

Synthesis, molecular structure and catalytic activity of chiral benzamidinate nickel complexes

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Abstract

Two new nickel complexes containing the chiral benzamidinate ligation: $[\text{PhC}(\text{N}-\text{SiMe}_3)(\text{N}'\text{-myrtanyl})_2\text{Ni}(\text{py})_2$ (**3**) and $\{[\text{PhC}(\text{NH})(\text{N}'\text{-myrtanyl})_2\text{Ni}]_2\}$ (**6**) have been synthesized and characterized. The solid-state molecular structures of these complexes have been determined by low-temperature X-ray diffraction analysis. Complex **3** was obtained via two different procedures. In complex **3**, the metal adopts a nearly ideal octahedral environment, whereas in complex **6** the two divalent nickel metals are coordinated in a square-planar geometry, forming a dimer. Complex **3** activated with MAO has been found to oligomerize propylene producing a mixture of dimers, trimers and tetramers with a turnover frequency of 5200 h^{-1} , whereas complex **6** being activated with MAO oligomerizes ethylene to a mixture of dimers and trimers with a high turnover frequency of $15,400 \text{ h}^{-1}$. In addition, when activated with MAO both complexes showed a good activity for the vinyl-type polymerization of norbornene.

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Keywords: Chiral nickel complexes; Chiral benzamidinates; Polymerization; Ethylene oligomerization; Propylene oligomerization; Nickel; X-ray structure

1. Introduction

During the last decade, enormous advancements have been made in the design and the synthesis of late-transition-metal complexes for the polymerization of olefins [1,2]. Their reduced oxophilicity and, hence, their enhanced functional group tolerance allows to produce functionalized linear polyolefin materials with unusual microstructures and properties [3]. However, due to polymerization chain termination via a β -hydrogen elimination process, these complexes are mainly utilized for the production of dimers or oligomers of ethylene [4].

Among the numerous late-transition-metal complexes, the neutral nickel complexes are considered to be very promising catalysts for the polymerization of α -

olefins and their copolymerization with polar monomers [1,2]. The well-known examples of neutral nickel complexes are the SHOP-type catalysts containing monoanionic (P–O) ligands for the oligomerization of ethylene to linear α -olefins [5,6]. The modified SHOP-type catalysts with bulky anthracenyl-derived (P–O) ligation were found to be an efficient catalytic system for copolymerization of ethylene with methyl methacrylate (MMA), producing a functionalized polyethylene in which the incorporated MMA-group appears at the chain ends [7].

Most attention has been directed to neutral nickel complexes with different anionic (N–O) ligations [8–11]. The new class of complexes are based on bulky *ortho*-substituted salicylaldehyde ligands that operates as single-component catalysts for the homo-polymerization of ethylene exhibiting good functional group tolerance and remaining active in the presence of polar solvents [12].

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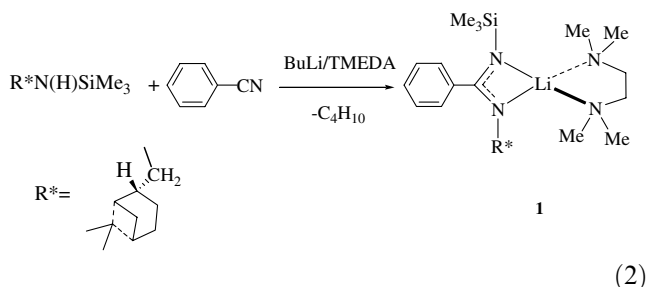
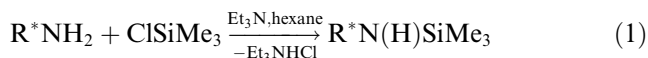
While the monoanionic (N–N) based ligands are among the most widely investigated chelating system, their nickel complexes are still extremely rare. Within the (N–N) chelating ancillary ligation, a variety of bulky β -diketiminato nickel complexes have received an increasing attention [13]. In a recent communication, nickel complexes containing six-membered anilido-imine ligands, which combine the exceptional features of β -diketiminato and salicylaldiminate ligations have been described [14]. When activated with MAO (methylalumoxane) these complexes show high activity for the polymerization of norbornene, while low activity for the oligomerization of ethylene, producing the mixture of butenes and hexenes.

Our recent developments in the polymerization of α -olefins using as catalysts early-transition metal complexes containing the benzamidinate ancillary ligations (N–N) encourage us to investigate the reactivity of the nickel metal towards those ligations. Here, we reported on the synthesis and structural X-ray diffraction studies on two new neutral Ni(II) complexes containing a chiral benzamidinate ligation forming four- and five-membered rings and their activity in a number of catalytic processes.

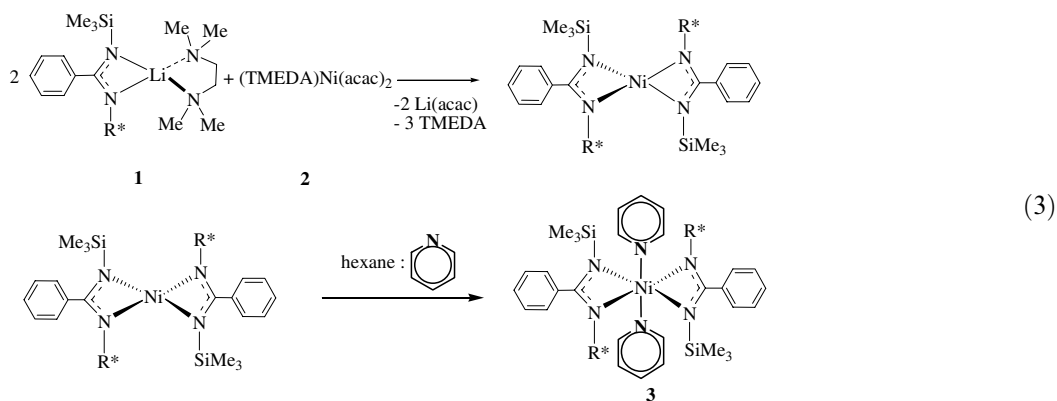
2. Results and discussion

2.1. Synthesis of the complex bis-[(N-trimethylsilyl)(N'-myrtanyl)benzamidinate]Ni(Py)₂ (6)

SiMe₃ as the sole product. In the absence of the triethylamine the reaction yields a quantitative conversion up to 50% due to the formation of the chiral salt R*NH₃Cl. In both cases, no double silylation product was formed, presumably due to bulkiness of the myrtanyl moiety.



