



Acetamidine complexes as catalysts for ethylene polymerization

Carolina Valdebenito^a, María Teresa Garland^{b,d}, Raul Quijada^{a,d}, Rene Rojas^{c,d,*}

^aDepartamento de Ingeniería Química, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile

^bDepartamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile

^cDepartamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago-22, Chile

^dCentro para la Investigación Interdisciplinaria Avanzada en Ciencias de Materiales (CIMAT), Chile

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ABSTRACT

The reaction of (2,6-diisopropyl-phenyl)-acetimidoyl chloride or (2,6-dimethyl-phenyl)-acetimidoyl chloride with 2,6-dimethylaniline in the presence of triethylamine yields a mixture of isomers N'-(2,6-diisopropyl-phenyl)-N-[1-(2,6-diisopropyl-phenylimino)-ethyl]-N-(2,6-dimethyl)-acetamidine (**1a**) and N-(2,6-diisopropyl-phenyl)-N-[1-(2,6-diisopropyl-phenylimino)-ethyl]-N'-(2,6-dimethyl)-acetamidine (**1b**), and N,N'-bis-(2,6-dimethyl-phenyl)-N-[1-(2,6-dimethyl-phenylimino)ethyl]-acetamidine (**2**), respectively. The addition of isomers (**1a** + **1b**) to nickel (II) dibromide 2-methoxyethyl ether, (NiBr₂[O-(C₂H₄OME)₂]) gives a mixture of new nickel complexes, [NiBr₂{N'-(2,6-diisopropyl-phenyl)-N-[1-(2,6-diisopropyl-phenylimino)-ethyl]-N-(2,6-dimethyl)-acetamidine}] (**3a**) and [NiBr₂{N-(2,6-diisopropyl-phenyl)-N-[1-(2,6-diisopropyl-phenylimino)-ethyl]-N'-(2,6-dimethyl)-acetamidine}] (**3b**). Similarly, ligand **2** reacts with nickel (II) dibromide 2-methoxyethyl ether to afford the complex [NiBr₂{N,N'-bis-(2,6-dimethyl-phenyl)-N-[1-(2,6-dimethyl-phenylimino)ethyl]-acetamidine}] (**4**). The structures of the ligands and nickel complexes have been determined by single crystal X-ray diffraction.

The addition of MAO to these complexes generates catalytically active species for the homopolymerization of ethylene. The polymer products are high molecular weight (80–169 K). At temperatures of up to 60 °C both catalysts are a single site giving a monomodal molecular weight distribution. However, at 70 °C the mixture (**3a** + **3b**) shows a bimodal molecular weight distribution.

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1. Introduction

The tailoring of polyolefin bulk properties by synthetic control is a major focus of many industrial and academic research groups [1]. After the development of metallocene catalysts, and the discovery of their activation with MAO and other alkylaluminums in the 1980s many groups began to focus on alternatives to the traditional group 4 metal complexes [2]. Design of the catalyst structure enables control over the polymer microstructure and therefore of important bulk properties [3]. The sensitivity of the group 4 metals such as zirconium and titanium led to the development of late transition metals such as iron, nickel and palladium [4,1c,1d]. The SHOP process for the production of higher olefins from ethylene has a long history, and familiarity with the molecular weight distributions dependence on steric effects on led to the development of the Keim oligomerization catalysts nearly 30 years ago [5]. In these systems it was observed that the ligand bulk could

have pronounced effects on the molecular weight and chain distribution of the product. Subsequently, a number of research groups began investigating ligand structures for the use with late transition metal polymerization catalysts. A large number and varieties of ligands (bi, tri and tetra dentate organic molecules) available for use in the production of these post-metallocene catalysts have been reported [4a]. The bidentate molecules typically bind in a NN [6], NO [7], NP, [8,10d] PO [9] or PP [10] coordination modes, either neutrally or monoanionically coordinated to late transition metals [4c]. While the possibilities of ligand structures are nearly endless, a few general categories have emerged which describe the structure of the catalyst. Brookhart catalyst [11] offer a simplicity of synthesis and an unconfined 5-member ring structure, Bazan α -iminocarboxamide ligands allow for the remote coordination of Lewis acid activators [12].

Substantial variation in geometry and electronics of the ligand and have been explored in both late and early transition metals in the Grubbs salicylaldiminato and FI Catalysts [13]. Brookhart-Gibson catalysts represent a departure from these catalysts in that they are tridentate, sharing the bisimino structure of the Brookhart systems but containing an additional interaction through a backbone integrated pyridine. This leads to a more planar and rigid ligand geometry in addition to substantial changes to the

* Corresponding author. Address: Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago-22, Chile. Tel.: +56 2 3547557; fax: +56 2 3544744.

E-mail address: rrojasg@uc.cl (R. Rojas).

electronics of the metal center. In addition to the N,N,N interaction for the Gibson style ligands [14] other tridentate molecules (neutral or monoanionic), which bind through NNO [15] and NPN [16] coordination modes have been reported. The reactivity, in these type of complexes is mostly dependent on the atoms which are bound to the metal center and how sterically closed the metal center is.

The simplicity and symmetry of the Brookhart and Gibson catalysts structures was striking and led us to design a family of catalysts which we suspect will allow for great flexibility in ligand design and synthesis. While the systems described in this contribution share some structural similarities to the Brookhart and Gibson systems, they possess an additional location from which to incorporate steric and electronic modifications, which has previously demonstrated to be practical [5e,17]. In addition these heteroatoms may potentially allow for the Lewis acid activation of the catalysts, through remote locations [12,18,19]. In this contribution we report on the progress in the synthesis of new (N)-imidoylamidine ligands and their use in the formation of nickel complexes which are active for the polymerization of ethylene. The activity of **3a + 3b** and **4** in presence of MAO towards the homopolymerization of ethylene is described along with the characterization of the products.

