and NaH (10.4 mg, 0.43 mmol) under argon. THF (5 mL) was added and deprotonation proceeded at RT for 3 h. The suspension was cannula transferred to another

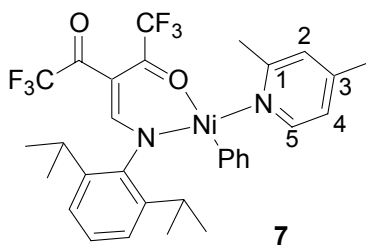
flask containing $(\text{PPh}_3)_2\text{Ni}(\text{o-tol})(\text{Cl})$ (0.1019 g, 0.14 mmol) in 5 mL THF. The reaction mixture was filtered through a pad of dry celite after 1 h at RT. After the removal of volatile compounds, the residue was crystallized from toluene/pentane at $-30\text{ }^\circ\text{C}$. Yield: 39 mg (34%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.98 (d, $J=\text{Hz}$, 1H), 7.61~7.20 (aromatic H, 22H), 4.43, 2.70, 2.66, Anal. Cald. $(\text{C}_{43}\text{H}_{40}\text{F}_6\text{NNiO}_2\text{P})$: C, 64.04; H, 5.00; N, 1.74. Found: C, 64.61; H, 5.12; N, 1.48.

Synthesis of 5f. A flame-dried Schlenk flask was charged with ligand **6** (0.100 g, 0.25 mmol) and $[(\eta^2\text{-CH}_2\text{C}(\text{CO}_2\text{Me})\text{CH}_2)\text{NiBr}]_2$ (60.2 mg, 0.13 mmol) in the glovebox. Toluene (5 mL) was added to the mixture, quickly followed by Et_3N (0.35 mL). The solution was stirred at RT for 40 min then cannula-transferred to another flask containing AgSbF_6 . The suspension was stirred at RT for 15 min, then chilled to $-20\text{ }^\circ\text{C}$ without stirring for 10 min. The mixture was filtered through a pad of dry celite at RT. After the removal of volatiles, the residue was crystallized from toluene/pentane at $-30\text{ }^\circ\text{C}$. Yield: 50.0 mg (35%). ^1H NMR (CD_2Cl_2 , 500 MHz): 7.89 (s, vinylic-H, 1H), 4.07 (d, $J=2.5\text{ Hz}$, H_4 , 1H), 3.87 (s, CH_3 , 3H), 3.71 (septet, $J=7\text{ Hz}$, $^i\text{PrCH}$, 1H), 3.10 (s, H_3 , 1H), 2.24 (d, $J=0.5\text{ Hz}$, H_2 , 1H), 1.73 (d, $J=1\text{ Hz}$, H_1 , 1H), 1.36 (d, $J=6.5\text{ Hz}$, $^i\text{PrCH}_3$, 3H), 1.28 (d, $J=6.5\text{ Hz}$, $^i\text{PrCH}_3$, 3H), 1.13 (d, $J=6.5\text{ Hz}$, $^i\text{PrCH}_3$, 3H), 0.97 (d, $J=6.5\text{ Hz}$, $^i\text{PrCH}_3$, 3H).



[(2, 6-Diisopropyl)anilinoenone]Ni(2,4-lutidine)(Ph) 7. A flame-dried Schlenk flask was charged with ligand **6** (0.200 g, 0.51 mmol) and NaH (24.3 mg, 1.0 mmol) under argon. Ether (20 mL) was added and deprotonation proceeded at RT for 3 h. The solution

was cannula-transferred to another flask containing (TMEDA)Ni(Ph)(Cl) in ether (20 mL), followed by addition of 2,4-lutidine (0.12 mL, 1.0 mmol). The reaction proceeded at RT for 1 h. The reaction mixture was filtered through a pad of dry celite. After the removal of volatiles, the residue was crystallized from ether and pentane and stored in the freezer (-30 °C). Yield: 0.218 g (68%). ¹H NMR (CD₂Cl₂, 400 MHz): δ 9.00 (d, J=6Hz, *H*₅, 1H); 7.68 (s, vinylic-*H*, 1H); 7.07 (br s, *H*₄ and *H*₂, 2H); 6.96-6.79 (m, Ar-*H* and Ph-*mH*, 5H); 6.42-6.35 (m, Ph-*o* and *p-H*, 3H); 4.00 (septet, J=6.8Hz, ⁱPrCH, 1H); 3.71 (septet, J=6.8Hz, ⁱPrCH, 1H); 3.63 (s, C₁CH₃, 3H); 2.24 (s, C₃CH₃, 3H); 1.38 (d, J=6.8Hz, ⁱPrCH₃, 3H); 1.22 (d, J=6.8Hz, ⁱPrCH₃, 3H); 1.04 (d, J=6.8Hz, ⁱPrCH₃, 3H); 1.00 (d, J=6.8Hz, ⁱPrCH₃, 3H). ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ 177.7 (q, J=34Hz, CO); 170.0 (q, J=36Hz, CO); 163.3, 159.2, 149.9, 149.5, 145.2, 140.8, 135.7 (br s, C₄ and C₂ on 2,4-lutidine); 126.7, 126.4, 125.2, 123.3, 123.1, 123.0, 122.2, 118.7 (q, J=284Hz, CF₃); 117.2 (q, J=292Hz, CF₃); 28.9, 28.7, 25.8, 25.5, 25.4, 22.7, 22.6, 20.9. ¹⁹F NMR (CD₂Cl₂, 376 MHz): δ -71.6, -71.9. Anal. Cald. (C₃₁H₃₂F₆N₂NiO₂): C, 58.42; H, 5.06; N, 4.40. Found: C, 58.35; H, 5.06; N, 4.14.



Bis(2,6-diisopropylanilinoenone)Ni, 8. A flame-dried Schlenk flask was charged with ligand **6** (50.0 mg, 0.13 mmol) and NaH (3.1 mg, 0.13 mmol) under argon. THF (5 mL) was added and deprotonation proceeded at RT for 1 h, then the mixture was cannula-transferred to another flask containing (DME)NiBr₂ (20.0 mg, 0.07 mmol) in THF (5 mL). After 1 h at RT, the mixture was filtered through a pad of dry celite and volatiles were removed. The residue was crystallized from toluene/pentane at -30 °C. Yield: 20.1 mg (40%).

^1H NMR (CDCl_3 , 400 MHz): δ 7.31 (s, vinylic-*H*, 2H), 7.29 (t, $J=8\text{Hz}$, Ar-*pH*, 2H), 7.14 (d, $J=8\text{Hz}$, Ar-*mH*, 4H), 4.12 (septet, $J=6.8\text{Hz}$, $^i\text{PrCH}$, 4H), 1.47 (d, $J=6.8\text{Hz}$, $^i\text{PrCH}_3$, 12H), 1.20 (d, $J=6.8\text{Hz}$, $^i\text{PrCH}_3$, 12H). ^{19}F NMR (CDCl_3 , 376 MHz): δ -68.8, -71.50. Anal. Calcd. ($\text{C}_{36}\text{H}_{36}\text{F}_{12}\text{N}_2\text{NiO}_4$) C, 51.03; H, 4.28; N, 3.31. Found: C, 50.79; H, 4.25; N, 3.31.

X-ray crystal structures. Diffraction data was collected on a Bruker SMART 1K diffractometer, at $-100\text{ }^\circ\text{C}$. Refinement was carried out with the full-matrix least-squares method on F (NCRVAX) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atoms. Complete details of X-ray data collection for **7** and **8** are given in Table 3.7.

