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Olefin Metathesis

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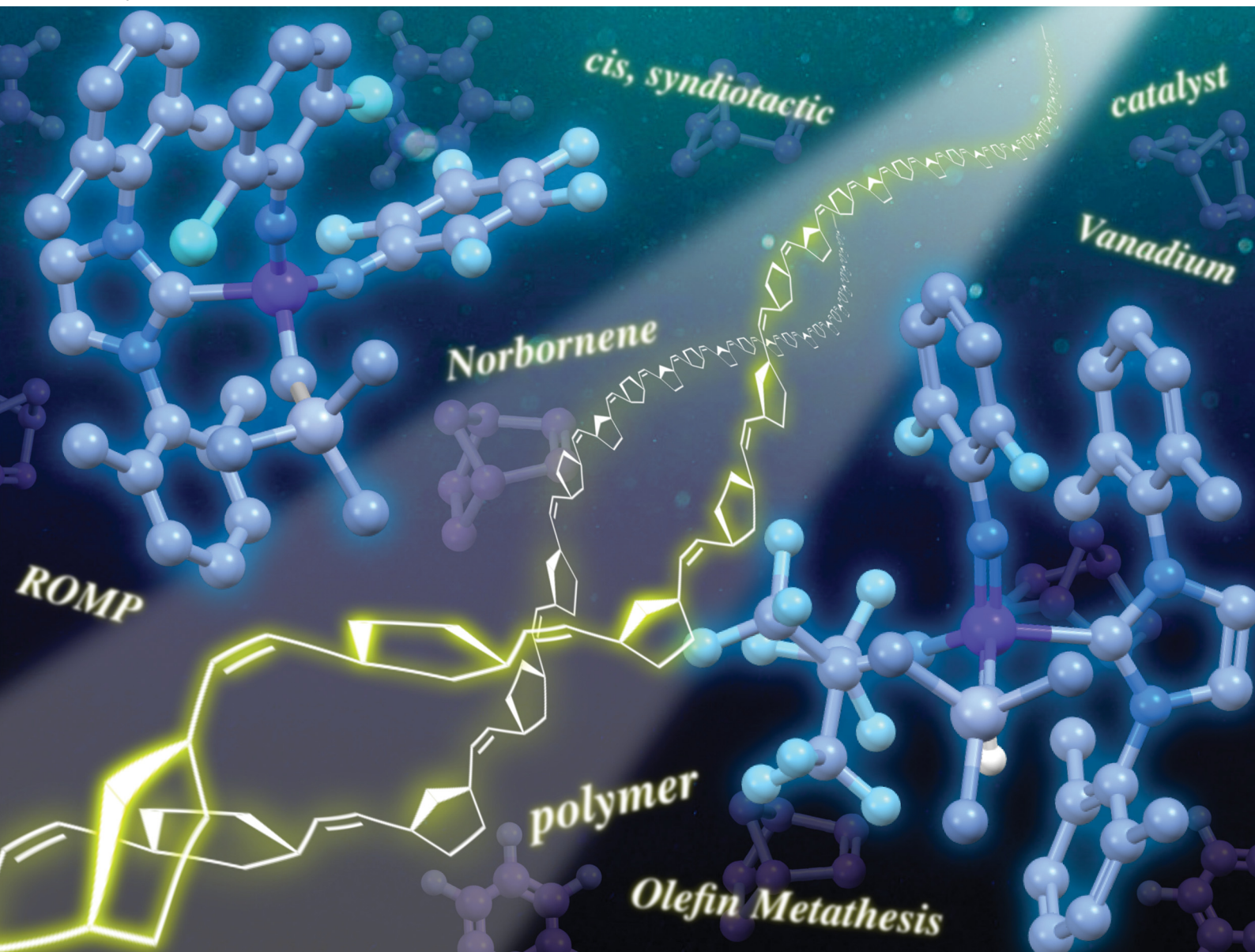
Vanadium(v) arylimido alkylidene N-heterocyclic carbene complexes containing fluorinated alkoxide or halogenated phenoxide ligands for the syndiospecific ROMP of cyclic olefins†

Kotohiro Nomura, [iD] *[a] Shuko Kuwahara,‡[a] Jirapa Suthala,‡[a] Yuta Kawamoto,[a] Daisuke Shimoyama[a] and Michael R. Buchmeiser [iD] *[bc]

[V(N-2,6-Cl$_2$C$_6$H$_3$)(CHSiMe$_3$)(OC$_6$X$_5$)(NHC)] [X = F (**1**), Cl (**2**), NHC = 1,3-bis-(2,6-dimethylphenyl)-imidazol-2-ylidene], exhibited remarkable catalytic activities [TOF = 133–193 s^{-1} (**1**), 90.9–126 s^{-1} (**2**)] for ring opening metathesis polymerisation (ROMP) of norbornene (NBE) at 25 °C to afford ring-opened polymers not only with high *cis*-(93–98%) selectivity, but also with exclusive syndiotactic stereo-regularity. These polymerisations proceeded in a living manner under optimised conditions. The activity improved at 50 °C with decreasing in the *cis* specificity. Synthesis and the structural analysis of the fluorinated alkoxide complexes, [V(N-2,6-X$_2$C$_6$H$_3$)(CHSiMe$_3$){OC(CF$_3$)$_3$}(NHC)] [X = F (**3**), Cl (**4**)] have been studied, and the difluorophenylimdo complex (**3**) exhibited comparable catalytic activities for ROMP of NBE. The *cis* selectivities in the resultant polymers prepared by **3** were low (88%) and the selectivities in the ring-opened poly(tetracyclododecene) (TCD) were low (61–66%) compared to those in poly(NBE)s. The resultant ring opened poly(TCD) possessed syndiotactic stereo-regularity confirmed by DSC thermogram of the hydrogenated polymers.
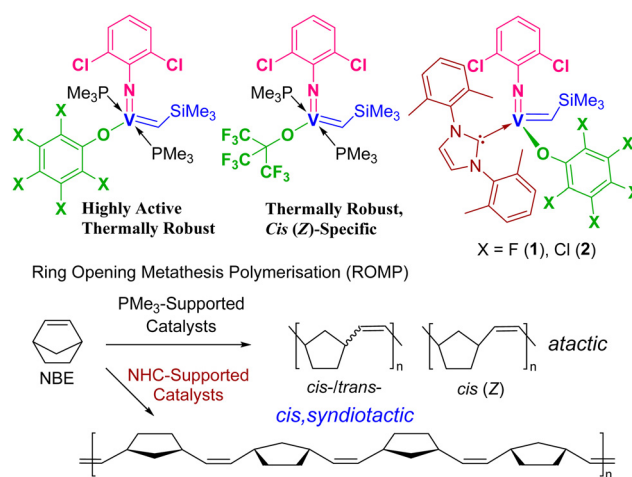
1. Introduction

