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Four-coordinated bipyridine complexes of nickel for ethene polymerization — the role of ligand structure

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Abstract

Four-coordinated bipyridine complexes of nickel, (2,2′-bipyridine)$NiBr_2$ (**1**), (6,6′-dimethoxycarbonyl-2,2′-bipyridine)$NiBr_2$ (**2**), (2,2′-biquinoline)$NiBr_2$ (**3**) and (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)$NiBr_2$ (**4**), were synthesized. Single crystal X-ray structures were determined for compounds **2** and **4**. Both structures were monoclinic with space group $P21/c$. For **2** $a = 8.4289(7)$, $b = 13.5013(14)$, $c = 14.7341(15)$ Å, $Z = 4$. For complex **4** $a = 12.8143(4)$, $b = 22.5687(8)$, $c = 7.8172(2)$ Å, $Z = 4$, respectively. Catalytic activities of complexes were studied in ethene polymerization using MAO as a cocatalyst. Complexes **2** and **3** showed a modest activity producing high-density polyethene. Polymerization temperature had a clear effect on the activities of the complexes. Reactions carried at 50°C yielded more polyethene than reactions at 30 or 70°. The effect of ligand structure on catalytic activity was also observed, the bulky substituents increased activity. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Nickel; Bipyridine; Polymerization; Ethene

1. Introduction

Polymerization of α-olefins has been traditionally done in a heterogeneous catalyst system. Industry mainly produces commercial polyethene on supported transition metal compounds, e.g. titanium tetrachloride (Ziegler–Natta catalysis) and metal oxides (Indiana, i.e. Standard Oil and Phillips processes). Advances of more selective homogeneous catalysis have stimulated studies on ethene polymerization with single site organometallic complexes. After the discovery of catalytic properties of metallocenes [1] the applications of homogeneous catalysis for ethene polymerization started to appear.

Late transition metal complexes for polymerization has been studied following the promising results with P$\frown$O-chelated ylide complex of nickel [2]. The breakthrough in ethene polymerization with late transition metals was reported by Brookhart et al. in the middle of the past decade, when four-coordinated complexes of Ni and Pd containing bidentate nitrogen donor ligand were reported to polymerize ethene in the presence of excess of cocatalyst [3]. Theoretical and experimental studies on catalytic properties of nickel and palladium complexes have been widely reported [4]. As a summary of those studies [4], following trends can clearly be notified.

The catalytic properties of α-diimine complexes of Ni and Pd (Brookhart-type catalysts) in ethene polymerization process depend on the electronic and steric effects of the metal site. The convenient steric hindrance around the metal center yields more active catalysts, while the branching rate of polyethene increases with bulky ligands. Nickel has been found to be more active metal than palladium, whereas bipyridine complexes of platinum have shown no catalytic activity in ethene polymerization. Palladium complexes have been reported to produce more branched polyethene than nickel complexes. Branching rate of the product depends also on reaction conditions, such as temperature and monomer pressure. Brookhart-type catalysts were the first polymerization catalyst systems, where simple variation of polymerization conditions controlled productivity and polymer structure.

The area of Brookhart-type catalysts is expanded here to the structural and activity studies of Ni(II) complexes based on bipyridine ligand (Scheme 1). Crys-