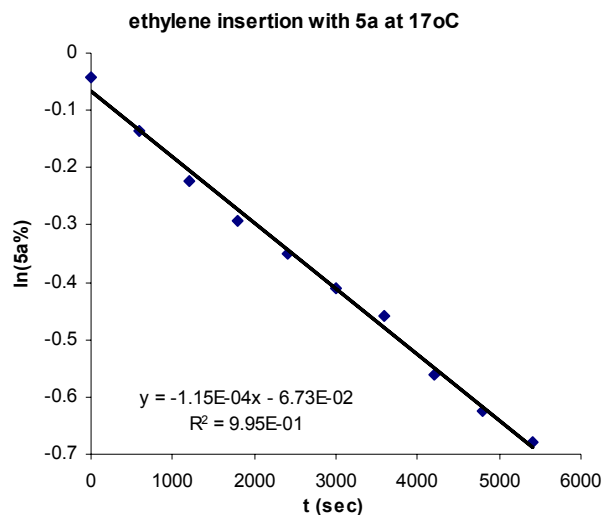
Table 3.7. Crystallographic Data Collection Parameters for **7** and **8**

	7	8
Formula	C ₃₁ H ₃₁ F ₆ N ₂ NiO ₂	C ₃₆ H ₃₆ F ₁₂ N ₂ NiO ₄
mol wt	636.29	847.38
Cryst syst	Triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
a (Å)	10.5682(6)	9.5184(7)
b (Å)	11.4422(8)	10.9055(8)
c (Å)	12.3889(8)	11.0898(8)
α (deg)	94.911(4)	99.053(4)
β (deg)	97.499(5)	112.247(4)
γ (deg)	94.937(5)	111.829(4)
V(Å ³)	1472.66(16)	927.62(12)
D _{calc} (mg/m ³)	1.435	1.517
Scan mode	ω and ψ	ω and ψ
μ (mm ⁻¹)	0.728	0.625
Cryst dims (mm)	0.20x0.15x0.05	0.20x0.15x0.05
2 θ range	1.95-22.50	2.14-28.00
no. of reflns	7605	19242
no. of unique reflns	3849	4456
No. of obsd data (I> 2.5 σ (I))	3849	4456
No. of refined params	386	322
hkl range	(-11,11)(-11,12)(-13,13)	(-12,12)(1-4,14)(-14,14)
R _F , %	0.1259	0.0282
R _w , %	0.2684	0.0672
GOF	0.967	1.056
Z	2	1

General Procedure for Ethylene Insertion Studies with (N,O)Ni(Ph)(L), L: PPh₃ (5a) and 2,4-lutidine (7). A screw-capped NMR tube was charged with either **5a** or **7** dissolved in CD₂Cl₂ (0.6 mL) under Ar in a glovebox. The sealed tube was cooled to -80 °C in an isopropanol and dry ice bath. Ethylene (5 mL) was injected into the tube using a gas-tight syringe at RT. The sample was warmed up to the desired temperature inside the NMR probe, and the insertion was monitored by ¹H and/or ¹⁹F NMR spectroscopy. For **5a**, the original peaks were 3.62 ppm(¹H), -71.5 ppm and -71.7 ppm(¹⁹F); the propagating species had chemical shifts at 3.85 ppm(¹H), -71.3 ppm and -71.8 ppm(¹⁹F). For **7**, the original peaks in use had chemical shifts at 2.22 ppm(¹H), -71.7 ppm and -71.9 ppm(¹⁹F); the propagating products had peaks at 2.43 ppm(¹H), -71.5 ppm and -72.1 ppm(¹⁹F). The rate of insertion was calculated by plotting ln(mole fraction of starting material) vs. time.

Example: Table 3.1 entry 2, ethylene insertion into Ni-Ph of **5a** at 17 °C by ¹H NMR.

t(sec)	Mole fraction of 5a	ln(mole fraction of 5a)
0	0.958	-0.04291
600	0.873	-0.13582
1200	0.799	-0.22439
1800	0.747	-0.29169
2400	0.704	-0.35098
3000	0.663	-0.41098
3600	0.633	-0.45728
4200	0.57	-0.56212
4800	0.536	-0.62362
5400	0.507	-0.67924



General Procedure for Studies of the equilibrium between 5a, 7, PPh₃ and 2,4-lutidine. A screw-capped NMR tube was charged with specified amounts of **7** and PPh₃ under argon in the glovebox. CD₂Cl₂ (0.6 mL) was used to dissolve the solids at RT (22 °C). The concentrations of **5a**, **7**, PPh₃ and free 2,4-lutidine were measured from the integrals of ¹H, ¹⁹F and ³¹P NMR spectra. The equilibrium was fast and the constant was calculated from $K_{eq} = \frac{[5a][2,4-lutidine]}{[7][PPh_3]}$.

General Procedure for Thermal Studies of 5a with or without ligand 6. A J-Young tube was charged with **5a** (10.6 μmol), ligand **6** (10.9 μmol) and toluene-d₈ (0.5 mL) at RT under Ar in the glovebox. The mixture was heated in an oil bath at 80 °C for days, and the reaction was monitored by ¹H, ¹⁹F and ³¹P NMR spectroscopy at RT. A similar procedure was used for the thermolysis of **5a** with **6**, but in a 50 °C oil bath.

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CHAPTER FOUR

New Neutral Nickel(II) Complexes Based on Anilinotropone Ligands Bearing Electron Withdrawing Nitro Substituents for Ethylene Polymerization and Copolymerization

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Abstract: A series of nitro-substituted anilinotropone-based neutral (N,O)Ni(Ph)(PPh₃) catalysts **4** and **5b-c** were synthesized and characterized. Ethylene polymerizations were performed and compared with unnitrated parent catalysts **8** and **9**. These new nitrated catalysts polymerize ethylene with extremely high activities without activators into high molecular weight PEs with few branches. Catalyst **5b** is the most active neutral Ni(II) catalyst for ethylene polymerization to date. The measured TOF of $2 \times 10^6 \text{ h}^{-1}$ is likely an underestimation as both mass transfer problems and impurities present in solvents at low catalyst loadings would decrease the catalyst productivity.

Introduction.

There has been growing interest in studying single-site neutral Ni(II) catalysts for polymerization of ethylene as well as for copolymerization of ethylene and readily available polar monomers.¹⁻³ Compared with early metals and cationic Ni/Pd catalysts, the reduced oxophilicity and neutral charge of the coordinated metal complex is expected to result in more tolerance of polar functionalities in neutral Ni(II) catalysts, as well as enable better productivities in incorporating polar monomers during polymerization.⁴⁻⁶ However, most neutral Ni(II) catalysts require cocatalysts for chain initiation and propagation which has complicated mechanistic investigations and restricted applications of these catalysts.⁷ It is therefore desirable to develop neutral Ni(II) catalysts without the requirement of activators for polymerization.

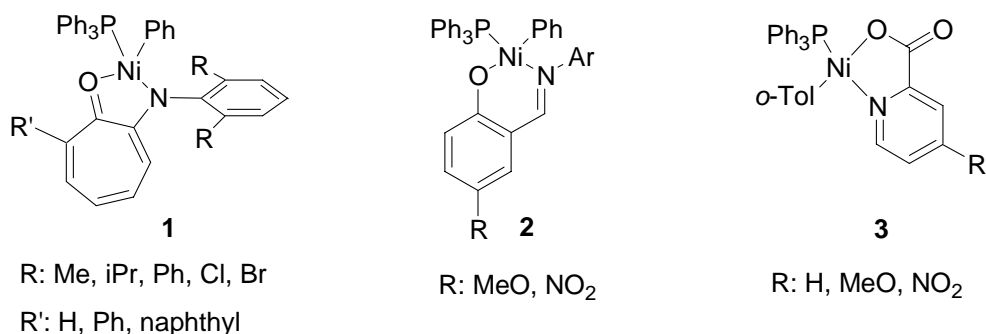


Figure 4.1. Neutral (N,O)Ni catalysts **1** (Brookhart), **2** (Grubbs) and **3** (Cavell).

