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Vinyl-addition polymerization of norbornene catalyzed by (pyrazol-1-ylmethyl)pyridine divalent iron, cobalt and nickel complexes

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ABSTRACT

Complexes of 2-((3,5-dimethyl)-1H-pyrazol-1-ylmethyl)pyridine (L1), 2-((3,5-ditert-butyl-1H-pyrazol-1-yl)methyl)pyridine (L2), 2-((3,5-dipenyl)-1H-pyrazol-1-yl)methyl)pyridine (L3), 2-((3,5-bis(trifluoro-methyl)-1H-pyrazol-1-yl)methyl)pyridine (L4) and 2,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)methyl) pyridine (L5) with cobalt(II), iron(II) and nickel(II), Ni(L1)Cl₂ (1), Co(L1)Cl₂ (2), Fe(L1)Cl₂ (3), Ni(L2)Cl₂ (4), Ni(L3)Cl₂ (5), Co(L3)Cl₂ (6), Fe(L3)Cl₂ (7), Ni(L4)Cl₂ (8) and Ni(L5)Cl₂ (9), were used as catalyst precursors to produce vinyl-addition type norbornene polymers. Both the identity of the metal center and nature of ligand affected the polymerization behaviour of the resultant catalysts. Nickel catalysts were generally more active than the corresponding iron and cobalt analogues. The polynorbornene produced have high molecular weights $(0.5-2.1 \times 10^6 \text{ g/mol})$ and narrow molecular weight distributions. Analyses of polymer microstructure using NMR and IR spectroscopy confirmed the polymers produced to be vinyl-addition polynorbornene.

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1. Introduction

Polynorbornene is a high performance speciality polymer prepared from bicycle-[2.2.1]hept-2-ene, commonly known as norbornene [1]. Norbornene polymerization can be achieved *via* three pathways, namely; ring opening metathesis polymerization (ROMP), cationic or radical polymerization and vinyl or addition polymerization [2]. Polymers derived from free radical process have undesirable properties such as low molecular weights and irregular polymer microstructure. As such, these polymers are not suitable for applications that require high tensile strength. On the other hand, polynorbornene, produced *via* the vinyl-addition process [3] exhibits superior properties such as good mechanical strength, high chemical resistance, optical transparency, low birefringence, high glass transition temperatures, low dielectric constant and large refractive indices [4]. Vinyl-addition polymerization is usually catalyzed by transition metal complexes [5].

Several complexes of iron, cobalt and nickel have been reported as catalysts for vinyl-addition polymerization of norbornene and strained cyclic olefins in general [5,6]. Among these complexes, catalysts derived from nickel appear to be the most active in the vinyladdition polymerization of norbornene. For example, nickel(II) complexes bearing phosphoraniminato ligands exhibit high catalytic activities for the polymerization of norbornene to produce high molecular weight polymers [6b]. In another related work, vinyl-addition polymerization of norbornene catalyzed by neutral salicylaldiminato nickel(II) complexes was reported to give very high activities of up to 2.86×10^6 g polymer/mol Ni h [6c]. Indeed a number of nitrogen-donor nickel complexes have been found to be very good catalysts for the vinyl polymerization of norbornene [7].

To date, there are few reports in literature that employ pyrazole or pyrazolyl-based metal complexes as catalysts for norbornene polymerization. For instance, nickel and palladium complexes of pyridine-pyrazolyl ligands display moderate activities of 100 kg polymer/mol Ni h [8]. Over the past 10 years, we have extensively demonstrated the versatility of late transition metal pyrazole and pyrazolyl metal complexes as olefin oligomerization and polymerization catalysts [9] and showed that the advantage of using pyrazolyl ligands as nitrogen donor lies in the weaker σ -donor ability of pyrazoles compared to pyridines, imines or other commonly used nitrogen donors. Thus pyrazolyl metal complexes produce electrophilic metal centers that promote coordination of substrates for subsequent catalytic transformations. This therefore makes pyrazolyl metal complexes attractive for catalysis that involves coordination such as vinyl-addition polymerization of norbornene. In the current work, we have investigated pyrazolyl complexes of iron(II), cobalt(II) and nickel(II) as catalysts for the polymerization of norbornene and herein report our results.



