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Note

Synthesis, characterization and catalytic behaviors of water-soluble phosphine-sulfonato nickel methyl complexes bearing PEG-amine labile ligand

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ABSTRACT

Two novel water-soluble phosphine-sulfonato nickel (II) methyl complexes [(P^O)NiMeL] (P^O = κ^2-*P,O*-2-(2-MeO-C_6H_4)$_2$P$C_6H_4SO_3$, L = $H_2N(CH_2CH_2O)_n$Me, *n* = *ca.* 52, **2a**; *n* = *ca.* 16, **2b**) have been prepared and characterized by ^{1}H, ^{31}P NMR and elemental analysis, and their reactivity towards ethylene was studied.

1. Introduction

Olefin polymerization by d^8 metal complexes has been studied intensely [1–7]. These late transition metal complexes are much more tolerant towards polar reagents in general by comparison to their highly oxophilic early transition metal counterparts. Thus, they can react with olefins to form polyethylene or copolymer with electron-deficient vinyl monomers such as acrylates [8–11]. In some cases polymerizations reaction can be carried out in aqueous systems to afford dispersions of submicron particles [12,13]. The water-soluble catalytic precursors, for example, Ni(II) salicylaldiminato complexes [(N^O)NiMe(L)], could afford nanoparticles with sizes of only *ca.* 10–30 nm – a size range which is challenging to access by any given polymerization type [14,15]. Such particles can be served as crystalline mesoscopic building blocks for ultrathin films [16–18].

In 2002 Drent et al. described for the first time the use of chelating SHOP-type phosphine-sulfonato ligand [P^O]$^-$ (Scheme 1) to stabilize Pd(II) catalytic system that could generate linear copolymers by random incorporation of ethylene and a variety of acrylates monomers [19]. This seminal report brings a series of successful incorporations of polar comonomers in linear copolymer chains [20–32]. Compared with increasing reports of palladium complexes, little attention has been focused on the corresponding nickel complexes with sulfonato phosphine ligands [33–35]. Several lipophilic neutral nickel [(κ^2-[P^O])NiPh(PPh_3)] [33], {[(κ^2-[P^O])NiMe]$_2$(TMEDA)}(**1**) [35], and [(κ^2-[P^O])NiMe(-Pyr)] [35] have been synthesized and their catalytic behaviors in toluene and other organic media have also been carefully investigated.

Previously we have prepared several water-soluble PEG-amine Pd(II) phosphine-sulfonato methyl complexes [(κ^2-[P^O])PdMe(L)] (L = tri(sodiumphenylsulfonate) phosphine; $NH_2(CH_2CH_2O)_n$Me, *n* = *ca.* 52), and showed that their aqueous solutions could polymerize ethylene to *ca.* 20 nm particles of low molecular weight linear polyethylene [36]. Herein we wish to report the hydrophilic phosphine-sulfonato nickel(II) methyl complexes [(κ^2-[P^O])NiMe(L)] (Scheme 2) comprising PEG-amine labile groups, and their reactivities towards ethylene and catalytic properties in aqueous media and non-aqueous systems were also investigated.

2. Results and discussion

Reactions of {[(κ^2-[P,O])NiMe)]$_2$($NMe_2CH_2CH_2NMe_2$)} (**1**) [22] with 1.0 equiv. of $H_2N(CH_2CH_2O)_n$Me (*n* = *ca.* 52 or 16) (for short, PEG-amine) in DMF afforded the corresponding hydrophilic nickel complexes **2a** and **2b** (Scheme 1). Both **2a** and **2b** are soluble in degassed water (solubility > 100 μmol/L) and stable in the solid state under inert atmosphere at room temperature. The identity and purity of these complexes were unambiguously established by NMR and elemental analysis. The ambient-temperature ^{1}H NMR spectra of PEG-amine complexes **2a** and **2b** contain one doublet for the Ni–CH_3 hydrogens ($^3J_{PH}$ = 6.8 Hz) resonance. The ^{31}P NMR spectra contain two singlets at δ 14.55 for **2a** and 14.58 ppm for **2b**, respectively (Fig. 1).