Olefin metathesis is an efficient method for synthesis of the fine chemicals, and advanced polymers.[1–5] Ring opening metathesis polymerisation (ROMP) especially offers access to the functional polymeric materials.[2] In this catalysis, metal-carbene (alkylidene) complexes act as the key intermediate,[3–5] and development of the alkylidene catalysts with earth abundant metal has thus been the important subject in long term. The PMe$_3$-supported vanadium–alkylidenes, [V(N-2,6-X$_2$C$_6$H$_3$)(CHSiMe$_3$)(OR)(PMe$_3$)$_2$] [X = F, Cl; R = C$_6$F$_5$, C$_6$Cl$_5$, C(CF$_3$)$_3$, Scheme 1, display high potentials in the ROMP of cyclic olefins,[4,6] particularly in *Z* specific ROMP at 80 °C,[6a,b] in the high temperature controlled ROMP of low

strain cyclic olefins (cycloheptene, *cis*-cyclooctene),[6d] and in the *Z/E* specific synthesis of bottlebrush polymers.[6g]

N-Heterocyclic carbenes (NHC) have been known to stabilise high oxidation state organometallic complexes with early transition metals,[7,8] as demonstrated *e.g.* for molybdenum, tungsten,[3g,i,7] and vanadium.[6f,8] Recently, we communicated that ROMP of

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† Electronic supplementary information (ESI) available: (i) Additional results for ring-opening metathesis polymerisation of norbornene, (ii) selected NMR spectra of the polymers, (iii) selected DSC thermograms of the polymers after hydrogenation, and (iv) additional adda including crystal data and collection parameters for structural analysis of [V(CHSiMe$_3$)(N-2,6-X$_2$C$_6$H$_3$){OC(CF$_3$)$_3$}(NHC)] (X = F, Cl). CCDC 2358163 and 2358164. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4nj02537g
‡ SK and JS: equal contribution.

Scheme 1 Reported (arylimido)vanadium–alkylidene complexes supported by PMe$_3$ or NHC ligands,[6] and *cis*, syndiospecific ROMP of NBE by catalysts **1** and **2**.[6f]

norbornene (NBE) by the vanadium–alkylidene NHC complexes containing perhalogenated phenoxide ligands, [V(N-2,6-Cl$_2$C$_6$H$_3$)(CHSiMe$_3$)(OC$_6$X$_5$)(NHC)] [X = F (**1**), Cl (**2**); NHC = 1,3-bis-(2,6-di-methylphenyl)-imidazol-2-ylidene (IXy)] gave *cis*-, syndiotactic ring-opened polymers (Scheme 1).[6f] High stereo-control in ROMP has also been reported for cationic molybdenum and tungsten imido or oxo alkylidene NHC initiators.[7]

We herein report the ROMP of NBE using catalysts **1** and **2** affording highly *cis* ring-opened polymers with exclusive syndiotactic stereoregularity even at 50 °C. The controlled (living) polymerisation could be demonstrated under optimised (diluted) conditions. Moreover, synthesis and structural analysis of the fluorinated alkoxide complexes, [V(N-2,6-X$_2$C$_6$H$_3$)(CHSiMe$_3$){OC(CF$_3$)$_3$}(NHC)] [X = F (**3**), Cl (**4**)], and their use as the catalysts for ROMPs of NBE, tetracyclo-dodecene (TCD) has been explored.

2. Results and discussion

2.1. Ring opening metathesis polymerisation of norbornene (NBE) by [V(N-2,6-Cl$_2$C$_6$H$_3$)(CHSiMe$_3$)(OC$_6$X$_5$)(NHC)] [X = F (**1**), Cl (**2**)]

As communicated previously,[6f] the ring opening metathesis polymerisations (ROMPs) of NBE by the vanadium catalysts (**1**, **2**) reaches completion within 1 or 2 minutes (runs 1, 4, 8, Table 1). Therefore, the ROMPs of NBE were conducted in benzene at 25 °C and 50 °C, respectively, applying different conditions (NBE/benzene = 2.12 mmol/4.8 mL or 4.24 mmol/9.6 mL, initial NBE conc. 0.44 mmol mL^{-1}). Table 1 summarises the results.

It should be noted that the pentafluoro phenoxide complex (**1**) showed higher catalytic activities (TOF 193 s^{-1}, run 3) than the pentachloro phenoxide (**2**, TOF 147 s^{-1}, run 11) when ROMP was conducted at 25 °C. The observed catalytic activities with **1** and **2** were at a similar level than those observed for the PMe$_3$-supported catalyst, [V(N-2,6-Cl$_2$C$_6$H$_3$)(CHSiMe$_3$)(OC$_6$F$_5$)–(PMe$_3$)$_2$] (TOF 153 s^{-1}), conducted under the similar conditions.[6a] The resultant poly(NBE)s prepared at 25 °C displayed high *cis* contents [92–94% (by **1**), 95–98% (by **2**)] and possessed high molecular weights with unimodal molecular weight distributions. The *cis* selectivity of **2** was slightly higher than that of **1**.

It was revealed that the catalytic activity slightly increased when the ROMPs (by **1**, **2**) were conducted at 50 °C, whereas the *cis* selectivity apparently decreased in all cases (runs 5, 6, 8, 10). The observed catalytic activity by **2** at 50 °C was improved by *in situ* addition of small amount of PMe$_3$ (1–3 equiv.), whereas the *cis* selectivity decreased by addition of PMe$_3$. The further addition suppressed the activity and the *cis* selectivity (runs 21–24).

