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Bimetallic nickel complexes of macrocyclic tetraiminodiphenols and their ethylene polymerization

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Abstract

Schiff's base condensation of 2,6-diformyl-4-R-phenol and 4,4″-diamino-3,3″,5,5″-R'_4-*o*-terphenyl affords 34-membered macrocyclic tetraiminodiphenol compounds, *o*-$C_6H_4\{(R'_2C_6H_2)$–*N*=CH–$[RC_6H_2(OH)]$–HC=$N(R'_2C_6H_2)\}_2$(*o*-C_6H_4) (R = H and R′ = *i*Pr, **1**; R = Me and R′ = *i*Pr, **2**; R = F and R′ = *i*Pr, **3**; R = Me and R′ = Et, **4**; R = F and R′ = Et, **5**) in good yields (47–62%), from which dinuclear nickel complexes, *o*-$C_6H_4\{[(R'_2C_6H_2)$–N=CH–$(RC_6H_2$-O)–HC=$N(R'_2C_6H_2)$-κ^2-N,O]Ni(η^1-CH_2Ph)$(PMe_3)\}_2$(*o*-C_6H_4) (R = H and R′ = iPr, **6**; R = Me and R′ = *i*Pr, **7**; R = F and R′ = *i*Pr, **8**) are prepared. Molecular structures of **2**, dipotassium salt of **1**, and **7** were confirmed by X-ray crystallography. Addition of $B(C_6F_5)_3$ to a toluene solution of **6**–**8** gives insoluble precipitates which show good activity for ethylene polymerization.

Keywords: Macrocyclic compounds; Nickel complexes; Ethylene polymerization; Dinuclear complexes

1. Introduction

Macrocyclic compounds have drawn extensive attention as hosts in the supramolecular chemistry [1]. Schiff's base condensation reactions are versatile in constructing the macrocyclic compounds [2] and the macrocyclic dinuclear complexes constructed by [2 + 2] Schiff's base condensation of 2,6-diformylphenol and diamino-compounds in the presence of metal template are specially named as Robinson-type complexes, which have been extensively prepared to study cooperative metal–metal interactions in spin exchange couplings, redox activities and bimetallic reactivities [3]. However, template-free Robinson-type macrocyclic compounds have been rarely reported due to the uncontrolled oligomerization process in the absence of template and the proclivity of the hydrolytic cleavage of the formed C=N linkage. A template-free [3 + 3] cyclocondensed macrocyclic compound was constructed from the reaction between 2,6-diformyl-4-methylphenol and *trans*-(R,R)-1,2-diaminocyclohexane, but the ring structure is destroyed during the metallation [4]. The reaction between 2,6-diformyl-4-methylphenol and 1,2-diaminobenzene afforded undesired partially reduced diiminodiaminodiphenol macrocycle [5]. Recently, an efficient proton-template synthesis of 18- to 38-membered tetraiminodiphenol macrocycles was reported but the ring structure was easily destroyed either by the lack of the hydrolytic stability of the formed C=N bond [3]. One of the ways to make the C=N bond persistent to the hydrolytic cleavage is the construction of the bond using aniline compounds bearing bulky *ortho*-substituents. We have recently developed a synthetic route for 4,4″-diamino-*o*-terphenyl derivatives which bear bulky *N*-aryl *ortho*-substituents and used them for construction of macrocyclic bis(anilido-aldimine) compounds [6]. We report herein preparations of template-free Robinson-type macrocyclic compounds using the 4,4″-diamino-*o*-terphenyl derivatives, which are stable for the hydrolytic cleavage by the

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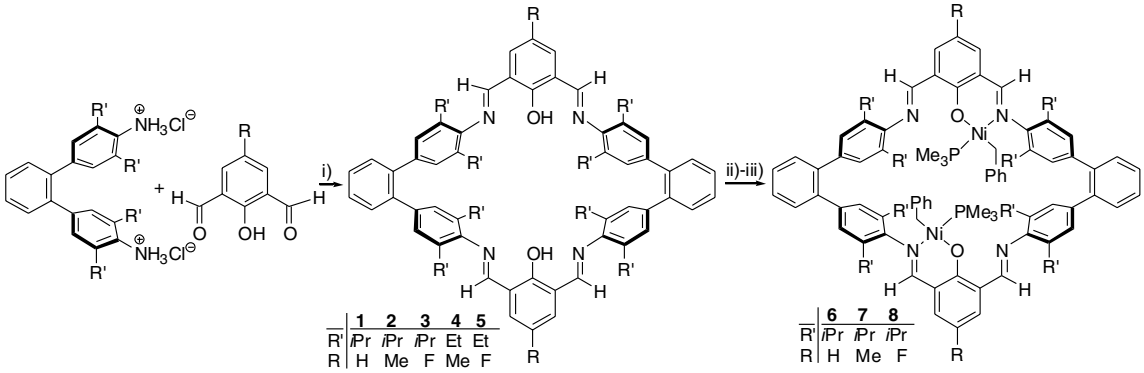
presence of bulky *N*-aryl *ortho*-substituents, and their dinuclear nickel complexes.

2. Results and Discussion

2.1. Synthesis and characterization

Reaction of equimolar amount of HCl salt of 4,4″-diamino-3,3″,5,5″-R'_4-*o*-terphenyl (R′ = *i*Pr, Et) and 2,6-diformyl-4-R-phenol (R = H, Me, F) in anhydrous ethanol (7.0 mM) furnishes HCl salt of the macrocyclic compound, which is neutralized with aqueous $NaHCO_3$ solution to give the desired neutral template-free macrocyclic compounds (Scheme 1). The macrocyclic compounds are hydrolytically so stable that they are not destroyed even on silica gel surface. Yields are fairly good (47–62%). The signals in the ^{1}H NMR spectra of the neutral macrocycles are very broad. The similar broadening was also observed



Legend: (i) EtOH, 70 °C then aqueous $NaHCO_3$; (ii) KH (2.0 eq); (iii) (η^3-$CH_2C_6H_5$)NiCl(PMe_3).

Scheme 1.

