

Nitrogen- and phosphorus-coordinated nickel(II) complexes as catalysts for the oligomerization of ethylene

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Abstract

Nitrogen- and phosphorus-coordinated nickel(II) complexes **1** and **2** are active precatalysts together with the cocatalyst MAO for the oligomerization of ethylene mainly favoring the production of butenes. The nickel(II) complex **2b** reveals a good selectivity at higher ethylene pressure for the production of 1-butene.

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1. Introduction

The oligomerization of ethylene is one of the major industrial processes for the production of linear α -olefins [1–3]. Those oligomers in the range C_6 – C_{20} , in particular 1-hexene, are used as comonomers in the polymerization of ethylene to give linear low-density polyethylene (LLDPE) or for the preparation of detergents and synthetic lubricants. Catalysts currently used in industry for the Shell Higher Olefin Process (SHOP) contain Ni(II) complexes bearing bidentate monoanionic ligands [4–15]. Furthermore, cationic Ni(II) α -diimine complexes were intensively investigated [16–29], and especially Brookhart and co-workers have described differently substituted α -diimine ligands to form stable nickel(II) complexes which are highly effective ethylene oligomerization or polymerization catalysts [17–25]. N,P-coordinated nickel or palladium complexes were also described as active compounds for the oligomerization and polymerization of ethylene [30–34]. The dimerization of ethylene to butenes is used industrially for generating powering components in fuel with homogeneous titanium catalysts and special cocatalysts in the

alaphutol process (IFP) [35]. 2-Butene is also produced with the Phillips Petroleum process by dimerization of ethylene [35].

We have investigated new nitrogen- and phosphorus-coordinated nickel(II) complexes as suitable catalysts for oligomerization and dimerization reactions of ethylene. The results of the catalytic ethylene oligomerization and dimerization with the precatalysts **1** and **2** together with MAO as cocatalyst will be presented.

2. Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. NMR spectra were recorded on a Bruker spectrometer 250 MHz (1H) and 62.9 MHz (^{13}C) at 293 K. Mass spectra were obtained using electron ionization (EI), electron spray ionization (ESI) or field ionization (FI). Oligomer products were analyzed by GC with a flame ionization detector, using a 50-m DB1 column, injector temperature 40 °C and the following temperature program: 40 °C/5 min, 40–300 °C, 5 °C/10 min⁻¹. The individual products were integrated, using *n*-tridecane as internal standard.

Materials: MAO (10% solution in toluene) and all reactants were purchased from Aldrich and used as received.

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2.1. Synthesis of ligands

2.1.1. *N*-[(2-Chlorophenyl)methylene]-*N*-(1-pyridin-2-ylethyl)amine (**1a**)

A solution of 2-chlorobenzaldehyde (2.1 g, 15 mmol) in 20 ml of methanol was added dropwise to a solution of 1-pyridine-2-ylethanamine (1.8 g, 15 mmol) in 15 ml of methanol at ambient temperature. The mixture was then heated under reflux for 5 h. The solvent was removed under reduced pressure, and a dark yellow oil was obtained which was dried under vacuum. Yield: 3.2 g (13 mmol, 85%). ¹H NMR (CDCl₃) δ 8.28 (s, 1H, N=CH), 8.50 (d, 1H, Pyr-N=CH), 8.11 (t, 1H, Ar-H), 7.58 (t, 1H, Ar-H), 7.47 (d, 1H, Ar-H), 7.29–7.16 (m, 3H, Ar-H), 7.07 (t, 1H, Ar-H), 4.70 (q, 1H, CH₃CH), 1.59 (d, 3H, CH₃); EI⁺-MS: *m/z* = 245 [M⁺].

2.1.2. Dimethyloxalic acid-bis(2-methylphenyl)imidoate (**1b**) [36]

Oxalic acid-bis(2-methylphenyl)-bisimidoyldichloride (3.04 g, 10 mmol) was suspended in 50 ml of methanol, and then triethylamine (2.8 ml, 20 mmol) was added. The mixture was heated under reflux as long as the product was no longer visible through TLC (on SiO₂, eluant toluene/acetone = 10:1). After the methanol was evaporated under reduced pressure, the residue was taken up in toluene. After the precipitated HNet₃Cl was filtered, the toluene was removed under reduced pressure. The residue was crystallized from methanol. Yield: 1.99 g (6.7 mmol, 67%). ¹H NMR (CDCl₃): δ 6.86–6.92 (m, 6H), 6.54 (d, 2H), 3.83 (s, 6H), 1.24 (s, 6H); EI⁺-MS: *m/z* 296 [M⁺].