Fig. 1a shows ^{13}C NMR spectrum (in CDCl$_3$ at 50 °C) of the hydrogenated polymer sample (run 19) prepared by treating with 4-MeC$_6$H$_4$SO$_2$NHNH$_2$ (excess) in toluene at 130 °C,[9,10] and Fig. 1b showed the extended resonances around 31–32 ppm for the estimation of tacticity of the polymers prepared under different conditions (catalyst, temperature); the other selected spectra are shown in ESI.† Note that the resultant hydrogenated polymer prepared by **2** showed a sole resonance at 31.7 ppm,

Table 1 Ring opening metathesis polymerisation (ROMP) of norbornene (NBE) by [V(N-2,6-Cl$_2$C$_6$H$_3$)(CHSiMe$_3$)(OC$_6$X$_5$)(NHC)] [X = F (**1**), Cl (**2**)][a]

Run	Cat. (μmol)	NBE/mmol	PMe$_3$[b]/equiv.	Temp./°C	Time/min	Yield/%	TON[c]	TOF[c]/h^{-1} (s^{-1})	M_n[d] × 10^{-5}	M_w/M_n[d]	*cis*[e]/%
1[f]	**1** (0.3)	2.12	—	25	1	97	6860	412 000 (114)	4.72	2.26	93
2	**1** (0.3)	2.12	—	50	1	>99	7040	423 000 (117)	6.21	1.98	81
3	**1** (0.1)	2.12	—	25	1	55	11 600	695 000 (193)	6.96	2.29	94
4	**1** (0.1)	2.12	—	25	2	88	18 600	558 000 (155)	7.51	2.89	94
5	**1** (0.1)	2.12	—	50	1	59	12 500	752 000 (209)	7.76	2.42	86
6	**1** (0.1)	2.12	—	50	2	91	19 300	580 000 (161)	8.96	3.02	86
7	**2** (0.5)	2.12	—	25	1	90	3800	228 000 (63.4)	3.73	1.65	97
8	**2** (0.5)	2.12	—	50	1	98	4140	249 000 (69.0)	4.67	1.73	91
9	**2** (0.3)	2.12	—	25	1	77	5450	327 000 (90.9)	4.44	1.86	97
10	**2** (0.3)	2.12	—	50	1	88	6200	372 000 (103)	5.44	2.07	91
11[f]	**2** (0.1)	2.12	—	25	1	42	8830	530 000 (147)	5.66	2.16	98
12[f]	**2** (0.1)	2.12	—	25	2	62	13 300	399 000 (111)	6.62	2.19	97
13[f]	**1** (0.5)	4.24	—	25	1	96	8150	489 000 (136)	6.17	2.15	93
14	**1** (0.5)	4.24	—	25	1	94	7990	479 000 (133)	5.86	2.12	92
15	**1** (0.3)	4.24	—	25	1	75	10 500	633 000 (176)	8.92	2.05	95
16	**1** (0.3)	4.24	—	50	1	77	10 900	656 000 (182)	7.11	2.52	88
17[f]	**2** (0.5)	4.24	—	25	1	75	6400	384 000 (107)	6.64	1.77	97
18	**2** (0.5)	4.24	—	50	1	75	6390	384 000 (107)	6.12	1.96	89
19	**2** (0.3)	4.24	—	25	1	53	7540	452 000 (126)	6.55	1.76	95
20	**2** (0.3)	4.24	—	50	1	60	8460	508 000 (141)	4.31	2.26	90
21[g]	**2** (0.5)	2.12	—	50	3	54	2290	45 900 (12.7)	5.29	1.66	88
22[g]	**2** (0.5)	2.12	1.0	50	3	73	3080	61 600 (17.1)	6.42	1.83	76
23[g]	**2** (0.5)	2.12	3.0	50	3	70	2950	59 000 (16.4)	6.29	1.95	72
24[g]	**2** (0.5)	2.12	10	50	3	68	2890	57 800 (16.0)	5.72	2.09	64

[a] Reaction conditions: NBE 2.12 mmol, benzene total 4.8 mL, or NBE 4.24 mmol, benzene total 9.6 mL. [b] Molar ratio to V. [c] TON (turnovers) = NBE reacted (mol)/mol-V, TOF = TON/time. [d] By GPC data in THF *vs.* polystyrene standards. [e] *cis* percentage (%) estimated by ^{1}H NMR spectra (selected data are shown in ESI). [f] Cited from ref. 6f. [g] Conditions: NBE 200 mg (2.12 mmol) benzene total 9.6 mL (initial NBE conc. 0.22 mmol mL^{-1}). PMe$_3$ was premixed in benzene at 25 °C for 1 min.
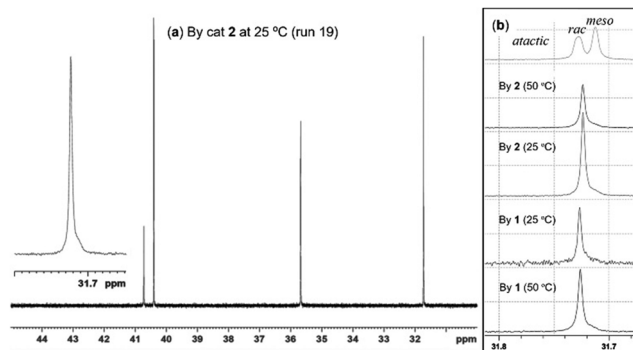
Fig. 1 ^{13}C NMR spectra (in $CDCl_3$ at 50 °C) for hydrogenated ring opened poly(NBE)s prepared by (a) [V(N-2,6-$Cl_2C_6H_3$)(CHSiMe$_3$)(OC$_6$Cl$_5$)(NHC)] (**2**) at 25 °C (run 19) and (b) expanded charts (31.7–31.8 ppm) for the polymer samples [from top to bottom: atactic sample for ref. 6b prepared by **2** at 25 °C (run 19), 50 °C (run 18), by [V(N-2,6-$Cl_2C_6H_3$)(CHSiMe$_3$)(OC$_6$F$_5$)(NHC)] (**1**) at 25 °C (run 15), 50 °C (run 16), respectively].