In the second reaction, the deprotonated chiral amine reacts with benzonitrile with the concomitant 1,3-sigmatropic shift to obtain the lithium ligation. The reaction of the previously described (TMEDA)Ni(acac)₂ (acac = acetylacetonate) (2) complex [16] with two equivalents of the ligand 1, in toluene at ambient temperature, afforded the compound [PhC(N-SiMe₃)(N'-myrtanyl)]₂Ni (Eq. (3)).



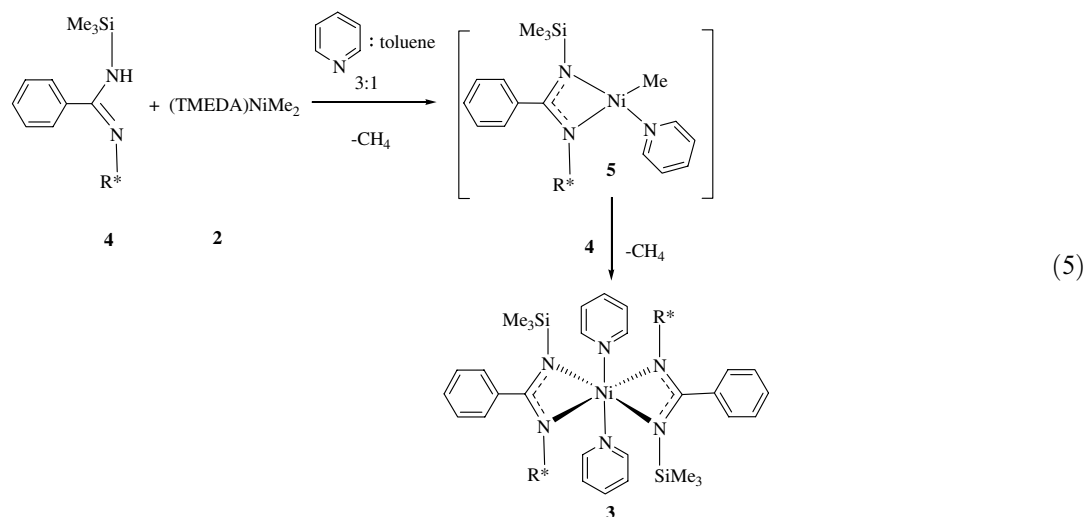
The chiral ligand lithium PhC(N-SiMe₃)(N'-myrtanyl)Li(TMEDA) (1) was obtained from the silylated chiral amine according to a modified literature procedure [15] in 82% yield (Eqs. (1) and (2)).

The formation of compound 1 consists of two consecutive reactions. In the first reaction an equimolar amount of the stronger base triethylamine was added in order to obtain the exchange product R*N(H)-

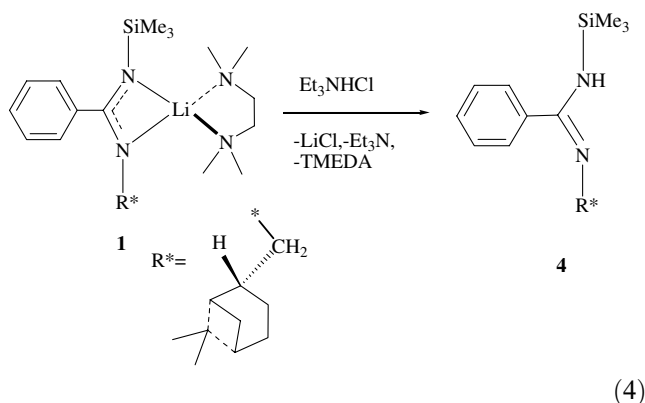
Attempts to crystallize the tetrahedral bis(benzamidinate) nickel complex [PhC(N-SiMe₃)(N'-myrtanyl)]₂Ni from a variety of solvents were unsuccessful. Only in the presence of a strong coordinating polar solvent, pyridine (hexane:pyridine = 1:1), it was possible to obtain single green color crystals suitable for X-ray measurements in 54% yield. In addition, in a second procedure, complex 3 was also synthesized by the metathesis of

(TMEDA)NiMe₂ [12d,16] with the neutral ligation PhC(NHSiMe₃)(N'-myrtanyl) (**4**). The latter ligation was prepared by the protonolysis of the ancillary ligand **1** with Et₃NHCl in toluene at ambient temperature in

complex **3**. The complex is precipitated from the reaction mixture with toluene and recrystallized from a supersaturated solution of toluene at -30 °C for two weeks (Eq. (5)).



92% yield (Eq. (4)). Interestingly, the reaction is quantitatively regioselective since the protonolysis only inserts the proton at the silicon containing nitrogen group, as expected for the silicon effect, stabilizing a better anion at the α -position.



The reaction of (TMEDA)NiMe₂ with the neutral ligand **4** in a solution mixture of toluene:pyridine (1:3) initially produced the expected mono methyl complex **5**, which can be observed by following the crude reaction by ¹H NMR ($\delta = -0.32$, corresponding to the mono Ni-CH₃ and the formation of methane). This plausible assumption is due to the large paramagnetic contact-shifted signals in the range from -15 to -4 and 60–90 ppm, which makes difficult to assure the structure of the product, although paramagnetic Ni-methyl complexes have been shown to exhibit a ¹H NMR around $\delta = -0.32$ [12d,16a]. As a function of time, this signal disappears to yield the corresponding