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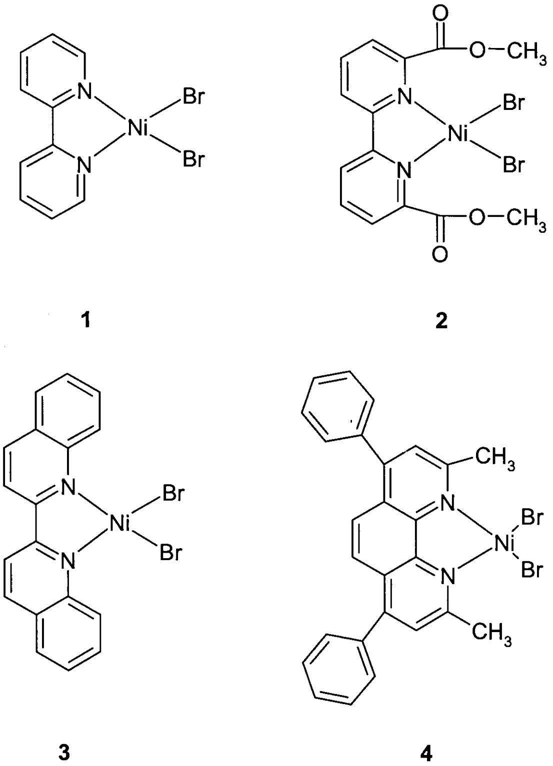
tal structure determinations for two synthesized complexes provide the further information of Ni(II) bipyridine complexes [5]. Catalytic properties of all synthesized complexes were tested for ethene homopolymerization. As in traditional Brookhart-type diimine systems, the role of ligand structure in bipyridine complexes plays an important role in the catalytic behavior. In addition to ligand structure, polymerization temperature also affects the activity.

2. Experimental

2.1. Materials

6,6′-Dimethoxycarbonyl-2,2′-bipyridine was synthesized according to a literature method [6]. The reagents for the three-step synthesis of this disubstituted bipyridine were 2,2′-bipyridyl-*N*,*N*′-dioxide (Aldrich, 98%), benzoyl chloride (Merck, 99%), KCN, acetonitrile (Sigma, + 99.9%), 8% NaOH (aq.), concentrated HCl, Na_2CO_3, 1,2-dimethoxyethane (Aldrich, 99 + %) and ethereal diazomethane azeotrope [7]. All other nitrogen donor ligands were commercially available and they were used without any purification. These ligands were 2,2′-bipyridyl (Aldrich, + 99%), 2,2′-biquinoline (Fluka, + 99%) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Aldrich 98%).



Scheme 1. Synthesized bipyridine complexes of Ni(II).

Metal precursors for complexes were commercially available: Nickel(II)dibromide trihydrate (Merck) and nickel dibromide ethyleneglycol dimethyl ether complex [(DME)$NiBr_2$] (Aldrich, 97%). Solvents and other chemicals were toluene (Lab-Scan, 99.5%), ethanol (Primalco, Aa), dichloromethane (FF-Chemicals, p.a.), tetrahydrofurane (THF) (Riedel de Haën, p.a.), methanol (Baker, p.a.)

2.2. Syntheses

*2.2.1. (2,2′-Bipyridine)NiBr$_2$ (**1**)*

Synthesis of unsubstituted bipyridine complex of Ni (2,2′-bipyridine)$NiBr_2$ (**1**) was based on reported method [8]. Yield of synthesis was 45% of theoretical amount. Elemental analysis results of complex **1**. Anal. Found: C, 32.14; H, 2.14; N, 7.47. Calc. for $C_{10}H_8N_2NiBr_2$: C, 32.06; H, 2.15; N, 7.48%.

*2.2.2. (6,6′-Dimethoxycarbonyl-2,2′-bipyridine)NiBr$_2$ (**2**)*

6,6′-Dimethoxycarbonyl-2,2′-bipyridine (200 mg) and 226 mg of (DME)$NiBr_2$ were suspended in dry, nitrogen–flushed dichloromethane (20 ml). After 24 h stirring at room temperature an orange solution was separated from light solid. The product crystallized as red needles when the solution was dried under a slow nitrogen flow. Crystals were washed with distilled tetrahydrofuran. Yield 17 mg (4.7%). Elemental analysis results for complex **2**. Anal. Found: C, 33.78; H, 2.32; N, 5.52. Calc. for $C_{14}H_{12}Br_2N_2NiO_4$: C, 34.26; H, 2.46; N, 5.71%.

