Synthesis, characterization, and norbornene polymerization of η3-benzylnickel(II) complexes of N-heterocyclic carbenes

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ABSTRACT

Neutral η1-benzylnickel carbene complexes, [Ni(η1-CH2C6H5)(IiPr)(PMe3)(Cl)] (3) (IiPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene) and [Ni(η1-CH2C6H5)(SIiPr)(PMe3)(Cl)] (4) (SIiPr = 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene), were prepared by the reaction between [Ni(η3-CH2C6H5)(PMe3)(Cl)] and an equivalent amount of the corresponding free N-heterocyclic carbene. The preparation of η3-benzylnickel carbene complexes, [Ni(η3-CH2C6H5)(IiPr)(Cl)] (5) and [Ni(η3-CH2C6H5)(SIiPr)(Cl)] (6) were carried out by the abstraction of PMe3 from 3 and 4 by the treatment of B(C6F5)3. The treatment of AgX on 5 and 6 produced the anion-exchanged complexes, [Ni(η3-CH2C6H5)(NHC)(X)] (7, NHC = IiPr, X = O2CCF3; 8, NHC = IiPr, X = O3SCF3; 9, NHC = SIiPr, X = O2CCF3; 10, NHC = SIiPr, X = O3SCF3). The solid state structures of 3 and 10 were determined by X-ray crystallography. The η3-benzyl complexes of IiPr (5, 7, and 8) alone, in the absence of any activators such as borate and MAO, showed good catalytic activity towards the vinyl-type norbornene polymerization. The catalyst was thermally robust and the activity increases as the temperature rises to 130 °C.

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1. Introduction

Since the discovery of stable N-heterocyclic carbenes (NHCs) [1], much attention has been focused on these compounds as ancillary ligands for a number of transition metal complexes. NHCs are versatile ligands that share many of the coordination properties of phosphanes [2]. They are more potent σ-donors than the phosphanes with a reduced π-back bonding ability. As a consequence, NHC complexes are more stable towards dissociation or degradation. There have been some reports of NHC metal complexes utilized as catalyst precursors for olefin polymerizations [3–9]. In this study, we report the preparation, characterization, and olefin polymerization reactivity of η3-benzylnickel complexes of the NHC ligands, 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (IiPr) and 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene (SIiPr). The η3-benzyl fragment is chosen because η3-benzyl complexes have displayed much faster rates of initiation in olefin polymerizations than the more frequently used η3-allyl complexes [10–13]. Even though some nickel complexes, such as the shell higher olefin process (SHOP) catalyst [14–17] and the salicylaldimine-based neutral nickel complexes [18–22], can be used as an "activator free" catalyst in olefin oligomerization or polymerization, most of the nickel complexes require activators such as meth-ylaluminoxane (MAO), B(C6F5)3, or [B(C6F5)4]−. The η3-benzylnickel complexes reported herein show activity for norbornene polymerization without the requirement of any activator.

2. Experimental

2.1. General

All the manipulations were carried out under an inert atmosphere using standard glove box and Schlenk techniques. Toluene, pentane, and C6D6 were distilled from benzophenone ketyl. The 1H (400 MHz), 13C (100 MHz), 31P (162 MHz), and 19F (376 MHz) spectra were recorded on a Varian Mercury Plus 400. The 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 the Waters Model 150-C+ GPC and the data were analyzed using a polystyrene analyzing curve.

2.2. Synthesis of η1- and η3-benzylnickel carbene complexes

2.2.1. Complex 3

The carbene, 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (IiPr) [23] (0.30 g, 0.77 mmol) and [η3-(CH2C6H5)NiCl(PMe3)] [24] (0.20 g, 0.77 mmol) were placed in a vial and toluene (2.5 mL) was added. The reaction mixture was stirred for 2 h at room