clearly suggesting that the resultant polymer possessed exclusive *syndiotactic* stereoregularity.[7e,10] Similar exclusive selectivity was also found by catalyst **1**. Noteworthy from Fig. 1b that the exclusive selectivity was not affected by the polymerisation temperature (25 or 50 °C), since the spectra showed sole resonance irrespective of catalysts (**1** or **2**) or the polymerisation temperature conducted (25 or 50 °C). The DSC thermograms of the hydrogenated polymers revealed melting temperature of 136.2 °C (run 5, Fig. S17, ESI†) and 137.8 °C (run 9, Fig. S18, ESI†), respectively, in line with a *syndiotactic* stereobase, as reported previously.[10]
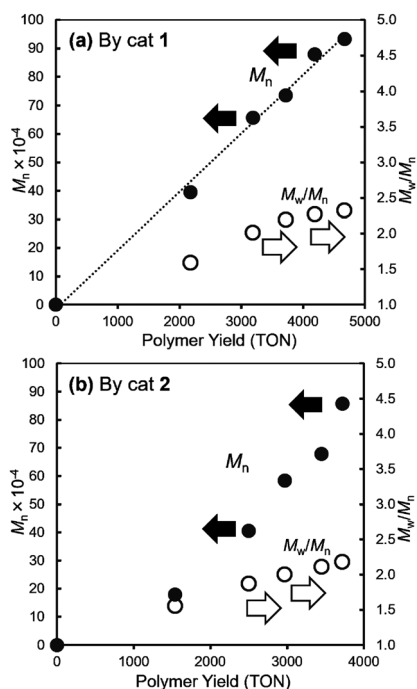

Fig. 2 Plots of M_n values *vs.* polymer yields (TON, turnover numbers based on polymer yield) in ROMP of norbornene (NBE) by (a) catalyst **1**, (b) catalyst **2**. Detailed data are shown in Table S1, ESI.†

In order to explore the catalyst performance and the polymerisation kinetics in more details, polymerisations were conducted under dilute conditions (initial NBE conc. 0.11 mmol mL^{-1}) at low catalyst loading (0.20 μmol) at 25 °C. The detailed results are summarised in Table S1, ESI.†

It was revealed that (TON) and the M_n values in the resultant polymers increased upon increasing the polymer yields (TON, turnover numbers based on NBE consumed) linearly in both polymerisation runs by catalysts **1** (Fig. 2a) and **2** (Fig. 2b), whereas the M_w/M_n values seemed increasing over the time course probably due to increase in the viscosity of the reaction mixture. The similar trends, linear relationships between the polymer yields and the M_n values, were observed, when these polymerisations were conducted under higher catalyst loadings (0.30 μmol) at 25 and even 50 °C (Fig. S1, and the data are summarised in Table S2, ESI†). These results clearly suggest that these polymerisations by catalysts **1**, **2** proceeded in a living manner without significant catalyst deactivation.[11]

2.2. Synthesis of [V(N-2,6-$X_2C_6H_3$)(CHSiMe$_3$){OC(CF$_3$)$_3$}(NHC)] [X = F (**3**), Cl (**4**)] and their use as catalysts for ROMP of NBE, tetracyclododecene (TCD).

It was demonstrated that the PMe$_3$-supported fluorinated alkoxide, [V(N-2,6-$Cl_2C_6H_3$)(CHSiMe$_3$){OC(CF$_3$)$_3$}(PMe$_3$)$_2$] (Scheme 1), exhibited exclusive *cis* specificity in the ROMP of NBE and the high *cis*-specificity did not decrease even at 80 °C in the presence of PMe$_3$. It was assumed that both the small arylimido ligand and the large fluorinated alkoxide ligands are responsible for the observed stereo-specificity by favouring an ene$_{syn}$ addition of NBE to a *syn*-alkylidene. We thus have an interest in the question whether the corresponding alkylidene NHC complexes, [V(N-2,6-$X_2C_6H_3$)(CHSiMe$_3$){OC(CF$_3$)$_3$}(NHC)] [X = F (**3**), Cl (**4**)], would display the similar high *cis* specificity or not.

These complexes (**3** and **4**) could be prepared by treating the corresponding dialkyl complexes, [V(N-2,6-$X_2C_6H_3$)–(CH$_2$Si-Me$_3$)$_2$],[6g] with NHC [1,3-bis-(2,6-dimethylphenyl)-imidazol-2-ylidene (IXy)] in benzene at 50 °C for 8 h (through α-hydrogen abstraction, Scheme 2), whereas the similar reactions for syntheses of **1** and **2** from [V(N-2,6-$Cl_2C_6H_3$)–(CH$_2$SiMe$_3$)$_2$(OC$_6$X$_5$)] completed within 1 h in benzene at room temperature. The resultant complexes were characterized by NMR spectroscopy and elemental analysis. As shown in Fig. 3 (shown below), the structures of **3** and **4** were determined by X-ray crystallographic analysis.

The structural analyses revealed that these complexes fold a distorted tetrahedral geometry around vanadium [N–V–C(7),
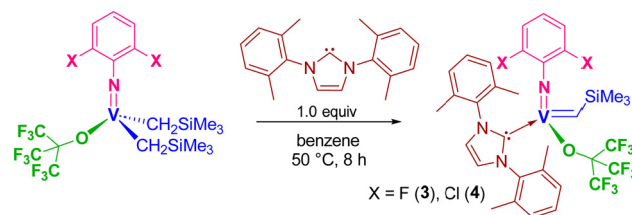
Scheme 2 Synthesis of [V(N-2,6-$X_2C_6H_3$)(CHSiMe$_3$){OC(CF$_3$)$_3$}(NHC)] [X = F (**3**), Cl (**4**)].

