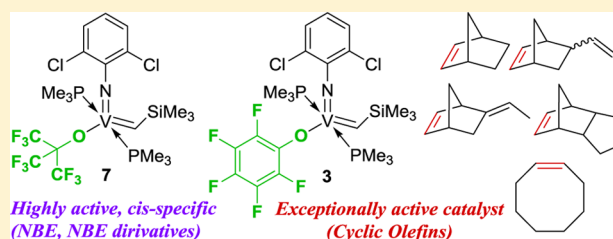# Ring-Opening Metathesis Polymerization of Cyclic Olefins by (Arylimido)vanadium(V)-Alkylidenes: Highly Active, Thermally Robust *Cis* Specific Polymerization

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Ⓢ *Supporting Information*

ABSTRACT: Ring-opening metathesis polymerization (ROMP) of various cyclic olefins especially using three (arylimido)vanadium(V)-alkylidene catalysts, $V(CHSiMe_3)(N-2,6-Cl_2C_6H_3)$ (OC_6F_5) $(PMe_3)_2$ (**3**), $V(CHSiMe_3)$ $(NR)[OC(CF_3)_3](PMe_3)_2$ [R = Ph (**6**), 2,6-$Cl_2C_6H_3$ (**7**)] have been explored. Complex **3** exhibited the highest catalytic activity (ex. TOF = 603 000 h^{-1}, 168 s^{-1}) for ROMP of norbornene (NBE) among a series of (imido)vanadium(V)-alkylidenes, and the *cis*-specific living ROMPs of NBE proceeded with remarkable activities (TOF = 125 000−157 000 h^{-1} at 25 °C) by the fluorinated alkoxo analogues (**6**, **7**). The activities by **6**, **7** increased at high temperature (50 and 80 °C) and/or upon addition of PMe_3 without decrease in the *cis* selectivity (98%). The ROMPs in the presence of 1-hexene by **3**, **7** proceeded without significant decrease in the activities, and the M_n values could be controlled by degree of chain transfer (cross metathesis). These dichlorophenylimido analogues (**3**, **7**) were effective for ROMPs of various norbornene derivatives; ROMP of cyclooctene took place by **3**, and the activity increased at high temperature (50, 80 °C).

Highly active, cis-specific (NBE, NBE dirivatives)   *Exceptionally active catalyst (Cyclic Olefins)*

■ INTRODUCTION

Olefin metathesis is an important and useful method for efficient carbon−carbon bond formation applied for synthesis of various organic compounds and polymeric, advanced materials,[1−8] and metal-carbene (alkylidene) complex play a key role in this catalysis. Both ruthenium-carbene (so-called Grubbs type) and molybdenum-alkylidene (so-called Schrock type) catalysts (Chart 1) are the well-known successful examples.[1−5] Moreover, several examples have also been reported recently as effective Z selective (*cis*-specific) catalysts for ring-opening metathesis polymerization (ROMP), cross metathesis, and ring-closing metathesis reactions (exemplified in Chart 1).[6−8]

High-oxidation-state early transition metal−alkylidene complexes are known to play a key role as catalysts in the olefin metathesis and Wittig type coupling,[2] and many examples are reported especially by molybdenum and tungsten.[2,3,6] Study on synthesis and reaction chemistry of vanadium(V)-alkylidene complexes has also been considered as an attractive subject,[3f] not only because of promising characteristics (notable reactivity toward olefins etc.) demonstrated by classical Ziegler type vanadium catalyst systems,[9] but also because of their potentials in catalysis as well as of fundamental importance in organometallic chemistry with vanadium.[10] We reported that (imido)vanadium(V)-alkylidene complexes containing ketimide,[10a] aryloxo,[10b,e,f,h] imidazolidin-2-iminato[10g] ligands (Chart 2) exhibited from moderate to high catalytic activities for ROMP of norbornene (NBE). In particular, we recently communicated that the arylimido complexes containing

fluorinated phenoxy ligand, $V(CHSiMe_3)(N-2,6-X_2C_6H_3)$ (OC_6F_5) $(PMe_3)_2$ [X = Me (**2**), Cl (**3**)], exhibited the remarkable activities, and the activities were higher than that by the adamantylimido analogue (**1**), probably due to an electronic effect (formation of more electron deficient metal−alkylidene).[10h] The ROMP by **1**, **2** proceeded in a living manner affording ultrahigh molecular weight polymers with low PDI (M_w/M_n) values (ca. by **2**: $M_n = 1.64 \times 10^6$ g/mol, M_w/M_n = 1.18).[10h] Moreover, *cis* specific ROMP has been achieved by the fluorinated alkoxo analogues, $V(CHSiMe_3)(N-2,6-X_2C_6H_3)[OC(CH_3)$ $(CF_3)_2](PMe_3)_2$ [X = Me (**4**), Cl (**5**)]; both the activity and the selectivity by **5** increased upon addition of PMe_3 even at 50 °C.[10h] We speculated that high *cis* selectivity would be thus achieved due to a proposed (metallacyclobutane) intermediate affected by the small arylimido and the large alkoxo ligands, which is analogous to the molybdenum catalysis.[6b]

Although many successful achievements have been reported by adopting the molybdenum and tungsten catalysts,[3] in fact, reported examples in thermally robust *cis* specific (Z selective) olefin metathesis catalysts, ROMP of certain monomers such as cyclooctene[11−14] etc. have been limited and challenging subjects. Moreover, the activities by the *cis*-specific ROMP catalysts (communicated as thermally robust catalyst especially by **5**)[10h] were, however, much lower than those by the OC_6F_5 analogues (**1−3**), and the *cis* selectivity decreased at 80 °C
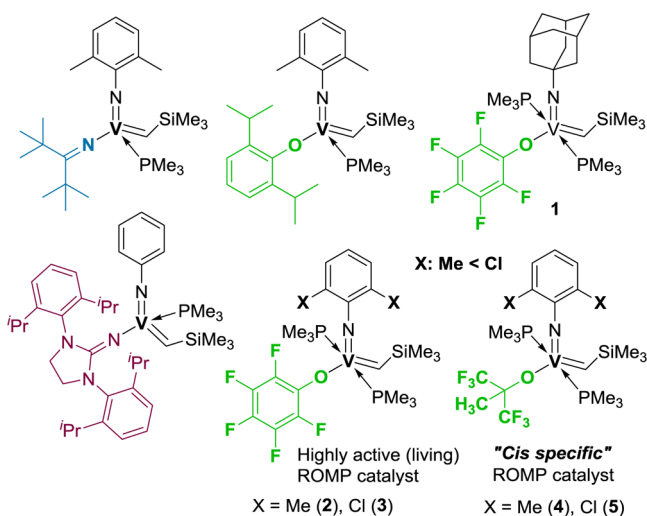
Chart 1. Typical Mo (Schrock type) and Ru (Grubbs type) Olefin Metathesis Catalysts and "Cis-Specific (Z Selective)" Olefin Metathesis Catalysts
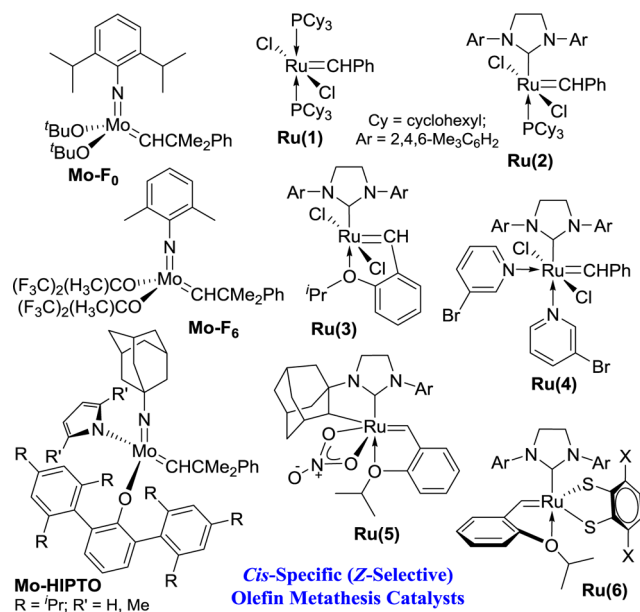
Chart 2. Selected Vanadium(V)-Alkylidene Catalysts for Ring-Opening Metathesis Polymerization (ROMP) of Norbornene (NBE)


