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Large-ring P/O chelate nickel complex catalyzed oligomerization of ethylene to linear α-olefins

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1,1-(Bicyclononyl-9-phosphino)hendecanoic acid and potassium 1,1-(biscyclohexylphosphino) hendecylate were synthesized. A model nickel complex $[\eta^3{-}C_8H_{13}]\overbrace{Ni[(C_8H_{14})P(CH_2)_{10}CO}O]$ containing a 14-membered chelate ring was also synthesized. The catalytic activity of this large chelate ring nickel complex for the oligomerization of ethylene was studied and compared with that of six-membered ring chelate nickel complexes. The influence of the chelate ring was rationalized in terms of intramolecular rotation. The 14-membered ring P/O chelate nickel complex was shown to have efficient catalytic activity for the oligomerization of ethylene to α-olefins. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

Chelate nickel complexes of P/O ligands have been used as catalyst precursors for the oligomerization of ethylene in the Shell SHOP process for more than 20 years.[1] This catalyst has three advantages—(1) the product can be separated from the catalyst solution by itself because of natural demixing; (2) the catalyst is reusable; (3) the catalyst has high selectivity to linear α-olefins—that are in keeping with the demands of the modern chemical industry for environmental protection and good use of resources. Therefore this kind of catalyst has always been of interest for the following study.[2,3]

The components and structure of the chelate nickel catalysts have been studied in depth. The substituents of phosphine can be phenyl, alkyl, naphthenic base, acetoxyl and heterocyclic radicals etc.; oxygen-containing chelate groups have been developed, ranging from carboxylic to phenolic groups, ketone and sulfo groups; and these structural changes have been proved to have a great influence on catalytic activity and product distribution. But all the ligands reported in the literature are four or five atoms in length, and therefore the chelate ring is five- or six-membered. This catalyst model has not been superceded.[4] Usually, in five- or six-membered chelate rings, the tetrahedral configuration of the carbon atom is slightly distorted, and the corresponding cyclo compound is stable. But some large-ring cyclo compounds also exist in many natural compounds, such as musk and civetone. Because of the flexibility of the long carbon chain in a large ring, the tetrahedral configuration has almost no distortion and therefore the large ring is also stable; accordingly we assumed that large-ring chelate nickel catalysts also have catalytic activity for the oligomerization of ethylene, and also that conformational changes of the large ring caused by intramolecular rotation of δ-bonds, and the strong movements of the large ring have a great influence on catalytic activity. Inquiring into this question not only has significance in theory, but could also lead to development of a new kind of catalyst for the oligomerization of ethylene. Here, we report the synthesis of two types of long-chain P/O bidentate ligand, the synthesis of 14-membered ring chelate nickel complexes, and the use of these complexes as the catalyst precursor for the oligomerization of ethylene.

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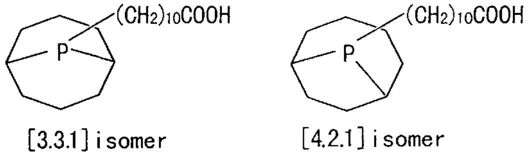
RESULTS AND DISCUSSION

Synthesis of long-chain P/O bidentate ligands

The following operations were carried out under N_2.

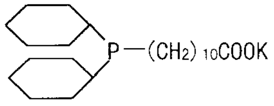
Synthesis of 11(bicyclononyl-9-phosphino) hendecanoic acid (1)



