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PAPER

Synthesis, structure, and ethylene polymerization behavior of nickel complexes based on benzoylmethylenetri(2-alkoxylphenyl)phosphorane†

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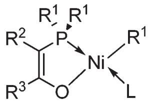
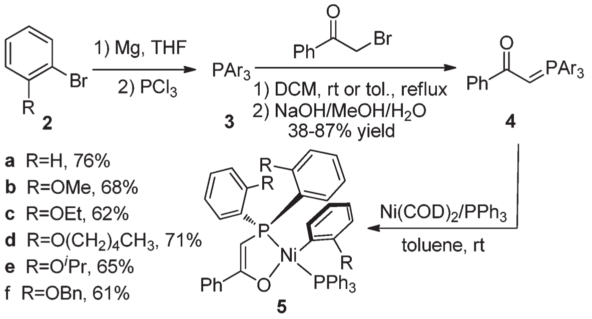
Several new nickel complexes are prepared by the treatment of the stabilized ylide benzoylmethylenetri(2-alkoxylphenyl)phosphorane with Ni(cod)$_2$ in the presence of PPh$_3$. X-Ray diffraction studies reveal that a distorted square planar geometry around Ni(II) is adopted. Upon treatment with Ni(cod)$_2$, the nickel complexes are sufficiently robust for ethylene polymerization. The existence of 2-alkoxyl-aryl substituents on phosphorus improves the catalytic activities. The highest activity (2.1×10^6 g mol^{-1} h^{-1}) is achieved when tri(2-isopropoxy-phenyl)phosphorane is employed (**5e**), which is one order higher than the corresponding SHOP catalyst. NMR analysis shows that the polyethylene mainly contains terminal double bonds and is highly linear.

Introduction

In recent years, late-transition metal based complexes as catalysts for the polymerization of olefins and functionalized olefins under moderate conditions have been of considerable interest because of their high functional group tolerance.[1] Of the catalysts developed, the family of nickel and palladium complexes based on either α-diimine[2] or salicylaldimine[3] have been investigated extensively. SHOP (Shell Higher Olefin Process)[4–6] type catalysts have been known for their unusual selectivity-controlling effect in the oligomerization of ethylene. They were also useful in catalyzing the ethylene into a polymer in the presence of bis(cyclooctadiene)nickel (Ni(cod)$_2$). To date, efforts have been made to improve their activity and broaden the scope of their application. Most of the modifications are focused on R^2 and R^3 groups of the chelating carbon backbone and/or the ligand **L** (Scheme 1).[7] For example, Ostoja-Starzewski and Witte disclosed a kind of nickel complex which is highly active leading to highly linear polyethylene.[7a] Gibson and his co-workers successfully enhanced the ethylene polymerization activity on introduction of bulky substituents at the site adjacent to the oxygen donor group (Scheme 2).[7e,f] However, very few examples involved the influence of the properties of R^1 on the catalytic olefin polymerization behaviors. The only example was reported by Gibson *et al.*, in which they had found that the introduction of *ortho*-methylphenyl groups on the phosphorus resulted in the reduction of the activity compared with the parent [P,O]Ni catalyst.[7e] During our ongoing research into ylide chemistry[8] and metal complex catalyzed olefin polymerization,[9] we found recently that the 2-alkoxyl group of the phenyl of phosphorane in SHOP-type nickel complexes could enhance the activity of ethylene polymerization significantly. In this paper, we will report the results.



Scheme 1 Structure of SHOP-type complexes.



Scheme 2 Synthesis of the ylides and nickel complexes.

