

(Arylimido)vanadium(V)-Alkylidene Complexes as Catalysts for Ring-opening Metathesis Polymerization (ROMP) of Cyclic Olefins: Ligand Design for Exhibiting the High Activity

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Abstract (Imido)vanadium(V)-alkylidene complexes of type $V(\text{CHSiMe}_3)(\text{NR})(\text{OR}')(\text{PMe}_3)_2$ [$\text{R} = \text{Ad}, \text{C}_6\text{H}_5, 2,6\text{-Me}_2\text{C}_6\text{H}_3, 2,6\text{-Cl}_2\text{C}_6\text{H}_3$; $\text{R}' = 2,6\text{-Me}_2\text{C}_6\text{H}_3, 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3, 2,6\text{-F}_2\text{C}_6\text{H}_3, \text{C}_6\text{F}_5, \text{C}_6\text{Cl}_5$] exhibited from moderate to remarkable catalytic activities for ring-opening metathesis polymerization (ROMP) of norbornene (NBE). The catalytic activities were affected by the ligand substituents, and $V(\text{CHSiMe}_3)(\text{N-}2,6\text{-Cl}_2\text{C}_6\text{H}_3)(\text{OC}_6\text{X}_5)(\text{PMe}_3)_2$ ($\text{X} = \text{F}, \text{Cl}$) demonstrated the exceptionally high catalytic activities for ROMP of NBE. The complexes polymerized cycloheptene (CHPE) and *cis*-cyclooctene (COE), and ROMP of COE by the OC_6Cl_5 analogue proceeded in a living manner even at 80 °C, and the activity increased with increasing the temperature up to 120 °C. Highly active catalysts for ROMP of cyclic olefins (NBE, cyclopentene, and CHPE) can be generated *in situ* by premixing isolated $V(\text{CHSiMe}_3)(\text{NC}_6\text{F}_5)(\text{O-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)(\text{PMe}_3)_2$ with 1.0 equiv. of $\text{C}_6\text{F}_5\text{OH}$ or $\text{C}_6\text{Cl}_5\text{OH}$ via immediate phenoxy exchange; the activity was affected by the kind of phenol added [TOF in the ROMPs of NBE: $4.62 \times 10^4 \text{ min}^{-1}$ (upon addition of $\text{C}_6\text{F}_5\text{OH}$) versus 37.3 min^{-1} (none)].

Keywords Olefin metathesis; Molecular catalyst; Ring-opening metathesis polymerization; Cyclic olefin; Vanadium catalyst

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INTRODUCTION

Olefin metathesis has been recognized as the useful method applied for synthesis of various organic compounds and functional polymers,^[1–18] and metal-carbene (alkylidene) complexes have been known to play a key role in this catalysis.^[3–10] Ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization have been widely used in synthesis of advanced polymeric materials.^[11–18] These are addition type polymerization induced by ring strain (ROMP) or condensation polymerization accompanied by production of small molecule (such as ethylene or propylene, ADMET).

Olefin metathesis catalysts are generally classified into three types:^[1,2,18] (i) transition metal alkylidene (carbene) complexes or metallacycles, (ii) transition metal compounds with metal alkyl cocatalysts (generating active species *in situ*), and (iii) others (generating active species *in situ* without alkylating reagent). Both ruthenium-carbene [so called Grubbs type, exemplified as **Ru(1)**–**Ru(4)**; neutral carbene] and molybdenum-alkylidene [so called Schrock type, **Mo-F₀**, **Mo-F₆**; nucleophilic carbene] catalysts (Chart 1) are the

known successful examples.^[1–8]

ROMP is a promising method affording polymers (especially by ROMP of norbornene derivatives) which possess rather linear structures compared to ordinary vinyl polymers such as poly(acrylate)s and poly(acrylamide)s.^[11,18,19] The unique characteristics thus contribute to better maintaining the nature of functionality at the side chain and the chain end. Schrock type molybdenum catalysts are useful initiators for the living ROMP of substituted norbornenes and norbornadienes.^[4–7,11,13,16,17] The absence of chain-transfer (intermolecular or intramolecular metathesis with internal olefins in the resultant ring-opened polymer) and termination (catalyst deactivation) in the ROMP enables synthesis of the homopolymers and the block copolymers with narrow molecular weight distributions (Scheme 1).^[5–7,11,16,18] Note that the exclusive end functionalization can be achieved by treating the propagating ROMP polymer chain end with aldehyde (called Wittig-type coupling, cleavage). Precise control of not only the functionality in both the initiation and the termination sites,^[5–7,11,16,18] but also the monomer repeat unit (by varying the monomer/catalyst molar ratios due to the exclusive initiation efficiency especially by **Mo-F₀**) can be possible under the living conditions. The ROMP thus demonstrates tremendous utility as a powerful tool in preparing macromolecular materials displaying promising biological, electronic, and mechanical properties.

As described above, both ruthenium and molybdenum

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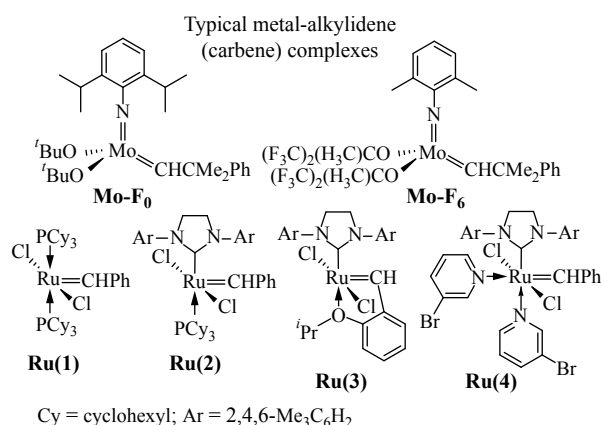
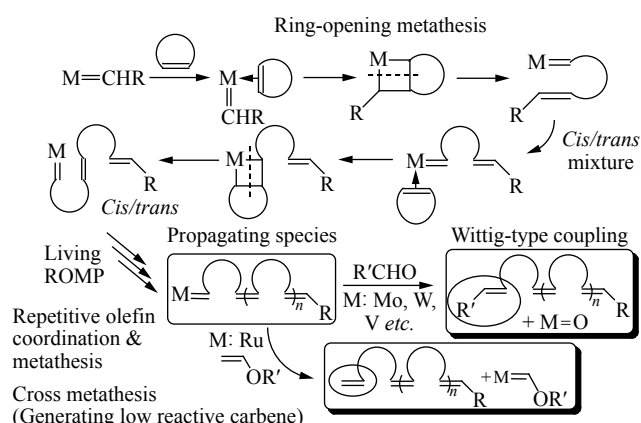


