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Synthesis and Characterization of a Cationic Cyclopentadienyl Nickel(II) Complex of Bis(mesityl-imino)acenaphthene and its Evaluation as a New Catalyst Precursor for Ethylene Polymerization

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O complexo catiônico ciclopentadienílico de níquel(II) contendo o ligante bis(mesitil-imino)acenafteno, de fórmula [Ni(η^5-C$_5$H$_5$)(Mes-BIAN)]PF$_6$ (Mes = mesitil = 2,4,6-Me$_3$-C$_6$H$_2$; Mes-BIAN = bis(mesitil-imino)acenafteno), foi sintetizado através de duas estratégias alternativas, tendo sido obtido com rendimentos moderado a quantitativo. Apesar de ser electronicamente saturado, este novo complexo foi testado na polimerização de etileno e propileno na presença do cocatalisador metilaluminoxano (MAO), mostrando ser um precursor catalítico eficiente da polimerização de etileno em condições suaves de reação (baixa temperatura e pressão), enquanto que se revelou inativo em relação ao propileno. Os polietilenos obtidos apresentam ramificações metílicas e um baixo teor em ramificações longas.

A cationic cyclopentadienyl nickel(II) complex of bis(mesityl-imino)acenaphthene, [Ni(η^5-C$_5$H$_5$)(Mes-BIAN)]PF$_6$ (Mes = mesityl = 2,4,6-Me$_3$-C$_6$H$_2$; Mes-BIAN = bis(mesityl-imino)acenaphthene), was synthesized via two alternative routes, being obtained in moderate to quantitative yields. Although electronically saturated, this new complex was tested in the polymerization of ethylene and propylene in the presence of the cocatalyst methylaluminoxane (MAO), and found to behave as an efficient catalyst precursor for the polymerization of ethylene under mild reaction conditions (low temperature and pressure), whereas it was inactive towards propylene. The polyethylenes produced show methyl branching and a low content of long branches.

**Keywords:** α-diimine, catalyst, cyclopentadienyl, nickel complexes, polymerization of ethylene

Introduction

The development of new nickel and palladium based catalysts for the preparation of high molecular weight polyethylenes with controlled branching has been a subject of interest both in academia and industry.[1] A major breakthrough occurred nearly two decades ago when neutral and cationic Ni(II) and Pd(II) catalysts bearing bulky α-diimine ligands of the aryl-diazadiene (DAD) or aryl-BIAN (aryl-BIAN = bis(aryl-imino)acenaphthene; An = acenaphthyl) types were prepared by Brookhart *et al.* (Scheme 1, **A** and **B**).[2] The presence of these sterically

hindered ligands was shown to be crucial for blocking the axial coordination sites on the metal center towards the incoming monomer and reduction of chain transfer reactions. These electronically unsaturated neutral complexes (Scheme 1, **A**) polymerized ethylene, propylene and 1-hexene when activated with methylaluminoxane (MAO), whereas the corresponding 16-electron cationic methyl nickel complexes (Scheme 1, **B**) were shown to be equally active without requiring the use of an alkylaluminium cocatalyst,[3] since the initiation of the polymerization process occurs through migratory insertion of coordinated ethylene into the Ni-alkyl bond. The obtained polyethylenes exhibited high molecular weights and relatively narrow molecular weight distributions, but were highly branched (ca. 100 branches/1000 carbon

A

B

M = Ni, Pd; Ar = ; Ar' = ; R' = H, Me, An

C ; Ar =
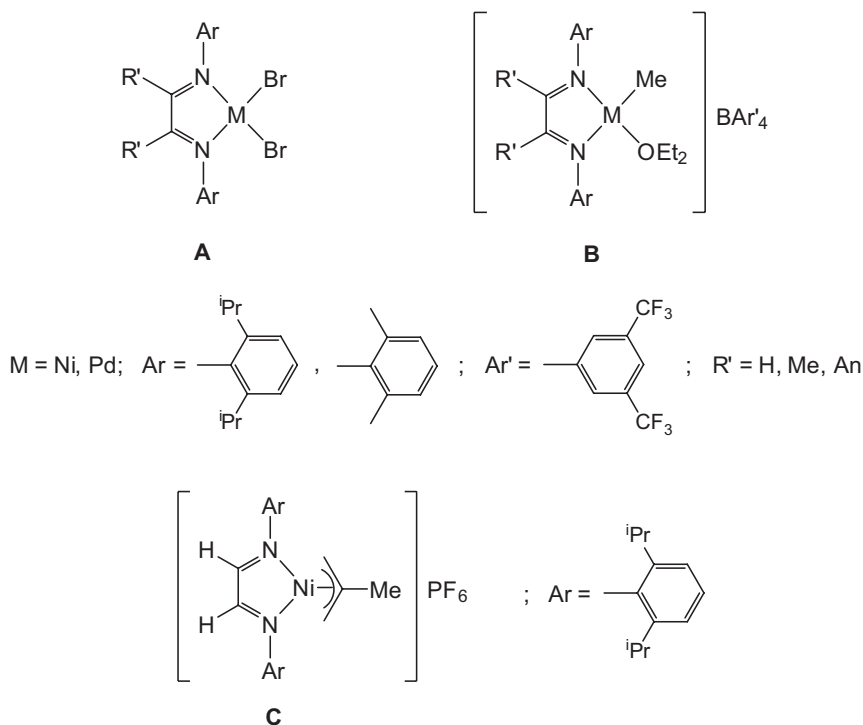
Scheme 1. α-diimine complexes prepared by Brookhart (**A** and **B**)[2,3] and de Souza (**C**).[4]

atoms), particularly those prepared with the Pd(II) catalysts. The major disadvantage associated with these catalyst systems was the need for a large excess of the aluminium cocatalyst, MAO, which is a very expensive material.

