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Synthesis, Characterization and Ethylene Oligomerization Behavior of Neutral Nickel Complexes Bearing *N*-Fluorinated Phenyl Salicylaldiminato Chelate Ligands

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A series of neutral nickel complexes featuring *N*-fluorinated phenyl salicylaldiminato chelate ligands was synthesized, and the novel molecular structure of complex **C14** was further confirmed by X-ray crystallographic analysis. The neutral nickel complexes showed high activity up to 9.96×10^5 g oligomers/(mol Ni•h) and high selectivity of C_6 in catalyzing ethylene oligomerization using methylaluminoxane (MAO) as cocatalyst. It was observed that the strong electron-withdrawing effect of the fluorinated salicylaldiminato ligand was able to significantly increase the catalytic activity for oligomerization of ethylene. In addition, the influence of reaction parameters such as Al/Ni molar ratio, reaction temperature, a variety of cocatalyst and ethylene pressure on catalytic activity was investigated.

Keywords neutral nickel complex, *N*-fluorinated phenyl salicylaldiminato ligand, crystal structure, ethylene oligomerization

Introduction

During the past decades, considerable advances have been achieved in the design and application of late transition metal complexes for oligomerization and polymerization of olefins.[1] Compared with early transition metal complexes, late transition metals are generally more tolerant of polar media because of their less oxophillic nature. Therefore, it is possible to catalyze not only olefin polymerization, polar-functionalized α-olefins polymerization, but also copolymerization of ethylene and α-olefins.[2] The commercially practiced Shell High Olefin Process (SHOP) based on the pioneering research of Keim produced olefins in the range of C_4—C_{30} at the rate of more than one million tons every year.[3] Recently, cationic nickel α-diimine catalyst was reported by Brookhart's group,[4] following the report, iron and cobalt complexes with mono-alkyl substituted bis(imino)pyridyl ligands were reported by Brookhart[5] and Gibson.[6] These iron and cobalt complexes exhibited high activity in ethylene oligomerization, and the oligomers consisted of $>95\%$ linear α-olefins. A series of neutral nickel complexes based on salicylaldiminato ligands with bulky imino substitnents was reported by Grubbs[7] and showed interesting properties for ethylene polymerization. Meanwhile, fluorinated ligands and their complexes have been investigated with a vast array of metals.[8] More recently, a series of novel nickel complexes as catalyst for olefins oligomerization or polymerization was reported.[9] Herein, we wish to report the synthesis of a series of arylnickel phosphine complexes featuring salicylaldiminato ligands with fluoro-substituents in different positions on the imine aryl and their reactivity and selectivity in ethylene oligomerization.

Results and Discussion

Synthesis and characterization of the ligands and complexes

Based on our modification of a procedure reported by Fujita *et al*.[8a,8b] and Nomura *et al*.,[8c] all ligands were prepared by condensation of fluorinated anilines with corresponding salicyaldehydes at 100 ℃ for 8 h without solvents. Pure ligands were then obtained in excellent yields by either re-crystallization in proper solvents or column chromatography on silica gel. All the ligands were characterized by ^{1}H NMR and ^{19}F NMR. A series of novel nickel complexes **C6**, **C7** and **C9**—**C14** were synthesized in good yields (Scheme 1) according to the previously reported procedues.[10] Unfortunately, the designed complex **C8** was not obtained under the same reaction conditions, although we tried

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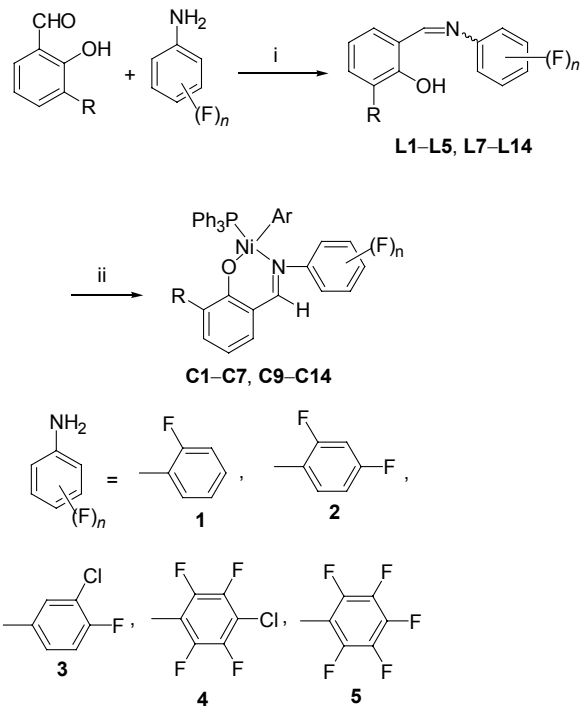
several methods to improve the reaction conditions, but the result was fail.

Scheme 1 Synthesis of ligands and complexes



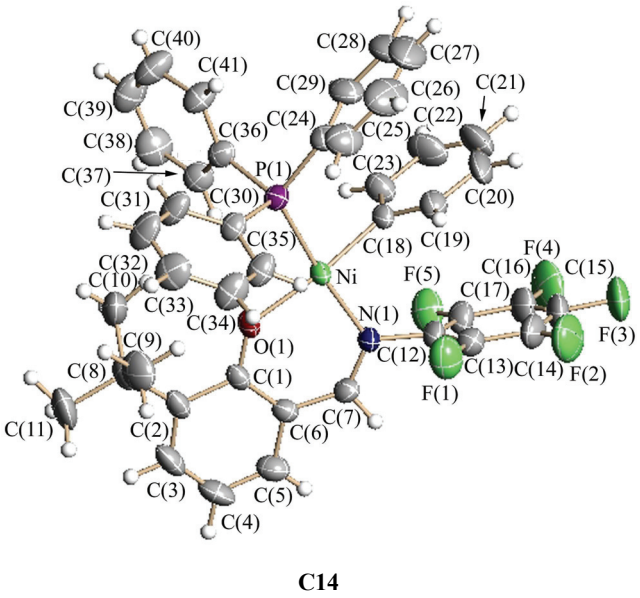
Reagents and conditions: (i) solvent-free, 100 ℃, 8 h; (ii) THF, NaH, *trans*-Ni(Ar)(Cl)(PPh_3)$_2$

