Supporting Information for:

Norbornene polymerization and copolymerization with 1alkenes by neutral palladium complexes bearing aryloxide imidazolin-2-imine ligand

Mingyuan Li,^a Hu Zhang,^a Zhengguo Cai *^a and Moris S. Eisen *^b

^aState Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China ^bSchulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa, 32000, Israel

Table of Contents

1. Polymerization results	.S2
2. NMR spectra of the complexes Pd1–Pd3	
3. High resolution mass spectrometry (HRMS) of the complexes Pd1–Pd3.	S7
4. X-ray crystallography of the complexes Pd1–Pd3	S8
5. NMR spectra of norbornene homopolymers and copolymers	S9–S21
6. GPC data of norbornene homopolymers and copolymers	
7. DSC data of norbornene homopolymers and copolymers	

1. Polymerization results

		1 1		J - 1			,	
ent.	cat.	co-cat.	Al/Pd	<i>T</i> (°C)	yield(g)	act. ^b (10 ⁶)	$M_{\rm n}^{\rm c}(10^4)$	PDIc
1	Pd2	MAO	1000	40	1.392	1.67	_d	_d
2	Pd2	MMAO	1000	40	1.209	1.45	_d	_d
3	Pd2	Et ₂ AlCl	500	40	0.074	0.09	0.97	2.55
4	Pd2	EtAlCl ₂	500	40	0.896	1.08	9.12	2.35
5	Pd3	MAO	1000	40	1.190	1.43	_d	_d
6	Pd3	MAO	1000	40	1.122	1.35	_d	_d
7	Pd3	Et ₂ AlCl	500	40	0.105	0.13	2.17	1.62
8	Pd3	EtAlCl ₂	500	40	0.853	1.02	9.26	1.94

Table S1. Norbornene polymerization by complexes Pd2 and Pd3 with different cocatalysts^a

^aPolymerization conditions: Pd complexes, 5 μ mol; co-cat., MAO, 1.4 M in toluene; MMAO, 2.43 M in toluene; Et₂AlCl, 0.9 M in *n*-hexane; EtAlCl₂, 1.8 M in toluene; norbornene, 20 mmol, 1.883 g; V_{total} (toluene)= 15 mL; t = 10 min. ^bAcitivity in units of g·mol⁻¹·h⁻¹. ^cGPC data in 1,2,4-trichlorobenzene at 150 °C with polystyrene standards, M_n in units of g·mol⁻¹. ^dInsoluble polymers.

2. NMR spectra of the complexes Pd1-Pd3.



Figure S1. ¹H NMR spectrum of complex Pd1 (*Solvent: CH₂Cl₂ and impurities).



Figure S2. ¹³C NMR spectrum of complex Pd1.



Figure S3. ³¹P NMR spectrum of complex Pd1.



Figure S4. ¹H NMR spectrum of complex Pd2 (*Solvent: *n*-hexane and impurities).



Figure S5. ¹³C NMR spectrum of complex Pd2 (*Solvent: *n*-hexane).



Figure S6. ³¹P NMR spectrum of complex Pd2.



Figure S7. ¹H NMR spectrum of complex Pd3 (*Solvent: *n*-hexane, toluene, THF and CH_2Cl_2).



Figure S8. ¹³C NMR spectrum of complex Pd3 (*Solvent: *n*-hexane, toluene, THF and CH_2Cl_2).

3. High resolution mass spectrometry (HRMS) of the complexes

Pd1-Pd3.



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Form	ula					
692.2971	692.2961	1.0	1.4	13.5	268.9	0.0	C37	H53	N3	0	P	Pd	

40.0

Maximum:

10.0

Figure S10. High Resolution Mass Spectrometry (HRMS) of complex Pd2.



Figure S11. High Resolution Mass Spectrometry (HRMS) of complex Pd3.