2. Results and discussion

2.1. Synthesis and characterization of ligands

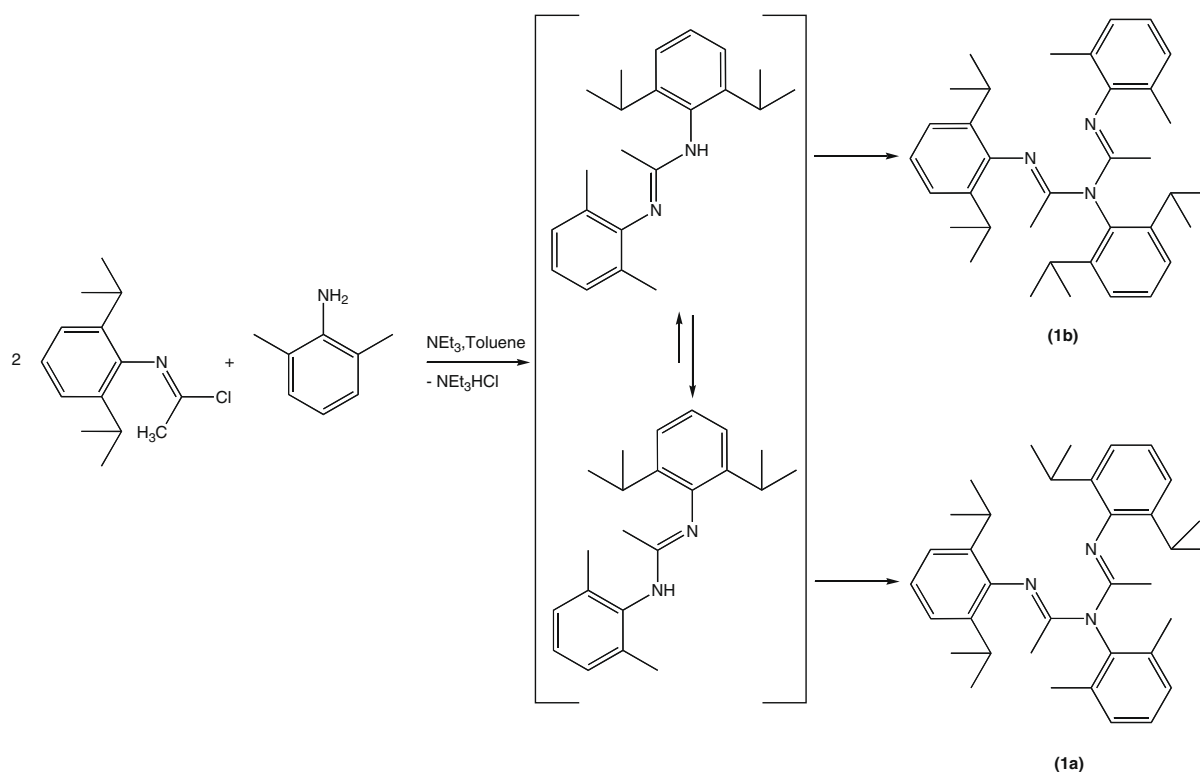
The (N)-imidoylamidine ligand isomers, 2,6-MeC₆H₃N(CMe)₂NC₆H₃-2,6-*i*-Pr₂ (**1a**) and 2,6-*i*-PrC₆H₃N(CMe)₂NC₆H₃-2,6-*i*-Pr-*(CMe)*NC₆H₃-2,6-Me (**1b**) were synthesized by reacting 2 equiv. of imidoyl chloride [20] with 2,6-dimethylaniline in presence of Et₃N in toluene and heating at reflux for 3 h.

The suspension was allowed to cool to room temperature, was filtered, and extracted three times with H₂O. The organic layer was dried with Na₂SO₄, filtered and the solvent removed under vacuum which provided a white solid. Compound **1** was isolated in 85% yield after purification by crystallization from methanol. Two isomers of **1** in a 10:1 ratio were observed by ¹H and ¹³C NMR spectroscopy. Particularly diagnostic peaks are those assigned to the isopropyl groups on the phenyl ring, which in the more symmetric isomer **1a** appear at 2.92 ppm, while the minor and less symmetric isomer has two peaks for the isopropyl groups, one of which is shifted downfield to 3.41 ppm and the second appears at 2.86 ppm.

Single crystals of both isomers suitable for X-ray analysis were separated by slow crystallization from methanol followed by physical separation based upon crystal size (the major isomer forms larger crystals). ¹H and ¹³C NMR studies were performed on the isolated compounds and the structures of the isomers correspond to those shown in Scheme 1. We suspect that the two isomers (Schemes 1, **1a** and **1b**) are formed by the transposition of the hydrogen in the intermediate, N-(2,6-diisopropylphenyl)-N'-(2,6-dimethylphenyl)-acetimidine. When the hydrogen atom is located over the less crowded nitrogen the more symmetric ligand **1a** is generated, while when the hydrogen is located on the more crowded nitrogen the less symmetric ligand is produced **1b**.

The ORTEP structures of the isomers are shown in Fig. 1. In solid state the ligands adopt a non planar arrangement similar to 2,6-*i*-PrC₆H₃N(CMe)₂NC₆H₃-2,6-*i*-Pr₂ recently reported [21].

In the minor isomer, Fig. 1, (right) two of nitrogen atoms, N(2) and N(3) occupy a common plane with C(13) and C(27), while the third, N(1), is twisted out of this plane and is nearly perpendicular. The N(3)–C(27) and N(2)–C(27) bond distances are 1.273(2), consistent with a double bond, and 1.386(2), with single bond character, respectively, Table 1. The N(1)–C(13) distance of the



Scheme 1. Synthesis of (N)-imidoylamidine ligands.