Ligand	L1	L7	L8	L9	L10	L11	L12	L13	L14
R=	H	CH_3	CH_3	CH_3	CH_3	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu
Ar_f=	1	1	2	3	5	1	2	3	5
Ar=	*p*-MePh	Ph	—	Ph	Ph	Ph	Ph	Ph	Ph
Complex	C6	C7	—	C9	C10	C11	C12	C13	C14

Usually, the C=N stretching vibration of ligands in IR spectra was distributed in the range from 1630 to 1640 cm^{-1}, approximately, while in the corresponding complexes the C=N stretching vibration was distributed in the range from 1603 to 1613 cm^{-1}; these shifts were attributed to the formation of N—Ni complex bonds. The strong absorption bands at about 1435 (ν_{P-C}) and 693 (ν_{Ni-P}) cm^{-1} could confirm the existence of PPh_3.[11] The weak absorption bands of complexes in 572—576 and 460—464 cm^{-1} might be attributed to ν_{Ni-N} and ν_{Ni-O}, respectively.[12] The signals for the triphenylphosphine ligand in the ^{31}P NMR spectra of complexes **C7**, **C9**—**C14** are observed between δ 27.6 and 42.5. Compared with the corresponding N-fluorinated phenyl salicylaldiminato chelate ligands, the signals for the fluorine atoms in ^{19}F NMR spectra of complexes **C1**—**C7**, **C9**—**C14** showed the similar patterns.

Crystal structures

In addition to the ^1H NMR, the single crystal X-ray diffraction result further confirmed the structure of **C14** (Figure 1).[13]



C14

Figure 1 Molecular structure of complex **C14** [2-((N-C_6F_5)-CHN)-η-6-*t*-Bu-C_6H_3O]Ni(Ph)(PPh_3).

Because of the obvious structural similarity, complex **C14** had a molecular structure (Figure 1) similar to complex **C4**.[10b] The four-coordinate atoms [C(18), N(1), O(1) and P(1)] and the central Ni atom were also in the same planar. Due to the repulsion between bulkier *tert*-butyl substituent attached on salicylaldiminato ligand and PPh_3 ligand, the O(1)-Ni-P(1) angle [93.56(5)°] for complex **C14** was larger than that of the corresponding angle of the complex **C4** [88.34(7)°], whereas the C(18)-Ni-P(1) angle [85.43(8)°] for complex **C14** was smaller than that of the corresponding angle of the complex **C4** [89.17(10)°]. In addition, the bond length of Ni—O [1.9224(16) Å] for complex **C14** was much longer than that of the corresponding length [1.898(2) Å] for complex **C4**; and the bond length of Ni—N [1.925(2) Å] for complex **C14** was much shorter than that of the corresponding length of complex **C4** [1.935(2) Å], suggesting that in the solid state there was an obvious steric interaction between the *tert*-butyl substituent and the triphenylphosphine ligand compared with the unsubstituted analogues.

Ethylene oligomerization

The catalyst precursors **C1**—**C7** and **C9**—**C14** could be activated for ethylene oligomerization with methylaluminoxane (MAO). Firstly, the complexes **C1**—**C6** were chosen to investigate the catalytic activities. The results with 12 atm of ethylene were summarized in Table 1. As shown in Table 1, the complexes **C1**—**C6** showed good catalytic activities and high catalytic selectivity for ethylene oligomerization, the major oligomers were C_6 component (containing

1-hexene, 2-methyl-pentene-2, 2-hexene, 3-hexene, respectively), along with the minor oligomers C_4 component (containing 1-butene exclusively), and no ethylene polymers were detected. In the cases of precatalysts **C4** and **C5**, no remarkable increase in catalytic activity could be seen by further increasing the amount of fluorine atoms in salicylaldiminato ligands. (for **C4**, 5.30×10^5 g/(mol Ni•h), for **C5**, 5.08×10^5 g/(mol Ni•h) (Entries 4 and 5, Table 1). Compared with the complex **C1**, the complex **C6** bearing methyl substituent on *para* position of phenyl group attached to nickel hardly affected the catalytic activity and selectivity for ethylene oligomerization because the methyl substituent was irrelevant in the catalytic active species (Ni-alkyl species) in terms of oligomers distribution (Entries 6 and 7, Table 1).

Svejda and Brookhart proposed the mechanism of chain isomerization and chain transfer with diimine nickel complexes in ethylene oligomeriztion.[14] Analogously, we supposed the possible mechanism of ethylene oligomerization with complex **C1** (Scheme 2). After ethylene insertion and chain propagation occurred (Scheme 2, Path A), if chain transfer (β-H elimination) took place, α-olefins could be formed. On the contrary, if chain isomerization took place, the formation of internal olefins was inevitable (Scheme 2, Path B).

The data in Table 1 demonstrated the electrophillic characteristic of center nickel atom was one of the most important factors determining the rate of chain propagation. The more electrophillic the nickel center, the higher the rate of ethylene oligomerization. This was because the introduction of fluorine atom(s) into the salicylaldimine ligand could weaken the electron releasing ability of the ligands and enhanced the electrophillic characteristic of the center nickel atom, benefiting chain propagation.