2.2. Synthesis of nickel(II) complexes

2.2.1. General procedure for the synthesis of the nickel complexes (**1a–2b**)

The appropriate ligand in dry DMF was added to a green solution of NiBr₂(dme) in dry DMF in a Schlenk flask under argon. The mixture was stirred for 3 h at room temperature, then the solvent was removed and finally the product was dried in vacuum.

2.2.2. *N*-[(2-Chlorophenyl)methylene]-*N*-(1-pyridine-2-ylethyl)-aminenickel(II) dibromide (**1a**)

N-[(2-Chlorophenyl)methylene]-*N*-(1-pyridine-2-ylethyl)-amine **1a** (200 mg, 0.82 mmol), NiBr₂(dme) (252 mg, 0.82 mmol), DMF 10 mL. Compound **1a** was obtained as a dark green solid, yield 261 mg (0.56 mmol, 69%). ESI⁺-MS: *m/z* 463 [M⁺]; C₁₄H₁₃N₂ClBr₂Ni: Calcd C 36.30, H 2.82, N 6.05; Found C 36.57, H 3.01, N 6.14.

2.2.3. Dimethyloxalic acid-bis(2-methylphenyl)-imidoatenickel(II) dibromide (**1b**)

A solution of dimethyl-*N,N'*-bis(2-methylphenyl)ethane diimidoate (**1b**) (1.10 g, 3.7 mmol) in 15 ml of DMF was added dropwise to a solution of nickel(II) bromide dimethoxyethane (1.15 g, 3.7 mmol) in 20 ml of DMF in a Schlenk flask under argon while stirring. The mixture was stirred for 5 h at room temperature. Then the solvent was removed under vacuum and a pale blue powder was obtained. The nickel complex was obtained in 95% yield and stored under argon. ESI⁺-MS: *m/z* 515 [M⁺]. C₁₈H₂₀N₂O₂Br₂Ni: Calcd C 41.99, H 3.92, N 5.44; Found C 42.18, H 4.21, N 5.73.

2.2.4. 2-[(Diisopropylphosphino)methyl]-pyridinenickel(II) dibromide (**2a**)

2-[(Diisopropylphosphino)methyl]pyridine **IIa** [37] (272 mg, 1.3 mmol) in 10 mL of DMF, NiBr₂(dme) (400 mg, 1.3 mmol) in 40 mL of DMF. Compound **2a** was obtained as a purple red powder, yield 505 mg (1.18 mmol, 91%). EI⁺-MS: *m/z* (%) 427 [M⁺, 10], 348 [M⁺ – Br, 100]. C₁₂H₂₀NPBr₂Ni: Calcd C 33.69, H 4.71, N 3.27; Found C 33.97, H 4.95, N 3.03.

2.2.5. 2-(Diisopropyl)phosphinobenzyl-*N,N*-dimethylaminenickel(II) dibromide (**2b**)

2-(Diisopropyl)phosphinobenzyl-*N,N*-dimethylamine **IIb** [38] (326 mg, 1.3 mmol) in 10 mL of DMF, NiBr₂(dme) (400 mg, 1.3 mmol) in 40 mL of DMF. Compound **2a** was obtained as a blue powder, yield 568 mg (1.21 mmol, 93%). EI⁺-MS: *m/z* (%) 391 [M⁺ – Br, 100]. C₁₅H₂₆NPBr₂Ni: Calcd C 38.35, H 5.58, N 2.98; Found C 38.47, H 5.77, N 3.15.

