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Nickel pre-catalysts bearing [(*N*)-imidoylamidine] ligands; influence of the presence of pyridine and pentafluorophenyl groups in ligand backbone on the reactivity in ethylene polymerizations

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ABSTRACT

In this contribution the synthesis and polymerization activity of the nickel complexes [NiBr$_2${*N*′-(2,6-diisopropylphenyl)-*N*-[1-(2,6-diisopropylphenylimine)ethyl]-*N*-(2,3,4,5,6-pentafluorophenyl)acetamidine}] (**2**), [NiBr$_2${*N*′-(2,6-diisopropylphenyl)-*N*-[1-(2,6-diisopropylphenylimine)ethyl]-*N*-(2,3,4,5,6-pentafluorophenylimine)ethylacetamidine}] (**2a**) and [NiBr$_2${*N*-(2,6-diisopropylphenyl)-*N*-[1-(2,6-diisopropylphenylimine)]-*N*-(pyridin-4-yl)acetamidine}] (**3**) are reported. The variation of the phenyl substituents on the β amine was found to influence the polymerization activity of the complexes. The electron withdrawing/donating capacity of the substituted ring was found to be correlated with the polymerization activity, with the pentafluoro substituted ring increasing the polymerization activity and the pyridine ring decreasing the activity. The ligands and complexes were characterized using standard techniques and the polymer properties analyzed.

1. Introduction

The β-diketiminate class of ligands, generally denoted as “nacnac”, or {ArNC(R)}$_2$CH (where Ar = aryl and R = CH$_3$ or bulkier group), rightfully occupies a place alongside a narrow list of popular ancillary supports, given its ability to stabilize or generate unique coordination environments and to support reactive organometallic reagents [1]. The popularity of nacnac and derivatives amongst synthetic chemists is driven by the mono-anionic nature of the β-diketiminate group and also in the strong coordination capacity of the neutral species [2]. As is well known with neutral imine ligands, including α and β diimines and acetamidines, the substituent at the nitrogen donor atom can provide steric protection and electronic influence at the metal center, something which is not possible in many other compounds [1,3,4]. Recently there has been a great deal of interest focused on late transition metal complexes as polymerization catalysts. This is justified by the properties of the polymers produced, the ability to control and adapt the ligand base, and the functional group tolerance, these properties facilitate the synthesis of new materials with previously unattained structures and properties [5–7].

Due to the influence of the ligand framework on the reactivity of the metal center, the design of the ligand is a key step in the development of new catalyst systems. For example the existence of a basic functionality on the ligand framework makes it susceptible to coordination by Lewis acids, which in some cases can be used to activate the metal center [8–12]. This can also have an electronic and steric effect over the metal center influencing the properties of the catalyst systems.

Recently, we discussed that the activation of [(*N*)-imidoylamidine]NiBr$_2$ with MAO (MAO = methylaluminoxane) generates an active site that is capable of polymerizing ethylene (Fig. 1) [13]. As expected, the polymerization reaction shows an increase in molecular weight with increasing pseudo-axial bulk around the nickel center, however, the reactivity was moderate.

The imidoylamidine based systems also offer the potential for ligand variation via the modification of the backbone amine [14]. It is well known that pseudo-axial bulk around the nickel center is necessary to produce high molecular weight polymers [5,15]. As demonstrated by the activity of similar complexes which do not bear a phenyl ring in the backbone, this steric bulk is not necessary to achieve high molecular weight materials [16]. The presence of

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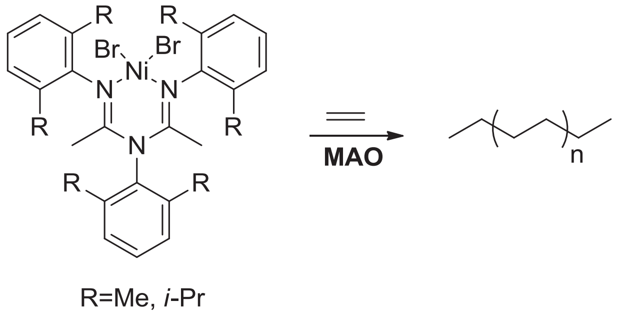


Fig. 1. In the presence of ethylene and MAO, [(*N*)-imidoylamidine]$NiBr_2$ produces polyethylene of high molecular weight.

this group however offers the opportunity to modify the electronics at the transition metal center without significantly altering the steric environment. It is suspected that the modification of the electronic properties at the metal center will increase the activity while maintaining the high molecular weight of the polymer. Therefore, in this contribution, the synthesis, characterization and reactivity of ligand–metal combinations which are structurally similar to compound **1** are discussed. The activity of the compounds in the presence of MAO toward ethylene is described along with the characterization of the products.

2. Results and discussion

2.1. Synthesis of ligands

The general synthesis of the ligands and nickel complexes has previously been discussed in detail and only a general discussion will be presented here [17]. Two synthetic targets for ligands were pursued (Fig. 2), and were selected on the basis of how it was thought the metal center once ligated would be affected. It was thought that the pentafluorophenyl ring in compound **2** would reduce the charge at the metal center in comparison to the diisomethylphenyl group present in compound **1**, which was previously reported by our group, whereas the use of the pyridinyl group in compound **3** would increase the electron density at the metal center due to the basicity of the substituent, thus producing changes in the ethylene polymerization activity and polymer properties.

The synthesis of the supporting ligand for compound **2** (symmetric ligand **2Ls**) proceeds through the addition of 2 equiv of (2,6-diisopropylphenyl)acetimidoyl chloride to pentafluoroaniline in the presence of triethylamine (Scheme 1). A pure white powder was obtained after crystallization from ethanol, the ^1H, ^{13}C and ^{19}F NMR analysis reveal that the synthesis was clean and only a single, pure compound was produced. The characteristic signals of the compound include (in ppm): ^1H NMR 7.11–7.02 (m, 6H, *H*-Ph), 2.84 (sep, 4H, *CH*-*i*-Pr), 2.00 (s, 6H, CH_3), 1.21 (d, 12H, CH_3-*i*-Pr), ^{19}F NMR −147.29, −156.66, −160.35.