O–V–C(15), N(1)–V(1)–C(15), C(7)–V(1)–O(1) = 108.98(18)°, 111.05(13)°, 102.43(14)°, 111.76(18)° (complex **3**); 114.2(3)°, 105.98(17)°, 103.95(17)°, 107.6(3)° (complex **4**), respectively]. The V–N–C bond angles in the arylimido ligand were rather linear, only slightly bent [164.8(3)°, 175.1(4)° for complexes **3**, **4**, respectively] with a rather short V–N distance [1.673(3) Å, 1.652(4) Å for complexes **3**, **4**, respectively]. These values are comparable to those reported for [V(N-1-adamantyl)(CHSiMe₃)–(OC₆F₅)(PMe₃)₂] [173.3(3)°, 1.660(3) Å, respectively][12] and [V(N-adamantyl)(CHSiMe₃)(CH₂SiMe₃)(NHC-DIP)] [165.0(2)°, 1.637(2) Å, respectively; NHC-DIP = 1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene].[8b] The V–C distances in the alkylidene [1.829(4), 1.784(7) Å, for complexes, **3**, **4**, respectively] and NHC [2.124(3), 2.142(4) Å, respectively] are close to that found in [V(N-adamantyl)(CHSiMe₃)(CH₂SiMe₃)–(NHC-DIP)][8b] [1.829(3), 2.172(2) Å, respectively]. These findings are also corresponded to the observation of broad resonances ascribed to the alkylidene carbon in the ¹³C NMR spectra (341.7, 340.3 ppm, respectively), clearly indicating the presence of vanadium-alkylidene bond, whereas the NHC ligand coordinates to vanadium as a neutral donor (Table 2).

The ROMPs of NBE by catalysts **3** and **4** were conducted in toluene, and the selected results are summarised in Table 3. It was revealed that the 2,6-dichlorophenyl complex (**4**) exhibited low catalytic activities even under the high initial NBE concentration conditions (run 25–28), whereas the resultant polymers possess olefinic double bond with high *cis* selectivity (92–93%); nevertheless, the observed *cis* selectivity in the olefinic double bonds was lower than that by catalyst **2**. The activity improved at 50 °C (run 29), whereas the *cis* selectivity slightly decreased upon increase in the reaction temperature.

In contrast, the 2,6-difluorophenylimido complex (**3**) exhibited superior catalytic activity at 25 °C (TOF = 150–337 s⁻¹), and the activity increased at 50 °C (run 33); the polymerisation run at 80 °C completed even after 6 s (run 34). However, the *cis* selectivity decreased upon increasing the polymerisation temperature. In all cases, the resultant polymers were hardly soluble in THF or chloroform for GPC analysis, suggesting that the resultant polymers possessed very high molecular weights.[6f]
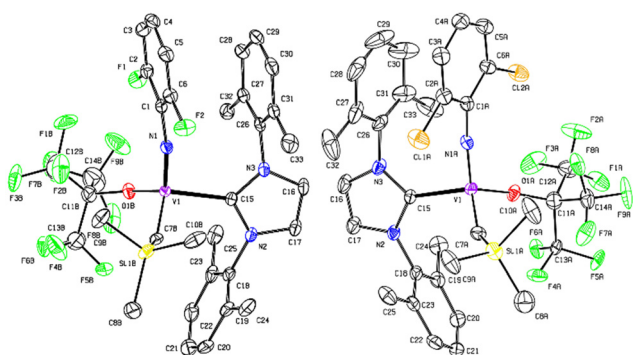
Table 2 Selected bond distances (Å) and angles (°) for [V(N-2,6-X₂C₆H₃)(CHSiMe₃){OC(CF₃)₃}(NHC)] [X = F (**3**), Cl (**4**)][a]

	X = F (**3**)	X = Cl (**4**)
Bond distances (Å)		
V(1)–N(1)	1.673(3)	1.652(4)
V(1)–C(7)	1.829(4)	1.784(7)
V(1)–O(1)	1.882(3)	1.946(5)
V(1)–C(15)	2.124(3)	2.142(4)
Bond angles (°)		
N(1)–V(1)–C(15)	102.43(14)	103.95(17)
N(1)–V(1)–O(1)	119.34(15)	117.4(2)
N(1)–V(1)–C(7)	108.98(18)	114.2(3)
C(7)–V(1)–C(15)	101.44(17)	106.8(2)
C(7)–V(1)–O(1)	111.76(18)	107.6(3))
O(1)–V(1)–C(15)	111.05(13)	105.98(17)
C(1)–N(1)–V(1)	164.8(3)	175.1(4)

[a] CCDC 2358163 (complex **3**) and 2358164 (complex **4**) contain the supplementary crystallographic data in detail.

Table 4 summarises the results in ROMPs of tetracyclododecene (TCD) by catalysts **3** and **4** in benzene at 25 °C. As observed in the ROMPs of NBE, catalyst **4** showed low catalytic activity, whereas the polymerisation with high catalyst loading resulted in poly(TCD) with a rather high *trans* content (*trans* 82%, runs 35, 36). In contrast, catalyst **3** showed much higher catalytic activity compared to **4**, affording the ring opened polymers with substantial *cis* selectivity (61–66%). We assume that these results are probably due to rotational isomer (*syn/anti*), once formed *syn* isomer would convert to (thermodynamically stable) *anti* form before TCD insertion; these probably affect the *cis* specificity in these catalyses. As observed in the ROMPs of TCD by the other vanadium-alkylidene catalysts,[6a,b] as well as niobium–alkylidene catalysts,[13] the resultant polymers were hardly soluble in THF (chloroform) for GPC analysis.

Nevertheless, selected poly(TCD)s were successfully hydrogenated by 4-MeC₆H₄SO₂NHNH₂ (excess) in toluene at 130 °C.[9,10] The corresponding DSC thermograms showed that the resultant hydrogenated polymers are amorphous and possessed sole glass transition temperature at 168.6–169.6 °C (Fig. 4) in all cases, clearly suggesting that the resultant polymers possess *syndiotactic* stereobase.[9b,10]

Fig. 3 ORTEP drawings for [V(N-2,6-X₂C₆H₃)(CHSiMe₃)[OC(CF₃)₃](NHC)] [X = F (**3**, left), Cl (**4**, right)]. Hydrogen atoms were omitted for clarity and thermal ellipsoids are drawn at 30% probability level. Additional data including crystal data and collection parameters for structural analysis are shown in ESI.†