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2. Experimental

2.1. Materials and methods

All reactions were carried out under inert atmosphere using standard Schlenk techniques. Solvents were dried over appropriate drying reagents prior to use. Bicycle-[2.2.1]hept-2-ene (norbornene) and methylaluminoxane (MAO) were purchased from Sigma Aldrich and used without further purification. The ligands 2-(3,5dimethylpyrazolylmethyl)pyridine (L1), 2-((3,5-ditert-butyl-1 H-pyrazol-1-yl)methyl)pyridine (L2), 2-((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine (**L3**), 2-(3,5-bis(trifluoromethyl)-1 H-pyrazol-1-yl)methyl)pyridine (L4) and 2,6 bis-(3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (L5) [10] and complexes Ni(L1)Cl₂ (1), Ni(L2)Cl₂ (4) and Ni(L5)Cl₂ (9) were synthesized according to literature procedures [10,11]. NMR spectra were recorded on a Varian Gemini 3000 instrument. IR spectra were recorded using a Bruker Tensor 27 FTIR using an Attenuated Total Reflector (ATR) attachment. Microanalyses were performed on a Vario Elementar III microcube CHNS analyser. High resolution mass spectra for the Schiff base ligands were recorded on a Waters API Q-TOF Ultima. Differential scanning calorimetry (DSC) analysis was conducted on a Mettler Toledo DSC822. Molecular weight and molecular weight distribution of polymers were determined by size exclusion chromatography (SEC) on a WGE Q1000 Gel Permeation Chromatograph.

2.2. Synthesis of iron and cobalt complexes

2.2.1. [{2-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine}CoCl₂] (**2**) To a suspension of CoCl₂ (0.10 g, 0.75 mmol) in dichloromethane (20 mL) was added a solution of **L1** (0.14 g, 0.75 mmol) in dichloromethane (20 mL). The solution was allowed to stir for 24 h and the complex precipitated by slow addition of hexane to afford compound **2** as a blue solid. Recrystallization from CH₂Cl₂/ hexane mixture at $-4 \,^{\circ}$ C gave single crystals suitable for X-ray analyses. Yield = 0.17 g (69%). *Anal.* Calc. for C₁₁H₁₃Cl₂N₃Co: C, 41.67; H, 4.13; N, 13.25. Found: C, 41.41; H, 4.54; N, 13.60%. ESI-MS (*m*/z): 316 {[M]⁺(³⁵Cl), 100%}, 318 {[M]⁺(³⁷Cl), 64.1%}. IR (ATR, cm⁻¹): 1083 (C-C), 1590 (C=N).

Compounds **3**, **6**, **7** and **8** were prepared using the procedure described for **2**.

2.2.2. [$\{2-((3,5-dimethyl-1H-pyrazole-1-yl)methyl)pyridine\}FeCl_2$] (3)

Complex **3** was prepared from FeCl₂ (0.10 g, 0.75 mmol) and **L1** (0.14 g, 0.75 mmol) and isolated as a brown solid. Yield = 0.18 g (77%). *Anal.* Calc. for $C_{11}H_{13}Cl_2N_3Fe: C, 42.08; H, 4.17; N, 13.38. Found: C, 41.72; H, 4.04; N, 13.80%. ESI-MS ($ *m/z* $): 312 {[M]⁺(³⁵Cl), 100%}, 314 {[M]⁺(³⁷Cl), 62.5%}. IR (ATR, cm⁻¹): 1086 (C–C), 1592 (C=N).$

2.2.3. [2-((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine}NiCl₂] (5)

Complex **5** was prepared from NiCl₂ (0.05 g, 0.42 mmol) and **L3** (0.13 g, 0.42 mmol) as a green solid. Yield = 0.13 g (72%). *Anal.* Calc. for C₂₁H₁₇Cl₂N₃Ni: C, 57.20; H, 3.89; N, 9.53. Found: C, 57.33; H, 3.52; N, 9.73%. ESI-MS (m/z): 439 {[M]⁺(³⁵Cl), 100%}, 441 {[M]⁺(³⁷Cl), 97.6%}. IR (ATR, cm⁻¹): 1093 (C–C), 1594 (C=N).