The ORTEP structure of compound **2Ls** (Fig. 3), shows that in the solid state the ligand adopts a non-planar arrangement similar to the previously reported 2,6-$MeC_6H_3N(C(Me)NC_6H_3$-2,6-*i*-$Pr)_2$ [13].

A notable difference in the solid state between compound **2Ls** and 2,6-$MeC_6H_3N(C(Me)NC_6H_3$-2,6-*i*-$Pr)_2$, is that the nitrogen atoms, N(1), N(2) and N(3) nearly occupy a common plane and only a minimal distortion was observed (Table 1). The N(1)–C(1) and C(2)–N(3) bond distances of 1.267(3) Å and 1.262(3) Å are consistent with double bonds. The C(1)–N(2) and N(2)–C(2) bond distances of 1.422(3) Å and 1.422(3) Å, respectively, are consistent with an amine N(2).

It was previously observed that the use of imidoyl chloride in the synthesis of these types of ligands can result in the formation of distinct compounds depending on the conditions used for the reaction, in particular the order of addition and base selection were found to be critical [18]. In the course of preparing **2Ls** it was found that the intermediate could be isolated by carefully selecting the reaction conditions. The intermediate, *N*-1-(2,6-diisopropylphenyl)-*N′*-(2,3,4,5,6-pentafluorophenyl)acetamidine (**2I**) was generated by reaction of 1 equiv of (2,6-diisopropylphenyl)acetimidoyl chloride with pentafluoroaniline (Scheme 2).

The pentafluoroaniline was added to a toluene solution of (2,6-diisopropylphenyl)acetimidoyl chloride at room temperature then the reaction was heated at reflux for 4 h to afford crude **2I•HCl**. The crude material was treated with aqueous NH_3 (25%) in dichloromethane (DCM), the organic phase dried over Na_2SO_4, followed by solvent evaporation and crystallization from methanol which provided a white solid of (**2I**) in 70% yield. ^1H NMR spectroscopy confirmed the structure of intermediate. Diagnostic peaks include (in ppm): 3.22 (*CH*-*i*-Pr), 2.04 ($CH_3C{=}N$), and 5.96 (NH).

The ^{19}F NMR presented three peaks at −146.60, −153.99, −162.61 ppm. Single crystals of **2I** suitable for X-ray diffraction were obtained by crystallization from methanol at room temperature. The resulting structure is shown in Fig. 4.

The structure shows that both nitrogen atoms and the carbon of the methyl are sharing a plane, in a trigonal-planar geometry around the C(7) carbon, while the two substituted phenyl rings are perpendicular to that plane. The trigonal-planar geometry around C(7) is slightly distorted. The N(2)–C(7)–N(1), C(8)–C(7)–N(1) and N(2)–C(8)–C(7) angles are 120.0(2)°, 124.5(2)° and 115.5(2)° respectively. The bond distances around the C(7); C(7)–N(1), C(7)–N(2) and C(7)–C(8) are 1.298(2) Å, 1.339(2) Å and 1.502(2) Å, respectively, indicating that the C(7)–N(1) and C(7)–N(2) bonds have a great deal of double bond character due to the level of conjugation. As expected the C(7)–C(8) bond (Table 1) is of single bond character.

The addition of a second equivalent of (2,6-diisopropylphenyl) acetimidoyl chloride to **2I** in toluene solution produced **2La**

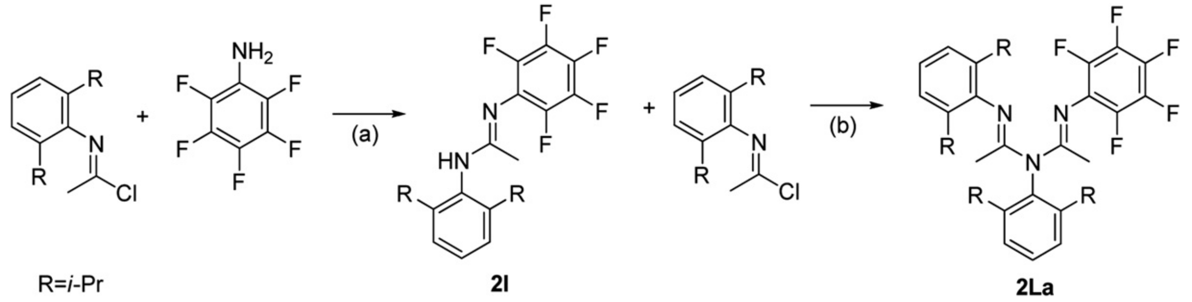
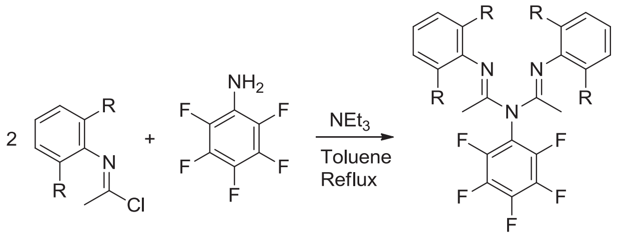


Fig. 2. Synthetic targets in this contribution.



2Ls, R=*i*-Pr

Scheme 1. Synthesis of compound **2Ls**.