Results and discussion

Design, synthesis, and characterization of complexes

It was found that introducing a pendant donor in the ligand can either stabilize a Lewis acidic metal center or modify the

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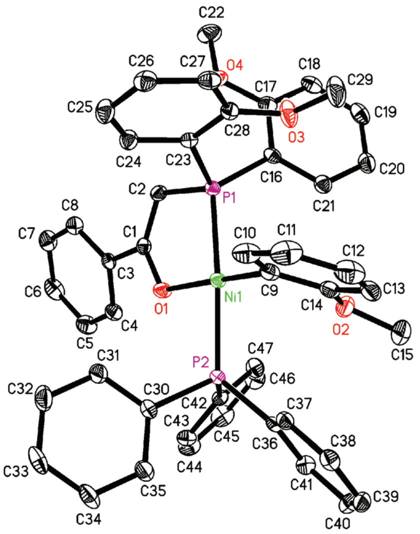

Fig. 1 Molecular structure of complex **5b**.

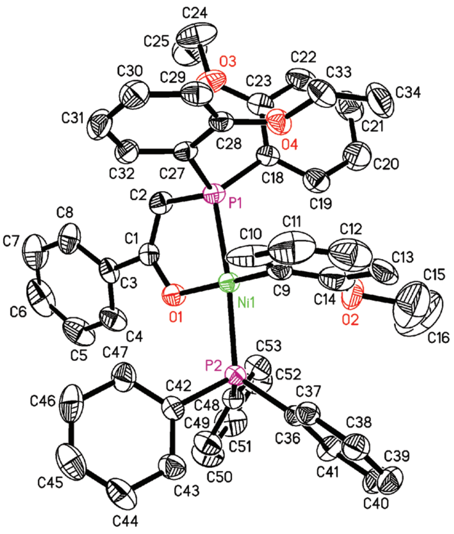

Fig. 2 Molecular structure of complex **5c**.

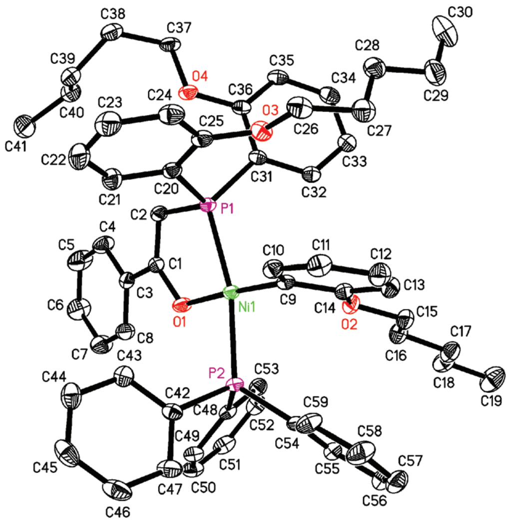

Fig. 3 Molecular structure of complex **5d**.

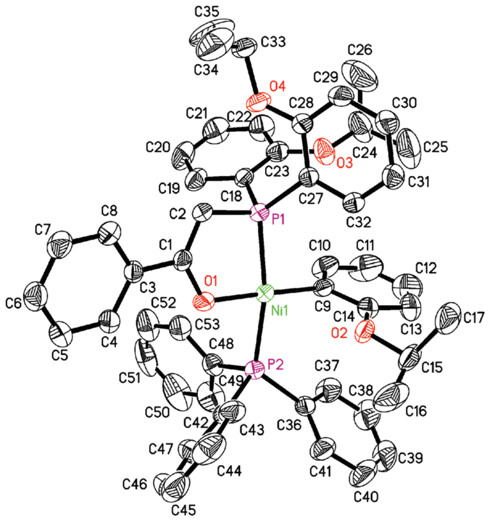

Fig. 4 Molecular structure of complex **5e**.

geometry around the metal and thus tune the catalytic behaviors of the complexes.[10] By employing this strategy, we recently designed several catalysts for olefin polymerization, which showed unique properties such as increasing activity and improving tolerance of impurity.[9] On the basis of these studies, we designed and synthesized nickel complexes based on benzoylmethylenetri(2-alkoxylphenyl)phosphorane **5**.

