

Retro-Brook rearrangement induces the formation of an octahedral nickel(benzamidinate) complex; synthesis, structure and catalytic activity

Elza Nelkenbaum, Moshe Kapon, Moris S. Eisen *

Department of Chemistry and Institute of Catalysis Science and Technology, Technion – Israel Institute of Technology, Kyriat Hatechion, Haifa 32000, Israel

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Abstract

The neutral octahedral nickel complex (PhC(NSiMe₃)NC(Ph)=CHSiMe₃)Ni(acac)(TMEDA) (**7**), has been synthesized and characterized including X-ray diffraction analysis. The complex was formed by the reaction of Ni(acac)₂(TMEDA) with the lithium salt of the corresponding β-diketiminato ligand. The formation of the benzamidinate motif from the corresponding β-diketiminato is a consequence of a retro-Brook isomerization that is operative only at the nickel centre. A plausible mechanism for the metal mediated isomerization is proposed. When complex **7** was activated with MAO it showed a good catalytic activity for the addition polymerization of norbornene. Furthermore, this catalytic system has been found to oligomerize ethylene to a mixture of butenes and hexenes with a high turnover frequency, $\eta = 29,300 \text{ h}^{-1}$, when the reaction is performed in dichloromethane.
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Keywords: Diketiminates; Polymerization; Retro brook isomerization; Ethylene oligomerization; Nickel; X-ray structure

1. Introduction

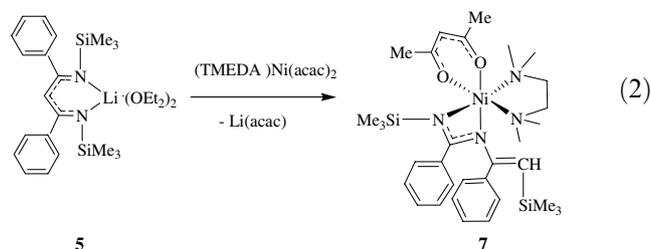
Brookhart's introduction of highly active cationic nickel (II) and palladium (II) catalysts with bulky α-diimine ligations [1] has encouraged a great interest in the development and exploring of late-transition-metal catalysts for the polymerization of α-olefins [2]. The decreased electrophilicity of late transition metals as compared to group 4 complexes allows the copolymerization of ethylene with polar monomer producing functionalized polyolefin materials with unusual microstructures [3]. However, due to rapid β-hydrogen elimination process, many neutral late transition-metal complexes have been mainly utilized for the production

of dimers and oligomers of ethylene [4]. For example, neutral nickel-ylide complex containing a P–O chelate ancillary ligation was employed in the Shell Higher Olefin process (SHOP) for the synthesis of linear oligomers of ethylene in the C₄–C₂₀ range [5]. These catalysts were also demonstrated to polymerize ethylene to high molecular weight polymer under severe conditions [6]. Hence, modified SHOP-type catalysts were introduced allowing the polymerization of α-olefins in polar media or their copolymerization with monomers containing a polar functional group in a remote position from the polymerising vinyl group [7]. Therefore, a renewed interest was aimed in developing neutral nickel (II) catalysts for using with various functionalized monomers and polar solvents.

Grubbs's family of neutral nickel (II) complexes bearing bulky *ortho*-substituted salicylaldimine ligands is

* Corresponding author. Tel.: +972 482 92680; fax: +972 482 95703.
E-mail address: chmoris@techunix.technion.ac.il (M.S. Eisen).