(Scheme 2), which was isolated as a yellow solid in 60% yield following crystallization from ethanol. The ^{1}H, ^{13}C and ^{19}F NMR analysis reveal that the synthesis was clean and only a single compound was produced. The characteristic signals of the compound include (in ppm): 7.38–7.22 (m, 3H, *H*-Ph), 3.26 (sep, 2H, *CH*-*i*-Pr), 2.79 (sep, 2H, *CH*-*i*-Pr), 2.18 (s, 3H, *CH*$_3$), 1.91 (s, 3H, *CH*$_3$), 1.25 (dd, 12H, *CH*$_3$-*i*-Pr), 1.17 (d, 12H, *CH*$_3$-*i*-Pr), 0.94 (d, 12H, *CH*$_3$-*i*-Pr), ^{19}F NMR −146.16, −157.55, −156.65. Single crystals of **2La** suitable for X-ray diffraction were obtained by crystallization from ethanol at room temperature. The resulting structure is shown in Fig. 5. EI-MS $[2La + H]^{+}$ analysis revealed a mass of 586.2 which is consistent with the structure.

In isomer **2La** (Fig. 5) two of the nitrogen atoms, N(1) and N(2) occupy a common plane with C(7), C(9) and C(8) while the third, N(3), is slightly twisted out of this plane, more similar to 2,6-MeC$_6$H$_3$N(C(Me)NC$_6$H$_3$-2,6-*i*-Pr)$_2$ [13] than the **2Ls** isomer. The distances between the atoms N(1)–C(7) and N(3)–C(9) are 1.285(2) Å and 1.264(2) Å, which are consistent with a double bond and the distances between N(2)–C(7) and N(2)–C(9) are 1.383(2) Å and 1.437(2) Å which are consistent with a single bond (Table 1).

In a comparison with complex **2Ls** where the distances C(2)–N(2) and C(1)–N(2) are the same (1.422(3) Å) we can find a significant difference in the C(9)–N(2) bond distance which is 0.054 Å longer than C(7)–N(2). This is consistent with asymmetry of the ligand and the less steric hindrance exerted by the pentafluoroaniline group in the asymmetric compound. The ORTEP structure of the more symmetric ligand (Fig. 3) shows that the substituted phenyl ring in the ligand shares a similar planar arrangement, but in **2La** it is observed that the planes in the molecule are not completely orthogonal (Fig. 5).

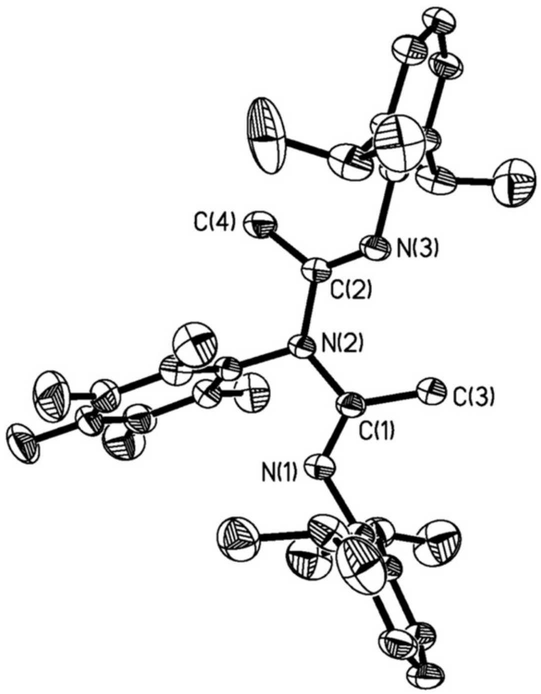


Fig. 3. ORTEP drawing of **2Ls** drawn at 50% probability. Hydrogen atoms were omitted for clarity.

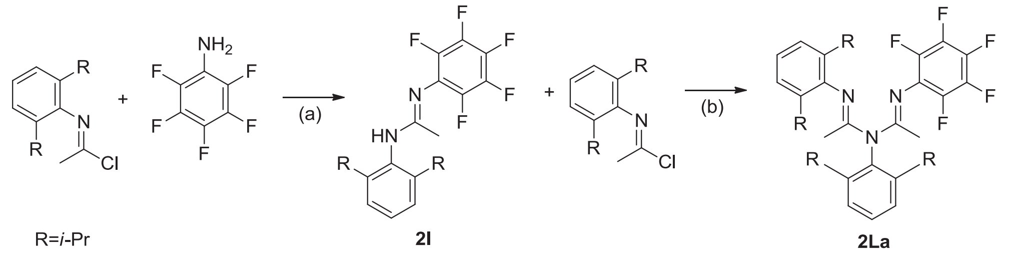
The symmetric ligand **3Ls**, precursor of complex **3** (Fig. 2) was produced using a similar synthetic pathway as compound **2Ls** with 1 equiv of 4-aminopyridine being added to 2 equiv of (2,6-diisopropylphenyl)acetimidoyl chloride in toluene in the presence of triethylamine. The product was washed and purified via column chromatography. A yellow solid was recovered in 50% yield. The ^{13}C and ^{1}H NMR are consistent with a single product. The characteristic signals include (in ppm) ^{1}H NMR: δ 8.69 (d, 2H, $^{3}J_{HH} = 6.8$ Hz, *H*-pyridine), 7.25 (d, 2H, $^{3}J_{HH} = 6.8$ Hz, *H*-pyridine), 7.12 (d, 4H, $^{3}J_{HH} = 6.8$ Hz, *p*-*H*-Ph), 7.04 (m, 2H, $^{3}J_{HH} = 6.8$ Hz, *m*-*H*-Ph), 2.90 (sep, 4H, $^{3}J_{HH} = 6.8$ Hz, *CH*-*i*-Pr), 1.97 (s, 6H, *CH*$_3$), 1.23 (d, 12H, $^{3}J_{HH} = 6.8$ Hz, *CH*$_3$-*i*-Pr), 1,09 (d, 12H, $^{3}J_{HH} = 6.8$ Hz, *CH*$_3$-*i*-Pr). Attempts to isolate the intermediate compound, as was accomplished in the synthesis of **2La** (Scheme 2) were not successful.