Complex **5** was readily prepared in 61–76% yields by the oxidative addition of the β-keto phosphorus(V) ylide **4** to Ni(cod)$_2$ in the presence of PPh$_3$ according to the literature method.[4] The ylides **4** were easily available from the corresponding phosphonium salts, which were synthesized by treating tri(2-alkoxyaryl)phosphines with α-bromoacetophenone in CH$_2$Cl$_2$ at room temperature or in refluxed toluene. All complexes were well characterized by ^{1}H NMR, ^{31}P NMR, ^{13}C NMR, and elemental analysis. The ^{31}P NMR analysis of the complexes shows a typical AB signal at around 20 ppm. The molecular structures of **5** were further determined by X-ray diffraction (Fig. 1–4) and the selected bond lengths (Å) and angles (°) of **5b**, **5c**, **5d**, and **5e** are summarized in Table 1.

As shown in Fig. 1, nickel complex **5b** adopts a distorted square planar geometry around nickel. The P1, C9, P2 and O1 atoms are nearly coplanar, with P1 and P2 occupying the trans position (bond angles of P2–Ni–P1 and O1–Ni–C9: 170.37(3)° and 173.18(10)°). The 2-MeOC$_6$H$_4$ rings on phosphorus are inclined by 82.51° and 64.27° to this plane. Comparing with the reported SHOP nickel complexes,[4,7e] the bond length of Ni–P1 is lengthened (2.1833(7) Å *vs.* 2.168 and 2.165(1) Å) because of the introduction of steric hindrance around phosphorus. Whereas both the length of Ni–P2 and Ni–O1 are shorter than those of **5a** (2.2184(7) Å *vs.* 2.230 Å and 1.9048(16) Å *vs.* 1.914 Å). Noticeably, the distance between Ni and O2 is shorter than the sum of the Ni and O van der Waals radii (2.985 Å *vs* 3.15 Å),[11] indicating a weak interaction between O2 and Ni atoms.

The molecular structures of **5c**, **5d**, and **5e** are similar to that of **5b**. In all cases, a distorted square planar geometry around

Table 1 Selected bond lengths (Å) and angles (°) for **5b**, **5c**, **5d**, and **5e**

	5b	**5c**	**5d**	**5e**
Ni(1)–C(9)	1.889(3)	1.898(6)	1.881(5)	1.890(2)
Ni(1)–P(2)	2.2184(7)	2.2168(14)	2.2243(13)	2.2078(7)
Ni(1)–O(1)	1.9048(17)	1.901(3)	1.905(3)	1.8959(17)
Ni(1)–P(1)	2.1833(7)	2.1928(14)	2.1768(13)	2.1785(7)
O(1)–C(1)	1.313(3)	1.306(6)	1.317(4)	1.313(3)
C(1)–C(2)	1.355(3)	1.339(7)	1.337(5)	1.360(3)
C(2)–P(1)	1.775(2)	1.768(5)	1.768(4)	1.772(2)
C(9)–Ni(1)–O(1)	173.18(10)	172.1(2)	177.76(18)	176.77(9)
C(9)–Ni(1)–P(1)	96.21(8)	95.11(16)	95.20(13)	96.72(7)
O(1)–Ni(1)–P(1)	86.21(6)	85.82(11)	86.07(9)	86.15(5)
C(9)–Ni(1)–P(2)	92.96(8)	93.91(16)	90.17(13)	91.97(7)
O(1)–Ni(1)–P(2)	85.00(6)	85.28(11)	88.99(9)	85.43(5)

nickel atom is adopted. P1, C9, P2 and O, and Ni are nearly coplanar. All 2-ROC_6H_4 rings are oriented nearly orthogonally to this plane (to phenyl ring A: 75.62° (**5c**) to 73.72° (**5d**); to phenyl ring B: 63.22° (**5c**) to 69.70° (**5d**)). No matter the steric hindrance of the OR group, the angles around phosphorus are similar: C2–P1–Ni varied from 98.14(19)° to 98.98(2)°. All of the distances between Ni and O2 are shorter than the sum of the Ni and O van der Waals radii,[11] and the distances of Ni–O2 decrease in the order of OEt (2.963 Å, **5c**) > $O(CH_2)_4CH_3$ (2.904 Å, **5d**) > O^iPr (2.871 Å, **5e**), suggesting a gradually stronger O2⋯Ni interaction in the complexes with the increasing of steric hindrance. We attempted to develop crystals of complex **5f** suitable for X-ray analysis but failed.