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temperature. All volatiles were removed using a vacuum pump. The remaining oily residue was dissolved in pentane (2 mL). Recrystallization from the pentane gave **3** as a yellowish brown colored solid. The yield was 0.47 g (94%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.51 (d, $^2J_{PH}$ = 8.4 Hz, 9H, PMe_3), 0.99 (br, 6H, iPr–CH_3), 1.11 (br, 6H, iPr–CH_3), 1.23 (br, 6H, iPr–CH_3), 1.50 (d, $^3J_{PH}$ = 9.6 Hz, 2H, benzyl-CH_2), 1.70 (br, 6H, iPr–CH_3), 2.85 (br, 2H, iPr–CH), 3.80 (br, 2H, iPr–CH), 6.61 (s, 2H, carbene-CH), 6.87 (d, J = 7.2 Hz, 3H), 6.98–7.08 (m, 3H), 7.26 (t, J = 8.0 Hz, 3H), 7.36 (d, J = 6.0 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 3.88 (d, $^1J_{PC}$ = 24.9 Hz), 12.63 (d, $^2J_{PC}$ = 23.5), 22.23, 23.67, 26.85, 29.20, 123.25, 123.48, 123.86, 124.75, 126.99, 129.38, 129.99, 137.06, 146.10, 148.29, 149.50, 188.96 (d, $^2J_{PC}$ = 109.9 Hz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 25 °C): δ = −1.40 ppm. Anal. Calc. for $C_{37}H_{52}ClN_2NiP$: C, 68.37; H, 8.06; N, 4.31. Found: C, 68.11; H, 8.28; N, 4.27%.

2.2.2. Synthesis of complex 4

The complex was synthesized by the same conditions and procedure as for **3**, using 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene (SIiPr) [25] (0.10 g, 0.26 mmol). Yield was 0.14 g (84%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.46 (d, $^2J_{PH}$ = 8.4 Hz, 9H, PMe_3), 1.09 (d, J = 6.8 Hz, 6H, iPr–CH_3), 1.20 (d, J = 6.8 Hz, 6H, iPr–CH_3), 1.31 (d, J = 6.8 Hz, 6H, iPr–CH_3), 1.53 (d, $^3J_{PH}$ = 9.6 Hz, 2H, benzyl-CH_2), 1.77 (d, J = 6.8 Hz, 6H, iPr–CH_3), 3.14 (septet, J = 6.4 Hz, 2H, iPr–CH), 3.49 (t, J = 8.4 Hz, 2H, carbene-CH_2), 3.70 (t, J = 8.4 Hz, 2H, carbene-CH_2), 4.09 (septet, J = 6.4 Hz, 2H, iPr–CH), 6.74- 6.88 (m, 3H), 7.00 (d, J = 7.6 Hz, 2H), 7.15–7.27 (m, 4H), 7.30 (d, J = 7.2, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 3.59 (d, $^1J_{PC}$ = 24.2 Hz), 12.53 (d, $^2J_{PC}$ = 23.5), 23.27, 24.56, 27.36, 29.17, 53.77, 123.19, 123.86, 125.18, 126.86, 129.20, 129.46, 137.45, 147.07, 149.49, 217.07 (d, $^2J_{PC}$ = 103.9 Hz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 25 °C): δ = −1.47 ppm. Anal. Calc. for $C_{37}H_{54}ClN_2NiP$: C, 68.16; H, 8.35; N, 4.30. Found: C, 68.14; H, 8.36; N, 4.23%.

2.2.3. Synthesis of complex 5

To a vial containing **3** (0.23 g, 0.35 mmol) and $B(C_6F_5)_3$ (0.18 g, 0.35 mmol) was added toluene (2.5 mL) at room temperature. The reaction mixture was stirred for 2 h. The white precipitates of $B(C_6F_5) \cdot PMe_3$ were removed by filtration over Celite. Finally, the solvent was removed to give the product as a violet colored powder. Yield was 0.21 g (99%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.02 (s, 2H, benzyl-CH_2), 1.05 (d, J = 6.8 Hz, 12H, iPr–CH_3), 1.46 (d, J = 6.8 Hz, 12H, iPr–CH_3), 3.14 (septet, J = 6.8 Hz, 4H, iPr–CH), 6.17 (d, J = 7.6 Hz, 2H, benzyl-ortho H), 6.61 (s, 2H, carbene-CH), 6.89 (t, J = 7.6 Hz, 2H, benzyl-meta H), 7.20 (t, J = 7.6 Hz, 1H, benzyl-paraH), 7.25 (d, J = 8.0 Hz, 4H), 7.33 (t, J = 8.0 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 19.53, 23.14, 26.58, 29.02, 114.49, 115.87, 124.22, 124.78, 127.23, 130.19, 133.48, 136.74, 146.75, 183.49 ppm. Anal. Calc. for $C_{34}H_{43}ClN_2Ni$: C, 71.16; H, 7.55; N, 4.88. Found: C, 70.82; H, 8.15; N, 4.85%.