Chart 1 Typical olefin metathesis catalysts



Scheme 1 General scheme for ring-opening metathesis polymerization (ROMP): basic mechanism and probable chain transfer reactions

Metathesis with internal olefins (chain transfer reactions)

Intermolecular cross metathesis (chain transfer)

Intramolecular cross metathesis (chain transfer)

Cyclic

catalysts demonstrated unique attractive characteristics,^[1–18] while there are still concerns such as thermal stability, catalyst deactivation over time course, and subsequent isomerization and/or generating radicals, *etc.* The catalyst development has thus been considered as an important topic. Study on synthesis and reaction chemistry of vanadium-alkylidene complexes has been considered as an attractive subject,^[10] not only due to their potentials in catalysis displayed by classical Ziegler type vanadium catalyst systems (*e.g.* VOCl₃, VCl₄, VCl₃-AlBr₃, AlCl₃-AlPh₃, AlⁱBu₃, SnPh₄) for the synthesis of ultrahigh molecular weight polymers (such as EP-

DM, cyclic olefin copolymers) *via* olefin coordination/insertion polymerization,^[20–22] but also due to fundamental importance in organometallic chemistry with vanadium.^[9,10,20,22] However, limited examples were known for synthesis of vanadium-alkylidene (carbene) complexes;^[9,10] in particular, examples for olefin metathesis active vanadium-alkylidene catalysts have been limited until recently.^[9,10]

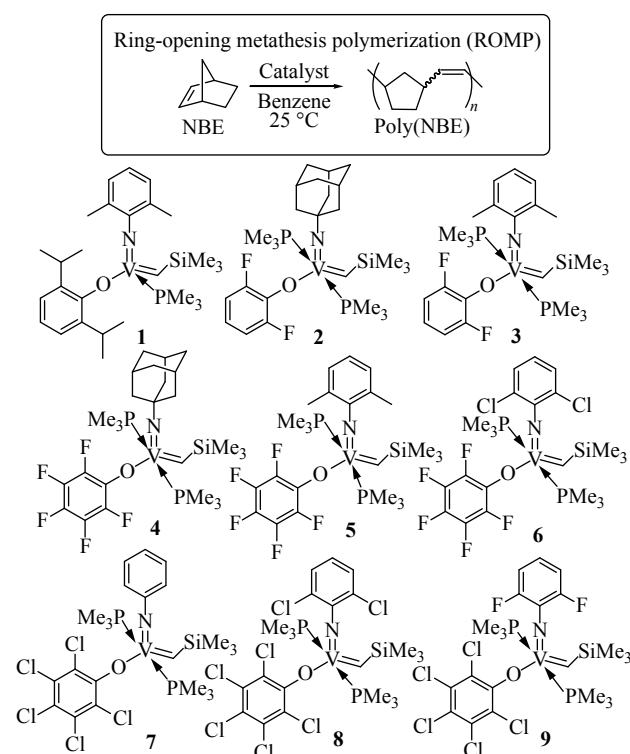
In this feature article, a series of vanadium-alkylidene complexes which exhibit catalytic activities for ROMP of cyclic olefins have thus been introduced.

EFFECTS OF LIGANDS ON RING-OPENING METATHESIS POLYMERIZATION (ROMP) OF CYCLIC OLEFINS USING VANADIUM(V)-ALKYLIDENE CATALYSTS

Ring-opening Metathesis Polymerization (ROMP) of Norbornene (NBE) Using Phenoxide-modified (Imido)vanadium-alkylidene Catalysts: Ligand Effects for Exhibiting the High Activity

(Imido)vanadium(V)-alkylidene complexes containing phenoxide ligands (1–9, shown in Scheme 2) exhibited from moderate to high catalytic activities for ROMP of norbornene (NBE), and the activities were affected by both the imido and the anionic donor ligands.^[9,10,23–27] The selected results in the ROMP of norbornene (NBE) are summarized in Table 1.^[23–27]

It turned out that the activity in ROMP was affected by the phenoxide substituents and the imido substituents, and



Scheme 2 Ring-opening metathesis polymerization (ROMP) of norbornene (NBE) using V(CHSiMe₃)(NR)(OR')(PMe₃)₂ [R = Ad, C₆H₅, 2,6-Me₂C₆H₃, 2,6-Cl₂C₆H₃, 2,6-F₂C₆H₃; R' = 2,6-ⁱPr₂C₆H₃, 2,6-F₂C₆H₃, C₆F₅, C₆Cl₅]

Table 1 Ring-opening metathesis polymerization (ROMP) of norbornene (NBE) by $V(\text{CHSiMe}_3)(\text{NR})(\text{OR}')(\text{PMe}_3)_2$ [$\text{R} = 1\text{-adamantyl (Ad), C}_6\text{H}_5, 2,6\text{-Me}_2\text{C}_6\text{H}_3, 2,6\text{-Cl}_2\text{C}_6\text{H}_3, 2,6\text{-F}_2\text{C}_6\text{H}_3$; $\text{R}' = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3, 2,6\text{-F}_2\text{C}_6\text{H}_3, \text{C}_6\text{F}_5, \text{C}_6\text{Cl}_5$] at 25 °C ^a[23–27]