(86%). In this article, we thus introduce our explored results concerning the effect of imido and alkoxo ligands toward the catalytic activities for ROMP of NBE (as model reaction), ROMP of NBE in the presence of a chain transfer (cross metathesis) reagent (1-hexene), norbornene derivatives, and of the other cyclic olefins such as cyclopentene and *cis*-cyclooctene.[15] Through these studies, we wish to demonstrate the importance of "fine-tuning" of ligands toward highly efficient ROMP of cyclic olefins (with wide monomer scope), thermally robust and highly active *cis*-specific ROMP catalysts even at 80 °C.

■ **RESULTS AND DISCUSSION**

1. Synthesis of V(CHSiMe₃) (NR)[OC(CF₃)₃](PMe₃)₂ [R = C₆H₅ (Ph, 6), 2,6-Cl₂C₆H₃ (7)] and Ring-Opening Meta-

thesis Polymerization (ROMP) of Norbornene (NBE). Three (imido)vanadium(V)-alkylidene complexes, shown Scheme 1, have been chosen for this study, and V(CHSiMe₃)-

Scheme 1. Synthesis of (Arylimido)vanadium(V)-Alkylidene Complexes Containing Fluorinated Aryloxo, Alkoxo Ligands
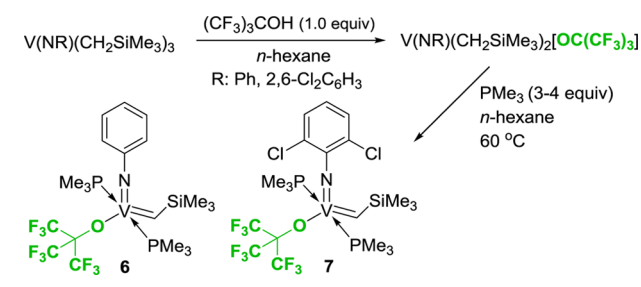
$(N\text{-}2,6\text{-}Cl_2C_6H_3)$ (OC_6F_5) $(PMe_3)_2$ (3) was prepared according to a reported procedure.[10h] The nonafluoro alkoxo analogues, $V(CHSiMe_3)$ $(NR)[OC(CF_3)_3](PMe_3)_2$ [R = C_6H_5 (Ph, 6), 2,6-$Cl_2C_6H_3$ (7)], have been prepared from the corresponding dialkyl analogues, $V(NR)$ $(CH_2SiMe_3)_2[OC(CF_3)_3]$, which were prepared by the reaction of $V(NR)$ $(CH_2SiMe_3)_3$ with $HOC(CF_3)_3$, by α-hydrogen abstraction in *n*-hexane in the presence of PMe_3 (Scheme 1).[16] These are established procedures for synthesis of (imido)vanadium(V)-alkylidene complexes with this series, and the resultant complexes were identified by NMR spectra and elemental analysis.[16] Attempted synthesis of the dialkyl complex containing 2,6-dimethylphenylimido ligand, $V(N\text{-}2,6\text{-}Me_2C_6H_3)$ $(CH_2SiMe_3)_2[OC(CF_3)_3]$, by reaction of $V(N\text{-}2,6\text{-}Me_2C_6H_3)$ $(CH_2SiMe_3)_3$ with $(CF_3)_3COH$ failed, probably due to a steric bulk (incompletion of the reaction after 2 days at 25 °C).[16]

A relatively sharp (but broad due to a coupling with vanadium) resonance and additional tiny resonance ascribed to proton in the alkylidene were observed in the ¹H NMR spectra of **6-7** (in C_6D_6),[16] as observed in the spectra of $V(CHSiMe_3)$ $(NR)[OC(CH_3) (CF_3)_2](PMe_3)_2$ [R = 2,6-$Me_2C_6H_3$ (4), 2,6-$Cl_2C_6H_3$ (5)], and $V(CHSiMe_3)(N\text{-}2,6\text{-}Cl_2C_6H_3)$ (OC_6F_5) $(PMe_3)_2$ (3).[10h] The ratios did not change upon addition of PMe_3, suggesting that complexes (**6, 7**) are a mixture of *syn/anti* forms.[16] Moreover, their VT-NMR (¹H, ³¹P and ⁵¹V) spectra suggest that there is a fast equilibrium between coordination and dissociation of PMe_3 in solution, as demonstrated previously;[10g,h] resonances ascribed to PMe_3 in the NMR spectra were broad but became rather sharp at low temperature.[16] These results also suggest the presence of a fast equilibrium.

Ring-opening metathesis polymerization (ROMP) of norbornene (NBE) by **3, 6, 7** were conducted in benzene at 25 °C (Scheme 2, initial NBE conc. 0.44 mmol/mL). The results by $V(CHSiMe_3)$ (NR) (OC_6F_5) $(PMe_3)_2$ [R = 1-adamantyl (Ad, **1**), 2,6-$Me_2C_6H_3$ (**2**)], **4, 5** conducted under the same conditions[10h] are also placed for comparison. The results are summarized in Table 1.

As reported previously,[10h] the activities by the OC_6F_5 analogues, $V(CHSiMe_3)$ (NR) (OC_6F_5) $(PMe_3)_2$ (**1−3**), increased in the order: R = Ad (TOF = 99 000 h⁻¹, run 1) < 2,6-$Me_2C_6H_3$ (230 000, run 3) < 2,6-$Cl_2C_6H_3$ (552 000, run 7). The dichlorophenylimido analogue (**3**) exhibited the highest activity and the activity seemed improving upon addition of PMe_3 (runs 7, 8), whereas the activity by the dimethylpheny-

Scheme 2. Ring-Opening Metathesis Polymerization (ROMP) of Norbornene (NBE) by V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$) (OC$_6$F$_5$) (PMe$_3$)$_2$ (3), V(CHSiMe$_3$) (NR)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ [R = C$_6$H$_5$ (6), 2,6-Cl$_2$C$_6$H$_3$ (7)]
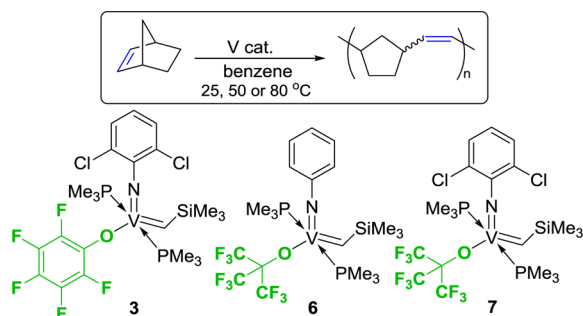
limido analogue (2) decreased even upon addition of small amount of PMe$_3$ [TOF = 24 200 h^{-1} (0.1 equiv, run 4), 3960 h^{-1} (0.5 equiv, run 5)].[10h] The resultant polymers possessed ultrahigh molecular weights with low PDI (M_w/M_n) values, suggesting a possibility of living polymerization, as observed in the ROMP by 1 and 2.[10h,17] As communicated previously,[10h] the activity by 3 is higher than that by known active catalyst Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ (Mo–

F$_6$,[18] TON 17 300 after 3 min, TOF 346 000 h^{-1} under the same conditions for run 6).