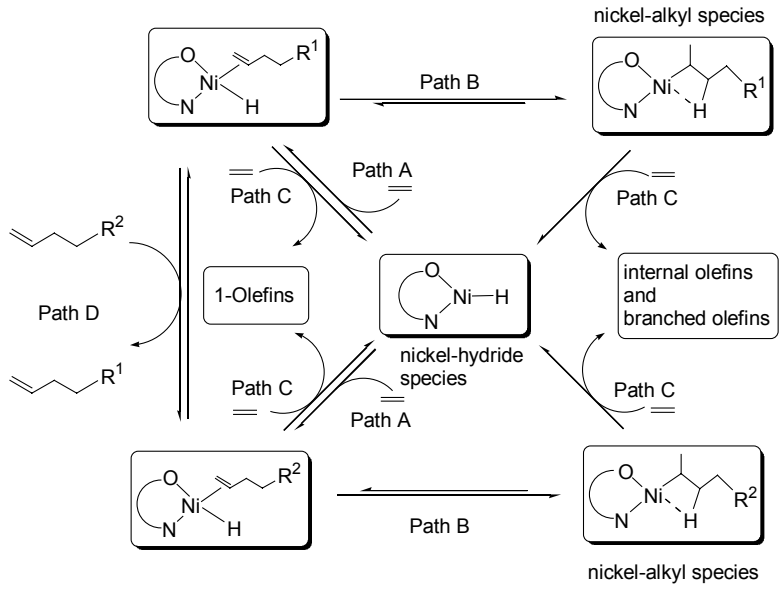
Owing to the fact that complex **C4** showed the highest activity under the same conditions among these complexes, **C4** was selected as the precatalyst and was

Table 1 Ethylene oligomerization using **C1**-**C6**/MAO system and their oligomers distribution[a]

Entry	Reaction condition			Oligomers distribtion/%		Distribution of C_4/%	Distribution of C_6[b]/%				Activity/
	Cat	Cocat	Al∶Ni	C_4	C_6	1-Butene	1-Hex	2MP	2-Hex	3-Hex	[10^5 g/(mol Ni•h)]
1	**C1**	MAO	2000	16.6	83.4	100	21.4	25.5	19.0	34.1	2.53
2	**C2**	MAO	2000	15.4	84.6	100	20.4	30.5	26.2	22.9	4.52
3	**C3**	MAO	2000	14.6	85.4	100	19.2	23.9	26.1	30.8	3.77
4	**C4**	MAO	2000	13.6	86.4	100	21.8	26.2	18.3	33.7	5.30
5	**C5**	MAO	2000	14.0	86.0	100	19.1	34.5	18.1	28.3	5.08
6	**C6**	MAO	1000	8.8	91.2	100	24.8	19.2	25.9	30.1	1.18
7	**C1**	MAO	1000	5.6	94.4	100	25.9	18.1	24.8	31.2	1.25

[a] Conditions: cat.: 1.5 μmol, solvent: toluene, total volume: 30.0 mL, ethylene pressure: 12.0 atm, temperature: 30 ℃, reaction time: 0.5 h.
[b] 1-Hex: 1-hexene; 2MP: 2-methyl-pentene-2; 2-Hex: 2-hexene; 3-Hex: 3-hexene.

Scheme 2 Proposed mechanism of ethylene oligomerization



Path A: ethylene in sertion and chain propagation, Path B: chain isomerization, Path C: chain transfer (β-H elimination), Path D: the reinsertion of previously formed olefins

carefully investigated its catalytic activity through varying reaction conditions, such as the molar ratio of cocatalyst (MAO) to nickel complex (Al/Ni), reaction temperature, and the pressure of ethylene, for the optimum.

Effects of ethylene pressure on the catalytic activity

For the complex **C4**/MAO, it was very clear that, with the fixed molar ratio of Al/Ni, the ethylene pressure largely affected the catalytic performance (Table 2). The oligomerization activity increased significantly along with the increase of ethylene pressure. Furthermore, the reaction gave C_4 component as the major oligomer (55.8%) at 3.0 atm of ethylene pressure (Entry 1, Table 2), by comparison of the reaction performed at higher ethylene pressure (Entries 2—4, Table 2). Higher ethylene pressure meant the enhancement of ethylene concentration in toluene. As explained above, Scheme 2 illustrated that ethylene concentration affected not only the steps of ethylene insertion and chain propagation (Path A), but also the step of chain transfer (Path C).[15] Therefore, in principle, higher ethylene pressure improved the catalytic activities and the content of C_6 fraction. However, as shown in Path B, ethylene pressure should have less influence on the step of chain isomerization. As a result, the distribution of both C_6 olefins and C_4 olefin did not change.

Effects of Al/Ni molar ratio

The variation of Al/Ni molar ratio in catalytic system of **C4**/MAO was explored at 30 ℃. As shown in Table 3, at Al/Ni molar ratio of 500∶1, the catalytic activity was relatively low [2.84×10^5 g/(mol Ni•h)]. When the Al/Ni molar ratio was increased, the catalytic activity efficiently increased. The best Al/Ni molar ratio for this catalytic system was 2000. Further increasing the Al/Ni molar ratio up to 2500, the catalytic activity was slightly decreased. However, the distribution of resultant oligomers was almost the same. The fact that a large excess of MAO did not significantly increase the activity suggested that catalytic active species (Ni-alkyl species) could be possibly deactivated by the reaction with excess MAO, or the enveloping of excess MAO on the surface of active species.[16]