2.2.4. [$\{2-((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine\}CoCl_2$] (6)

Complex **6** was prepared from $CoCl_2$ (0.06 g, 0.48 mmol) and **L3** (0.15 g, 0.48 mmol) as a blue solid. Single crystals suitable for X-ray analyses were grown by slow diffusion of hexane into a dichloromethane solution of **6**. Yield: 0.13 g (59%). *Anal.* Calc. for $C_{21}H_{17}Cl_2N_3Co$: C, 57.17; H, 3.88; N, 9.52. Found: C, 57.00; H,

2.2.5. [{2-((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine}FeCl₂] (7)

Complex **7** was prepared from FeCl₂ (0.05 g, 0.35 mmol) and **L3** (0.11 g, 0.35 mmol) and isolated as a yellow solid. Yield = 0.10 g (66%). *Anal.* Calc. for $C_{21}H_{17}Cl_2N_3Fe: C, 57.57; H, 3.91; N, 9.59.$ Found: C, 57.21; H, 4.25; N, 9.91%. ESI-MS (*m*/*z*): 436 {[(M⁺(³⁵Cl), 100%}, 438 {[(M⁺(³⁷Cl), 63.0%}]. IR (ATR, cm⁻¹): 1084 (C–C), 1593 (C=N).

2.2.6. [{2-((3,5-bis(trifluoromethyl)-1H-pyrazol-1-

yl)methyl)pyridine}NiCl₂] (8)

Complex **8** was prepared from [NiCl₂ (0.05 g, 0.40 mmol) and **L4** (0.09 g, 0.40 mmol) as a green solid. Yield = 0.06 g (68%). *Anal.* Calc. for $C_{11}H_7Cl_2F_6N_3Ni$: C, 31.10; H, 1.66; N, 9.89. Found: C, 30.94; H, 1.36; N, 9.73%. ESI-MS (*m*/*z*): 422 {[(M⁺(³⁵Cl), 99.7%), 424 {[(M⁺(³⁷Cl), 97.1%). IR (ATR, cm⁻¹): 1156 (C–C), 1607 (C=N).

2.3. Polymerization of norbornene

Polymerization reactions were carried out in a Schlenk tube equipped with a magnetic stirrer bar. In a typical procedure, complex **1** (6 mg, 20 μ mol) was placed in a dry Schlenk tube, evacuated and degassed toluene (30 mL) was added. The Schlenk tube was flushed with nitrogen and norbornene monomer (5 mL) in toluene (10 mL) added *via* a cannula. Polymerization was initiated by the addition of 10 mL of methylaluminoxane (MAO) as co-catalyst. After 1 h of reaction time, the polymer formed was precipitated by addition of methanol to the reaction mixture. The polymer was isolated by filtration and dried under vacuum.

2.4. Single crystal X-ray crystallography

A typical experiment is described here for **2**. Suitable crystals were selected under oil. under ambient conditions and attached to the tip of a MiTeGen MicroMount[©]. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the Xray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with MoK α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 10 s per frame. A total of 67 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 6406 strong reflections from the actual data collection. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.71 Å. A total of 9431 data were harvested by collecting four sets of frames with 0.3° scans in ω and one set with 0.45° scans in φ with an exposure time 20 s per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [12].

The systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ and P1. The *E*-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement [13] A successful solution by the direct methods provided most nonhydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined



 $\begin{array}{l} R = Me, M = Ni, (1); R = Me, M = Co, (2); R = Me, M = Fe (3); R = {}^{t}Bu, M = Ni, (4); \\ R = Ph, M = Ni, (5); R = Ph, M = Co, (6); R = Ph, M = Fe, (7); R = CF_3, M = Ni, (8). \end{array}$



with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The crystal proved to be a non-merohedral twin with the minor component contribution of approximately 15%. The refinements based on data from both twin components were worse than the one based on the reflections from the major component; thus the results of based on the major component are presented herein. The final least-squares refinement of 156 parameters against 3581 data resulted in residuals *R* (based on F^2 for $I \ge 2\sigma$) and *wR* (based on F^2 for all data) of 0.0385 and 0.1080, respectively. The final difference Fourier map was featureless. The molecular diagram is drawn with 50% probability ellipsoids.