[3.3.1] isomer [4.2.1] isomer

1

To a 100-ml three-necked flask equipped with reflux condenser and constant-pressure dropping funnel, 8.6 g (0.06 mol) 9-phosphinobiscyclononane, 16 ml hendecanoic acid and 20 ml toluene were added, then a solution of 0.5 g azobisisobutyronitrile in 15 ml toluene was added slowly at 70–75 °C with stirring. The final solution was stirred for 3 h. Then toluene was distilled under normal pressure, unreacted $C_8H_{14}PH$ (58–60 °C/ 0.5 mmHg) and hendecanoic acid (138–140 °C/ 0.5 mmHg) were distilled under reduced pressure and the solid product came out of the residual solution with a pale yellow color. A colorless crystalline product was obtained by recrystalization from chloroform: m.p. 39–40 °C. Elementary analysis ($C_{19}H_{35}O_2F$): calcd: C, 69.90; H, 10.81; Found: C, 69.55; H, 10.83%. IR (cm^{-1}): ν_{OH} 3600–2500, ν_{CH} 2922.4, 2851.0, $\nu_{\mathrm{C=O}}$ 1709.4, ν_{CH} 1452.5, 1421.0, ν_{CP} 1197.1, 1114.2, ^{31}P NMR (δ ppm): [4,2,1] isomer, −2.4; [3,3,1]isomer, −37.2 ^{1}H NMR (δ, ppm): 10.86 (COOH), 2.82 (CH in ring), 2.51 (CH_2COOH), 2.19 (CH_2P), 1.82 (CH_2 in ring), 1.49 (CH_2 in chain). ^{13}C NMR (δ, ppm): 178.9 (COOH), 34.3 and 29.4–29.1 (CH_2 in chain), 39.5 and 38.9 (PC), 35.6, 34.9, 34.0, 33.7, 25.8, 25.2 (C in ring).



2

Synthesis of potassium 11-(biscyclohexyl phosphino)hendecylate (2)

To a 100-ml three-necked flask equipped with reflux condenser and constant-pressure dropping funnel, 12 g (0.06 mol) $(C_6H_{11})_2PH$ and 0.07 mol hendecanoic acid and 40 ml toluene were added. Then a solution of 0.82 g azobisisobutyronitrile in 20 ml toluene was added slowly at 75 °C with stirring, and the final solution was stirred for 3 h. Then toluene, unreacted$(C_6H_{11})_2PH$ and hendecanoic acid were distilled under reduced pressure (170 °C/0.5 mmHg), leaving a pale yellow residual solution, to which 20 ml anhydrous ethyl ether and a solution of 10 g KOH/anhydrous ethyl ether solution were added. By filtration 8 g of a pale yellow solid powder was obtained. Elementary analysis ($C_{23}H_{42}O_2PK$): Calcd: C, 65.67; H, 10.06; Found: C, 65.31%; H 10.24%. IR (cm^{-1}): ν_{CH} 2924.3, 2851.0 $\nu_{\mathrm{CO_2^-}}$ 1564.4, 1413.9, ν_{PC} 1467.9. ^{31}P NMR (δ, ppm): −6.0.

Large-ring P/O chelate nickel complex catalyzed oligomerization of ethylene

Catalyst precursors were prepared *in situ* $NiCl_2{\cdot}6H_2O$ (0.0173 mmol) and 0.0173 mmol of

Table 1 Large-ring chelate nickel complexes compared with six-membered ring chelate nickel complexes in catalytic oligomerization of ethylene

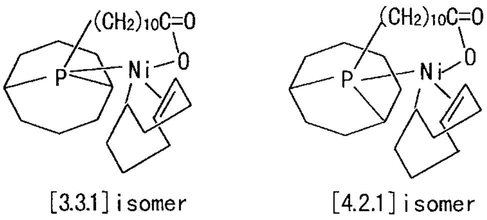
Ligand[a] (L)	Temp. (°C)	Reaction time(h)	Activity g/(gNi.h)	Product distribution (%)			Chelate ring
				C_4[b]	C_{6-10}[b]	C_{12+}[b]	
1	90	1.50	1416	70.9	29.1	0	14-membered
2	130	1.25	82	37.8	57.0	5.2	14-membered
4	125	1.25	2783	25.4	42.1	32.1	6-membered
5	80	1.50	1543	88.4	10.8	0	6-membered

[a] Ligands **1** and **2** are identified in the text. **4** Sodium biscyclohexylphosphinopropionate; **5** Sodium 9-phosphinobiscyclononylpropionate. Ligand L, $NaBH_4$ and Ni were used in the molar proportion L/$NaBH_4$/Ni = 1:2:1.
[b] Carbon atoms contained in product.