2.3. Oligomerization procedure

- Low-pressure tests.* The precatalyst was dissolved in 30 mL of solvent in a Schlenk flask under argon. A complete solution was obtained by leaving the flask in an ultrasonic bath for several minutes. A 150-mL glass reactor was evacuated and then filled with argon. The precatalyst solution was added under argon into the reactor vessel. Under stirring the cocatalyst MAO (0.6 mL, approx. 100 equiv. of a 10 mol.% MAO solution in toluene) and *n*-tridecane standard solution were added under argon. For several minutes ethylene was introduced while streaming through the reactor to displace the argon. Then the reactor was closed and pressurized to 3 bar with ethylene. The reactor pressure maintained constant throughout the oligomerization run by manually controlled addition of ethylene. Runs were terminated by venting off volatiles and extracting the solution with dilute hydrochloric acid and water. Quantitative GC analysis of the organic layer was performed immediately after the extraction.
- High-pressure tests.* Same procedure as described for low-pressure tests. Instead of a glass reactor was used a

150-mL stainless steel reactor with cooling mantle. After the reactor was closed, it was pressurized to 30 bar with ethylene. The temperature of the reaction was controlled by cooling the reactor vessel with water.

3. Results and discussion

Nitrogen- and phosphorus-substituted nickel(II) complexes **1** and **2** were prepared to compare their catalytic abilities as precatalysts for the oligomerization and dimerization of ethylene together with the cocatalyst methylaluminoxane (MAO) [39].

The imine nickel(II) complex **1a** represents a typical class of active neutral nickel(II) precursors for ethylene oligomerization. Both the selectivity for formed oligomers and the α -selectivity are low, a broad spectrum of oligomers C₄–C₂₆ and small amounts of polymer being obtained (Table 1, entry 1). The distribution of oligomers obtained in the catalyzed ethylene oligomerization with **1a** follows Schulz–Flory rules for oligomers >C₄, which can be characterized by the constant α representing the probability of chain propagation (α = rate of propagation/[rate of propagation + (rate of chain transfer)] = (moles of C_{n+2})/(moles of C_n)) [40–43]. Because olefins with long chain lengths are obtained in the catalytic oligomerization of ethylene with **1a**, α has a high value of 0.8.

α -Diimine nickel(II) complexes were already examined as suitable catalysts for ethylene oligomerization [17]. Like the imine precursor **1a**, α -diimine nickel(II) complexes can produce oligomers in the range C₄–C₂₆ [17]. Instead of a glyoxal- or α -diketo-diimine, the α -diimine nickel(II) complex **1b** contains the diimino ester of oxalic acid: the electron-withdrawing methoxy groups influence the product distribution of formed oligomers in the ethylene oligomerization catalysis with **1b** and MAO towards the production of olefins with low chain lengths. Butenes are formed at 3 bar ethylene pressure as main product in 89% yield (Table 1, entry 2). Higher ethylene pressure with a shorter reaction time has nearly no effect on the activity of the catalyst and mostly produces butenes and hexenes (Table 1, entry 3). For both imine complexes **1a** and **1b** the α -selectivities of the formed

Table 2
Yield (%) of oligomers in the experiments 1–6

Fraction (%)	1	2	3	4	5	6
C ₄	9.3	89.0	78	73.0	73.5	80.8
C ₆	16.7	6.5	17	23.0	18.7	13.7
C ₈	16.2	3.8	4.6	3.5	4.0	3.6
C ₁₀	11.5	0.2	0.4	0.5	1.3	1.2
C ₁₂	9.5	0.15	–	0.1	0.7	0.4
C ₁₄	8.4	0.13	–	–	0.5	0.1
C ₁₆	6.4	0.1	–	–	0.4	0.05
C ₁₈	5.2	0.07	–	–	0.3	0.03
C ₂₀	4.8	–	–	–	–	–
C ₂₂	4.5	–	–	–	–	–
C ₂₄	4.1	–	–	–	–	–
C ₂₆	3.3	–	–	–	–	–

oligomers are low to moderate (Table 1, entries 1–3), derived from a favored chain isomerization in the α -hydride elimination reinsertion step to give linear isomeric olefins [17,18,29].