Rieger et al. have showed that nickel phenyl complex [(κ^2-[P^O])NiPh(PPh_3)] could be used in an emulsion polymerization

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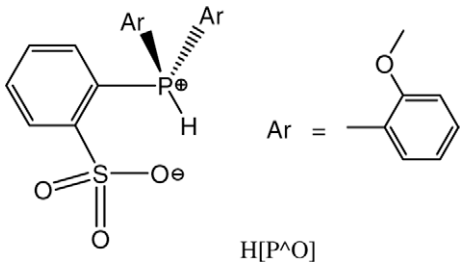


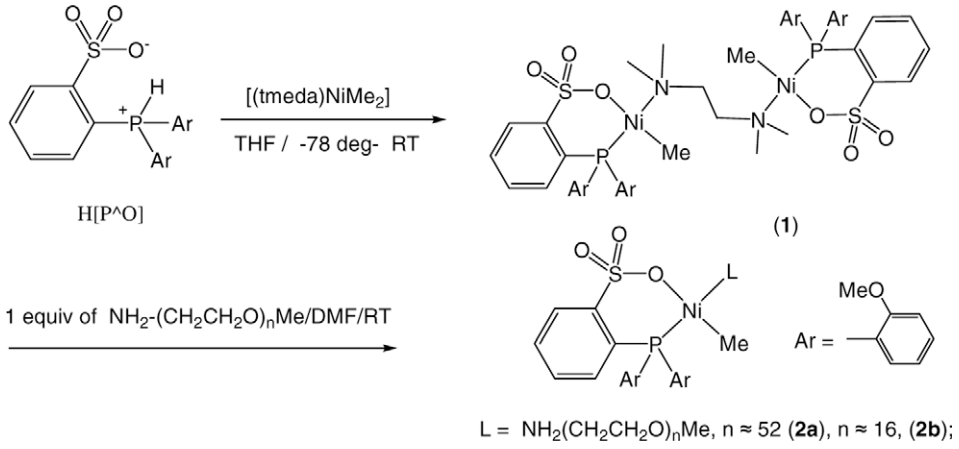
Scheme 1. The phosphine-sulfonato fragment.

to afford a latex of low molecular weight polyethylene in a very low yield [33]. A similar palladium methyl complex [(κ^2-[P^O])Pd-Me(PPh_3)] has also been prepared by Jordan and co-workers [25]. For comparison, nickel methyl complex [(κ^2-[P^O])NiMe(PPh_3)] (**3**) was synthesized. In the NMR spectra of **3**, a $^3J_{PH}$ (10 Hz) triplet resonance at −1.24 ppm for the methyl group, and a large $^2J_{PP}$ value (292 Hz) with two doubles at δ 25.16 and 2.17 ppm are observed, consistent with a *cis* arrangement of the methyl and the phosphine group (Fig. 2). The similar ^{31}P resonances and coupling constant $^2J_{PP}$ have been achieved for [(κ^2-[P^O])NiPh(PPh_3)] (δ = 18.1(d), 3.02(d), $^2J_{PP}$ = 285.0 Hz) [33] and [(κ^2-[P^O])NiPh(PPh_3)] (δ = 27.3(d), 7.90(d), $^2J_{PP}$ = 403 Hz) [25].

Table 1 summaries the ^{1}H and ^{31}P NMR data of reported nickel and palladium complexes with phosphine-sulfonato ligand [P^O]. In the whole, the chemical shifts of Ni–CH_3 are located at lower field region of about 1.0 ppm than those of Pd–CH_3. In ^{31}P NMR spectra, the same shift tendency of phosphine signals (no less 5.0 ppm) and bigger coupling constant (*ca.* 290 vs. 405) were observed.