	Complex (μmol)		PMe ₃ (equiv.)	Time (min)	Yield (%)	TON ^b	TOF ^b ($\text{h}^{-1} (\text{s}^{-1})$)	$M_n^c \times 10^{-4}$	M_w/M_n^c
	R	R'							
1 (5.0) ^d	2,6-Me ₂ C ₆ H ₃	2,6- ⁱ Pr ₂ C ₆ H ₃	–	60	7	150	150 (0.04)	3.1	1.10
2 (0.5)	Ad	2,6-F ₂ C ₆ H ₃	–	5	32	1380	1.65×10^4 (4.58)	29	1.53
3 (0.5)	2,6-Me ₂ C ₆ H ₃	2,6-F ₂ C ₆ H ₃	–	5	78	3300	3.97×10^4 (11.0)	59	1.41
3 (0.3)	2,6-Me ₂ C ₆ H ₃	2,6-F ₂ C ₆ H ₃	–	3	54	3820	7.63×10^4 (21.2)	122	1.08
4 (0.3)	Ad	C ₆ F ₅	–	3	70	4950	9.90×10^4 (27.5)	79.0	1.15
5 (0.1)	2,6-Me ₂ C ₆ H ₃	C ₆ F ₅	–	3	54	1.15×10^4	2.30×10^5 (63.9)	164	1.18
5 (0.3)	2,6-Me ₂ C ₆ H ₃	C ₆ F ₅	–	1	80	5650	3.39×10^5 (94.2)	117	1.22
5 (0.3)	2,6-Me ₂ C ₆ H ₃	C ₆ F ₅	0.1	3	17.1	1210	2.42×10^4 (6.7)	61.8	1.10
5 (0.3)	2,6-Me ₂ C ₆ H ₃	C ₆ F ₅	0.5	3	2.8	198	3960 (1.1)	12.4	1.03
6 (0.1)	2,6-Cl ₂ C ₆ H ₃	C ₆ F ₅	–	3	> 99	2.12×10^4	4.24×10^5 (118)	110	1.27
6 (0.1)	2,6-Cl ₂ C ₆ H ₃	C ₆ F ₅	–	2	87	1.84×10^4	5.52×10^5 (153)	205	1.12
6 (0.1)	2,6-Cl ₂ C ₆ H ₃	C ₆ F ₅	3.0	2	95	2.01×10^4	6.03×10^5 (168)	179	1.11
7 (0.1)	C ₆ H ₅	C ₆ Cl ₅	–	2	38	4000	1.20×10^5 (33.3)	107	1.61
7 (0.1)	C ₆ H ₅	C ₆ Cl ₅	–	3	50	5300	1.06×10^5 (29.5)	114	1.81
8 (0.1)	2,6-Cl ₂ C ₆ H ₃	C ₆ Cl ₅	–	2	78	1.66×10^4	4.98×10^5 (138)	128	1.57
8 (0.1)	2,6-Cl ₂ C ₆ H ₃	C ₆ Cl ₅	–	3	92	1.95×10^4	3.90×10^5 (108)	132	1.60
9 (0.1)	2,6-F ₂ C ₆ H ₃	C ₆ Cl ₅	–	2	75	1.59×10^4	4.77×10^5 (133)	152	1.55
9 (0.1)	2,6-F ₂ C ₆ H ₃	C ₆ Cl ₅	–	3	90	1.91×10^4	3.82×10^5 (106)	158	1.66
	Mo-F₀ (1.0) ^e		–	10	63	1340	8040 (2.2)	19.0	1.02
	Mo-F₆ (0.1) ^e		–	3	81.5	1.73×10^4	3.46×10^5 (96.1)	186	1.20

^a Conditions: NBE 2.12 mmol, benzene 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 versus polystyrene standards; ^d Initial NBE 0.89 mmol/mL; ^e In toluene

OC₆F₅ analogues (**4–6**) showed higher activities than those of O-2,6-F₂C₆H₃ (**2** and **3**) and O-2,6-ⁱPr₂C₆H₃ (**1**) analogues.^[25,26] The activities by the OC₆F₅ analogues, $V(\text{CHSiMe}_3)(\text{NR})(\text{OC}_6\text{F}_5)(\text{PMe}_3)_2$ (**4–6**), increased in the order: $\text{R} = \text{Ad}$ (**4**, $\text{TOF} = 9.90 \times 10^4 \text{ h}^{-1}$) < 2,6-Me₂C₆H₃ (**5**, $\text{TOF} = 2.30 \times 10^5 \text{ h}^{-1}$) < 2,6-Cl₂C₆H₃ (**6**, $\text{TOF} = 5.52 \times 10^5 \text{ h}^{-1}$). The 2,6-Cl₂C₆H₃ analogue (**6**) exhibited the highest activity and the activity seemed improving upon addition of PMe₃, whereas the activity by the 2,6-Me₂C₆H₃ analogue (**5**) decreased even upon addition of small amount of PMe₃.^[25,26]

The resultant polymers held a ring-opened structure (confirmed by NMR spectra) with a mixture of *cis/trans* olefinic double bonds. They possessed ultrahigh molecular weights with low PDI (M_w/M_n) values, suggesting a possibility of living polymerization, as described below. The activity by **6** was also higher than those by the known active molybdenum catalysts, **Mo-F₆** ($\text{TOF} 3.46 \times 10^5 \text{ h}^{-1}$ after 3 min)^[24] and **Mo-F₀** (8040 h^{-1} after 10 min).^[25]

It also turned out that the activity by the OC₆Cl₅ analogues, $V(\text{CHSiMe}_3)(\text{NR})(\text{OC}_6\text{Cl}_5)(\text{PMe}_3)_2$ (**7–9**), was affected by the imido ligand employed, and the activity (after 2 min) increased in the order: Ph (**7**, $\text{TOF} = 1.20 \times 10^5 \text{ h}^{-1}$) < 2,6-Cl₂C₆H₃ (**8**, $\text{TOF} = 4.98 \times 10^5 \text{ h}^{-1}$) and 2,6-F₂C₆H₃ (**9**, $\text{TOF} = 4.77 \times 10^5 \text{ h}^{-1}$).^[27] Both the 2,6-dichlorophenylimido analogue (**8**) and the 2,6-difluorophenylimido analogue (**9**) showed higher activities than that of the phenylimido (**7**) analogue; 2,6-dimethylphenylimido analogue showed the lowest activity ($4.80 \times 10^4 \text{ h}^{-1}$). The results suggest that an electronic factor in the arylimido ligand plays a role toward the activity.^[27] Taking into account these results, it is clear that the introduction of electron-withdrawing groups on both the imido and the phenoxide ligands, generating electron-de-

ficient alkylidene species, leads to higher activity; $V(\text{CHSiMe}_3)(\text{N-2,6-Cl}_2\text{C}_6\text{H}_3)(\text{OC}_6\text{F}_5)(\text{PMe}_3)_2$ (**6**) thus showed the highest activity among these vanadium catalysts for the ROMP of NBE.