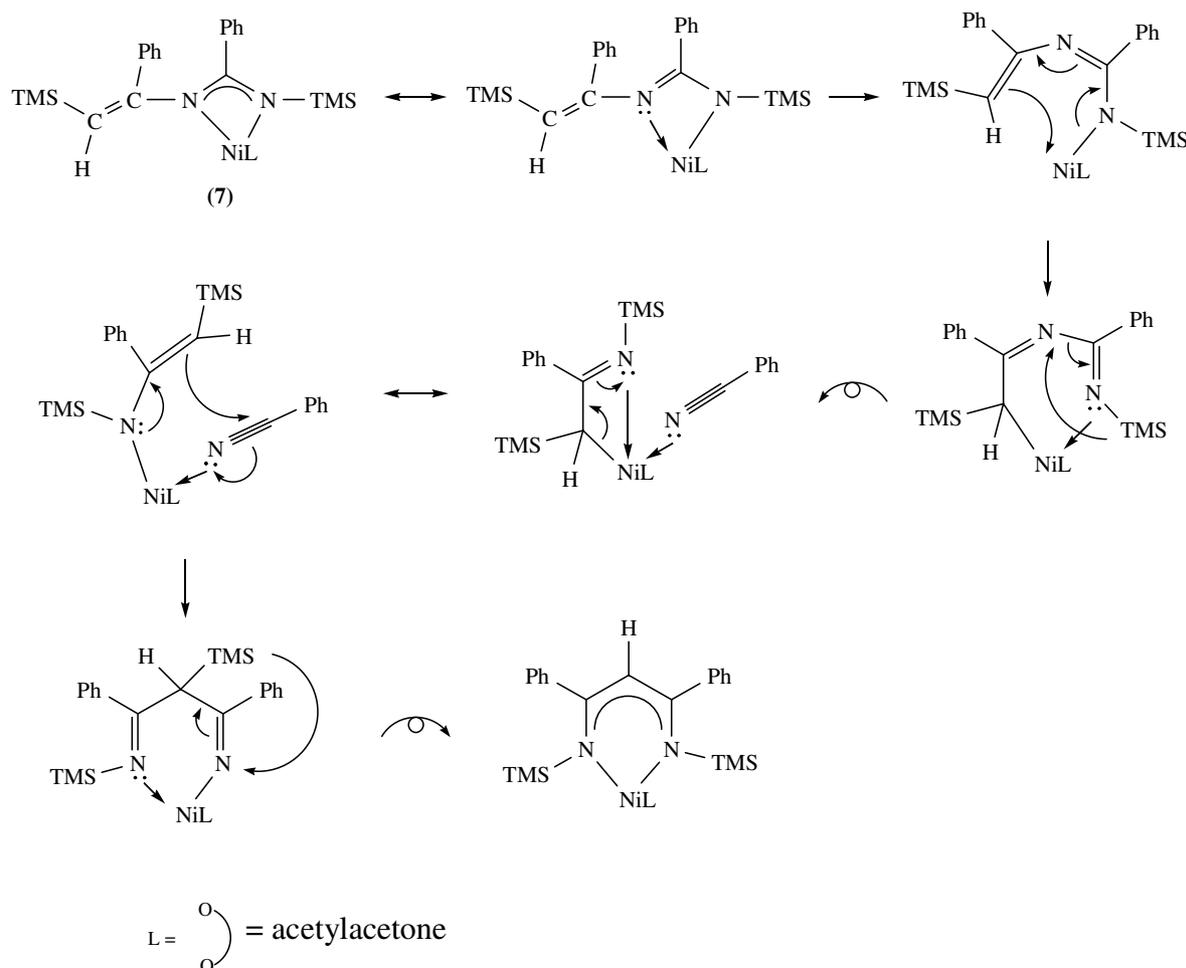
following the literature procedures. Reaction of (TMEDA)Ni(acac)₂ with an equimolar amount of complex **5** in toluene at ambient temperature provided complex (PhC(NSiMe₃)NC(Ph)=CHSiMe₃)Ni(acac)(TMEDA) (**7**), bearing the 1,3-diazaallyl ligand, which is formed through the isomerization of the corresponding β-diketiminato moiety (Eq. (2)).



The isomerization of the ketimidate ligation has been suggested to be a consequence of steric hindrance [29]. Therefore, temperature-dependent NMR studies of the corresponding lithium β-diketiminato (**5**) was studied at temperatures ranging from –25 to 90 °C, to determine if this isomerization is dynamically operative

or operative at the ligand. It is worth noting that no signal changes were observed, in the ¹H and ¹³C NMR, for complex **5** between the ranges of measured temperatures indicating its stability. Hence, since in the synthesis of complex **7** the pure β-ketimidate ligand **5** was utilized, implicates that the isomerization of the β-diketiminato ligand to the benzamidinate form was mediated by the nickel metal. This isomerization presumably occurs via a retro-Brook rearrangement [21]. A plausible mechanism for this Ni mediated isomerization is suggested in Scheme 1. The proposed mechanism is shown starting from the amidinate ligand, since it is easier to follow the process from this direction. The process involves changes in the binding of the ligand to the metal center, from metal–nitrogen to metal–carbon bond, followed by rearrangement of the TMS group from a nitrogen atom to another one. Additional metal–nitrogen bond change, nucleophilic attack of the carbanion on a coordinated nitrile followed by a second TMS rearrangement generates the formation of the final product.