Our lab has reported a group of anilinetropone-based neutral Ni(II) catalysts, **1**^{8,9} (Figure 4.1), that are active for ethylene polymerization without activators. Polymerization results showed that variation of substituents, R, at the *ortho*-aryl position had minor effects on catalyst activities, whereas an increase in steric bulk at R' on the tropone ring dramatically

enhanced catalyst stabilities, and activities at lower temperatures. Extensive mechanistic investigations of anilinetropone-based neutral Ni(II) catalysts for ethylene polymerization were reported by our group, and an ethylene insertion barrier of $\Delta G^\ddagger=16\sim17$ kcal/mol was discovered.⁶ This value was intermediate between cationic diimine Ni(II) (13.5~14.0 kcal/mol)¹⁰ and Pd(II) (18.0-18.5 kcal/ mmol)¹¹ catalysts. DFT/stochastic studies¹² of **1** catalyzed ethylene polymerization were also performed and results are consistent with those from experiments. The computations also suggested that anilinetropone-based neutral Ni(II) catalysts should have better functional group tolerance than salicylaldimine-based neutral Ni(II) catalysts of type **2**^{1,7} reported by Grubbs, due to formation of more stable π -complexes than carbonyl oxygen coordinated adducts when the polar monomer is methyl acrylate.

To further our study with the anilinetropone-based neutral Ni(II) catalysts, we decide to examine the effect on catalyst activity and stability of adding strong electron-withdrawing NO₂ groups to the tropone ring. Previously, Cavell reported that the introduction of NO₂ at R of the pyridyl ring transformed **3** (Figure 4.1) from an oligomerization catalyst to a polymerization catalyst of higher productivity.¹³ The polyethylene (PE) produced had high density and high molecular weight (MW) ($T_m = 129.5$ °C). Salicylaldimine-based neutral Ni(II) catalyst **2** with R = NO₂ also displayed high activity for polymerization of ethylene into high MW polymer with fewer branches than the unnitrated catalysts.⁷

Originally, nitro-substituted anilinetropone (N,O)Ni(II) catalyst **4** (Figure 4.2) was designed, where the *para*-position of the aryl ring is occupied by a methyl group to block the possible nitration at that position. Previous studies with cationic diimine Ni/Pd catalysts showed that replacement of a methyl group by an *i*Pr group at the *ortho*-N-aryl position influenced the resulting polymer properties by increasing both molecular weight and

branching numbers.^{14,15} Also reported in this chapter are the effects of NO₂ groups in isopropyl-substituted analog **5**. With the diisopropyl-substituted anilinetropone ligand, by carefully controlling the nitric acid concentration, the first nitration occurs on the tropone ring, but gives a mixture of two mononitrated isomers **7a** and **7a'** upon workup. As the reaction time and nitric acid concentration increase, the next two nitrations occur stepwise at the tropone and aryl groups to yield dinitro- and trinitro-substituted ligands **7b** and **7c**, correspondingly. These nitro-substituted anilinetropone-based neutral Ni(II) catalysts **4** and **5b-c** are extremely active for ethylene polymerization and results are compared with their unnitrated parent complexes.

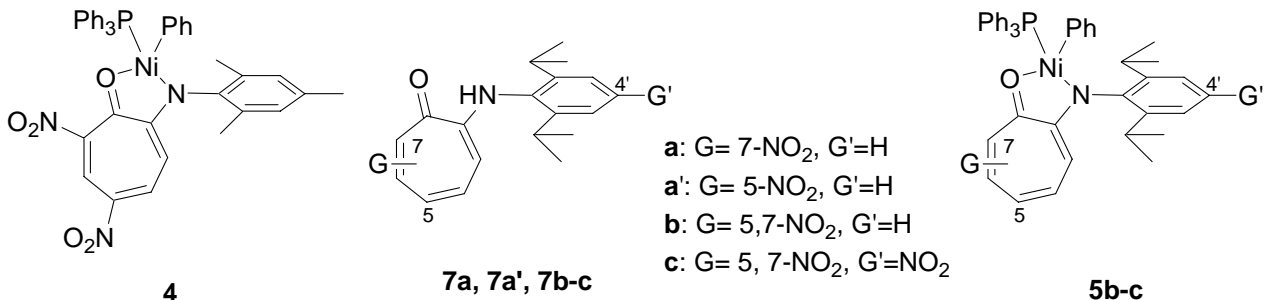
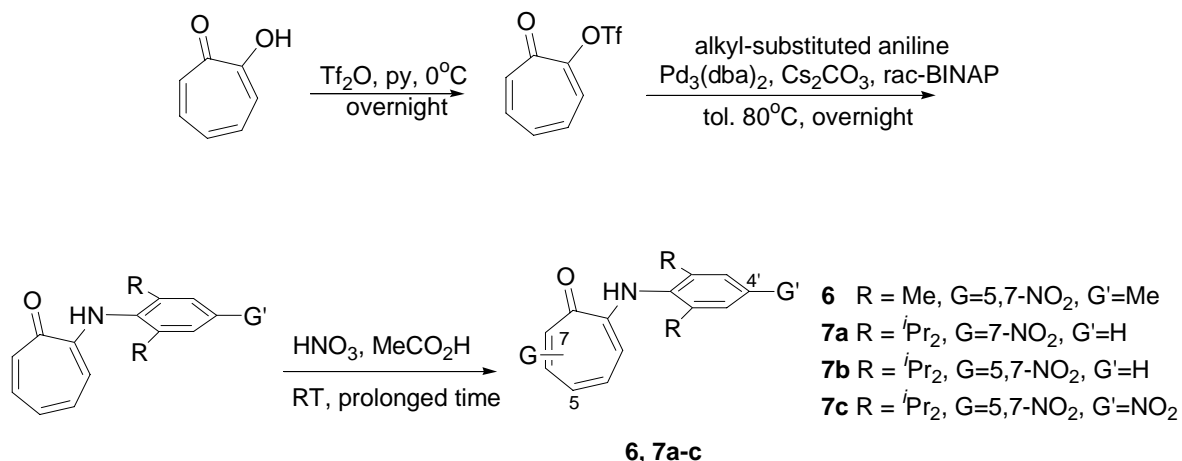


Figure 4.2 Nitro-substituted anilinetropone-based neutral Ni(II) catalysts **4** and **5a-c**.

Results and Discussion.

Synthesis of nitro-substituted anilinetropone ligands 6, 7a, 7a' and 7b-c, and their corresponding Ni complexes 4 and 5b and 5c. The unnitrated anilinetropone was synthesized following previously reported procedures (Scheme 4.1).⁸ Nitration of 2,4,6-trimethylanilinetropone dissolved in acetic acid by a solution of nitric acid and acetic acid (1:1 by volume) at RT afforded within 1 h a mixture of the mononitro- and dinitro substituted species. However, extending the reaction time to 2 h resulted in complete formation of

dinitro ligand **6**. Pure product was obtained in good yield after purification by flash chromatography. However when the conditions similar to synthesis of **6** were applied, nitration of 2,6-diisopropylanilinetropone was relatively slow, as the addition of the first NO₂ group took 2 h to reach completion. The unchanged splitting patterns of *meta*-H and *para*-H of the aryl ring in the ¹H NMR spectrum (doublet and triplet, respectively) indicated that nitration took place at the tropone ring instead of at the expected *para*-position of the aryl ring which has higher electron density. According to ¹H NMR analysis, the NO₂ group originally appeared at the C7-position of the tropone ring (**7a**), adjacent to carbonyl group as two triplet resonances (at 6.93 ppm and 7.48 ppm in CDCl₃) were observed for the tropone ring. However, the compound isomerized into a mixture of two isomers having the NO₂ group at either the C5- or the C7-position upon workup. Upon slightly increasing the nitric acid concentration, a mixture of mononitro (at C5-position, **7a'**) and dinitro **7b** was obtained. Attempts to separate **7a'** from **7b** were unsuccessful due to the same R_f value on the TLC plate in various eluents and the same solubility in crystallizing solvents. By increasing the nitric acid concentration and/or the reaction time, nitration proceeded cleanly to give **7b** as the only product. A third NO₂ group was added to the *para*-position of aryl ring under more concentrated nitric acid condition and prolonged time.