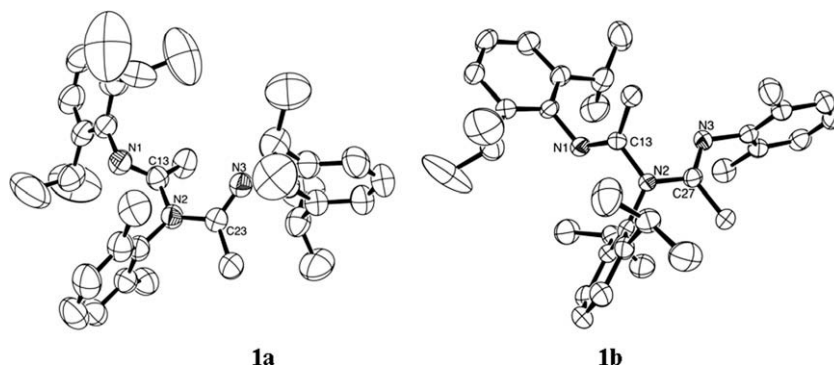
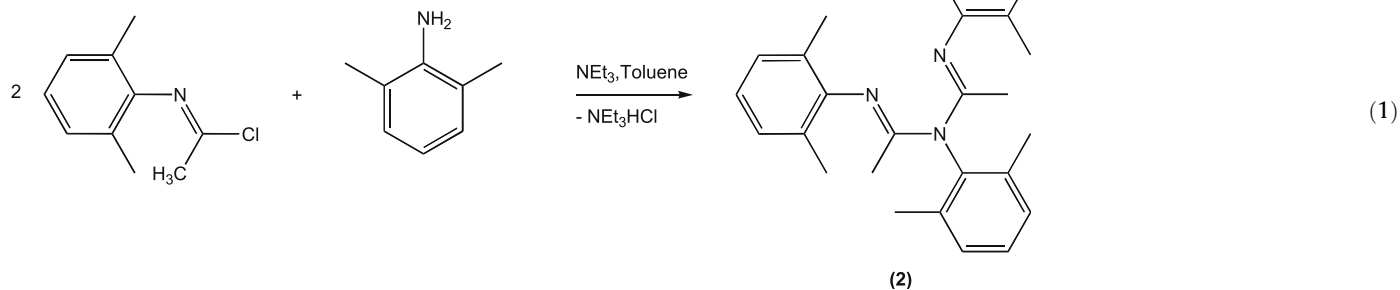


Fig. 1. ORTEP of **1a** and **1b** drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distance (Å) and angle (°) for (N)-imidoylamidine ligand.

	1a	1b
N(1)–C(13)	1.2690(19)	1.258(2)
N(2)–C(13)	1.4197(19)	1.446(2)
N(2)–C(27)		1.386(2)
N(2)–C(23)	1.3945(19)	
N(3)–C(27)		1.273(2)
N(3)–C(23)	1.2689(19)	
N(1)–C(13)–N(2)	117.19(13)	116.73(16)
C(13)–N(2)–C(27)		117.67(14)
C(13)–N(2)–C(23)	120.74(12)	
N(3)–C(27)–N(2)		118.42(16)
N(3)–C(23)–N(2)	118.48(13)	

With the goal of accessing a wide variety of (N)-imidoylamidine ligands, we prepared 2,6-dimethylphenylimidoyl chloride following literature procedures [20,21]. Subsequently, a fully symmetric (N)-imidoylamidine, N,N'-bis-(2,6-dimethyl-phenyl)-N-[1-(2,6-dimethyl-phenylimino)ethyl]-acetamidine **2** was synthesized by reacting 2 equiv. of 2,6-dimethylphenylimidoyl chloride with 2,6-dimethylaniline in presence of Et₃N in toluene and heating at reflux for 3 h (Eq. (1)). Compound **2** was isolated in 87% yield by crystallization from ethanol. The ¹H NMR and ¹³C NMR show only a single isomer. Characteristic signals include: 2.46 ppm (s, 6H, Ph-CH₃), 2.19 (s, 12H, Ph-CH₃), 1.95 (s, 6H, (C=N)CH₃).



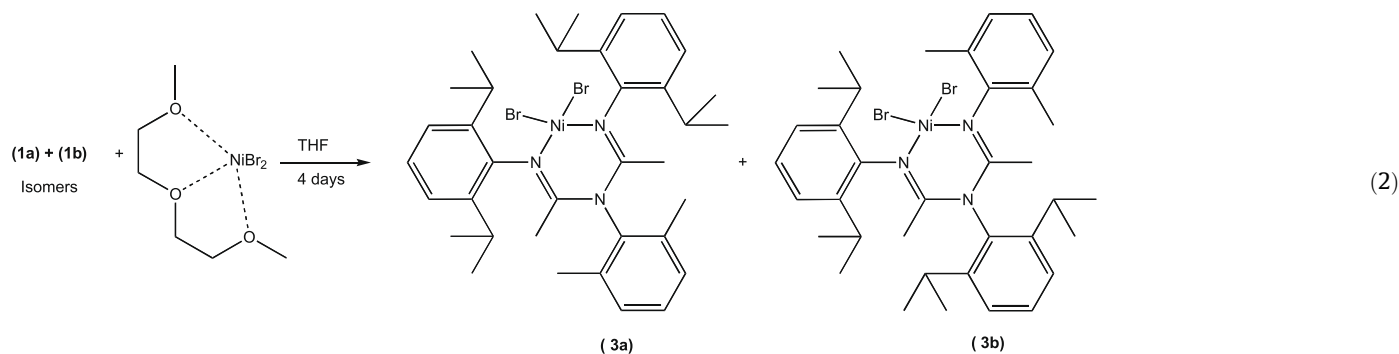
out of plane imine is 1.2690(19), slightly shorter than the one in the plane which could be due more sterically crowded environment around N(3) and C(27).