3. Results and discussion

3.1. Synthesis and characterization of metal complexes

The general procedure for the preparation of complexes **1–8** is shown in Scheme 1. Whereas the nickel complexes **1**, **4** and **9** are known [11], the rest of the complexes are new.

Due to the paramagnetic nature of the isolated iron, cobalt and nickel complexes, ¹H NMR spectra of these complexes were broad and showed large contact shifts; hence NMR spectroscopy was not useful in their characterization. A combination of micro-analyses, mass spectrometry and single crystal X-ray crystallography for **2** and **6** were thus used to elucidate their structures. Indeed molecular ions from the mass spectra were consistent with the molecular weights of monometallic compounds. For instance, the molecular ions of **2** and **3** were observed at $M^+ = 318$ and 314, respectively correspond to the molecular formulae of these compounds proposed in Schemes 1 and 2. The solid state structures of **2** and **6**

from single crystal X-ray crystallographic analyses confirmed these structures.

Crystals of complexes **2** and **6** suitable for single crystals X-ray analyses were grown by slow diffusion of hexane into a CH₂Cl₂ solution of the corresponding complex at -4 °C. The data collection and refinement parameters are given in Table 1 while selected bond lengths and angles of 2 and 6 are listed in Table 2. Molecular structures of **2** and **6** are shown in Figs. 1 and 2, respectively. In the solid state structures of 2 and 6, the cobalt center adopts a distorted tetrahedral geometry, in which the coordination sphere around the metal centers consist of either the bidentate ligand L1 or L3 and two chloride atoms. The Co-N and Co-Cl distances in **2** and **6** fall in the usual ranges [14]. The coordination environment of the Co center is 6 is substantially more distorted than that in 2. Two parameters are very indicative. There first one is the dihedral angle between the planes defined by atoms Co1, N1, N3 and Co1, Cl1, Cl2. In **6**, this angle is $98.37(13)^\circ$, whereas in **2** it is closer to 90° at 86.23(5)°. The second parameter is the angle between the midpoint between atoms N1 and N3, Co1 and the midpoint between Cl1 and Cl2. This angle is 180° in an ideal tetrahedron, but in 2 it is 178.9° and a dramatic 169.9° in 6. Ligand L3 occupies 41.8% of the Co coordination sphere in 6 whereas L1 shields only 38.6% of the metal center in 2. The closer position of the N atoms to the Co center in 6 results in a slightly wider N-Co–N angle in 6. Thus, the apparent bulk of the L3 ligand in 6 and the mutual molecular arrangement in the lattice cause the distortion. Interestingly, the two N atoms in 6 approach the metal center somewhat closer than in 2 despite the fact that ligand L3 is substantially more sterically demanding than L1.

3.2. Polymerization of norbornene

Complexes **1–9** were investigated for their ability to catalyze the polymerization of norbornene using MAO as the co-catalyst. Table 3 contains the optimization results for the norbornene polymerization using catalyst **1**, while Table 4 shows all the polymerization data for catalysts **1–9**.

First, catalyst **1** was used to investigate the effect of co-catalyst to catalyst ratio by varying the Al/Ni ratio from 250:1 to 1500:1. The optimum ratio was found to be 1000:1 (Table 3, entries 1–4). It was clear that lower ratios produced fewer active sites to initiate the polymerization reaction than at 1000:1, leading to reduced activity. Similar observations have been reported for the [(3,5-di-methyl-pyrazol-1-yl)-phenyl-methylene]-phenyl-amine nickel complex by Wang and co-workers, where a decrease in Al/Ni ratio from 800:1 to 400:1 resulted in a decrease in the activity from 6.64×10^5 to 2.21×10^5 g/mol [15]. Increasing reaction time for catalyst **1** from 60 to 90 min resulted in significant increase in percentage conversion from 90% to 99% (Table 3, entries 3 and 6). This indicates the stability of catalyst **1** in the norbornene polymerization reaction. It is also well known that monomer concentration



Scheme 2. Synthesis of 2,6-bis(3,5-dimethylpyrazolylmethyl)pyridine nickel complex 9.