Note that the activity by the nonafluoro alkoxo analogues (6, 7) were much (more than 20 times) higher than those by the hexafluoro alkoxo analogue (4,5) [TOF: 99 000 h^{-1} (6, run 14) > 78 800 h^{-1} (7, run 20) ≫ 3000 (5, run 11) > 1010 (4, run 10)]. This would be due to an activation of the alkylidene species by introduction of the electron-withdrawing alkoxide as observed in (imido)molybdenum(VI)-alkylidene catalysts.[2c,3b] The activities by the phenylimido analogue (6) were slightly higher than those by the 2,6-Cl$_2$C$_6$H$_3$ analogue (7) under these conditions, and the results are reproducible (runs 14, 15, and additional data in SI).[16] Moreover, the activities by 6, 7 increased upon addition of PMe$_3$ (1.0–3.0 equiv), no significant differences in the activity were observed between 6 and 7. However, the activities decreased by excess additions (30–100 equiv, runs 16–19 by 6, runs 24–28 by 7), suggesting that excess PMe$_3$ suppresses coordination of NBE for proceeding the ROMP. The resultant polymers prepared by 6, 7 (PMe$_3$/V = 0–3, molar ratio) possessed ultrahigh molecular weights (1.33–2.10 × 10^6 g/mol) with low PDI values (M_w/M_n = 1.08–1.23); these results also suggest a possibility of living polymerization under these conditions, as demonstrated below. Although the M_n values in the resultant polymers prepared by 6 (and 7) in the presence of PMe$_3$

Table 1. ROMP of NBE by V(CHSiMe$_3$) (NR) (OC$_6$F$_5$) (PMe$_3$)$_2$ [R = 1-adamantyl (1), 2,6-Me$_2$C$_6$H$_3$ (2), 2,6-Cl$_2$C$_6$H$_3$ (3)], V(CHSiMe$_3$) (NR)[OC(CH$_3$) (CF$_3$)$_2$](PMe$_3$)$_2$ [R = 2,6-Me$_2$C$_6$H$_3$ (4), 2,6-Cl$_2$C$_6$H$_3$ (5)], V(CHSiMe$_3$) (NR)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ [R = C$_6$H$_5$ (Ph, 6), 2,6-Cl$_2$C$_6$H$_3$ (7)]: Effect of Imido and Fluorinated Aryloxo/Alkoxo Ligand[a]

run	cat. (μmol)	PMe$_3$/equiv	time/min	polymer/mg	yield/%	TON[b]	TOF[b]/h^{-1}	M_n^c × 10^{-4}	M_w/M_n^c	cis/%[d]
1[e]	1 (0.3)	–	3	140	70	4950	99 000	79	1.15	
2[e]	2 (0.3)	–	1	160	80	5650	339 000	117	1.22	
3[e]	2 (0.1)	–	3	108	54	11 500	230 000	164	1.18	
4[e]	2 (0.3)	0.1	3	34.2	17.1	1210	24 200	61.8	1.10	
5[e]	2 (0.3)	0.5	3	5.6	2.8	198	3960	12.4	1.03	
6[e]	3 (0.1)	–	3	200	>99	21 200	424 000	110	1.27	45
7	3 (0.1)	–	2	174	87	18 400	552 000	205	1.12	
8	3 (0.1)	3	2	190	95	20 100	603 000	179	1.11	
9[e,f]	4 (1.0)	–	60	10.2	5	108	108	6.4	1.49	96
10[g]	4 (1.0)	–	20	31.7	16	337	1010	80.0, 7.0	1.29, 1.20	85
11[e]	5 (1.0)	–	20	95	48	1000	3000	52.5	1.38	92
12	5 (1.0)	3	20	196	98	2090	6270	95	1.15	97
13[h]	6 (0.5)	–	3	371	93	7880	157 000	210	1.11	
14	6 (0.3)	–	3	140	70	4950	99 000	160	1.08	98
15	6 (0.3)	–	3	139	70	4910	98 200	160	1.08	98
16	6 (0.3)	3	3	189	95	6700	134 000	176	1.18	
17	6 (0.3)	10	3	169	85	5990	120 000	139	1.22	98
18	6 (0.3)	50	3	59.7	30	2110	42 200	78.8	1.15	
19	6 (0.3)	100	3	49.3	25	1740	34 800	56.6	1.54	
20	7 (0.5)	–	3	186	93	3940	78 800	151	1.16	
21	7 (0.3)	–	3	102	51	3620	72 400	133	1.17	98
22	7 (0.3)	–	5	148	74	5240	62 900	154	1.18	
23	7 (0.3)	–	10	191	96	6750	40 500	171	1.19	
24	7 (0.3)	1	3	120	60	4240	84 800	155	1.19	98
25	7 (0.3)	3	3	177	89	6250	125 000	142	1.23	98
26	7 (0.3)	10	3	130	65	4590	91 800	129	1.25	98
27	7 (0.3)	30	3	74.8	37	2640	52 800	114	1.17	98
28	7 (0.3)	50	3	61.3	31	2160	43 200	85.7	1.22	98

[a]Reaction conditions: NBE 200 mg (2.12 mmol), benzene total 4.8 mL, initial NBE conc. 0.44 mmol/mL. [b]TON (turnovers) = NBE reacted (mmol)/V(mmol), TOF = TON/time. [c]GPC data in THF vs polystyrene standards (M_n in g/mol). [d]Cis percentage (%) estimated by ^{1}H NMR spectra. [e]Cited from ref 10h. [f]In toluene at −20 °C. [g]Two peaks were observed on GPC trace. [h]NBE 400 mg, initial NBE conc. 0.88 mmol/mL.

decreased upon increasing the PMe$_3$/V molar ratios (with decreasing the activity), a fairly good linear trend was observed between the TON (corresponding to the polymer yield, conversion) and the M_n values (in all polymerization runs conducted under the same initial concentration conditions) consistent with low PDI values. It also turned out that the M_n values in the resultant polymers were higher than those estimated on the basis of TON values (and the yields), although the M_n values measured by GPC were estimated vs polystyrene standards [ex. M_n = 160 vs $M_{n(theo)}$ = 46.6 (run 14) by **6**; M_n = 154 vs $M_{n(theo)}$ = 49.3 (run 22) by **7**; $M_{n(theo)}$: calculated on the basis of TON values]. These results suggest that certain percentage of the catalytically active species play a role in this catalysis. The activity was also dependent upon the NBE concentration charged; high TOF value was observed when the ROMP by **6** was conducted under rather high initial NBE concentration conditions (run 13, TOF 157 000 h^{-1}, 43.6 s^{-1}).