Scheme 4.1. Nitro-substituted anilinetropone ligand **6** and **7a-c** synthesis.

One of the diagnostic features used to judge the reaction conversion and number of NO₂ groups added was the large difference in ¹H chemical shift of the NH before and after nitration. For 2,6-diisopropylanilinetropone, the NH had chemical shift at 8.40 ppm before nitration. This resonance then moved to 8.95 ppm and 9.05 ppm (mononitrated **7a** and **7a'**, respectively), 9.51 ppm (dinitrated **7b**) and 9.40 ppm (trinitrated **7c**). The changes in chemical shift seem consistent with changes in NH acidity, as decreasing electron density on the tropone ring by adding one or two NO₂ groups increases the acidity of the NH. However, decreasing electron density on the aryl ring seemed to oppositely affect the NH chemical shift, though the change was minor. Both ligands **6** and **7b** which had two NO₂ groups on the tropone ring had ¹H chemical shifts of NH, at 9.53 ppm and 9.51 ppm, respectively.

Ligand **6** was also analyzed by single crystal X-ray diffraction (Figure 4.3.). The N-aryl ring was perpendicular to the tropone (87.9°) to minimize steric interactions. The N(15)-tropone C(14) bond distance was shorter than that of N(15)-aryl C(16) indicating that the lone electron pair on N was delocalized onto the tropone ring instead of onto aryl group due to the formation of a stable H-bond between O and N. This conjugation caused the

electrophilic nitration to occur at the C5- and C7-positions of the tropone ring where the electron densities are higher; the addition of the third NO₂ group on the aryl group seems to have little effect on *NH* acidity. The O(1)-C(2) bond distance was lengthened as a result of delocalized electron density along the seven-membered tropone structure.

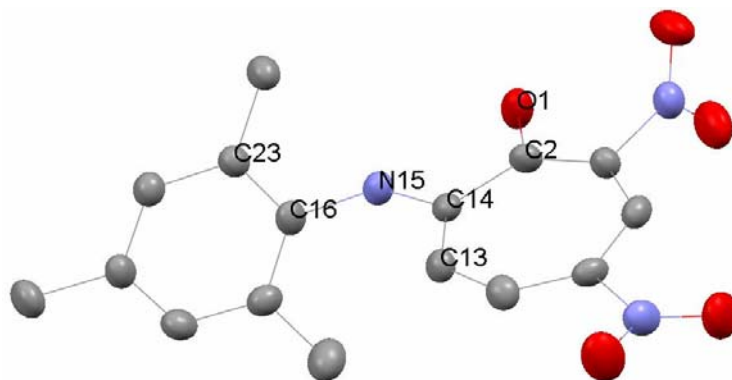
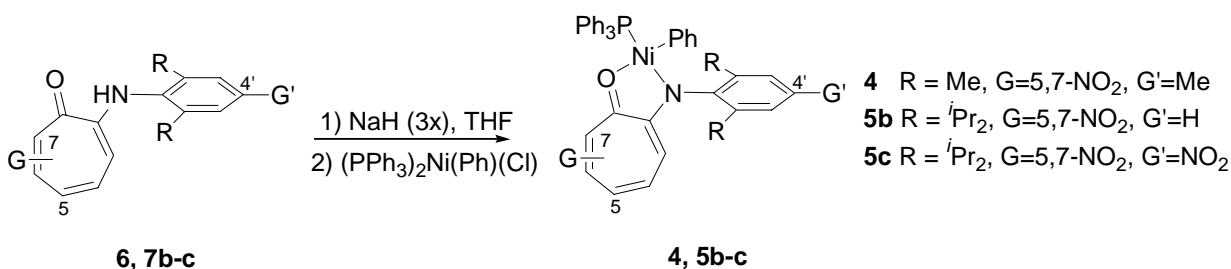


Figure 4.3. Thermal ellipsoid plot of ligand **6**. Selected interatomic (Å) distances and torsion angles (degree): O(1)-C(2)=1.239(4), C(14)-N(15)=1.332(4), N(15)-C(16)=1.443(4), C(13)-C(14)-C(16)-C(23)=87.9(3), N(15)-C(14)-C(2)-O(1)=0.44(3).

Except **7a** and **7a'** which exist as a mixture, nitro-substituted anilinetropone ligands **6** and **7b-c** were converted to their corresponding neutral Ni(II) complexes **4** and **5b-c** in good yields, following literature procedures (Scheme 4.2). Increasing the number of nitro groups caused catalyst **5c** to be less soluble in toluene or Et₂O. While **4** and **5b** were crystallized from toluene/pentane, pure **5c** was obtained by crystallization using CH₂Cl₂/pentane at -30 °C.



Scheme 4.2. Synthesis of neutral Ni catalyst **4** and **5b-c**.

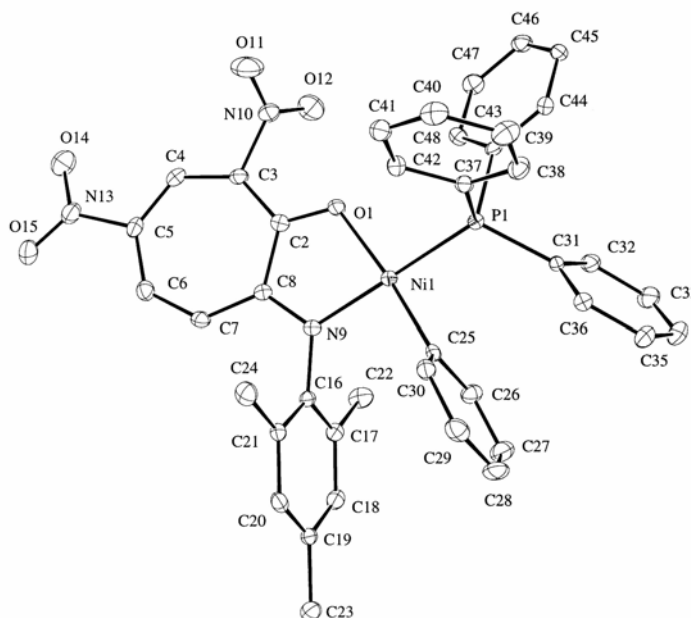


Figure 4.4 ORTEP drawing of catalyst **4**. Ni(1)-C(25)=1.878(3), Ni(1)-P(1)=2.1716(10), Ni(1)-N(9)=1.931(3), Ni(1)-O(1)=1.9343(22), O(1)-C(2)=1.274(4), C(8)-N(9)=1.317(4), N(9)-C(16)=1.450(4), O(1)-Ni(1)-P(1)=98.8(8), O(1)-Ni(1)-N(9)=81.39(11), N(9)-Ni(1)-C(25)=173.26(), N(9)-Ni(1)-C(25)-C(30)=-89.1(5), C(17)-C(16)-N(9)-C(8)=101.3(7).

Catalysts **4** and **5b-c** were characterized by ¹H, ¹³C and ³¹P NMR spectroscopy. The solid state structure of **4** was also analyzed by single-crystal X-ray diffraction (Figure 4.4). Ni has adopted almost perfect square planar geometry, with the sum of the angles around Ni being 359.75°. Phosphine was *trans* to N and the N-aryl group was perpendicular to the five-membered Ni chelate. Similar to ligand **6**, catalyst **4** has a shorter N-C(tropone) bond length

than N-C(aryl), indicating that the lone pair electrons were delocalized into the tropone ring. In the ^1H NMR spectrum, there was only one singlet for two *ortho*-methyl groups in **4** and two doublets for the four *ortho*-*i*Pr methyl groups in **5b-c**. This implied that all Ni catalysts have Cs symmetry where the mirror plane contains the tropone ring and bisects the N-aryl ring. There was only one ^{31}P NMR resonance for each catalyst, indicating the existence of one isomer in solution. Similar to **4**, catalysts **5b-c** all have P *trans* to amine N.