Table 1

Crystal and structure refinement data for complexes 2 and 6.

Parameters	2	6
Empirical formula		C H CLCoN
Formula weight	317.07	AA2 22
Temperature (K)	100(2)	100(2)
Wavelength $(Å)$	0.71073	15/178
Crystal system	triclinic	triclinic
Space group	nī	P2.2.2.
	p1 9.126(2)	7 6595(2)
$u(\Lambda)$	0.130(2) 9.732(2)	15 2401(6)
$D(\mathbf{A})$	0.722(2) 10.206(2)	15.5491(0)
c (A)	10.200(3) 85.602(4)	10.3800(0)
<i>C</i> ()	70.772(4)	90
p()	64.061(4)	90
$\gamma()$ Volumo (Å ³)	641 0(2)	30 1025 40(12)
7	041.0(3)	1923.49(13)
Σ (mg/m ³)	1642	4
D_{calc} (IIIg/III) Absorption coefficient (mm ⁻¹)	1.045	0.618
F(0.00)	277	008
Theta range for collection (°)	2 60-30 06	5 40-64 40
Index ranges	10 < h < 11	8 < h < 8
index ranges	$-10 \le 1 \le 11$ 12 < k < 12	$-0 \leq n \leq 0$ 14 < k < 17
	$-12 \leqslant k \leqslant 12$ 0 < 1 < 14	$-14 \le k \le 17$ 10 < 1 < 10
Reflections collected	3581	20011
Independent reflections	$3581 [R_{\odot} = 0.0483]$	$3086 [R_{\odot} = 0.0470]$
Completeness to theta = 25.0°	99.8%	92 7%
Maximum and minimum	0.8457 and 0.5157	0.3678 and 0.1251
Pofinement method	full matrix loast	full matrix loast
Refinement method	squares F ²	squares F ²
Data/rostraints/paramotors	2591/0/156	2086/0/245
$Coodpess_of_Fit (COF) on F^2$	0.001	1 03/
Final R indices $[I > 2\sigma(I)]$	$R_{\rm c} = 0.0385$	$R_{\rm c} = 0.0401$
Final K multes $[1 \ge 20(1)]$	$K_1 = 0.0383$, WP = 0.1044	$K_1 = 0.0491,$ WP = 0.1201
Pindicos (all data)	$WR_2 = 0.1044$ $P_1 = 0.0462$	$R_2 = 0.1201$
A multes (all uata)	$n_1 = 0.0403$, $m_{R_1} = 0.1080$	$m_1 = 0.0333$, $m_{R_2} = 0.1230$
Largest difference peak and hole (e $Å^{-3}$)	1.346 and -0.489	1.12 and -0.66

Table 2

Selected bond lengths (Å) and angles (°) for complexes 2 and 6.

2		6	
Bond length (Å)			
Co(1)-N(1)	2.0503(19)	Co(1)-N(1)	2.023(4)
Co(1)-N(3)	2.0609(19)	Co(1)-N(3)	2.048(4)
Co(1)-Cl(1)	2.2236(8)	Co(1)-Cl(1)	2.2457(12)
Co(1)-Cl(2)	2.2250(9)	Co(1)-Cl(2)	2.2331(11)
Bond angles (°)			
N(1)-Co(1)-N(3)	90.97(8)	N(1)-Co(1)-N(3)	93.29(14)
N(1)-Co(1)-Cl(2)	113.45(6)	N(1)-Co(1)-Cl(2)	123.04(10)
N(3)-Co(1)-Cl(2)	108.55(6)	N(3)-Co(1)-Cl(2)	103.89(10)
N(1)-Co(1)-Cl(1)	110.00(6)	N(1)-Co(1)-Cl(1)	106.60(10)
N(3)-Co(1)-Cl(1)	114.93(5)	N(3)-Co(1)-Cl(1)	116.12(5)
Cl(1)-Co(1)-Cl(2)	116.30(3)	Cl(1)-Co(1)-Cl(2)	116.12(5)