Ethylene polymerization

In the presence of a phosphine scavenger $Ni(cod)_2$, complexes **5a–f** were investigated as catalysts for ethylene polymerization. As shown in Table 2, in contrast to the parent SHOP catalyst, the introduction of the alkoxyl group at the *ortho* position of the phenyl group on the phosphorus improved the activity evidently. For instance, compared with **5a**, the installation of OMe group nearly quadrupled the activity when ethylene was polymerized under a 10 atmosphere pressure at 60 °C for 1 hour (entries 1 and 2). Under the same conditions, replacing OMe with the OEt group further increased the activity to 7.28×10^5 g mol^{-1} h^{-1} (entries 2 and 3). When OBn was introduced, the activity reached 6.26×10^5 g mol^{-1} h^{-1} (entry 8). These results suggest that the steric hindrance of the alkoxyl groups on phosphorus influences the catalytic behavior apparently. The influence of the steric hindrance on the activity was further supported by comparing the results of ethylene polymerization promoted by complexes **5d** and **5e**. By employing complex **5e** bearing O^iPr groups, the highest activity of 21.06×10^5 g mol^{-1} h^{-1} was obtained, which is one order higher than that of **5a** (entries 5 *vs.* 1). In the presence of **5e** and $Ni(cod)_2$, increasing the polymerization temperature from 60 °C to 75 °C, a slightly reduced activity was observed (entries 5 *vs.* 6). Further increasing the polymerization temperature to 90 °C halved the activity, demonstrating that this catalyst is quite stable considering the solubility of ethylene in toluene at 90 °C is lower than that at 60 °C (entry 7). We proposed that the introduced alkoxyl group can stabilize the active species. For example, in the case of **5d** being applied in the ethylene polymerization at 60 °C and 10 atm, the activity was nearly sustained when the reaction time was lengthened from 1 h to 4 h (entries 4 *vs.* 10), which is clearly different from that of **5a**. These results showed that the modification by introduction of an alkoxyl group at the 2-position of a phenyl group on the phosphorus of a SHOP-type catalyst could improve the catalytic behavior of ethylene polymerization. The probable reason is that there is a weak interaction between nickel and the oxygen (either O3 or O4) of the alkoxyl group, which tuned the electronic properties and stabilized the catalytic species. Many attempts to grow a single-crystal without a PPh_3 group failed. The true role will be further investigated.

Table 2 Ethylene polymerization results with complexes **5**

Entry^a	Catalyst	Temp (°C)	Time (hour)	Yield (g)	$M_v{}^b$ (g mol^{-1})	Activity (10^5 g mol^{-1} h^{-1})
1	**5a**	60	1	0.52	3500	1.04
2	**5b**	60	1	1.98	1700	3.96
3	**5c**	60	1	3.64	1100	7.28
4	**5d**	60	1	2.06	1400	4.12
5	**5e**	60	1	10.53	1300	21.06
6	**5e**	75	1	8.75	1800	17.50
7	**5e**	90	1	5.14	1600	10.28
8	**5f**	60	1	3.13	4300	6.26
9	**5a**	60	4	0.95	5500	0.47
10	**5d**	60	4	8.76	2800	4.38

[a] Conditions: 5 μmol catalyst, 50 μmol $Ni(cod)_2$, solvent: toluene, V_{total} 50 mL, ethylene pressure: 10 atm. [b] M_v measured as ASTM D 1601.

^1H NMR analysis shows that the polyethylene generated consists of about 90% terminal double bonds and high linearity. When OR is an alkoxyl group, a low molecular weight is obtained no matter the steric bulk of R. While a higher molecular weight for PE was observed in the case of R being a benzyl group.