Complex **7** was successfully crystallized from a hexane solution to obtain bright-green color single crystals



Scheme 1. Proposed mechanism for the nickel-mediated isomerization of β-diketiminates.

suitable for X-ray measurements in 73% yield. ^1H NMR spectroscopy reveals that complex **7** is paramagnetic, giving broad contact-shifted signals in the range of -23 to -10 and of 50 – 90 ppm. The ORTEP crystal structure of complex **7** is presented in Fig. 1. Selected bond lengths and angles and crystallographic data and structure refinement details for the complex, are collected in Tables 1 and 4, respectively.

The low temperature X-ray diffraction analysis reveals that complex **7** contains one κ^2 -chelating substituted benzamidinate, one κ^2 -acetylacetonate and one κ^2 -TMEDA ligand around the nickel centre with distorted octahedral coordination geometry. The axial position is occupied by one oxygen and one nitrogen from the benzamidinate ligand with a transaxial angle of $\text{O}(2)\text{--Ni--N}(1) = 166.92(7)^\circ$, whereas the second oxygen atom $\text{O}(1)$, and the nitrogen atoms $\text{N}(2)$, $\text{N}(3)$ and $\text{N}(4)$ occupy the equatorial position with the sum of the equatorial angles of 360.91° ($\text{N}(2)\text{--Ni--N}(4) = 97.50(8)^\circ$, $\text{N}(3)\text{--Ni--N}(4) = 83.48(8)^\circ$, $\text{O}(1)\text{--Ni--N}(3) = 89.59(8)^\circ$, $\text{O}(1)\text{--Ni--N}(2) = 90.34(8)^\circ$) [30]. The benzamidinate ligand is a partially puckered as shown by the small dihedral angle $\text{N}(1)\text{--C}(3)\text{--N}(2)\text{--Ni} = 4.1^\circ$.

The core units of complex **7** comprises a five-membered ring Ni--N--C--C--N , a four-membered ring Ni--N--C--N and a six-membered ring Ni--O--C--C--C--O . The bond lengths between the metal centre and the nitrogen atoms of the coordinative TMEDA ligand are slightly different ($\text{Ni--N}(3) = 2.168(2)$, $\text{Ni--N}(4) = 2.213(2)$ Å) in contrary to other isolobal octahedral nickel benzamidinate TMEDA complexes as in $\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})(\text{TMEDA})$ ($2.197(2)$ and $2.221(2)$ Å) or in $p\text{-MePhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})(\text{TMEDA})$ ($2.188(5)$ and $2.208(5)$ Å) [31]. It is important to point out that in all the compared complexes the nitrogen atoms of the TMEDA ligand are disposed always *trans* to the same type of atoms of the additional ligands, as in complex **7**. Interestingly, is the relationship between the nickel (II) *N*-silylated benzamidinate distances. In complex **7** both Ni--N (amidinate) distances ($\text{Ni--N}(1) = 2.150(2)$, $\text{Ni--N}(2) = 2.132(2)$ Å) are almost identical, opposite again to those observed in the isolobal octahedral complexes where the M--N (amidinate) are different ($2.096(2)$ and $2.215(2)$ Å) for $\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})(\text{TMEDA})$, ($2.101(4)$ and $2.228(4)$ Å) for $p\text{-MePhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})(\text{TMEDA})$). The Ni--O bond lengths in all the complexes are similar ($\text{Ni--O}(2) = 2.011(2)$, $\text{Ni--O}(1) = 2.037(2)$ Å) and ($2.027(2)$ and $2.031(2)$ Å) for $\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})(\text{TMEDA})$ and ($2.029(4)$ and $2.041(3)$ Å) for $p\text{-MePhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})(\text{TMEDA})$) [31].