2.2.4. Synthesis of complex 6

The complex was synthesized according to the same conditions and procedure as for **5**, using **4** as a starting material. The product was obtained as a violet colored powder. Yield was 94%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.05 (s, 2H, benzyl-CH_2), 1.16 (d, J = 6.8 Hz, 12H, iPr–CH_3), 1.53 (d, J = 6.8 Hz, 12H, iPr–CH_3), 3.50 (septet, J = 6.8 Hz, 4H, iPr–CH), 3.52 (s, 4H, CH_2), 6.14 (d, J = 7.2 Hz, 2H, benzyl-orthoH), 6.85 (t, J = 7.2 Hz, 2H, benzyl-metaH), 7.20 (t, J = 7.6 Hz, 1H, benzyl-paraH), 7.23 (d, J = 6.8 Hz, 4H), 7.30 (t, J = 6.8 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 20.16, 24.00, 27.08, 28.97, 53.83, 115.14, 117.45, 124.68, 127.44, 129.43, 133.19, 137.21, 147.88, 214.91 ppm. Anal. Calc.

for $C_{34}H_{45}ClN_2Ni$: C, 70.91; H, 7.88; N, 4.86. Found: C, 70.51; H, 8.49; N, 4.82%.

2.2.5. Synthesis of complex 7

To a vial containing compound **5** (0.02 g, 0.03 mmol) and CF_3COOAg (0.007 g, 0.03 mmol) was added C_6H_6 (0.5 mL). The vial was covered with aluminium foil and the reaction mixture was stirred for 8 h at room temperature. The precipitates of AgCl were removed by filtration over Celite. The recrystallization from pentane produced a red colored crystalline compound **7**. Yield was 0.016 g (80%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.98 (s, 2 H, benzyl-CH_2), 1.00 (d, J = 6.8 Hz, 12H, iPr–CH_3), 1.39 (d, J = 6.8 Hz, 12H, iPr–CH_3), 2.88 (septet, J = 6.8 Hz, 4H, iPr–CH), 6.32 (d, J = 7.6 Hz, 2H, benzyl-orthoH), 6.53 (s, 2H, carbene-CH), 6.95 (t, J = 7.6 Hz, 2H, benzyl-metaH), 7.11 (t, J = 7.6 Hz, 1H, benzyl-paraH), 7.22 (d, J = 8.4 Hz, 4H), 7.31 (t, J = 8.4 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 18.28, 22.81, 22.94, 26.33, 28.89, 113.62, 124.44, 124.85, 127.56, 130.37, 133.38, 135.99, 145.99, 180.80 ppm. $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6, 25 °C): δ = −74.36 ppm. Anal. Calc. for $C_{36}H_{43}F_3N_2NiO_2$: C, 66.38; H, 6.65; N, 4.30. Found: C, 65.91; H, 7.24; N, 4.26%.

2.2.6. Synthesis of complex 8

To a vial containing compound **5** (0.012 g, 0.02 mmol) and CF_3SO_3Ag (0.006 g, 0.02 mmol) was added C_6H_6 (0.5 mL). The vial was covered with aluminium foil and the reaction mixture was stirred for 3 h at room temperature. The AgCl precipitates were removed by filtration over Celite. Recrystallization from pentane gave a red colored crystalline compound **8**. Yield was 0.012 g (89%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.93 (s, 2H, benzyl-CH_2), 1.01 (d, J = 6.8 Hz, 12H, iPr–CH_3), 1.50 (d, J = 6.8 Hz, 12H, iPr–CH_3), 3.01 (septet, J = 6.8 Hz, 4H, iPr–CH), 6.51 (s, 2H, carbene-CH), 6.52 (d, J = 7.6 Hz, 2H, benzyl-orthoH), 7.01 (t, J = 7.6 Hz, 2H, benzyl-metaH), 7.07 (t, J = 7.6 Hz, 1H, benzyl-paraH), 7.23 (d, J = 8.0 Hz, 4H), 7.31 (t, J = 6.8 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 16.58, 23.10, 26.36, 29.06, 116.25, 124.61, 125.34, 126.17, 129.08, 130.53, 134.54, 135.96, 145.88, 176.96 ppm. $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6, 25 °C): δ = −77.04 ppm. Anal. Calc. for $C_{35}H_{43}F_3N_2NiO_3S$: C, 61.15; H, 6.30; N, 4.07. Found: C, 60.73; H, 6.89; N, 4.02%.