The crystal structure of complex **3** is presented in Fig. 1. Selected bond lengths and bond angles and crystallographic data and structure refinement details are listed in Tables 1 and 3, respectively. The low-temperature X-ray diffraction analysis reveals that the nickel atom adopts a nearly ideal octahedral coordination geometry chelated by two chiral η^2 -benzamidinate ligands and two pyridine molecules. The axial positions are occupied by the two nitrogen atoms from the pyridine moieties with a transaxial angle of N(3)–Ni(1)–N(4) = 180.00(1)°, whereas the four nitrogen atoms from the two benzamidinates form the equatorial plane with the sum of equatorial angles of 360.24° (N(2)–Ni(1)–N(1) = 63.69(9)°, N(2)#1–Ni(1)–N(1)#1 = 63.69(9)°, N(2)–Ni(1)–N(1)#1 = 116.43(9)°, N(2)#1–Ni(1)–N(1) = 116.43(9)°). The two four-membered rings are planar with a dihedral angle of N(1)–C(4)–N(2) = 0.1°. The disposition of the benzamidinate ligation is not symmetrical around the metal as observed by the corresponding bond lengths Ni(1)–N(1) = 2.150(2) and Ni(1)–N(2) = 2.115(2) Å. The same trend is observed by the distances within the diazaallyl C–N bond lengths N(1)–C(4) = 1.350(4), N(2)–C(4) = 1.316(4) Å, which is a result of the different hardness of the two amidine nitrogens when substituted with either a silyl or an alkyl group. Compared to other (N'-myrtanyl)benzamidinate complexes, the Ni–N distances are somewhat longer than in PhC(N-SiMe₃)(N'-myrtanyl)(THF)TiCl₃ (2.030(9) and 2.070(9) Å) [15b], while slightly shorter than in [PhC(N-SiMe₃)(N'-myrtanyl)]₃ZrCl-toluene (2.249(5) and 2.293(5) Å) [15b], and in [PhC(N-SiMe₃)(N'-myrtanyl)]₃ZrMe (2.217(13) and 2.26(2) Å) [15b]. By comparison to early-transition-

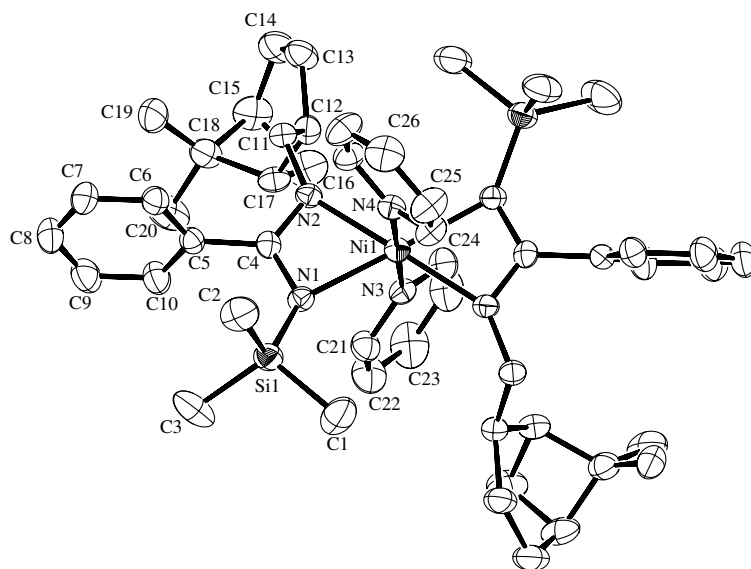


Fig. 1. ORTEP plot of the molecular structure of the complex **3**. All hydrogens were removed for clarity and thermal ellipsoids are given at 50% probability.

metals complexes the N(2)–C(4)–N(1) angle in complex **3** ($115.1(2)^\circ$), is slightly larger than that in the complexes of $\text{PhC}(\text{N}-\text{SiMe}_3)(\text{N}'\text{-myrtanyl})(\text{THF})\text{TiCl}_3$ ($111.0(10)^\circ$), $[\text{PhC}(\text{N}-\text{SiMe}_3)(\text{N}'\text{-myrtanyl})]_3\text{ZrMe}$ ($112.0(2)^\circ$), similar to that in $[\text{PhC}(\text{N}-\text{SiMe}_3)(\text{N}'\text{-myrtanyl})]_3\text{ZrCl-toluene}$ ($114.6(5)^\circ$) [15b], while smaller than the angle in other octahedral nickel complexes bearing the N-silylated-benzamidinate moiety as in $\text{PhC}(\text{NSiMe}_3)_2\text{-Ni}(\text{acac})\text{-(TMEDA)}$ ($117.95(19)^\circ$) [17] and $p\text{-MePhC}(\text{N}-\text{SiMe}_3)_2\text{-Ni}(\text{acac})\text{-(TMEDA)}$ ($118.1(5)^\circ$) [17].

2.2. Synthesis of the complex [tetra-(*N*-myrtanyl)(benzaminate)]Ni dimer (**6**)

Reaction of compound **2** with two equivalent of ligand **1** in a solution mixture of toluene:pyridine (2:3) at ambient temperature afforded the unexpected complex $\{[\text{PhC}(\text{NH})(\text{N}'\text{-myrtanyl})]_2\text{Ni}\}_2$ (**6**) (Eq. (6)).

Complex **6** was successfully crystallized from a toluene solution to obtain green color single crystals suitable for X-ray measurements in 62% yield. The crystal structure of complex **6** is presented in Fig. 2. Selected bond lengths and bond angles and crystallographic data and structure refinement details are listed in Tables 2 and 3, respectively.

The low-temperature X-ray diffraction analysis shows that complex **6** crystallizes with one molecule of toluene. The most peculiar fact regarding complex **6** is the total replacement of all trimethylsilyl groups by hydrogen atoms during the course of reaction. A plausible mechanism for this replacement is suggested in Scheme 1. The formation of complex **6** instead of complex **3** is the result of using the solvent pyridine already at the beginning of the reaction. The presence of pyridine reduces the chelating effect of the acetylacetonate ligation (step 1), allowing the lithium benzamidinate to act as a base removing the hydrogen from the methyl of the