Effects of oligomerization temperature

With the fixed Al/Ni molar ratio of 1000∶1, the reaction temperature significantly affected the catalytic activity. And the good oligomerization activity was obtained at 30 ℃ (Entry 1, Table 4). Along with elevating reaction temperature in the range of 30 to 90 ℃, the oligomerization activity significantly declined. In addition, the ratio of C_4 component of the resultant oligomers increased obviously at higher reaction temperature. However, temperature had no effect on the distribution of trimer. This result was consistent with the above explanation, in which the solubility of ethylene in toluene decreased dramatically while increasing the temperature.[17]

Effects of co-catalyst

Combined with the complex **C5**, a variety of cocatalyst affecting the catalytic activity was also explored. As shown in Table 5, when 2 equiv. of $Ni(COD)_2$ was used as the cocatalyst, the catalytic activity was slightly decreased to 2.76×10^5 g/(mol Ni•h), and the reaction

Table 2 Influence of ethylene pressure on **C4**/MAO catalytic system and their oligomers distribution[a]

Entry	Reaction condition		Oligomers distribution/%		Distribution of C_4/%	Distribution of C_6[b]/%				Activity/ [10^5 g/(mol Ni•h)]
	Cat.	$p_{ethylene}$/atm	C_4	C_6	1-Butene	1-Hex	2MP	2-Hex	3-Hex	
1	**C4**	3	55.8	44.2	100	17.2	32.3	29.3	21.2	0.52
2	**C4**	6	19.6	80.4	100	19.0	30.0	27.6	23.4	1.43
3	**C4**	9	16.7	83.3	100	20.2	28.6	22.6	28.6	2.09
4	**C4**	12	16.4	83.6	100	18.9	32.3	19.9	28.9	4.22

[a] Conditions: cat.: 1.5 μmol, Al∶Ni=1000, reaction temperature: 30 ℃, solvent: toluene, total volume: 30.0 mL, reaction time: 0.5 h. [b] 1-Hex: 1-hexene; 2MP: 2-methyl-pentene-2; 2-Hex: 2-hexene; 3-Hex: 3-hexene.

Table 3 Influence of Al/Ni molar ratio on **C4**/MAO catalytic system and their oligomers distribution[a]

Entry	Reaction condition		Oligomers distribution/%		Distribution of C_4/%	Distribution of C_6[b]/%				Activity/[10^5 g/(mol Ni•h)]
	Cat.	Al∶Ni	C_4	C_6	1-Butene	1-Hex	2MP	2-Hex	3-Hex	
1	**C4**	500	15.1	84.9	100	17.8	38.1	21.6	22.5	2.84
2	**C4**	1000	16.4	83.6	100	18.9	32.3	19.9	28.9	4.22
3	**C4**	1500	15.5	84.5	100	19.6	29.7	21.6	29.1	4.71
4	**C4**	2000	13.6	86.4	100	21.8	26.2	18.3	33.7	5.30
5	**C4**	2500	13.3	86.7	100	19.7	29.5	22.8	27.9	4.98

[a] Conditions: cat.: 1.5 μmol, $p_{ethylene}$=12.0 atm., reaction temperature: 30 ℃, solvent: toluene, total volume: 30.0 mL, reaction time: 0.5 h. [b] 1-Hex: 1-Hexene; 2MP: 2-methyl-pentene-2; 2-hex: 2-hexene; 3-hex: 3-hexene.

CHINESE JOURNAL OF CHEMISTRY

gave the C_8 component predominately, without formation of the longer carbon chain oligomers. It should be indicated that, in the absence of the co-catalyst such as MAO or $Ni(COD)_2$, no ethylene oligomerization or polymerization product was detected by GC analysis. It was well known that phosphine scavengers, such as $Ni(COD)_2$, played an important role in the removal of PPh_3 in the course of olefin oligomerization and polymerization.[7,18] In combining with $Ni(COD)_2$, SHOP-type oligomerization catalysts could also convert ethylene to polyethylene with molecular weights over 1000000. Interestingly, when phosphine scavenger was applied to the neutral fluorinated salicylaldiminato-nickel catalytic system, the molecular weights of oligomers only slightly increased, and no polymer could be obtained. Although **C5**/$Ni(COD)_2$ showed moderate activity to produce olefin oligomers, as a non-organoaluminium activator, $Ni(COD)_2$ played a crucial role in the stabilization of the catalytic active site.

Effects of the coordination environment

It was well known that the catalytic activity of the nickel complex was greatly affected by arched environment of corresponding ligand, and the bulkier the substituents, the higher the catalytic activity.

With this aim of view, to verify the role of the R substituent attached to the salicylaldiminato ligands in the catalytic performance, the complexes **C7**, **C9**—**C14** bearing the methyl or *tert*-butyl attached on the salicylaldiminato moieties were also studied for ethylene oligomerization. As shown in Table 8, under the optimal conditions, the complexes **C7**, **C9**—**C14** displayed the higher oligomerization activities than that of un-substituted analogs **C1**—**C5**. Furthermore, a remarkable increase in catalytic activity could be observed by introduction of the bulky substituent in salicylaldiminato ligands [for **C5**, 5.30×10^5 g/mol•Ni•h], for **C10**, 6.50×10^5 g/(mol Ni•h), for **C14**, 9.96×10^5 g/(mol Ni•h)]. It was very clear that the bulkier group was recognized to increase the catalytic activity of late-transition metal complexes, the highest activity up to 9.96×10^5 g oligomers/(mol Ni•h) could be obtained by **C14**/MAO catalytic system. This result was consistent with the previous work in which bulky substituents on the phenolic ring might decrease the rate of catalyst deactivation.[7] It should be noted that the steric effects