4. X-ray crystallography of the complexes Pd1–Pd
--

Complexes	Pd1 ^a	Pd2 ^b	Pd3 ^a
Identification code	Moris563b	Moris558b	Moris565b
Empirical formula	$C_{32}H_{42}C1_2N_3OPPd$	$C_{46}H_{61}N_3OPPd$	$C_{79}H_{64}C1_2N_3OPd$
Formula weight	692.96	809.34	1248.63
Temperature/K	200.15	296.15	296.15
Crystal system	triclinic	monoclinic	triclinic
Space group	P-1	$P2_1/c$	P-1
a/Å	13.5869(9)	16.510(7)	11.1555(12)
b/Å	14.2487(10)	10.817(5)	13.2102(14)
c/Å	19.0045(13)	24.396(10)	21.891(2)
α/°	104.6320(10)	90	75.266(2)
β/°	90.5370(10)	99.031(11)	86.560(2)
γ/°	111.5870(10)	90	88.068(2)
Volume/Å ³	3288.7(4)	4303 (3)	3113.7(6)
Z	4	4	2
$\rho_{calc}g/cm^3$	1.400	1.249	1.332
μ/mm^{-1}	0.804	0.505	0. 434
F(000)	1432.0	1708.0	1294.0
Crystal size/mm ³	0.3 \times 0.12 \times	0.21 \times 0.15 \times	0.18 \times 0.15 \times
	0.09	0.09	0.12
Radiation	MoK α (λ =	MoK α (λ =	MoK α (λ =
Radiation	0.71073)	0.71073)	0.71073)
2Θ range for data collection/°	2.23 to 48.318	2.498 to 50.82	1.926 to 50.72
	-15 \leqslant h \leqslant 15, -	-19 \leqslant h \leqslant 18, -	-12 \leqslant h \leqslant 12, -
Index ranges	$16 \leqslant k \leqslant 16$, -	$12\leqslantk\leqslant12$, –	$15 \leqslant k \leqslant 15$, -
	$21 \leqslant 1 \leqslant 21$	$29 \leqslant 1 \leqslant 29$	$26 \leq 1 \leq 25$
Reflections collected	34596	38659	36061
	10458	$7830 [R_{int} =$	10774 [R _{int} =
Independent reflections	$[R_{int} = 0.0646,$	0.0825, R_{sigma} =	0.0728, $R_{sigma} =$
	$R_{sigma} = 0.0525$]	0.0759]	0.0771]
Data/restraints/parameters	10458/0/741	7830/0/469	10774/243/787
Goodness-of-fit on F ²	1.003	0.985	1.048
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0294,$	$R_1 = 0.0441,$	$R_1 = 0.0547,$
	$wR_2 = 0.0685$	$wR_2 = 0.0869$	$wR_2 = 0.1368$
Final R indexes [all data]	$R_1 = 0.0411,$	$R_1 = 0.0670,$	$R_1 = 0.0908,$
i mai it mueres [un uata]	$wR_2 = 0.0733$	$wR_2 = 0.0763$	$wR_2 = 0.1556$
Largest diff. peak/hole / e Å-3	0.43/-0.55	0.67/-1.53	1.15/-1.08

Table S2. Crystal	data and structur	re refinement for	r the complexes P	d1-Pd3

^aThere are cocrystallized CH_2Cl_2 molecules in the unit cell. ^bThere are cocrystallized benzene molecules in the unit cell.

5. NMR spectra of norbornene homopolymer and copolymers



Figure S12. Selected ¹H NMR spectrum (600 MHz, $CDCl_3$, r.t.) of norbornene homopolymer obtained by Pd2 (Table 1, entry 8).



Figure S13. Selected ¹H NMR spectra of (a) poly(NB-co-1-dodecene) and (b) poly(NB-co-1-octadecene) obtained by Pd/EtAlCl₂ system.



Figure S14. ¹H NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by **Pd1** (Table 2, (a) entry 1; (b) entry 2; (c) entry 3).



Figure S15. ¹H NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by **Pd2** (Table 2, (a) entry 4; (b) entry 5; (c) entry 6).



Figure S16. ¹H NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by **Pd3** (Table 2, (a) entry 7; (b) entry 8; (c) entry 9).



Figure S17. ¹H NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by **Pd1** (Table 2, (a) entry 10; (b) entry 11; (c) entry 12).



Figure S18. ¹H NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by **Pd2** (Table 2, (a) entry 13; (b) entry 14; (c) entry 15).



Figure S19. ¹H NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by **Pd3** (Table 2, (a) entry 16; (b) entry 17; (c) entry 18).



Figure S20. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by Pd1 (Table 2, entry 1).



Figure S21. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by **Pd1** (Table 2, entry 2).



Figure S22. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by **Pd1** (Table 2, entry 3).



Figure S23. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by Pd2 (Table 2, entry 4).



Figure S24. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by **Pd2** (Table 2, entry 5).



Figure S25. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by Pd2 (Table 2, entry 6).



Figure S26. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by **Pd3** (Table 2, entry 7).



Figure S27. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by Pd3 (Table 2, entry 8).



Figure S28. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-dodecene)s obtained by **Pd3** (Table 2, entry 9).



Figure S29. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by Pd1 (Table 2, entry 10).



Figure S30. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by **Pd1** (Table 2, entry 11).



Figure S31. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by Pd1 (Table 2, entry 12).



Figure S32. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by **Pd2** (Table 2, entry 13).



Figure S33. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by **Pd2** (Table 2, entry 14).



Figure S34. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by **Pd2** (Table 2, entry 15).



Figure S35. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by **Pd3** (Table 2, entry 16).



Figure S36. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by **Pd3** (Table 2, entry 17).



Figure S37. ¹³C NMR spectra (600 MHz, CDCl₃, r.t.) of poly(NB-co-1-octadecene)s obtained by **Pd3** (Table 2, entry 18).



6. GPC data of norbornene homopolymers and copolymers

Figure S38. GPC trace of PNB obtained by Pd2 from table 1, entry 8.

Figure S39. GPC trace of PNB obtained by Pd1 from table 1, entry 12.

Figure S40. GPC trace of PNB obtained by Pd3 from table 1, entry 19.