Importantly, as observed by **5**, the olefinic double bonds in the resultant polymers prepared by **6**, **7** at 25 °C possess high *cis* selectivity (98%), whereas the resultant polymers prepared by **1**-**3** possess a mixture of *cis*/*trans* olefinic double bonds, confirmed by ^{1}H and ^{13}C NMR spectra (shown below and in the Supporting Information).[16] The *cis* percentages in the resultant polymers were not affected upon addition of PMe$_3$.

As shown in Figure 1, good linear correlations between TON (turnover number, polymer yield on the basis of V) and M_n value consistent with low PDI (M_w/M_n) values were observed in the ROMPs of NBE by V(CHSiMe$_3$)(N-2,6-X$_2$C$_6$H$_3$)[OC-(CF$_3$)$_3$](PMe$_3$)$_2$ [X = H (**6**), Cl (**7**)].[16] As suggested from Table 1, the M_n values in the resultant polymers were higher than those estimated on the basis of TON values (detailed data are shown in the SI).[16] It also turned out that linear relationships between ln[NBE]$_t$/[NBE]$_0$ and the polymerization time were observed ([NBE]$_0$, [NBE]$_t$ are the NBE concentration at the initial, the certain time, respectively), suggesting that the reaction rates were following a first order kinetics. These are the similar trends observed in the ROMP of NBE when **1** and **2** were used, communicated previously.[10h,16] The facts thus strongly suggest a possibility of living polymerization without deactivation, affording ultrahigh molecular weight ring-opened polymers with narrow molecular weights distributions (ex. M_n = 2.39 × 10^6 g/mol, M_w/M_n = 1.05 by **6**, after ca. 20 min).[16] Moreover, as described above, the resultant polymers possessed high *cis* olefinic double bonds.[16] Reported examples for the fast living ROMP affording ultrahigh molecular weight polymers have been limited, and these catalysts clearly demonstrate precise "*cis*-specific" living ROMP; this is thus one of the unique characteristics by adopting this catalysis. Since the resultant poly(NBE)s prepared at 50 and 80 °C also possessed low PDI values (M_w/M_n = 1.06−1.25, runs 32−37, 40, 41), the results thus suggest a possibility of living polymerization.

Table 2 summarizes the ROMP of NBE using **6** and **7** conducted at 50 and 80 °C in the presence (or without addition) of PMe$_3$. The results by **5** are also placed for comparison.[10h] As observed in the ROMP by **5** (runs 11, 12, 29−31),[10h] the catalytic activity by **6** (without addition of PMe$_3$) increased at 50 °C but decreased at 80 °C [activity (TOF) by **6**: 98 200 h^{-1} (run 15, at 25 °C), 93 400 (run 36, at 80 °C) < 109 000 (run 32, at 50 °C)]. However, it should be noted that the activities increased upon addition of PMe$_3$ and the reactions completed even at 80 °C, affording ultrahigh
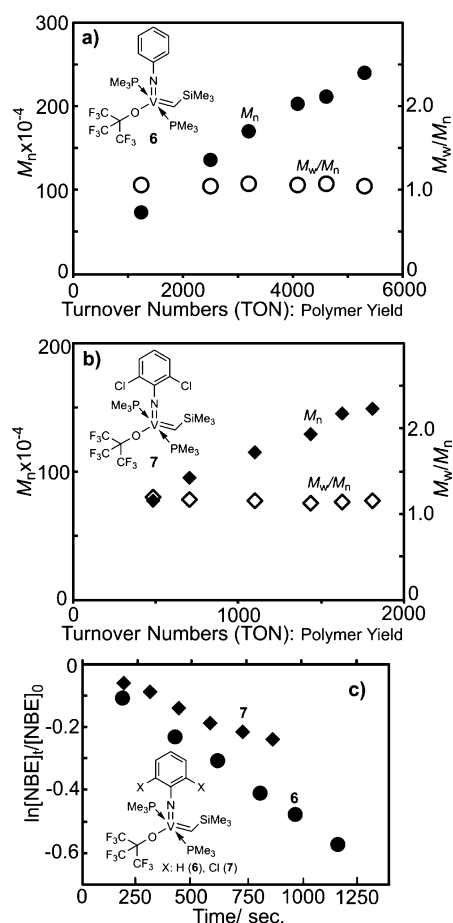
Figure 1. Plots of (a,b) M_n (g/mol, plotted as ●, ◆) and M_w/M_n (plotted as ○, ◇) vs turnover numbers (TON, polymer yield on the basis of V), and (c) ln[NBE]$_t$/[NBE]$_0$ vs time in ROMP of NBE by V(CHSiMe$_3$)(N-2,6-X$_2$C$_6$H$_3$)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ [X = H (**6**), Cl (**7**)]. Conditions: NBE 8.48 mmol in benzene (initial NBE conc. 0.22 mmol/mL) at 25 °C. [NBE]$_0$ and [NBE]$_t$ are the NBE concentration at the initial and the certain time, respectively. Detailed data are shown in the Supporting Information.[16]

molecular weight polymers with low PDI values (runs 33, 34, 37−39; M_n = 1.61−1.95 × 10^6 g/mol, M_w/M_n = 1.09−1.19); the results were reproducible (runs 35−38). Similarly, the activity by **7** at 80 °C increased upon addition of PMe$_3$ (runs 40, 41). Decrease in the activities (as observed in the ROMP at 25 °C) were not observed even addition of 10 equiv of PMe$_3$ (runs 34, 39). It thus probably seems likely that excess PMe$_3$ would play a role to stabilize the catalytically active species in this catalysis.

Note that the olefinic double bonds in the resultant polymers prepared by **6**, **7** possess high *cis* selectivity (97, 98%) when the ROMPs were conducted at 50 and 80 °C in the presence of PMe$_3$ (run 37, 39, 41). Moreover, it is also noteworthy that the *cis* percentage in the resultant polymers prepared by **5**−**7** without addition of PMe$_3$ at 80 °C increased in the order: 86% (**5**, run 31)[10h] < 93% (**6**, run 36) < 98% (**7**, run 40). The results clearly indicate that the highly *cis* specificity has been achieved by modification of both the imido and the anionic donor ligands in this catalysis. Although examples have been known concerning *cis* specific olefin metathesis reactions including ROMP using molybdenum and ruthenium complexes catalysts,[6,7] examples at high temperature have been very limited so far (these reactions were conducted mostly at room