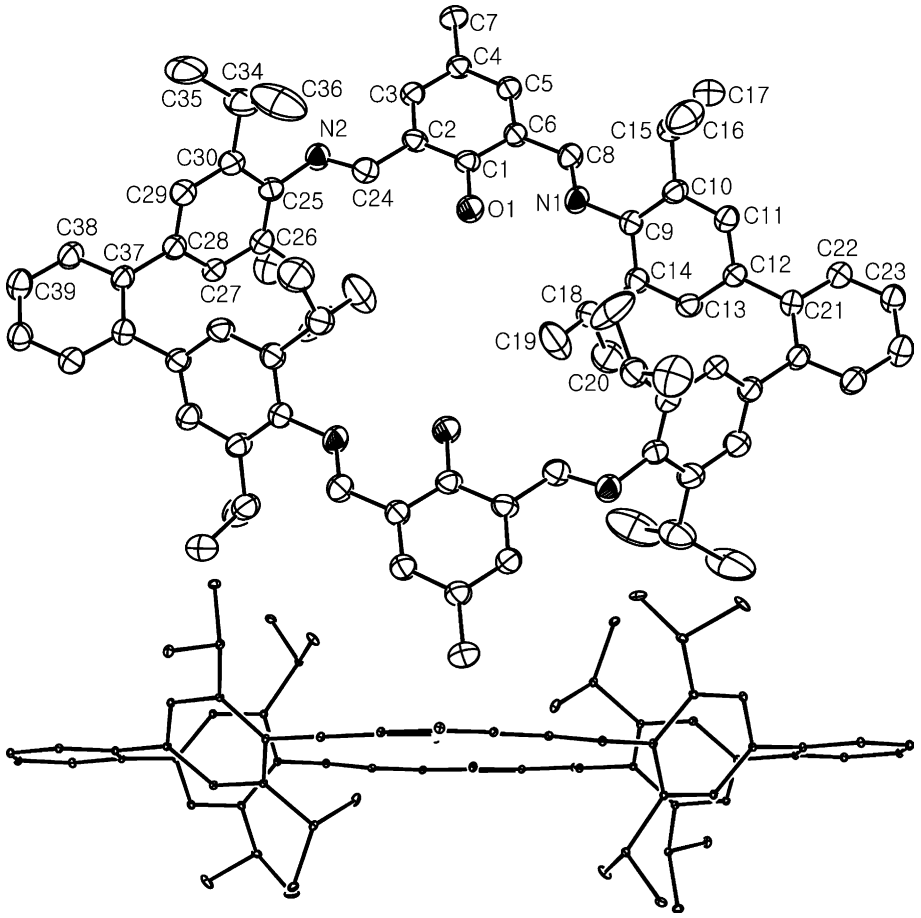
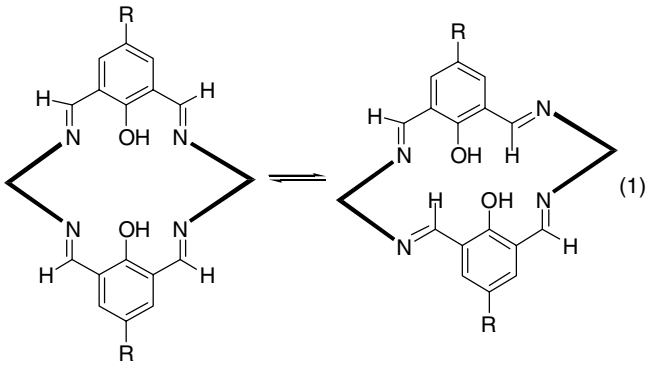


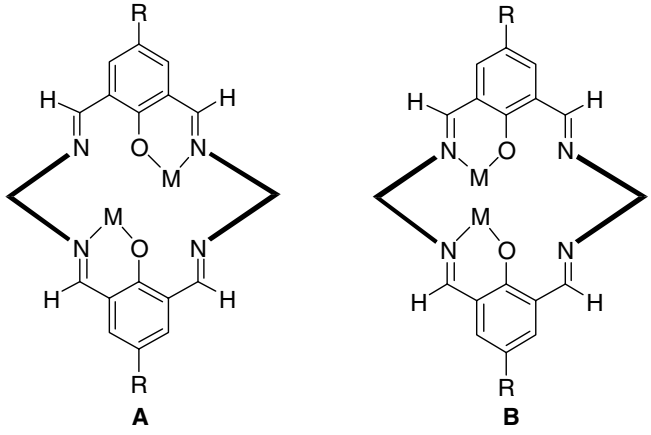
Fig. 1. Thermal ellipsoid plot (30% probability level) of **2** and its side view (below).

for the macrocycles constructed by the condensation of 2,6-diformyl-4-methylphenol and α,ω-diaminoalkanes. [3] When the temperature is raised to 80 °C in the NMR study, sharp signals, which are unambiguously assignable, are observed but the N=CH and phenol-*meta*-H signals are still broad. The broad signals may be attributed either to slow changing of the hydrogen bonding direction between the two nitrogens or to a slow conformational change shown in equation 1. The fast atom bombardment (FAB) mass data are in agreement with the ring structure either. The X-ray crystallographic studies of a single crystal of **2** confirmed the macrocyclic structure (Fig. 1).



Neutral Ni(II) complexes are attractive as polyolefin catalysts [7,8]. They may not require cocatalysts such as methylaluminoxane (MAO) or borate and they are compatible with polar groups enabling incorporation of polar monomers. When **1**–**5** are reacted with (tmeda)$NiMe_2$ in order to prepare phosphine free nickel complexes, [9] broad signals are observed in the ^1H NMR spectra, which are not clearly assignable. Treatment of KH in THF affords cleanly the dipotassium salts. Contrast with the observation of broad signals for the neutral compounds **1**–**5**, sharp NMR signals are observed for the dipotassium salts even at room temperature, indicating the fluxional motions existing in **1**–**5** are absent in the dipotassium salts. Only a single signal is observed respectively for N=CH, phenol-*meta*-H, phenol-*para*-H, and $C_6R'_2H_2$-ring proton(s) and signals of AA′BB′ spin system, which is characteristic for symmetrically *otho*-disubstituted benzene ring protons [10], are observed for the C_6H_4-protons. These observations indicate that the molecule is symmetrical not only vertically but also horizontally. Only 12 aromatic carbon signals are observed in the ^{13}C NMR spectra. The dipotassium salts are crystalline and a structure was elucidated by the X-ray crystallography (Fig. 2).

Addition of (η^3-$CH_2C_6H_5$)NiCl(PMe_3) [11] to the dipotassium salts of **1**–**3** affords cleanly the desired dinuclear η^1-benzyl nickel complexes. The same reaction to the dipotassium salts of **4** and **5** does not furnish the desired η^1-benzyl complexes. The ^1H NMR signals of the dinuclear η^1-benzyl complexes are more complex than those observed for the dipotassium salts but they can be fully assigned. Two configurations (**A** and **B**) are possible by the N,O-chelation. If the configuration is **B**, one should observe two distinct signal-sets of AA′BB′ spin system for right and left side C_6H_4-protons, respectively. If the configuration is **A**, the C_6H_4-benzene ring is not symmetrically *ortho*-disubstituted and hence one cannot observe the characteristic AA′BB′ signal-pattern. Observation of two doublets and two triplets instead of AA′BB′ signals indicates the configuration of **A**. Two N=CH signals, one of which is split by the coupling with phosphorus as doublet, and two phenol-*meta*-H signals are observed separately, respectively, and four signals are observed for $C_6R'_2H_2$-ring protons in the ^1H NMR spectra. Two methylene protons on the benzyl are diastereotopic each other and rather broad signals of AB spin system are observed at 0.7 and 1.6 ppm. Total 30 aromatic carbon-signals are observed in the ^{13}C NMR spectra. The 24 signals are counted for the ring carbons on the phenol, the C_6H_4-ring, and the two $C_6R'_2H_2$-rings, none of which are equivalent each other. The 4 signals are counted for ring carbons on the benzyl and the rest two signals, one of which is split by the coupling with phosphorus as doublet, are counted for the carbons on the imine.



$B(C_6F_5)_3$ has been frequently used for PMe_3-abstracting agent to generate phosphine-free η^3-benzyl complexes which show fast initiation for olefin polymerization [12]. The insoluble side product, $PMe_3 \cdot B(C_6F_5)_3$ can be removed by filtration if the generated η^3-benzyl complexes are soluble in toluene or benzene. Addition of 2 equiv. of $B(C_6F_5)_3$ to **6**–**8** in benzene or toluene results in formation of insoluble complexes, hampering isolation of the phosphine-free η^3-benzyl complexes. Addition of $B(C_6F_5)_3$ in more polar solvent such as CD_2Cl_2 does not provide assignable NMR spectra.