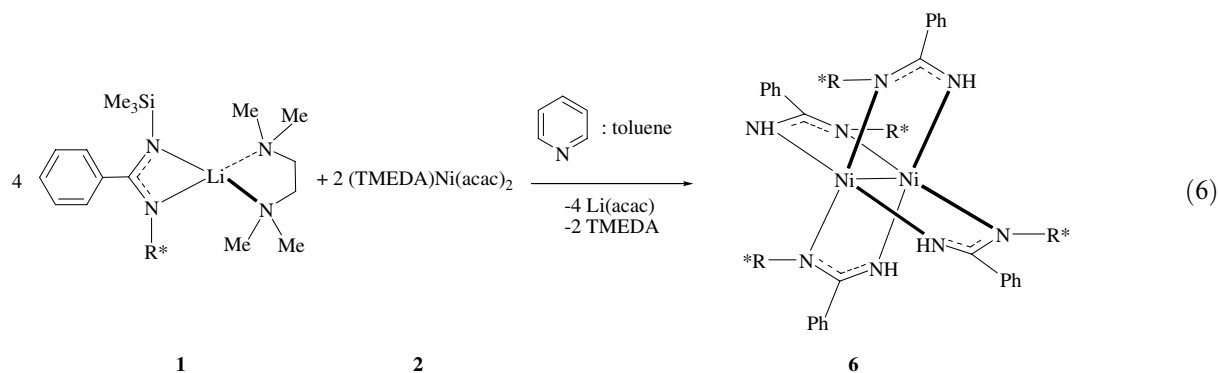


Table 1
Selected Bond Lengths [Å] and Angles [deg] for complex 3

Ni(1)–N(2)	2.115(2)
Ni(1)–N(1)	2.150(2)
N(1)–C(4)	1.350(4)
N(2)–C(4)	1.316(4)
N(3)–Ni(1)–N(4)	180.00(1)
N(2)#1–Ni(1)–N(1)#1	63.69(9)
N(2)–Ni(1)–N(1)#1	116.43(9)
N(2)–C(4)–N(1)	115.1(2)
N(2)–Ni(1)–N(1)	63.69(9)
N(2)#1–Ni(1)–N(1)	116.43(9)

acetylacetonate ligation (step 2). The formed enolate anion is highly nucleophilic towards the trimethylsilyl moiety and will react again with the neutral benzamidinate ligand forming the lithium benzamidinate without the trimethylsilyl group (step 3). This ligand will again react either with the new nickel complex containing the silyl group or with another molecule of complex 2 forming ultimately complex 6.

Diffraction measurements on complex 6 reveal an interesting “cross”-like tetrameric structure with two nickel metal centers adopting a slightly distorted square-planar geometry. The sums of the angles around the nickel atoms are 359.6° (N(1)–Ni(1)–N(4) = 90.8(3)°, N(7)–Ni(1)–N(4) = 89.7(3)°, N(1)–Ni(1)–N(6) = 89.1(3)°, N(7)–Ni(1)–N(6) = 90.0(3)°) and 359.7° (N(5)–Ni(2)–N(8) = 91.1(3)°, N(8)–Ni(2)–N(3) = 89.7(3)°, N(5)–

Table 2
Selected bond lengths (Å) and bond angles (°) for complex 6

Ni(2)–N(2)	1.918(7)
Ni(1)–N(4)	1.900(7)
Ni(1)–N(6)	1.920(7)
Ni(2)–Ni(8)	1.894(7)
Ni(1)–N(1)	1.882(7)
Ni(2)–N(3)	1.904(6)
Ni(2)–N(5)	1.876(7)
Ni(1)–N(7)	1.894(7)
Ni(1)–Ni(2)	2.4484(13)
N(1)–C(1)	1.316(9)
N(2)–C(1)	1.351(10)
N(1)–C(4)	1.350(4)
N(2)–C(4)	1.316(4)
N(3)–C(18)	1.318(10)
N(4)–C(18)	1.349(9)
N(5)–C(35)	1.345(10)
N(6)–C(35)	1.323(10)
N(7)–C(52)	1.349(9)
N(8)–C(52)	1.310(10)
N(1)–Ni(1)–N(4)	90.8(3)
N(7)–Ni(1)–N(4)	89.7(3)
N(1)–Ni(1)–N(6)	89.1(3)
N(7)–Ni(1)–N(6)	90.0(3)
N(5)–Ni(2)–N(8)	91.1(3)
N(8)–Ni(2)–N(3)	89.7(3)
N(5)–Ni(2)–N(2)	88.3(3)
N(3)–Ni(2)–N(2)	90.6(3)
N(1)–C(1)–N(2)	120.2(7)
N(8)–C(52)–N(7)	120.2(8)

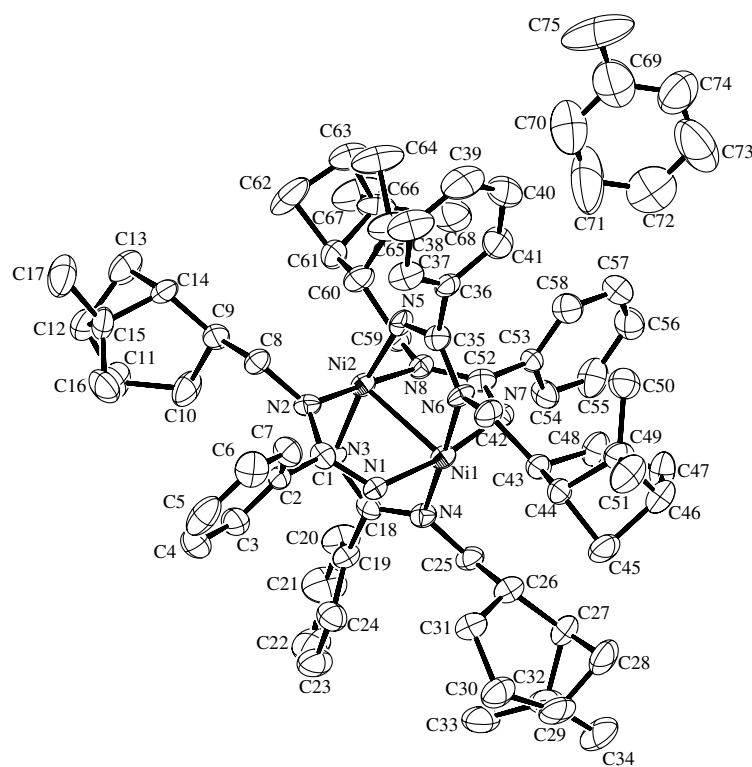


Fig. 2. ORTEP plot of the molecular structure of the complex 6. All hydrogens were removed for clarity and thermal ellipsoids are given at 50% probability.