As shown in Fig. 1, good linear relationships were observed between TON (turnover number, corresponding to the polymer yield, conversion) and the M_n values (in all polymerization runs conducted under the same initial NBE concentration conditions) accompanied with low PDI values, irrespective of the kind of ligand set employed (**4** and **5**). Importantly, linear relationships between $\ln[\text{NBE}]_t/[\text{NBE}]_0$ and the polymerization time were also observed, where $[\text{NBE}]_0$ and $[\text{NBE}]_t$ are the NBE concentration at the initial and certain time, respectively. These results strongly suggest that the reaction rates followed the first order kinetics without catalyst deactivation.^[25,26] Therefore, the ROMPs proceeded in a living manner under these conditions, affording ultrahigh molecular weight polymers with low PDI (M_w/M_n) values.

Ring-opening Metathesis Polymerization (ROMP) of Cycloheptene (CHPE) and *Cis*-cyclooctene (COE)

It has been postulated that the driving force in ROMP (addition polymerization *via* ring-opening) is the release of ring strain,^[1–3,28] and several reports concerning the effect of ring strain toward the catalytic activity in ROMP [of called low ring strain monomers, cyclopentene (CPE), cycloheptene (CHPE), and *cis*-cyclooctene (COE)] using neutral ruthenium-carbene catalysts^[29,30] and Fischer-type tungsten-carbene catalyst^[31] were known; reports in the ROMP of COE using alkylidene complexes with early transition metals were limited.^[26,27,32–38]

Table 2 summarizes the results in ROMPs of CPE and

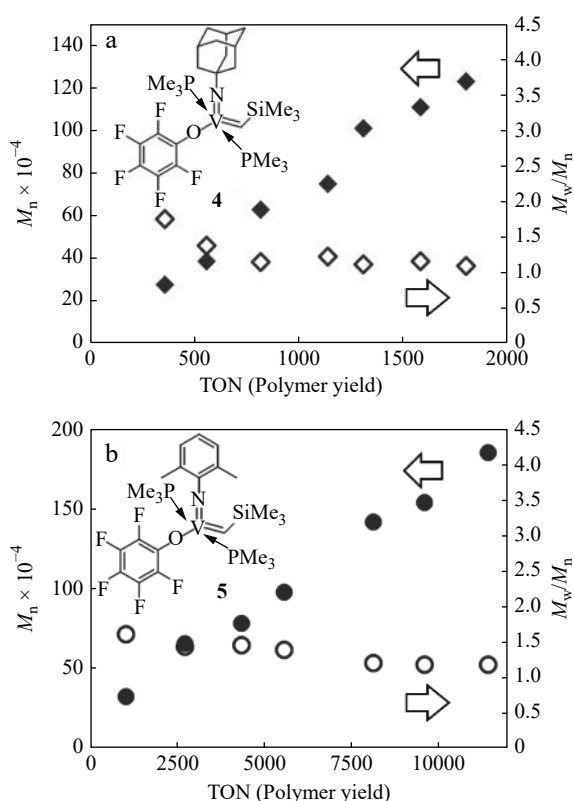


Fig. 1 Plots of M_n and M_w/M_n versus TON (polymer yield) in ROMP of NBE using (a) $V(\text{CHSiMe}_3)(\text{NAd})(\text{OC}_6\text{F}_5)(\text{PMe}_3)_2$ (**4**) or (b) $V(\text{CHSiMe}_3)(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)(\text{OC}_6\text{F}_5)(\text{PMe}_3)_2$ (**5**). Conditions: cat. 1.0 μmol (**4**) or 0.30 μmol (**5**), NBE 8.48 mmol in benzene, initial NBE concentration 0.22 mmol/mL at 25 $^\circ\text{C}$.^[25]

CHPE using $V(\text{CHSiMe}_3)(\text{N-2,6-Cl}_2\text{C}_6\text{H}_3)(\text{OC}_6\text{F}_5)(\text{PMe}_3)_2$ (**6**), $V(\text{CHSiMe}_3)(\text{NR})(\text{OC}_6\text{Cl}_5)(\text{PMe}_3)_2$ [$\text{R} = 2,6\text{-Cl}_2\text{C}_6\text{H}_3$ (**8**), $2,6\text{-F}_2\text{C}_6\text{H}_3$ (**9**)].^[27] As described above, the activity was affected by the ligand substituents, and it increased in ROMP of CPE in the order (TOF after 5 min): **9** (2240 min^{-1}) < **6** (3460 min^{-1}) < **8** (5840 min^{-1}). The M_n value in the resultant polymers prepared by **9** increased upon increasing the polymer yields with low PDI values ($M_w/M_n = 1.16\text{--}1.24$), and the similar trend was observed in the ROMP by **6**, although the molecular weight distributions were rather broad.^[27] In contrast, the resultant polymers prepared by **8** after 1 min possessed ultrahigh molecular weights with broad molecular weight distributions, and the M_n values decreased after 5 min with broadening of the molecular weight distributions; the polymer yield (TON) did not increase after 10 min. The results thus suggest that certain degree of intramolecular chain transfer or backbiting, in which the active vanadium-alkylidene species containing polymer chain reacted with a double bond, occurred leading decrease in the M_n values.^[27]