2.2. Synthesis of nickel complexes

The [NiBr$_2${*N*′-(2,6-diisopropylphenyl)-*N*-[1-(2,6-diisopropylphenylimine)ethyl]-*N*-(2,3,4,5,6-pentafluorophenyl)acetamidine}] (**2**), [NiBr$_2${*N*′-(2,6-diisopropylphenyl)-*N*-[1-(2,6-diisopropylphenylimine)ethyl]-*N*-(2,3,4,5,6-pentafluorophenylimine)ethylacetamidine}] (**2a**) and [NiBr$_2${*N*-(2,6-diisopropylphenyl)-*N*-[1-(2,6-diisopropylphenylimine)]-*N*-(pyridin-4-yl)acetamidine}] (**3**) were obtained by the addition of **2Ls**, **2La** or **3Ls** to a suspension of nickel (II) dibromide 2-methoxyethyl ether in DCM and stirring at 60 °C for 4 days. The resulting purple (for **2Ls** and **2La**) and blue (for **3Ls**)

Table 1
Selected bond distance (Å) and angles (deg) for *N*-imidoylamidine ligands **2Ls** and **2La** and intermediate **2I**.

2I		**2Ls**		**2La**	
N(1)–C(6)	1.401(2)	C(1)–N(1)	1.267(3)	C(7)–N(1)	1.285(2)
N(1)–C(7)	1.298(2)	C(1)–C(3)	1.483(3)	C(7)–C(8)	1.503(2)
N(2)–C(7)	1.339(2)	C(1)–N(2)	1.422(3)	C(7)–N(2)	1.383(2)
N(2)–C(9)	1.430(2)	C(2)–N(2)	1.422(3)	C(9)–N(2)	1.437(2)
C(7)–C(8)	1.502(2)	C(2)–C(4)	1.498(3)	C(9)–C(10)	1.500(2)
N(1)–C(7)–N(2)	120.0(2)	C(2)–N(3)	1.262(3)	C(9)–N(3)	1.264(2)
N(1)–C(7)–C(8)	124.5(2)	N(1)–C(1)–N(2)	114.3(2)	N(1)–C(7)–N(2)	117.1(1)
N(2)–C(7)–C(8)	115.5(2)	N(1)–C(1)–C(3)	126.2(2)	N(1)–C(7)–C(8)	125.7(1)
C(7)–N(1)–C(6)	118.2(2)	N(3)–C(2)–N(2)	119.0(2)	N(3)–C(9)–N(2)	116.5(1)
C(7)–N(2)–C(9)	124.9(2)	N(2)–C(2)–C(4)	114.1(2)	N(2)–C(9)–C(10)	117.4(1)
		C(2)–N(2)–C(1)	126.8(2)	C(9)–N(2)–C(7)	119.7(1)



Scheme 2. Asymmetric ligand synthesis (**2La**). (a) Toluene, reflux 4 h. (b) Toluene, reflux 24 h.

complexes can be isolated after filtration, solvent evaporation and recrystallization from DCM–Ether in 77%, 70%, and 73% yields respectively.

NMR characterization of the complexes was poor due to the paramagnetic nature of the pseudo-tetrahedral nickel centers, and structural identification inconclusive. Monocrystals of all three of the complexes were obtained, however, only the structure of **2a** was resolvable, due to twinning in complexes **2** and **3**. Crystals of compound **2a** were successfully obtained via the slow evaporation of a dilute DCM solution. X-ray analysis of the crystals revealed the molecular structure shown in Fig. 6. Bond angles and distances are given in Table 2.

The molecular structure confirms a six member chelate ring formed by the ligand in a *N,N* binding mode to the nickel dibromide. The tetrahedral geometry around nickel is distorted. For example, Br(1) is almost perpendicular to the plane of the metal containing ring. This can be observed in the corresponding angle N(3)–Ni–Br(1), 103.1(5)° while the angle of N(3)–Ni–Br(1) is 122.0(5)°. The N(1)–C(7), N(3)–C(9), N(2)–C(7) and N(2)–C(9) bond distances are 1.294(3) Å, 1.286(3) Å, 1.397(3) Å and 1.413(3) Å respectively, indicating the double and single bond character around the imines and amine nitrogen respectively (Table 2).

It was noticed in the synthesis of the ligands and the corresponding nickel complexes, that the production of single crystals for X-ray analysis was a great deal more difficult than similar ligands and complexes, in particular the nacnac complexes. It is thought that the presence of the nitrogen in the α position relative to the imines in these ligands causes a disruption in the planarity of the ligand backbone, making the isolation of crystals suitable for X-ray crystallization more difficult. In addition, the crystallization behavior of the complexes **2** and **2a** was interesting as one of the complexes (**2a**) crystallized after a relatively short time, however, the other symmetric complex required substantially longer periods of time to form crystals even under various solvent pairs/conditions. Even when crystals were obtained the structures were unresolvable due to twinning. FT-IR and elemental analysis were consistent with the proposed structures.