Table 2. ROMP of NBE by 5, 6, 7: Temperature Dependence[a]

run	cat. (μmol)	PMe$_3$/equiv	temp./°C	time/min	polymer/mg	yield/%	TON[b]	TOF[b]/h^{-1}	$M_n^c \times 10^{-4}$	M_w/M_n^c	cis/%[d]
11[e]	5 (1.0)	–	25	20	95	48	1000	3000	52.5	1.38	92
12[e]	5 (1.0)	3	25	20	196	98	2090	6270	95	1.15	97
29	5 (1.0)	–	50	20	138	69	1460	4380	49	1.30	77
30[e]	5 (1.0)	3	50	10	200	>99	2120	12 700	83	1.37	96
31[e]	5 (0.5)	33	80	5	196	98	3920	47 000	54.6	1.36	86
15	6 (0.3)	–	25	3	139	70	4910	98 200	160	1.08	98
16	6 (0.3)	3	25	3	189	95	6700	134 000	176	1.18	
32	6 (0.3)	–	50	3	155	78	5480	109 000	189	1.06	96
33	6 (0.3)	3	50	3	199	>99	7030	141 000	168	1.17	95
34	6 (0.3)	10	50	3	194	>97	6850	137 000	195	1.15	96
35	6 (0.3)	–	80	3	122	61	4320	86 400	147	1.11	
36	6 (0.3)	–	80	3	132	66	4670	93 400	156	1.09	93
37	6 (0.3)	3	80	3	195	>98	6900	138 000	161	1.19	97
38	6 (0.3)	3	80	3	195	>98	6900	138 000			
39	6 (0.3)	10	80	3	197	>98	6960	139 000	146	1.20	97
23	7 (0.3)	–	25	10	191	96	6750	40 500	171	1.19	
25	7 (0.3)	3	25	3	177	89	6250	125 000	142	1.23	98
40	7 (0.3)	–	80	3	128	64	4530	90 600	121	1.28	98
41	7 (0.3)	3	80	3	194	>97	6850	137 000	128	1.25	97

[a]Reaction conditions: NBE 200 mg (2.12 mmol), benzene total 4.8 mL, initial NBE conc. 0.44 mmol/mL. [b]TON (turnovers) = NBE reacted (mmol)/V(mmol), TOF = TON/time. [c]GPC data in THF vs polystyrene standards (M_n in g/mol). [d]Cis percentage (%) estimated by ^{1}H NMR spectra. [e]Cited from ref 10h.

temperature). Taking into account these, the present catalysts (especially **6** and **7**) are very rare examples as thermally robust, highly efficient *cis* specific ROMP catalysts.

Figure 2 shows ^{1}H and ^{13}C NMR spectra in the resultant poly(NBE)s. The olefinic double bonds in the resultant polymers prepared by **7** possess high *cis* selectivities even if the polymerization was conducted at 80 °C (98%, Figure 2a,c, runs 21, 40, respectively), whereas the *cis* selectivity in the

Figure 2. (a−c) ^{1}H NMR spectra (in CDCl$_3$ at 25 °C) of poly(NBE)s prepared by V(CHSiMe$_3$)(N-2,6-X$_2$C$_6$H$_3$)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ [(a,c) X = Cl (**7**, runs 21, 40, respectively), (b) X = H (**6**, run 36)], (d) ^{13}C NMR spectra (in CDCl$_3$ at 25 °C) of poly(NBE) prepared by **7** (run 40). More detailed data are shown in the Supporting Information.[16]

resultant polymer prepared by **6** at 80 °C was rather low (93%, run 36, Figure 2b). Only one resonance due to ccc sequence (in carbon ascribed to C$_{2,3}$) was also observed in the ^{13}C NMR spectrum (Figure 2d, run 40), strongly suggesting the high *cis* selectivity in the resultant ROMP polymer.[19]

Since olefinic double bonds in the resultant polymers prepared by **6** possessed high *cis* selectivity (98%, run 14, Table 1), we analyzed the tacticity by measurement of ^{13}C NMR spectra with hydrogenated samples (details are shown in the SI).[16] Although ordinary measurement showed a simple set of 4 resonances, careful analysis using cryoprobe showed broad two resonances in 31.7 ppm (ascribed to cyclopentane unit, 5, 6 position) and three resonances in 40.7 ppm (ascribed to carbon in bridgehead, 7 position).[20] The result thus clearly indicates that the resultant polymer prepared by **6** is atactic, and the tacticity control should be thus the next target. Moreover, samples prepared by different catalysts [runs 6 (by **3**), 11 (by **5**), 21 (by **7**)] were also measured to explore ligand effect toward the tacticity (Figure 3).[16] Although samples prepared by **3,5,6** possessed atactic (*meso/racemo* = ca. 6/4, on the basis of carbons in 5, 6 positions), sample by **7** possessed rather high *racemo* selectivity (*meso/racemo* = ca. 3/7, Figure 3b).[16,20] These results suggest that tacticity would be control by the ligand modification (both imido and anionic ancillary donor ligands).

The ROMPs of NBE in the presence of chain transfer reagent (1-hexene, commonly employed in industry)[21] were conducted in the presence of V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$)(OC$_6$F$_5$) (PMe$_3$)$_2$ (**3**), V(CHSiMe$_3$) (NR)[OC(CF$_3$)$_3$]-(PMe$_3$)$_2$ [R = Ph (**6**), 2,6-Cl$_2$C$_6$H$_3$ (**7**)].[21] The results are summarized in Table 3.

The activities by **3** slightly decreased upon increasing 1-hexene concentration (runs 44−47), when the polymerization was conducted without addition of PMe$_3$, but the activity increased upon addition of PMe$_3$ (run 42); exceptionally high TOF value (1 210 000 h^{-1}, 336 s^{-1}) has been achieved. The M_n values decreased upon increasing the 1-hexene concentration
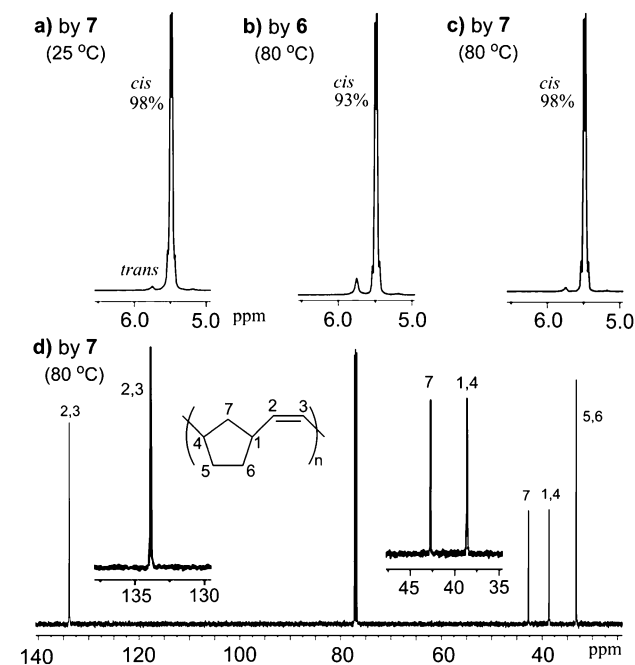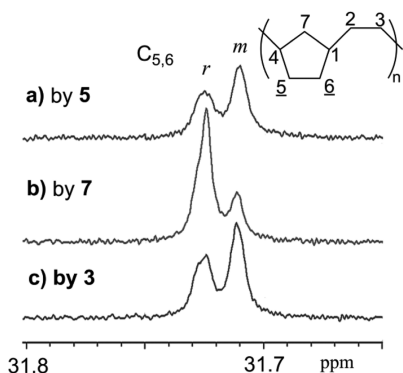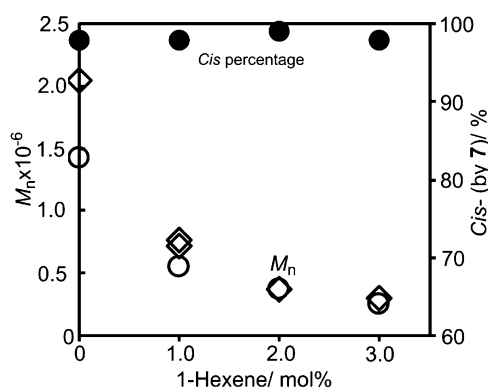
Figure 3. ^{13}C NMR spectra (in CDCl$_3$ at 60 °C) of hydrogenated poly(NBE)s prepared by (a) V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$)[OC-(CH$_3$) (CF$_3$)$_2$](PMe$_3$)$_2$ (**5**, run 11), (b) V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ (**7**, run 21), and by (c) V(CHSiMe$_3$)-(N-2,6-Cl$_2$C$_6$H$_3$) (OC$_6$F$_5$) (PMe$_3$)$_2$ (**3**, run 6)]. Detailed conditions are shown in the Supporting Information.[16]