It turned out that the OC_6Cl_5 analogue (**8**) showed higher activity than the OC_6F_5 analogue (**6**) in the ROMP of CHPE. As shown in Fig. 2, the M_n value in the resultant polymer prepared by **8** increased upon increasing the polymer yields (TON) consistent with rather low PDI (M_w/M_n) values, clearly suggesting that the ROMPs proceeded without chain transfer or termination (in a living manner). The observed facts by **8** are in unique contrast to those displayed by the ROMP of CPE, in which certain degree of chain transfer (backbiting) was observed. The polymer yields by 2,6-difluorophenyl-imido (**9**) and 2,6-dimethylphenylimido analogues were, however, negligible.^[27]

Table 2 ROMP of cyclopentene (CPE) and cycloheptene (CHPE) using $V(\text{CHSiMe}_3)(\text{N-2,6-Cl}_2\text{C}_6\text{H}_3)(\text{OC}_6\text{F}_5)(\text{PMe}_3)_2$ (**6**) or $V(\text{CHSiMe}_3)(\text{NR})(\text{OC}_6\text{Cl}_5)(\text{PMe}_3)_2$ [$\text{R} = 2,6\text{-Cl}_2\text{C}_6\text{H}_3$ (**8**), $2,6\text{-F}_2\text{C}_6\text{H}_3$ (**9**)]^a ^[27]

Cyclic olefin	Cat. (μmol)	CPE ^b (mol/L)	Time (min)	TON ^c	TOF ^d (min^{-1} (s^{-1}))	$M_n \times 10^{-4}$ ^e	M_w/M_n ^e
CPE	6 (0.1)	2.08	5	1.73×10^4	3460 (57.7)	44.8	1.65
CPE	6 (0.1)	2.08	10	2.13×10^4	2130 (35.5)	51.3	1.47
CPE	6 (0.1)	2.08	15	2.51×10^4	1670 (27.8)	55.2	1.52
CPE	8 (0.1)	2.08	1	1.47×10^4	1.47×10^4 (245)	149	1.70
CPE	8 (0.1)	2.08	5	2.92×10^4	5840 (97.3)	149	1.69
CPE	8 (0.1)	2.08	10	3.26×10^4	3260 (54.3)	129	1.87
CPE	8 (0.1)	2.08	15	3.42×10^4	2280 (38.0)	98.9	1.89
CPE	9 (0.1)	2.08	1	4700	4700 (78.3)	45.3	1.24
CPE	9 (0.1)	2.08	5	1.12×10^4	2240 (37.3)	63.5	1.23
CPE	9 (0.1)	2.08	10	1.38×10^4	1380 (23.0)	66.9	1.20
CPE	9 (0.1)	2.08	15	1.40×10^4	933 (15.6)	73.6	1.16
CHPE	6 (1.0)	2.08	5	759	152 (2.53)	21.2	1.37
CHPE	6 (1.0)	2.08	10	1330	133 (2.22)	35.3	1.40
CHPE	6 (1.0)	2.08	15	1730	115 (1.92)	40.0	1.59
CHPE	8 (1.0)	2.08	5	1340	268 (4.47)	31.6	1.55
CHPE	8 (1.0)	2.08	10	2100	210 (3.50)	56.3	1.54
CHPE	8 (1.0)	1.04	1	530	530 (8.83)	14.6	1.11
CHPE	8 (1.0)	1.04	5	613	123 (2.05)	16.4	1.12
CHPE	8 (1.0)	1.04	10	1200	120 (2.00)	42.9	1.31
CHPE	8 (1.0)	1.04	15	1660	111 (1.85)	65.3	1.29
CHPE	8 (1.0)	1.04	20	1780	89.0 (1.48)	80.0	1.38
CHPE	9 (1.0)	1.04	30	510	17.0 (0.28)	17.2	1.55

^a Conditions: CPE or CHPE 10.0 mmol (initial conc. 2.08 mol/L) or 5.0 mmol (initial conc. 1.04 mol/L), CPE or CHPE + benzene total 4.8 mL; ^b Initial CPE or CHPE conc. in mmol/mL (mol/L); ^c TON (turnover) = CPE or CHPE reacted (mmol)/vanadium (mmol); ^d TOF = TON/time; ^e GPC data in THF versus polystyrene standards

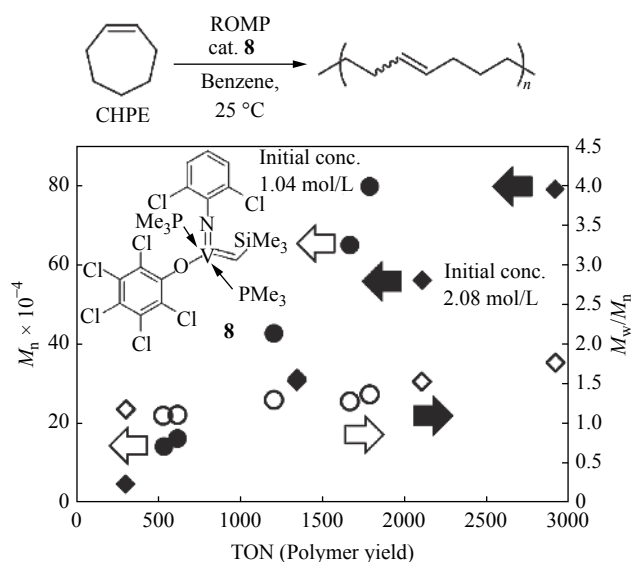


Fig. 2 Plots of M_n and M_w/M_n versus TON (polymer yield) in ROMP of CHPE using $V(\text{CHSiMe}_3)(\text{N}-2,6\text{-Cl}_2\text{C}_6\text{H}_3)(\text{OC}_6\text{Cl}_5)(\text{PMe}_3)_2$ (**8**). Conditions: cat. 1.0 μmol (**8**), 10.0 mmol (initial conc. 2.08 mol/L) or 5.0 mmol (initial conc. 1.04 mol/L) in benzene at 25 °C^[27]

Table 3 summarizes the results in ROMP of *cis*-cyclooctene (COE) using the OC_6F_5 analogue (**6**) or the OC_6Cl_5 analogue (**8**) in benzene under high COE initial concentration conditions (5.59 mol/L, COE 10.0 mmol and benzene 0.5 mL).^[26,27,38] The polymer yield in the ROMP by **6** increased over time course and the activity increased at high temperature (25–80 °C), but the activities at 100 °C were

lower than those conducted at 80 °C.^[26,27,38] Moreover, the M_n value in the resultant polymer increased over time course even at 50–80 °C (and 100 °C) without significant changes in the PDI (M_w/M_n) values.