Table 4 Influence of temperature on **C4**/MAO catalytic system and their oligomers distribution[a]

Entry	Reaction condition		Oligomers distribution/%		Distribution of C_4/%	Distribution of C_6/%				Activity/
	Cat.	T/℃	C_4	C_6	1-Butene	1-Hex	2MP	2-Hex	3-Hex	[10^5 g/(mol Ni•h)]
1	**C4**	30	16.4	83.6	100	18.9	32.3	19.9	28.9	4.22
2	**C4**	60	39.4	60.6	100	21.2	21.2	23.4	34.2	2.08
3	**C4**	90	52.8	47.2	100	22.5	29.5	26.4	21.4	2.29

[a] Conditions: Cat.: 1.5 μmol, Al∶Ni=1000, $p_{ethylene}$=12.0 atm, solvent: toluene, total volume: 30.0 mL, reaction time: 0.5 h. [b] 1-Hex: 1-hexene; 2MP: 2-methyl-pentene-2; 2-Hex: 2-hexene; 3-Hex: 3-hexene.

Table 5 Influence of co-catalyst on **C5** complex and their oligomers distribution[a]

Entry	Reaction Condition[a]			Oligomers distribution/%			Activity/[10^5 g/(mol Ni•h)]
	Cat.	Cocat.	Cocat.∶Cat.	C_4	C_6	C_8	
1	**C5**	MAO	1000	8.7	91.3	—	3.90
2	**C5**	$Ni(COD)_2$	2	10.1	15.6	74.3	2.76
3	**C5**	—	—	—	—	—	—

[a] Conditions: cat.: 1.5 μmol, solvent: toluene, total volume: 30.0 mL, ethylene pressure: 12.0 atm, temperature: 30 ℃, reaction time: 0.5 h.

Table 6 Ethylene oligomerization using **C7**, **C9**—**C14**/MAO catalytic system and their oligomers distribution[a]

Entry	Reaction condition			Oligomers distribution/%		Activity/[10^5 g/(mol Ni•h)]
	Cat.	Cocat.	Cocat.∶Cat.	C_4	C_6	
1	**C7**	MAO	2000	9.9	90.1	6.35
2	**C9**	MAO	2000	8.6	91.4	5.93
3	**C10**	MAO	2000	12.3	87.7	6.50
4	**C11**	MAO	2000	7.7	92.3	7.35
5	**C12**	MAO	2000	5.8	94.2	9.67
6	**C13**	MAO	2000	15.7	84.3	7.19
7	**C14**	MAO	2000	7.3	92.7	9.96

[a] Conditions: Cat.: 1.5 μmol, solvent: toluene, total volume: 30.0 mL, ethylene pressure: 12.0 atm, temperature: 30 ℃, reaction time: 0.5 h.

of the bulkier R substituents had little influence on the oligomer distribution, and the main oligomer was C_6 component.

Experimental

General

All manipulations involving air- and/or moisture-sensitive compounds were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were refluxed over the appropriate drying reagents and distilled under argon prior to use. Melting points (m.p.) were determined with a digital electrothermal apparatus without calibration. IR spectra were recorded on a Nicolet AV-360 spectrophotometer using KBr pellet. ^{1}H and ^{19}F NMR spectra were recorded on Bruker AM-300 or AM-500 instruments with Me_4Si and $CFCl_3$ (with upfield negative) as the internal and external standards, respectively. The ^{31}P NMR spectra were recorded on a Bruker AM-300 instrument with H_3PO_4 (85%) as the external standard. Mass spectra were determined with a Finnigan GC-MS 4021 instrument using the electron impact ionization technique (70 eV). The elemental analyses were performed on a Flash EA 1112 microanalyzer. Distribution of oligomers obtained was measured on a Varian VISTA 6000 GC spectrometer (SE-30 capillary column, 30 m×0.25 mm) and an HP 5971A GC-MS detector. *trans*-Ni(Ar)(Cl)$(PPh_3)_2$ and $Ni(COD)_2$ were prepared according to the literatures.[10,19]

General procedure for preparation of ligands

In a 10 mL round bottle flask was placed 5.0 mmol of salicylaldehyde and 5.5 mmol of fluorinated aniline. The mixture was stirred at 100 ℃ for 8 h. After cooling to room temperature, the resultant crude product was purified by recrystallization with ethyl acetate/petroleum (*V*/*V*=1/9).

***N*-2-Fluorophenyl-3-methyl-salicylaldimine (L7)** Yellow solid, yield 82%; m.p. 60—62 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 13.41 (s, 1H, OH), 8.72 (s, 1H, CH=N), 7.33—6.86 (m, 7H, aromatic-H), 2.34 (s, 3H, CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −125.88 (m, 1F, 2-F).

***N*-2,4-Difluorophenyl-3-methyl-salicylaldimine (L8)** Yellow solid, yield 83%; m.p. 76—78 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 13.23 (s, 1H, OH), 8.68 (s, 1H, CH=N), 7.430—6.85 (m, 6H, aromatic-H), 2.33 (s, 3H, CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −112.17 (m, 1F, 2-F), −121.04 (m, 1F, 4-F).

***N*-3-Chloro-4-fluorophenyl-3-methyl-salicylaldimine (L9)** Yellow solid, yield 85%; m.p. 98—99 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 13.05 (s, 1H, OH), 8.56 (s, 1H, CH=N), 7.35—6.84 (m, 6H, aromatic-H), 2.31 (s, 3H, CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −118.38 (d, *J*=8.18 Hz, 1F, 4-F).