Figure 4. Plots of M_n (g/mol) vs 1-hexene conc. in the ROMP of NBE by V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$) (OC$_6$F$_5$) (PMe$_3$)$_2$ (**3**, plotted as ◇), V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ (**7**, plotted as ○), and *cis*-percentage in the resultant ROMP polymer (plotted as ●) vs 1-hexene concentration in the ROMP of NBE by **7**. Data are shown in Table 3.

with broadening of the M_w/M_n values, clearly suggesting that a chain transfer reaction occurred with certain degree under these conditions (runs 42−44, 46, 47, Figure 4). In contrast, the activity by **6** decreased upon addition of 1-hexene with decreasing the M_n values in the resultant polymers; the decreases in the activity were slightly improved upon addition of PMe$_3$ (runs 48−52).

Note that a clear decrease in the M_n value without decreasing the activity (as seen by **6**) was observed upon presence of 1-hexene (run 21 vs run 53) in the ROMP using **7**. Also note that the activities increased upon addition of PMe$_3$ and remarkable decrease in the activity was not observed upon increasing the 1-hexene concentration charged (runs 55−57). The M_n values decreased upon increasing the 1-hexene concentration with

broadening of the M_w/M_n values, clearly suggesting that certain degree of chain transfer reaction occurred under these conditions (runs 25, 55−57, Figure 4). Moreover, importantly, the resultant polymers prepared by **7** (as well as **6**) possessed highly *cis* selectivity (96−99%, Figure 4) irrespective of presence of 1-hexene. These results would suggest that uses of dichlorophenylimido analogues (**3** and **7**) are highly effective for the ROMP of NBE in the presence of chain transfer reagent, although the exact reason is not clear at this moment. Since chain transfer reaction means cross metathesis reaction of metal−alkylidene containing polymer chain with 1-hexene, the results would also suggest a possibility of application to various cross metathesis reactions.

Table 3. ROMP of NBE by 3, 6, 7] in the Presence of 1-Hexene as Chain Transfer Reagent[a]

run	cat. (μmol)	PMe$_3$/equiv	1-hexene/mol %	time/min	polymer/mg	yield/%	TON[b]	TOF[b]/h^{-1}	$M_n{}^c \times 10^{-4}$	$M_w/M_n{}^c$	cis[d]/%
7	**3** (0.1)	−	−	2	174	87	18 400	552 000	205	1.12	
8	**3** (0.1)	3.0	−	2	190	95	20 100	603 000	179	1.11	
42	**3** (0.1)	3.0	1.0	2	192	96	20 300	609 000	62.2	1.39	
43	**3** (0.05)	3.0	1.0	2	190	95	40 300	121 0000	44.0	1.63	
44	**3** (0.1)	−	1.0	2	178	89	18 800	564 000	71.8	1.38	
45	**3** (0.1)	−	1.0	2	184	92	19 500	585 000	76.4	1.20	
46	**3** (0.1)	−	2.0	2	132	66	14 000	420 000	36.5	1.51	
47	**3** (0.1)	−	3.0	2	130	65	13 800	414 000	29.6	1.45	
15	**6** (0.3)	−	−	3	139	70	4910	98 200	160	1.08	98
17	**6** (0.3)	10.0	−	3	169	85	5990	120 000	139	1.22	98
48	**6** (0.3)	−	1.0	3	24	12	848	17 000	17.6	1.74	
49	**6** (0.3)	−	1.0	3	26	13	918	18 400	17.0	1.67	
50	**6** (0.3)	−	1.0	10	46	23	1620	9720	20.1	2.4	95
51	**6** (0.3)	3.0	1.0	3	35	18	1240	24 800	17.2	1.77	96
52	**6** (0.3)	10.0	1.0	3	49	25	1730	34 600	17.0	1.74	97
21	**7** (0.3)	−	−	3	102	51	3620	72 400	133	1.17	98
53	**7** (0.3)	−	1.0	3	85	43	3000	60 000	86.4	2.59	96
54	**7** (0.3)	−	1.0	10	197	>98	6960	41 700	78.8	3.07	98
25	**7** (0.3)	3.0	−	3	177	89	6250	125 000	142	1.23	98
55	**7** (0.3)	3.0	1.0	3	178	89	6250	125 000	55.0	1.56	98
56	**7** (0.3)	3.0	2.0	3	156	78	5510	110 000	37.4	1.66	99
57	**7** (0.3)	3.0	3.0	3	152	76	5370	107 000	24.8	1.83	98

[a]Reaction conditions: NBE 200 mg (2.12 mmol), benzene total 4.8 mL (initial NBE conc. 0.44 mmol/mL), 25 °C. [b]TON (turnovers) = NBE reacted (mmol)/V(mmol), TOF = TON/time. [c]GPC data in THF vs polystyrene standards (M_n in g/mol). [d]Cis percentage (%) estimated by ^{1}H NMR spectra.

Table 4. ROMP of 5-Vinyl-2-norbornene (VNBE), 5-Ethylidene-2-Norbornene (ENB), Dicyclopentadiene (DCPD), and Norbornadiene (NBD) by 3, 6, 7[a]

run	monomer	cat.	PMe$_3$/equiv	time/min	polymer/mg	yield/%	TON[b]	TOF[b]/h^{-1}	M_n[c] $\times 10^{-4}$	M_w/M_n[c]
58	VNBE	**6** (1.0)	−	10	64.7	26	540	3240	0.22	1.50
59	VNBE	**6** (1.0)	3.0	10	125	49	1040	6240	0.24	1.59
60	VNBE	**7** (0.3)	−	3	49.0	19	1360	27 200	1.35	1.77
61	VNBE	**7** (0.3)	3.0	3	133	52	3730	74 600	1.69	1.56
62	VNBE	**3** (0.2)	−	3	200	79	8350	167 000	4.00	2.24
63	VNBE	**3** (0.2)	3.0	3	240	95	10 000	200 000	3.18	2.37
64	ENB	**6** (0.5)	−	3	243	96	4060	81 200	17.1	2.74
65	ENB	**7** (0.5)	−	2	254	>99	4240	127 000	12.8	2.39
66	ENB	**3** (0.2)	−	2	254	>99	10 600	318 000	80.5	1.34
67	DCPD	**6** (1.0)	−	5	273	98	2070	24 800	70.1	1.15
68	DCPD	**7** (0.5)	−	3	204	73	3090	61 800	119	1.24
69	DCPD	**3** (0.2)	−	3	135	48	5110	102 000	−[d]	−
70	TCD	**6** (1.0)	−	5	317	94	1980	23 800	−[d]	−
71	NBD	**6** (0.3)	−	2	53.5	27	1890	56 700	−[d]	−
72	NBD	**7** (0.3)	−	2	173	87	6110	183 000	−[d]	−