*2.2.3. (2,2′-Biquinoline)NiBr$_2$ (**3**)*

2,2′-Biquinoline (0.400 g) was dissolved in 20 ml dichloromethane and $NiBr_2{\cdot}3H_2O$. (0.426 g) in methanol (20 ml). Solutions were combined and the mixture was then stirred for 1 h. Red solid formed and it was collected by filtration using needle-technique. Solid was dried under vacuum. Reprecipitation from toluene gave a pink solid, which was washed with toluene and dried. Yield 0.042 g (5.7%). Elemental analysis results for complex **3**. Anal. Found: C, 45.31; H 2.57; N, 5.89. Calc for $C_{18}H_{12}Br_2N_2Ni$: C, 45.53; H, 2.54; N, 5.90%.

*2.2.4. (2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline)-NiBr$_2$ (**4**)*

2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (0.500 g) and 0.378 g of $NiBr_2{\cdot}3H_2O$ were suspended in methanol (50 ml). After 30 h stirring at room temperature a pink precipitate was formed and filtered from green solution. The solid product was washed by refluxing in toluene, an orange solution formed and a pink solid was recovered by filtration. The pink solid was dried under vacuum. Yield 0.099 g (12.3%). Product

Table 1
Crystallographic data for (6,6′-dimethoxycarbonyl-2,2′-bipyridine)NiBr$_2$ (**2**), and (2,9′-dimethyl-4,7′-diphenyl-1,10-phenanthroline)NiBr$_2$ (**4**)

	2	**4**
Empirical formula	$C_{14}H_{12}Br_2N_2NiO_4$	$C_{26}H_{20}Br_2N_2Ni$
Formula weight	490.79	578.97
Crystal system	Monoclinic	Monoclinic
Crystal size (mm)	$0.4 \times 0.2 \times 0.1$	$0.3 \times 0.1 \times 0.1$
Space group	$P2_1/c$	$P2_1/c$
Temperature (K)	120	120
λ (Å)	0.71073	0.71073
a (Å)	8.4283(7)	12.8143(4)
b (Å)	13.5013(14)	22.5687(8)
c (Å)	14.7341(15)	7.8172(2)
α (°)	90	90
β (°)	103.467(7)	99.134(2)
γ (°)	90	90
V (Å^3)	1630.5(3)	2232.08(12)
Z	4	4
D_{calc} (g cm^{-3})	1.999	1.723
μ (mm^{-1})	6.110	4.466
θ range (°)	3.91–27.35	3.15–25.04
Limiting indices	$-9 \leq h \leq 9$ $-17 \leq k \leq 17$ $-18 \leq l \leq 18$	$-15 \leq h \leq 15$ $-26 \leq k \leq 26$ $-9 \leq l \leq 9$
Max/min transmission	0.5801 and 0.1937	0.6637 and 0.3476
Parameters	210	282
Unique reflections	3312	3880
Observed reflections [a]	2463	3024
R_{int}	0.0454	0.0367
R_1	0.0392	0.0485
wR_2	0.0872	0.1195
Largest difference peak and hole (e Å^{-3})	0.630 and −0.606	1.130 and −0.510

[a] $I > 2\sigma(I)$.

was crystallized for structural analysis from dichloromethane yielding orange–red crystals. Elemental analysis results for complex **4**. Anal. Found: C, 52.55; H, 3.47; N, 4.77. Calc. for $C_{26}H_{20}Br_2N_2Ni$: C, 53.94; H, 3.48; N, 4.84%.