A significant difference is observed in the N(2)–C(13) bond distance which is 0.06 Å longer than N(2)–C(27). This is consistent with conjugation in the direction of the N(3) atoms, likely with the assistance of the lone pair of N(2). The ORTEP structure of the more symmetric ligand (Fig. 1 left) shows that the ligand shares a similar planar arrangement but in this instance the N(1) is less twisted out of the plane, and is nearly coplanar with the rest of the backbone. The bond distances observed in the more symmetric ligand are similar to those observed in **1b** and are in agreement with what would be expected in a conjugated bond, between N(2)–C(23)–N(3).

Full details of the crystal structure parameters of the ligand **2** are available in the supporting information.

2.2. Synthesis of nickel complexes

Eq. (2) depicts the synthesis of [NiBr₂{N'-(2,6-diisopropyl-phenyl)-N-[1-(2,6-diisopropyl-phenylimino)-ethyl]-N-(2,6-dimethyl)-acetamidine}] (**3a**) and [NiBr₂{N-(2,6-diisopropyl-phenyl)-N-[1-(2,6-diisopropyl-phenylimino)-ethyl]-N'-(2,6-dimethyl)-acetamidine}] (**3b**) by the addition of **1** as a mixture of isomers to nickel (II) dibromide 2-methoxyethyl ether in THF at room temperature for 4 days. Crystallization from THF–Ether allows isolation of **3a** and **3b** isomers as air and thermally stable dark purple crystals in 70% yield.



Single crystals of **3a** and **3b** suitable for X-ray diffraction studies were obtained by diffusion of ether into a THF solution at room temperature. The results are shown in Fig. 2. The molecular structures show a six member chelate ring formed by the ligand in a N,N-binding mode to the nickel dibromide as expected. In both isomers the tetrahedral geometry around nickel is slightly distorted. For example in complex **3a** (the most symmetric), Br(2) is almost perpendicular to the plane of the ring. This can be observed in the corresponding angle N(1)–Ni–Br(2) (101.32(9)°) while the angle of N(1)–Ni–Br(1) is 122.18(9)°. The N(3)–C(27), N(1)–C(13) and N(2)–C(27), N(2)–C(13) bond distances are 1.293(5), 1.279(5) and 1.392(5), 1.405(5), respectively, Table 2. The second isomer **3b** shows nearly the same bond distances for N(3)–C(23), N(1)–C(9) and N(2)–C(23), N(2)–C(9); 1.283(3), 1.287(3) and 1.411(3), 1.402(3), respectively. If we compare the **3b** distances with those of the pure ligand **1b**, we find that the N–C distances of the amine fragment (N(2)–C(23), N(2)–C(9)) become similar in length, due to the coordination of the ligand to the nickel center.

The amine bound phenyl ring rests orthogonal to the plane of the chelated ring with distances of the N(2)–C(15), 1.444(4) Å similar to that of the complex N(2)–C(11), 1.470(3) Å.

Another noticeable characteristic of this type of ligand frameworks bound to the nickel is the planar line configuration of the chelated ring, which is not observed in the case of (CH₂(C(Me)NC₆H₃-2,6-*i*-Pr)₂)NiBr₂ [6b].

The synthesis of the less crowded and more symmetric complex was prepared by reaction of N,N-(2,6-dimethyl-phenyl)-N-[1-(2,6-

Table 2

Selected bond distance (Å) and angle (°) for (N)-imidoylamidine nickel complexes.

	3a	3b	4
Ni–Br(1)	2.3428(6)	2.3218(4)	2.3874(10)
Ni–Br(2a)	2.3660(7)	2.3862(4)	2.3543(9)
Ni–Br(2b)		2.473(7)	
Ni–N(1)	1.979(3)	1.9764(17)	1.984(4)
Ni–N(3)	1.981(3)	1.9759(17)	1.977(4)
N(3)–C(23)	1.293(5)	1.283(3)	
N(3)–C(27)			1.294(6)
N(3)–C(19)		1.287(3)	1.284(6)
N(1)–C(9)			
N(1)–C(13)	1.280(5)		
N(2)–C(23)		1.411(3)	
N(2)–C(27)	1.293(5)		
N(2)–C(9)		1.402(3)	1.403(6)
N(2)–C(13)	1.405(5)		
N(2)–C(19)			1.399(6)
N(3)–Ni–N(1)	90.30(13)	89.76(7)	90.06(16)
Br(1)–Ni–Br(2a)	119.12(3)	122.473(15)	118.98(3)
N(3)–Ni–Br(1)	115.91(10)	115.83(5)	108.92(13)
N(1)–Ni–Br(1)	122.18(9)	115.57(5)	104.69(12)

dimethyl-phenylimino)-ethyl]-acetamidine with nickel (II) dibromide 2-methoxyethyl ether in dichloromethane (DCM) at 75 °C for 48 h, Eq. (3). Compound **4** is obtained in near quantitative yields, after filtration, solvent evaporation and recrystallization from DCM.

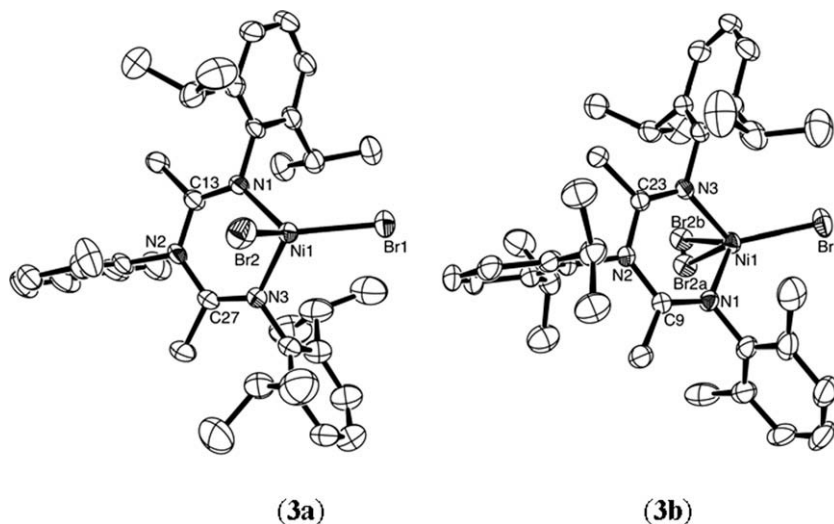


Fig. 2. ORTEP drawing of **3a** and **3b** drawn at 50% probability. Hydrogen atoms are omitted for clarity.