The coordinating ligand **IIa** of the nickel complex **2a** was synthesized from 2-picoline and chloro-diisopropylphosphane with *n*-butyllithium according to Ref. [37]. The 2-(Diisopropylphosphino-methyl)-pyridine (**IIa**) was then reacted with (dme)NiBr₂ to give the nickel(II) dibromide complex **2a**. A similar 6-aryl-substituted 2-(diarylphosphinomethyl)-pyridine-nickel(II) dibromide complex was recently investigated as precatalyst for the di- and trimerization of ethylene [32]. **2a** mostly produces butenes and hexenes and shows a similar oligomer distribution (Table 2, No. 4) compared with the 6-aryl-substituted 2-(diarylphosphinomethyl)-pyridine-nickel(II) dibromide complex in [32] (70.5% butenes, 29.5% hexenes). **2a** has a low overall α -selectivity of 46% (Table 1, entry 4), similar to the more bulky substituted nickel(II) complex in [32]. **2a** bears less bulky substituents and has a lower catalytic activity (Table 1). The N,P nickel(II) complex **2b** is less reactive than **2a**, but shows a much better selectivity for the production of α -olefins. The α -value is low, so the dimerization of ethylene is favored in the catalytic reaction with **2b** and MAO. A longer reaction time provides a better yield, even at lower ethylene pressure, indicating a substantial lifetime of the catalyst (Table 1, entries 5 and 6).

Table 1
Results of oligomerization of ethylene with catalysts **1** and **2**

No.	Catalysts ^a	Loading (μ mol)	Time (h)	<i>p</i> (bar)	<i>T</i> (°C)	Yield (g) ^b	TON	TOF (h ⁻¹)	Solvent	α	α -Olefins (%) ^b
1	1a	10	1	30	22–30	2.7 ^c	9526	9526	Toluene	0.80	33
2	1b	10	4.5	3	22	<0.1	281	62	Toluene	0.26	58
3	1b	10	1	30	22–31	<0.1	43	43	Toluene	0.24	40
4	2a	10	1.7	30	22–31	4.4	15792	9024	Toluene	0.24	46
5	2b	10	2	30	22–30	0.2	758	379	CH ₂ Cl ₂	0.35	77
6	2b	10	5	3	22	0.4	1446	290	Toluene	0.36	50

^a All precatalysts were first dissolved in 30 mL of solvent in an ultrasonic bath and then activated with approx. 100 equiv. MAO (0.6 mL of a 10 mol% MAO solution in toluene).

^b The yield and the 1-olefin content C₄–C₂₆ were determined by GC and a flame ionization detector using calibration curves with standard solutions.

^c Small amounts of polymer formed in the reaction.

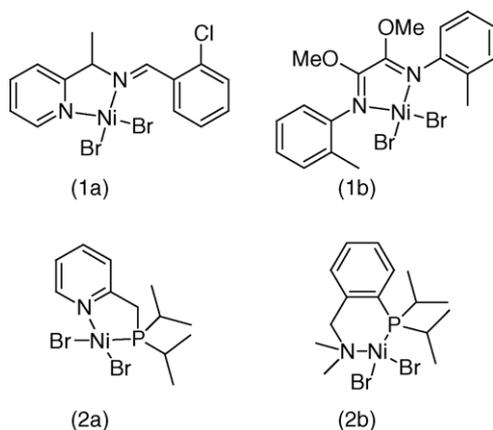


Fig. 1. Structure of the precatalysts **1** and **2**.