long-chain P/O bidentate ligand **1** or **2** was added to a 200 ml steel high-pressure autoclave equipped with a magnetic stirrer. The autoclave was flushed out with ethylene at least three times, and 45 ml 1,4-butanediol was introduced. At 25–35 °C. 0.5 M $NaBH_4$/DMF solution was added dropwise, then stirred for 30 min. In this way the catalyst precursor was prepared and reduced *in situ*. After reaction for 1–1.5 h at the chosen temperature (80–130 °C) and pressure (7.5–8.5 MPa), the autoclave was cooled to room temperature, and the product was analyzed by GC. The experimental results for two large-ring chelate nickel complexes and comparison with six-membered ring chelate nickel complexes are shown in Table 1.

From Table 1, it can be concluded that large-ring P/O chelate nickel complexes of ligands **1** and **2** are active for the oligomerization of ethylene. Therefore the catalytic model of a five or six-membered chelate ring in the SHOP process was extended. When the substituent group of the phosphine and the chelate atom are the same, the catalytic activity of the large-ring P/O chelate nickel complex was lower than that of six-membered ring chelate nickel complexes. Also the high proportion of (α)-olefins produced by large-ring chelate complex decreased compared with six-membered ring chelate complexes. When the substituent was 9-phosphinobicyclononyl (having a small volume,) the catalytic activity decreased slightly. When the substituents were biscyclohexyl (having a large volume,) the activity decreased greatly. The effect on product distribution is similar to that of six-membered ring chelate nickel, that is, the complex containing the 9-phosphinobicyclononyl group has higher selectivity to lower (α)-olefins than the complex containing the two cyclohexyl groups. These results can be rationalized by the concept of intramolecular rotation. In Table 1, the 14-membered ring in the nickel complex consists of ten C–C binds, one Ni–O bond, one Ni–P bond, one P–C bond and one C–O bond. Because of the rotation of these single bonds, the large chelate ring has many configurations in space, which shift constantly; some conformations have steric hindrance to active sites, which is unfavorable to the formation of long-chain (α)-olefins. Therefore large-ring chelate nickel has higher selectivity to lower (α)-olefins than six-membered chelate nickel, and the activity is lower than that of the six-membered ring chelate nickel. Regarding the substituent on the phosphine, smaller one have less influence than larger ones on the chelate ring and less steric hindrance to the active site, and the chelate ring is more stable. Therefore the catalytic activity of complexes containing 9-phosphinobicyclononyl (having less volume) decreased slightly, and the catalytic activity of complexes containing biscyclohexyl (having greater volume) decreased greatly.

The above rationalization was based on the assumption that a 14-membered ring chelate nickel complex was produced, so the key aim in this paper is to improve the survival of this complex.



[3.3.1] isomer [4.2.1] isomer

3

Synthesis and characterization of large-ring P/O chelate model complex $[\eta^3{-}C_8H_{13}]\overline{Ni[(C_8H_{14})P(CH_2)_{10}COO}]$ (3)

A model nickel complex (**3**) containing a 14-membered chelate ring was synthesized by the reaction of 6 mmol $Ni(cod)_2$ (cod, cyclo-octadiene) with 4.7 mmol $C_8H_{14}P(CH_2)COOH$ at room temperature in toluene.[5] After reaction for 1.5 h, low-boiling compounds, such as toluene and 1,5-cyclooctadiene, were distilled under reduced pressure. The residue solid was dissolved in 20 ml toluene and 10 ml 1-octene, $Ni(cod)_2$ was filtered out, at −30 °C and after evaporation under vacuum red crystals came out of the filtrate: m.p. 225–226 °C. Elementary analysis: Calcd: C, 65.47; H, 9.97; P, 6.25; Ni, 11.96; Found: C, 65.28; H, 9.41%; P, 6.11; Ni, 11.85%. The characterization by NMR and IR is listed in Table 2.