affect the rates of olefin polymerization reactions [15]. Doubling the norbornene/Ni ratio from 2500:1 to 5000:1 resulted in an increase in polymer yield, but showed a drastic drop in percentage conversion from 90% to 60% (Table 3, entries 3 and 5). We attribute this decrease in percentage conversion to reduced number of active sites of the catalyst that is accessible to the monomer. A similar observation was also made by Myagmarsuren and co-workers [16] where they reported a slight increase in polymer yield but a large decrease in turn-over number with increase in monomer concentration.

Generally high molecular weight polymers of up to 10.5×10^5 g/mol were obtained, typical of vinyl-addition type polynorbornene [1]. Changing the reaction conditions also affected the polymer molecular weight. For example, an increase in Al/Ni ratio



Fig. 1. Molecular structure of complex 2. All hydrogen atoms have been omitted for clarity.



Fig. 2. Molecular structure of complex 6. All hydrogen atoms have been omitted for clarity.

from 500:1 to 2500:1 was followed by a slight decrease in molecular weight from 10.5×10^5 to 9.6×10 g/mol. This trend contrast the observations made for salicylaldimnato nickel(II) catalysts where an increase in Al/Ni from 500:1 to 2000:1 resulted in an increase in polymer molecular weight from 5.73×10^5 to 8.40×10^5 g/mol [7b]. We, however, observed that there was no significant influence of monomer concentration on polymer molecular weight at norbornene/Ni ratios of 2500:1 and 5000:1. This is also consistent with vinyl-addition polymerization process where chain termination occurs *via* β -hydride elimination but not transfer of polymer chain to the monomer [17].

The effect of catalyst structure on norbornene polymerization activity was also investigated under the optimized conditions of

Table 3

Influence of reaction parameters on the norbornene polymerization activity of catalyst $\mathbf{1.}^{\mathrm{a}}$

Entry	Al:Ni	[NBE/Ni]	Yield (g) ^b	Yield (%) ^c	$M_{ m w} imes 10^{5 m d}$	$M_{\rm w}/M_{\rm n}^{\rm d}$
1	250	2500	1.26	25	9.55	2.22
2	500	2500	2.80	56	10.05	2.25
3	1000	2500	4.50	90	9.58	2.21
4	1500	2500	4.45	89	9.56	2.21
5	1000	5000	6.00	60	9.57	2.31
6 ^e	1000	2500	4.95	99	9.53	2.20

^a Polymerization conditions: reaction time, t = 60 min; catalyst: 20 µmol; Al/ Ni = 1000; monomer concentration [NBE/Ni] = 2500; solvent: toluene (40 mL); ratio of norbornene monomer (NBE) to the nickel catalyst.

^b Mass of polymer obtained.

^c Mass of polymer/mass of monomer × 100.

^d Determined by gel permeation chromatography.

^e Time of reaction, t = 90 min.

Table 4

Effect of catalyst structure on polymerization of norbornene.^a

Entry	Catalyst	Yield (g) ^b	Yield (%) ^c	$M_{ m w} imes 10^{5d}$	$M_{\rm w}/M_{\rm n}^{\rm d}$
1	1	4.50	90	5.13	2.38
2	2	1.50	31	6.05	2.76
3	3	3.05	61	6.47	3.01
4	4	3.50	70	5.33	2.18
5	5	3.70	74	nd ^e	-
6	6	1.35	27	nd ^e	-
7	7	2.50	50	nd ^e	-
8	8	3.02	61	5.17	2.64
9	9	3.21	64	21.01	2.44

^a Polymerization conditions: reaction time, *t* = 60 min; catalyst: 20 μmol; Al/ Ni = 1000; [NBE/Ni] = 2500; solvent: toluene (40 mL).

^b Mass of polymer obtained.

^c Mass of polymer/mass of monomer × 100.

^d Determined by gel permeation chromatography.