In 1997, de Souza *et al.*[4] reported the 16-electron cationic Ni(II) complex [Ni(η^3-methallyl)(^{i}Pr$_2$-DAD)] PF$_6$ (Scheme 1, **C**), which, despite bearing an allyl group coordinated to Ni, was revealed to be highly active in the polymerization of ethylene only in the presence of organoaluminium activators (MAO or AlEt$_2$Cl), under mild reaction conditions, and at low Al/Ni ratios. The obtained polymers covered a large range of properties, between high density polyethylene (HDPE) and low density polyethylene (LDPE).

We have been interested in complexes of nickel containing either aryl-BIAN[5] or cyclopentadienyl (η-C$_5$H$_5$)[6,7] ligands. In transition metal complexes on the left side of the periodic table, the η^5-cyclopentadienyl ligand is essentially a non-reactive fragment, in contrast to later electron-rich transition metals in which it may not be a pure spectator. In the case of cyclopentadienyl nickel complexes, this ligand can display reactivity, in particular, undergoing η^5 to η^1 ring-slippage processes upon coordination of further ligands to the metal center.[8]

In the present work, we report the synthesis of the first cationic nickel(II) complex bearing simultaneously a cyclopentadienyl ring and an α-diimine ligand, its characterization by multinuclear nuclear magnetic

resonance (NMR) spectroscopy and X-ray diffraction, as well as its application as an efficient catalyst precursor for the polymerization of ethylene when activated with MAO, despite being an electronically saturated (18-electron) compound.

Experimental

General procedures

All experiments dealing with air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques. Nitrogen gas was supplied in cylinders by specialized companies (Air Liquide, etc.) and purified by passage through 4 Å molecular sieves. Unless otherwise stated, all reagents were purchased from commercial suppliers (e.g., Acrös, Aldrich, Fluka) and used without further purification. All solvents to be used under inert atmosphere were thoroughly deoxygenated and dehydrated before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen. The following drying agents were used: sodium [for diethyl ether, and tetrahydrofuran (THF)], calcium hydride (for dichloromethane, chlorobenzene and *o*-dichlorobenzene), Na/K alloy (toluene for the polymerization reactions). Solvents and solutions were transferred using a positive pressure of nitrogen through stainless steel cannulae and

mixtures were filtered in a similar way using modified cannulae that could be fitted with glass fiber filter disks. Ethylene and propylene were supplied by Air Liquide, and were dried by passage through 4 Å molecular sieves. As cocatalyst, solutions of 10% of MAO (Aldrich) or MMAO (Akzo Nobel) in toluene were used.

The NaCp (Cp = C_5H_5)[9] and the α-diimine bis(mesityl-imino)acenaphthene (Mes-BIAN)[10] ligand precursors, the complexes [NiBr$_2$(DME)] (DME = 1,2-dimethoxyethane),[11] [NiCl$_2$(PPh$_3$)$_2$][12] and [NiBr$_2$(Mes-BIAN)] (**1**)[10] were prepared according to literature procedures.

The NMR spectra were recorded on a Varian Unity 300 (^{1}H, 299.995 MHz; ^{13}C, 75.4296 MHz; ^{31}P 121.44 MHz) spectrometer, at room temperature. Deuterated solvents were dried by storage over 4 Å molecular sieves and degassed by the freeze-pump-thaw method. Spectra were referenced internally using the residual protio solvent resonance relative to tetramethylsilane ($\delta = 0$) or, in the case of ^{31}P spectra, relative to H$_3$PO$_4$ ($\delta = 0$). All chemical shifts are quoted in δ (ppm) and coupling constants (J) given in Hz. Multiplicities were abbreviated as follows: singlet (s), doublet (d), triplet (t), septet (sept) and multiplet (m). The samples were prepared in J. Young NMR tubes. Polymer samples were prepared in a mixture of 1,2,4-trichlorobenzene and C$_6$D$_6$ (75:25 v/v) and recorded at 120 °C.

The elemental analyses were obtained from the Instituto Superior Técnico elemental analysis services.

