Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganic Chemistry Communications 9 (2006) 548–550

INORGANIC CHEMISTRY COMMUNICATIONS

www.elsevier.com/locate/inoche

Binuclear neutral nickel complexes bearing bis(bidentate) salicylaldiminato ligands: Synthesis, structure and ethylene polymerization behavior

Wei-Hua Wang, Guo-Xin Jin *

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200 433, China

Received 24 December 2005; accepted 20 February 2006
Available online 3 April 2006

Abstract

Reaction of sodium salts of the bridging [O,N,N,O]-type bisalylaldimine ligands [O,N,N,O = [3-phenyl-2-OH-(CH=N)]$_2$-L (L = $CH_2CH_2CH_2$ **3a**, 1,4-C_6H_4 **3b**)] with *trans*-bis(triphenylphosphane)phenylnickel (II) chloride result in neutral bis(bidentate) binuclear nickel (II) complexes **4a** and **4b**. The structure of **4b** has been confirmed by X-ray crystallography. **4a** shows moderate activity for polymerization of ethylene in the presence of methylaluminoxane (MAO). Catalytic activities, molecular weights and molecular weight distribution of polyethylene have been investigated under the various reaction conditions.

Keywords: Nickel; Catalyst; Binuclear; Molecular structure; Polymerization of ethylene

Late transition metal catalysts for polymerization of olefins have attracted more and more attention over the past decade [1–4]. Due to the less oxophillic properties of late transition metal, these catalysts are more tolerate to polar functional groups in the monomers than those metallocene olefin polymerization catalysts, therefore, the copolymerization of olefins with polar monomers become possible [5–7]. Among them, neutral salicylaldimine based nickel (II) catalysts developed by Grubbs and coworkers are of high importance [8], which can produce polyethylene with high molecular weight. Grubbs reported that introducing bulky substituent into the ortho position of the phenoxyl group can retard the rate of chain termination and increase the catalytic activity [8]. But the influence of the modification at the other side of the imino fragment have been rarely investigated [9]. Here we report new neutral binuclear nickel (II) complexes with [N,O,O,N]-type bridging di(bidentate) ligands and their catalysis properties for ethylene polymerization.

The free ligands **3a**–**b** were prepared by condensation of 1,3-diaminopropane (**2a**) or *p*-diaminobenzene (**2b**) and the substituted salicylaldehyde (**1**) in appropriate yields (Scheme 1). The substituted salicylaldehyde **1**, containing bulky aromatic phenyl group was prepared by formylation of the corresponding phenol with paraformaldehyde with the catalysis of $SnCl_4$ according to reference [10].

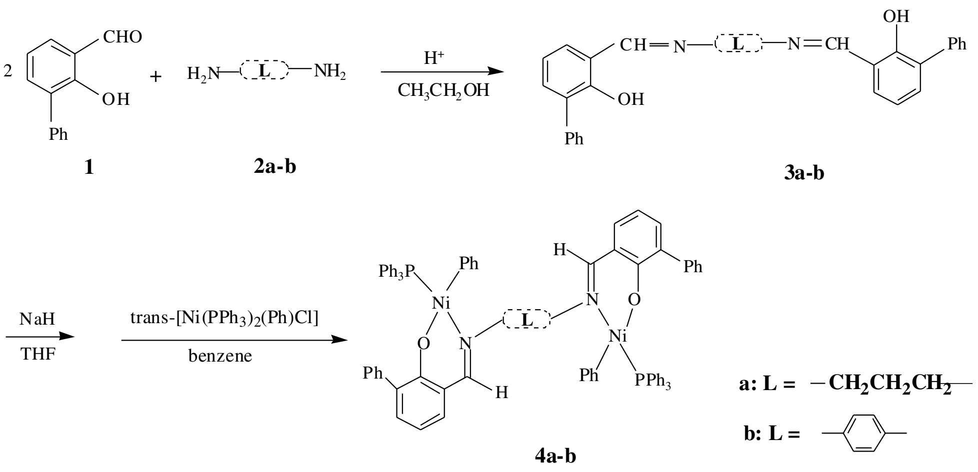
Binuclear complexes **4a**–**b** were prepared in a similar procedure of reference [8], by the reaction of 2 equiv of *trans*-[Ni(PPh$_3$)$_2$(Ph)Cl] with the sodium salts of the free ligands **2a**–**b**, which were obtained via deprotonation by excess sodium hydride in anhydrous tetrahydrofuran at room temperature. After several times of recrystallization in hexane/benzene, pure powders of **4a**–**b** were obtained, which are light brown and dark brown respectively. Complexes **4a** and **4b** are neutral, diamagnetic and air-sensitive in solution, and insoluble in *n*-hexane, soluble in CH_2Cl_2 or THF.

Crystals of **4b** suitable for X-ray structure determination were grown from slow diffusion of hexane into a benzene solution of **4b** [11]. The molecular structure of **4b** is depicted in Fig. 1.