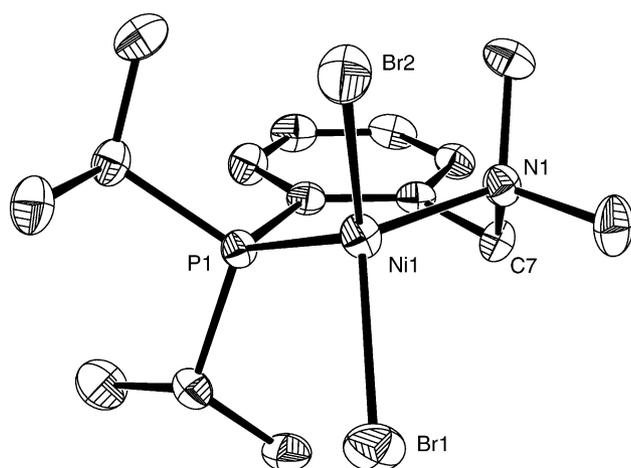


Fig. 2. Molecular structure of **2b**. Selected bond distances (Å) and angles (°): Ni1–N1 2.042(2), Ni1–P1 2.308(1), Ni1–Br1 2.363(1), Ni1–Br2 2.381(1), N1–C7 1.493(3), N1–Ni1–P1 96.61(6), C7–N1–Ni1 111.91(2), Br1–Ni1–N1 112.47(6), Br1–Ni1–P1 101.73(3), Br2–Ni1–N1 103.74(6), Br2–Ni1–P1 123.98(2).

Similar built palladium iminophosphine complexes showed a comparable reactivity in the ethylene oligomerization, but they mainly form hexenes, octenes, and higher oligomers [34]. The X-ray structure analysis of **2b** shows a distorted tetrahedral nickel(II) ion connected to its neighbouring nitrogen- and phosphorus atoms in the ligand (Figs. 1 and 2). Observed bond lengths are in the range of published data [44].

4. Conclusions

In summary, the described nickel(II) imine and diimine complexes **1** and the N,P-substituted nickel(II) complexes **2** reveal differences in their behavior as precatalysts for the oligomerization of ethylene. **2a** has a good activity with ethylene in the presence of MAO as cocatalyst for the dimerization of ethylene, while **2b** mainly produces butenes with an α -selectivity of 77%. The complexes **1b–2b** show small

Table 3
Crystallographic data

	2b
Empirical formula	C ₁₅ H ₂₆ Br ₂ NPNi
CCDC No.	252695
fw (g mol ⁻¹)	469.87
Temperature (K)	293(2)
Wavelength λ (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 10.116(3) Å, α = 90° <i>b</i> = 16.605(4) Å, β = 94.06(3)° <i>c</i> = 11.064(3) Å, γ = 90°
<i>V</i> (Å ³)	1853.8(9)
<i>Z</i>	4
$\rho_{\text{calcd.}}$ (g cm ⁻³)	1.684
μ (mm ⁻¹)	5.435
<i>F</i> (000)	944
Crystal size (mm ³)	0.6 × 0.2 × 0.1
Theta range for data collection (°)	2.22–28.30
Index ranges	–13 ≤ <i>h</i> ≤ 13, –21 ≤ <i>k</i> ≤ 21, –14 ≤ <i>l</i> ≤ 14
Reflections collected	19385
Independent reflections	4516 [R(int) = 0.0536]
Data/restraints/parameters	4516/0/192
Goodness-of-fit on <i>F</i> ²	1.001
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> 1 = 0.0293, <i>wR</i> 2 = 0.0657
<i>R</i> indices (all data) ^a	<i>R</i> 1 = 0.0438, <i>wR</i> 2 = 0.0698

^a $R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|$, $wR2 = \left[\frac{\sum w(|F_o^2 - F_c^2|)^2}{\sum w(F_o^2)} \right]^{1/2}$, $w = 1/[(\sigma F_o)^2 + (aP)^2]$. The value of *aP* was obtained from structure refinement.

Schulz–Flory α -values, which prove a low chain propagation with preference for the production of 1-butenes and isomers.

4.1. Crystal structure determination

The intensity data for the compounds were collected by a Siemens Smart 1000 CCD diffractometer (compound **2b**) using graphite-monochromated Mo-K α radiation. The X-ray analyses were performed with an irradiation time of 10 s per frame collecting a full sphere of data. Data were corrected for Lorentz and polarization effects, an experimental absorption correction was performed with SADABS [45].

The structures were resolved by direct methods and refined by full-matrix least-squares techniques against *F*_o² (SHELXL-97 [46]). The hydrogen atoms were localized by difference Fourier synthesis and refined isotropically. The data are deposited in the Cambridge Crystallographic Data Centre [47] (see Table 3).

All non-hydrogen atoms were refined anisotropically [46]. XPMA was used for visual analysis of the structure reported [48], and Ortep [49] was used for structure representations.

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- [47] CCDC 252695 (**2b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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