***N*-2,3,4,5,6-Pentafluorophenyl-3-methyl-salicylaldimine (L10)**[8a] Yellow solid, yield 89%; m.p. 121—122 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.51 (s, 1H, OH), 8.83 (s, 1H, CH=N), 7.34 (d, *J*=7.5 Hz, 1H, aromatic-H), 7.26 (d, *J*=7.5 Hz, 1H, aromatic-H), 6.91 (t, *J*=7.5 Hz, 1H, aromatic-H), 2.34 (s, 3H, CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −152.33 (dd, *J*=22.56, 5.64 Hz, 2F, 2-F, 6-F), −158.67 (t, *J*=22.56 Hz, 1F, 4-F), −162.57—−162.74 (m, 2F, 3-F, 5-F).

***N*-2-Fluorophenyl-3-*tert*-butyl-salicylaldimine (L11)**[8b] Yellow solid, yield 89%; m.p. 55—56 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 13.71 (s, 1H, OH), 8.70 (s, 1H, CH=N), 7.42—6.85 (m, 7H, aromatic-H), 1.47 (s, 9H, *t*-Bu); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −125.97 (m, 1F, 2-F).

***N*-2,4-Difluorophenyl-3-*tert*-butyl-salicylaldimine (L12)**[8c] Yellow sticky oil, yield 89%; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 13.60 (s, 1H, OH), 8.69 (s, 1H, CH=N), 7.45—6.88 (m, 6H, aromatic-H), 1.49 (s, 9H, *t*-Bu); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −112.30 (m, 1F, 2-F), −121.07 (m, 1F, 4-F).

***N*-3-Chloro-4-fluorophenyl-3-*tert*-butyl-salicylaldimine (L13)** Yellow solid, yield 93%; m.p. 58—59 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 13.49 (s, 1H, OH), 8.58 (s, 1H, CH=N), 7.45—6.88 (m, 6H, aromatic-H), 1.48 (s, 9H, *t*-Bu); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −118.47 (d, *J*=8.18 Hz, 1F, 4-F).

***N*-2,3,4,5,6-Pentafluorophenyl-3-*tert*-butyl-salicylaldimine (L14)**[8a] Yellow solid, yield 93%; m.p. 70—71 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.87 (s, 1H, OH), 8.80 (s, 1H, CH=N), 7.46 (d, *J*=7.5 Hz, 1H, aromatic-H), 7.23 (d, *J*=7.5 Hz, 1H, aromatic-H), 6.89 (t, *J*=7.5 Hz, 1H, aromatic-H), 1.45 (s, 9H, *t*-Bu); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −152.33 (dd, *J*=21.15, 6.20 Hz, 2F, 2-F, 6-F), −158.80 (t, *J*=21.43 Hz, 1F, 4-*F*), −162.61—−162.79 (m, 2F, 3-F, 5-F)

General procedure for preparation of complexes

A solution of the Schiff base (1.5 mmol) in THF (20.0 mL) was added to 80% sodium hydride (70.0 mg, 2.5 mmol). The resulting mixture was stirred for 1 h at ambient temperature. After filtered, the filtrate was reduced in vacuum. The solid residue was washed with *n*-hexane (10.0 mL) and dried in vacuum. The salt was immediately used in next step without further purification. The sodium salt of ligand and *trans*-NiCl(Ar)$(PPh_3)_2$ (1.44 mmol) dissolved in toluene (30.0 mL) were in a Schlenk flask and stirred for 8 h at room temperature. After this time, the reaction mixture was filtered by cannula filtration, and the filtrate was concentrated to *ca*. 5.0 mL. *n*-Hexane (30.0 mL) was added to the reaction. A brown-yellow needle crystal was isolated by cannula filtration to give the complexes.

{2-[(*N*-2-F-C_6H_4)-CHN]-η-C_6H_4O}Ni(*p*-MePh)-(PPh_3) (C6) Brown solid, yield 71%; m.p. 120 ℃ (decomposed); ^{1}H NMR (300 MHz, C_6D_6) δ: 7.85 (d, J_{H-P}=8.4 Hz, 1H, N=CH), 7.71—7.65 (m, 6H), 7.11—7.08 (m, 3H, ArH), 7.03—6.91 (m, 9H, ArH), 6.88—6.85 (m, 1H, ArH), 6.57—6.33 (m, 7H, ArH), 6.20 (d, *J*=7.5 Hz, 1H, ArH), 1.97 (s, 3H, CH_3); ^{19}F NMR (282

MHz, d_6-C_6D_6) δ: −122.0 (s, 1F, ArF); IR (KBr pellet) v: 3048 (w), 2915 (w), 1613 (vs), 1581 (vs), 1530 (s), 1498 (s), 1451 (s), 1444 (s), 1434 (s), 1337 (m), 1178 (m), 1146 (m), 1095 (m), 750 (vs), 693 (vs), 529 (vs), 508 (vs) cm^{-1}. Anal. calcd for $C_{38}H_{31}FNNiOP$: C 72.88, H 4.95, N 2.24; found C 72.65, H 4.89, N 2.21.

{2-[(*N*-2-F-C_6H_4)-CHN]-η-6-CH_3-C_6H_3O}Ni(Ph)-(PPh_3) (C7) Brown solid, yield 85%; m.p. 114−116 ℃, ^{1}H NMR (300 MHz, C_6D_6) δ: 7.92 (d, J_{H-P}=8.7 Hz, 1H, N=CH), 7.73—7.67 (m, 6H, m, ArH), 7.22 (d, J=8.1 Hz, 2H, ArH), 7.11—6.81 (m, 11H, ArH), 6.57—6.29 (m, 8H, ArH), 1.40 (s, 3H, CH_3); ^{19}F NMR (282 MHz, C_6D_6) δ: −122.2 (m, 1F, ArF); ^{31}P NMR (121 MHz, C_6D_6) δ: 42.0 (m, Ph_3P); IR (KBr pellet) v: 3047 (w), 1605 (vs), 1562 (s), 1544 (m), 1495 (m), 1434 (m), 1382 (m), 1335 (m), 1224 (m), 1179 (m), 1079 (m), 1084 (m), 864 (s), 803 (s), 757 (vs), 742 (vs), 730 (vs), 693 (vs), 532 (s), 510 (s) cm^{-1}. Anal. calcd for $C_{38}H_{31}FNNiOP$: C 72.88, H, 4.95, N 2.24; found C 73.51, H 5.21, N, 1.92.