2.2. X-ray structures of *2*, dipotassium salt of *1*, and *7*

Solid state structure of **2** is shown in Fig. 1. One nitrogen atom (N(1)) is situated not only close to the oxygen but also on the phenolic benzene plane (dihedral angle of

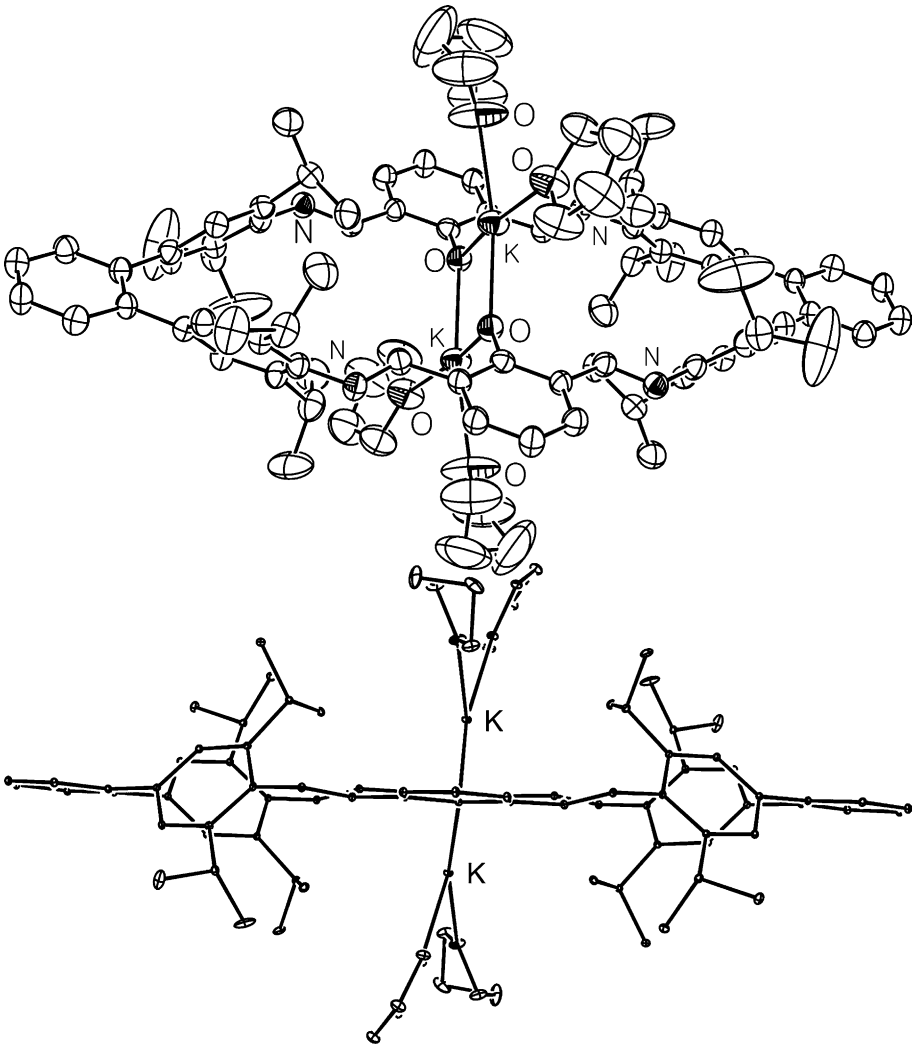


Fig. 2. Thermal ellipsoid plot (30% probability level) of the dipotassium salt of **1** and its side view (below).

C(1)–C(6)–C(8)–N(1), 3.7°), surely acting as hydrogen bonding acceptor. The other nitrogen atom (N(2)) is situated away from the oxygen atom and slightly out of the phenolic benzene plane (dihedral angle of C(1)–C(2)–C(24)–N(2), 6.9°). The phenolic benzene plane and the C_6H_4-benzene plane is situated almost in a plane (the angles between the planes, 5(1)°), consequently showing a macrocyclic planar structure (side view in Fig. 1). The C_6H_2(iPr)-benzene planes are situated skew to the macrocyclic plane. The O–O separation distance is 5.804 Å.

Single crystals of dipotassium salt of **1** suitable for X-ray crystallography were obtained in benzene/THF solution by slow evaporation of the solvent and its molecular structure is shown in Fig. 2. The final *R* value after refinement is rather big (R_1, 14.5%). Attempts to improve the *R* value by variation of crystal growing methods were unsuccessful. The nitrogen atoms do not coordinate to the potassium and both nitrogen atoms are situated away from the oxygen atom. The C_6H_4-rings and the phenolic rings are also situated in a plane (angle between the rings, 1.9(5)°) showing a macrocyclic planar structure with the $C_6H_2i\mathrm{Pr}_2$-rings being situated skew to the macrocylic plane (side view in Fig. 2). The two potassium atoms are situated symmetrically on both axial sites of the macrocyclic plane and are coordinated by the two phenoxy and two THF molecules with the coordination geometry of the distorted square plane. Considering the van der Waals radius of the potassium atom (2.75 Å) [13] and K–K distance (4.54 Å) in metallic state [14], the K–K separation distance (3.769(4) Å) is fairly short but such short separations were also observed in the structures of water-bridged dipotassium complexes of calixarenes [15]. The O–O separation distance in the macrocyclic ring (3.635 Å) is severely contracted when compared with that observed for **2**. Molecular structure revealed by the X-ray crystallography is in agreement with the ^{1}H and ^{13}C NMR spectra, which implies that main feature of the solid structure may persist in the solution.

Single crystals of **7** were obtained in toluene solution at −30 °C and its solid structure is shown in Fig. 3. Attempts to improve the *R* value were unsuccessful in this case either