Table 3
Crystal data collection for complexes **3** and **6**

Identification code	Complex 3	Complex 6
Empirical formula	C ₅₀ H ₇₂ N ₆ NiSi ₂	C ₇₅ H ₁₀₀ N ₈ Ni ₂
Formula weight	872.03	1231.05
<i>T</i> (K)	230.0(1)	230.0(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C</i> 2	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions		
<i>a</i> (Å)	16.7700(15)	11.64200(10)
<i>b</i> (Å)	14.2200(13)	12.67700(10)
<i>c</i> (Å)	11.9050(12)	45.6020(6)
α (°)	90	90
β (°)	117.543(4)	90
γ (°)	90	90
<i>V</i> (Å ³)	2517.2(4)	6730.20(12)
<i>Z</i>	2	4
<i>D</i> _{calc} (mg/m ³)	1.151	1.215
Absorption coefficient (mm ⁻¹)	0.471	0.608
<i>F</i> (000)	940	2648
Crystal size (mm)	0.30 × 0.30 × 0.13	0.15 × 0.24 × 0.28
θ Range for data collection (°)	1.93–24.76	2.20–22.00
Limiting indices	−19 ≤ <i>h</i> ≤ 19, −16 ≤ <i>k</i> ≤ 14, −13 ≤ <i>l</i> ≤ 13	−12 ≤ <i>h</i> ≤ 12, −13 ≤ <i>k</i> ≤ 13, −47 ≤ <i>l</i> ≤ 48
Reflections collected/unique (<i>R</i> _{int})	3609/3609 (0.0000)	8072/4605 (0.0650)
Completeness to θ	97.9% ($\theta = 24.76^\circ$)	97.9% ($\theta = 22.00^\circ$)
Maximum and minimum transmission	0.9413 and 0.8716	
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3609/1/306	4605/0/749
Goodness-of-fit on <i>F</i> ²	0.887	0.967
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0378, <i>wR</i> ₂ = 0.0813	<i>R</i> ₁ = 0.0509, <i>wR</i> ₂ = 0.1139
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0601, <i>wR</i> ₂ = 0.0849	<i>R</i> ₁ = 0.0869, <i>wR</i> ₂ = 0.1247
Absolute structure parameter	0.014(15)	0.38(3)
Extinction coefficient		0.0007(3)
Largest difference in peak and hole (e Å ⁻³)	0.196 and −0.214	0.350 and −0.447

Ni(2)–N(2) = 88.3(3)°, N(3)–Ni(2)–N(2) = 90.6(3)°. Each nickel atom is σ -bonded to two myrtanyl-substituted and two H-substituted nitrogen atoms of the benzamidinate moiety. Interestingly, are the almost equal Ni–N–myrtanyl bond lengths (Ni(2)–N(2) = 1.918(7), Ni(1)–N(4) = 1.900(7), Ni(1)–N(6) = 1.920(7), Ni(2)–Ni(8) = 1.894(7) Å) and nearly equidistance Ni–N–hydrogen bond lengths (Ni(1)–N(1) = 1.882(7), Ni(2)–N(3) = 1.904(6), Ni(2)–N(5) = 1.876(7), Ni(1)–N(7) = 1.894(7) Å). The bridging benzamidinates are disposed in a *trans* fashion around the two nickel centers.

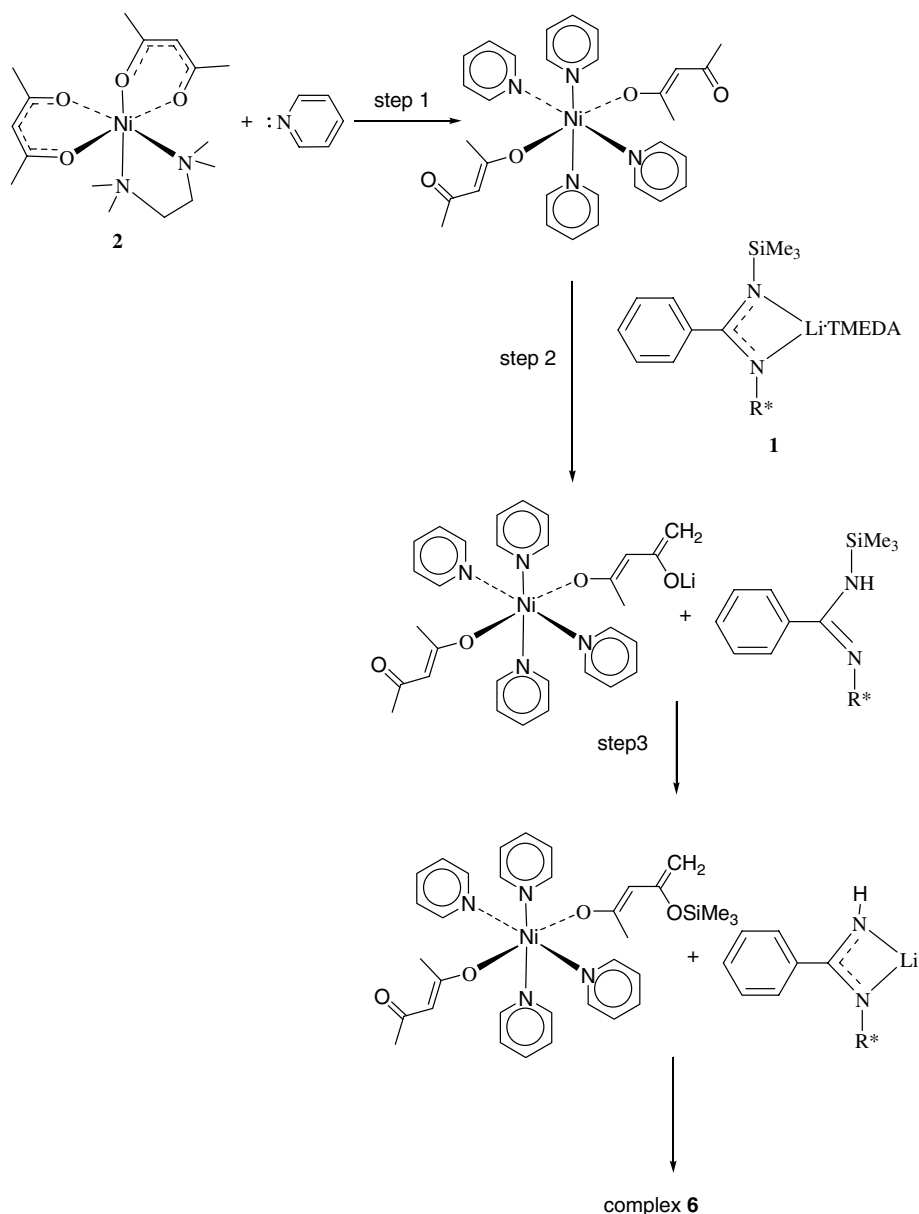
The core units of complex **6** comprised four five-membered Ni–N–C–N–Ni rings that are not completely planar as shown by the torsion angles N(1)–Ni(1)–Ni(2)–N(2) = 15.2° and N(4)–Ni(1)–Ni(2)–N(3) = 15.5°. The analogous deviation from planarity has been observed for similar binuclear benzamidinate-bridged nickel complexes, which is consisted of two five-membered rings (the torsion angle of 13.5°) [17].