The molecular weights of the polyethylenes obtained were determined by gel permeation chromatography/ size exclusion chromatography (GPC/SEC), on a GPC Waters 150 CV chromatograph. The solvent used as eluent was filtered through 0.50 μm membranes from Fluoropore (Millipore), and degassed by ultrasound for 45 min. The polymer samples were always filtered through 0.45 μm Durapore filters (Millipore). A mixture of *o*-dichlorobenzene (ODCB) and the radical stabilizer butylated hydroxytoluene (BHT) (0.01%) was used as eluent, at a flow rate of 1.0 mL min^{-1}, and the temperature was thermostated at 135, 135 and 60 °C, respectively, in the injector, column and pump compartments. The permeation of polymers was performed with two Waters Styragel HT linear columns. The molecular weights were calibrated relative to polystyrene standards (TSK Tosoh Co.). The acquisition and data processing were performed with the program Millennium[32] (version 3.05.01).

The thermal analyses of polyethylene samples were performed by differential scanning calorimetry (DSC) using a Setaram DSC 121 calorimeter. The samples were heated between 20 and 300 °C at 10 °C min^{-1}. The temperature of the maximum of the peak(s) was registered as the melting temperature and the area under the peak(s) was associated to the melting enthalpy of each polymer sample. During the experiments the sample holder was continuously purged with argon.

Synthesis of [Ni(η^5-C$_5$H$_5$)(PPh$_3$)$_2$]PF$_6$ (**2**)

The following procedure was adapted from the literature:[6] a suspension of NaCp (0.52 g, 5.90 mmol) in Et$_2$O (20 mL) was added to a suspension of [NiCl$_2$(PPh$_3$)$_2$] (3.89 g, 5.94 mmol) in the same solvent (60 mL), at room temperature. The dark-green suspension turned to light yellowish-green, with a dark red supernatant solution. This mixture was stirred overnight. After filtration and washings with Et$_2$O, THF was added and a violet solution was obtained. TlPF$_6$ was added to the mixture and the reaction was stirred for 1 h. All volatiles were evaporated and the resulting residue was washed with *n*-hexane and extracted with dichloromethane (filtered through Celite®) until extracts were colorless. The greenish solution was concentrated (ca. 50%) and Et$_2$O was added with concomitant precipitation of a microcrystalline light green powder of **2**. Yield: 2.36 g, 50%; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 7.45 (m, Ph of PPh$_3$, 30H), 5.20 (s, C$_5$H$_5$, 5H); ^{31}P{^{1}H} NMR (121.44 MHz, CD$_2$Cl$_2$) δ 35.7 (s, PPh$_3$), −143.7 (sept, PF$_6^-$, $^1J_{PF}$ 712 Hz). Anal. calc. for C$_{41}$F$_6$H$_{35}$NiP$_3$: C, 61.82; H, 4.44, found: C, 62.07; H, 4.45.

## Synthesis of [Ni(η^5-C$_5$H$_5$(Mes-BIAN)]PF$_6$ (**3**)

Method (a)

A solution of NaCp (0.19 g, 2.16 mmol) in THF (30 mL) was added to a suspension of [NiBr$_2$(Mes-BIAN)] (**1**) (1.43 g, 2.25 mmol) in the same solvent (100 mL), at room temperature. The mixture was stirred overnight, leading to a violet solution and a white precipitate (NaBr). The solution was filtered to another Schlenk tube, and TlPF$_6$ (0.76 g, 2.18 mmol) was added, an immediate color change to dark green being observed. The final solution was then stirred for 2 h. All volatiles were evaporated under vacuum and the resulting residue was washed with *n*-hexane, extracted with dichloromethane, and filtered through Celite® until extracts were colorless. The solution was concentrated (to ca. 50%) and double-layered with Et$_2$O (1:3). Dark green crystals of **3** precipitated, which were further washed with Et$_2$O and dried under vacuum. Yield 0.59 g, 45%.

Method (b)

A solution of bis(mesityl-imino)acenaphthene (0.83 g, 1.99 mmol) in ODCB (30 mL) was added to a solution of

$[Ni(\eta^5\text{-}C_5H_5)(PPh_3)_2]PF_6$ (**2**) (1.63 g, 2.05 mmol) in the same solvent (100 mL), at 45 °C. The mixture was stirred overnight, leading to a dark green solution. All volatiles were evaporated under vacuum and the resulting residue was washed with *n*-hexane, extracted with dichloromethane until extracts were colorless. The solution was concentrated (to ca. 25%) and double-layered with Et_2O (1:5). Dark green crystals of **3** precipitated, which were further washed with Et_2O and dried under vacuum. Yield 1.40 g, 100%.
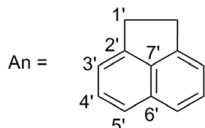
^{1}H NMR (300 MHz, CDCl$_3$) δ 8.06 (d, $^3J_{HH}$ = 8.1 Hz, H5', 2H), 7.46 (t, $^3J_{HH}$ = 8.1 Hz, H4', 2H), 7.06 (s, H$_{meta}$ mesityl, 4H), 6.61 (d, $^3J_{HH}$ = 7.2 Hz, H3', 2H), 5.22 (s, C$_5$H$_5$, 5H), 2.37 (s, CH$_{3\,para}$ mesityl, 6H), 2.30 (s, CH$_{3\,ortho}$ mesityl, 12H); ^{13}C{^{1}H} NMR (75.43 MHz, CDCl$_3$) δ 163.2 (C1'), 148.5 (C$_{ipso}$ mesityl), 145.7 (C7'), 141.8 (C$_{para}$ mesityl), 138.7 (C6'), 131.5 (C2'), 130.2 (C$_{meta}$ mesityl) 129.3 (C5'), 127.7 (C4'), 124.9 (C$_{ortho}$ mesityl), 124.1 (C3'), 95.6 (C$_5$H$_5$), 21.1 (CH$_{3\,para}$ mesityl), 17.5 (CH$_{3\,ortho}$ mesityl); ^{31}P{^{1}H} NMR (121.44 MHz, CDCl$_3$) δ –143.7 (sept, PF$_6^-$, $^1J_{PF}$ = 712 Hz); Anal. calc. for C$_{35}$H$_{33}$F$_6$N$_2$PNi: C, 61.54; N, 4.05; H, 4.85, found: C, 61.34; N, 4.08; H, 4.85.