{2-[(*N*-3-Cl-4-F-C_6H_3)-CHN]-η-6-CH_3-C_6H_3O}Ni-(Ph)(PPh_3) (C9) Brown solid, yield 56%; m.p. 118—120 ℃; ^{1}H NMR (300 MHz, C_6D_6) δ: 7.78 (d, J_{H-P}=8.4 Hz, 1H, N=CH), 7.67—7.62 (m, 6H, ArH), 7.12 (d, J=7.8 Hz, 1H, ArH), 7.00—6.91 (m, 12H, ArH), 6.58—6.50 (m, 2H, ArH), 6.40—6.28 (m, 4H, ArH), 6.20—6.22 (m, 1H, ArH), 1.42 (s, 3H, CH_3); ^{19}F NMR (282 MHz, C_6D_6) δ: −121.7 (m, 1F, ArF); ^{31}P NMR (121 MHz, C_6D_6): 40.6 (m, Ph_3P); IR (KBr pellet) v: 3047 (w), 2966 (w), 1609 (vs), 1584 (s), 1541 (m), 1490 (m), 1448 (m), 1433 (m), 1377 (m), 1334 (m), 1259 (m), 1186 (m), 1096 (m), 869 (m), 753 (vs), 730 (vs), 692 (vs), 532 (vs), 519 (vs), 509 (vs), 439 (m) cm^{-1}. Anal. calcd for $C_{38}H_{30}ClFNNiOP$: C 69.07, H 4.54, N 2.12; found C 69.73, H 4.59, N 2.10.

{2-[(N-C_6F_5)-CHN]-η-6-CH_3-C_6H_3O}Ni(Ph)(PPh_3) (C10) Brown solid. yield 79%; m.p. 178—180 ℃; ^{1}H NMR (300 MHz, C_6D_6) δ: 7.73 (d, J_{H-P}=8.1 Hz, 1H, N=CH), 7.62—7.58 (m, 6H, ArH), 7.21 (d, J=6.9 Hz, 2H, ArH), 7.09 (d, J=6.7 Hz, 1H, ArH) , 6.96—6.90, (m, 4H, ArH), 6.86—6.82 (m, 6H, ArH), 6.47 (t, J=7.5 Hz, 1H, ArH), 6.33—6.27 (m, 3H, ArH), 1.31 (s, 3H, CH_3); ^{19}F NMR (282 MHz C_6D_6) δ: −147.4 (dd, J=24.0, 6.0 Hz, 2F, ArF), −161.3 (t, J=24.0 Hz, 1F, ArF), −164.2 (td, J=24.0, 6.0 Hz, 2F, ArF); ^{31}P NMR (121 MHz, C_6D_6): 42.5 (m, Ph_3P); IR (KBr pellet) v: 3044 (w), 3016 (w), 2973 (w), 1609 (vs), 1583 (vs), 1543 (s), 1515 (vs), 1435 (s), 1375 (m), 1227 (s), 1097 (s), 1000 (vs), 967 (s), 869 (m), 753 (s), 733 (s), 693 (vs), 533 (vs), 508 (s) cm^{-1}. Anal. calcd for $C_{38}H_{27}F_5N$-NiOP: C 65.36, H 3.87, N 2.00; found C 65.16, H 3.85, N 1.95.

{2-[(*N*-2-F-C_6H_4)-CHN]-η-6-*t*-Bu-C_6H_3O}Ni(Ph)-(PPh_3) (C11) Brown solid, yield 65%; m.p. 140—142 ℃ (decomposed); ^{1}H NMR (300 MHz, C_6D_6) δ: 7.83—7.74 (m, 6H, ArH), 7.36 (d, J_{H-P}=7.5 Hz, 1H, N=CH), 6.98—6.86 (m, 13H, ArH), 6.58—6.40 (m, 5H, ArH), 6.25—6.15 (m, 3H, ArH), 0.86 [s, 9H, $C(CH_3)_3$]; ^{19}F NMR (282 MHz, C_6D_6) δ: −122.9 (s, 1F, ArF); ^{31}P NMR (121 MHz, C_6D_6) δ: 27.7 (m, Ph_3P); IR (KBr pellet) v: 3047 (w), 2947 (m), 2905 (w), 1591 (vs), 1564 (m), 1533 (s), 1493 (s), 1436 (s), 1416 (s), 1228 (m), 1176 (m), 1146 (m), 1096 (m), 754 (s), 741 (s), 730 (s), 693 (vs), 529 (s), 511, 496 (s) cm^{-1}. Anal. calcd for $C_{41}H_{37}FNNiOP$: C 73.69, H 5.54, N 2.10; found C 73.78, H 5.58, N 1.89.