2.3. Activation with MAO and reactivity toward ethylene polymerization

Polymerization studies using the nickel complexes **2**, **2a** and **3** activated with MAO were carried out and the results summarized

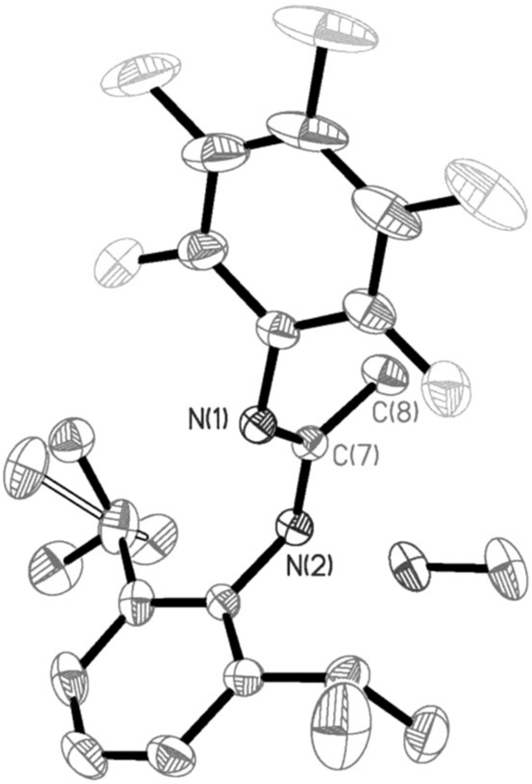


Fig. 4. ORTEP drawing of **2l** drawn at 50% probability. Hydrogen atoms are omitted for clarity.

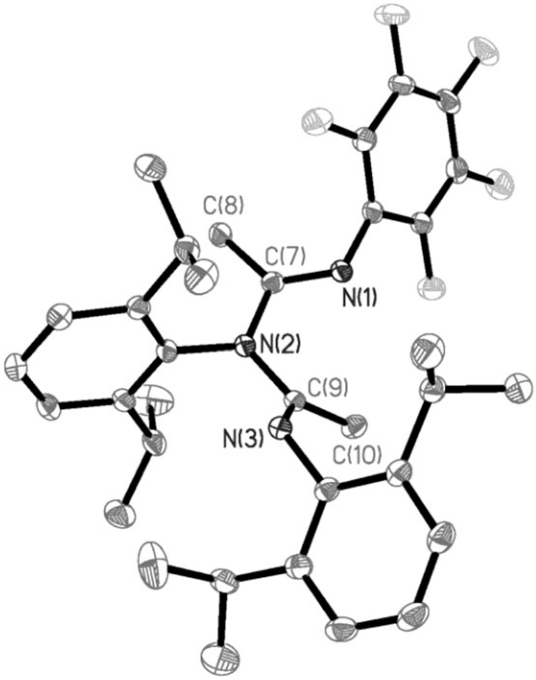


Fig. 5. ORTEP drawing of **2La** drawn at 50% probability. Hydrogen atoms are omitted for clarity.

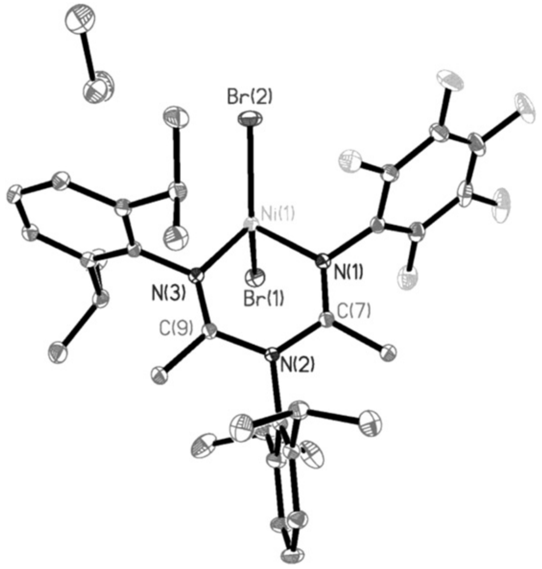


Fig. 6. ORTEP structure of complex **2a** drawn at 50% probability.

in Table 3. The results for compound **1** were previously reported and are used for comparison purposes. In each case, the formation of high molecular weight linear polyethylene was observed. Catalysts which bear more negatively charged ligands (meaning that the metal center has a greater positive charge) **2** and **2a**, entries 2 and 4, show an increase in activity compared to compound **1**, entry 1.

This is likely due to the decreased insertion barriers, similar to those predicted theoretically in NiDAB systems by Ziegler et al. [19]. The melting points of the polymers produced by **2** and **2a** decrease by 1–2 °C compared to **1**, indicating that the polymers are less linear. Increasing the relative charge on the Ni center, compound **3**, results in a large reduction, ca. 85%, in activity compared to complex **2**. The melting temperature of the material produced by **3**, entry 7, decreased by 6 °C compared to those produced by **2**. This indicates that not only does the presence of the pyridinyl group on the ligand backbone reduce the activity, but that the reduced charge increases chain branching. When the polymerization temperature is increased to 70 °C the activities of both **2** and **2a** decrease substantially, entries 3 and 5, while the activity of **3** actually increases by ca. 50%. This is likely due to the decomposition of the complexes **2** and **2a** at elevated temperatures.

Table 2
Selected bond distances (Å) and angles (deg) for the *N*-imidoylamidine nickel complex **2a**.

2a	
N(1)–C(7)	1.294(3)
N(2)–C(7)	1.397(3)
N(2)–C(9)	1.413(3)
N(3)–C(9)	1.286(3)
Ni–N(1)	1.976(2)
Ni–N(3)	1.965(2)
Ni–Br(1)	2.371(4)
Ni–Br(2)	2.316(4)
N(1)–Ni–N(3)	88.13(7)
N(3)–Ni–Br(1)	100.10(5)
N(3)–Ni–Br(2)	122.00(5)
N(1)–Ni–Br(1)	110.10(5)
N(1)–Ni–Br(2)	113.21(5)
C(7)–N(2)–C(9)	126.09(2)

Table 3
Ethylene polymerization reactions.[a]

Entry	Precatalyst	Temp. (°C)	Activity[b]	M_w (kg/mol)	M_w/M_n	T_m (°C)
1	**1**	60	95	112	1.9	136
2	**2**	60	468	84	2.1	133
3	**2**	70	70	184	1.5	135
4	**2a**	60	387	162	2.5	134
5	**2a**	70	145	122	1.6	134
6	**3**	60	68	102	1.8	126
7	**3**	70	110	98	2.0	129

[a] Polymerizations were carried out in 500 mL autoclave reactor with 8 μmol of precatalyst, Al/Ni ratio of 2000 in 100 mL of toluene; reaction time, 30 min; ethylene pressure 4 bar; temperature controlled by external bath.
[b] kg polymer/(mol Ni)(h).