From the comparison of IR data of complex **3** with the corresponding ligand **1**, the chelate oxygen atom existed as —COOH (1704 cm^{-1}) in ligand **1**, but in complex **3** it existed as $—COO^-$ (IR absorption at 1572. and 1408.1 cm^{-1}, showing that oxygen coordinated with nickel). The ^{31}P NMR (δ)-values of phosphine in ligand **1** are −37.2 ppm for the [3.3.1] isomer and −2.4 ppm for the [4.2.1] isomer; after reaction with $Ni(cod)_2$ they shifted to −3.6, −9.6, −15.5 ppm and 40.2, 33.6, 28.8 ppm, respectively, showing that phosphine coordinated with nickel. At the same time complex **3** was also characterized by MS; fragments such as

Table 2 NMR and IR data of large-ring chelate nickel complex **3**

	—CO_2—	—CH=CH—	—CH=CH=CH—	—CH_2—		—CH—	Ni—CH—	P
^{1}H NMR δ (ppm)		5.54	4.79 4.05	2.26–1.6 (ring) 1.32 (chain)		2.35 (ring)	0.85	
^{13}C NMR δ (ppm)	183.7	128.3 77.0		33.7, 34.0 24.8	29.1–29.4 20.0	25.2–25.8		
IR ν (cm^{-1})	1572.1 1408.1	1508.4		3036.2 2854.9	2924.3 2818.2			
^{31}P NMR δ (ppm)								[4.2.1] [3.3.1] 40.2 – 3.6 33.6 – 9.6 28.8 – 15.5

Table 3 ^{31}P NMR data of some nickel chelate complexes

Complex	Chemical shift (ppm)
$[\eta^3\text{-}C_8H_{13}]\overline{\mathrm{Ni}[(C_8H_{14})P(CH_2)_{10}COO}]$ **(3)**	[3.3.1] isomer: −3.6, −9.6, −15.5 [4.2.1] isomer: 40.2, 33.6, 28.8
$[\eta^3\text{-}C_8H_{13}]\overline{\mathrm{Ni}[Ph_2P(CH_2)_{10}COO}]$	28.8
$[\eta^3\text{-}C_8H_{13}]\overline{\mathrm{Ni}[Ph_2PCH_2COO}]$	−3.2
$[\eta^3\text{-}C_8H_{13}]\overline{\mathrm{Ni}[Ph_2PC_6H_4COO}]$	15.6

$H\overline{\mathrm{Ni}[(CH_2)_{10}COO}(C_8H_{13})]$ and C_8H_{13} were detected. Overall, the above statements show that a 14-membered chelate nickel complex **3** was produced by reaction of ligand **1** with $Ni(cod)_2$.

The model complex **3** had three signals in the ^{31}P NMR spectrum for both the [3.3.1] isomer and the [4.2.1] isomer. We also studied some similar chelate nickel complexes, and found that these other complexes had single signals in the ^{31}P NMR spectra (see Table 3.) It is suggested that the three signals of **3** were probably due to three different conformations caused by intramolecular interaction of large groups; their structures were difficult to assign exactly, and so further studies on the structures are needed.

In order to study the structure of chelate nickel catalysts under real oligomerization conditions, our group has studied the *in situ* IR spectra by using $[\eta^3\text{-}C_8H_{13}]\overline{\mathrm{Ni}[Ph_2PCH_2COO}]$ as the catalyst precursor,[6] the result showed that IR absorption of the carbonyl ($\nu_{C=O}$) had no evident shift, indicating that the catalyst keeps its chelate structure under oligomerization conditions.

CONCLUSION

Two kinds of long-chain bidentate ligands, 11-(bicyclononyl-9-phosphino)hendecanoic acid (**1**) and potassium 11-(biscyclohexylphosphino)hendecylate **(2)**, were synthesized, and when they were used as the ligands in the SHOP P/O chelate nickel catalyst the catalytic activity was efficient. A model complex $[\eta^3\text{-}C_8H_{13}]\overline{\mathrm{Ni}[(C_8H_{14})P(CH_2)_{10}COO}]$ **(3)** containing a 14-membered chelate ring was also synthesized. The large-ring chelate nickel complex proved to have efficient catalytic activity for the oligomerization of ethylene, adding new types of catalyst for the SHOP-process.

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