3. Conclusions

We have shown that perhalogenated phenoxide alkylidene complexes, V(N-2,6-Cl₂C₆H₃)(CHSiMe₃)(OC₆X₅)(NHC)[6f] [X = F (**1**), Cl (**2**)], exhibited remarkable catalytic activities [TOF = 133–193 s⁻¹ (**1**), 90.9–126 s⁻¹ (**2**)] for ring-opening metathesis polymerisation (ROMP) of norbornene (NBE), and the resultant ring opened polymers prepared at 25 °C possessed high *cis* selectivity (93–98%); the pentachlorophenoxide catalyst (**2**) showed rather higher *cis* specificity (95–98%). Under diluted polymerisation conditions, linear relationships between the M_n values and the polymer yields were demonstrated (Fig. 1), strongly suggesting that these polymerisations proceeded in a living manner without significant catalyst decomposition. The catalytic activities by **1**, **2** slightly increased at 50 °C, whereas the *cis*

Table 3 ROMP of NBE by [V(N-2,6-X$_2$C$_6$H$_3$)(CHSiMe$_3$){OC(CF$_3$)$_3$}(NHC)] [X = F (**3**), Cl (**4**)]^a

Run	Cat. (μmol)	Temp./°C	Time	Yield/mg	TON^b	TOF^b/h^{-1} (s^{-1})	cis^c/%
25^d	**4** (10)	25	0.5 h	Trace			
26	**4** (10)	25	3 h	13.8	15	5	93
27	**4** (10)	25	16 h	35	37	2	92
28	**4** (10)	25	21 h	42.3	45	2	93
29	**4** (10)	50	1.0 h	16.6	18	18	90
30	**3** (5.0)	25	1.0 min	95	201	720 000 (200)	88
31	**3** (5.0)	25	1.5 min	106	225	539 000 (150)	88
32	**3** (10)	50	0.20 min	216^e	220	66 000 (18.3)	79
33	**3** (5.0)	50	0.25 min	40	84	121 000 (337)	81
34	**3** (10)	80	0.10 min	202^e	200	126 000 (35.0)	65

^{a} Reaction conditions: NBE 200 mg (2.12 mmol), toluene 1.2 mL. ^{b} TON (turnovers) = NBE reacted (mol)/mol-V. TOF (turnover frequency) = TON/h. ^{c} cis percentage (%) estimated by ^{1}H NMR spectra. ^{d} Benzene 4.8 mL in place of toluene 1.2 mL. ^{e} Yield > 99%.

Table 4 ROMP of tetracyclododecene (TCD) by [V(N-2,6-X$_2$C$_6$H$_3$)-(CHSiMe$_3$){OC(CF$_3$)$_3$}(NHC)] [X = F (**3**), Cl (**4**)]^a

Run	Cat. (μmol)	Time	Yield/mg	TON^b	TOF^b/h^{-1}	cis^c/%
35	**4** (5.0)	24 h	17.9	22.3	0.9	18
36	**4** (10)	24 h	100.3	62.6	2.6	18
37	**3** (5.0)	4 min	38.5	48.0	721	61
38	**3** (10)	3 min	61.0	38.1	761	62
39	**3** (10)	4 min	83.4	52.0	781	64
40	**3** (20)	3 min	113.8	35.5	710	64
41	**3** (20)	3 min	116.0	36.2	724	66

^{a} Reaction conditions: TCD 340 mg (2.12 mmol), benzene 1.2 mL. ^{b} TON (turnovers) = TCD reacted (mol)/mol-V. TOF (turnover frequency) = TON/h. ^{c} cis percentage (%) estimated by ^{1}H NMR spectra.

specificity decreased upon increasing the polymerisation temperature. Further increase in the activity was observed upon addition of 1.0 equiv. of PMe$_3$ with decreasing the cis specificity. The resultant polymers possessed exclusive syndiotactic stereoregularity irrespective of the polymerisation temperature on the basis of ^{13}C NMR spectra for the hydrogenated polymers (Fig. 2).

Synthesis and structural analysis of the perfluorinated alkoxide complexes, [V(CHSiMe$_3$)(N-2,6-X$_2$C$_6$H$_3$){OC(CF$_3$)$_3$}(NHC)] [X = F (**3**), Cl (**4**)], have been studied, and these complexes possessed a distorted tetrahedral geometry around vanadium containing NHC ligand as a neutral donor. The 2,

Fig. 4 DSC thermograms for hydrogenated ring opened poly(TCD) prepared by catalysts **3** and **4**.

6-difluorophenylimido complex (**3**) showed comparable catalytic activities for ROMP of NBE conducted at 25 °C, whereas the 2,6-dichlorophenylimido complex (**4**) showed extremely the low catalytic activities. The resultant polymers possessed high cis selectivities (88–93%) which were lower than those conducted by **1**, **2**. The activity by **3** increased at 50 °C with decreasing the cis specificity. The resultant ring opened polymers prepared by ROMP of tetracyclododecene (TCD) by **4** possessed highly trans selectivity (82%) in the olefinic double bond, whereas polymers prepared by **3** possessed cis (61–66%). We assume that these results are probably due to rotational isomer (syn/anti), once formed syn isomer would convert to (thermodynamically stable) anti form before TCD insertion; these probably affect the cis specificity in these catalyses. The resultant poly(TCD) possessed syndiotactic stereoregularity confirmed by DSC thermograms for hydrogenated polymers.

As described above, the cis selectivity in the resultant poly(NBE) prepared by the fluorinated alkoxides (**3**,**4**) at 25 °C were comparable or rather low (cis 88–93%, Table 3) compared to those prepared by the perhalogenated phenoxides (cis 91–97%, Table 1) under the same conditions. The observed fats are clear contrast to those reported in the PMe$_3$-supported catalysts.[6a,b] As discussed in the ROMPs of TCD by catalysts **3** and **4**, isomerization of syn rotational isomer to the (thermally stable) anti form can be thus considered before coordination of cyclic olefins. These should be clarified as the future subject.

Through this research, we have demonstrated that the present vanadium–alkylidene catalysts show promising potential for ring opening metathesis polymerisation and the ligand modification plays an important role for control of cis/trans and the tacticity control. In particular, on the basis of results by the fluorinated alkoxide catalysts (**3**, **4**), we are currently exploring more ligand modification for development of catalysts affording exclusive cis, syndiotactic polymers. Moreover, these catalysts also showed promising characteristics in ring closing metathesis reactions.[14] We highly hope to introduce further results in the near future.