Ethylene Polymerization Studies. Ethylene polymerizations catalyzed by **4** and **5b-c** were studied and results were compared with their parent unnitrated catalysts **8** and **9** (Table 4.1. and Figure 4.5.). Like the parent complexes, these new catalysts were active for ethylene polymerization without activators, indicating that under the employed polymerization conditions, phosphine displacement by ethylene readily occurs for **4** and **5b-c**.



Figure 4.5. Unnitrated anilinetropone Ni complexes **8** and **9**.

Catalyst **4** was initially studied for polymerization at 200 psig ethylene pressure. As the polymerization temperature was increased from 60 °C to 80 °C, TON increased from 65,000 to 230,000 (entries 4 and 2), indicating that **4** had good thermal stability at higher temperature. Similar thermal stabilities were also observed with other neutral five-membered (N,O)Ni(II) chelate complexes, such as anilinetropone-based Ni(II) catalysts **1**^{8,9} and catalysts **3**,¹³ where higher activities were achieved at higher temperatures (60 °C vs 80 °C).

For salicylaldimine-based Ni(II) catalysts **2**, the best activities were reached at 45 ~ 50 °C,¹ and previously studied anilinoenone neutral Ni(II) catalysts displayed best activities at 50~60 °C.¹⁶ It seemed that the better thermal stability of neutral (N,O)Ni(II) complexes was related to the more rigid metallacycle structures, where five-member (N,O)Ni(II) chelates are more constrained than six-member Ni(II) chelates.

As the polymerization temperature was increased from 60 °C to 80 °C, the polymer MW decreased while branching increased. The trend was similar to those observed previously for both neutral Ni(II) catalysts and cationic Ni/Pd catalysts.^{9,15,17} The addition of two NO₂ groups dramatically enhances catalyst activities at 80 °C (entries 6 vs 4) from a TON of 33,000 to 164,000 while the MWs of PE were comparable. Extending the reaction time from 10 min to 60 min resulted in a doubling in TONs for **4** while the increase of TON was only modest for **8**, implying catalyst **4** had longer lifetime than **8** (entries 3, 4 vs. 5, 6).

Table 4.1 Ethylene polymerizations with **4** and **5b-c**.

Entry	Cat	Cat (μ mol)	t (min)	T (°C)	PE (g)	TON	Mw	MWD	Tm (°C)	Br (/1000C)
1	4	5.5	60	60	4.4	28,000	289,000	2.9	123	10
2	4	6.9	10	60	2.6	13,000	230,000	2.7	123	8
3	4	2.0	60	80	19.3	345,000	128,000	2.4	118	18
4	4	2.1	10	80	9.6	164,000	65,000	3.5	118	16
5	8	5.2	30	80	6.3	43,100				
6	8	5.2	10	80	4.7	32,600	73,000	1.7		61
7	5b	0.9	10	60	0.6	24,000				
8	5b	0.45	60	80	3.0	239,000				
9	5b	0.9	10	80	12.1	478,000			121	2
10	5c	0.5	10	80	3.3	233,000				7
11	9	5.2	60	80	9.2	62,100	162,000	1.8		61
12	9	5.2	10	80	7.6	52,400	165,000	1.8		61

All ethylene polymerizations were carried out in a 1 L Parr reactor with 200 mL toluene and 200 psig ethylene pressure. Polymerization temperature was well-controlled with less than ± 2 °C fluctuation.

Similar to **4**, the addition of two or three NO₂ groups led to dramatically enhanced catalytic activities of diisopropyl analog **5b-c**, with a TON of 478,000 for **5b** (entry 9) and 233,000 for **5c** (entry 10) compared with unnitrated parent catalyst **9** (entry 12). The activities of catalysts **9** and **5b-c** correlate well with the acidities of the NH group in the corresponding ligand. The more acidic the ligand NH is, the more active the catalyst. The addition of a third NO₂ on the aryl ring did not apparently further enhance catalytic activity. Polymerizations catalyzed by **5b** and **5c** were very exothermic thus very small catalyst loadings were required to better control temperature. Stock solutions of **5b** (0.9 μmol/mL) and **5c** (1.0 μmol/mL) were used for polymerizations. However, the decreased catalysts' loading makes the catalytic species more susceptible to decomposition in the presence of minor impurities in the large quantity of toluene used. Moreover, after quenching the polymerizations catalyzed by **5b** or **5c**, the solvent-swollen PE was found to aggregate on the reactor cooling coil. Therefore the TONs listed in Table 4.1 are likely affected by the inaccessibility of propagating Ni(II) centers to ethylene (mass transfer) and likely are an underestimation of the true catalytic activities under those conditions. Catalyst **5b** is the most active neutral Ni(II) catalyst prepared to date with a turnover frequency (TOF) > 2x10⁶ /h, approaching TOFs of classical early metal metallocene catalysts.

All PEs produced by nitro-substituted catalyst **4** and **5b-c** had lower branching densities than those of parent catalysts **8** and **9** (entry 4 vs 6 and entries 9,10 vs. 12). The exact reason for the lower branching number is unknown, but similar results were also observed for catalysts **2** and **3** when NO₂ groups were present in the ligand backbones. All PEs had monomodal GPC traces and molecular weight distributions (MWD) between 2 and 4, implying that single-site species were present for catalysts **4** and **5a-c** during polymerizations.

Ethylene Copolymerizations and α -Olefin Oligomerization Studies. One reason to study neutral Ni(II) catalysts is to copolymerize ethylene and readily available polar monomers, as stated in the Introduction. Vinyltrimethoxysilane was chosen as the polar monomer for copolymerization studies using catalyst **4** (Table 4.2.). Copolymers containing silyl ether groups have many commercial applications as these groups are easily hydrolyzed to form crosslinked materials for insulating purposes and can be covalently attached to modify surfaces. DuPont has used cationic diimine Ni(II) catalysts to polymerize ethylene and vinyl- or allylsilanes productively.¹⁸ Catalyst **4** was able to incorporate vinyltrimethoxysilane into polyethylene, but at a reduced rate compared to ethylene homopolymerization (entry 1). The copolymer was sensitive to moisture and crosslinked after exposure to air for a period of time (entry 2). Reduced activities were also observed for ethylene and 1-hexene copolymerizations (entries 3 and 4). The exact amount of 1-hexene incorporated in the polymer was difficult to estimate due to complications from chain walking and similar backbone structures of polyethylene and poly(1-hexene).

Table 4.2. Copolymerization of ethylene and polar or nonpolar olefins using **4**.^a

Entry	Cat. (μ mol)	VTMoS (mmol)	1-hex. (mmol)	T ($^{\circ}$ C)	t (h)	Yield (g)	TON	M _w ^b	MWD	VTMoS ^c (%mol)	Br (/1000C)	T _m ^d ($^{\circ}$ C)
1	10	13.1	0	80	1	3.2	11,000	47,000	3.2	1.5	16	97
2	10	13.1	0	80	1	3.1	--	--	--	--	--	109
3	5.8	0	40.0	50	0.5	1.8	--	--	--	--	--	121
4	6.1	0	40.0	80	3	0.8	--	--	--	--	--	--

a. Copolymerizations were run at 80 $^{\circ}$ C in a 1 L Parr reactor with 198 mL toluene and 200 psig ethylene pressure. Reaction temperature was well-controlled with variation less than ± 2 $^{\circ}$ C. b. M_w, weight average molecular weight of polymer was determined by GPC at 135 $^{\circ}$ C in 1,2,4-trichlorobenzene. c. Molar ratio of VTMoS incorporated measure from 1 H NMR spectroscopy. d. melting temperature was measured by DSC.

1-Hexene or 1-octene oligomerization was also studied with catalysts **4** or **5b** (Table 4.3.). 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.