General procedure for the polymerization tests with ethylene and propylene

Polymerizations were carried out in 250 mL crown capped pressure bottles sealed with neoprene septa and pump filled with nitrogen atmosphere (the bottles were previously dried in the oven at 140 °C for several days), and with magnetic stirring (600 rpm). To each polymerization bottle, 50 mL of freshly distilled solvent were added, which were subsequently thermostated in ice (0 °C), water or oil baths. After removal of the N$_2$ atmosphere by vacuum, the solvent was saturated with the gas monomer at a relative pressure of 1 bar, which was maintained throughout the polymerization reactions. Then the appropriate amount of MAO cocatalyst was added via a glass syringe at the defined Al/Ni ratio. Solutions were then brought to the desired temperature and allowed to equilibrate for 15 min. The polymerization reactions were initiated by the addition of a solution of the desired amount of catalyst in 1 mL of ODCB via a glass syringe. The polymerizations were terminated after 60 min (or less) by quenching the mixture with 150 mL of an acidic methanol (2% HCl) solution. The polymers obtained were

then filtered, washed several times with methanol and dried in a vacuum oven at 60 °C for 3 days.

X-ray diffraction

Crystals of compound **3** were grown from a dichloromethane solution double-layered with Et$_2$O, at −20 °C, and isolated by filtration. A specimen was chosen under an inert atomsphere, covered with paratone-*N* oil, and mounted on the end of a glass fiber. Data were collected at 125 K on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å), as summarized below (Crystal data). The images were processed with the DENZO and SCALEPACK programs.[13] Corrections for Lorentz and polarization effects were performed. Structure solution and refinement were performed using direct methods with the programs SIR92,[14] included in the package of programs WINGX-Version 1.80.05.[15] Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom, with C–H distances of 0.95, 0.98 and 0.99 Å for aromatic, methyl and methylene H atoms, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$. Graphic presentations were prepared with ORTEP-III.[16] Data for **3** was deposited in Cambridge Crystallographic Data Centre (CCDC) under the deposit number 1018192.

Crystal data

C$_{35}$H$_{33}$NiPF$_6$N$_2$·CH$_2$Cl$_2$, M = 770.24 g mol^{-1}, triclinic, *a* = 10.8610(4) Å, *b* = 13.0500(4) Å, *c* = 14.1750(5), α = 70.439(2), β = 75.195(2), γ = 68.5330(10), *V* = 1735.44(10) Å^3, space group *P-1*, Z = 2, D$_{calc}$ = 1.474 g cm^{-3}, μ = 0.821 mm^{-1}, crystal dimensions 0.5 × 0.55 × 0.6 mm, θ$_{max}$ = 25.02°, total data = 5757, unique data = 5341, R [I > 2σ(I)] = 0.03, R$_w$ = 0.08, goodness of fit = 1.046, ρ$_{min}$ = −0.484, ρ$_{max}$ = 0.351.

Results and Discussion

The reaction of [NiBr$_2$(Mes-BIAN)] (**1**) with NaCp, followed by treatment with TlPF$_6$ [Scheme 2, route (a)], in THF, at room temperature, leads to the formation of the cationic complex [Ni(η^5-C$_5$H$_5$(Mes-BIAN)]PF$_6$ (**3**), bearing simultaneously an α-diimine ligand and a η-cyclopentadienyl ring, which was obtained as dark green crystals, in 45% yield. The Ni(II) complex **3**, which is stable in air and soluble in chlorinated solvents, such as dichloromethane, chloroform, chlorobenzene and ODCB,
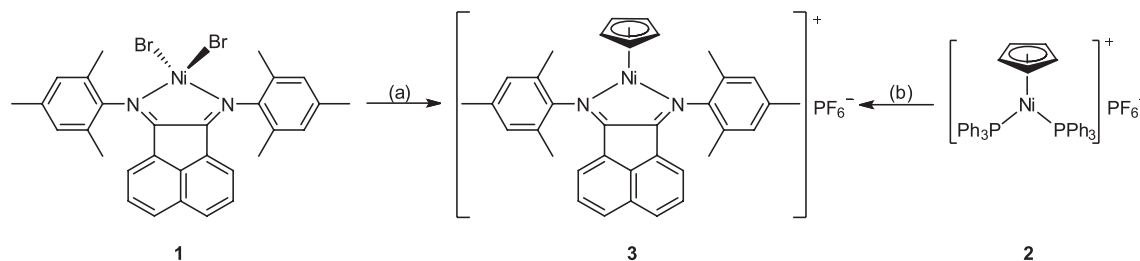
Scheme 2. (a) (*i*) NaCp, THF, room temperature, overnight; (*ii*) TlPF$_6$, THF, room temperature, 1 h (45%); (b) mesityl-BIAN, *o*-dichlorobenzene, 45 °C (100%).