Ethylene polymerizations employing the water-soluble nickel complexes **2a** and **2b** in neat water have been carefully tested. Unfortunately, both of them are inactive towards ethylene under this condition. The same result was also obtained for hydrophilic complexes **2a** and **2b** and lipophilic complex **3** using an emulsion process in CH_2Cl_2/H_2O solution or in the presence of cocatalyst $Ni(COD)_2$.

For further understanding of the loss of activity of this kind of organonickel catalysts in water, the reactivity of complex **2a** towards water was studied by NMR spectroscopy (Fig. 3). Firstly, the ^{1}H NMR spectrum of **2a** in neat DMSO-d^6 solution showed no obvious change even after the solution was heated to 70 °C. Secondly, the similar ^{1}H NMR study indicates that **2a** is stable in DMSO-d^6/D_2O (v/v: 2/1) solution. The Ni–Me signal coalesces with each other to a broader peak at 70 °C, which may be a simple dynamics of **2a**. Thirdly, the DMSO-d^6/D_2O (v/v: 2/1) solution of **2a** is stable at room temperature upon addition of ethylene to



Scheme 2. Synthesis of the hydrophilic phosphine-sulfonato nickel methyl complexes.

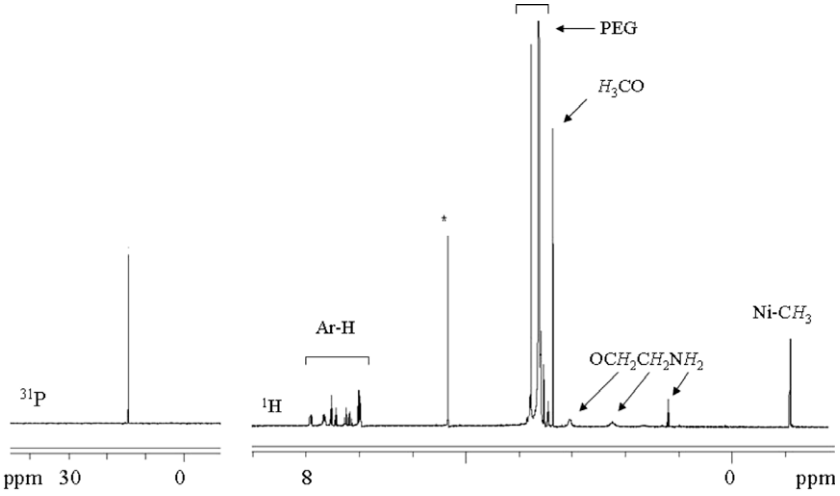


Fig. 1. The ^{1}H NMR spectra (right), and ^{31}P (left) NMR spectra of CD_2Cl_2 solution of **2a** acquired at 25 °C. The asterisk presents the ^{1}H chemical shift signal of residual undeuterated CD_2Cl_2 solvent.