4. Experimental

4.1. General procedures

The experiments were conducted under a nitrogen atmosphere on Vacuum Atmospheres Drybox. Anhydrous grade of octane,
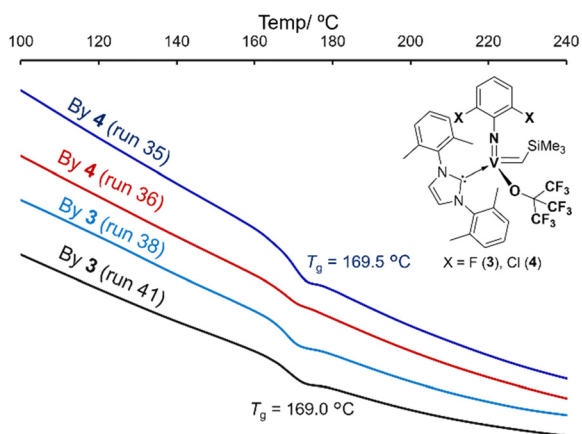
dichloromethane, *n*-hexane, benzene, and toluene (Kanto Chemical Co., Inc.) were transferred into bottles containing a mixture of molecular sieves (3A 1/16, 4A 1/8, and 13 × 1/16) inside the drybox. These solvents were purified by flushing an alumina short column under nitrogen stream in the dry-box prior to use. [V(N-2,6-Cl$_2$C$_6$H$_3$)(CH$_2$SiMe$_3$)$_2${OC(CF$_3$)$_3$}],[6a] [V(N-2,6-Cl$_2$C$_6$H$_3$)(CHSiMe$_3$)(OC$_6$X$_5$)(NHC)][6f] [X = F (**1**), Cl (**2**)] and NHC (IXy) ligand[6f] used were prepared following the previously reported procedures. Norbornene (NBE, Tokyo Chemical Industry Co., Ltd.) was distilled in the presence of sodium before use. Tetracyclododecene (TCD, Zeon corporation) were purified by passing through alumina short column, and then dried in the presence of molecular sieves. *p*-Toluenesulfonyl hydrazide (4-MeC$_6$H$_4$SO$_2$NHNH$_2$, Sigma-Aldrich Co. LLC.) for hydrogenation of polymers was used without further purification.

All ^{1}H, ^{13}C, ^{19}F, ^{31}P and ^{51}V NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C, 470.54 MHz for ^{19}F, 202.45 MHz for ^{31}P and 131.55 MHz for ^{51}V). All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Chemical shifts are given in ppm and are referenced to SiMe$_4$ (δ 0.00 ppm, ^{1}H, ^{13}C), CFCl$_3$ (δ 0.00, ^{19}F), and VOCl$_3$ (δ 0.00, ^{51}V). Coupling constants and half-width values, $\Delta\nu_{1/2}$, are given in Hz. The ratio of *cis/trans* of polymers were calculated by the integration of ^{1}H NMR spectra. ^{13}C NMR spectra of hydrogenated poly(NBE)s were recorded on a Bruker Avance III 500 MHz spectrometer (500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C) with CryoprobeTM DCH 500/3 at 50 °C (reference chloroform at 77.2 ppm for ^{13}C).

Gel-permeation chromatography (GPC) was performed to estimate the molecular weights (M_w, M_n) and their distributions, HPLC grade THF (degassed prior to use) was used as eluent. GPC was performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt% of 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL min^{-1}). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm diameter, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from <10^2 to 2 × 10^7 MW) were calibrated *versus* polystyrene standard samples.

4.2. Synthesis of [V(N-2,6-F$_2$C$_6$H$_3$)(CH$_2$SiMe$_3$)$_2${OC(CF$_3$)$_3$}][6g]

Into a *n*-hexane solution (30 mL) containing V(N-2,6-F$_2$C$_6$H$_3$)(CH$_2$SiMe$_3$)$_3$ (501 mg, 1.14 mmol) was added (CF$_3$)$_3$COH (538 mg, 2.28 mmol, 2.0 equiv.) at −30 °C. The solution was then gradually warmed to room temperature and was stirred for 12 h. The solution was passed through a Celite pad and washed with *n*-hexane. The combined filtrate and the wash were taken to dryness *in vacuo* resulted in dark-brown oil product. Yield: 635 mg (1.08 mmol, 94.9% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C): δ 6.40 (t, 2H, *J* = 8.00 Hz, Ar-*H*), 6.26 (t, 1H, *J* = 7.20 Hz, Ar-*H*), 3.03 (br, 4H, V–C*H*$_2$SiMe$_3$), 0.11 (s, 18H, SiMe$_3$). ^{19}F NMR (C$_6$D$_6$, 25 °C): δ −74.11 (s), −117.49 (s). ^{51}V NMR (C$_6$D$_6$, 25 °C): δ 725.32 ($\Delta\nu_{1/2}$ = 291 Hz).

4.3. Synthesis of [V(CHSiMe$_3$)(N-2,6-F$_2$C$_6$H$_3$){OC(CF$_3$)$_3$}(NHC)] (3)

Into a benzene solution (10 mL) containing [V(N-2,6-F$_2$C$_6$H$_3$)(CH$_2$SiMe$_3$)$_2${OC(CF$_3$)$_3$}] (635 mg, 1.08 mmol), NHC [NHC = 1,3-bis-(2,6-dimethylphenyl)-imidazol-2-ylidene, 298 mg, 1.08 mmol,