There are similar differences observed in the N–C distances as presented above, indicating the different electronic delocalization within N–C–N framework (N(1)–C(1) = 1.316(9), N(2)–C(1) = 1.351(10), N(3)–C(18) = 1.318(10), N(4)–C(18) = 1.349(9), N(5)–C(35) = 1.345(10), N(6)–C(35) = 1.323(10), N(7)–C(52) =

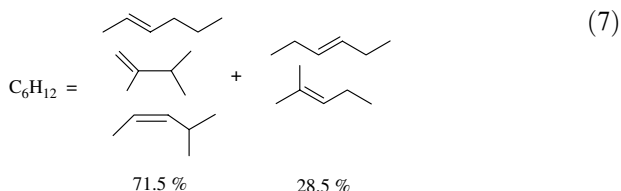
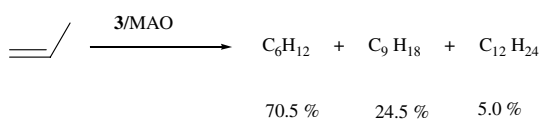
1.349(9), N(8)–C(52) = 1.310(10) Å). Comparing the benzamidinate ligation with other nickel complex reveals a small difference between the N–C–N angles in complex **6** (120.6° (average)), and those in (μ_2)₂–(N,N′-bis-(trimethylsilyl)benzamidinate Ni(I)) dimer (122.25°) [17]. Interestingly, the Ni–Ni distance in complex **6** (2.4484(13) Å) is longer than in N-silylated-benzamidinate nickel(I) complex (2.2990(12) Å) [17].

2.3. Oligomerization of propylene by complex **3** activated with MAO

Complex **3** was tested as a pre-catalyst for the oligomerization of propylene after being activated by MAO (Al:Ni = 200). Performing the oligomerization reaction at liquid propylene (10 bar) and room temperature for 20 h without additional solvents leads to a mixture of dimers (70.5%), trimers (24.5%) and tetramers (5.0%) of propylene with a turnover frequency of 5200 h⁻¹ (Eq. (7)). Among the various dimerization products two mixtures of hexenes containing both primary dimerization products (71.5%, *trans*-2-hexene, 2,3-dimethyl-1-butene, *cis*-4-methyl-2-pentene) and isomerization products (28.5%, *trans*-3-hexene, 2-methyl-2-pentene) were obtained (Eq. (7)).



Scheme 1. Proposed mechanism for SiMe₃-H exchange in the ligand PhC(N-SiMe₃)(N'-myrtanyl)Li(TMEDA).

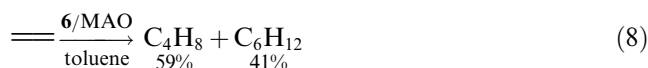


Interestingly, in comparison with complex 3 non-chiral bis-N-silylated-benzamidinate nickel pre-catalyst shows a large selectivity towards dimers (>98%) with

different product distribution (42% of the primary dimerization products and 58% of isomerization products) with a high turnover frequency of 9040 h⁻¹ [17].

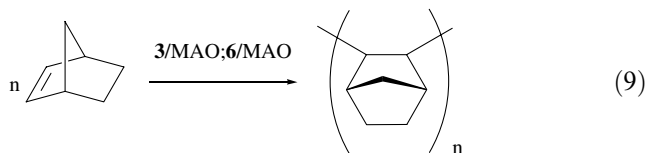
2.4. Oligomerization of ethylene with complex 6/MAO

When activated with MAO complex 6 showed a high activity toward the oligomerization of ethylene. Performing the oligomerization reaction in toluene at ambient temperature and a constant ethylene pressure of 30 atm complex 6 yield a mixture of dimers (59%) and trimers (41%) with a high turnover frequency of 16,400 h⁻¹ (Eq. (8)). A similar product distribution (52% of butenes and 48% of hexenes) and turnover frequency of 17,100 h⁻¹ were observed for the pre-catalyst PhC(NSiMe₃)₂Ni(acac) using toluene as the solvent [17].



2.5. Polymerization of norbornene with complex 3/MAO and complex 6/MAO

Complexes **3** and **6** were also tested as the catalytic precursors for the addition polymerization of norbornene (Eq. (9)).



The preliminary results indicate that both complex **3** and complex **6** being activated with MAO exhibit a good catalytic activity for the polymerization of norbornene in toluene at ambient temperature (for complex **3** atactic polynorbornene (PNB) yield = 42.4% for 1 h at Al:Ni = 150, [monomer]:[Ni] = 1500; for complex **6** yield = 59.4% for 1 h at Al:Ni = 100, [monomer]:[Ni] = 1000). As compared to other nickel complexes activated by MAO, complexes **3** and **6** were found to be less active than PhC(NSiMe₃)₂Ni(acac) at the molar ratio Al:Ni = 100 and 150 (for PhC(NSiMe₃)₂Ni(acac) yield = 65.9% for 1 h) [17]. Interestingly, when the polymerization was performed at a MAO:Ni ratio of 200 the activities of both complex **6** and PhC(NSiMe₃)₂Ni(acac) were alike (yield = 72.0% for complex **6** and 70.0% for PhC(NSiMe₃)₂Ni(acac)). The formation in all cases of atactic polymers indicates the lack of ability to induce stereospecific interactions presumably due to the large distance of the chiral center to the metal center.