It turned out that **8** led to higher activity than **6**; the observed activities became high when these ROMPs by **8** were conducted under low catalyst concentrations. The activity by **8** further increased at 100 °C, whereas the activity by **6** decreased. The initial activities by **8** at 120 °C seemed lower than that conducted at 100 °C probably due to the catalyst decomposition, but the activity at 120 °C after 5 min improved upon presence of small amount of PMe_3 .

Fig. 3 shows plots of M_n values with polymer yields (TON) in the ROMP of COE by **8**. A linear relationship between the polymer yields (TON) and the M_n values was demonstrated without significant changes in the PDI (M_w/M_n) values till the relatively high COE conversion (ca. 50%).^[27] The results thus clearly demonstrate the high temperature ROMP of COE by **8** proceeded at 80 °C without catalyst decomposition or chain transfer. As far as we know, this is a very rare demonstration of high temperature (quasi) living ROMP using transition metal catalysts.^[27]

Facile *in Situ* Generation of Highly Active ROMP Catalysts by Immediate Phenoxy Ligand Exchange

Study on the synthesis and reaction chemistry of vanadium (V)-alkylidenes has been recognized as an important fundamental subject in organometallic chemistry and catalysis.^[9,10] On the basis of observed rapid phenoxy exchanges in the dialkyl complexes, $V(\text{NAr})(\text{CH}_2\text{SiMe}_3)_2(\text{OAr})$ ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) and $V(\text{NAr})(\text{CH}_2\text{SiMe}_3)(\text{OAr})_2$,^[39] and the alkyl-

Table 3 ROMP of *cis*-cyclooctene (COE) using $V(\text{CHSiMe}_3)(\text{N}-2,6\text{-Cl}_2\text{C}_6\text{H}_3)(\text{OC}_6\text{X}_5)(\text{PMe}_3)_2$ [$\text{X} = \text{F}$ (**6**), Cl (**8**)]^a ^[26,27,38]

Cat. (μmol)	Temp (°C)	Time (min)	TON ^b	TOF ^c ($\text{min}^{-1} (\text{h}^{-1})$)	$M_n^d \times 10^{-3}$	M_w/M_n^d
6 (20)	25	30	45	1.5 (90)	10.5	1.34
6 (20)	25	120	132	1.1 (66)	27.0	1.59
6 (10)	50	5	47	9.4 (564)	19.3	1.51
6 (10)	50	10	110	11.0 (660)	32.0	1.59
6 (10)	50	15	160	10.7 (640)	41.9	1.60
6 (10)	80	5	164	32.8 (1970)	52.0	1.46
6 (10)	80	10	259	25.9 (1550)	62.1	1.64
6 (10)	100	5	118	23.6 (1420)	42.2	1.60
6 (10)	100	10	140	14.0 (840)	54.6	1.36
8 (20)	25	120	147	1.2 (74)	47.8	1.61
8 (20)	25	360	290	0.8 (73)	71.2	1.54
8 (20)	50	1	83	83.0 (4980)	5.8	1.45
8 (20)	50	5	169	33.8 (2030)	28.2	1.51
8 (1.0)	25	10	390	39.0 (2340)		
8 (1.0)	25	30	799	26.6 (1600)	9.50	1.15
8 (1.0)	50	5	889	178 (1.07×10^4)	55.4	1.45
8 (1.0)	50	10	1660	166 (9960)	80.3	1.47
8 (1.0)	50	15	1920	128 (7690)	90.1	1.49
8 (1.0)	80	2	1060	531 (3.19×10^4)	126	1.18
8 (1.0)	80	5	2490	497 (2.98×10^4)	226	1.24
8 (1.0)	100	5	2770	554 (3.32×10^4)	126	1.59
8 (1.0)	100	10	6450	645 (3.87×10^4)	509	1.32
8 (1.0)	120	2	2030	1020 (6.09×10^4)	44.4	1.55
8 (1.0)	120	5	2400	480 (2.88×10^4)	113	1.57
8 (1.0) ^e	120	5	2900	580 (3.48×10^4)	126	1.60

^a Conditions: COE 10.0 mmol, benzene 0.5 mL; ^b TON (turnover) = COE reacted (mmol)/vanadium (mmol); ^c TOF = TON/time; ^d GPC data in THF versus polystyrene standards (g/mol); ^e Addition of PMe_3 (3.0 equiv.)

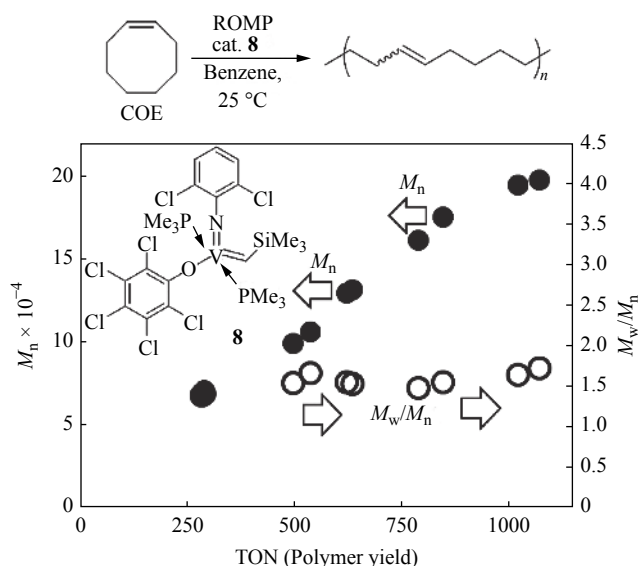


Fig. 3 Plots of M_n and M_w/M_n versus TON (polymer yield) in ROMP of COE using $V(\text{CHSiMe}_3)(\text{N}-2,6\text{-Cl}_2\text{C}_6\text{H}_3)(\text{OC}_6\text{Cl}_5)(\text{PMe}_3)_2$ (**8**). Conditions: cat. 5.0 μmol (**8**), COE 10.0 mmol (initial conc. 2.08 mol/L) in benzene at 80 $^\circ\text{C}$ [27]