[a]Reaction conditions: monomer 2.12 mmol, total solvent (benzene) 4.8 mL (initial monomer conc. 0.44 mmol/mL), 25 °C. [b]TON (turnovers) = monomer reacted (mmol)/V(mmol), TOF = TON/time. [c]GPC data in THF vs polystyrene standards (M_n in g/mol). [d]Insoluble (in THF, CDCl$_3$) for GPC measurement.

2. Ring-Opening Metathesis Polymerization (ROMP) of Cyclic Olefins by V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$) (OC$_6$F$_5$)(PMe$_3$)$_2$ (3), V(CHSiMe$_3$) (NR)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ [R = Ph (6), 2,6-Cl$_2$C$_6$H$_3$ (7)].

Table 4 summarizes the results for ROMP of 5-vinyl-2-norbornene (VNBE), 5-ethylidene-2-norbornene (ENB), dicyclopentadiene (DCPD), tetracyclododecene (TCD), and norbornadiene (NBD), shown in Scheme 3, by V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$) (OC$_6$F$_5$) (PMe$_3$)$_2$ (3), V(CHSiMe$_3$) (NR)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ [R = Ph (6), 2,6-Cl$_2$C$_6$H$_3$ (7)].

Scheme 3. List of NBE Derivatives Employed for ROMPs by V(CHSiMe$_3$)(N-2,6-Cl$_2$C$_6$H$_3$) (OC$_6$F$_5$) (PMe$_3$)$_2$ (3), V(CHSiMe$_3$) (NR)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ [R = Ph (6), 2,6-Cl$_2$C$_6$H$_3$ (7)], and ROMP of Cyclopentene (CP), Cyclooctene (CO) by 3
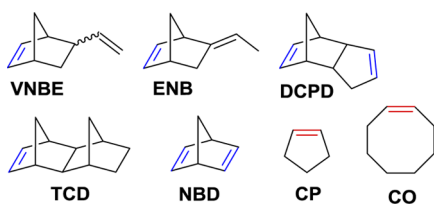
It turned out that the catalytic activities in the ROMP of VNBE (without addition of PMe$_3$ increased in the order: TOF (h^{-1}) = 3240 (**6**, run 58) < 27 200 (**7**, run 60) < 167 000 (**3**, run 62). The activity by **7** was much higher than that by **6** under the same conditions (runs 58, 60), and the activities by **3** and **7** increased upon addition of PMe$_3$ (runs 61 and 63). The activity by **3** was also higher than those by the 2,6-Me$_2$C$_6$H$_3$, adamantylimido analogues [TOF = 81 300 h^{-1} (**2**), 2770 (**1**), respectively].[10h] The resultant polymer possessed low molecular weights with uniform but rather broad molecular weight distributions (M_w/M_n = 1.50−2.37), suggesting a possibility of certain chain transfer in this catalysis, and the M_n values were not affected by addition of PMe$_3$.

In contrast, the ROMP of ENB by **3** afforded ultrahigh molecular weight polymer with relatively narrow molecular weight distribution (run 66), and the observed activity was higher than those for VNBE conducted under the similar conditions (runs 62, 66; initial monomer conc. 0.44 mmol/mL, at 25 °C). Moreover, **7** showed higher activity than **6**, affording rather low molecular weight polymers with uniform molecular weight distributions, suggesting a possibility of certain chain transfer (runs 64, 65). It seems likely that these ROMP results are somewhat related to those in the ROMP of NBE in the presence of 1-hexene, but certain chain transfer by **3** might not take place (or the degree was low). Thus, uses of dichlorophenylimido analogues (**3** and **7**) were effective for the ROMP of NBE derivatives. Although we highly expected that olefinic double bonds in the resultant polymers prepared by **6** and **7** possessed highly *cis* selectivity, as demonstrated by ROMP of NBE, however, it in fact seemed difficult to assign all resonances, estimate *cis-/trans-* ratios (by ^{13}C NMR spectra).[16] This is because that VNBE and ENB are a mixture of *endo-/exo-* forms, and resultant polymers is a mixture of head-to-head, head-to-tail, and tail-to-tail repeat units.

Although the resultant polymers in the ROMP of DCPD prepared by **6** and **7** afforded high molecular weights with low PDI values (M_w/M_n = 1.15, 1.24, runs 67, 68), the resultant polymer prepared by **3** was insoluble in ordinary GPC runs in THF (and ordinary GPC analysis in hot *o*-dichlorobenzene at 145 °C). The result by **3** clearly suggesting a possibility of certain cross-linking by olefin metathesis of two olefinic double bonds (norbornene and cyclopentene units). The results by **3** also suggests that **3** shows higher reactivity than the others (**6**, **7**) toward various cyclic olefins, as demonstrated below. ROMP of TCD and NBD by **6** (and **7**) afforded polymers that were insoluble for ordinary GPC analysis;[22] it seemed difficult to terminate the ROMP of NBD at the initial stage due to high reactivities toward the olefinic double bond(s).

Table 5 summarizes results in reactions with cyclopentene (CP) and *cis*-cyclooctene (CO) using **3**, **6**, and **7** under high monomer concentration conditions (Scheme 3). It turned out that ROMP of CP by **3** afforded ring-opened polymers with rather high efficiency (runs 73−75),[16] and the resultant polymers possessed high molecular weights with uniform molecular weight distributions (M_n = 83 600−105 000, M_w/M_n = 1.73−1.91). These ROMPs (with/without addition of PMe$_3$)

Table 5. ROMP of Cyclopentene (CP), *cis*-Cyclooctene (CO) by 3, 6, 7[a]

run	monomer	cat.	PMe₃/equiv	temp./°C	time	polymer/mg	yield/%	TON[b]	M_n[c] × 10⁻⁴	M_w/M_n[c]
73	CP	**3**	–	25	5 min	259	38	190	8.36	1.74
74	CP	**3**	–	25	10 min	272	40	199	9.51	1.73
75	CP	**3**	–	25	30 min	569	84	417	10.5	1.91
76	CP	**3**	10.0	25	10 min	38	6	28	2.58	1.66
77	CP	**3**	3.0	25	2 h	243	36	178	8.94	1.79
78	CP	**3**	10.0	25	2 h	209	32	153	7.60	1.66
79	CP	**6**	–	25	20 h	trace				
80	CP	**7**	–	25	20 h	trace				
81	CO[d]	**3**	–	25	12 h	140	64	63	3.31	1.70
82	CO	**3**	–	25	30 min	100	9	45	1.05	1.34
83	CO	**3**	–	25	2 h	290	26	132	2.70	1.59
84	CO	**3**	–	50	5 min	358	32	162	2.61	1.75
85	CO	**3**	–	80	5 min	545	49	247	3.95	1.84
86	CO	**3**	3.0	25	12 h	trace	–	–	–	
87	CO	**3**	10.0	50	30 h	trace				
88	CO	**6**	–	25	20 h	trace				
89	CO	**7**	–	25	20 h	trace				
90	CO	**Mo−F₆**[e]	–	25	5 min	960	87	436	9.03	1.86
91	CO	**Mo−F₀**[e]	–	25	2 h	trace				