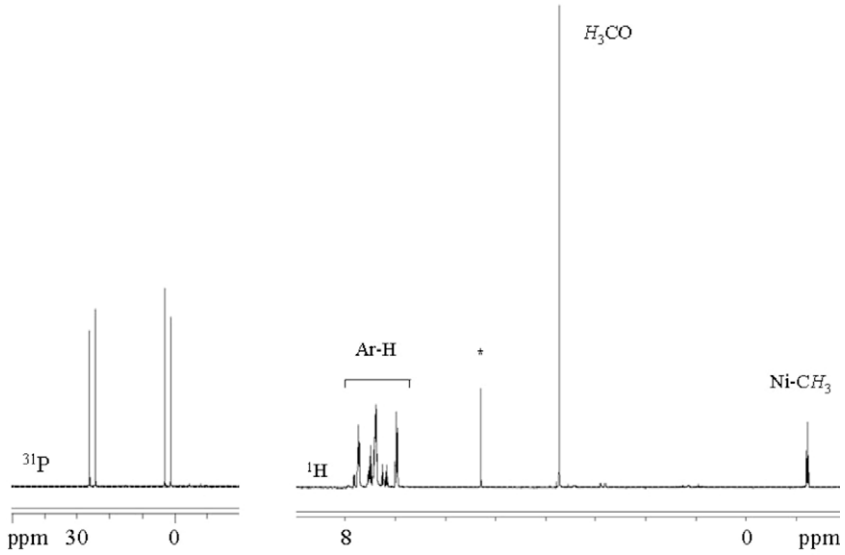


Fig. 2. The ^{1}H NMR spectra (right), and ^{31}P (left) NMR spectra of CD_2Cl_2 solution of **3** acquired at 25 °C. The asterisk presents the ^{1}H chemical shift signal of residual undeuterated CD_2Cl_2 solvent.

Table 1
Selected ^{1}H and ^{31}P NMR data of some phosphine-sulfonato nickel and palladium complexes.

Compound	^{1}H NMR δ [ppm] [M−CH_3] (M = Ni, Pd)	^{31}P NMR δ [ppm]	Reference
{(κ^2-[P,O])NiMe(Pyr)}	−0.99 (d, $^{3}J_{PH}$ = 7.2 Hz)	16.22 (s)	[35]
{(κ^2-[P,O])NiMe(NH$_2$(CH$_2$CH$_2$O)$_n$Me)} ($n \approx 52$) (**2a**)	−1.17 (d, $^{3}J_{PH}$ = 6.8 Hz)	14.55 (s)	This work
{(κ^2-[P,O])NiMe(NH$_2$(CH$_2$CH$_2$O)$_n$Me)} ($n \approx 16$) (**2b**)	−1.17 (d, $^{3}J_{PH}$ = 6.8 Hz)	14.58 (s)	This work
{(κ^2-[P,O])NiMe(PPh$_3$)} (**3**)	−1.24 (t, $^{3}J_{PH}$ = 10 Hz)	25.16 (d, $^{2}J_{PP}$ = 292 Hz), 2.17 (d, $^{2}J_{PP}$ = 292 Hz)	This work
{(κ^2-[P,O])Ni(Ph)(PPh$_3$)}	–	18.10 (d, $^{2}J_{PP}$ = 285 Hz), −3.02 (d, $^{2}J_{PP}$ = 285 Hz)	[33]
{(κ^2-[P,O])PdMe(Pyr)}	0.24 (s)	21.54 (s)	[22]
{(κ^2-[P,O])PdMe(NH$_2$(CH$_2$CH$_2$O)$_n$Me)} ($n \approx 52$)	0.04 (d, $^{3}J_{PH}$ = 2.8 Hz)	19.18 (s)	[36]
{(κ^2-[P,O])PdMe(PPh$_3$)}	−0.12 (t, $^{3}J_{PH}$ = 6.0 Hz)	27.3 (d, $^{2}J_{PP}$ = 403 Hz), 7.90 (d, ^{2}JPP = 403 Hz)	[25]

NMR conditions: 25 °C; $C_2D_2Cl_2$, ^{1}H: 400 MHz, ^{31}P: 161.8 MHz.