can also be prepared quantitatively by substitution of the PPh$_3$ ligands by the mesityl-BIAN bidentate ligand in the complex [Ni(η^5-C$_5$H$_5$)(PPh$_3$)$_2$]PF$_6$ (**2**), in ODCB, at 45 °C [Scheme 2, route (b)]. Compound **3** was characterized by ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR, the corresponding spectra revealing the expected resonances and chemical shifts typical of the η-cyclopentadienyl and bis(mesityl-BIAN) ligands and PF$_6^-$ anion.

The molecular structure of complex **3** was determined by single-crystal X-ray diffraction, at 125 K. The molecular structure of the cation is depicted in Figure 1, whereas selected bond distances and angles are presented in Table 1.
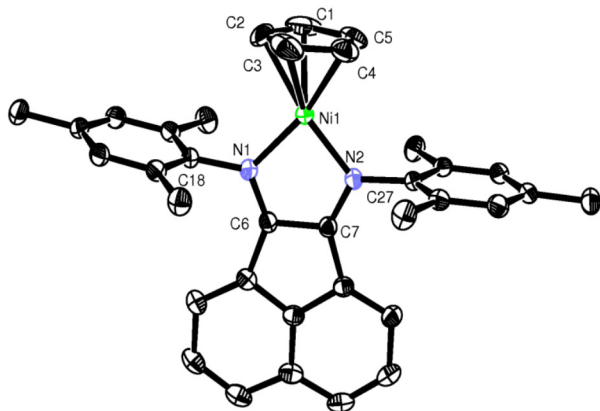
Figure 1. Perspective view of the molecular structure of the cation of **3**. The ellipsoids were drawn at 50% probability level. All the hydrogen atoms, the anion PF$_6^-$ and a dichloromethane solvent molecule were omitted for clarity.

Complex **3** displays a trigonal geometry around the nickel center, the sum of the three internal angles about the Ni atom being 360° (considering the Cp centroid as one of the coordination positions). The Cp ligand is coordinated to the metal center with η^5 hapticity, being perpendicular to the best {NiN$_2$} plane, as can be observed by the estimated values of the dihedral angle between the planes of Cp and N(1)-Ni(1)-N(2), which are close to 90° (88.99°). The Cp plane is nearly parallel to the plane defined by the mesityl rings (2.04°), the latter being practically perpendicular to the imino-acenaphthene plane. According to the classification

Table 1. Selected bond distances (Å), angles (degree) and other relevant structural parameters for complex [Ni(η^5-C$_5$H$_5$)(Mes-BIAN)]PF$_6$ (**3**)

Bond distances / Å		Bond angles / degree	
Ni(1)-N(1)	1.8865(15)	N(1)-Ni(1)-N(2)	85.13(6)
Ni(1)-N(2)	1.8793(15)	N(1)-Ni(1)-C(1)	122.01(9)
Ni(1)-C(1)	2.107(2)	N(2)-Ni(1)-C(1)	132.59(11)
Ni(1)-C(2)	2.041(2)	N(1)-Ni(1)-C(2)	103.53(9)
Ni(1)-C(3)	2.122(2)	N(2)-Ni(1)-C(2)	170.66(10)
Ni(1)-C(4)	2.099(2)	N(1)-Ni(1)-C(3)	118.36(8)
Ni(1)-C(5)	2.070(2)	N(2)-Ni(1)-C(3)	138.35(11)
C(1)-C(2)	1.399(5)	N(1)-Ni(1)-C(4)	153.66(8)
C(1)-C(5)	1.368(4)	N(2)-Ni(1)-C(4)	108.14(8)
C(2)-C(3)	1.419(5)	N(1)-Ni(1)-C(5)	158.97(8)
C(3)-C(4)	1.372(4)	N(2)-Ni(1)-C(5)	105.36(8)
C(4)-C(5)	1.429(3)	Ni(1)-N(1)-C(18)	126.07(12)
Ni(1)-Cp$_{centroid}$	1.717	Ni(1)-N(1)-C(6)	112.77(12)
		Ni(1)-N(2)-C(27)	129.42(12)
		Ni(1)-N(2)-C(7)	112.49(12)

Distance A^a	0.122 (C2)	Dihedral χ ^{b}	88.99

^{a}Shortest distance between a carbon atom of the Cp ring (in brackets) and the plane N(1)-Ni(1)-N(2); ^{b}Dihedral χ = angle between the plane N(1)-Ni(1)-N(2) and the average plane of the Cp ring.