Table 4.3 1-Hexene or 1-octene oligomerization.^a

Entry	Cat	Cat. (μ mol)	olefin	olefin (mmol)	T ($^{\circ}$ C)	t (h)	Yield (g)	TON	M_n^b (g/mol)	Br (/1000C)
1	4 ^c	6.7	1-hex	8	40	3	0.016	28	308	138
2	5b ^d	10	1-oct.	15.9	80	6.5	1.25	1100	521	76

a. Oligomerizations were run in sealed Kontes flask. Reaction temperature was well-controlled with variation less than ± 2 $^{\circ}$ C. b. M_n , number average molecular weight was measured from ^1H NMR spectroscopy in CDCl_3 at RT. c. Total of 1 mL toluene was used. d. Total of 5 mL was used.

Conclusions.

A group of neutral anilinetropone nickel catalysts, **4** and **5b-c**, with strong electron-withdrawing nitro groups were synthesized and studied for ethylene polymerization. Catalysts **4** and **5b-c** were active for polymerizations without activators. Catalysts **5b** and **5c** were extremely active and exothermic, such that low loadings were required for temperature control. Catalyst **5b** is the most active neutral Ni(II) catalyst discovered to date with a TOF larger than 2×10^6 /h.

Experimental Section.

General Considerations. All manipulations of air- and/or water sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Solid organometallic compounds were transferred in an argon-filled drybox and, unless stated otherwise, were stored at room temperature. The ^1H , ^{13}C and ^{31}P NMR spectra were acquired using Bruker 400 or 500 MHz spectrometers. Chemical shifts were reported in δ units, parts per million (ppm) and referenced against residual deuterated solvent peaks (^1H , ^{13}C) or external standard H_3PO_4 (^{31}P). Flash chromatography was performed using 60 Å silica gel (SAI). High temperature gel permeation chromatography (GPC) was performed by DuPont (Wilmington, DE) in 1,2,4-trichlorobenzene at 135 °C using Waters HPLC 150C equipped with Shodex columns. All calibration curves were established with polystyrene standards and universal calibration was applied using Mark-Houwink constants for polyethylene ($k = 4.34 \times 10^{-4}$; $\alpha = 0.724$). Thermal analysis of the polymer melting temperature (T_m) was performed on a Seiko Instruments DSC220C differential scanning calorimeter. A Hewlett-Packard 6850 GC with a flame ionization detector on a 25 m x μm DB-1 capillary column (J&W Scientific) and a HP 3396 Series III integrator were used for gas chromatography analysis. Elemental analyses were performed by Altantic Microlab Inc. of Norcross, GA.

Materials. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through alumina columns under an argon or nitrogen atmosphere. NMR solvents were vacuum-transferred from CaH_2 , degassed by repeated freeze-pump-thaw cycles and stored over 4 Å molecular sieves. 2,6-Diisopropylaniline,

2,4,6-trimethylaniline, NaH, tropolone, Pd₂dba₃, *rac*-BINAP, Cs₂CO₃, and Tf₂O were used as received. Polymer-grade ethylene was used as received for bulk polymerizations and NMR experiments. 2,6-Diisopropylanilinotropone⁸ and (PPh₃)₂Ni(Ph)(Cl)¹⁹ were prepared following the literature procedures. Yields refer to isolated yields of compounds of greater than 95% purity as estimated by ¹H NMR analysis and elemental analysis.

Analysis of Polymer Branching by ¹H NMR Spectroscopy. ¹H NMR spectra were recorded in either CDCl₃ at room temperature or C₆D₅Br at 100 °C. Assignment of peaks and calculation of polymer branching were carried out following the previously published method.²⁰

Analysis of Vinyltrimethoxysilane Incorporation by ¹H NMR spectroscopy. ¹H NMR spectra were recorded in C₆D₅Br at 100 °C. The integrals of methoxy H and all other H (alkyl and olefinic regions) were used to determine the incorporation ratio by the following

$$\text{formula: } n_{C_2H_4} = \frac{H_{alkyl} + H_{olefinic} - 3 \times \frac{H_{MeO}}{9}}{4} \quad \text{and} \quad VTMOs\% = \frac{\frac{H_{MeO}}{9}}{n_{C_2H_4} + \frac{H_{MeO}}{9}} \cdot (H_{alkyl}: \text{ the}$$

integral of H in the alkyl region; H_{olefinic}: the integral of H in the olefinic region; H_{MeO}: the integral of H belonging to VTMOs fraction.)

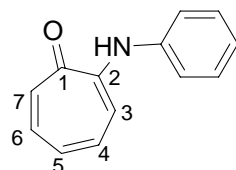
General Polymerization/Oligomerization Procedure. All ethylene homopolymerizations were carried out in 1L Parr reactor equipped with an automatic heating and cooling controller. Before polymerization, the reactor was heated at 120 °C under vacuum for 1-2 h, then backfilled with argon and cooled to the desired polymerization temperature. After 190 mL toluene was injected, the reactor was purged with ethylene (3x100 psig). A solution of catalyst in 10 mL toluene was added to the vented reactor via

cannula. The reactor was sealed and pressurized to the desired polymerization pressure with the stirring motor engaged. After the reaction time was reached, ethylene pressure was released, and the reaction was quenched with 250 mL MeOH. Polymer was collected by suction filtration and dried in a vacuum oven overnight at 80 °C.

For ethylene and vinyltrimethoxysilane copolymerizations, a procedure similar to ethylene homopolymerization was followed, but 188 mL toluene and 2 mL VTMoS were injected instead of 190 mL toluene into the 1 L Parr reactor before ethylene purging. 10 mL Et₃N was added to MeOH (250 mL) to prevent the silyl groups being hydrolyzed during quenching and workup steps.¹⁸

1-Hexene and 1-octene oligomerizations were carried out in Kontes flasks with magnetic stir bars. Complex **4** was pre-dissolved in 1 mL toluene in the flask while **5b** was pre-dissolved in 5 mL toluene. After injection of olefin for both oligomerizations, the flask was sealed and placed in a pre-heated oil bath (40 or 80 °C). When the desired time was reached, the reaction was quenched by MeOH (20 mL). The solution was filtered through a pad of Celite. After the removal of volatiles, the residue was dried in a vacuum oven at 80 °C overnight and weighed to calculate the conversion.

Synthesis of ligands **6**, **7a-c** and their corresponding Ni complexes **4**, **5a-c**.



Synthesis of 2,4,6-trimethylanilinotropone. A method similar to the previously reported procedure was used.⁹ Triflatotropone (0.561 g, 2.2 mmol), Pd₂dba₃ (10 mg, 0.011 mmol), *rac*-BINAP (14 mg, 0.022 mmol) and Cs₂CO₃ (1.00 g, 3.1 mmol) were added to a

flame-dried Schlenk flask under Ar. Toluene (10 mL) was added, followed by 2,4,6-trimethylaniline (0.4 mL, 2.6 mmol). The reaction proceeded at 80 °C in toluene for 18 h. After the flask cooled down to RT, the mixture was filtered through a pad of silica with the aid of 100 mL Et₂O. The organic phase was dried using MgSO₄, and volatiles were removed in vacuo to give crude product. Purification by flash chromatography with ethyl acetate:hexane (1:3) yielded 0.372 g (70%) pure product. ¹H NMR (CD₂Cl₂, 400 MHz): δ 8.32 (br s, *NH*), 7.30 (td, *J*=0.8, 8.8 Hz, *H*₆, 1H), 7.18 (d, *J*=11.6 Hz, *H*₇, 1H), 7.06 (t, *J*=10 Hz, *H*₄, 1H), 7.00 (s, Ar-*m-H*, 2H), 6.69 (t, *J*=9.6 Hz, *H*₅, 1H), 6.18 (d, *J*=10.4 Hz, *H*₃, 1H), 2.32 (s, *p-CH*₃, 3H), 2.10 (s, *o-CH*₃, 6H). ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ 177.0, 155.3, 137.9, 137.7, 136.7, 136.2, 132.8, 130.1, 129.8, 123.7, 110.1, 21.4, 18.3. Anal. Calcd. (C₁₆H₁₇NO): C, 80.30; H, 7.16; N, 5.85. Found: C, 80.32; H, 7.16; N, 5.83.