3. Conclusions

The ability to remotely modify the electronic properties of a metal center without significantly altering the steric environment is particularly important in late transition metal catalyst systems. As the ligand, variation in the complexes described in this contribution occur remotely, in the ligand backbone, and uses groups which are about the same size, there is little effect on the steric environment around the metal center. Thus the changes in the polymerization activity and polymer properties are due to variations in the electronic environment of the metal center. This provides access to a convenient method to explore the relationship between electronic properties and polymerization activities. Comparison of the dimethylphenyl substituted [(*N*)-imidoylamidine] (compound **1**) with compounds **2** and **3**, shows that the activity of the catalyst system is very dependent on the electronic effects of the ligand. Compound **2**, in which the nickel center is more electron deficient, shows a greatly increased polymerization activity, whereas compound **3**, which bears a pyridine substituted [(*N*)-imidoylamidine] ligand, and should be slightly more electropositive than compound **1**, shows a reduced polymerization activity. This is consistent with previously observed results in exocyclically activated compounds, in which reduction of the electron density at the metal center resulted in an increased polymerization activity.

4. Experimental section

4.1. General remarks

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from Aldrich unless otherwise specified. Ethylene was purchased from Matheson Tri-Gas (research grade, 99.99% pure) and was further purified by passage through an oxygen/moisture trap BASF R3-11 and 4 Å molecular sieves. Toluene, THF, hexane, and pentane were distilled from benzophenone ketyl and DCM was distilled from calcium hydride. The synthesis of compounds **1**–**3** used recently reported procedures. NMR spectra were obtained using Varian Unity 200 and Bruker Avance-400 spectrometers using deuterated solvents and TMS as internal standard. Polymers were dried overnight under vacuum, and the polymerization activities were calculated from the mass of product obtained. These values were to within 5% of the calculated mass by measuring the ethylene consumed by use of a mass flow controller. The polymers were characterized by GPC analysis at 135 °C in trichlorobenzene (in a Waters Alliance 2000 GPC). Polymer melting points were measured on a TA Instruments model DSC 2920 modulated differential scanning calorimeter at a rate of 10 °C/min for two cycles using a temperature range of 0–160 °C.

Elemental analysis was performed on a Leeman Labs Inc. CE440 elemental analyzer and a Control Equipment Corporation 440 elemental analyzer. Electron impact (EI) mass spectra were obtained at 70 eV on a Thermo-Finnigan MAT95 XP High Resolution Mass Spectrometer using perfluorokerosene (PFK) as reference. FT-IR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets and in solution using C_6D_6 as solvent.

4.2. Synthesis and characterization of compounds

*4.2.1. N-1-(2,6-Diisopropylphenyl)-N′-(2,3,4,5,6-pentafluorophenyl) acetamidine (**2l**)*

(2,6-Diisopropylphenyl)acetimidoyl chloride [18] (1.00 g, 4.2 mmol) was added to a solution of 2,3,4,5,6-pentafluoro phenylaniline (0.77 g, 4.2 mmol), in 20 ml of toluene and stirred for 4 h under reflux. A white solid (**2l•HCl**) was collected by filtration washed with toluene (5 ml). The solid **2l•HCl** was dissolved in DCM and washed three times with 25% of aqueous NH_3 solution. The organic phase was dried over Na_2SO_4. The solvent was removed under vacuum to yield a white solid. Crystallization from methanol gives white crystals in 73% of yield.

^{1}H NMR (399.95 MHz, $CDCl_3$, 298 K): δ/ppm = 7.33–7.20 (m, 3H, *H*-Ph), 5.95 (s, 1H, NH), 3.22 (m, 2H, *CH*-*i*-Pr), 2.04 (s, 3H, *CH*$_3$), 1.29 (d, 6H, $^3J_{HH}$ = 6.4 Hz, *CH*$_3$-*i*-Pr), 1.23 (d, 6H, $^3J_{HH}$ = 6.8 Hz, *CH*$_3$-*i*-Pr). ^{13}C NMR (399.95 MHz, $CDCl_3$, 298 K): δ/ppm = 159.78, 146.08, 132.27, 128.95, 124.16, 123.85, 29.05, 28.65, 24.44, 23.46, 23.04, 18.51. ^{19}F NMR (200 MHz, $CDCl_3$, 298 K): δ/ppm = −146.60, −153.99, −162.61. FT-IR (KBr Pellet, cm^{-1}): 3402(s), 3061(w), 2968(s), 2929(m), 2869(m), 1638(s). EI-MS(+): *m*/*z* = 385.16.

*4.2.2. N′-(2,6-Diisopropylphenyl)-N-[1-(2,6-diisopropylphenylimine) ethyl]-N-(2,3,4,5,6-pentafluorophenylimine)ethylacetamidine (**2La**)*