[a]Reaction conditions: cat. 20 μmol, monomer 10.0 mmol (molar ratio of monomer:V = 500:1), total solvent (benzene) 0.5 mL, initial monomer conc. 20.0 M (mmol/mL), 25 °C. [b]TON (turnovers) = monomer reacted (mmol)/V(mmol). [c]GPC data in THF vs polystyrene standards (M_n: g/mol). [d]CP 2.0 mmol (4.0 M). [e]**Mo−F₆**: Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)[OC(CH₃)(CF₃)₂]₂, **Mo−F₀**: Mo(CHCMe₂Ph)(N-2,6-ⁱPr₂C₆H₃)-(OᵗBu)₂.

proceeded without deactivation (runs 73−75, 77, 78), but the activity decreased upon addition of PMe₃ (runs 76−78). In contrast, the ROMPs of CP by the fluorinated alkoxo analogues (**6**, **7**) did not take place at 25 °C even after 20 h.

Note that ROMP of CO by **3** took place and the activity increased at high temperature (50 and 80 °C, runs 84, 85), affording rather high molecular weight polymers with uniform molecular weight distributions (M_n = 10 500−39 500, M_w/M_n = 1.34−1.84). The ROMPs by **3** did not occur upon addition of PMe₃. As observed in the reaction of CP, the ROMPs of CO by the fluorinated alkoxo analogues (**6**, **7**) did not take place at 25 °C. As described in the introductory,[11−14] reported examples in ROMP of CO using alkylidene complexes with early transitions metals (especially without aid of AlCl₃ etc.) have been limited so far,[12,13] we thus believe that this is one of the unique characteristics for using this catalyst.

We also conducted the ROMP of CO using known molybdenum-alkylidene catalysts, Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)[OC(CH₃)(CF₃)₂]₂ (**Mo−F₆**),[18] Mo(CHCMe₂Ph)-(N-2,6-ⁱPr₂C₆H₃)(OᵗBu)₂ (**Mo−F₀**),[23] under the same conditions for comparison. Although the ROMP by **Mo−F₀** did not take place, the ROMP by **Mo−F₆**, that has been known as the highly active catalyst among them, showed higher catalytic activity at 25 °C. This is also, in fact, the first clear demonstration of ROMP of CO by (Schrock type mononuclear) molybdenum-alkylidene catalyst.[14a] In this regards, complex **3** is one of the effective catalysts for ROMP of CO especially at high temperature.

■ SUMMARY

In this paper, we explored ring-opening metathesis polymerization (ROMP) of various cyclic olefins especially using three (imido)vanadium(V)-alkylidene catalysts, V(CHSiMe₃)(N-2,6-Cl₂C₆H₃)(OC₆F₅)(PMe₃)₂ (**3**), V(CHSiMe₃)(NR)[OC-(CF₃)₃](PMe₃)₂ [R = Ph (**6**), 2,6-Cl₂C₆H₃ (**7**)], including

synthesis and identification of complexes **6** and **7**. Contents in this paper can be summarized as follows.

(1) Complex **3** exhibited the highest catalytic activity for ROMP of norbornene (NBE) among a series of (imido)vanadium(V)-alkylidenes employed in this study; effect of imido ligand toward the activity by V(CHSiMe₃)(NR)(OC₆F₅)(PMe₃)₂ [R = 1-adamantyl (**1**) < 2,6-Me₂C₆H₃ (**2**) < 2,6-Cl₂C₆H₃ (**3**)], has been demonstrated.

(2) *Cis*-specific (Z selective) ROMPs of NBE have been achieved with remarkable catalytic activities by the fluorinated alkoxo analogues (**6**, **7**), and the activity increased upon addition of PMe₃. The activities increased at high temperature (50 and 80 °C) without decreasing the *cis* selectivity (98%) in the resultant polymers. Since most of Z-selective metathesis reactions were conducted at room temperature (22 °C), these catalysts (**6** and **7**) should be promising candidates as thermally robust *cis*-specific (Z selective) metathesis catalysts. The ROMPs by **6** and **7** at 25 °C proceeded in a living manner, and the resultant poly(NBE)s prepared at 50 and 80 °C also possessed low PDI values (M_w/M_n = 1.06−1.25), suggesting a possibility of living polymerization.

(3) ROMPs of NBE in the presence of 1-hexene (chain-transfer reagent) by the 2,6-dichlorophenylimido analogues (**3** and **7**) proceeded without significant decrease in the catalytic activities; the M_n values can be controlled by 1-hexene concentration charged with certain degree of chain transfer (cross metathesis) reactions. The resultant poly(NBE)s prepared by **7** possessed high *cis* selectivity.

(4) These (imido)vanadium(V)-alkylidenes (**3**, **6**, and **7**) were effective for ROMPs of various norbornene derivatives, and ROMPs by 2,6-dichlorophenylimido analogues (**3** and **7**) proceeded with high catalytic activities. ROMPs of cyclopentene, even *cis*-cyclooctene (CO) proceeded

by **3**, and the activity in the ROMP of CO increased at high temperature (50 and 80 °C).

In particular, the highly *cis*-specific (and living) ROMP with remarkable activities have been achieved in these catalyzes (**6** and **7**) even at high temperature [ex. TOF 137 000 − >141 000 h⁻¹, at 50 or 80 °C, Table 2], and we highly believe that this is one of the unique characteristics for using these catalysts. Unique ligand effect of imido ligands (**3** and **7**) has also been demonstrated not only in the ROMPs of NBE derivatives, but also in the ROMP of NBE with chain-transfer reagent. Moreover, ROMP of CO took place by **3**, as the first clear demonstration of the ROMP using early transition metal alkylidene catalyst without additives. These are, we believe, potentially important information for the catalyst design as well as better understanding in organometallic chemistry. We are now exploring the role of PMe₃ and exploring to find more active, stereospecific catalysts (better tacticity control) in this subject. We hope to introduce our more data in the near future.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06330.

> Experimental details, NMR spectra for attempted synthesis of V(N-2,6-Me₂C₆H₃) (CH₂SiMe₃)₂[OC-(CF₃)₃] from V(N-2,6-Me₂C₆H₃) (CH₂SiMe₃)₃, NMR spectra (including VT-NMR spectra, upon addition of PMe₃) of the alkylidene complexes, V(CHSiMe₃) (NR)[OC(CF₃)₃](PMe₃)₂ [R = C₆H₅ (**6**), 2,6-Cl₂C₆H₃ (**7**], additional ROMP results (experimental data for the living ROMP), and selected NMR data for resultant polymers (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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