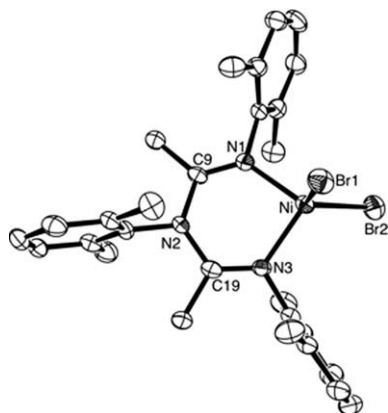
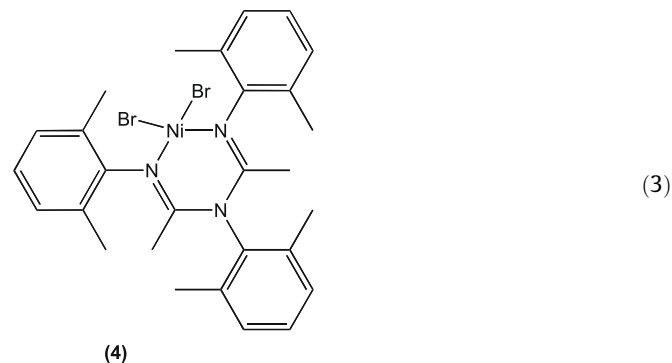
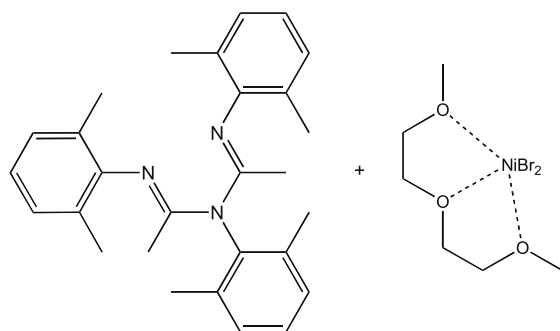


Fig. 3. ORTEP drawing of **4**, drawn at 50% probability. Hydrogen atoms are omitted for clarity.



Single crystals of **4** suitable for X-ray diffraction studies were obtained by diffusion of ether into a DCM solution at room temperature. The results of this study are shown in Fig. 3. The molecular structure shows a six-member chelate ring. The reduction in steric bulk around the nickel center allows for a more tetrahedral geometry compared to the more crowded nickel complexes Fig. 2. The imine N(1)–C(9) and N(3)–C(19) bond lengths are 1.284(6) and 1.294(6), respectively similar to the corresponding distances in complexes **3a** and **3b**, Table 2.

2.3. Activation with MAO and reactivity towards ethylene

Polymerization studies with the family of N-imidoamidinate nickel complexes ($[\text{Ni}(\text{N-imidoamidinate})] = 8.0 \times 10^{-5} \text{ M}$) acti-

vated with MAO, 2000 equiv. of Al, were carried out, and the results are summarized in Table 3. Reactions were performed inside a 500 mL glass reactor in toluene (100 mL) at an ethylene pressure of 2–4 bar. The reactions used an external water bath to maintain the temperature constant at 60–70 °C. Entry 1 corresponds to the reactivity previously reported for $\text{CH}_2(\text{C}(\text{Me})\text{NC}_6\text{H}_3\text{-2,6-}i\text{-Pr})_2\text{NiBr}_2/\text{MAO}$ [6b] and is provided for comparison. Entries 2 and 3 show the results obtained at different reaction pressure for **3a** + **3b** precatalyst. Comparison of these entries shows that the ethylene consumption increases at higher pressure.

The results obtained with **4**/MAO, entries 6 and 7 demonstrate that this combination also yields ethylene polymerization sites. A comparison of these results with catalyst **3a** + **3b** under the same reaction conditions (entries 2, 5 and 3, 6) shows that the polymerization activity decreases with a reduction of the steric bulk on the N-imidoamidinate ligand.

Table 3
Ethylene polymerization reactions.^a

Entry	Precatalyst	Temperature (°C)	Pressure (bar)	Activity ^b	M_w (g/mol)	M_w/M_n	T_m (°C)
1	Ref. Catalyst ^c	60	2	119	–	–	–
2	3a + 3b	60	2	141	160.000	1.9	132
3	3a + 3b	60	4	547	169.000	1.7	132
4	3a + 3b	70	4	540	87.000, 21.000	1.7, 1.04 ^d	136
5	4	60	2	45	98.000	1.8	138
6	4	60	4	95	112.000	1.9	136

^a Polymerizations were carried out in 500 mL autoclave reactor with 8 μmol of precatalyst, Al/Ni ratio, 2000 in 100 mL of toluene; reaction time, 30 min.; temperature controlled by thermo bath.

^b kg polymer/(mol Ni)(h).

^c Catalysts prepared as a reference.

^d Bimodal distribution.

Thermal analysis was performed using differential scanning calorimetry (DSC). Results are shown in Table 3. Samples were scanned from 0 °C to 160 °C at 10 °C/min (taking the data from the second cycle). One sharp thermal transitions at 132 °C are observed for the PE obtained from compound **3a** and **3b** when the reaction are performed at 60 °C, increasing 4° when the reaction temperature was increased to 70 °C, indicating the production of linear PE. The polymer obtained with complexes **4**/MAO yield also unbranched PE with a melting transition of 137 °C (average).