(2,6-Diisopropylphenyl)acetimidoyl chloride (0.5 g, 2.1 mmol) was added to a solution of *N*-1-(2,6-diisopropylphenyl)-*N*′-(2,3,4,5,6-pentafluorophenyl)acetamidine (**2l**) (0.8 g, 2.1 mmol) in 20 mL of toluene. The reaction mixture was heated at reflux for 24 h. The slightly cloudy mixture was filtered and the filtrate was washed three times with 25% of aqueous NH_3 solution and dried over Na_2SO_4. The solvent was removed under vacuum to yield a yellow oil. Crystallization from ethanol gives a white solid in 68% yield. ^{1}H NMR (399.95 MHz, $CDCl_3$, 298 K): δ/ppm = 7.38–7.22 (m, 3H, *H*-Ph), 7.09–6.99 (m, 3H, *H*-Ph), 3.26 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, *CH*-*i*-Pr), 2.79 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, *CH*-*i*-Pr), 2.12 (s, 3H, *CH*$_3$), 1.91 (s, 3H, *CH*$_3$), 1.26 (dd, 12H, $^3J_{HH}$ = 6.8 Hz, *CH*$_3$-*i*-Pr), 1.17 (d, 12H, $^3J_{HH}$ = 6.8 Hz, *CH*$_3$-*i*-Pr), 0.96 (d, 12H, $^3J_{HH}$ = 6.8 Hz, *CH*$_3$-*i*-Pr). ^{13}C NMR (399.95 MHz, $CDCl_3$, 298 K): δ/ppm = 163.25, 157.78, 147.59, 144.25, 137.09, 136.79, 129.34, 124.53, 123.49, 123.14, 29.12, 28.20, 24.69, 24.41, 23.62, 22.66, 20.23, 19.52. ^{19}F NMR (200 MHz, $CDCl_3$, 298 K): δ/ppm = −146.16, −157.56, −158.64. EI-MS[2La + H]$^+$: *m*/*z* = 586.2.

*4.2.3. N′-(2,6-Diisopropylphenyl)-N-[1-(2,6-diisopropylphenylimine) ethyl]-N-(2,3,4,5,6-pentafluorophenyl)acetamidine (**2Ls**)*

(2,6-Diisopropylphenyl)acetimidoyl chloride (2.00 g, 8.4 mmol) was added to a solution of 2,3,4,5,6-pentafluorophenylaniline (0.77 g, 4.2 mmol), triethylamine (0.85 g, 8.4 mmol) in 60 ml of toluene. The reaction mixture was heated at reflux for 3 h. The slightly cloudy mixture was washed three times with water, and dried over Na_2SO_4. The solvent was removed under vacuum to yield a yellow solid. Crystallization from methanol gives a white solid in 82% yield.

^{1}H NMR (399.95 MHz, $CDCl_3$, 298 K): δ/ppm = 7.11–7.02 (m, 6H, *H*-Ph), 2.84 (sep, 4H, $^3J_{HH}$ = 6.8 Hz, *CH*-*i*-Pr), 2.00 (s, 6H, *CH*$_3$), 2.21 (d, 12H, $^3J_{HH}$ = 7.2 Hz, *CH*$_3$-*i*-Pr), 1.08 (d, 12H, $^3J_{HH}$ = 6.8 Hz, *CH*$_3$-*i*-Pr). ^{13}C NMR (399.95 MHz, $CDCl_3$, 298 K): δ/ppm = 155.99, 144.03, 137.26, 123.81, 123.26, 29.92, 28.36, 23.44, 22.89, 18.99. ^{19}F NMR (200 MHz, $CDCl_3$, 298 K): δ/ppm = −147.29, −156.66, −160.35. FT-IR (KBr Pellet, cm^{-1}): 3402(s), 2968(s), 2929(m), 2869(m), 1638(s). EI-MS[2Ls + H]$^+$: *m*/*z* = 586.32.

*4.2.4. N-(2,6-Diisopropylphenyl)-N-1-(2,6-diisopropylphenylimine)-N-(pyridine-4-yl)acetamide (**3Ls**)*

(2,6-Dimethylphenyl)acetimidoyl chloride (1.00 g, 4.2 mmol) was added to a solution of 4-aminopyridine (0.20 g, 2.1 mmol) and triethylamine (0.42 g, 4.2 mmol) in 60 ml of toluene. The reaction was heated at reflux with stirring for 6 h. The resulting solution was washed three times with distilled water and dried with Na_2SO_4. The solvent was removed under vacuum and a brown solid was obtained. The product was purified using column chromatography (ether/hexanes) and a yellow solid obtained (after solvent evaporation) in a 50% yield.

^{1}H NMR (399.95 MHz, $CDCl_3$, 298 K): δ/ppm = 8.69 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *H*-pyridine), 7.25 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *H*-pyridine), 7.12 (d, 4H, $^3J_{HH}$ = 6,8 Hz, *p*-*H*-Ph), 7.04 (m, 2H, $^3J_{HH}$ = 6.8 Hz, *m*-*H*-Ph), 2.90 (sep, 4H, $^3J_{HH}$ = 6.8 Hz, *CH*-*i*-Pr), 1.97 (s, 6H, *CH*$_3$), 1.23 (d, 12H, $^3J_{HH}$ = 6.8 Hz, *CH*$_3$-*i*-Pr), 1.09 (d, 12H, $^3J_{HH}$ = 6.8 Hz, *CH*$_3$-*i*-Pr). ^{13}C NMR (399.95 MHz, $CDCl_3$, 298 K): δ/ppm = 157.82; 151.31; 151.25; 144.64; 137.15; 123.86; 123.69; 123.23; 28.44; 23.68; 23.03; 19.77. FT-IR (KBr Pellet, cm^{-1}): 2959(s), 2930(w), 2867(w), 1652(s), 1239(s).

*4.2.5. [NiBr$_2${N′-(2,6-diisopropylphenyl)-N-[1-(2,6-diisopropylphen ylimine)ethyl]-N-(2,3,4,5,6-pentafluorophenylimine)acetamidine}] (**2**)*

1 equiv of nickel (II) dibromide 2-methoxyethyl ether (0.14 g, 4.17 mmol) was added to a solution of compound **2Ls**, (0.16 g, 4.17 mmol) in DCM. The mixture was stirred under reflux for 4 days. The reaction showed a progressive change of color from light to dark purple. The resulting solution was filtered, the solvent evaporated and the solid extracted with ether. The product was a purple solid and obtained in a 67% yield. NMR characterization was not possible because the compound is paramagnetic. Elemental analysis (%) $C_{34}H_{40}Br_2F_5N_3Ni$ (*M* = 803.09 g/mol): calculated C 50.78, H 5.01, N 5.23; found. C 60.14, H 5.21, N 4.93.