By comparison to other metal amidinate moieties the Ni--N (amidinate) bond lengths in complex **7** are shorter than in the similar uranium complex (2.40 and 2.45 Å) [23] and in the corresponding zirconium complex (2.242 and 2.269 Å) [22], while these bonds are longer

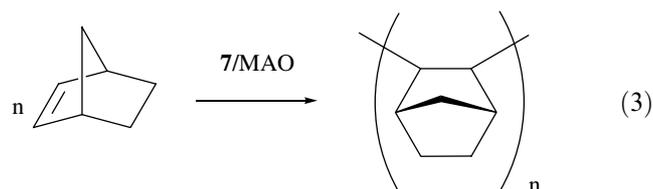
than in chromium (II) ($2.096(4)$ Å (average)) [32] and copper (II) ($1.984(4)$ and $2.029(4)$ Å) [33] complexes.

Comparing the benzamidinate ligand with other lanthanide/actinide and early/late-transition-metal complexes reveals a small difference between the $\text{N}(2)\text{--C}(3)\text{--N}(1)$ angle in complex **7** ($116.3(2)^\circ$), and those of analogous complexes of neodymium (121.4°) [34], in yttrium (119.8°) [35], in titanium (IV) (112.9°) [36], in zirconium (IV) ($113.2(3)^\circ$) [22], in nickel (II) ($117.95(19)^\circ$) [31], and copper (II) ($114.2(4)^\circ$) [33]. The acute angle of the benzamidinate ligation in complex **7** $\text{N}(2)\text{--Ni--N}(1) = 63.46(7)^\circ$ is identical to that in other octahedral *N*-silylated benzamidinate nickel (II) complex ($63.56(7)^\circ$) [31]; whereas smaller than in tetrahedral (benzamidinate)nickel compound ($67.65(13)^\circ$) [31]; although larger as compared to that in zirconium complex ($59.51(12)^\circ$) [22] due to the hardness of the latter metal as compared to nickel. Interestingly, there are no significant differences observed in the $\text{C}(3)\text{--N}(1)\text{--C}(2)$ angle in complex **7** ($122.14(19)^\circ$), in uranium ($125(2)^\circ$) [23], and in zirconium ($123.1(3)^\circ$) [22] complexes bearing the 1,3-diazaallyl ancillary ligation indicating the lack of coordination of the double bond.

Within the benzamidinate ligation, the $\text{N}(2)\text{--C}(3) = 1.319(3)$ and $\text{N}(1)\text{--C}(3) = 1.335(3)$ Å bond lengths are almost identical indicating similar electronic delocalization within N--C--N framework. The similar N--C distances fashion is observed for analogous *N*-silylated copper (II) benzamidinate ($1.319(6)$ and $1.334(6)$ Å) [33], for tetrahedral (amidinate)nickel compound ($1.323(5)$ and $1.327(5)$ Å) [31] and $\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})(\text{TMEDA})$ ($1.322(3)$ and $1.329(3)$ Å) [31]. The $\text{N}(1)\text{--C}(2)$ ($1.403(3)$ Å) and the $\text{C}(1)\text{--C}(2)$ ($1.350(3)$ Å) bond lengths in complex **7** are similar to the zirconium complex ($\text{N--C} = 1.442(5)$ Å), and (C=C double bond = $1.331(6)$), reflecting almost no degree of delocalization within the N--C--C framework, and a lack of conjugation within the amidine moiety [22].

2.2. Polymerization of norbornene

Complex **7** was tested as a catalytic precursor for the vinyl polymerization of norbornene (Eq. (3))



The preliminary results indicate that when complex **7** is activated with MAO exhibits a good catalytic activity for the polymerization of norbornene in toluene (polynorbornene (PNB) yield = 66.9% at $\text{Al:Ni} = 200$, 25°C). The comparison of the catalytic activity of complex **7** with other nickel complexes activated by