2.3. X-ray data collection and structure solution for (6,6′-dimethoxycarbonyl-2,2′-bipyridine)NiBr$_2$ (2) and (2,9′-dimethyl-4,7′-diphenyl-1,10-phenatroline)NiBr$_2$ (4)

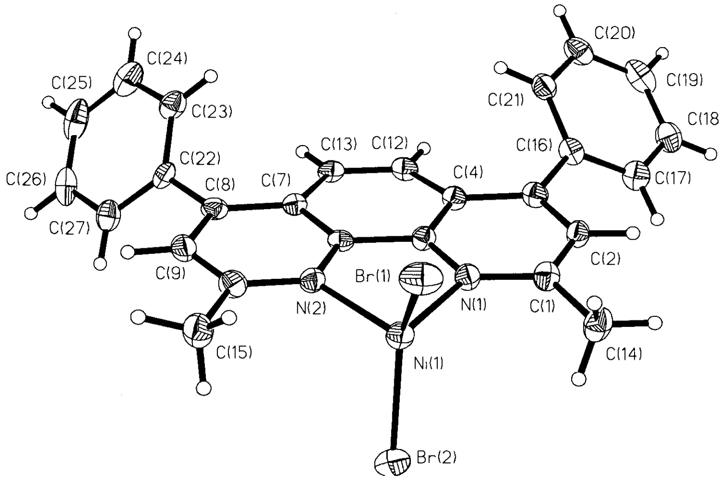
All data were collected on a Nonius KappaCCD diffractometer with a Collect data collection program [9] using ϕ-scan mode and Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Cell refinement and data reduction were done by Denzo and Scalepack programs [10]. A multi-scan absorption correction, based on equivalent reflections (XPREP in SHELXTL version 5.1) [11], was applied to all data. The structures were solved by direct methods and successive difference Fourier synthesis using the SHELXS-97 or SIR-97 programs [12,13]. The structure refinement was carried out with the SHELXL-97 program [14]. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed at calculated positions (aromatic hydrogens at 120 K: C–H = 0.95 Å and $U_{iso} = 1.2$ U_{iso} of the parent carbon, hydrogens in CH_3 at 120 K: C–H = 0.98 Å and 1.2 U_{iso} of the parent carbon). Crystallographic data are summarized in Table 1 and selected bond lengths and angles in Table 2. Thermal motion ellipsoid plots of structurally characterized complexes are shown in Fig. 1.

2.4. Ethene polymerization experiments

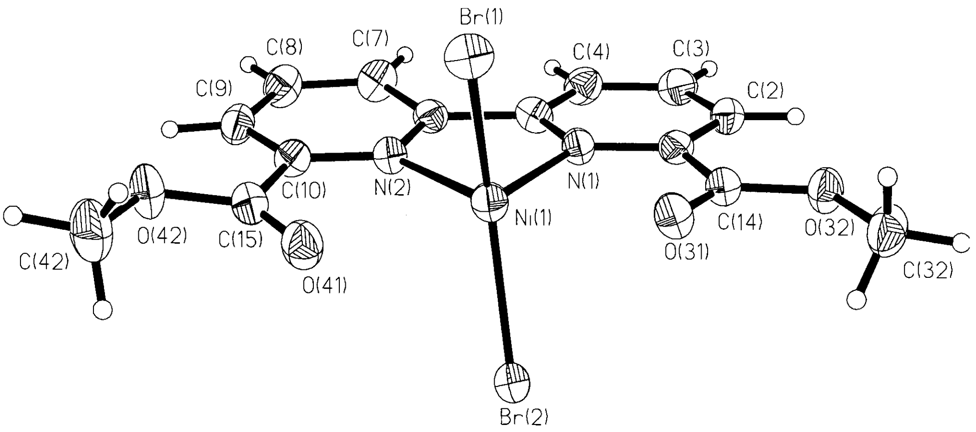
Catalytic properties of synthesized bipyridine complexes of nickel were tested in ethene polymerization. Complexes were activated with methylalumoxane (10%-MAO in toluene). Polymerization experiments were carried out in a stainless steel autoclave (Büchi Miniclave Drive 200 ml) using temperature and pressure controlled system. Polymerization temperature was varied from 30 to 70°C, and the initial ethene pressure was typically 5 bar. The Al:Ni ratio of 1000:1 was used. Polymerization time was 3 h. Because of low yields of polymer, the relatively long reaction time was needed to get enough polymer for thermal and spectroscopic analyses. Melting points of polymeric products were determined by DSC. The sample was heated (10°C min^{-1}) to 150°C, then cooled (−10°C min^{-1}) back to 25°C and finally T_m were measured by heating (10°C min^{-1}) to 150°C.