Synthesis of ligand 6. 2,4,6-Trimethylanilinetropone (0.364 g, 1.5 mmol) was dissolved in acetic acid (4 mL). A solution (3 mL) of acetic acid and nitric acid (1:1 by volume) was added. The reaction proceeded at RT for 4 h, then was quenched with water (35 mL). The precipitate was collected via suction filtration and crude solid was purified by flash chromatography with hexane/ethyl acetate (3:1) as eluent. Yield: 0.343 g (69%). ¹H NMR (CDCl₃, 400 MHz): δ 9.45 (br s, *NH*, 1H), 8.98 (d, *J*=2.4 Hz, 1H), 8.53 (dd, *J*=2.4, 12 Hz, 1H), 7.04 (s, Ar-*mH*, 2H), 6.39 (d, *J*=12 Hz, 1H), 2.35 (s, Me, 3H), 2.09 (s, Me, 6H). ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ 166.7, 160.1, 145.9, 140.1, 138.6, 136.5, 134.8, 130.3, 129.6, 126.6, 107.1 (aromatic H), 21.3 (*p-CH*₃), 18.1 (*o-CH*₃). Anal. Calcd. (C₁₆H₁₅N₃O₅): C, 58.4; H, 4.59; N, 12.76. Found: C, 58.01; H, 4.50; N, 12.42.

Synthesis of ligand 7a and 7a'. 2,6-Diisopropylanilinetropone (0.753 g, 2.7 mmol) was dissolved in 8 mL acetic acid. A solution (6 mL) of acetic acid and HNO₃ (1:1) was

added and the mixture was stirred at RT for 2 h and then diluted with 50 mL water. The precipitate was collected, washed several times with water and purified by chromatography with ethyl acetate/hexane (1:3). Yield: 0.43 g (50%) of **7a/7a'** in 1:2 ratio. ^1H NMR (CDCl_3 , 400 MHz): δ 9.05 (s, NH, 1H, **7a'**), 8.95 (s, NH, 0.5H, **7a**), 8.46 (dd, $J=2.8, 12.8$ Hz, H_6 , 1H, **7a'**), 8.35 (dd, $J=2.6, 12.8$ Hz, H_7 , 1H, **7a'**), 7.71 (d, $J=8.8$ Hz, H_6 , 0.5H, **7a**), 7.45~7.26 (m, Ar- H and H_5 , 5H); 7.19 (d, $J=12.8$ Hz, H_4 , 1H, **7a'**), 6.72 (t, $J=9.6$ Hz, H_4 , 0.5H, **7a**), 6.42 (t, $J=10.8$ Hz, H_3 , 0.5H, **7a**), 6.21 (d, $J=11.6$ Hz, H_3 , 1H, **7a'**), 2.81-2.72 (m, $^i\text{Pr-CH}$, 3H, **7a** and **7a'**); 1.19-1.13 (m, $^i\text{Pr-CH}_3$, 18H, **7a** and **7a'**). Anal. Cald. ($\text{C}_{19}\text{H}_{22}\text{O}_3\text{N}_2$): C, 69.92; H, 6.79; N, 8.58. Found: C, 68.77; H, 6.71; N, 7.96.

Synthesis of ligand 7b. 2,6-Disopropyl-anilinetropone (0.782 g, 2.4 mmol) dissolved in 8 mL acetic acid at RT. $\text{HNO}_3\text{:MeCOOH}$ (1:1, 6 mL) was added at RT, the reaction was stirred for 6 h and quenched with 200 mL water. The precipitate was collected and dried in vacuo. Purification by flash chromatography with ethyl acetate: hexane (1:3) yielded 0.47 g (53%) of **7b**. ^1H NMR (CDCl_3 , 400 MHz): δ 9.51 (s, NH, 1H); 9.02(d, $J=2\text{Hz}$, H_5 , 1H); 8.53 (dd, $J=2, 12\text{Hz}$, H_4 , 1H); 7.49 (t, $J=8\text{Hz}$, Ni-Ph- p - H , 1H); 7.33 (d, $J=8\text{Hz}$, Ni-Ph- m - H , 2H); 6.42 (d, $J=12$, H_3 , 1H); 2.68 (septet, $J=7\text{Hz}$, $^i\text{Pr-CH}$, 2H); 1.23 (d, $J=7\text{Hz}$, $^i\text{Pr-CH}_3$, 6H); 1.21 (d, $J=7\text{Hz}$, $^i\text{Pr-CH}_3$, 6H). ^{13}C $\{^1\text{H}\}$ (CDCl_3 , 100 MHz): δ 166.4, 161.0, 146.0, 145.5, 138.6, 135.9, 130.7, 129.4, 126.5, 125.0, 107.3, 28.9, 24.3, 23.3. Anal. Cald ($\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}_5$): C, 61.45; H, 5.70; N, 11.31. Found: C, 61.39; H, 5.81; N, 10.94.

Synthesis of ligand 7c. 2,6-Diisopropylanilinetropone (2.21 g, 7.0 mmol) was dissolved in 6 mL acetic acid. Nitric acid (10 mL) was added and reaction was proceeded and were monitored by ^1H NMR spectroscopy. After 18 h, another 10 mL nitric acid was added. After 42 h, another 15 mL nitric acid was added. The reaction ran at RT for total of 3 d and

quenched with 200 mL H₂O. The precipitate was collected and purified by chromatography (ethyl acetate:hexane=1:3). Yield: 1.64 g (50%). ¹H NMR (CDCl₃, 400 MHz), 9.40 (br s, NH, 1H), 9.02 (d, J=2.4Hz, H₆, 1H); 8.57 (dd, J=2.4, 12Hz, H₄, 1H); 8.19 (s, Ar-*m*-H, 2H), 6.34 (d, J=12Hz, H₃, 1H), 2.82 (septet, J=7Hz, ⁱPr-CH, 2H), 1.23 (d, J=7Hz, ⁱPr-CH₃, 6H), 1.20 (d, J=7Hz, ⁱPr-CH₃, 6H). ¹³C {¹H} (CDCl₃, 100 MHz): δ 166.4, 160.2, 149.3, 148.5, 146.7, 139.5, 136.0, 135.1, 126.6, 120.3, 106.8, 29.4, 24.1, 23.0. Anal. Cald. (C₁₉H₂₀N₄O₇): C, 54.81; H, 4.84; N, 13.46. Found: C, 55.16; H, 4.97; N, 13.05.

Synthesis of catalyst 4. A method similar to the previously reported procedure was used.⁹ Ligand **6** (0.100 g, 0.30 mmol) and NaH (22 mg, 0.90 mmol) were added under Ar to a flame-dried Schlenk flask. 15 mL THF was injected and the deprotonation proceeded at RT for 2 h. The mixture was cannula-transferred to another flask containing (PPh₃)₂Ni(Ph)(Cl) (0.212 g, 0.30 mmol) dissolved in 10 mL THF. The reaction ran at RT for 1 h and was then filtered through a pad of dry Celite. After the removal of volatiles, the residue was crystallized from toluene/pentane (1:10) at -30 °C to yield red needle-like crystals of **4** (0.144 g, 66%). ¹H NMR (CDCl₃, 400 MHz): δ 8.61 (d, J=1.6Hz, H₆, 1H), 7.83 (dd, J=2, 12.8Hz, H₄, 1H), 7.41~7.26 (m, PPh₃, 15H), 6.64 (d, J=7.6Hz, Ni-Ph-*o*-H, 2H), 6.51 (s, Ar-*o*-H, 2H), 6.31~6.24 (m, Ni-Ph-*p*-H and H₃, 2H), 6.17 (t, J=7.6Hz, Ni-Ph-*m*-H, 2H), 2.08 (s, *m*-CH₃, 6H), 2.05 (s, *p*-CH₃, 3H). ¹³C {¹H} NMR (CD₂Cl₂, 100 MHz): δ 146.1, 145.6, 141.4, 140.5, 138.3, 136.1, 135.5, 134.6, 134.3, 130.7, 130.2, 129.8, 128.9, 128.6, 128.4, 126.1, 125.7, 122.3, 117.0, 20.7, 18.3. ³¹P NMR (CD₂Cl₂, 162 MHz): δ 26.1. Anal. Cald. (C₄₀H₃₄O₅N₃PNi): C, 66.14; H, 4.72; N, 5.78. Found: C, 67.12; H, 4.80; N, 5.60.