1.0 equiv.] was added at 50 °C, and the reaction mixture was further stirred for 8 h. The solution was then placed to a rotary evaporator in the drybox to remove volatiles. The benzene solution containing the resultant residue was passed through a Celite pad. The filter cake was washed twice with benzene, and volatiles in the combined filtrate and the wash were removed *in vacuo*. The resultant solid was then dissolved in a minimum amount of benzene, and the solution was added dropwise into a stirred cold *n*-hexane solution (pre-cooled at −30 °C) resulted in dark-brown solid. Yield: 261 mg (0.336 mmol, 31.1% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C): δ 16.24 (s, 1H, V=C*H*SiMe$_3$), 6.84 (s, 6H, Ar-*H*), 6.41 (t, 2H, *J* = 7.52 Hz, Ar-*H*), 6.27 (t, 1H, *J* = 7.00 Hz, Ar-*H*), 5.93 (s, 2H, NC*H*), 2.07 (s, 6H, Ar-C*H*$_3$), 1.85 (s, 6H, Ar-C*H*$_3$), 0.26 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 340.3 (br), 161.5, 159.5, 138.7, 135.6, 135.3, 134.7, 133.6, 130.9, 129.5, 128.7, 125.6, 123.2, 123.0, 122.3, 121.7 (t), 120.9, 118.6, 110.4 (dd), 84.5 (br), 17.8, 17.6, 1.5. ^{19}F NMR (C$_6$D$_6$, 25 °C): δ −74.59 (s), −118.80 (s). ^{51}V NMR (C$_6$D$_6$, 25 °C): δ 166.53 ($\Delta\nu_{1/2}$ = 230 Hz). Anal. calcd. for C$_{33}$H$_{33}$F$_{11}$N$_3$OSiV (+0.08 × *n*-hexane): C, 51.39; H, 4.40; N, 5.37. Found: C, 51.27; H, 4.58; N, 5.39.

4.4. Synthesis of [V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$){OC(CF$_3$)$_3$}(NHC)] (4)

Into a benzene solution (10 mL) containing [V(N-2,6-Cl$_2$C$_6$H$_3$)(CH$_2$SiMe$_3$)$_2${OC(CF$_3$)$_3$}] (423 mg, 0.682 mmol), NHC [NHC = 1,3-bis-(2,6-dimethylphenyl)-imidazol-2-ylidene, 188 mg, 0.680 mmol, 1.0 equiv.] was added at 50 °C, and the solution was stirred for 8 h. The solution was then placed to a rotary evaporator in the drybox to remove volatiles. The benzene solution containing the resultant residue was passed through a Celite pad. The filter cake was washed twice with benzene, and volatiles in the combined filtrate and the wash were removed *in vacuo*. The resultant solid was then dissolved in a minimum amount of benzene, and the solution was added dropwise into a stirred cold *n*-hexane solution (pre-cooled at −30 °C) resulted in dark-brown solid. Yield 158 mg (0.195 mmol, 28.7% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C): δ 15.85 (s, 1H, V=C*H*SiMe$_3$), 6.93–6.79 (m, 8H, Ar-*H*), 6.25 (t, 1H, *J* = 7.40 Hz, Ar-*H*), 5.94 (s, 2H, NC*H*), 2.03 (s, 6H, Ar-C*H*$_3$), 1.89 (s, 6H, Ar-C*H*$_3$), 0.17 (s, 9H, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 341.7 (br), 155.2 (br), 138.6, 135.5, 135.4, 134.3, 133.0, 131.4, 129.6, 129.0, 128.5, 128.3, 127.3, 125.7, 123.3, 122.9, 122.3, 121.0, 118.7, 84.4 (br), 18.1, 17.9, 1.5. ^{19}F NMR (C$_6$D$_6$, 25 °C): δ −73.74 (s). ^{51}V NMR (C$_6$D$_6$, 25 °C): δ 196.00 ($\Delta\nu_{1/2}$ = 242 Hz). Anal. calcd. for C$_{33}$H$_{33}$Cl$_2$F$_9$N$_3$OSiV (+0.12 × *n*-hexane): C, 49.46; H, 4.27; N, 5.13. Found: C, 49.33; H, 4.35; N, 5.35.

4.5. ROMP of NBE and TCD

Into a 15-mL vial, NBE (4.24, 2.12 or 1.06 mmol) or TCD (2.12 mmol) was dissolved in benzene (4.8 or 9.6 mL). A prescribed amount of catalyst dissolved in benzene was added to the above mixture to start the polymerisation for a prescribed time. The polymerisation was then quenched by addition of benzaldehyde in excess. The resultant mixture was stirred for an additional 30 min at room temperature for completion, then poured into 100 mL of methanol. The resultant solid was

collected by filtration, washed with methanol, and then dried *in vacuo*.

Poly(NBE): ^{1}H NMR (CDCl$_3$ at 25 °C): δ 5.35 (1H, *trans*), 5.21 (1H, *cis*) 2.80 (1H, *cis*), 2.44 (1H, *trans*), 1.89–1.80 (3H), 1.36 (2H), 1.04 (1H). ^{13}C NMR (CDCl$_3$ at 25 °C): δ 134.0, 133.2, 43.6, 42.8, 38.8, 38.6, 33.4, 33.1, 32.5, 32.3. Detailed assignments are shown in the ESI† (Fig. S2 and S3, ESI†).

Poly(TCD): ^{1}H NMR (CDCl$_3$ at 25 °C): δ 5.51 (2H), 2.97–2.70 (2H), 2.28–2.20 (2H), 2.02 (2H), 1.73–1.65 (1H), 1.43–1.28 (4H), 1.05 (2H), 0.91 (1H). ^{13}C NMR (CDCl$_3$ at 25 °C): δ 135.2, 131.2, 130.4, 53.0, 48.6, 46.2, 37.9, 36.0, 29.8.

4.6. Hydrogenation of poly(NBE) and poly(TCD).[9]

The resultant polymers (120 mg) were transferred to a Schlenk tube and dissolved in toluene (20 mL). 4-MeC$_6$H$_4$SO$_2$NHNH$_2$ (4 equiv.) was added. The Schlenk tube was then placed into an oil bath heated to 130 °C, and the solution mixture was stirred for 12 h. After the reaction was complete, the mixture was cooled to room temperature and poured into 100 mL of methanol. The resultant solid was collected by filtration, washed with methanol, and then dried *in vacuo*.

Author contributions

KN designed the project (conceptualization, catalyst design, methodology, supervision) including funding acquisition and project administration. MMB contributed to the conceptualization and the catalyst design. SK and JS conducted synthesis of complexes **3** and **4**, polymerisation, analysis of polymers in investigation and YK prepared complexes **1**, **2**. DS helped crystallographic analysis. KN wrote the original manuscript, and both MMB and KN revised the manuscript. All authors have discussed the results and approved the final version of the manuscript.

Data availability

Data is contained within the article and the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

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