*4.2.6. [NiBr$_2${[N′-(2,6-diisopropylphenyl)-N-[1-(2,6-diisopropylph enylimine)ethyl]-N-(2,3,4,5,6-pentafluorophenylimine)ethyl] acetamidine}] (**2a**)*

1 equiv of nickel (II) dibromide 2-methoxyethyl ether (0.14 g, 4.17 mmol) was added to a solution of compound **2La**, (0.16 g, 4.17 mmol) in DCM. The mixture was stirred at reflux for 4 days. The reaction showed a progressive change of color from light to dark purple. The resulting solution was filtered, the solvent evaporated and the solid extracted with ether. The product was a purple solid and obtained in a 77% yield. NMR characterization was not possible because the compound is paramagnetic. FT-IR (KBr Pellet, cm^{-1}): 3047(w), 2968(s), 2928(s), 2870(w), 1635(s), 1300(s). Elemental analysis (%) $C_{34}H_{40}Br_2F_5N_3Ni$ (*M* = 803.09 g/mol): calculated C 50.78, H 5.01, N 5.23; found. C 49.84, H 5.46, N 5.33.

*4.2.7. [NiBr$_2${N-(2,6-diisopropylphenyl)-N-[1-(2,6-diisopropylp henylimine)]-N-(pyridine-4-yl)acetamide}] (**3**)*

1 equiv of nickel (II) dibromide 2-methoxyethyl ether (0.11 g, 3.1 mmol) was added to a solution of compound **3L**, (0.15 g, 3.1 mmol) in DCM. The mixture was stirred at room temperature for 4 h. The reaction showed a progressive change of color from green to blue. The resulting solution was filtered, the solvent evaporated and the solid extracted with ether. The product was a purple solid and obtained in a 73% yield. NMR characterization was not possible because the compound is paramagnetic. EI-MS(+): *m*/*z* = 715.3(M$^+$). Elemental analysis (%) $C_{33}H_{44}Br_2N_4Ni$

($M = 715.23$ g/mol): calculated C 55.42, H 6.20, N 7.83; found. C 55.92, H 5.90, N 7.43.

4.3. Typical reaction with ethylene

A solution of (*N*)-imidoylamidine complex (8 μmol) in DCM and MAO solution in toluene (Al/Ni = 2000), were added to a 500 mL glass Parr reactor such that the final volume of the toluene solution was 100 mL. The solution was stirred under nitrogen and brought to temperature. The reactor was then attached to an ethylene line, and the gas fed continuously into the reactor at the specified pressure. After the specified reaction time, the ethylene was vented and acidified methanol (10 wt% HCl) was added to quench any residual MAO in the polymerization. The precipitated polymer was collected by filtration and dried overnight under vacuum.

4.4. Crystallographic characterization

The monocrystal was mounted on a glass fiber and transferred to a *Bruker* CCD platform diffractometer. The SMART program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data) [20]. The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis [21]. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}).

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Appendix. Supplementary material

Additional details about the study for compound **2a** are available in the supporting material. Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.11.035.

References

[1] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169–1204.
[2] L. Bourget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031–3066.
[3] G.W. Coates, Chem. Rev. 100 (2000) 1223–1252.
[4] V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283–316.
[5] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414–6415.
[6] S. Mecking, L.K. Johnson, L. Wang, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 888–899.
[7] P. Kuhn, D. Semeril, D. Matt, M.J. Chetcuti, P. Lutz, Dalton Trans. (2007) 515–528.
[8] Z.J.A. Komon, G.M. Diamond, M.K. Leclerc, V. Murphy, M. Okazaki, G.C. Bazan, J. Am. Chem. Soc. 124 (2002) 15280–15285.
[9] Y. Chen, G. Wu, G.C. Bazan, Angew. Chem., Int. Ed. 44 (2005) 1108–1112.
[10] D.J. Parks, W.E. Piers, M. Parvez, R. Atencio, M.J. Zaworotko, Organometallics 17 (1998) 1369–1377.
[11] A.R. Cabrera, Y. Schneider, M. Valderrama, R. Frohlich, G. Kehr, G. Erker, R.S. Rojas, Organometallics 29 (2010) 6104–6110.
[12] R.S. Rojas, B.C. Peoples, A.R. Cabrera, M. Valderrama, R. Fröhlich, G. Erker, G. Kehr, T. Weigand, H. Eckert, Organometallics (2011). doi:10.1021/om200536z.
[13] C. Valdebenito, M.T. Garland, R. Quijada, R. Rojas, J. Organomet. Chem. 694 (2009) 717–725.
[14] M.N. Kopylovich, A.J.L. Pombeiro, Coord. Chem. Rev. 255 (2011) 339–355.
[15] L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 267–268.
[16] J.D. Azoulay, R.S. Rojas, A.V. Serrano, H. Ohtaki, G.B. Galland, G. Wu, G.C. Basan, Angew. Chem., Int. Ed. 48 (2009) 1089–1092.
[17] R.T. Boere, V. Klassen, G. Wolmershauser, Dalton Trans. (1998) 4147–4154.
[18] R. Caris, B.C. Peoples, M. Valderrama, G. Wu, R. Rojas, J. Organomet. Chem. 694 (2009) 1795–1801.
[19] M.J. Szabo, N.M. Galea, A. Michalak, S.-Y. Yang, L.F. Groux, W.E. Piers, T. Ziegler, J. Am. Chem. Soc. 127 (2005) 14692–14703.
[20] SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc, Madison, WI, 1999.
[21] International Tables for X-Ray Crystallography, Kluwer Academic Publishers, Dordrecht, 1992.