Comparison of the entries 2 and 3 with 5 and 6 shows that the molecular weight of the resulting polymers decreases with a reduction of the steric bulk on the N-imidoamidinate ligand, while the PDIs (M_w/M_n ratios) are approximately 1.8. However, both

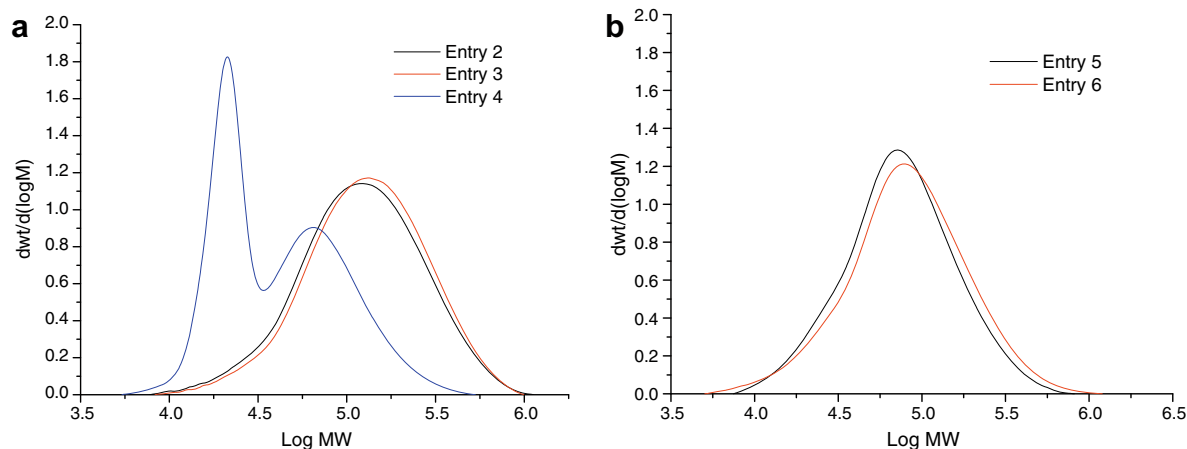


Fig. 4. GPC analysis of the polyethylene isolated from: (a) catalysts **3a** + **3b** and (b) catalyst **4**, Table 3, relative to polystyrene standards at 135 °C.

systems show a slightly increase in the molecular weights when the ethylene pressure was varied from 2 to 4 bar, Table 3 and Fig. 4a trace red¹ and black for catalyst **3a** + **3b** and Fig. 4b for catalyst **4**. This behavior can be associated with an increased propagation rate at higher ethylene concentration. Under these conditions the PDI of the polyethylene obtained remained constant. When the temperature was increased at 70 °C the systems which are composed of isomers, shows a bimodal molecular weight distribution, indicating a second site generate polymers, giving a low molecular weight fraction ($M_w = 21$ K). The deconvolution of the trace in Fig. 4a (blue trace), shows that the second reactive site behaves as a living catalyst (PDI = 1.04). Work in progress, involves isolating the isomers to determine the identity of living site in these systems.

3. Conclusion

In conclusion, we have described the synthesis and characterization of stable symmetrical and non-symmetrical (N)-imidoylamidine ligands and the nickel complexes produced through reaction with nickel (II) dibromide 2-methoxyethyl ether. This synthetic route represents a general pathway into a wide variety of ligand and NiBr₂{(N)-imidoylamidine} complexes. Separation of the complexes (**3a** + **3b**) was achieved by crystallization and the physical separation of the isomers. The catalytic activity for the polymerization of ethylene in the presence of MAO has also been investigated. The polymers properties indicate that the product is a linear and high molecular weight (80–169 K) polyethylene.

4. Experimental

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. All polymerization reactions were carried out in a Parr autoclave reactor as described below. Toluene for polymerization was distilled from sodium-benzophenone ketyl. The synthesis of compounds **1a**, **b** and **2** used procedures similar to the literature procedure [20,21] and were purified by recrystallization. NMR

spectra were obtained using Varian Unity 200 and 400 Bruker spectrometers using deuterated solvent with 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 Polymers Laboratories, high-temperature chromatograph, PI-GPC 200). Polymer melting points were measured on a TA Instruments differential scanning calorimeter (model DSC 290 modulate TA Instruments) 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 FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets and in solution using C₆D₆ as solvent.

4.2. Synthesis and characterization of compounds

4.2.1. N'-(2,6-diisopropyl-phenyl)-N-[1-(2,6-diisopropyl-phenylimino)-ethyl]-N-(2,6-dimethyl)-acetamidine (**1a**)

(2,6-diisopropylphenyl)acetimidoyl [20] (2 g, 8.4 mmol) was added to a solution of 2,6-dimethylaniline (0.51 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 Na₂SO₄. The solvent was removed under vacuum to yield a yellow solid. Crystallization from ethanol gives a white solid in 85% of yield. The ¹H NMR spectrum shows two isomers in a 10:1 ratio, N'-(2,6-diisopropyl-phenyl)-N-[1-(2,6-diisopropyl-phenylimino)-ethyl]-N-(2,6-dimethyl)-acetamidine (**1a**) and N-(2,6-diisopropyl-phenyl)-N-[1-(2,6-diisopropyl-phenylimino)-ethyl]-N'-(2,6-dimethyl)-acetamidine (**1b**), respectively. ¹H NMR (399.95 MHz, [d₃]-chloroform, 298 K): Major isomer **1a**, δ = 7.26–7.00 (m, 9H, H-Ph), 2.92 (sep, 4H, ³J_{HH} = 6.8 Hz, CH-iPr), 2.42 (s, 6H, CH₃), 1.92 (s, 6H, CH₃), 1.19 (d, 12H, ³J_{HH} = 6.8 Hz, CH₃-iPr), 1.06 (d, 12H, ³J_{HH} = 6.8 Hz, CH₃-iPr). Minor isomer **1b**, δ 7.34–6.84 (m, 6H, H-Ph), 3.41 (sep, 2H, ³J_{HH} = 6.8 Hz, CH-iPr), 2.86 (sep, 2H, ³J_{HH} = 6.8 Hz CH-iPr) 2.08 (s, 6H, CH₃), 2.01 (s, 3H, CH₃), 1.82 (s, 3H, CH₃), 1.28 (d, 6H, ³J_{HH} = 6.4 Hz, CH₃-iPr), 1.27 (d, 6H, ³J_{HH} = 6.4 Hz, CH₃-iPr) 1.18 (d, 6H, ³J_{HH} = 6.8 Hz, CH₃-iPr), 0.94 (d, 6H, ³J_{HH} = 6.8 Hz, CH₃-iPr). ¹³C NMR (125.7 MHz, [d₃]-chloroform, 298 K): Major isomer **1a**, 156.47, 147.86, 137.32, 137.22, 128.38, 127.23, 122.87, 122.78, 28.10, 24.43, 22.94, 19.18, 18.40; Minor isomer **1b**, 158, 147.89,