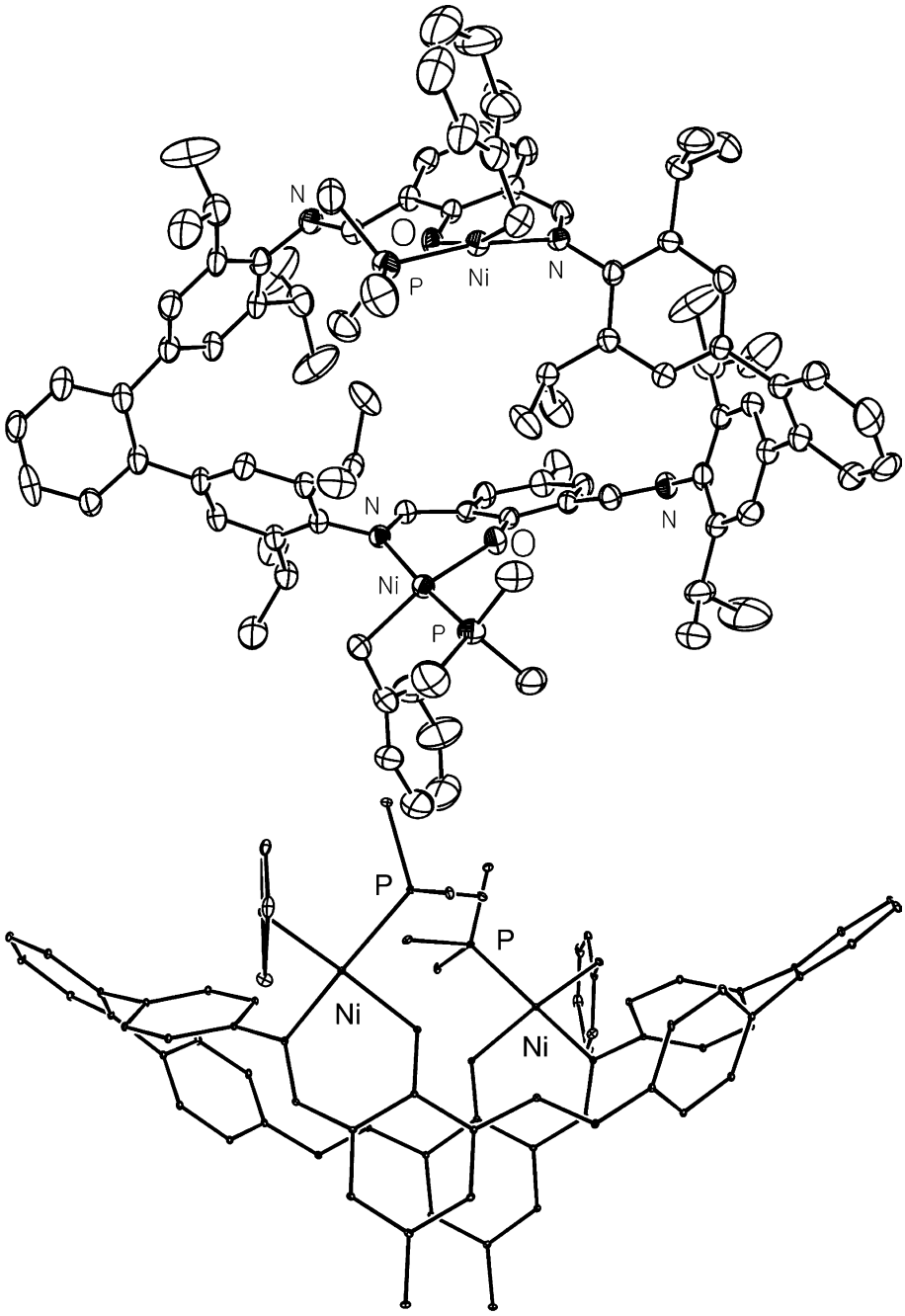


Fig. 3. Thermal ellipsoid plot (30% probability level) of **7** and its side view (below). Isopropyl groups are removed for clarity in the side view.

and the final R value after refinement is rather big (R_1, 15.5%). Geometry around nickel is not unusual: distorted square planar structure with *trans*-relationship between the neutral phosphine ligand and the neutral imine ligand. The C_6H_4-ring and the phenolic ring are situated almost perpendicularly consequently showing a bowl-shape structure (side view in Fig. 3), which is in sharp contrast with the observation of the macrocyclic planar structures for **2** and dipotassium salt of **1**. The O–O separation distance (7.255 Å) is severely elongated by the conformational change. The Ni–Ni separation distance is 8.869 Å, which is slightly longer than the O–O separation distance.

2.3. Polymerization studies

Even though the isolation and characterization of the phosphine-free η^3-benzyl complexes are unsuccessful presumably due to their low solubility in the hydrocarbon solvent, we are encouraged to do the polymerization reaction with the precipitates obtained from **6** to **8** by the addition of $B(C_6F_5)_3$ because polymerization reactions have been frequently carried out with the insoluble activated metallocene catalyst in slurry phase in non-polar solvent such as hexane [16]. When ethylene is added to a reactor containing the precipitates at low temperature (30 °C),

Table 1
Ethylene polymerization results[a]

Entry	Catalyst	Temperature (°C)[b]	Activity (kg/mol Ni h)	M_w	M_w/M_n	Branches[c]
1	**6**	30–72	620	8700	8.1	32
2	**7**	30–58	380	37000	5.1	44
3	**8**	30–58	360	8100	9.4	56
4	**6**	40–73	390	6700	7.7	40
6	**7**	40–59	180	38000	8.5	55
7	**8**	40–55	150	7800	6.3	46
8	**6–9**	60	Negligible			

[a] Polymerization conditions: 30 ml toluene, 20 μmol Ni + 20μmol of $B(C_6F_5)_3$, 100 psig ethylene, 10 min.
[b] Initial temperature–maximum temperature.
[c] Determined by the ^{1}H NMR, and corresponds to the number of branches/1000 carbons.

the solution temperature rises rapidly by the exothermic reaction. The activities are fairly good (360–620 kg/mol Ni h) when considering the insoluble nature of the injected catalyst. Complex **6** shows the highest activity among the dinuclear complexes. When the initial polymerization temperature is raised to 40 °C, the activities are reduced to about half. When the temperature is raised further to 60 °C, almost negligible activities are observed, indicating that the catalysts are thermally unstable. Lack of thermal stability has been an issue for the late transition metal-based catalysts and much endeavors has been devoted to overcome this problem [17].

Polymers obtained by the macrocyclic complexes contain branches (32–55 branches/1000C). Analysis of the ^{13}C NMR spectrum of the polymer obtained by **6** at 30 °C (entry 1) indicates most of the branches are methyl [18]. Molecular weights of the polymers obtained by the macrocyclic complex **7** is significantly higher (M_w, 37000–38000) than those for **6** and **8** (6700–8700) and rather broad molecular weight distributions (M_w/M_n, 5–10) are observed presumably due to the failure of temperature control or the lack of solubility of the active catalysts (see Table 1).

3. Experimental

3.1. General considerations

All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Toluene, pentane, THF, and C_6D_6 were distilled from benzophenone ketyl. Toluene used for polymerization reactions was purchased from Aldrich (anhydrous grade) and purified further over Na/K alloy. Ethylene was purchased from Conley Gas (99.9%) and purified by contacting with molecular sieves and copper for several days under the pressure of 200 psig. The ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (376 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on a Varian Mercury plus 400. The ^{19}F NMR, ^{11}B NMR, ^{31}P NMR spectra were calibrated and reported downfield from external α,α,α-trifluorotoluene, $BF_3 \cdot OEt_2$ and PPh_3, respectively. Mass spectra were obtained on a Micromass VG Autospec. Elemental analyses were carried out at the Inter-University Center Natural Science Facilities, Seoul National University. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using Waters Model 150-C+ GPC and the data were analyzed using a polystyrene analyzing curve. 2,6-Diformylphenol [19], 2,6-diformyl-4-methylphenol, and 4-fluoro-2,6-diformylphenol [20] were prepared by the literature method.

3.2. Compound *1*

To a stirred solution of HCl salt of 4,4″,-diamino-3,3″,5,5″-tetraisopropyl-*o*-terphenyl (0.972 g, 1.94 mmol) in anhydrous ethanol (280 ml) at 70 °C was added 2,6-diformylphenol (0.291 g, 1.94 mmol) in anhydrous ethanol (200 ml). The solution was stirred at 70 °C for 3 days to give yellow precipitates. The solution was cooled to room temperature and filtered to isolate the solid, which was washed with diethyl ether. The solid was dissolved in methylene chloride (200 ml) and the resulting solution was washed with saturated aqueous $NaHCO_3$ solution (100 ml × 3). The organic phase was collected and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporator to give a yellow solid, which was used for the next reaction without further purification. Yield was 0.980 g (47%). M.p. > 300 °C (dec). IR (NaCl): 1627 (C=N), 3449 (N–H) cm^{-1}. ^{1}H NMR (C_6D_6:$CDCl_3$ = 10:1, 80 °C): δ 1.01 (d, J = 6.8 Hz, 24H, CH_3), 2.99 (septet, J = 6.8 Hz, 4H, CH), 6.74 (t, J = 7.6 Hz, 1H, phenol-*p*H), 6.96 (s, 4H, *i*Pr$_2$C$_6$–H), 7.21–7.24 (AA′BB′, 2H, C_6H_4–H), 7.42–7.45 (AA′BB′, 2H, C_6H_4–H), 7.52–7.80 (br, 2H, phenol-*m*H), 8.32-8.56 (br, 1H, N=CH) ppm. HRMS (FAB): *m*/*z* calcd ($[M + H]^+$ $C_{76}H_{85}N_4O_2$) 1085.6673, found 1085.6667.