3. Conclusions

Two new chiral nickel complexes bearing the chelating benzamidinate ligation have been synthesized. Their solid-state molecular structures have been determined by low-temperature X-ray diffraction analysis. Complex **3** being activated with MAO oligomerizes propylene, producing a mixture of dimers, trimers and tetramers. Complex **6** activated with MAO has been found to oligomerize ethylene to the mixture of dimers and trimers. Moreover, both complex **3**/MAO and complex **6**/MAO have been shown to be good catalytic systems for the addition polymerization of norbornene.

4. Experimental

4.1. General procedure

All manipulations were performed with the exclusion of oxygen and moisture using flamed Schlenk-type glass-

ware on a dual-manifold Schlenk line, or interfaced to a high vacuum (10⁻⁵ Torr) line. For storage of air-sensitive materials, a nitrogen-filled “Vacuum Atmospheres” glovebox with a medium capacity recirculator (1–2 ppm O₂) was used.

NMR spectra were recorded on Bruker AM-300 and AM-500 spectrometers. Chemical shifts for ¹H NMR and were referenced to internal solvent resonances and reported relative to tetramethylsilane. Low-temperature X-ray diffraction experiments were carried out on a Nonius-KappaCCD diffractometer with graphite monochromatized Mo K α radiation. The crystals were placed in dry and degassed Parathon-N (Du-Pont) oil in a glovebox. Single crystals were mounted on the diffractometer under a stream of cold N₂ at 230 K. Cell refinements and data collection and reduction were carried out with the Nonius software package [18]. The structure solution was carried out by the SHELXS-97 [19] and SHELXSL-97 [20] software packages. The ORTEP program incorporated in the TEXRAY structure analysis package was used for molecular graphics [21].

4.2. Materials

Argon and nitrogen were purified by passage through a MnO oxygen removal column and a Davison 4 Å molecular sieves column. Analytically pure solvents were distilled under argon from Na/K alloy (diethyl ether, hexane), Na (toluene), P₂O₅ (dichloromethane), or BaO (pyridine, triethylamine). All solvents for vacuum line manipulations were stored in a vacuum over Na/K alloy. Nitrile compounds (Aldrich) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were degassed and freshly distilled under argon. Methylalumoxane (MAO) (Witco) was prepared from a 30% suspension in toluene by vacuum evaporation of the solvent at 25 °C/10⁻⁵ Torr. (–)-*cis*-Myrtanylamine, Me₃SiCl, BuLi, norbornene (bicyclo[2.2.1]hept-2-ene) were purchased and used as received (Aldrich). Et₃NHCl (Aldrich) was sublimated under vacuum at 200 °C. Bis-(acetylacetonate)nickel(II)–(TMEDA)Ni(acac)₂ [16], (TMEDA)NiMe₂ [12d,16] were prepared via the literature procedures.

4.3. Synthesis of ligand [PhC(*N*-SiMe₃)(*N'*-myrtanyl)]Li(TMEDA) (**1**)

4.3.1. Synthesis of Me₃SiH(*N*-myrtanyl)

To a well-stirred solution of 5.65 g (33.1 mmol) (–)-*cis*-myrtanylamine and 33.5 g (33.1 mmol) of freshly distilled Et₃N in hexane (150 mL) 3.6 g (33.1 mmol) of Me₃SiCl was dropwise added over 1 h at room temperature. The resulting mixture was stirred with reflux for 17 h. After filtration of the solid Et₃NHCl and evaporation of the solvent by vacuum, the product was distilled under vacuum at 50–52 °C producing 6.3 g (85%) of

transparent oil. For spectroscopic characterization and for the second step of the preparation of ligand **1** see [15b].

Anal. Calc. for $C_{20}H_{31}N_2LiSi \cdot 1/2TMEDA$ (392.2): C, 70.39; H, 9.95; N, 10.71. Found: C, 69.61; H, 9.00; N, 9.65%.

4.4. Synthesis of neutral ligand $PhC(NHSiMe_3)-(N'-myrtanyl)$ (**4**)

1.03 g (7.47 mmol) of Et_3NHCl was added to a solution of the ligand **1** (2.5 g, 7.47 mmol) in 40 mL of toluene. The mixture was stirred at room temperature for 20 h. The solution was isolated via filtration through celite and the solvent was evaporated under vacuum producing transparent yellow oil. The product was washed with additional 25 mL of toluene and dried under vacuum overnight to obtain 2.25 g (92%) of ligand **4** as a viscous oil. Anal. Calc. for $C_{20}H_{32}N_2Si$ (328.1): C, 73.15; H, 9.75; N, 8.53. Found: C, 72.80; H, 9.70; N, 8.87%.

1H NMR (C_6D_6 , 300 MHz): δ = 7.19 (m, 5H, Ph), 3.48 (s, 1H N-H), 3.22 (m, 2H, N- CH_2CH), 2.40 (m, 2H, N- $CH_2CHCHC(CH_3)_2$), 1.93 (m, 5H, C- CH_3 + $CHCH_2CH_2$), 1.54 (m, 1H, $CH_2CHC(CH_3)_2$), 1.21 (m, 5H, C- CH_3 + CH_2CH_2CH), 1.11 (m, 1H, $CHCHCH$), 0.76 (m, 1H, $CHCHCH$), 0.4 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (C_6D_6 , 75 MHz): δ = 161.0 (N-C=N), 130.4, 129.7, 129.0, 128.2 (Ph), 58.8 (HN- CH_2CH), 45.8 ($CH_2CH(CH_2)_2$), 43.5 ($CHCHC(CH_3)_2$ + $CH_2CHC(CH_3)_2$), 40.3 ($C(CH_3)_2$), 35.4 ($CHCH_2CH$), 29.7 (CH_3), 28.2 (CH_2CH_2CH), 24.8 (CH_3), 21.7 ($CHCH_2CH_2$), 1.8 ($SiCH_3$).

