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Synthesis, crystal structure, and olefin oligomerization activity of neutral arylnickel(II) phosphine catalyst with 2-oxazolinylphenolato N–O chelate ligand $\stackrel{\text{tr}}{\Rightarrow}$

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Abstract

A novel neutral arylnickel(II) phosphine complex 1 bearing 2-oxazolinylphenolato ligand is synthesized by the reaction of *trans*-Ni(Ph)(Cl)(PPh₃)₂ with 2-(4,5-dihydro-oxazol-2-yl)phenol in the presence of NEt₃, and the molecular structure is determined by X-ray single crystal diffraction. Complex 1 exhibits high activity and selectivity in catalyzing olefin oligomerization when various organoaluminum cocatalysts or Ni(COD)₂ are used (TOF values up to 507 kg oligomers/(mol Ni·h)). © 2003 Elsevier B.V. All rights reserved.

Keywords: Nickel complex; Oxazoline ligand; Crystal structure; Olefin oligomerization

Recently, due to some potential application values in both academic and commercial fields, many attentions are focused on the olefin oligomerization and polymerization catalyzed by late transition metal complexes [1– 3]. Compared with early transition metal complexes, late transition metal complexes are generally more tolerant of polar media because of their less oxophilic nature. Therefore, it is possible for them to catalyze olefin polymerization, polar-functionlized α -olefin polymerization as well as copolymerization of ethylene and α olefin. Keim [4] firstly revealed that the late transition metal nickel catalysts [(PONi(R)(L)] containing α -ketoylide ligands could oligomerize ethylene to produce linear α -olefin, and also could polymerize ethylene in the presence of phosphine scavenger [5]. Brookhart and co-workers [6] reported that nickel and palladium complexes bearing α -diimine ligands could convert ethylene to highly branched polymers. Furthermore, the cationic (α -diimine) nickel catalysts had the ability to copolymerizing ethylene and polar-functionlized α olefins [7]. A series of salicylaldiminato nickel catalysts with bulky imino substituents were described by Grubbs [8]. These neutral nickel catalysts exhibited high activity in ethylene polymerization, and excellent tolerance to polar functional groups. Recently, arylnickel phosphine complexes are paid more attention because of their various catalytic polymerization behavior besides olefin polymerization and oligomerization [9–12]. Therefore, it is the tendency in exploring some novel ligands for arylnickel(II) phosphine catalysts.

We report here the synthesis of the nickel-oxazoline olefin oligomerization catalyst 1 (Scheme 1). The reaction of *trans*-Ni(Ph)(Cl)(PPh₃)₂ with 2-(4,5-dihydro-oxazol-2-yl)phenol in the presence of NEt₃ gives out the target complex 1 in moderate yields. Although it also gives out the by-product 2, the separation of these two

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complexes is very easy according to their different solubility in toluene.

The single crystal X-ray diffraction result confirms the structure of 1 [13] (Fig. 1). In solid-state, the coordination geometry around Ni atom is typically square-planar



Fig. 1. the molecular structure of complex **1**. Selected bond lengths (Å) and angles (°): Ni–C(10) 1.884(3), Ni–O(2) 1.891(2), Ni–N(1) 1.907(2), Ni–P 2.1709(9), O(2)–C(9) 1.291(4), N(1)–C(3) 1.282(4), C(10)–Ni–O(2) 175.08(13), N(1)–Ni–P 177.37(8), C(10)–Ni–N(1) 91.53(11), O(2)–Ni–N(1) 91.49(10), C(10)–Ni–P 86.13(9), O(2)–Ni–P 90.76(7).

Table 1				
Ethylene	oligomerization	with	complex 1	l ^a

with the triphenylphosphane ligand in the trans-position to the N atom, which is similar to some known neutral arylnickel(II) phosphine complexes. We note that the bond lengths of Ni–O(2) (1.891(2) A), and Ni–N(1) (1.907(2) A) are shorter than that of known (NO)Ni complexes which are 1.906-1.931 Å and 1.921-1.975 Å [14–16], respectively. These facts suggest that the π backbonding from metal atom to the ligand is stronger than that of other nickel complexes. It should also be noted that there are seven rings in the molecular: five phenyl groups, one oxazoline group, and one six-membered chelate ring containing the metal atom. Therefore, it is possible to form a large plane composed of 15 atoms in complex 1. The large rigid π -coplanar structure may have dramatic effects on the catalytic activity in the formation of low carbon oligomers by decreasing the steric hindrance.