---

* Corresponding author. Tel.: +86 21 65643776; fax: +86 21 65641740.
E-mail address: gxjin@fudan.edu.cn (G.-X. Jin).

1387-7003/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2006.02.015



Scheme 1. Synthesis of complexes **4a**–**4b**.

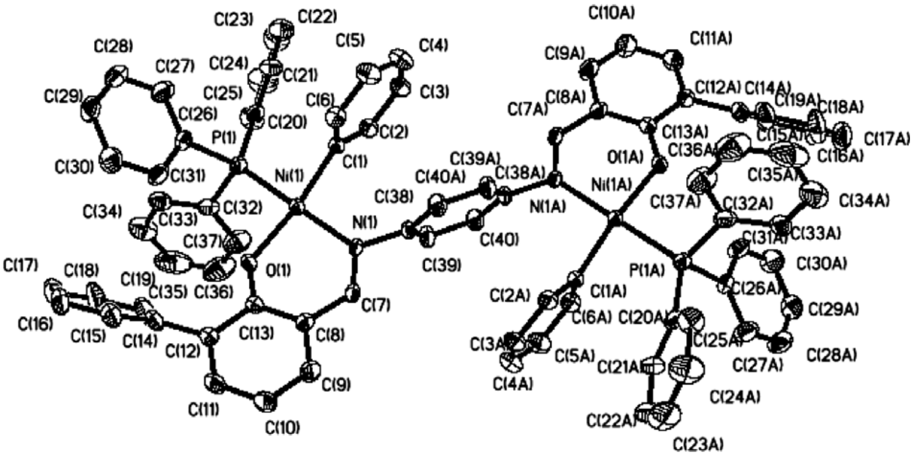


Fig. 1. Molecular structure of complex **4b**. Selected distances (Å) and angles(°C):Ni(1)—C(1) = 1.891(6), Ni(1)—O(1) = 1.910(4), Ni(1)—N(1) = 1.926(4), Ni(1)—P(1) = 2.1735(18); C(1)—Ni(1)—O(1) = 165.0(2), C(1)—Ni(1)—N(1) = 90.6(2), O(1)—Ni(1)—N(1) = 92.74(17), C(1)—Ni(1)—P(1) = 89.63(17), O(1)—Ni(1)—P(1) = 89.87(12), N(1)—Ni(1)—P(1) = 168.99(15).

In the solid state, the molecule adopts a nearly square-planar coordination geometry with both Ni atoms displaced approximately 0.067 Å (Ni1) and 0.078 Å (Ni2) from the planes of their ligands respectively. Meanwhile, the bridging phenyl plane is almost perpendicular to the two coordination planes with Ni centers. The triphenylphosphine occupies the position *trans* to the N atom with a nearly linear N(1)—Ni(1)—P(1) angle (168.99(15)°). The phenyl group attached to Ni lies *trans* to O atom with an C(1)—Ni(1)—O(1) angle of 165.0(2)°. The Ni(1)—O(1), Ni(1)—N(1), Ni(1)—P(1) and Ni(1)—C(1) bond distances are similar to those in known neutral nickel complexes [9,12].

The tests of ethylene polymerization with complexes **4a**–**b** were carried out by dissolving the corresponding catalysts in toluene, followed by the injection of a toluene solution of different amount of MAO. The results of polymerizations are listed in Table 1.

Neither complexes **4a** nor **4b** could be used as single component catalyst to polymerize ethylene, while Grubbs' catalysts with bulky phenyl group or larger groups at the ortho position of the phenoxy group can catalyze ethylene polymerization without cocatalyst [8]. It is clear that binuclear **4a**–**b** are different from mononuclear Grubbs' catalysts. When activated with MAO, complex **4b** still show no catalytic activity to polymerization of ethylene, which is agree to the case of neutral nickel complexes reported by Li and coworkers [12] and is similar to the case of the neutral palladium complexes reported by Novak and coworkers [13].

The ration of Al/Ni is essential for complex **4a** to polymerize ethylene. Under 1 bar ethylene pressure, only trace product was obtained at 1000:1 ratio, while activity of 3.76×10^5 gPE/mol Ni · h was obtained when the Al/Ni was increased to 2000:1. At high pressure of 10 bar, less MAO was needed to activate the catalyst precursor **4a**. At the Al/Ni ratio of 400:1, complex **4a** showed an activity of 2.67×10^4 gPE/mol Ni · h. When the Al/Ni ratio was increased to 2000:1, the according activity was increased

Table 1
Results of polymerization of ethylene[a]

Entry	Complex (amt, μmol)	Al/Ni	T (°C)	P (bar)	Yield (g)	Activity (gPE/mol Ni · h)	M_w	M_w/M_n
1	**4a** (13.625)	0	40	10	0	0	–	–
2	**4a** (3.406)	1000:1	25	1	Trace	–	–	–
3	**4a** (3.406)	2000:1	25	1	1.282	3.76×10^5	440000	2.2
4	**4a** (3.406)	400:1	40	10	0.091	2.67×10^4	n.d.[b]	n.d.[b]
5	**4a** (3.406)	2000:1	40	10	2.262	6.71×10^5	n.d.[b]	n.d.[b]
6	**4b** (13.625)	0	40	10	0	0	–	–

[a] Conditions: Total volume of toluene, 50 ml; Cocatalyst, MAO; 800 rpm; Time of polymerization, 30 min.