2.2.7. Synthesis of complex 9

The complex was synthesized according to same conditions and procedure as for **7** using **6**. Yield was 78%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.13 (d, J = 6.8 Hz, 12H, iPr–CH_3), 1.34 (s, 2H, benzyl-CH_2), 1.48 (d, J = 6.8 Hz, 12 H, iPr–CH_3), 3.22 (septet, J = 6.8 Hz, 4H, iPr–CH), 3.36 (s, 4H, CH_2), 6.22 (d, J = 7.6 Hz, 2H, benzyl-orthoH), 6.92 (t, J = 7.6 Hz, 3H, benzyl-meta and paraH), 7.21 (d, J = 8.0 Hz, 4H), 7.31 (t, J = 8.0 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 20.14, 23.58, 26.84, 28.94, 54.06, 114.27, 116.74, 124.95, 127.48, 129.59, 133.09, 136.13, 146.95, 211.62 ppm. $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6, 25 °C): δ = −74.03 ppm. Anal. Calc. for $C_{36}H_{45}F_3N_2NiO_2$: C, 66.17; H, 6.94; F, 8.72; N, 4.29. Found: C, 65.74; H, 7.48; N, 4.30%.

2.2.8. Synthesis of complex 10

The complex was synthesized according to same conditions and procedure as for **8** using **6**. Yield was 86%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.13 (d, J = 6.4 Hz, 12H, iPr–CH_3), 1.21 (s, 2H, benzyl-CH_2), 1.53 (d, J = 6.4 Hz, 12H, iPr–CH_3), 3.23 (septet, J = 6.4 Hz, 4H, iPr–CH), 3.31 (s, 4H, CH_2), 6.23 (d, J = 7.6 Hz, 2H, benzyl-orthoH), 7.03 (t, J = 7.6 Hz, 3H, benzyl-meta and paraH), 7.24 (d, J = 7.6 Hz, 4H), 7.34 (t, J = 7.6 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 19.28, 23.96, 26.69, 29.06, 54.42, 116.15, 117.14, 125.32, 126.17, 129.76, 134.50, 135.99, 146.56, 208.14 ppm. $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6, 25 °C): δ = −77.48 ppm.

Anal. Calc. for $C_{35}H_{45}F_3N_2NiO_3S$: C, 60.97; H, 6.58; N, 4.06. Found: C, 60.63; H, 7.11; N, 4.06%.

2.3. General procedure for norbornene polymerization

To a vial containing 5 g of norbornene solution in toluene (30 wt%) was added the catalyst inside the glove box. The solution was vigorously stirred. When the stirring was ceased, the viscous solution was taken out from the glove box and poured into a flask containing acetone. The white precipitates were collected by filtration and dried under a vacuum. The polymerization at 130 °C was carried out using a bomb reactor. The ^{1}H NMR spectra were obtained at 100 °C in $C_2D_2Cl_4$. The ^{13}C-CPMAS spectrum was measured at room temperature, with a pulse angle of 90°, and a relaxation delay of three seconds on a Bruker 500.