{2-[(*N*-2,4-$F_2C_6H_3$)-CHN]-η-6-*t*-Bu-C_6H_3O}Ni(Ph)-(PPh_3) (C12) Brown solid, yield 66%; m.p. 138—140 ℃; ^{1}H NMR (300 MHz, C_6D_6) δ: 7.85—7.79 (m, 6H, ArH), 7.40 (d, J_{H-P}=7.2 Hz, 1H, N=CH), 7.05 (d, J=9.6 Hz, 2H, ArH), 6.95—6.92 (m, 10H, ArH), 6.57 (t, J=7.5 Hz, 1H, ArH), 6.32—6.144 (m, 7H, ArH), 0.87 [s, 9H, $C(CH_3)_3$]; ^{19}F NMR (282 MHz, C_6D_6) δ: −115.2 (m, 1F, ArF), −118.0 (m, 1F, ArF); ^{31}P NMR (121 MHz, C_6D_6) δ: 27.6 (m, Ph_3P); IR (KBr pellet) v: 3048 (w), 2952 (w), 2865 (w), 1602 (vs), 1536 (s), 1500 (s), 1435 (m), 1418 (m), 1174 (s), 1137 (s), 1097 (s), 963 (s), 849 (s), 745 (vs), 731 (vs), 691 (vs), 528 (vs), 511 (vs) cm^{-1}. Anal. calcd for $C_{41}H_{36}F_2NNiOP$: C 71.75, H 5.25, N 2.04; found C 71.67, H 5.36, N 1.95.

{2-[(*N*-3-Cl-4-FC_6H_3)-CHN]-η-6-*t*-Bu-C_6H_3O}Ni-(Ph)(PPh_3) (C13) Brown solid, yield 99%; m.p. 123—125 ℃; ^{1}H NMR (300 MHz, C_6D_6) δ: 7.81—7.75 (m, 6H, ArH), 7.40 (d, J_{H-P}=6.9 Hz, 1H, N=CH), 6.95—6.90 (m, 13H, ArH), 6.63—6.56 (m, 2H, ArH), 6.32—6.18 (m, 5H, ArH), 0.89 [s, 9H, $C(CH_3)_3$]; ^{19}F NMR (282 MHz, C_6D_6) δ: −121.7 (m, 1F, ArF); ^{31}P NMR (121 MHz, C_6D_6) δ: 40.6 (m, Ph_3P); IR (KBr pellet) v: 3046 (w), 2960 (w), 2906 (w), 2867 (w), 1604 (vs), 1586 (s), 1536 (s), 1490 (s), 1420 (m), 1181 (s), 1094 (s), 726 (s), 692 (vs), 529 (s), 514 (s) cm^{-1}. Anal. calcd for $C_{41}H_{36}ClFNNiOP$: C 70.07, H 5.13, N 1.99; found C 70.25, H 5.22, N 1.83.

{2-[(*N*-C_6F_5)-CHN]-η-6-*t*-Bu-C_6H_3O}Ni(Ph)(PPh_3) (C14) Brown solid, yield 58%; m.p. 168—170 ℃; ^{1}H NMR (300 MHz, C_6D_6) δ: 7.76—7.72 (m, 6H, ArH), 7.40 (d, J_{H-P}=6.9 Hz, 1H, N=CH), 7.19—7.17 (m, 2H, ArH), 6.95—6.91, (m, 4H, ArH), 6.87—6.84 (m, 7H, ArH), 6.56 (t, J=7.5 Hz, 1H, ArH), 6.33—6.27 (m, 3H, ArH), 0.79 [s, 9H, $C(CH_3)_3$]; ^{19}F NMR (282 MHz, C_6D_6) δ: −147.5 (dd, J=22.5, 5.4 Hz, 2F, ArF), −161.6 (t, J=25.5 Hz, 1F, ArF), −165.0 (t, J=25.5 Hz, 2F, ArF); ^{31}P NMR (121 MHz, C_6D_6): 41.4 (m, Ph_3P); IR (KBr pellet) v: 3051 (w), 2942 (w), 2865 (w), 1604 (vs), 1593 (vs), 1535 (s), 1509 (vs), 1415 (s), 1347 (m), 1148 (m), 1099, 995 (vs), 751 (s), 732 (s), 696 (vs), 534 (s), 509 (s) cm^{-1}. Anal. calcd for $C_{41}H_{33}F_5NNiOP$: C 66.51, H 4.46, N 1.89; found C 66.37, H 4.60, N 1.90.

Oligomerization procedure

A 100 mL autoclave, equipped with a magnetic stir bar, was preheated at 100 ℃ under vacuum for 30 min and then cooled to the required temperature. Toluene was injected into the reactor and pressured with ethylene to 1 atm. After equilibrating for 20 min, the appropriate volume of catalysts solution and cocatalysts were

injected to start the reaction. The ethylene pressure was kept constant during the reaction. After the desired run time, the reactor was vented and the reaction mixture was terminated by ethanol. *n*-Heptane was added to the mixture as internal standard for GC analysis. An upper-layer clear solution was separated from the reaction mixture to analyze and quantify the soluble components by GC and GC-MS.

X-ray crystallography measurements

Single crystal X-ray diffraction studies for complex **C14** was carried out on a Bruker P4 diffractometer with graphite-monochromated Mo Kα radiation (k=0.71073) at 293(2) K. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 Package.

Conclusions

In summary, neutral arylnickel phosphine complexes **C1**—**C7**, **C9**—**C14** bearing *N*-fluorinated phenyl salicylaldimine chelate ligand showed considerable activities and high selectivies in oligomerization of ethylene. The complexes with more fluoro-substituents on the ligands exhibited higher activity than those with less fluoro-substituents. The catalytic activity and selectivity of the nickel complex were greatly affected by arched environment of corresponding ligand, the variation of Al/Ni molar ratio, the variety of cocatalyst, the reaction temperature and the pressure of ethylene.

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[13] CCDC 752856 and 752857 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (1223)336033.

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