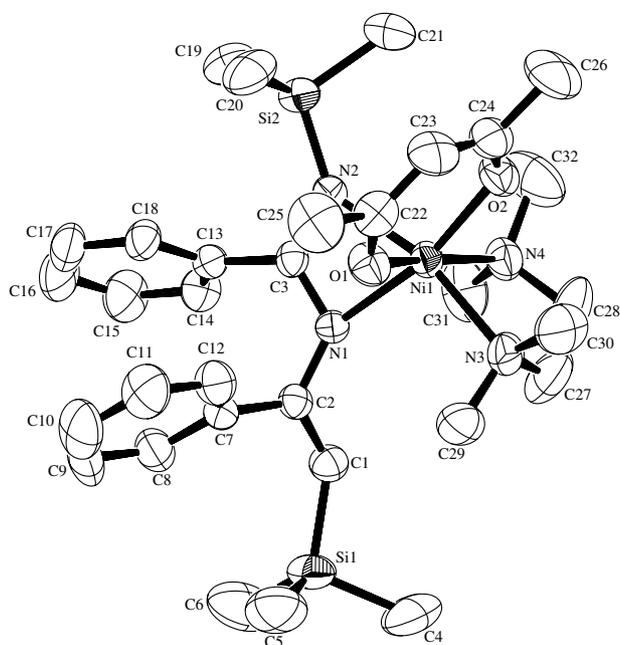


Fig. 1. ORTEP plot of the molecular structure of the complex **7**. All hydrogens were removed for clarity and thermal ellipsoids are given at 50% probability.

MAO, $\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})$ [31] and $\text{Ni}(\text{acac})_2$ [37], is presented in Table 2. Complex **7** was found to be less active than $\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})$ at the molar ratio $\text{Al}:\text{Ni} = 100$ (compare entries 1 and 4 in Table 2). However, longer reaction time leads to a significant increasing in the polymer yield for the former complex (compare entries 1 and 2 in Table 2) as compared to a modest increasing in the yield for the latter complex (entries 4 and 5). As regards to $\text{Ni}(\text{acac})_2$, complex **7** was found to be more active (compare entries 2 and 7 or 3 and 8). Interestingly when running the reaction with a MAO:Ni ratio of 200 complex **7** was found to be more active than the complexes $\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})$ and $\text{Ni}(\text{acac})_2$ (compare entries 3, 6 and 8). It is important to point out that in toluene MAO does not induce the polymerization of norbornene. Regarding to the molec-

Table 1
Selected bond lengths (Å) and angles (°) for complex **7**

Ni–N(1)	2.150(2)
Ni–N(2)	2.137(2)
Ni–N(3)	2.168(2)
Ni–N(4)	2.213(2)
N(1)–C(3)	1.335(3)
N(2)–C(3)	1.319(3)
N(1)–C(2)	1.403(3)
C(1)–C(2)	1.350(3)
O(2)–Ni–N(1)	166.92(7)
O(1)–Ni–N(2)	90.34(7)
O(1)–Ni–N(3)	89.59(8)
N(2)–Ni–N(4)	97.50(8)
N(3)–Ni–N(4)	83.48(8)
N(2)–Ni–N(1)	63.46(7)
N(2)–C(3)–N(1)	116.3(2)
C(3)–N(1)–C(2)	122.14(2)

ular weight of the polymer under all the studied conditions, complex **7** yield the higher molecular weight polynorbornenes.

2.3. Oligomerization of ethylene

Complex **7** was also tested as a pre-catalyst for the oligomerization of ethylene being activated with MAO ($\text{Al}:\text{Ni} = 200$). When performing the reaction in toluene at ambient temperature and a constant ethylene pressure of 30 atm, complex **7** affords a mixture of dimers (83%) and trimers (17%) with a high turnover frequency of $13,100 \text{ h}^{-1}$ (see entry 1 in Table 3). Interestingly, a different product distribution is observed for the pre-catalyst $\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})$ using toluene as the solvent (52% of butenes and 48% of hexenes) however with a better turnover frequency of $17,100 \text{ h}^{-1}$ [31]. Since all the reactions were carried out for 1 h the turnover frequency equals the turnover number ($\text{TOF} = \text{TON}$).

$$\alpha = \frac{\text{rate of propagation}}{\text{rate of propagation} + \text{rate of chain transfer}} = \frac{\text{moles of } C_{n+2}}{\text{moles of } C_n} \quad (4)$$

Table 2
Comparison in the polymerization of norbornene by complex **7**, $\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})$ and $\text{Ni}(\text{acac})_2$

Entry	Complex	Time (h)	Al/Ni	Yield (%)	Mw $\times 10^{-3}$	Reference
1	7	0.25	100	32.6	737	This paper
2	7	1	100	56.5	821	This paper
3	7	0.25	200	66.9	637	This paper
4	$\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})$	0.25	100	52.0	408	[31]
5	$\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})$	1	100	65.9	354	[31]
6	$\text{PhC}(\text{NSiMe}_3)_2\text{Ni}(\text{acac})$	0.25	200	59.3	399	[31]
7	$\text{Ni}(\text{acac})_2$	4	100	40.0	593	[37]
8	$\text{Ni}(\text{acac})_2$	4	200	53.0	609	[37]