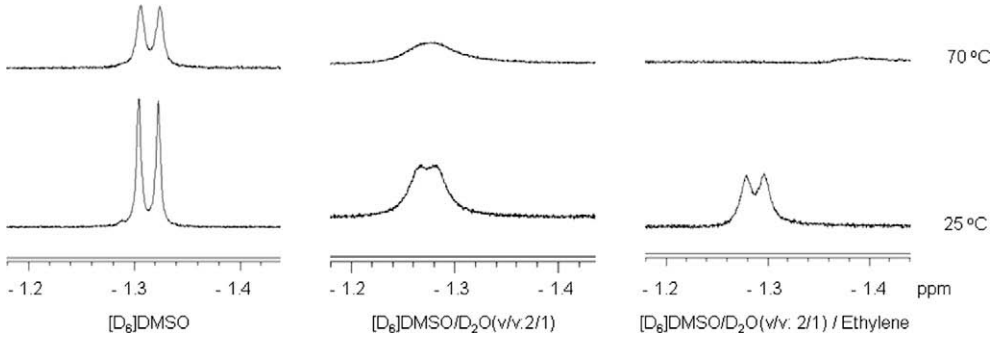


Fig. 3. High field region of ^{1}H NMR region of the Ni–Me signals of compound **2a** in DMSO-d^6 (left) and DMSO-d^6/D_2O (v/v: 2/1) with (right) or without ethylene (middle) at 25 °C and 70 °C. ^{1}H chemical shifts referenced to residual undeuterated DMSO solvent signal (δ 2.54 ppm).

the NMR tubes, which can be seen from its doublet signal of Ni–Me. Finally, when the above DMSO-d^6/D_2O solution of **2a** was heated to high-temperature in the presence of ethylene, Ni–Me signal disappeared quickly, which means that ethylene plays a role for the loss of activity of such neutral phosphine-sulfonato nickel methyl catalysts [37]. Moreover, unlike phosphine-sulfonato palladium methyl complexes, no nickel metal could be observed after NMR determinations at high-temperature in presence of 1 atm of ethylene [36].

Given that these phosphine-sulfonato nickel methyl complexes were inactive toward ethylene in aqueous media, we undertook the ethylene polymerization in non-aqueous toluene. Preliminary ethylene polymerization reactions were performed to find that unlike phenyl nickel complexes, these methyl nickel complexes showed high activities without $B(C_6F_5)_3$ or $Ni(COD)_2$ as scavengers. These nickel catalysts polymerize ethylene in toluene at 70 °C with activity over the TON range of 29 000–346 000 mol $[C_2H_4] \times mol^{-1}$ [Ni] h^{-1}. Ethylene polymerization results in toluene are summarized in Table 2.

The polymers have the similar chain structures to those produced by previously reported phosphine-sulfonato nickel catalysts but are slightly different from those obtained by

Table 2
Ethylene polymerization using nickel catalysts **1**–**3**.[a]

Entry	Catalyst	Time (min)	Yield (g)	TON[b]	M_n[c]	Internal unsat. (%)[c]	Me branches per 1000 C[d]
1	**1**	15	5.85	83 600	1196	45	12
2	**2a**	30	4.69	33 500	1154	47	14
3	**2b**	15	2.03	29 000	1140	48	13
4	**3**	15	24.22	346 000	980	48	13

[a] Polymerization conditions: 10 μmol of [Ni], 40 bar of C_2H_4, 100 mL of toluene, 70 °C.
[b] Mol $[C_2H_4] \times mol^{-1}$ [Ni] h^{-1}.
[c] Determined by ^1H NMR assuming that one double bond per chain.
[d] Determined by ^{13}C NMR at 115 °C in $C_2D_2Cl_4$.