3.3. Compound *2*

The compound was synthesized using same conditions and procedures as for **1**. Yield was 62%. M.p. > 300 °C (dec). IR (NaCl): 1621 (C=N), 2468 (N–H) cm^{-1}. ^{1}H NMR (C_6D_6:$CDCl_3$ = 10:1, 80 °C): δ 1.06 (d, J = 6.8 Hz, 24H, CH_3), 2.24 (s, 3H, phenol-CH_3), 3.01 (septet, J = 6.8 Hz, 4H, CH), 6.97 (s, 4H, *i*Pr$_2$C$_6$–H), 7.29–7.36 (AA′BB′, 2H, C_6H_4–H), 7.46–7.54 (AA′BB′, 2H, C_6H_4–H), 7.44–7.75 (br, 2H, phenol-*m*H), 8.40-8.54 (br, 1H,

N=CH) ppm. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{78}H_{89}N_4O_2$) 1113.6986, found 1113.6984.

3.4. Compound 3

The compound was synthesized using same conditions and procedures as for **1**. Yield was 60%. M.p. > 300 °C (dec). IR (NaCl): 1637 (C=N), 3468 (N–H) cm^{-1}. ^1H NMR (C_6D_6:$CDCl_3$ = 10:1, 80 °C): δ 1.00 (d, $J = 6.8$ Hz, 24H, CH_3), 2.94 (septet, $J = 6.8$ Hz, 4H, CH), 6.95 (s, 4H, *i*Pr_2C_6–H), 7.22–7.28 (AA′BB′, 2H, C_6H_4–H), 7.43–7.50 (AA′BB′, 2H, C_6H_4–H), 8.22–8.41 (br, 1H, N=CH) ppm. The phenol-*m*H signal is missing presumably due to the severe broadening. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{76}H_{83}F_2N_4O_2$) 1121.6484, found 1121.6482.

3.5. Compound 4

The compound was synthesized using same conditions and procedures as for **1**. The protonated salt of the macrocyclic compound was not deposited as a solid in this case. The ethanol solution was treated with aqueous $NaHCO_3$ solution and the neutral macrocyclic compound was extracted with toluene. The compound was purified by trituration in ethyl acetate. Yield was 52%. M.p. > 300 °C (dec). IR (NaCl): 1621 (C=N), 3449 (N–H) cm^{-1}. ^1H NMR (C_6D_6:$CDCl_3$ = 10:1, 80 °C): δ 0.99 (t, $J = 7.2$ Hz, 12H, CH_3), 2.09 (s, 3H, phenol-CH_3), 2.39 (q, 8H, CH_2), 6.86 (s, 4H, *i*Pr_2C_6–H), 7.21–7.27 (AA′BB′, 2H, C_6H_4–H), 7.41–7.46 (AA′BB′, 2H, C_6H_4–H), 8.33-8.45 (br, 1H, N=CH) ppm. The phenol-*m*H signal is missing presumably due to the severe broadening. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{70}H_{73}N_4O_2$) 1001.5734, found 1001.5726.

3.6. Compound 5

The compound was synthesized using same conditions and procedures as for **1**. Yield was 55%. M.p. > 300 °C (dec). IR (NaCl): 1634 (C=N), 3461 (N–H) cm^{-1}. ^1H NMR (C_6D_6:$CDCl_3$ = 10:1, 80 °C): δ 0.97 (t, $J = 7.2$ Hz, 12H, CH_3), 2.34 (q, 8H, CH_2), 6.86 (s, 4H, *i*Pr_2C_6–H) 7.22–7.27 (AA′BB′, 2H, C_6H_4–H), 7.42–7.46 (AA′BB′, 2H, C_6H_4–H), 8.18–8.32 (br, 1H, N=CH) ppm. The phenol-*m*H signal is missing presumably due to the severe broadening. HRMS (FAB): *m/z* calcd ($[M+H]^+$ $C_{68}H_{67}F_2N_4O_2$), 1009.5232, found 1009.5236.

3.7. Compound 6

Compound **1** (500 mg, 0.460 mmol) was dissolved in THF (20 ml) and KH (37 mg, 0.920 mmol) was added. The solution was stirred overnight at room temperature. The solvent was removed by vacuum to give a dipotassium salt which was pure by the analysis of the ^1H and ^{13}C NMR spectra. ^1H NMR (C_6D_6:THF-d_8 = 10:1): δ 1.11 (d, $J = 6.8$ Hz, 12H, CH_3), 1.25 (d, $J = 6.8$ Hz, 12H, CH_3), 3.36 (septet, $J = 6.8$ Hz, 4H, CH_3), 6.63 (t, $J = 7.6$ Hz, 1H, phenol-*p*H), 7.10 (s, 4H, *i*Pr_2C_6–H), 7.28–7.38 (AA′BB′, 2H, C_6H_4–H), 7.60–7.70 (AA′BB′, 2H, C_6H_4–H), 8.57 (d, $J = 7.6$ Hz, 2H, phenol-*m*H), 8.83 (s, 2H, N=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6:THF-d_8 = 10:1): δ 23.35, 25.59, 28.26, 111.77, 125.51, 126.73, 127.15, 129.87, 131.50, 137.36, 137.45, 142.54, 149.35, 159.86, 173.45 ppm. The potassium salt was dispersed in toluene (20 ml) and (η^3-$CH_2C_6H_5$)NiCl(PMe_3) (240 mg, 0.920 mmol) was added. After the red solution was stirred overnight, it was filtered over Celite. Removal of solvent gave a red crystalline solid. Yield was 480 mg (85%). ^1H NMR (C_6D_6): δ 0.24 (d, $J = 6.8$ Hz, 3H, CH_3), 0.73 (AB, $J = 10.8$ Hz, 1H, benzyl-CH_2), 0.86 (d, $^2J_{PH} = 9.6$ Hz, 9H, PMe_3), 0.88 (d, $J = 6.8$ Hz, 3H, CH_3), 0.90 (d, $J = 6.8$ Hz, 3H, CH_3), 1.12 (d, $J = 6.8$ Hz, 3H, CH_3), 1.13 (d, $J = 6.8$ Hz, 3H, CH_3), 1.28 (septet, $J = 6.8$ Hz, 1H, CH), 1.32 (d, $J = 6.8$ Hz, 6H, CH_3), 1.61 (AB, $J = 10.8$ Hz, 2H, benzyl-CH_2), 1.69 (d, $J = 6.8$ Hz, 3H, CH_3), 2.64 (septet, $J = 6.8$ Hz, 1H, CH), 3.40 (septet, $J = 6.8$ Hz, 1H, CH), 3.48 (septet, $J = 6.8$ Hz, 1H, CH), 6.56 (s, 1H, *i*Pr_2C_6–H), 6.58 (t, $J = 7.6$ Hz, 1H, phenol-*p*H), 6.84 (s, 1H, *i*Pr_2C_6–H), 6.98 (t, $J = 7.2$ Hz, 1H, benzyl-*p*H), 7.06 (t, $J = 7.2$ Hz, 2H, benzyl-*m*H), 7.12 (dd, $J = 7.6$, 1.6 Hz, 1H, phenol-*m*H), 7.23 (td, $J = 7.6$, 1.2 Hz, 1H, C_6H_4–H), 7.30 (td, $J = 7.6$, 1.2 Hz, 1H, C_6H_4–H), 7.41 (s, 1H, *i*Pr_2C_6–H), 7.47 (d, $J = 7.6$ Hz, 1H, C_6H_4–H), 7.51 (s, 1H, *i*Pr_2C_6–H), 7.69 (d, $J = 7.6$ Hz, 1H, C_6H_4–H), 7.73 (d, $^4J_{HP} = 7.6$ Hz, 1H, NiN=CH), 7.79 (d, $J = 7.2$ Hz, 2H, benzyl-*o*H), 8.60 (dd, $J = 7.6$, 1.6 Hz, 1H, phenol-*m*H), 8.65 (s, 1H, N=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.32 (d, $^2J_{CP} = 32.1$ Hz), 12.13 (d, $^2J_{CP} = 25.7$ Hz), 20.64, 22.79, 23.95, 24.04, 24.19, 24.72, 24.96, 25.63, 27.96, 28.26, 28.39, 30.49, 114.47, 123.61, 123.66 (d, $J = 11.4$ Hz), 125.05, 125.67, 126.27, 126.59, 127.29, 128.17(br), 128.87, 129.35, 130.23, 130.52, 133.01, 135.99, 136.29, 137.24, 138.24, 140.01, 140.25, 140.57, 141.15, 141.77, 146.21, 149.19 (d, J = 3.8 Hz), 150.82, 160.00, 164.10, 167.56 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 9.58 ppm. Anal. Calc. ($C_{96}H_{114}N_4O_2P_2Ni_2$): C, 75.10; H, 7.48; N, 3.65%. Found: C, 75.48; H, 7.54 ; N, 3.38%.