Conclusions

In summary, a series of tri(2-alkoxylphenyl)phosphorane derived SHOP-type nickel complexes have been designed and synthesized by the reaction of benzoylmethylenetri(2-alkoxylphenyl)phosphorane with $Ni(cod)_2$. In the presence of ethylene. The highest activity of 2.1×10^6 g mol^{-1} h^{-1} was achieved when an O^iPr group was installed. X-Ray crystallographic studies confirmed the molecular structures and a gradually stronger O2⋯Ni interaction is observed with the increasing in the bulkiness of the R group. This provides an efficient way to modify SHOP catalysts for olefin polymerization. Further investigations are in progress in our laboratory.

Experimental section

General information

All air or moisture sensitive manipulations were carried out under a nitrogen atmosphere using Schlenk techniques. ^1H NMR, ^{13}C NMR, ^{31}P NMR spectra were recorded on Varian Mercury 300 spectrometer and Varian 400 MR spectrometer.

Table 3 Summary of crystallographic data for **5b–5e**

	5b	**5c**	**5d**	**5e**
Formula	$C_{47}H_{42}Ni_4O_4P_2$	$C_{50}H_{48}NiO_4P_2$	$C_{59}H_{66}NiO_4P_2$	$C_{53}H_{54}NiO_4P_2$
*F*w	791.46	833.53	959.79	875.61
Cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*C*2/*c*	*P*2(1)/*n*	*P*2(1)/*c*
a, Å	18.1954 (3)	41.597(3)	14.5218(3)	17.5838(15)
b, Å	10.2494(5)	10.8709(8)	23.7365(5)	13.0885(11)
c, Å	21.1754(10)	21.9171(16)	18.5141(4)	20.7174(18)
V, Å3	3935.2(3)	8712.7(11)	5893.8(2)	4726.7(7)
Z	4	8	4	4
D(calcd), Mg m^{-3}	1.336	1.271	1.179	1.230
2θ range, °	1.93 to 26.00	2.09 to 25.50	3.19 to 67.48	1.85 to 25.50
F(000)	1656	3504	2240	1848
Reflections collected/ unique	48 022/7714[*R*(int) = 0.0507]	22 539/8099[*R*(int) = 0.0686]	39 123/10 463[*R*(int) = 0,0240]	24 458/878[*R*(int) = 0.0916]
Data/restraints/parameters	7714/0/490	8099/25/518	10 463/7/624	8783/0/547
Goodness of fit	1.063	0.913	1.026	0.864
R_1 ($I > 2\sigma(I)$)	0.037	0.066	0.052	0.056
wR_2 ($I > 2\sigma(I)$)	0.095	0.160	0.152	0.127

Mass spectra were carried out with a HP5989A spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. M_V was measured by an Ubbelohde Viscometer for testing the dilute solution viscosity as ASTMD 1601 at 135 °C in decahydronaphthalene, the molecular weight correlating with intrinsic viscosity equation is $M_v = 5.37 \times 10^4\ [\eta]^{1.37}$. Toluene, hexane, CH_2Cl_2 and other solutions were purified by MB SPS-800 system. $Ni(cod)_2$ was purchased from Alfa Aesar.

X-Ray structure determination

Crystal data[12] and details of data collection and structure refinements are given in Table 3. Data for **5b**, **5c**, and **5e** were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo K (λ = 0.71073 Å) radiation. Data for **5d** were collected at 133 K on a Bruker APEXII diffractometer using Cu K (λ = 1.54178 Å) radiation. An empirical absorption was applied using the SADABS program. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F2 using the SHELXTL program package. All hydrogen atoms were geometrically fixed using the riding model.

Typical procedure for the synthesis of nickel complexes

Using **5b** as an example, to a solution of $Ni(cod)_2$ (2.0 g, 7.27 mmol) in toluene (50 mL) was added a mixture of ylide **4b** (1.91 g, 7.27 mmol) and PPh_3 (1.91 g, 7.27 mmol) in toluene (150 mL) at 0 °C. The resulting mixture was stirred for 24 hours at room temperature and 2 hours at 50 °C. After filtration, the solvent was removed under reduced pressure to afford yellow powder, which was recrystallized in toluene–hexane (v/v: 10/1) to give the pure product **5b**.