proposed by Andersen *et al.*,[17] the cyclopentadienyl ligand of complex **3** exhibits a diene-type distortion (Figure 2). The two non-adjacent bonds which are not intercepted by the {NiN$_2$} plane (C(1)-C(5) and C(3)-C(4)) have bond lengths lower than 1.40 Å, being considerably shorter than the remaining three bonds in the ring. As suggested by Andersen *et al.*,[17] a structure with a carbon atom "on" (< 0.10 Å) the Ni square plane has a diene distortion in the Cp ring. In complex **3**, the carbon atom C(2) is very close to this plane (0.122 Å), resulting in a stronger interaction with the metal center. In fact, the distance Ni–C(2) is the shortest of all Ni–C$_{Cp}$ bonds (Table 1). The Mes-BIAN ligand of **3** presents geometrical features similar to other aryl-BIAN or analogous ligands coordinated to nickel(II) complexes.[5,18]

The Cp-diimine-Ni(II) complex **3** was tested as catalyst for the polymerization of olefins, such as ethylene and
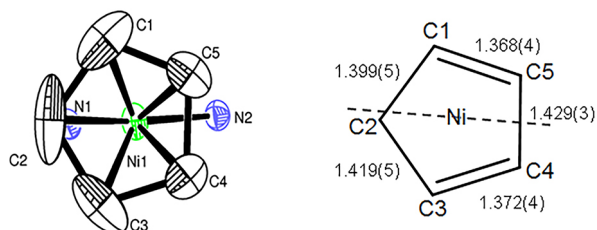
Figure 2. (a) Top view of the [CpNi(Mes-BIAN)]⁺ cation **3**; (b) diene-type distortion observed in the cyclopentadienyl ligand of **3** (the N(1)-Ni(1)-N(2) plane is indicated by a dashed line; distances in Å).

propylene. The results obtained are summarized in Table 2. In the absence of a cocatalyst, this complex was inactive towards the polymerization of ethylene, when used at low pressures (Table 2, entry 1). This inactivity can be attributed to its electronic saturation (18-electron count) and also possibly to the fact that the Cp-Ni⁺ bond is much stronger than that of a Ni⁺-ethylene bond. Therefore, a ring-slippage from η^5 to η^1 is unlikely to occur.

However, in the presence of the alkyl-aluminium cocatalyst MAO, complex **3** revealed to be an efficient catalyst precursor for the polymerization of ethylene (Table 2, entries 2-4 and 6-9), whereas it was inactive towards the polymerization of propylene (Table 2, entry 10). The catalytic activity towards ethylene, as well as the molecular weight, the structural and thermal characteristics of the resulting polyethylenes depend largely on the reaction temperature and solvent. The catalyst system **3**/MAO was inactive for a ratio [Al]/[**3**] of 10 (Table 2, entry 5), showing however similar activities for [Al]/[Ni] ratios of 100 and 1000 (Table 2, entries 6 and 7).

The polymerization of ethylene in the presence of **3** is very sensitive to the nature of the aromatic solvent employed: toluene (PhMe), chlorobenzene (PhCl) or ODCB (Table 2, entries 2-4). Among these solvents, the maximum

catalytic activity is observed when the reaction is performed in PhCl. The higher polarity of PhCl ($\varepsilon = 5.62$) compared to that of toluene (PhMe, $\varepsilon = 2.38$) favors the solubility of the cationic catalyst precursor and possibly increases the amount of cationic species in solution, which results in an enhancement of the catalytic activity due to an increase in the concentration of the metal active centers. This is in agreement with the observations of de Souza *et al.*[4] for the study of [Ni(η^3-methallyl)(α-diimine)]PF₆ as catalyst precursor for the polymerization of ethylene, although the activities achieved in the present work are considerably higher than those reported by that author for the MAO-based catalyst system. Despite the fact that the polarity of ODCB ($\varepsilon = 9.93$) is greater than that of PhCl, the latter gives rise to slightly higher activities. The molecular weights, melting temperatures and crystallinities of the polyethylenes obtained decrease in the order PhMe > PhCl > ODCB. Conversely, the polydispersity index (PDI = M_w/M_n) increases in the order PhMe < PhCl < ODCB (Table 2, entries 2-4). The catalytic activity increases with the reaction temperature from 0 to 30 °C (Table 2, entries 3, 6 and 8; Figure 3), going through a maximum and decreasing at 40 °C (Table 2, entry 9; Figure 3), which can be attributed to a deactivation of the catalyst (irreversible chain termination step). The increase in the reaction temperature caused a decrease in the polyethylene molecular weight since the β-hydrogen elimination, and therefore the chain transfer step, is favored. In fact, the highest molecular weight is obtained when the polymerization reaction was performed at 0 °C (Table 2, entry 6; Figure 3). The increase in the reaction temperature also causes a significant increase in the branching number, leading to the consequent decrease in the polyethylene melting temperature and crystallinity. These types of