2.4. X-ray crystallography

Crystals of **3** and **10** 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

Table 1
Crystallographic data and structure refinement for **3** and **10**[a]

	3	10
Molecular formula	$C_{36}H_{52}ClN_3NiP$	$C_{35}H_{45}F_3N_2NiO_3S$
Formula weight	650.93	689.50
Size (mm³)	$0.20 \times 0.17 \times 0.12$	$0.19 \times 0.13 \times 0.11$
Crystal system	Monoclinic	Monoclinic
Space group	C_2/c	Cc
a (Å)	34.6025(18)	16.400(13)
b (Å)	10.6917(5)	12.571(10)
c (Å)	20.5602(11)	16.321(13)
β (°)	104.3370(10)	98.768(15)
Volume (Å³)	7369.5(6)	3325(5)
Z	8	4
μ (mm⁻¹)	0.669	0.701
Number of data collected	37 439	15 949
Number of unique data	9146	8161
Number of data/restraints/ parameters	9146/0/391	8161/2/415
Final indices	$R_1 = 0.0491$	$R_1 = 0.0824$
$[I > 2\sigma(I)]$	$wR_2 = 0.1226$	$wR_2 = 0.1894$
GOF	0.996	0.880

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

$(\lambda = 0.7107 \text{ Å})$ was used for all structures. The structures were solved by the 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 1.

3. Results and discussion

3.1. Syntheses and characterization of η¹- and η³-benzylnickel carbene complexes

The η^1-benzylnickel(II) complexes $[Ni(\eta^1$-CH$_2$C$_6$H$_5$)(PMe$_3$)(Cl)(IiPr)]$ IiPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (**3**) and $[Ni(\eta^1$-CH$_2$C$_6$H$_5$)(PMe$_3$)(Cl)(SIiPr)]$ (**4**) (SIiPr = 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene) are prepared in high yields by the reaction between $[Ni(\eta^3$-CH$_2$C$_6$H$_5$)(PMe$_3$)(Cl)]$ and the corresponding free N-heterocyclic carbene. The complexes are fully characterized by the ^{1}H, ^{13}C, and ^{31}P NMR. In the ^{1}H NMR spectra, the PMe$_3$ signal is observed at 0.44–0.54 ppm as a doublet by coupling with phosphorous ($^2J_{PH}$ = 9.6 Hz), and the η^1-benzyl-CH$_2$ signal is observed at 1.48–1.55 ppm as a doublet by coupling with phosphorous ($^3J_{PH}$ = 9.6 Hz). In the ^{13}C NMR spectra, the η^1-benzyl carbon signal is observed at 3.4–4.0 ppm as a doublet by coupling with phosphorous ($^2J_{PC}$ = 25.0 Hz). In addition, the carbene carbon signals are observed at 189.0 ppm ($^2J_{PC}$ = 109.9 Hz) and at 217.0 ppm ($^2J_{PC}$ = 109.9 Hz) as a doublet for complexes **3** and **4**, respectively. B(C$_6$F$_5$)$_3$ has been commonly used as a PMe$_3$-abstracting reagent to yield phosphine-free η^3-benzyl complexes which show fast initiation in olefin polymerizations [10–13]. Addition of an equivalent amount of B(C$_6$F$_5$)$_3$ to **3** and **4** generates the desired η^3-benzyl complexes **5** and **6** in nearly quantitative yields (Scheme 1).

The ^{1}H and ^{13}C NMR spectra strongly support the formation of the PMe$_3$-free η^3-benzyl complexes. The methyl signal of PMe$_3$ disappears completely and the characteristic upfield-shifted η^3-benzyl signals [10–13] are observed at 6.15–6.18 ppm (doublet, ortho) and 6.85–6.88 ppm (triplet, meta). The upfield-shifted benzyl-CH$_2$ signals are observed at 1.02 ppm and 1.05 ppm for complexes **5** and **6**, respectively. The carbene carbon signals are observed as a singlet almost in the same region as observed for the η^1-benzyl complexes **3** and **4** (183.5 ppm and 214.9 ppm for compounds **5** and **6**, respectively). Preparation of related η^3-allyl IiPr Ni(II) complexes by the reaction between Ni(COD)$_2$ and allyl chloride in the presence of corresponding free NHC was reported

Scheme 1. Syntheses of Ni-complexes.