¹ For interpretation of color in Fig. 4, the reader is referred to the web version of this article.

137.00, 128.58, 127.88, 127.25, 124.06, 122.86, 122.82, 29.06, 27.94, 24.67, 24.45, 23.53, 22.58, 18.15.

4.2.2. *N,N'*-bis-(2,6-dimethyl-phenyl)-*N*-[1-(2,6-dimethyl-phenylimino)ethyl]-acetamidine (**2**)

To a solution of 2,6-dimethylaniline (0.38 g, 3.2 mmol), triethylamine (0.64 g, 6.4 mmol) in 60 ml of toluene was added (2,6-dimethylphenyl)acetimidoyl (1 g, 6.4 mmol). The reaction 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 ethanol gives a white solid in 87% of yield. ^1H NMR (399.95 MHz, $[\text{d}_3]$ -chloroform, 298 K): δ 7.18 (m, 3H, H-Ph), 7.04 (d, 4H, $^3J_{\text{HH}} = 7.6$ Hz, H-Ph), 6.87 (t, 2H, $^3J_{\text{HH}} = 7.6$ Hz, H-Ph) 2.46 (s, 6H, Ph- CH_3), 2.19 (s, 12H, Ph- CH_3), 1.95 (s, 6H, (C=N) CH_3). ^{13}C NMR (125.7 MHz, $[\text{d}_3]$ -chloroform, 298 K): 156.78, 147.53, 141.01, 137.08, 128.58, 127.99, 127.87, 127.05, 122.31, 18.96, 18.59, 18.52.

4.2.3. $[\text{NiBr}_2\{\text{N}'\text{-}(2,6\text{-diisopropyl-phenyl})\text{-N-[1-(2,6-diisopropyl-phenylimino)-ethyl]-N-(2,6-dimethyl)-acetamidine}\}]$ (**3a**) and $[\text{NiBr}_2\{\text{N-(2,6-diisopropyl-phenyl)-N-[1-(2,6-diisopropyl-phenylimino)-ethyl]-N'-(2,6-dimethyl)-acetamidine}\}]$ (**3b**)

One equivalent of nickel (II) dibromide 2-methoxyethyl ether (0.041 g, 1.34 mmol) was added to a solution of isomers mixture **1a** and **1b**, (0.07 g, 1.34 mmol) in THF was added. The mixture was stirred at room temperature for 4 days. The reaction showed a progressive change of color from green to 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 70% yield. NMR characterization was not possible because the compound is paramagnetic. FT-IR (KBr Pellet, cm^{-1}): 3439(m), 3063(w), 3021(w), 2961(s), 2925(m), 2867(m), 1644(s). EI-MS(+): $m/z = 662.31$ ($\text{M}^+ - \text{Br}$).

4.2.4. $[\text{NiBr}_2\{\text{N,N}'\text{-bis-(2,6-dimethyl-phenyl)-N-[1-(2,6-dimethyl-phenylimino)ethyl]-acetamidine}\}]$ (**4**)

One equivalent of nickel (II) dibromide 2-methoxyethyl ether (0.070 g, 2.3 mmol) was added to a solution of **2**, (0.10 g, 2.43 mmol) in DCM was added. The mixture was stirred at room temperature for 48 h. The reaction showed a progressive change of color from green to 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 86% yield. NMR characterization was not possible because the compound is paramagnetic. FT-IR (KBr Pellet, cm^{-1}): 3422(s), 3060(w), 2962(s), 2926(m), 2867(m), 1632(s). EI-MS(+): $m/z = 629.10$.

4.3. Typical procedure for polymerization of ethylene

Toluene, (N)-imidoylamidine complex (8 μmol) dissolved 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 under nitrogen. The reactor was attached to an ethylene line, and the gas fed continuously into the reactor at the specified pressure. The pressurized reaction mixture was stirred at a temperature controlled by an external bath. After a specific reaction time, the ethylene was vented and HCl–MeOH (10%) was added to quench the excess of MAO in the polymerization. The precipitated polymer was collected by filtration and dried overnight under vacuum.

4.4. Crystallography characterization

The monocrystal was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART [22] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction

Table 4
Crystal data and structure refinement for (N)-imidoylamidine ligand.