{[Ni(2-OMeC$_6$H$_4$)$_2$P═CHC(Ph)O][(2-OMeC$_6$H$_4$)PPh$_3$]} (5b). Yield 3.93 g, 68%. ^{1}H NMR (300 MHz, C_6D_6): δ 8.74 (dd, 1H, *J* = 7.8 Hz, 13.8 Hz), 7.81–7.70 (m, 8H), 7.55–7.52 (m, 2H), 7.03–6.80 (m, 16H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.53 (dd, *J* = 3.9 Hz, 5.1Hz, 1H), 6.42–6.32 (m, 2H), 5.73 (d, *J* = 7.8 Hz, 1H), 5.54 (s, 1H, –C═C*H*), 3.22 (s, 3H, –OC*H*$_3$), 3.12 (s, 3H, –OC*H*$_3$), 2.90 (s, 3H, –OC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.9, 179.8, 179.6, 179.5, 162.1, 162.1, 160.8(8), 160.8(4), 160.6, 138.6, 138.4, 137.2, 137.18, 136.2, 136.0, 134.4, 134.3, 133.0, 132.9, 132.8, 132.5(5), 132.5(1), 132.4, 132.2, 132.0, 131.9, 130.9, 130.3, 129.0, 128.7, 128.5, 128.4, 128.2, 127.7, 127.5, 127.4, 127.1, 127.0, 122.6, 122.1, 121.7, 121.6 120.3, 120.2, 120.0, 119.9, 118.6, 110.7(4), 110.7, 110.0(3), 110.0(0), 106.6, 78.7, 78.2, 77.3, 55.3, 55.1, 53.5. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 23.87 (d, *J* = 291.4 Hz), 17.51 (d, *J* = 291.4 Hz). Anal. calcd for $C_{47}H_{42}NiO_4P_2$: C, 71.32; H, 5.35; found: C, 70.79; H, 5.82.

{[Ni(2-OEtC$_6$H$_4$)$_2$P═CHC(Ph)O][(2-OEtC$_6$H$_4$)PPh$_3$]} (5c). Yield: 0.26 g, 62%. ^{1}H NMR (300 MHz, C_6D_6): δ 8.78–8.71 (m, 1H), 8.01–7.95 (m, 1H), 7.51–7.46 (m, 6H), 7.46–6.95 (m, 17H), 6.88 (t, *J* = 7.2 Hz, 1H), 6.57–6.50 (m, 2H), 6.50–6.40 (m, 2H), 6.15–6.02 (m, 1H), 5.66 (d, *J* = 7.5 Hz, 1H), 5.20 (s, 1H, –C═C*H*), 3.78 (t, *J* = 7.2 Hz, 1H, –OC*H*$_2$CH$_3$), 3.56 (t, *J* = 6.6 Hz, 1H, –OC*H*$_2$CH$_3$), 3.40 (t, *J* = 6.6 Hz, 2H, –OC*H*$_2$CH$_3$), 3.11 (t, *J* = 5.4 Hz, 1H, –OC*H*$_2$CH$_3$), 2.99 (t, *J* = 7.5 Hz, 1H, –OC*H*$_2$CH$_3$), 1.40 (t, *J* = 6.3 Hz, 3H, –OCH$_2$C*H*$_3$), 0.73 (t, *J* = 6.3 Hz, 3H, –OCH$_2$C*H*$_3$), 0.25 (s, 3H, –OCH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.1, 180.0, 179.8, 179.7, 161.8, 160.4, 160.0, 138.5, 138.3, 137.4, 136.1, 135.8, 134.5, 134.3, 132.3, 132.2, 131.8(9), 131.8(5), 131.8, 131.5, 130.3, 130.0, 129.2, 129.0, 127.7, 127.5, 127.4, 127.1, 127.0, 124.0, 123.3, 122.8, 122.2(3), 122.2(0), 121.8, 119.8, 119.6, 119.5, 118.2, 109.9, 107.3, 78.9, 78.2, 77.4, 63.0, 62.2, 61.5, 15.4, 13.8, 13.3. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 23.83 (d, *J* = 292.1 Hz), 19.84 (d, *J* = 293.5 Hz). Anal. calcd for $C_{50}H_{48}NiO_4P_2$: C, 72.05; H, 5.80; found: C, 72.12; H, 5.85.