3.8. Compound 7

The compound was synthesized using same conditions and procedures as for **6**. The isolated overall yield for the nickel complex was 92%. NMR data for the potassium salt: ^1H NMR (C_6D_6:THF-d_8 = 10:1): δ 1.01 (d, $J = 6.8$ Hz, 12H, CH_3), 1.13 (d, $J = 6.8$ Hz, 12H, CH_3), 2.15 (s, 3H, phenol-CH_3), 3.25 (septet, $J = 6.8$ Hz, 4H, CH), 6.97 (s, 4H, *i*Pr_2C_6–H), 7.21–7.28 (AA′BB′, 2H, C_6H_4–H), 7.48–7.56 (AA′BB′, 2H, C_6H_4–H), 8.23 (s, 2H, phenol-*m*H), 8.73 (s, 2H, N=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6:THF-d_8 = 10:1): δ 23.29, 25.61, 28.16, 119.50, 125.42, 126.17, 127.05, 129.83, 131.78, 137.22, 137.48, 142.49, 149.44, 159.98, 171.92 ppm. Analytical data for the nickel complex: ^1H NMR (C_6D_6): δ 0.28 (d, $J = 6.8$ Hz, 3H, CH_3), 0.73 (AB, $J = 11.2$ Hz, 1H, benzyl-CH_2), 0.87 (d, $^2J_{PH} = 9.6$ Hz,

9H, PMe_3), 0.88 (d, $J = 6.8$ Hz, 3H, CH_3), 0.89 (d, $J = 6.8$ Hz, 3H, CH_3), 1.12 (d, $J = 6.8$ Hz, 3H, CH_3), 1.14 (d, $J = 6.8$ Hz, 3H, CH_3), 1.27 (septet, $J = 6.8$ Hz, 1H, CH), 1.33 (d, $J = 6.8$ Hz, 6H, CH_3), 1.61 (AB, $J = 11.2$ Hz, 1H, benzyl-CH_2), 1.71 (d, $J = 6.8$ Hz, 3H, CH_3), 2.15 (s, 3H, phenol-CH_3), 2.70 (septet, $J = 6.8$ Hz, 1H, CH), 3.42 (septet, $J = 6.8$ Hz, 1H, CH), 3.52 (septet, $J = 6.8$ Hz, 1H, CH), 6.58 (s, 1H, iPr$_2$C$_6$–H), 6.85 (s, 1H, iPr$_2$C$_6$–H), 6.98 (t, $J = 7.6$ Hz, 1H, benzyl-pH), 7.08 (t, $J = 7.2$ Hz, 2H, benzyl-mH), 7.10 (d, $J = 1.2$ Hz, 1H, phenol-mH), 7.23 (td, $J = 7.6$, 2.0 Hz, 1H, C_6H_4–H), 7.30 (td, $J = 7.6$, 1.6 Hz, 1H, C_6H_4–H), 7.40 (s, 1H, iPr$_2$C$_6$–H), 7.47 (d, $J = 7.6$ Hz, 1H, C_6H_4–H), 7.52 (s, 1H, iPr$_2$C$_6$–H), 7.70 (d, $J = 7.6$ Hz, 1H, C_6H_4–H), 7.76 (d, $^4J_{HP} = 7.6$ Hz, 1H, NiN=CH), 7.84 (d, $J = 7.2$ Hz, 2H, benzyl-oH), 8.43 (d, $J = 2.4$ Hz, 1H, phenol-mH), 8.64 (s, 1H, N=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.43 (d, $^2J_{CP} = 34.1$ Hz), 12.01 (d, $^2J_{CP} = 25.8$ Hz), 20.26, 21.49, 22.96, 23.72, 24.10, 24.22, 24.74, 24.96, 25.72, 27.99, 28.23, 28.40, 30.51, 122.79, 123.59 (d, $J = 9.3$ Hz), 124.74, 125.49, 125.61, 126.41, 126.60, 127.31, 128.35, 128.47, 129.11, 129.39, 130.16, 130.57, 134.05, 135.94, 136.25, 136.94, 138.29, 140.09, 140.24, 140.69, 141.12, 141.79, 146.33, 149.40 (d, $J = 4.0$ Hz), 150.90, 160.23, 163.84, 166.01 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 9.65 ppm. Anal. Calc. ($C_{98}H_{118}N_4O_2P_2Ni_2$): C, 75.29; H, 7.61; N, 3.58%. Found: C, 75.57 ; H, 7.97 ; N, 3.19%.