Figure S41. GPC trace of poly(NB-co-1-dodecene) obtained by **Pd1** from table 2, entry 1.

Figure S42. GPC trace of poly(NB-co-1-dodecene) obtained by **Pd1** from table 2, entry 2.

Figure S43. GPC trace of poly(NB-co-1-dodecene) obtained by **Pd1** from table 2, entry 3.

Figure S44. GPC trace of poly(NB-co-1-dodecene) obtained by **Pd2** from table 2, entry 4.

Figure S45. GPC trace of poly(NB-co-1-dodecene) obtained by **Pd2** from table 2, entry 5.

Figure S46. GPC trace of poly(NB-co-1-dodecene) obtained by **Pd2** from table 2, entry 6.

Figure S47. GPC trace of poly(NB-co-1-dodecene) obtained by **Pd3** from table 2, entry 7.

MW Averag	ges							
Peak No.	Мр	Mn	Mw	Mz	Mz+1	Mv	PD	
1	99826	41642	95277	153260	221341	87566	2.288	
Processed P	eak Inform	ation						
Peak/Trac	Name	Start RT	Max RT	End RT	Height	Height	Area	Area
e No.		(mins)	(mins)	(mins)	(mV)	(%)	(mV.sec)	(%)
1		11.5667	13.05	15.7833	-39.6753	100	3054.48	100

Figure S48. GPC trace of poly(NB-co-1-dodecene) obtained by **Pd3** from table 2, entry 8.

Figure S49. GPC trace of poly(NB-co-1-dodecene) obtained by **Pd3** from table 2, entry 9.

Figure S50. GPC trace of poly(NB-co-1-octadecene) obtained by Pd1 from table 2, entry 10.

Figure S51. GPC trace of poly(NB-co-1-octadecene) obtained by Pd1 from table 2, entry 11.

Figure S52. GPC trace of poly(NB-co-1-octadecene) obtained by Pd1 from table 2, entry 12.

Figure S53. GPC trace of poly(NB-co-1-octadecene) obtained by Pd2 from table 2, entry 13.

Figure S54. GPC trace of poly(NB-co-1-octadecene) obtained by Pd2 from table 2, entry 14.

Figure S55. GPC trace of poly(NB-co-1-octadecene) obtained by Pd2 from table 2, entry 15.

Figure S56. GPC trace of poly(NB-co-1-octadecene) obtained by Pd3 from table 2, entry 16.

Figure S57. GPC trace of poly(NB-co-1-octadecene) obtained by Pd3 from table 2, entry 17.

Figure S58. GPC trace of poly(NB-co-1-octadecene) obtained by Pd3 from table 2, entry 18.

7. DSC data of norbornene homopolymers and copolymers

Figure S59. DSC curve of NB homopolymer obtained by Pd2 (Table 1, entry 8).

Figure **S60**. DSC curve of poly(NB-co-1-dodecene) obtained by **Pd1** (Table 2, entry 1).

Figure S61. DSC curve of poly(NB-co-1-dodecene) obtained by Pd1 (Table 2, entry 2).

Figure **S62**. DSC curve of poly(NB-co-1-dodecene) obtained by **Pd1** (Table 2, entry 3).

Figure **S63**. DSC curve of poly(NB-co-1-dodecene) obtained by **Pd2** (Table 2, entry 4).

Figure S. DSC curve of poly(NB-co-1-dodecene) obtained by Pd2 (Table 2, entry 5).

Figure **S64**. DSC curve of poly(NB-co-1-dodecene) obtained by **Pd2** (Table 2, entry 6).

Figure **S65**. DSC curve of poly(NB-co-1-dodecene) obtained by **Pd3** (Table 2, entry 7).

Figure **S66**. DSC curve of poly(NB-co-1-dodecene) obtained by **Pd3** (Table 2, entry 8).

Figure **S67**. DSC curve of poly(NB-co-1-dodecene) obtained by **Pd3** (Table 2, entry 9).

Figure **S68**. DSC curve of poly(NB-co-1-octadecene) obtained by **Pd1** (Table 2, entry 10).

Figure **S69**. DSC curve of poly(NB-co-1-octadecene) obtained by **Pd1** (Table 2, entry 11).

Figure S. DSC curve of poly(NB-co-1-octadecene) obtained by Pd1 (Table 2, entry 12).

Figure **S70**. DSC curve of poly(NB-co-1-octadecene) obtained by **Pd2** (Table 2, entry 13).

Figure **S71**. DSC curve of poly(NB-co-1-octadecene) obtained by **Pd2** (Table 2, entry 14).

Figure **S72**. DSC curve of poly(NB-co-1-octadecene) obtained by **Pd2** (Table 2, entry 15).

Figure **S73**. DSC curve of poly(NB-co-1-octadecene) obtained by **Pd3** (Table 2, entry 16).

Figure S. DSC curve of poly(NB-co-1-octadecene) obtained by Pd3 (Table 2, entry 17).

Figure **S74**. DSC curve of poly(NB-co-1-octadecene) obtained by **Pd3** (Table 2, entry 18).