Table 2
Selected bond lengths (Å) and angles (°) of complexes **2** and **4**

Complex **2**		Complex **4**	
Bond lengths			
Ni–N1	2.015(4)	Ni–N1	1.994(5)
Ni–N2	2.051(4)	Ni–N2	1.987(5)
N1–C5	1.340(6)	N1–C5	1.350(8)
N2–C6	1.350(6)	N2–C6	1.362(8)
Ni–Br1	2.391(1)	Ni–Br1	2.332(1)
Ni–Br2	2.404(1)	Ni–Br2	2.338(1)
Bond angles			
N(1)–Ni(1)–N(2)	79.4(2)	N(2)–Ni(1)–N(1)	82.8(2)
N(1)–Ni(1)–Br(1)	104.2(1)	N(2)–Ni(1)–Br(1)	110.7(2)
N(2)–Ni(1)–Br(1)	98.4(1)	N(1)–Ni(1)–Br(1)	107.9(2)
N(1)–Ni(1)–Br(2)	101.2(1)	N(2)–Ni(1)–Br(2)	103.3(2)
N(2)–Ni(1)–Br(2)	106.6(1)	N(1)–Ni(1)–Br(2)	106.2(2)
Br(1)–Ni(1)–Br(2)	147.1(3)	Br(1)–Ni(1)–Br(2)	134.0(4)



(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)NiBr$_2$ (**4**)



(6,6′-dimethoxycarbonyl-2,2′-bipyridine)NiBr$_2$ (**2**)

Fig. 1. X-ray crystal structures of M(II) bipyridine complexes (**2**) and (**4**).

3. Results and discussion

Syntheses of air-sensitive four-coordinated bipyridine complexes of Group 10 metals were done either via ligand substitution (complex **2**) or ligand addition (complexes **1**, **3** and **4**). The high purities of the products were confirmed by elemental analysis.

Crystallization of two synthesized complexes **2** and **4** succeeded and their structures were determined with X-ray crystallography. The structures show that nickel has a tetrahedral coordination geometry with bromines being located above and below the bipyridine plane. The coordination sphere of nickel atom in **2** and **4** is naturally dependent on the ligand system. Bond angles N1–Ni–N2 are slightly different, 79.4° for **2** and 82.8 for **4**. Typical Ni–N bond lengths [5a,b,15] are around 2 Å, which is also true for complexes **2** and **4**. The distance between Br and Ni for complex **2** is somewhat longer than typical values (2.4 instead of 2.3 Å). In addition to bond lengths, the more conspicuous divergence from typical values for complex **2** is an unusual wide Br1–Ni–Br2 angle (147.1°). This divergence is due to substituents of the bipyridine ligand. The oxygen atoms of the carbonyl groups in complex **2** lie 2.5 Å from Ni. The effect of these two oxygens on Br1–Ni–Br2 bond angle is noteworthy; the angle is 13° larger compared to the value of the corresponding angle in **4**. Crystal structure data reported in the literature [5a] for complex **3** show comparable bond lengths and angles with values for **4**.

In addition to synthetic and structural studies, catalytic properties of prepared bipyridine complexes were studied in ethene polymerization using MAO as a cocatalyst. The catalyst–cocatalyst system in toluene yielded polyethene after ethene was introduced into the reactor. Melting temperatures (T_m (°C)) of the pro-