[b] Not determined due to poor solubility in 1,2,4-trichlorobenzene.

to 6.71×10^5 gPE/mol Ni · h, which is higher than that of 1 bar ethylene pressure (entry 3).

GPC analysis of polyethylene obtained employing complexes **4a** at 1 bar ethylene pressure revealed molecular weight of 4.4×10^5g/mol (M_w), which is higher than that of polyethylenes obtained by Grubbs' catalysts [8] and a moderate molecular weight distribution of 2.2, which is similar to those of Brookhart's mononuclear nickel catalyst with anilinotropone ligand [6] amd Li's binuclear neutral nickel catalyst [12]. However, polyethylenes obtained under 10 bar ethylene pressure are difficult to dissolve in 1,2,4-trichlorobenzene, implying that the molecular weights may be higher. High-temperature ^{13}C NMR spectra showed that the polymers which was produced by the catalyst **4a** (entry 3) are moderately branched. Methyl branches predominate with ca. 15 methyl branches per 1000 carbon atoms. Additional weak signals suggested that higher branches, such as butyl, are also present.

New type of neutral di(bidentate) binuclear nickel (II) complexes **4a** and **4b** were synthesized, and the structure of **4b** has been determined by X-ray crystallography. When activated with methylaluminoxane (MAO), **4a** shows moderate activity for polymerization of ethylene (3.71×10^5 gPE/mol Ni · h). The molecular weight of the obtained polyethylene of up to 440 000 g/mol was observed. Catalytic activities, molecular weights and molecular weight distribution of polyethylene have been investigated under the various reaction conditions.

Acknowledgement

Financial support by the National Science Foundation of China for Distinguished Young Scholars (20421303, 20531020) and by the National Basic Research Program of China (2005CB623800) is gratefully acknowledged.

Appendix A. Supplementary data

Details on experimental section are deposited. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.02.015.

References

[1] S. Mecking, Angew. Chem. Int. Ed. Engl. 40 (2001) 534.

[2] L.S. Boffa, B.M. Novak, Chem. Rev. 100 (2000) 1479.

[3] J. Zhang, X. Wang, G-X. Jin, Coord. Chem. Rev. 250 (2006) 95.

[4] J.W. Strauch, G. Erker, G. Kehr, R. Frohlich, Angew. Chem. Int. Ed. Engl., 41 (2002) 2543.

[5] V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283.

[6] C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11664.

[7] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.

[8] T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Bansleben, Science 287 (2000) 460.

[9] (a) W.H. Wang, G.X. Jin, Inorg. Chem. Commun. 8 (2005) 109;
(b) D. Zhang, G.X. Jin, N.H. Hu, Chem. Commun. (2002) 574;
(c) D. Zhang, G.X. Jin, Eur. J. Inorg. Chem. 8 (2003) 1570;
(d) D. Zhang, G.X. Jin, N.H. Hu, Organometallics 22 (2003) 2851;
(e) X. Wang, G.-X. Jin, Chem. Euro. J. 11 (2005) 5758.

[10] G. Casiraghi, G. Casnati, G. Puglia, G. Sartori, G. Terenghi, J. Chem. Soc., Perkin I 9 (1980) 1862.

[11] *Crystal data for* **4b**: $C_{40}H_{31}NNiOP$, $M_r = 631.34$, Monoclinic, Space group, $P2(1)/c$, $a = 16.895(9)$ Å, $b = 13.063(7)$ Å, $c = 16.895(9)$ Å, $V = 3728(3)$ (Å^3), $Z = 4$, $D_c = 1.125$ (mg/m^3), $F(000) = 1316$, reflections measured (1.97°–25.00°), $R(wR) = 0.0769(0.2107)$ for 18,361 reflections with $I > 2\sigma(I)$. The diffraction data were collected on a Siemens SMART CCD diffractometer. The structures are solved using direct methods and refined on F^2 by full-matrix least-squares methods using the **SHELX** 97 program package. Crystallographic data for the structure of **4b** reported in this paper has been deposited in the Cambridge Crystallographic Data Centre Nos. CCDC-275670. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1233/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[12] Y.S. Li, Y.R. Li, X.F. Li, J. Organomet. Chem. 667 (2003) 185.

[13] G.L. Tian, H.W. Boone, B.M. Novak, Macromolecules 34 (2001) 7656.