Reaction conditions: $[\text{Ni}] = 1.06 \times 10^{-3} \text{ M}$; $[\text{monomer}]:[\text{Ni}] = 1000$; 25°C .
5 mL toluene; For complex $\text{Ni}(\text{acac})_2$ the $[\text{monomer}]:[\text{Ni}] = 1500$.

Table 3
Data in the oligomerization of ethylene with complexes **7**/MAO and PhC(NSiMe₃)₂Ni(acac)/MAO

Entry	Complex	Solvent	C ₄ H ₈ (%)	C ₆ H ₁₂ (%)	C ₈ –C ₁₂ ^a (%)	Schulz–Flory α	TOF ^b (η) (h ⁻¹)
1	7	Toluene	83	17	–	0.17	13,100
2	7	CH ₂ Cl ₂	86	14	Traces	0.14	29,300
3	PhC(NSiMe ₃) ₂ Ni(acac)]	Toluene	52	48	–	0.48	17,100
4	PhC(NSiMe ₃) ₂ Ni(acac)]	CH ₂ Cl ₂	28	44	28	0.72	43,600

Reaction conditions: [Ni] = 1.2 × 10⁻³ M, Al:Ni = 200, time = 1 h, 25 ± 3 °C; solvent 10 mL, 30 bar of ethylene.

^a C₈–C₁₂ = hydrocarbons with 8–12 carbons in the chain.

^b TOF = turnover frequency = mol of ethylene consumed/(mol of Ni catalyst × time in hours).

Table 4
Crystal data collection for complex **7**

Identification code	Complex 7
Empirical formula	C ₃₂ H ₅₂ N ₄ NiO ₂ Si ₂
Formula weight	639.67
Temperature (K)	230.0(1)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	10.4300(3)
<i>b</i> (Å)	12.6430(3)
<i>c</i> (Å)	15.0330(6)
α (°)	100.079(1)
β (°)	93.934(1)
γ (°)	106.978(2)
Volume (Å ³)	1851.5(1)
Z, calculated density (mg/m ³)	2, 1.147
Absorption coefficient (mm ⁻¹)	0.619
<i>F</i> (000)	688
Crystal size (mm)	0.18 × 0.24 × 0.28
Theta range for data collection (°)	2.01–25.05
Limiting indices	–11 ≤ <i>h</i> ≤ 12, –14 ≤ <i>k</i> ≤ 15, –17 ≤ <i>l</i> ≤ 17
Reflections collected/unique	11,338/6555 [<i>R</i> (int) = 0.03671]
Completeness to theta = 25.05 (%)	99.9
Refinement method	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6555/0/422
Goodness-of-fit on <i>F</i> ²	0.928
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0395, <i>wR</i> ₂ = 0.0924
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0667, <i>wR</i> ₂ = 0.0974
Largest difference peak and hole (e Å ⁻³)	0.343 and –0.371

Performing the oligomerization reaction in dichloromethane with complex **7** under the same reaction conditions also leads to the mixture of dimers and trimers of ethylene having similar products distribution (compare entries 1 and 2 in Table 3), but with a much higher turnover frequency $\eta = 29,300 \text{ h}^{-1}$. As a comparison, for PhC(NSiMe₃)₂Ni(acac), using dichloromethane as a solvent gives also oligomers of ethylene with a much higher turnover frequency and different product distribution with a considerable amount of the higher oligomers (compare entries 3 and 4 in Table 3) [31]. The oligomerization follows a Schulz–Flory distribution [38] that is

characterized by the constant α . This constant represents the probability for chain propagation as display in Eq. (4). An oligomer distribution with a small α value (e.g. $\alpha < 0.5$) is indicative for mainly dimers and lower oligomers. A high value will indicate higher oligomers. As presented in Table 3, mainly dimers are the oligomers obtained.