^a Not determined.



Fig. 3. Effect of catalyst structure on catalyst activity in norbornene polymerization.

Al/Ni of 1000, 1 h and norbornene/catalyst ratio of 2500:1 (Table 4). The nature of the metal was found to have a profound effect on the catalytic activity. Under similar conditions, nickel catalysts 1 and 5, exhibited much higher activities than the corresponding iron and cobalt complexes (2, 3, 6 and 7) (Fig. 3). For example, while the nickel catalysts 1 gave 90% conversion, the corresponding iron and cobalt catalysts, 2 and 3, gave conversions of 31% and 61%, respectively (Table 4, entries 1–3). This is consistent with higher catalytic activities generally observed for nickel in olefin transformation reactions compared to cobalt and iron analogues [18]. We have also recently observed similar trend in ethylene oligomerization where nickel complexes of L1 and L3 are highly active, while the palladium, cobalt and iron show very low activity [9e,11].

Both the electronic and steric properties of the ligands influenced the norbornene polymerization activity. For example, catalyst **1** bearing electron-donating methyl groups on the pyrazolyl motif showed greater activity (90%) than the corresponding catalyst (**8**) containing electron-withdrawing CF₃ groups (61%). It is generally believed that electron-donating groups increased the stability of the active species while electron-withdrawing groups reduces the stability of the active species [7a]. Steric factors also influenced the catalytic properties of the complexes used in this study. While the iron catalyst bearing methyl groups (**3**) showed conversions of 61%, the phenyl analogue (**7**) gave conversions of 50%. A similar trend was observed for the nickel and cobalt catalysts (Fig. 3). A possible reason for this decrease in activity with increased steric bulk could be reduced accessibility of the monomer to the vacant metal center. This hypothesis is also supported by the low activity of the crowded tridentate-bound catalyst **9** (64%) in comparison to the more accessible bidentate-bound analogue, **1**, (90%).

The molecular weight of the polynorbornene produced was also regulated by the structure of the catalysts. An increase in steric bulk from methyl group in **1** to *tert*-butyl group in **4** resulted in an increase in molecular weight from 5.13×10^5 to 5.33×10^5 . This is normal for addition polymerization reactions and results from reduced β -hydride elimination with increase in steric hindrance [17]. A more interesting observation made in this work was the extreme high molecular weights of polymers obtained using catalyst **9** containing the tridentate ligand **L5** which shields the metal atom by 59.6% [9e]; hence promoting chain propagation over chain termination as compared to the smaller bidentate ligands **L1–L5** which shields the metal atom by 38.8–46.5% [11].

All the polymers obtained were slightly soluble in benzene, chlorobenzene and other chlorinated solvents indicating low stereoregularity. Attempts to determine melting points and glass transition temperatures were not successful. TGA-DSC analyses showed the polymers decomposed before melting. Thus attempts to determine melting points and glass transition temperatures of the polymers were not successful.

The polymer microstructure was investigated by ¹H NMR, ¹³C NMR and IR spectroscopy. All the polymers showed very similar NMR and IR spectra, indicating that the type of polynorbonene produced is independent of the catalyst system and reaction

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conditions. The absence of signature peaks for C=C protons at 5.1 ppm in the ¹H NMR spectra is indicative of vinyl-addition type polymers and not ROMP-type polymers [19]. This is also supported by the absence of signals in the 1680–1620 cm⁻¹ range of the IR spectra, typical of vinyl-addition type polynorbonene [20]. The broad unresolved nature of the ¹³C NMR spectra made it impossible to assign the stereochemistry of the polymers.

4. Conclusions

We have demonstrated that nickel complexes of 2-(pyrazol-1-ylmethyl)pyridine and 2,6-bis(pyrazol-1-ylmethyl)pyridine ligands produce very active catalysts for the vinyl-addition polymerization of norbornene to give high molecular weight polymers. The corresponding iron and cobalt display low catalytic activities. The nature of the catalyst influences both the activity and polymer molecular weight.

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Appendix A. Supplementary data

CCDC 832409 and 832410 contain the supplementary crystallographic data for compounds **2** and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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