dene complex, $V(\text{CHSiMe}_3)(\text{NAd})(\text{OAr})(\text{PMe}_3)_2$ [40] with 1.0 equiv. of $\text{C}_6\text{F}_5\text{OH}$ in C_6D_6 at 25 $^\circ\text{C}$, it was assumed that the highly reactive alkylidene catalysts for the efficient ROMP of cyclic olefins would be generated *in situ* from a rather stable (and could be isolable) alkylidene upon addition of $\text{C}_6\text{F}_5\text{OH}$ (or $\text{C}_6\text{Cl}_5\text{OH}$) *via* rapid phenoxy ligand exchange (Scheme 3). [41]

Table 4 summarizes the results in ROMPs of NBE conducted in benzene at 25 $^\circ\text{C}$ by introducing a catalyst solution, which was prepared in advance by premixing $V(\text{CHSiMe}_3)(\text{NC}_6\text{F}_5)(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{PMe}_3)_2$ (**10**), isolated and identified, with 1.0 equiv. of ArOH in benzene for 1 min.

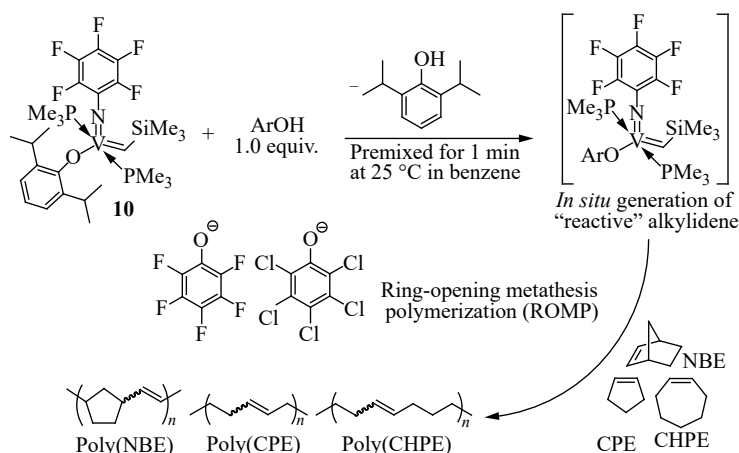
It should be noted that the ROMP by **10** completed within 1 min (even with low catalyst loading, 0.10 μmol) upon addition of 1.0 equiv. of $\text{C}_6\text{F}_5\text{OH}$ ($\text{TOF} > 4.24 \times 10^4 \text{ min}^{-1}$). The activity (TOF) with $\text{C}_6\text{F}_5\text{OH}$ under a low catalyst loading (0.05 μmol) was 770 s^{-1} ($4.62 \times 10^4 \text{ min}^{-1}$), one of the highest values in ROMPs using the reported vanadium(V)-

alkylidenes. [9,10,23–27] The activity was highly affected by the nature of phenol premixed with **10**, and increased in the order: none ($\text{TOF} = 155 \text{ min}^{-1}$) $\ll$ $2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{OH}$ ($\text{TOF} = 1.22 \times 10^4 \text{ min}^{-1}$) $<$ $\text{C}_6\text{Cl}_5\text{OH}$ ($\text{TOF} = 3.00 \times 10^4 \text{ min}^{-1}$) $<$ $\text{C}_6\text{F}_5\text{OH}$ ($\text{TOF} = 4.62 \times 10^4 \text{ min}^{-1}$). [41] This is a similar trend to that in the ROMPs using $V(\text{CHSiMe}_3)(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)(\text{OAr}')$ ($\text{Ar}' = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$, $2,6\text{-F}_2\text{C}_6\text{H}_3$, C_6F_5), [25] in which an introduction of electron withdrawing group into the phenoxide ligand enhances the activity. The polymer yields increased over time course without remarkable changes in the TOF values, suggesting that the ROMP proceeded without significant catalyst deactivation. [41]

It should also be noteworthy that the activity in ROMPs of CPE increased upon addition of $\text{C}_6\text{F}_5\text{OH}$ or $\text{C}_6\text{Cl}_5\text{OH}$, and the resultant polymers possessed high molecular weights with unimodal molecular weight distributions ($M_n = 2.69 \times 10^5$ – 6.60×10^5 , $M_w/M_n = 1.66$ – 2.19). [41] Moreover, similar trend was observed in ROMP of CHPE, and the resultant polymers possessed ultrahigh molecular weights with unimodal molecular weight distributions ($M_n = 2.01 \times 10^5$ – 10.84×10^5 , $M_w/M_n = 1.66$ – 2.38). [41]

CONCLUSIONS

In this feature article, effects of both imido and phenoxide ligands in the (imido)vanadium(V)-alkylidene complexes of type $V(\text{CHSiMe}_3)(\text{NR})(\text{OR}')(\text{PMe}_3)_2$ [$\text{R} = \text{Ad}$, C_6H_5 , $2,6\text{-Me}_2\text{C}_6\text{H}_3$, $2,6\text{-Cl}_2\text{C}_6\text{H}_3$; $\text{R}' = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, $2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$, $2,6\text{-F}_2\text{C}_6\text{H}_3$, C_6F_5 , C_6Cl_5] toward the catalytic activities for ring-opening metathesis polymerization (ROMP) of cyclic olefins have been summarized. $V(\text{CHSiMe}_3)(\text{N}-2,6\text{-Cl}_2\text{C}_6\text{H}_3)(\text{OC}_6\text{F}_5)(\text{PMe}_3)_2$ (**6**) exhibited the highest catalytic activity for ROMP of norbornene (NBE). In contrast, the activities in the ROMP of cyclopentene (CPE), cycloheptene (CHPE), and *cis*-cyclooctene (COE) by $V(\text{CHSiMe}_3)(\text{N}-2,6\text{-Cl}_2\text{C}_6\text{H}_3)(\text{OC}_6\text{Cl}_5)(\text{PMe}_3)_2$ (**8**) were higher than those by the OC_6F_5 analogue (**6**). The order in the activity in ROMP of cyclic olefins displayed as $\text{COE} \ll \text{CHPE} < \text{CPE} \ll \text{NBE}$, which is different not only from that in the ring strain energy, [28] but also from that reported in the ROMPs using ruthenium-carbene catalysts. [29,30] As far as we know, this is the first