4.5. Synthesis of the complex $[PhC(N-SiMe_3)(N'-myrtanyl)]_2Ni(Py_2)$ (**3**)

4.5.1. Method A

To a well-stirred solution of compound **2** (1.12 g 3.0 mmol) in 30 mL of diethyl ether 2.0 g (6.0 mmol) of ligand **1** was added. A color change from turquoise to a brown was observed. The resulting mixture was stirred for 10 h at room temperature and filtrated cold. The solvent was evaporated under vacuum producing brown color viscous oil. The product was washed with additional 25 mL of toluene and dried under vacuum. Attempts to crystallize this compound from any solvent were unsuccessful. After addition of a solution mixture of hexane:pyridine (20 mL, 1:1) to a nickel compound the solution was stirred for 1 h. Slow cooling of this solution at $-40^\circ C$ for two weeks provided the green color crystals of complex **3** (54%), which was isolated by filtration and drying under vacuum. Complex **3** is paramagnetic, giving broad contact-shifted signals in the range from -15 to -4 and 60 – 90 ppm. Anal. Calc.

for $C_{50}H_{72}N_6NiSi_2$ (872.03): C, 68.80; H, 8.25; N, 9.63. Found: C, 69.40; H, 8.14; N, 10.45%.

4.5.2. Method B

(TMEDA) $NiMe_2$ prepared by the reaction of (TMEDA) $Ni(acac)_2$ (0.66 g, 1.77 mmol) with 0.30 g (1.77 mmol) of (TMEDA) $MgMe_2$ was dissolved in 10 mL of a cooled ($-70^\circ C$) solution mixture of toluene:pyridine (3:1) and reacted with a toluene solution (3 mL) of ligand **4** (0.42 g, 1.28 mmol). The resulting mixture was warmed to $-20^\circ C$ and stirred at this temperature for 15 min and then for 3 h at room temperature giving a deep red solution. Bubbling was observed. The reaction initially provided the expected methyl complex **5** which could be observed by following the crude reaction in a NMR tube 1H NMR (δ = -0.32 , corresponding to the mono $Ni-CH_3$). However, after repeated washing of the precipitated complex with cold toluene and the re-crystallization at $-30^\circ C$ for 2 weeks, single crystals with green color of complex **3** have been obtained in 23% yield.

4.6. Synthesis of $[tetra-(N'-myrtanyl)(benzamidinate)]-Ni$ dimer (**6**)

To a well-stirred solution of 0.48 g (1.29 mmol) of complex **2** in toluene:pyridine mixture (25 mL, 2:3) 1.0 g (2.58 mmol) of ligand **1** was added. A color change from turquoise to a deep brown was immediately observed. The resulting mixture was stirred for 15 h at room temperature, filtrated and the solvents were evaporated under vacuum. The product was washed with additional 25 mL of toluene and after toluene evaporation, 15 mL of hexane was transferred under vacuum to the residue. Slow cooling of this solution to $-40^\circ C$ for two weeks provided the green color crystals of complex **6** in 62% yield.

Anal. Calc. for $C_{75}H_{100}N_8Ni_2$ (1231.05): C, 73.11; H, 8.12; N, 9.09. Found: C, 73.40; H, 8.14; N, 9.45%.

4.7. General procedure for the dimerization of propylene

Experiments at higher pressures were performed in a 100 mL stainless steel reactor. The reactor was charged inside a glovebox with a certain amount of the catalytic precursor, MAO, and a magnetic stirrer. The reactor was connected to a high vacuum line, pumped-down and frozen at liquid nitrogen temperature. 25 mL of liquid propylene was transferred under vacuum to the frozen reactor. The reactor was rapidly warmed to room temperature, and the solution stirred. After being stirred for a certain period, the mixture was quenched by exhausting the unreacted propylene. An aliquot of the reaction mixture was removed for GLC analysis whereas a set of ten different hexenes was used as internal reference.

4.8. General procedure for ethylene oligomerization

The catalytic oligomerization of ethylene activated by complex **6** and MAO was performed in 100 mL stainless steel reactors. The reactor was charged inside a glovebox with a certain amount of the catalytic precursor, MAO and a magnetic stirrer. The reactor was connected to a high vacuum line, and, after introduction of the solvent (10 mL) under an argon flow, it was frozen at liquid nitrogen temperature and evacuated under vacuum. The reactor was then warmed to room temperature, pressurized to 30 bar ethylene pressure and stirred for the desired reaction time. The reaction temperature was maintained using an external water-ice bath to control the reaction exotherm. After 1 h the reaction was stopped by cooling the reactor to $-15\text{ }^{\circ}\text{C}$ and depressurizing. The contents were transferred into a cold tarred 50 mL heavy duty glass Schlenk flask, sealed and weighed. The oligomers obtained were analyzed by GC/MS.

4.9. Norbornene polymerization procedure

A 50 mL three neck polymerization bottle, equipped with a retort and a magnetic stirrer, was charged inside a glovebox with a certain amount of MAO and 0.5 g of norbornene. The bottle was connected to a Schlenk vacuum line and, after introducing a toluene solution (5 mL) of precatalyst ($1.06 \times 10^{-3}\text{ M}$) via a syringe under an argon flow and stirring catalytic mixture for 5 min, the monomer was added from the retort in one portion. After being stirred for a desired amount of time, the reaction mixture was poured into acidified methanol (1:4) in order to quench the polymerization. The resulting precipitated polymer was separated by filtration, washed with water and acetone several times and finally dried under vacuum at $70\text{ }^{\circ}\text{C}$. The polynorbornene yield in percentage was calculated as the weight fraction of converted monomer over the total monomer.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 226901 and 226902 for complex **3** and complex **6**, respectively. Supplementary data

associated with this article can be found, in the online version at [doi:10.1016/j.jorganchem.2005.04.007](https://doi.org/10.1016/j.jorganchem.2005.04.007).

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