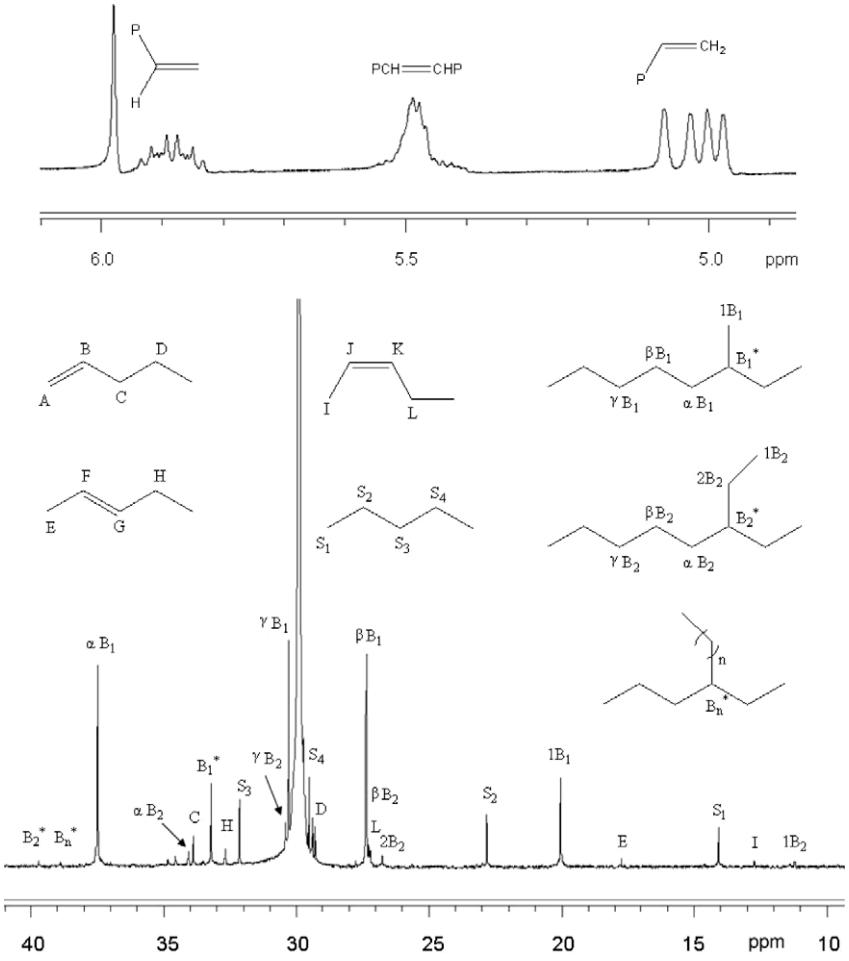


Fig. 4. The selected ^1H NMR (the above) and ^{13}C (the below) spectrum regions of polyethylene produced by nickel catalyst **2a** (Table 2, entry 2). The chemical shift is in units of δ. NMR conditions: 115 °C in $CDCl_2CDCl_2$.

palladium catalysts. Although these nickel complexes produce linear polyethylene with low levels of 10–14 methyl branches, ethyl and longer branches were observed from high-temperature ^{13}C NMR (Fig. 4). The ^1H NMR spectra of the polyethylenes contain resonances for internal double bonds chains (PCH═CHP′) besides terminal end group olefins (PCH═CH_2) (P and P′ represent polymer chain, Fig. 4). The mole ratio of internal-olefins and terminal-olefins seems a constant (near 1:1) although these nickel complexes have different labile ligands, such as tmeda (**1**), amine (**2a**, **2b**) and phosphine (**3**). Moreover, the polyethylenes obtained with these nickel complexes have number average molecular weight (M_n's) between 980 and 1420 which is much lower than polyethylene from other neutral nickel catalyst systems [38]. Another easily concluded point is that the labile ligand of nickel complexes has an influence to its catalytic activity. For example, complex **3** with a more labile phosphine-containing ligand, reveals a much higher activity than complexes **2a** and **2b** with nitrogen-containing ligands $NH_2(CH_2CH_2O)_nMe$ (Table 2, entry 4 vs. entries 2 and 3).

3. Conclusions

The coordination of hydrophilic poly(ethylene glycol)-substituted amine to the (κ^2-P,O-phosphine-sulfonato)NiMe fragment affords stable water-soluble complexes, which were isolated in high yield and fully characterized by NMR spectroscopy. These water-soluble neutral methyl nickel catalysts are stable in neat water, but revealed a rapid deactivation in the presence of ethylene. In spite of that these nickel complexes could efficiently catalyze ethylene polymerization to yield low molecular weight polyethylene.