3.9. Compound **8**

The compound was synthesized using same conditions and procedures as for **6**. The isolated overall yield for the nickel complex was 89%. NMR data for the potassium salt: ^1H NMR (C_6D_6:THF-d_8 = 10:1): δ 1.16 (d, $J = 6.8$ Hz, 12H, CH_3), 1.30 (d, $J = 6.8$ Hz, 12H, CH_3), 3.37 (septet, $J = 7.2$ Hz, 4H, CH), 7.16 (s, 4H, iPr$_2$C$_6$–H), 7.38–7.46 (AA′BB′, 2H, C_6H_4–H), 7.69–7.76 (AA′BB′, 2H, C_6H_4–H), 8.43 (d, $J = 8.8$ Hz, 2H, phenol-mH), 8.85 (d, $J = 2.4$ Hz, 2H, N=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6:THF-d_8 = 10:1): δ 23.10, 25.39, 28.14, 116.56 (d, $^2J_{CF} = 24$ Hz), 125.38, 126.51 (d, $^3J_{CF} = 8.1$ Hz), 127.07, 129.74, 137.34, 137.47, 142.26, 148.78, 151.95 (d, $^1J_{CF} = 227$ Hz), 159.14, 170.10 ppm. $^{19}F\{^1H\}$ NMR (C_6D_6:THF-d_8 = 10:1): δ −40.64 ppm. Analytical data for the nickel complex: ^1H NMR (C_6D_6): δ 0.21 (d, $J = 6.8$ Hz, 3H, CH_3), 0.70 (AB, $J = 10.4$ Hz, 1H, benzyl-CH_2), 0.84 (d, $^2J_{PH} = 9.6$ Hz, 9H, PMe_3), 1.07 (d, $J = 6.8$ Hz, 3H, CH_3), 1.11 (d, $J = 6.8$ Hz, 3H, CH_3), 1.22 (d, $J = 6.8$ Hz, 3H, CH_3), 1.28 (d, $J = 6.8$ Hz, 3H, CH_3), 1.30 (d, $J = 6.8$ Hz, 6H, CH_3), 1.38 (br, 6H, CH_3), 1.43 (septet, $J = 6.8$ Hz, 1H, CH), 1.56 (AB, $J = 10.4$ Hz, 1H, benzyl-CH_2), 1.65 (d, $J = 6.8$ Hz, 3H, CH_3), 2.63 (septet, $J = 6.8$ Hz, 1H, CH), 3.32 (septet, $J = 6.8$ Hz, 1H, CH), 3.38 (septet, $J = 6.8$ Hz, 1H, CH), 6.52 (d, $J = 1.6$ Hz, 1H, iPr$_2$C$_6$–H), 6.79 (d, $J = 1.6$ Hz, 1H, iPr$_2$C$_6$–H), 6.95 (dd, $J = 7.6$, 3.2 Hz, 1H, phenol-mH), 7.00 (t, $J = 7.6$ Hz, 1H, benzyl-pH), 7.09 (t, $J = 7.6$ Hz, 2H, benzyl-mH), 7.22 (td, $J = 7.6$, 1.6 Hz, 1H, C_6H_4–H), 7.29 (td, $J = 7.6$, 1.6 Hz, 1H, C_6H_4–H), 7.36 (d, $J = 1.6$ Hz, 1H, iPr$_2$C$_6$–H), 7.45 (d, $J = 7.6$ Hz, 1H, C_6H_4–H), 7.49 (d, $J = 1.6$ Hz, 1H, iPr$_2$C$_6$–H), 7.61 (d, $^4J_{HP} = 6.8$ Hz, 1H, NiN=CH), 7.68 (d, $J = 7.6$ Hz, 1H, C_6H_4–H), 7.79 (d, $J = 7.6$ Hz, 2H, benzyl-oH), 8.39 (dd, $J = 9.2$, 3.2 Hz, 1H, phenol-mH), 8.56 (d, $J = 2.8$ Hz, 1H, N=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.12 (d, $^2J_{CP} = 34.1$ Hz), 12.10 (d, $^2J_{CP} = 25.8$ Hz), 20.25, 20.92, 23.71, 24.12, 24.22, 24.74, 24.96, 25.72, 27.97, 28.22, 28.40, 30.50, 122.80 (d, $^2J_{CF} = 22$ Hz), 123.65 (d, $J = 9.3$ Hz), 124.70, 125.51, 125.61, 126.43 (d, $^3J_{CF} = 8.2$ Hz), 126.60, 127.31, 128.46 (br), 129.11, 129.40, 130.16, 130.60, 134.05, 135.94, 136.25, 136.97, 138.29, 140.10, 140.23, 140.70, 141.13, 141.80, 146.34, 149.40 (d, $J = 3.8$ Hz), 150.91 (d, $^1J_{CF} = 215$ Hz), 160.23, 163.85, 166.02 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 9.50 ppm. $^{19}F\{^1H\}$ NMR (C_6D_6): δ −48.17 ppm. Anal. Calc. ($C_{96}H_{112}N_4F_2O_2P_2Ni_2$): C, 73.38; H, 7.18; N, 3.57%. Found: C, 73.66; H, 7.51; N, 3.44%.

3.10. Ethylene polymerization

Nickel complex (20 μmol Ni), $B(C_6F_5)_3$ (20 μmol), and toluene (2 ml) were added in a vial and stirred for 30 min inside a glove box. The generated slurry was added into a 60 ml glass reactor containing stirring bar and toluene (30 ml). The reactor was assembled and brought out of the glove box. The reactor was immersed in an oil bath of which temperature had been set to a given value. The solution was stirred for 15 min, at which time the temperature of the solution reached the bath temperature. Ethylene was fed continuously for 10 min under pressure of 100 psig. Temperature of the solution was monitored. Reaction was quenched by release of the ethylene pressure and the reaction mixture was poured into a flask containing 100 ml acetone. White participates were collected by filtration and dried under vacuum. Branch numbers were calculated from integration value of methyl, methylene, methine proton regions in the ^1H NMR spectra. NMR spectra of the polymers were obtained at 100 °C in benzene-d_6 and 1,2,4-trichlorobenzene (v/v, 4:1).

3.11. Crystallographic studies

Crystals of **2**, dipotassium salt of **1**, and **7** were mounted in thin-walled glass capillaries and sealed under argon. The data sets were collected on a Bruker Smart CCD detector single diffractometer. Mo Kα radiation ($\lambda = 0.7107$ Å) was used for all structures. Each structure was solved by the application of direct methods using the SHELX-96 program and least-squares refinement using the SHELXL-PLUS (5.1) software package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the calculated positions. The crystal data and refinement results are summarized in Table 2.

Table 2
Crystallographic parameters of **2**, dipotassium salt of **1**, and **7**[a]

	2	Dipotassium salt of **1**	**7**
Formula	$C_{78}H_{86}N_4O_2$	$C_{76}H_{80}K_2N_4O_2 \cdot (C_4H_8O)_4$	$[C_{98}H_{118}N_4O_2P_2Ni_2] \cdot (C_7H_8)_3$
Formula weight	1111.51	1448.06	1811.50
Color	Yellow	Yellow	Red
Size (mm^3)	$0.196 \times 0.118 \times 0.088$	$0.227 \times 0.137 \times 0.136$	$0.309 \times 0.231 \times 0.180$
a (Å)	10.624(2)	24.418(6)	32.3720(15)
b (Å)	12.913(3)	13.656(4)	13.4733(6)
c (Å)	13.196(3)	28.425(8)	33.0202(15)
α (°)	98.930(5)	90	90
β (°)	91.510(5)	110.190(4)	114.2690(10)
γ (°)	107.402(4)	90	90
V ($Å^3$)	1701.3(6)	8897(4)	13129.2(10)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$C2/c$
D_{calc} ($g\,cm^{-1}$)	1.085	1.081	0.916
Z	1	4	4
μ (mm^{-1})	0.064	0.157	0.352
Number of data collected	18968	43746	67039
Number of unique data	8343	11242	16302
Number of variables	390	478	542
R_1[a] (%)	0.1285	0.1454	0.1548
R_w (%)	0.2450	0.3263	0.4167
Goodness of fit	0.883	1.033	1.432