Complex 1 exhibits considerable activity and high selectivity for ethylene oligomerization (Table 1). The highest activity up to 507 kg oligomers/(mol Ni·h) can be achieved by treatment with 1/MAO catalytic system. The activities of 1/DIBAL-H and 1/AlEt₃ are slightly lower than that of 1/MAO in the formation of ethylene oligomers. At the same time, the activities of 1/organoaluminum catalytic system are almost 10 times as high as that of $1/Ni(COD)_2$ catalytic system. In contrast, no oligomers are obtained when cocatalysts or phosphine scavenger are absent from the catalytic system.

Table 1 also shows that the product distribution greatly depends on the kinds of cocatalysts or phosphine scavenger. In 1/MAO, C₆-olefin is the major product, while C₄-olefin (2-methylpropylene) is the major product in 1/AlEt₃. Ni(COD)₂ being a phosphine scavenger has better selectivity in the formation of C₈-olefin. 84.9% (wt%) 1-octene is obtained in the catalytic system.

Table 2 verifies that 1 is an efficient catalyst for selective propylene dimerization to C₆-olefin in the presence of various cocatalysts or phosphine scavenger. The dimerization activities increase in the order of

Entry	Reaction conditions		Activity ^b	Distribution of oligomers (%)			
	Cocatalyst ^c	Ratio ^d		C_4	C_6	C_8	
1	DIBAL-H	500	487	54.0	28.7	17.4	
2	MAO	1300	507	12.6	77.3	10.0	
3	AlEt ₃	500	364	61.8	11.1	27.1	
4	Ni(COD) ₂	2	55.6	_	15.1	84.9	
5	_	_	0	_	_	-	

^a Conditions: 1.63 µmol of complex 1, solvent: toluene, total volume: 30 ml, ethylene pressure: 12 atm, temperature: 25 °C, reaction time: 0.5 h. ^b kg oligomers/(mol Ni·h).

^cDIBAL-H is diisobutylaluminum hydride, MAO is methylaluminoxane, and Ni(COD)₂ is di(1,5-cyclooctadiene)nickel.

^d The ratio of cocat. and cat.

ropyene unicidation with complex r						
Entry	Reaction conditions		Activity ^b	Distribution of C ₆ -olefin (%)		
	Cocatalyst	Ratio ^c		1-Hexene	Others	
1	MAO	1000	132	78.4	21.6	
2	AlEt ₃	500	38.1	26.5	73.5	
3	Ni(COD) ₂	2	24.3	76.0	24.0	
4	_	_	0	_	_	

 Table 2

 Propylene dimerization with complex 1^a

^a Conditions: 1.74 µmol of complex 1, solvent: toluene, total volume: 30 ml, propylene pressure: 1 atm, temperature: 25 °C, reaction time: 0.5 h. ^b kg oligomers/(mol Ni-h).

^c The ratio of cocat. and cat.

MAO > AlEt₃ > Ni(COD)₂. Amongst them, 1/MAO catalytic system shows the highest activity up to 132 kg oligomers/(mol Ni h) (entry 1). Notably, 1-hexene is the major product in entries 1 and 3. The fact that 1 can give out low carbon olefins indicates the consequence that chain transfer is faster than chain propagation in ethylene and propylene oligomerization because of the elimination of axial steric bulk in d⁸ square-planar system [17].

In summary, neutral arylnickel(II) phosphine complex 1 with chelating oxazoline ligand represents a novel kind of efficient olefin oligomerization catalyst. The molecular weight distribution of olefin oligomers greatly depends on the selection of cocatalysts or phosphine scavenger in catalytic system. A series of study on neutral nickel(II) catalysts containing substituted 2-oxazolinylphenolato ligand towards olefin oligomerization are also now in progress.

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