4. Experimental

4.1. Materials and instrumentation

Unless noted otherwise, all manipulations of metal complexes were carried out under an inert atmosphere using standard glovebox or Schlenk techniques. Toluene and diethyl ether were distilled from sodium/benzophenone, and methylene chloride and DMF from CaH_2 under argon. Chemicals, $H_2N(CH_2CH_2O)_nMe$ (n = *ca.* 52, 16), and [(TMEDA)$NiMe_2$] (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) were purchased commercially and used as received. The phosphine-sulfonic acids ligand [P^O]H was synthesized by modified multi-step literature routes developed by Drent et al. and Jordan and co-workers [19,24–26,39–42]. Preparation of complexes {[(κ^2-[P,O])NiMe)]$_2$($NMe_2CH_2CH_2NMe_2$)} (**1**) was accomplished by reaction of the respective H[PO] with 1 equiv. of [(TMEDA)$NiMe_2$] in THF under an inert atmosphere in 81% yield [36].

NMR spectra were recorded on a Varian Unity INOVA 400 spectrometer. Chemical shifts were referenced to the residual ^1H, and ^{13}C solvent resonances, and to external 85% H_3PO_4 (^{31}P), respectively. Elemental analyses were performed up to 950 °C on an Elementar Vario EL. For high-temperature NMR spectroscopy of polyethylenes, a mixture of polymer and $CDCl_2CDCl_2$ in an NMR tube was heated to 115 °C, affording a homogeneous solution. The tube was inserted into a preheated NMR probe at 115 °C, and NMR spectra were obtained after a 5 min temperature equilibration period. Methyl branches were quantified from ^{13}C NMR spectra according to [43,44].

4.2. Synthesis of water-soluble phosphine-sulfonato nickel methyl complexes **2a** and **2b**

Complex **1** (0.05 mmol) and PEG-amine (0.10 mmol) of were dissolved in 3 mL of dry dimethylformamide (DMF) in a glove box and stirred for 1 h. The volatiles were carefully removed under vacuum. The resulting solid was triturated with diethyl ether (*ca.* 5 mL), washed twice with ether, and dried under vacuum overnight to afford complex water-soluble phosphine-sulfonato nickel methyl complexes.

{(κ^2-[P,O])NiMe($NH_2(CH_2CH_2O)_nMe$)} ($n \approx 52$) (**2a**) was obtained as a yellow solid in 83% yield. ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ −1.17 (d, J_{HP} = 6.8 Hz, 3H, Ni–CH_3), 2.19 (t, J_{HH} = 7, 2H, NH_2), 2.99 (br s, 2H,$CH_2CH_2NH_2$), 3.08 (br s, 2H, CH_2CH_2-NH_2), 3.32 (s, 3H, $CH_2CH_2OCH_3$), 3.40–3.59 (m, (CH_2CH_2)$_n$ and OCH_3), 3.73 (m, 4H, $CH_2CH_2OCH_3$), 6.95–7.01 (m, 5H), 7.15 (dd, J_{HH} = 8, J_{PH} = 1, 1H), 7.24 (t, J_{HH} = 8, 1H), 7.42 (m, 1H), 7.50 (t, J_{HH} = 8, 2H), 7.64(m, 2H), 7.90 (dd, J_{HH} = 8, J_{PH} = 6, 1H). $^{31}P\{1H\}$ NMR (162 MHz, 25 °C, CD_2Cl_2): δ 14.55 (s). Anal. Calc. for $C_{126}H_{234}NNiO_{57}PS$ (M = 2796.91 g mol^{-1}): C, 54.11; H, 8.43; N, 0.50. Found: C, 54.01; H, 8.37; N, 0.54%.