Table 2. Catalytic performance of [Ni(η^5-C₅H₅)(Mes-BIAN)]PF₆ (**3**) activated by MAO in the polymerization of ethylene and attempt of propylene polymerization[a]

entry	[Al]/[Ni]	T / °C	Solvent	Polymer mass / g	Activity × 10⁻⁴ / (gPE mol⁻¹ h⁻¹)	M_n × 10⁻³ / (g mol⁻¹)	PDI	N[b]	T_m[c] / °C	ΔH_m[d] / (J g⁻¹)	Cryst.[e] / %
1[f]	0	22	PhCl	0	0	–	–	–	–	–	–
2[f]	100	22	PhMe	0.46	4.55	350	2.47	n.d.[i]	121.8	203.3	71.1
3[f]	100	22	PhCl	1.27	12.70	320	2.68	15	117.8	197.4	69.0
4[f]	100	22	ODCB	1.22	12.20	218	3.08	n.d.[i]	108.8	178.5	62.4
5[f]	10	0	PhCl	0	0	–	–	–	–	–	–
6[f]	100	0	PhCl	0.52	5.21	448	2.45	7	122.8	207.5	72.2
7[f]	1000	0	PhCl	0.31	3.10	n.d.[i]	n.d.[i]	n.d.[i]	122.2	208.0	72.7
8[f]	100	30	PhCl	1.68	16.8	125	2.51	29	99.1	146.5	51.2
9[f,g]	100	40	PhCl	0.89	8.9	37	1.90	67	66.5	93.1	32.5
10[h]	100	22	PhCl	0	0	–	–	–	–	–	–

[a]**3**: 10 µmol; t: 1 h; $V_{solvent}$: 50 mL; P_{olefin} (relative): 1 bar; [b]number of branches/1000 carbons (determined by ¹H NMR; reference 19); [c]melting temperature (determined by DSC). [d]enthalpy of fusion; [e]crystallinity % = ($\Delta H_m/285.9$) × 100 (reference 20); [f]olefin: ethylene; [g]several phase transitions, T_m being determined for the most intense transition and ΔH_m determined for all the transitions; [h]olefin: propylene; **3**: 17 µmol; t: 2 h; [i]n.d.: not determined.

variations in the T_m and polymer microstructure were also observed by de Souza *et al.*.[4]
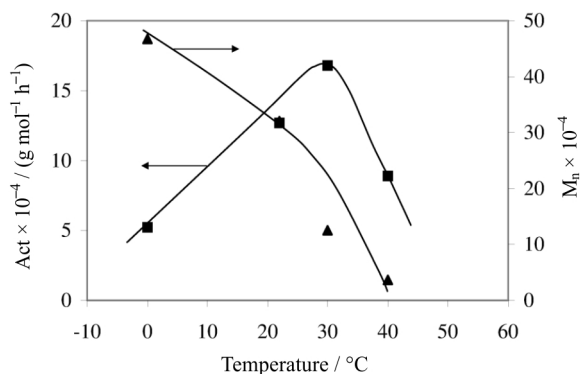
Figure 3. Influence of the reaction temperature on the catalytic activity (squares) of the catalyst system **3**/MAO and on the M_n (triangles) of the polyethylenes obtained.

The analysis of the microstructures of the polyethylenes prepared with the cationic system $[Ni(\eta^5\text{-}C_5H_5)$ (Mes-BIAN)]$^+$ activated with MAO was performed using ^{13}C NMR spectroscopy. The results showed branched polymers, in agreement with the results obtained by Brookhart and co-authors[21] and de Souza *et al.*[4,22] with nickel catalyst systems bearing α-diimine ligands. As an example, the ^{13}C{^{1}H} NMR spectrum of the product prepared under the reaction conditions of entry 3 (Table 2) is depicted in Figure 4. The assignment of the observed resonances was based on the data available in the literature.[22-24] The spectrum shown in Figure 4 displays a polyethylene essentially containing methyl branches attached to the main polymeric chain (resonances at 19.97, 33.53 and 34.72 ppm), and very few long branches ($N_L \geq 6$; resonance at 29.50 ppm). The absence of "branched branches" in the sample can be attributed to a hampered isomerization reaction, potentially caused by the presence of a bulky counter-anion derived from MAO.
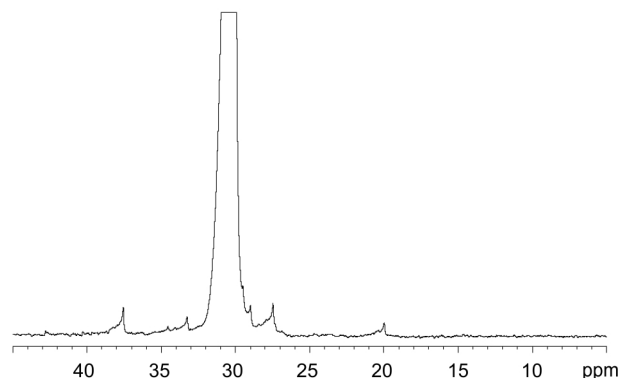
Figure 4. ^{13}C{^{1}H} NMR spectrum of polyethylene obtained with the catalyst system **3**/MAO (Table 2, entry 3) (75.43 MHz, 1,2,4-trichlorobenzene/C_6D_6 (75:25 v/v), 120 °C).