{[Ni(2-OC$_5$H$_{11}$C$_6$H$_4$)$_2$P═CHC(Ph)O][(2-OC$_5$H$_{11}$C$_6$H$_4$)PPh$_3$]} (5d). Yield: 0.68 g, 71%. ^{1}H NMR (300 MHz, C_6D_6): δ 9.19–9.14 (m, 1H), 8.37–8.36 (m, 1H), 7.75–7.60 (m, 6H), 7.60–7.50 (m, 2H), 7.28–7.20 (m, 2H), 7.14–6.80 (m, 14H), 6.70–6.61 (m, 2H), 6.47 (t, *J* = 8.4 Hz, 2H), 6.31 (t, *J* = 7.2 Hz, 1H), 5.86 (d, 1H, *J* = 7.8 Hz), 5.66 (s, 1H, –C═C*H*), 3.70–3.55 (m, 1H), 3.50–3.38 (m, 1H), 3.32–3.20 (m, 2H), 3.07–2.91(m, 2H), 1.97–0.30 (m, 27H). ^{13}C NMR (100 MHz, C_6D_6): δ 181.1, 180.9(2), 180.9(0), 180.8, 162.7, 161.4, 160.3, 139.2, 139.1, 137.9, 136.7, 135.0, 134.9, 133.0, 132.8, 132.7, 132.4, 130.8, 130.4, 129.5, 129.3, 127.8, 127.7, 127.6, 124.7, 123.4, 122.9, 122.4, 120.3, 119.1, 110.7, 110.3, 108.3, 79.6, 79.1, 67.7, 67.1, 31.9, 30.2, 29.2, 28.9, 28.5, 28.3, 28.1, 23.2, 23.0, 22.9, 22.8, 14.4, 14.3, 14.2. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ 22.86 (d, *J* = 291.2 Hz), 19.79 (d, *J* = 296.6 Hz) Anal. calcd for $C_{59}H_{66}NiO_4P_2$: C, 73.83; H, 6.93; found: C, 74.44, H, 7.15.

{[Ni(2-O^{i}PrC$_6$H$_4$)$_2$P═C(Ph)O][(2-O^{i}Pr-C$_6$H$_4$)PPh$_3$]} (5e). Yield: 0.57 g, 65%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (brs, 1H), 8.10–7.96 (m 1H),7.52–7.07 (m, 23H), 6.90 (t. *J* = 6.9 Hz, 1H), 6.70–6.58(m, 2H), 6.54 (t, *J* = 7.2 Hz, 1H), 6.32–6.24(m, 1H), 6.13 (t, *J* = 6.9 Hz, 1H), 6.06 (t, *J* = 6.9 Hz, 1H), 5.87 (d, *J* = 8.1 Hz, 1H), 5.36 (s, 1H, –C═C*H*), 4.40–4.36 (m, 1H, –OC*H*(CH$_3$)$_2$), 4.02–3.82 (m, 2H, –OC*H*(CH$_3$)$_2$), 1.52 (d, 3H, *J* = 4.8 Hz, –OCH(C*H*$_3$)$_2$), 1.22 (d, 3H, *J* = 5.1 Hz, –OCH(C*H*$_3$)$_2$), 1.15 (d, 3H, *J* = 5.1 Hz, –OCH(C*H*$_3$)$_2$), 0.78 (d, 3H, *J* = 5.7 Hz, –OCH(C*H*$_3$)$_2$), 0.69 (brs, 3H, –OCH(C*H*$_3$)$_2$), 0.27 (brs, 3H, –OCH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): 179.5, 179.3, 179.2, 179.1, 161.1, 159.4, 158.9, 157.9, 138.4, 1382, 137.8, 137.7, 137.0, 136.8, 134.5, 134.4, 132.8, 132.2, 132.1, 131.9, 131.8, 131.5, 131.1, 130.7, 130.3, 129.6, 129.0, 127.5, 127.4, 127.0, 127.0, 124.3, 124.1, 123.8, 123.6, 123.1, 123.0, 123.6, 122.4, 121.9, 119.6, 119.4, 119.0, 118.0, 111.4, 110.5, 109.6, 108.3, 80.1, 79.9, 79.5, 79.3, 69.0, 68.3, 67.8, 67.3, 22.8, 22.2, 21.8, 21.0, 20.3. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 21.24 (d, *J* = 296.3 Hz), 17.81 (d, *J* = 294.5 Hz) Anal. calcd for $C_{53}H_{54}NiO_4P_2$: C, 72.70; H, 6.22; found: C, 72.24; H, 6.54.

