An Additional Potential Donor-bearing Alkylidene-containing Latent NHC-Rutheniumbased Catalyst for Olefin Metathesis Polymerization

Dharmalingam Sivanesan^a, Bongkuk Seo^a, Choong-Sun Lim^a, Dongchen Choi^a, Taehee Kim^a and Hyeon-Gook Kim^a,*

Advanced Industrial Chemistry Research Center, Advanced Convergent Chemistry Division, Korea Research Institute of Chemical Technology (KRICT), 45 Jonggaro, Ulsan, 44412, Korea.

Contents

S.No		Title	Page No
1	Figure S1	¹ H NMR spectra of Ligand L1, complex 1 and SM	S3
2	Figure S2	¹ H NMR spectra of Ligand L2, complex 2 and SM	S3
3	Figure S3	¹ H NMR spectra of Ligand L3, complex 3 and SM	S4
4	Figure S4	¹ H NMR spectra of Ligand L3, complex 4 and SM	S4
5	Figure S5	Exotherm plot of ROMP of DCPD for 1, 2 and complex C at 80 °C.	S5
		Catalysts and DCPD ratio: 1:10000	
6	Figure S6	FT-IR spectra of ligands (L1-L4)	S 6
7	Figure S7	FT-IR spectra of compounds (1-4)	S 7
8	Figure S8	DSC curves for mixture of catalysts (1, 2, 3 and 4) and DCPD in	S 8
		the ration of 1:1000, heating rate 10 °C/min	
9	Table S1	FT-IR analysis data for ligand and complex (change in $-C=N$)	S9
10	Table S2	$T_{\rm g}$ of the PDCDP obtained from complexes 1-4 in the ration of cat:DCPD = 1:10000, N/R -not recorded	S9
11	Table S3	Crystal data and structure refinement for 4	S10
12	Table S4	Bond lengths [Å] and angles [°] for 4	S11
13	Table S5	Polymerization enthalpies of mixture of catalysts (1, 2, 3 and 4)	S11
		and DCPD in the ratio of 1:1000	
14	Table S6	Pot life of the precatalyst - DCPD mixtures at room temperatures	S12



Figure S1. ¹H NMR spectra of ligand L1, complex 1 and SM

Figure S2. ¹H NMR spectra of ligand L2, complex 2 and SM





Figure S3. ¹H NMR spectra of ligand L3, complex 3 and SM

Figure S4. ¹H NMR spectra of ligand L3, complex 4 and SM





Figure S5: Exotherm plot of ROMP of DCPD for 1, 2 and complex C at 80 °C. Catalysts and DCPD ratio: 1:10000

Figure S6. FT-IR spectra of ligands (L1-L4)



Figure S7. FT-IR spectra of compounds (1-4)





Figure S8. DSC curves for mixture of catalysts (1, 2, 3 and 4) and DCPD in the ratio of 1:1000, heating rate 10 °C/min.

Entry	Catalyst	Ligand	Catalyst v _(C=N) , cm ⁻¹	Ligand v _(C=N) , cm ⁻¹	Frequency change $\Delta v_{(C=N)}$
1	1	L1	1652	1665	13
2	2	L2	1649	1664	15
3	3	L3	1653	1665	12
4	4	L4	1644	1660	16

Table S1. FT-IR analysis data for ligand and complex (change in –C=N)

Table S2. The T_g of the PDCDP obtained from complexes **1-4** in the ration of cat:DCPD = 1:10000, N/R –not recorded

Entry	Catalyst	T _g of the PDCDP at	T _g of the PDCDP at
		30 and 60 °C	80 °C
1	1	96.45	144.21
2	2	107.82	149.21
3	3	108.14	N/R
4	4	114.41	N/R
5	complex C	130.91	153.98

Table 55. Crystal data and structure refinement fo	of 4		
CCDC number	1954315		
Empirical formula	C36 H46 Cl2 N3 Ru		
Formula weight	692.73		
Temperature	296(1) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2(1)/n		
Unit cell dimensions	a = 13.6977(4) Å	<i>α</i> = 90°.	
	b = 11.9911(3) Å	β= 96.9080(10)°.	
	c = 21.2056(5) Å	$\gamma = 90^{\circ}$.	
Volume	3457.75(16) Å ³		
Ζ	4		
Density (calculated)	1.331 Mg/m ³		
Absorption coefficient	0.636 mm ⁻¹		
F(000)	1444		
Crystal size	0.30 x 0.20 x 0.08 mm ³		
Theta range for data collection	1.88 to 26.79°		
Index ranges	-17<=h<=17, 0<=k<=15, 0<=l	<=26	
Reflections collected	7350		
Independent reflections	7350 [R(int) = 0.0000]		
Completeness to theta = 26.79°	99.8 %		
Absorption correction	Multi-scan		
Max. and min. transmission	0.9509 and 0.8321		
Refinement method	Full-matrix least-squares on F ²	2	
Data / restraints / parameters	7350 / 10 / 379		
Goodness-of-fit on F ²	1.055		
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1316		
R indices (all data)	R1 = 0.0617, wR2 = 0.1422		
Largest diff. peak and hole	1.039 and -0.706 e.Å ⁻³		

Ru(1)-C(22)	1.786(4)
Ru(1)-C(1)	2.043(3)
Ru(1)-N(3)	2.135(3)
Ru(1)-Cl(2)	2.3700(10)
Ru(1)-Cl(1)	2.3781(10)
C(22)-Ru(1)-C(1)	98.37(15)
C(22)-Ru(1)-N(3)	89.01(14)
C(1)-Ru(1)-N(3)	172.45(12)
C(22)-Ru(1)-Cl(2)	97.08(16)
C(1)-Ru(1)-Cl(2)	95.19(10)
N(3)-Ru(1)-Cl(2)	85.41(9)
C(22)-Ru(1)-Cl(1)	94.50(16)
C(1)-Ru(1)-Cl(1)	89.42(10)
N(3)-Ru(1)-Cl(1)	88.42(9)

Table S4.Bond lengths [Å] and angles [°] for 4

Table S5. Polymerization ΔH of mixture of catalysts (1, 2, 3 and 4) and DCPD in the ratio of 1:1000

Entry	Catalysts	$\Delta H \left(\mathrm{J/g} \right)$
1	1	-116
2	2	-98.2
3	3	-175
4	4	-126
5	G1 ^(reported)	-3471

Table S6. Pot life of the precatalyst - DCPD mixtures at room temperatures

Entry	Catalyst	Pot life of the precatalyst-DCPD mixtures at ambient		
		temperatures (1:10000, precatalyst:DCPD ratio)		
1	1	no gelation for 120 h		
2	2	no gelation for 120 h		
3	3	gelation was observed after 30 min		
4	4	gelation was observed after 6 min		
5	С	gelation was observed after 2 min		