[a] Data collected at 233(2) K with Mo Kα radiation ($\lambda(K\alpha) = 0.7107$ Å), $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 2.0\sigma(I)$, $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]^2]^{1/2}$ with $F_o > 2.0\sigma(I)$.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center (**2**: CCDC No. 275681; Dipotassium salt of **1**: CCDC No. 275682; **7**: CCDC No. 275683). Copies of this information may be obtained free of charge form The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033: e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) B.A. Blight, K.A. Van Noortwyk, J.A. Wisner, M.C. Jennings, Angew. Chem. Int. Ed. 44 (2005) 1499;
(b) Z.-B. Li, J. Lin, L. Pu, Angew. Chem. Int. Ed. 44 (2005) 1690;
(c) C. Miranda, F. Escarti, L. Lamarque, M.J.R. Yunta, P. Navarro, E. Garcia-Espana, M.L. Jimeno, J. Am. Chem. Soc. 126 (2004) 823;
(d) L.S. Evans, P.A. Gale, Angew. Chem. Int. Ed. 43 (2004) 1286;
(e) Y. Yamaguchi, S. Kobayashi, S. Miyamura, Y. Okamoto, T. Wakamiya, Y. Matsubara, Z.-i. Yoshida, Angew. Chem. Int. Ed. 43 (2004) 366;
(f) M.-X. Wang, X.-H. Zhang, Q.-U. Zheng, Angew. Chem. Int. Ed. 43 (2004) 838;
(g) M. Boiocchi, M. Bonizzoni, L. Fabbrizzi, G. Piovani, A. Taglietti, Angew. Chem. Int. Ed. 43 (2004) 3847;
(h) L. Fabbrizzi, F. Foti, S. Patroni, P. Pallavicini, A. Taglietti, Angew. Chem. Int. Ed. 43 (2004) 5073;
(i) W. Zhang, J.S. Moore, J. Am. Chem. Soc. 126 (2004) 12796;
(j) S. Shimizu, V.G. Anand, R. Taniguchi, K. Furukawa, T. Kato, T. Yokoyama, A. Osuka, J. Am. Chem. Soc. 126 (2004) 12280.

[2] P. Guerriero, S. Tamburini, P.A. Vigato, Coord. Chem. Rev. 139 (1995) 11.

[3] B. Dutta, P. Bag, B. Adhikary, U. Flörke, K. Nag, J. Org. Chem. 69 (2004) 5419, and references therein.

[4] (a) S.R. Korupoju, N. Mangayarkarasi, S. Ameerunisha, E.J. Valente, P.S. Zacharias, Dalton Trans. (2000) 2845;
(b) S.R. Korupoju, P.S. Zacharias, Chem. Commun. (1998) 1267.

[5] A. Aguiari, E. Bullita, U. Casellato, P. Guerriero, S. Tamburini, P.A. Vigato, Inorg. Chim. Acta 202 (1992) 157.

[6] (a) B.Y. Lee, H.Y. Kwon, S.Y. Lee, S.J. Na, S.-i. Han, H. Yun, H. Lee, Y.-W. Park, J. Am. Chem. Soc. 127 (2005) 3031;
(b) S.Y. Lee, S.J. Na, H.Y. Kwon, B.Y. Lee, S.O. Kang, Organometallics 23 (2004) 5382.

[7] (a) T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Banselben, Science 287 (2000) 460;
(b) C. Wang, S. Friedrich, T.R. Younkin, R.T. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149;
(c) E.F. Connor, T.R. Younkin, J.I. Henderson, S.J. Hwang, W.P. Roberts, J.J. Litzau, R.H. Grubbs, J. Polym. Sci. A1 40 (2002) 2842.

[8] (a) L.F. Groux, T. Weiss, D.N. Reddy, P.A. Chase, W.E. Piers, T. Ziegler, M. Parvez, J. Benet-Buchholz, J. Am. Chem. Soc. 127 (2005) 1854;
(b) M.A. Zuideveld, P. Wehrmann, C. Röhr, S. Mecking, Angew. Chem. Int. Ed. 43 (2004) 869;
(c) S.J. Diamanti, V. Khanna, A. Hotta, D. Yamakawa, F. Shimizu, E.J. Kramer, G.H. Fredrickson, G.C. Bazan, J. Am. Chem. Soc. 126 (2004) 10528;
(d) J.C. Jenkins, M. Brookhart, J. Am. Chem. Soc. 126 (2004) 5827;
(e) C. Müller, L.J. Ackerman, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Am. Chem. Soc. 126 (2004) 14960;
(f) L.-C. Liang, W.-Y. Lee, C.-C. Yin, Organometallics 23 (2004) 3538.

[9] E.F. Connor, T.R. Younkin, J.I. Henderson, A.W. Waltman, R.H. Grubbs, Chem. Commun. (2003) 2272.

[10] E.D. Becker, High Resolution NMR: Theory and Chemical Application, second ed., Academic Press, London, 1980, p. 171.

[11] (a) E. Carmona, M. Paneque, M.L. Poveda, Polyhedron 8 (1989) 285;

(b) C.B. Shim, Y.H. Kim, B.Y. Lee, Y. Dong, H. Yun, Organometallics 22 (2003) 4272.
[12] (a) B.Y. Lee, G.C. Bazan, J. Vela, Z.J.A. Komon, X. Bu, J. Am. Chem. Soc. 123 (2001) 5352;
(b) B.Y. Lee, X. Bu, G.C. Bazan, Organometallics 20 (2001) 5425;
(c) C.B. Shim, Y.H. Kim, B.Y. Lee, D.M. Shin, Y.K. Chung, J. Organomet. Chem. 675 (2003) 72.
[13] A. Bondi, J. Phys. Chem. 68 (1964) 441.
[14] Handbook of Chemistry and Physics, 72nd ed., Chemical Rubber Co., Cleveland, OH, 1992, p. 12-8.
[15] (a) T.A. Hanna, L. Liu, L.N. Zakharov, A.L. Rheingold, W.H. Watsona, C.D. Gutsche, Tetrahedron 58 (2002) 9751;
(b) K. Murayama, K. Aoki, Inorg. Chim. Acta 281 (1998) 36.
[16] (a) B.Y. Lee, J.S. Oh, Macromolecues 33 (2000) 3194;
(b) B.Y. Lee, J.W. Han, Y.K. Chung, S.W. Lee, J. Organomet. Chem. 587 (1999) 181.
[17] (a) S.A. Svejda, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 121 (1999) 10634;
(b) D.P. Gates, S.A. Svejda, E. Onate, C.M. Killian, L.K. Johnson, P.S. White, M. Brookhart, Macromolecules 121 (1999) 10634;
(c) S. Ikeda, F. Ohhata, M. Miyoshi, R. Tanaka, T. Minami, F. Ozawa, M. Yoshifuji, Angew. Chem. Int. Ed. 39 (2000) 4512;
(d) Z. Guan, W.J. Marshall, Organometallics 21 (2002) 3580;
(e) O. Daugulis, M. Brookhart, Organometallics 21 (2002) 5926;
(f) Y.H. Kim, T.H. Kim, B.Y. Lee, D. Woodmansee, X. Bu, G.C. Bazan, Organometallics 21 (2002) 3082.
[18] G.B. Galland, R.F. de Souza, R.S. Mauler, F.F. Nunes, Macromolecules 32 (1999) 1620.
[19] C. Zondervan, E.K. van den Beuken, H. Kooijman, A.L. Spek, B.L. Feringa, Tetrahedron Lett. 38 (1997) 3111.
[20] L.F. Lindoy, G.V. Meehan, N. Svenstrup, Synthesis (1998) 1029.