{[Ni(2-OBnC$_6$H$_4$)P═CHC(Ph)O][(2-OBnC$_6$H$_4$)PPh$_3$]} (5f). Yield: 0.62 g, 61%. ^{1}H NMR (300 MHz, C_6D_6): δ 9.25–9.22 (m, 1H), 8.37–8.35 (m, 1H),7.83–7.78 (m, 2H), 7.71–7.65 (m, 8H), 7.48–7.45 (m, 2H), 7.33–7.20 (m, 7H), 7.08–6.92 (m, 26H), 6.86–6.74 (m, 3H), 6.70–6.61 (m, 5H), 6.48 (d, *J* = 8.7 Hz, 1H), 6.39 (t, *J* = 7.2 Hz, 1H), 5.86 (d, *J* = 7.8 Hz, 1H), 5.67 (s, 1H, –C═C*H*), 4.57–4.43 (m, 4H, –OC*H*$_2$Ph), 4.30 (d, *J* = 11.7, 1H, –OC*H*$_2$Ph), 4.09–4.05 (d, *J* = 11.4, 1H, –OC*H*$_2$Ph). ^{13}C NMR (75 MHz, C_6D_6): δ 180.9, 180.8, 162.6(9), 162.6(6), 160.6(3), 160.8, 159.6, 139.1, 139.0, 138.96, 138.9, 138.0, 137.4, 136.8, 134.9(8), 134.9(2), 134.8, 133.9, 133.6, 133.4(4), 133.4(0), 133.3, 132.6, 132.5, 132.4, 132.2, 131.6, 131.1, 130.8, 129.5, 128.9(6), 128.9(0). 128.8, 128.7(1), 128.7(0), 128.5(4), 128.5(1), 128.4, 128.3, 127.9(3), 127.9(0), 127.8, 127.7(4), 127.7(0), 127.5(3), 127.5(0), 127.4(4), 127.4(0), 127.3(2), 127.3(0), 127.2, 127.1, 127.0, 122.6, 121.2, 121.1, 121.0, 120.9(4), 120.9(0), 120.8, 119.7, 111.8, 111.3, 109.0, 79.5, 79.0, 70.2, 69.7, 69.0. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 22.56 (d, *J* = 303.5 Hz), 18.78 (d, *J* = 291.4 Hz). Anal. calcd for $C_{65}H_{54}NiO_4P_2$: C, 76.56; H, 5.34; found: C, 76.33; H, 5.23.

Ethylene polymerization

A 300 mL stainless-steel autoclave was heated to 100 °C under vacuum before use. The reactor was charged with a solution of **5** in toluene, followed by a solution of Ni(cod)$_2$ (10 equiv.) in toluene at the desired temperature under nitrogen atmosphere. Then the autoclave was pressurized by ethylene for 1 or 4 h. The reaction was quenched by venting the autoclave. The mixture was poured into a solution of acidified ethanol (200 mL of 10% HCl) and stirred for 12 hours. The polymer was isolated by filtration, washed with ethanol and dried under vacuum at 70 °C to constant weight.

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