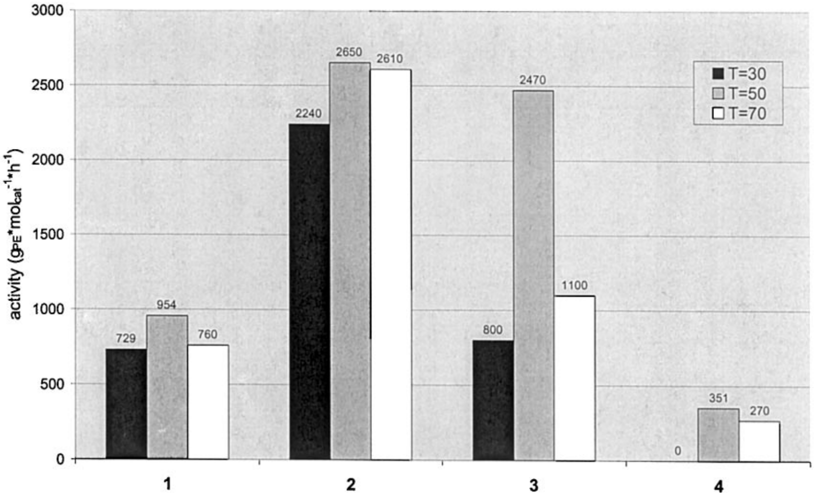


Fig. 2. Catalytic activities of Ni(II) bipyridine complexes **1**–**4** (3 h, 5 bar ethene, MAO content Al:Ni 1000:1).

duced polyethenes were 127 (catalyst **1**), 134(**2**), 137(**3**) and 132(**4**)°C indicating characters of the high-density character of polyethenes produced. Routine infrared spectral analyses of products were also done and the absence of bands of terminal hydrocarbon groups gave also the evidence of high-density properties of the products [16]. The major evidence was absence of the bands at 1377 (CH_3 or C_4H_9 deformation) and 1379 cm^{-1} (C_2H_4 deformation). Other characteristic bands of low density PE (terminal (vinyl) unsaturation) should have been present at 908 and 890 cm^{-1}. Also the absence of bands at 770 cm^{-1} (CH_3 rocking) indicates that products were not LDPE.

Productivity (g_{PE} mol_{cat}^{-1} h^{-1}) of Ni-complexes varied as a function of reaction temperature and ligand structure (Fig. 2). It was observed that reaction temperature of 70°C already decreased the catalytic activity compared to that at 50°C, thus activities reached their maxima at 50°C being 2650 for **2**, 2470 for **3**, 954 for **1** and 351 for **4**. The most active catalyst system at all temperatures was Ni(II) complex with 6,6′-disubstituted bipyridine ligand (complex **2**). Ester substituents in disubstituted bipyridine ligand in **2** yielded three times more active catalysts compared to unsubstituted bipyridine in **1**. Also aromatic rings of 2,2′-biquinoline ligand increased activity (**3**), yielding comparable activity with **2** at 50°C. The role of ligand structure is in agreement with reported results of Brookhart et al. [3]; the successful polymerization requires steric hindrance around metal center. Activity is still presumed to rise if more bulky substituents are closer to metal center and above and below the ligand plane. For the sake of comparison, shorter polymerization experiment with **2** (30°C, 15 min) showed lower activity (40% lower) than a longer experiment in similar conditions. This result indicates that complex **2** does not decay to a significant extent under used polymerization conditions.

4. Conclusions

X-ray diffraction determination for synthesized complexes gave new structural information of the four-coordinated M(II) bipyridine complexes of late transition elements. Structural studies on complex **2** showed that the dimethoxycarbonyl substituents at 6 and 6′ positions of the bipyridine ligand lie in the same plane with the bipyridine frame. The polymerization activity was observed to increase when the bulky dimethoxycarbonyl substituents were used. In addition to steric effects, the electron withdrawing property of ester group stabilizes the cationic form yielding a more active catalyst. The production of HDPE was also found to be dependent on polymerization temperature. Low temperature (50°C) was the most promising, and is close to the reaction temperatures commonly used with Brookhart-type catalysts.

5. Supplementary material

Crystallographic data for complexes **2** and **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 145273 and 145274, respectively. Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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