3. Conclusions

A new 1,3-diazaallyl-acetylacetonate nickel complex has been synthesized and characterized. The solid state molecular structure of complex **7** have been confirmed by single crystal X-ray diffraction studies. The chelating ring size effect as compared to other benzamidinato complexes is presented. Complex **7** activated with MAO has been shown to be a good catalytic system for the norbornene vinyl-type polymerization. In addition, this catalytic system has been found to oligomerize ethylene producing the mixture of dimers and trimers.

4. Experimental

4.1. General procedure

All manipulations were performed with the exclusion of oxygen and moisture using flamed Schlenk-type glassware 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 ¹³C NMR were referenced to internal solvent resonances and reported relative to tetramethylsilane. The NMR experiments of the complexes were conducted in Teflon valve-sealed tubes after vacuum transfer of the solvent in a high vacuum line. The NMR characterization of polynorbornenes was performed in deuterated 1,1,2,2-tetrachloroethane at 130 °C. The electronic spectra were recorded on a HP 8452A diode array spectrophotometer. GC/MS analysis was performed on a Finnigan MAT TSQ 700 mass-spec-

trometer with a DB-5 type capillary column of 30 m length and 0.25 mm internal diameter. Molecular weights of polymers were determined by the GPC method on a Waters-Alliance 2000 instrument using 1,2,4-trichlorobenzene (HPLC) as the mobile phase at 150 °C.

4.2. X-ray crystallography

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 (DuPont) 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 [39]. The structure solution was carried out by the SHELXS-97 [40] and SHELXL-97 [41] software packages, respectively. The ORTEP program incorporated in the TEXRAY structure analysis package was used for molecular graphics [42].

4.3. 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 nitrogen from Na/K alloy (diethyl ether, hexane), Na (toluene), P₂O₅ (dichloromethane). All solvents for vacuum line manipulations were stored in a vacuum over Na/K alloy. Methylalumoxane (MAO) (Witco) was prepared from a 30% suspension in toluene by vacuum evaporation of the solvent at 25 °C/10⁻⁵ Torr. Norbornene (bicyclo-[2.2.1]hept-2-ene) was purchased and used as received (Aldrich). The lithium β -diketiminatate [27] **5** and (TMEDA)Ni(acac)₂ (**6**) [28], were prepared via the literature procedures.

4.4. Synthesis of 1,3-diazaallyl(acetylacetonate)-Ni(TMEDA) complex (**7**)

To a well-stirred solution of compound **6** (1.3 g, 3.49 mmol) in 30 mL of toluene 1.3 g (3.49 mmol) of ligand **5** was added. A color change from turquoise to a deep green was observed. The resulting mixture was stirred for 10 h at room temperature, filtrated from Li(acac), and the solvent was vacuum evaporated. The product was washed with additional 25 mL of toluene and after toluene evaporation, 30 mL of hexane was vacuum transferred to a residue. Slow cooling of this solution at -40 °C for 50 h provided the bright-green color crystals of complex **7** (1.6 g, 73%), which was isolated by vacuum drying. Anal. Calc. for C₃₂H₅₂N₄NiO₂·Si₂ (639.35): C, 60.09; H, 8.19; N, 8.76. Found: C, 59.32; H, 7.74; N, 8.67%. UV/Vis (toluene): λ_{\max} = 630 nm. Mp = 85 °C (dec).

4.5. Norbornene polymerization procedure

In a 50 mL 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 × 10⁻³ M) via a syringe under an argon flow and stirring catalytic mixture for 5 min, the monomer from the retort was added 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 °C. The polynorbornene yield in percentage was calculated as the weight fraction of converted monomer over the total monomer.

4.6. General procedure for ethylene oligomerization

The catalytic oligomerization of ethylene activated by complex **7** 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 introducing the solvent (10 mL) under an argon flow, it was frozen at liquid nitrogen temperature and pumped-down. The reactor was then warmed to room temperature and maintained at temperature in the range of 25 ± 3 °C via a thermostated water bath to control the reaction exotherm, pressurized to 30 bars ethylene pressure and stirred for the desired reaction time. After 1 h the reaction was stopped by cooling the reactor to -15 °C and depressurizing. The contents were transferred into a cold tarred 50 mL heavy duty glass Schlenk flask, tightly sealed and weighed. The oligomers obtained were analyzed by GC/MS. The ratio among the oligomers was calculated based on the GC/MS and the total weight of the sample.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 261072 for complex **7**.

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