Scheme 3 ROMP of cyclic olefins by the vanadium(V)-alkylidene generated *in situ* from $V(\text{CHSiMe}_3)(\text{NC}_6\text{F}_5)(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{PMe}_3)_2$ (**10**) upon addition of 1.0 equiv. of ArOH ($\text{C}_6\text{F}_5\text{OH}$, $\text{C}_6\text{Cl}_5\text{OH}$) [41]

Table 4 ROMP of NBE, CPE, and CHPE by vanadium-alkylidenes formed *in situ* from V(CHSiMe₃)(NC₆F₅)(O-2,6-*i*-Pr₂C₆H₃)(PMe₃)₂ (**10**) upon addition of 1.0 equiv. of ArOH ^a

Cyclic olefin	Cat. (μmol)	Phenol	Time (min)	TON ^b	TOF ^c (min ⁻¹ (s ⁻¹))	M _n ^d × 10 ⁻⁵	M _w /M _n ^d
NBE	10 (2.0)	–	10	1550	155 (2.6)	11.2	2.04
NBE	10 (0.10)	C ₆ F ₅ OH	1	> 4.24 × 10 ⁴ ^e	> 4.24 × 10 ⁴ (> 706)	Insoluble	
NBE	10 (0.05)	C ₆ F ₅ OH	1	4.62 × 10 ⁴	4.62 × 10 ⁴ (770)	Insoluble	
NBE	10 (0.10)	C ₆ Cl ₅ OH	1	3.00 × 10 ⁴	3.00 × 10 ⁴ (499)	Insoluble	
NBE	6 (0.10)	–	2	2.06 × 10 ⁴ ^e	1.03 × 10 ⁴ (172)	10.4	1.31
NBE	8 (0.10)	–	2	1.66 × 10 ⁴	8300 (138)	12.8	1.57
NBE	10 (0.10)	2,6-Cl ₂ C ₆ H ₃ OH	1	1.22 × 10 ⁴	1.22 × 10 ⁴ (204)	Insoluble	
NBE	10 (0.10)	2,6-Cl ₂ C ₆ H ₃ OH	3	3.17 × 10 ⁴	1.06 × 10 ⁴ (176)	Insoluble	
CPE	10 (1.0)	–	1.5	5220	3480 (58)	5.11	2.19
CPE	10 (0.50)	C ₆ F ₅ OH	1	1.05 × 10 ⁴	1.05 × 10 ⁴ (175)	6.60	2.14
CPE	10 (0.10)	C ₆ F ₅ OH	1	1.77 × 10 ⁴	1.77 × 10 ⁴ (295)	2.69	1.66
CPE	10 (0.50)	C ₆ Cl ₅ OH	1	1.39 × 10 ⁴	1.39 × 10 ⁴ (232)	Insoluble	
CHPE	10 (3.0)	–	10	373	37.3	1.31	1.51
CHPE	10 (0.20)	C ₆ F ₅ OH	5	1620	325	2.01	2.01
CHPE	10 (0.50)	C ₆ F ₅ OH	5	1370	274	4.09	1.71
CHPE	10 (0.20)	C ₆ F ₅ OH	10	3990	399	4.33	1.66
CHPE	10 (0.20)	C ₆ F ₅ OH	20	4940	247	10.84	2.01
CHPE	10 (0.50)	C ₆ Cl ₅ OH	10	4240	424		

^a Reaction conditions: NBE 4.24 mmol in benzene 9.6 mL (initial conc. 0.44 mol/L) or CPE mmol in benzene 0.5 mL (initial conc. 7.06 mol/L) or CHPE 10.0 mmol in benzene 1.0 mL (initial conc. 4.61 mol/L), 25 °C. The catalyst solution was prepared *in situ* by premixing **10** with 1.0 equiv. of ArOH for 1 min at 25 °C (0.10 mmol/mL V, 200 r/min); ^b TON (turnovers) = monomer reacted (mmol)/vanadium complex (mmol); ^c TOF (min⁻¹) = TON/time; ^d GPC data in THF versus polystyrene standards; ^e Conversion > 98%

comprehensive demonstration of ROMP of (so called) low strain cyclic olefins with early transition metal-alkylidene, and these alkylidene catalysts are capable of polymerizing these monomers efficiently.

It should be noteworthy that the activity in the ROMP of COE increased at high temperature till 120 °C, and the ROMPs of CHPE and COE proceeded without chain-transfer or termination (nor catalyst decomposition); the (quasi) living nature was thus maintained even at 80 °C. As far as we know, these are also the very rare examples for high temperature living ROMP of cyclic olefins, demonstrated by ROMP of COE.

Highly efficient ROMP catalysts can be generated *in situ* by premixing V(CHSiMe₃)(NC₆F₅)(O-2,6-*i*-Pr₂C₆H₃)(PMe₃)₂ (**10**) with 1.0 equiv. of C₆F₅OH or C₆Cl₅OH *via* immediate phenoxy exchange. The present methodology should be applicable not only to *in situ* generation of highly active catalysts that are difficult to isolate, but also to the simplified catalyst screening from the isolable vanadium(V)-alkylidenes.

Through this feature article, we highly believe that a promising potential of vanadium(V)-alkylidene complexes has been demonstrated, and the organometallic chemistry including the catalyst development will be more fruitful in the near future.

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