The similarity of the results obtained in the present work with those reported by Brookhart and co-workers[2,3,21] and de Souza *et al.*[4] for the species [NiMe(α-diimine)]$^+$ and [Ni(methallyl)(α-diimine)]$^+$, respectively, led us to put forward a mechanism for the polymerization of ethylene catalyzed by **3**/MAO (Scheme 3) analogous to
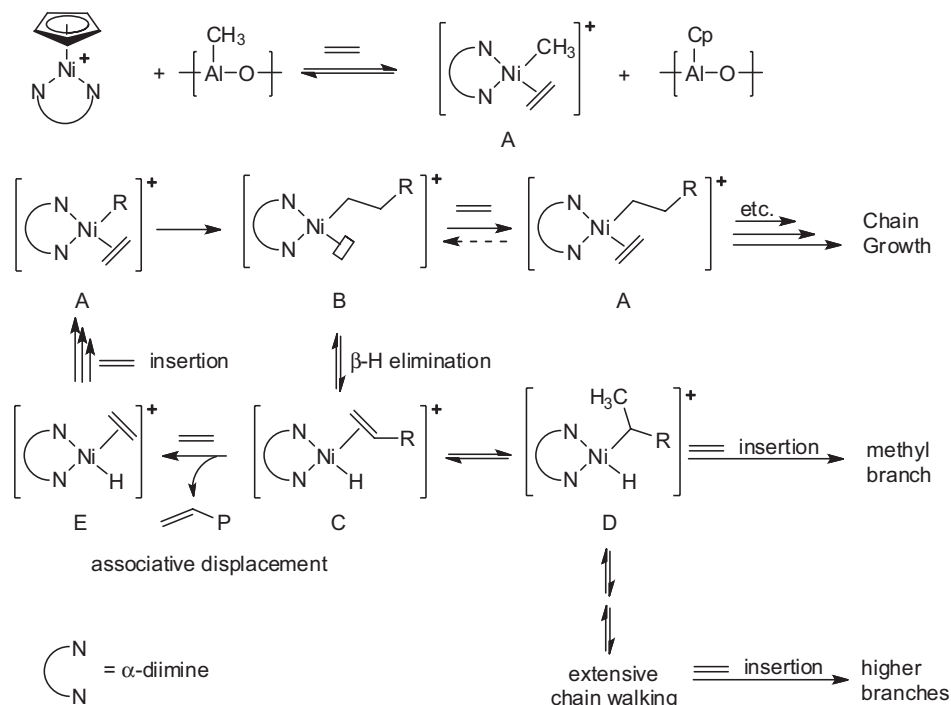
Scheme 3. Possible mechanism for the polymerization of ethylene with the catalyst system $[Ni(\eta^5\text{-}C_5H_5)(\alpha\text{-diimine})]^+$/MAO.

that suggested by Brookhart and co-workers,[1-3,21] except in the initiation step (transformation of catalyst precursor **3** into the active species). The initiation reaction, which we propose to be the exchange of the Cp ring of the Ni precursor with the alkyl groups of the MAO cocatalyst in the presence of ethylene, generating the cationic alkyl complex **A** (catalyst resting state), is followed by the three usual main processes: (1) chain propagation, (2) metal migration along the polymer chain ("chain walking"), and (3) chain transfer. These steps are common to all the other α-diimine nickel catalyst precursors, being well described and extensively discussed in the literature.[1-4,21,22,25]

Conclusions

The reaction of [NiBr$_2$(Mes-BIAN)] (**1**) with NaCp in the presence of TlPF$_6$ gave rise to the formation of the first cationic Ni(II) complex containing simultaneously a cyclopentadienyl and an α-diimine ligand, [Ni(η^5-C$_5$H$_5$)(Mes-BIAN)]PF$_6$ (**3**), in moderate yield. Alternatively, this compound can be prepared quantitatively by substitution of PPh$_3$ by the α-diimine ligand in the complex [Ni(η^5-C$_5$H$_5$)(PPh$_3$)$_2$]PF$_6$ (**2**). Although electronically saturated, complex **3** was shown to be an efficient catalyst precursor for the polymerization of ethylene when activated with MAO, whereas it was inactive towards propylene. Reaction conditions such as solvent and temperature were studied in the polymerization of ethylene, revealing that the higher catalytic activities were obtained in polar aromatic solvents, especially when chlorobenzene was employed. The average-number molecular weight, melting temperature and crystallinity decreased with an increase in the polarity of the reaction solvent. The catalytic activity increases with the reaction temperature, but only to a certain extent (from 0 to 30 °C), leading though to a decrease in the polyethylene average molecular weight, melting temperature and crystallinity.

Supplementary Information

The ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} NMR spectra and CIF file for compound **3** are provided as Supplementary Information and available free of charge at http://jbcs.sbq.org.br.

Crystallographic data (excluding structure factors) for the structure in this work were deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1018192. Copies of the data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving. html or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. E-mail: deposit@ccdc.cam.ac.uk.

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