[26,27]. The addition of AgX (X = CF$_3$COO, CF$_3$SO$_3$) to a solution of complexes **5** or **6** in toluene gives the corresponding anion-exchanged complexes **7**–**10** in good yields (78–90%). In case of the reactions with AgO$_3$SCF$_3$, the displacement of Cl anion by the CF$_3$SO$_3$ anion is completed within 3 h. In contrast, the reaction with AgO$_2$CCF$_3$ is rather slow. The reaction is not completed after 8 h and trace amounts of the original material (5–8%) still remain. The pure products are obtained from the reaction mixture in 78–80% yields by recrystallization. The structure of complexes **7**–**10** are in agreement with the ^{1}H, ^{13}C, and ^{19}F NMR spectra. Characteristic η^3-benzyl signals are observed at 6.22–6.52 ppm (doublet, *ortho*) and 6.92–7.03 ppm (triplet, *meta*). In the ^{13}C NMR spectra, the carbene carbon signals are observed at 178.0–180.8 ppm for complexes **7**–**8** and at 208.1–211.6 ppm for complexes **9**–**10**, which are slightly upfield-shifted from the chemical shifts observed for the corresponding chloride complexes **5**–**6**. The single signal is observed at the range of −74.0 to −77.5 ppm in the ^{19}F NMR spectra of **7**–**10**.

3.2. X-ray crystallographic studies

The single crystals of **3** suitable for X-ray crystallography are obtained from a pentane solution at −15 °C. The ORTEP drawing shows the square planar geometry around the Ni center with a *trans*-relationship between the Cl and the benzyl ligands (Fig. 1). The Ni–C(1) bond length (1.909(3) Å) is comparable to those observed for other Ni(II) carbene complexes (for *trans*-dichlorobis-(1,3-dicyclohexylimidazol-2-ylidene)nickel(II), 1.911(2) Å [28]; for [(^{tBu}CC^{meth})NiCl(PMe$_3$)] (^{tBu}CC^{meth} = 1,1′-methylene-3,3′-di-*tert*-butyldiimidazole-2,2′-diylidene), 1.942(4) Å) [29]. The imidazolylidene ring is situated perpendicularly to the square plane of the nickel (dihedral angle of N(1)–C(1)–Ni–Cl, 91.3°).

The single crystals of **10** suitable for X-ray crystallography are obtained from a solution in a cosolvent of pentane and toluene. Fig. 2 shows the structure of **10**. The Ni centre is best described as a distorted square planar with a *trans*-relationship between the OSO$_2$CF$_3$ ligand and the benzyl-CH$_2$ fragment (angles of O(1)–Ni–C(34), 166.7(3)°). The Ni–C(29) and Ni–C(28) distances

Fig. 2. ORTEP diagram of complex **10** (30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni–C(1), 1.858 (8); Ni–C(34), 1.917 (9); Ni–C(29), 2.112 (8); Ni–C(28), 2.327 (8); Ni–O(1), 1.950 (6); O(1)–S, 1.436 (6); C(29)–C(34), 1.445 (11); C(28)–C(29), 1.383(13); C(1)–N(2), 1.342 (9); C(1)–N(1), 1.352 (10); C(1)–O(1), 103.5 (3); C(28)–Ni–(O1), 99.5 (3); C(34)–Ni–C(1), 88.2 (3); C(34)–Ni–C(28), 68.6 (3); Ni–C(34)–C(29), 76.4 (5); Ni–C(29)–C(28), 80.5 (5); S–O(1)–Ni, 144.0 (4); Ni–C(1)–N(2), 129.6 (5); Ni–C(1)–N(1), 123.6 (5); C(1)–N(2)–C(16), 125.9(6); C(1)–N(1)–C(4), 123.2 (6).

(2.112(8) and 2.327(8) Å, respectively) indicates the chemical bonding between these two atoms, supporting the η^3-hapticity of the benzyl ligand. By changing the hapticity from η^1 to η^3, the H$_2$C–C^{ipso} distance is contracted (1.445(11) and 1.503(5) Å for **10** and **3**, respectively) while the C^{ipso}–C^{ortho} distance is almost invariable (1.383(13) and 1.380(5) for **10** and **3**, respectively). By forming the η^3-bonding, the Ni–C(34)–C(29) angle (76.4(5)°) becomes acute and severely deviated from the angle of the ideal sp^3 carbon atom (109.5°), which is highly comparable with the observations found in other η^3-benzyl complexes of Ni [10–13] and Rh [30]. The imidazolin-2-ylidene ring is not situated as perpendicularly to the square plane as is observed for **3** but is rather tilted (dihedral angle of N(1)–C(1)–Ni–O(1), 120.3°).