Synthesis of catalyst 5a. A procedure similar to the preparation of **4** was used. Ligand **7a** (0.117 g, 0.4 mmol), NaH (26 mg, 1.1 mmol), (PPh₃)₂Ni(Ph)(Cl) (0.25 g, 0.4

mmol) and 20 mL THF were used. Pure product was crystallized from Et₂O/pentane (1:5). Yield 0.126g (49%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.50~7.28 (m, PPh₃, 15H), 6.94-6.14 (m, Ar-*H*, tropone-*H*, Ni-Ph, 12H), 3.56 (septet, J=6.8Hz, ⁱPr-CH, 2H), 1.16 (d, J=6.8Hz, ⁱPr-CH₃, 6H), 0.96 (d, J=6.8Hz, ⁱPr-CH₃, 6H). ¹³C {¹H} NMR (CD₂Cl₂, 100 MHz): δ 179.9, 169.4, 149.1, 144.4, 142.4, 138.0, 134.6, 134.1, 133.3, 131.6, 130.1, 128.9, 128.2, 125.3, 125.1, 123.4, 122.2, 121.1, 120.6, 28.8, 25.8, 23.8. ³¹P NMR (CD₂Cl₂, 162 MHz): δ 28.4. Anal. Calcd. (C₄₃H₄₁N₂O₃PNi): C, 71.39; H, 5.71; N, 3.87. Found: C, 75.2; H, 6.18; N, 2.07.

Synthesis of catalyst 5b. A procedure similar to the preparation of **4** was used. Ligand **7b** (0.100 g, 0.27 mmol), NaH (19 mg, 0.81 mmol), (PPh₃)₂Ni(Ph)(Cl) (0.187 g, 0.27 mmol) and 20 mL THF were used. Pure product was crystallized from toluene/pentane (1:10). ¹H NMR (CDCl₃, 500 MHz): δ 8.57 (d, J=2.5Hz, *H*₆, 1H), 7.70 (dd, J=2.5, 12Hz, *H*₄, 1H), 7.45-7.30 (m, PPh₃, 15H), 7.02 (t, J=7.5Hz, Ar-*p-H*, 1H), 6.94 (d, J=7.5Hz, Ar-*m-H*, 2H), 6.67 (d, J=7.0Hz, Ph-*o-H*, 2H), 6.33 (t, J=7.0Hz, Ph-*p-H*, 1H), 6.31 (d, J=12Hz, *H*₃, 1H), 6.23 (t, J=7.0Hz, Ph-*m-H*, 2H), 3.31 (septet, J=7.0Hz, ⁱPr-CH, 2H), 1.18 (d, J=7Hz, ⁱPr-CH₃, 6H), 0.99 (d, J=7Hz, ⁱPr-CH₃, 6H). ¹³C {¹H} NMR (CDCl₃, 126 MHz): 174.2, 168.7, 144.5, 144.1, 141.8, 140.8, 138.4, 137.0, 134.3, 130.7, 130.1, 128.6, 127.6, 126.9, 126.1, 126.0, 122.4, 119.6, 29.3, 25.7, 23.0. ³¹P NMR (CDCl₃, 162 MHz): 25.9. Anal. Calcd. (C₄₃H₄₀N₃NiO₅P): H, 67.21; C, 67.35; N, 5.47. Found: C, 67.35; H, 5.31; N, 5.42.

Synthesis of catalyst 5c. A procedure similar to the preparation of **4** was used. Ligand **7c** (0.150 g, 0.36 mmol), NaH (26 mg, 1.08 mmol), (PPh₃)₂Ni(Ph)(Cl) (0.251 g, 0.36 mmol) and 30 mL THF were used. Pure product was crystallized from CH₂Cl₂/pentane (1:4). Yield: 0.199 g (68%). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.61 (s, *H*₆, 1H), 7.93 (d, J=12Hz, *H*₄, 1H), 7.79 (s, Ar-*m-H*, 1H), 7.45~7.34 (m, PPh₃, 15H), 6.63 (d, J=7.2Hz, Ni-Ph-*o-H*, 2H),

6.34 (t, $J=7.2\text{Hz}$, Ni-Ph-*p*-H, 1H), 6.24 (m, Ni-Ph-*m*-H and H_3 , 3H), 3.39 (septet, $J=6.8\text{Hz}$, $i\text{Pr-CH}$, 2H), 1.28 (d, $J=6.8\text{Hz}$, $i\text{Pr-CH}_3$, 6H), 1.03 (d, $J=6.8\text{Hz}$, $i\text{Pr-CH}_3$, 6H). ^{13}C $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): δ 174.0, 168.4, 148.3, 146.9, 143.5, 143.4, 143.1, 141.7, 138.9, 136.8, 134.3, 130.8, 129.5, 128.7, 126.4, 126.2, 119.7, 118.9, 29.7, 25.4, 23.4.. ^{31}P $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162 MHz): δ 25.8. The crystal of **5c** collected contained 0.5equiv of CH_2Cl_2 as determined by ^1H NMR in CDCl_3 . Anal. Calcd. ($\text{C}_{43}\text{H}_{39}\text{N}_4\text{NiO}_7\text{P}\cdot 0.5\text{CH}_2\text{Cl}_2$): C, 61.04; H, 4.72 N, 6.55. Found: C, 60.57; H, 4.68; N, 6.52.

X-ray crystal structures. Diffraction data was collected on a Bruker SMART 1K diffractometer, at $-100\text{ }^\circ\text{C}$. Refinement was carried out with the full-matrix least-squares method on F (NCRVAX) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atoms. Complete details of X-ray data collection for **4** and **6** are given in Table 4.4.

Table 4.4. Crystallographic Data Collection Parameters for **6** and **4**

	6	4
Formula	C ₁₆ H ₁₅ N ₃ O ₅	C ₄₀ H ₃₄ N ₃ NiO ₅ P
mol wt	658.62	726.40
Cryst syst	Monoclinic	triclinic
Space group	<i>P</i> 1 21/c 1	<i>P</i> $\bar{1}$
a (Å)	19.5960(14)	11.1880(3)
b (Å)	10.8488(6)	12.2142(3)
c (Å)	15.9295(8)	12.9510(3)
α (deg)	90	85.907(1)
β (deg)	113.812(4)	76.626(1)
γ (deg)	90	82.686(1)
V(Å ³)	3095.4(3)	1706.17(7)
D _{calc} (mg/m ³)	1.41	1.414
Scan mode	ω	ω
μ (mm ⁻¹)	0.107	0.67
Cryst dimens (mm)	0.20x0.30x0.30	0.30x0.20x0.15
2 θ range	3-25	5.00-50.00
No. of reflns	31200	12278
No. of unique reflns	7303	6019
No. of obsd data ($I > 2.5\sigma(I)$)	4092	4461
No. of refined params	434	451
hkl range	(-22,25)(-14,14)(-19,20) (-13,13)(0,14)(-15,15)	
R _F , %	0.087	0.047
R _w , %	0.197	0.053
GOF	0.966	1.5304
Z	8	2

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