	1a	1b
Empirical formula	$\text{C}_{36}\text{H}_{49}\text{N}_3$	$\text{C}_{36}\text{H}_{49}\text{N}_3$
Formula weight	523.78	523.78
Temperature (K)	150(2)	150(2)
Wavelength (\AA)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/c$	$P\bar{1}$
Unit cell dimensions		
<i>a</i> (\AA)	10.8098(4)	10.2414(11)
<i>b</i> (\AA)	13.8640(5)	10.6912(12)
<i>c</i> (\AA)	22.6187(7)	16.2338(18)
α ($^\circ$)	90	82.350(2)
β ($^\circ$)	95.2900(10)	74.429(2)
γ ($^\circ$)	90	73.118(2)
Volume (\AA^3)	3375.4(2)	1635.5(3)
Z	4	2
D_{calc} (Mg m^{-3})	1.031	1.064
Absorption coefficient (mm^{-1})	0.060	0.062
$F(000)$	1144	572
Crystal size (mm^3)	$0.59 \times 0.55 \times 0.46$	$0.19 \times 0.09 \times 0.08$
θ Range ($^\circ$)	1.89–27.90	1.99–27.77
Index ranges	$-14 \leq h \leq 13$ $-18 \leq k \leq 18$ $-29 \leq l \leq 28$	$-12 \leq h \leq 13$ $-13 \leq k \leq 13$ $0 \leq l \leq 21$
Reflections collected	27470	6711
independent reflections	7647 [$R_{\text{int}} = 0.0229$]	6711 [$R_{\text{int}} = 0.0529$]
Completeness to $\theta = 26.48^\circ$ (%) (for 1) and 28.52° (%) (for 1', 2)	100.0	96.9
Data/restraints/parameters	7647/3/364	6711/0/364
Goodness-of-fit on F^2	1.193	1.226
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0662$, $wR_2 = 0.2044$	$R_1 = 0.0632$, $wR_2 = 0.1042$
<i>R</i> indices (all data)	$R_1 = 0.0904$, $wR_2 = 0.2233$	$R_1 = 0.1193$, $wR_2 = 0.1220$
Largest difference in peak and hole ($e \text{\AA}^{-3}$)	0.337 and -0.221	0.262 and -0.226

Definitions: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum (F_o^2 - F_c^2)^2 / \sum (w(F_o^2)^2)]^{1/2}$, $\text{GOF} = [\sum (w(F_o^2 - F_c^2)^2) / (n - p)]^{1/2}$, where *n* is the number of the reflections and *p* is the total number of the parameters refined. min/max.

Table 5
Crystal data and structure refinement for (N)-imidoylamidine nickel complexes.

	3a	3b	4
Empirical formula	C ₃₆ H ₄₉ N ₃ Br ₂ Ni	C ₃₆ H ₄₉ N ₃ Br ₂ Ni	C ₂₈ H ₃₃ N ₃ NiBr ₂ × CCl ₂ H ₂
Formula weight	742.31	742.31	715.03
Temperature (K)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P $\bar{1}$	P2(1)/n	P2(1)/c
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	10.0112(9)	11.2211(8)	13.631(2)
<i>b</i> (Å)	11.1804(10)	17.8539(13)	3.0323(19)
<i>c</i> (Å)	16.9769(15)	18.2779(14)	18.203(3)
α (°)	90.3390(10)	90	90
β (°)	99.7510(10)	102.3690(10)	107.422(2)
γ (°)	108.0690(10)	90	90
Volume (Å ³)	1776.9(3)	3576.8(5)	3085.3(8)
<i>Z</i>	2	4	4
<i>D</i> _{calc} (Mg m ⁻³)	1.387	1.378	1.539
Absorption coefficient (mm ⁻¹)	2.822	2.804	3.415
<i>F</i> (000)	768	1536	1448
Crystal size (mm ³)	0.36 × 0.32 × 0.05	0.64 × 0.41 × 0.35	0.25 × 0.25 × 0.09
θ Range(°)	1.92–27.69	1.96–27.83	1.57–26.55
Index ranges	–12 ≤ <i>h</i> ≤ 13 4 ≤ <i>k</i> ≤ 14 –22 ≤ <i>l</i> ≤ 21	–14 ≤ <i>h</i> ≤ 14 –23 ≤ <i>k</i> ≤ 23 –23 ≤ <i>l</i> ≤ 23	–14 ≤ <i>h</i> ≤ 17 –15 ≤ <i>k</i> ≤ 16 –22 ≤ <i>l</i> ≤ 22
Reflections collected	17808	25610	19492
Independent reflections	7596 [<i>R</i> _{int} = 0.0298]	7905 [<i>R</i> _{int} = 0.0245]	612 [<i>R</i> _{int} = 0.0656]
Completeness to $\theta = 26.48^\circ$ (%) (for 1) and 28.52° (%) (for 1', 2)	98.8	99.9	95.2
Data/restraints/parameters	7596/0/392	7905/0/395	6112/0/342
Goodness-of-fit on <i>F</i> ²	1.059	1.059	1.260
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0521, <i>wR</i> ₂ = 0.1290	<i>R</i> ₁ = 0.0335, <i>wR</i> ₂ = 0.0800	<i>R</i> ₁ = 0.0552, <i>wR</i> ₂ = 0.1184
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0718, <i>wR</i> ₂ = 0.1386	<i>R</i> ₁ = 0.0443, <i>wR</i> ₂ = 0.0838	<i>R</i> ₁ = 0.1029, <i>wR</i> ₂ = 0.1409
Largest difference in peak and hole (e Å ⁻³)	1.457 and –0.602	0.860 and –0.415	1.357 and –0.543

Definitions: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum (F_o^2 - F_c^2)^2 / \sum (w(F_o^2))^2]^{1/2}$, $GOF = [\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$, where *n* is the number of the reflections and *p* is the total number of the parameters refined. min/max.

data). The raw frame data was processed using SAINT [23] and SADABS [24] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL [25] program. The structure was solved by direct methods and refined on *F*² by full-matrix least-squares techniques. The analytical scattering factors [26] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (*x*, *y*, *z* and *U*_{iso}) [27].

4.4.1. X-ray crystal structure determination parameters of ligand **1a** and **1b** (Table 4) and complexes **3a**, **3b** and **4** (Table 5)

See Tables 4 and 5.

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Appendix A. Supplementary material

CCDC 705306, 705307, 705308, 705309, 705310, and 705311 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.066.

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