3.3. Polymerization studies

The reactivity of the η^3-benzyl complexes **5**–**10** for ethylene polymerization or oligomerization is tested by adding ethylene gas to a sealable NMR cell containing a C$_6$D$_6$ solution of complexes **5**–**10** and the reaction is monitored by the ^{1}H NMR spectroscopy. A mixture of *cis*- and *trans*-2-butene is formed slowly, with the rate being so slow that it takes more than one day to transform all the gaseous ethylene to butene (turnover frequency, less than 0.5 h^{-1}).

Norbornene can be polymerized via the vinyl-addition polymerization [31]. Recently, Fink et al. reported that in the polymer prepared using *rac*-[iPr(Ind)$_2$ZrCl$_2$]/MAO, the chain is grown through an unexpected 2-*exo*,7′-*syn* linkage through the σ-bond metathesis [32,33]. Complexes **5**–**10** are tested for norbornene polymerization without the addition of any extra activators. There have been a number of publications regarding the norbornene polymerization with nickel complexes activated with MAO or B(C$_6$F$_5$)$_3$ [34–38], but the use of neutral nickel complexes as a catalyst without the addition of any activator has not been reported. The imidazolinylidene η^3-benzyl complexes **6**, **9**, and **10** show negligible activity toward norbornene polymerization. In contrast, the imidazolylidene η^3-benzyl complexes **5**, **7**, and **8** exhibit good activity (Table 2). When the complexes are added to the norbornene solution in toluene (30 wt%) with [norbornene]/[Ni] ratio of 5000 and the

Fig. 1. ORTEP diagram of complex **3** (30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni–C(1), 1.909 (3); Ni–C(31), 1.966 (4); Ni–Cl, 2.258 (10); Ni–P, 2.195 (12); N(2)–C(16), 1.451 (4); N(1)–C(4), 1.446 (4); C(1)–N(2), 1.364 (4); C(1)–N(1), 1.360 (4); N(1)–C(1)–N(2), 103.10 (3); C(1)–Ni–Cl, 89.72 (10); C(1)–Ni–C(31), 93.56(15); C(1)–Ni–P, 164.56 (10); Cl–Ni–P, 87.84 (4); Ni–C(1)–N(2), 122.2 (2); Ni–C(1)–N(1), 134.2 (2); Ni–C(31)–C(32), 115.5 (3); P–Ni–C(31), 92.79 (13).

Table 2
Norbornene polymerization results[a]

Entry	Catalyst	T (°C)	Time (min)	Yield (g)	Activity ($\times 10^{-3}$ g/mol h)	$M_w^{b} \times 10^{-3}$	M_w/M_n^{b}
1	**5**	25	120	0.26	40.6	410	2.4
2	**7**	25	150	0.17	21.4	323	2.5
3	**8**	25	120	0.32	50.0	341	2.6
4	**8**	50	90	0.30	62.5	229	3.2
5	**8**	80	60	0.42	131.3	226	3.3
6	**8**	100	35	0.51	274.8	156	2.9
7	**8**	130	20	0.35	328.0	120	3.1
8	**6**, **9**, **10**	25	120	Trace			

[a] Polymerization conditions: 5 g norbornene solution in toluene (30 wt%), 3.2 μmol complex, [monomer]/[catalyst] = 5000.
[b] Determined by GPC in 1,2,4-trichlorobenzene at 140 °C using polystyrene standards.