{(κ^2-[P,O])NiMe($NH_2(CH_2CH_2O)_nMe$)} (n = *ca.* 16) (**2b**) was obtained as yellow oil in 74% yield. ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ −1.17 (d, J_{HP} = 6.8 Hz, 3H, Ni–CH_3), 2.19 (t, J_{HH} = 7, 2H, NH_2), 2.99 (br s, 2H,$CH_2CH_2NH_2$), 3.09 (br s, 2H, CH_2CH_2-NH_2), 3.32 (s, 3H, $CH_2CH_2OCH_3$), 3.40–3.58 (m, (CH_2CH_2)$_n$ and OCH_3), 3.73 (m, 4H, $CH_2CH_2OCH_3$), 6.95–7.01 (m, 5H), 7.15 (dd, J_{HH} = 8, J_{PH} = 1, 1H), 7.24 (t, J_{HH} = 8, 1H), 7.42 (m, 1H), 7.50 (t, J_{HH} = 8, 2H), 7.64(m, 2H), 7.89 (dd, J_{HH} = 8, J_{PH} = 6, 1H). $^{31}P\{1H\}$ NMR (162 MHz, 25 °C, CD_2Cl_2): δ 14.58 (s). Anal. Calc. for $C_{54}H_{90}NNiO_{21}PS$ (M = 1211.02 g mol^{-1}): C, 53.56; H, 7.49; N, 1.16. Found: C, 53.29; H, 7.58; N, 1.22%.

4.3. Synthesis of {(κ^2-[P,O])NiMe(PPh_3)} (**3**)

Complex **2** (0.053 g, 0.05 mmol) and triphenylphosphine (0.026 g, 0.10 mmol) of were dissolved in 3 mL of dry DMF in a glove box and stirred for 1 h. The volatiles were carefully removed under vacuum. The resulting solid was triturated with diethyl ether (*ca.* 5 mL), washed twice with ether, and dried under vacuum overnight to afford a yellow solid in 87% yield. ^1H NMR (400 MHz, CD_2Cl_2): δ −1.24 (t, $^3J_{PH}$ = 10, 3H, Ni–*Me*), 3.74 (s, 6H, ArO*Me*),. 6.99–7.02 (m, 4H), 7.19 (dd, J_{HH} = 8, J_{PH} = 1, 1H), 7.27 (t, J_{HH} = 8, 1H), 7.47–7.38 (m, 10H), 7.49–7.58 (m, 4H), 7.76 (t, J_{HH} = 8, 6H), 7.83 (dd, J_{HH} = 8, J_{PH} = 6, 1H). $^{31}P\{1H\}$ NMR (162 MHz, CD_2Cl_2): δ 25.16 (d, J_{PP} = 292 Hz), 2.17 (d, J_{PP} = 292 Hz, PPh_3). Anal. Calc. for $C_{39}H_{36}NiO_5P_2S$ (M = 737.41 g mol^{-1}): C, 63.52; H, 4.92. Found: C, 63.41; H, 4.77%.

4.4. Ethylene polymerizations

The typical process for ethylene polymerizations of water-soluble complexes **2a** and **2b** in neat water, see Ref. [36].

The typical process for ethylene polymerizations of **2a**, **2b** and **3** of in emulsion process (CH_2Cl_2/H_2O), see Ref. [36].

The typical process for non-aqueous ethylene polymerizations of **2a**, **2b** and **3** of in toluene, see Ref. [36].

4.5. Variable temperature NMR experiments

Young-*J* NMR tubes were charged with solid complexes in a glove box. Generally, 10 mg of **2a** were dissolved in 500 μL of solvent. The tube was sealed, taken out of the box, and inserted into a preheated NMR probe at the desired temperature. NMR spectra were obtained after a 5 min temperature equilibration period.

For NMR experiments with ethylene, the Young-*J* NMR tube was charged with the solid complex and solvent in the glove box, and closed. The tube was removed from the box, and connected with a three way stopcock to the Schlenk line, and to the ethylene gas supply. The tube was cooled to −78 °C in a dry ice/isopropanol bath, and charged with *ca.* 1 atm of ethylene by several pump-fill cycles. The NMR tubes was sealed, warmed to room temperature, and shaken briefly prior to recording NMR spectra. For NMR experiments at elevated temperature, the tube was inserted into a preheated NMR probe at the desired temperature and NMR spectra were obtained after a 5 min temperature equilibration period.

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