solution is stirred, a very viscous solution is obtained within 2.5 h and the stirring is ceased. Among the three complexes, trifluoromethanesulfonato complex **8** shows the highest activity at room temperature (entries 1–3). Complex **8** is thermally robust and the activity increases as the temperature climbs to 130 °C (entries 4–7). The activity at 130 °C is 6.5 times higher than that observed at 25 °C and it reaches 3.3×10^5 g/molNi · h. The polynorbornenes prepared using **6**, **9**, and **10** are soluble in toluene, trichlorobenzene, or dichloroethane at a high temperature. The ^{1}H NMR spectrum of the obtained polynorbornene in $C_2D_2Cl_4$ confirms that it is obtained exclusively by the vinyl-type polymerization. Arndt et al. proposed three types of polynorbornene based on the investigation of the solid state ^{13}C-CPMAS NMR spectra [39]. Three broad signals are observed in the ^{13}C-CPMAS spectra of Type-1, which is observed for the polymers obtained using the catalytic system of [(Ni(acac)$_2$, Ni(2-ethylhexanoate)$_2$, or Ni(COD)$_2$)/MAO] or [(Cp$_2$ZrCl$_2$ or Me$_2$C(Cp)(Flu)ZrCl$_2$)/MAO]. The CPMAS-type II spectrum is closely related to type I spectrum. The type-II spectrum is observed for the polymers produced by a catalytic system of {rac-[Me$_2$Si(Ind)$_2$]ZrCl$_2$/MAO}. In type-III spectra, the number of signals is much more and it is observed for the polymers produced by the palladium complexes and the metallocene complexes, rac-[C$_2$H$_4$(IndH$_4$)$_2$]ZrCl$_2$ and meso-[Me$_2$Si(Ind)$_2$]ZrCl$_2$. The ^{13}C-CPMAS spectrum of the polynorbornene produced by **8** looks like a combination of type-I and type-III as was observed on the polymer obtained with a zwitterionic nickel complex (Fig. 3) [40]. Broad signals at 30, 40, and 50 ppm, which are typical type-I signals, are overlapped with the signals at 35 and 58 ppm, which are typical type-III signals.
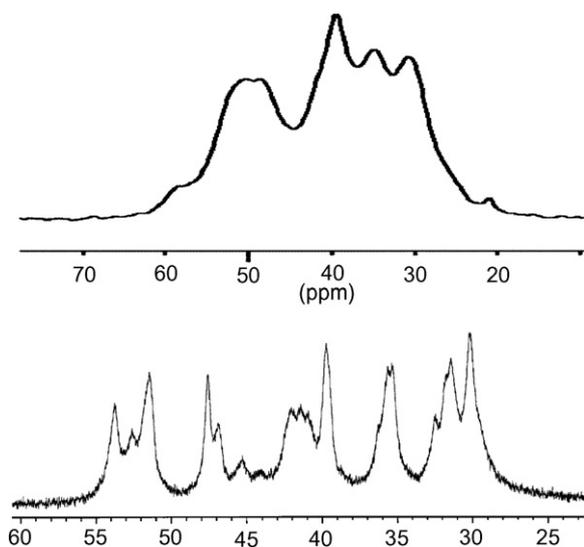
Fig. 3. Solid (CPMAS) and solution (CDCl$_3$) ^{13}C NMR spectra of polynorbornene.

Even though the determinations of the absolute molecular weights are limited [41], we can routinely measure the relative molecular weights on GPC using a polystyrene standard curve and compare the data with the previously reported ones. The molecular weights (M_w) of the polymers obtained by **5**, **7**, and **8** at room temperature (410, 323, and 341 × 10^3, respectively) are smaller than that of the polymer obtained either by Ni(acac)$_2$/MAO catalyst (3.8×10^6) [31] or by B(C$_6$F$_5$)$_3$-activated zwitterionic catalyst (633×10^3) [40]. Narrow molecular distribution (MWD = 2.4–3.4) indicate the presence of a single active species in the polymerization solution. The molecular weight decreases with increase in temperature (entries 3–7), which is a general trend observed in the polymerization process.

4. Conclusions

Some η^3-benzyl nickel complexes of NHC, [Ni(η^3-CH$_2$C$_6$H$_5$)-(NHC)(X)] (NHC = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene or 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene; X = Cl, O$_2$CCF$_3$, O$_3$SCF$_3$) are prepared and characterized in this study. While the imidazolinylidene complexes are inactive, the imidazolylidene-based η^3-benzyl complexes exhibit good activity for norbornene homopolymerization without the requirement of any activator. Moreover, the trifluoromethanesulfonato complex gives the highest activity. It is thermally robust and the activity increases as the temperature rises to 130 °C. The solid state ^{13}C-CPMAS spectrum reveals some unusual pattern.

5. Supplementary material

CCDC 649337 and 649338 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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