

(Arylimido)vanadium(V)–Alkylidene Complexes Containing Fluorinated Aryloxo and Alkoxo Ligands for Fast Living Ring-Opening Metathesis Polymerization (ROMP) and Highly *Cis*-Specific ROMP

Xiaohua Hou and Kotohiro Nomura*

Department of Chemistry, Faculty of Science and Engineering, Tokyo Metropolitan University, 1-1 minami Osawa, Hachioji, Tokyo 192-0397, Japan

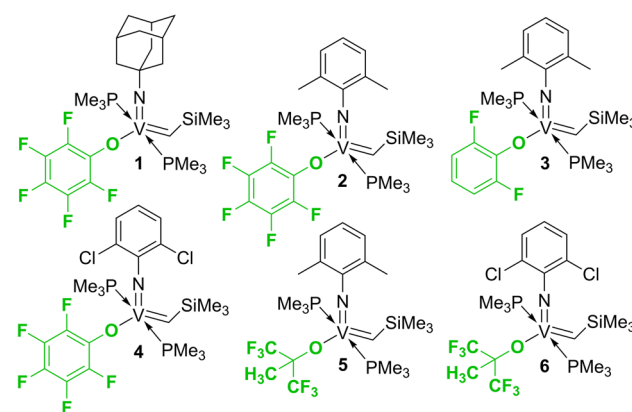
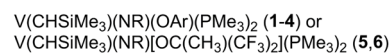
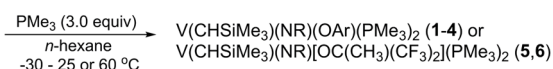
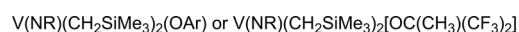
S Supporting Information

ABSTRACT: (Arylimido)vanadium(V)–alkylidene complexes, $V(\text{CHSiMe}_3)(N\text{-}2,6\text{-X}_2\text{C}_6\text{H}_3)(\text{OC}_6\text{F}_5)(\text{PMe}_3)_2$ [$X = \text{Me}$ (2), Cl (4)], exhibited remarkable catalytic activities for ring-opening metathesis polymerization (ROMP) of norbornene, and the ROMP by 2 proceeded in a living manner, affording ultrahigh molecular weight polymers. *Cis*-specific ROMP was achieved with the alkoxo analogues, $V(\text{CHSiMe}_3)(N\text{-}2,6\text{-X}_2\text{C}_6\text{H}_3)[\text{OC}(\text{CH}_3)(\text{CF}_3)_2](\text{PMe}_3)_2$ [$X = \text{Me}$ (5), Cl (6)]. Both the activity and the selectivity increased upon addition of PMe_3 , even at 50 °C.

High-oxidation-state early transition metal alkylidene complexes attract considerable attention^{1,2} because they play essential roles as catalysts in olefin metathesis, which is known as one of the most efficient carbon–carbon bond formation methods in the synthesis of organic compounds, polymers, and advanced materials,^{1–4} as demonstrated especially by molybdenum.^{1,2a,b,e,3a,c} Due to promising characteristics (notable reactivity toward olefins, etc.) demonstrated by classical Ziegler-type vanadium catalyst systems,⁵ the synthesis and reaction chemistry of vanadium–alkylidene complexes is thus considered to be of fundamental importance as well as having potential in catalysis.^{1d,2f,5d,6} We herein present that (arylimido)vanadium(V)–alkylidene complexes containing fluorinated aryloxo ligands are remarkably active for living ring-opening metathesis polymerization (ROMP) of norbornene (NBE); the activity can be tuned by ligand modification.⁷ We also demonstrate an efficient *cis*-specific ROMP, especially by $V(\text{CHSiMe}_3)(N\text{-}2,6\text{-Cl}_2\text{C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2](\text{PMe}_3)_2$.

$V(\text{CHSiMe}_3)(N\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)(\text{OAr})(\text{PMe}_3)_2$ [$\text{Ar} = \text{C}_6\text{F}_5$ (2), 2,6- $\text{F}_2\text{C}_6\text{H}_3$ (3), Scheme 1] in addition to $V(\text{CHSiMe}_3)(\text{NAd})(\text{OC}_6\text{F}_5)(\text{PMe}_3)_2$ (1)^{6e} have been chosen in this study, on the basis of our preliminary results in the ROMP of NBE using a series of dialkyl complexes in the presence of PMe_3 .⁸ The dichlorophenylimido analogue (4) has also been chosen, because $V(N\text{-}2,6\text{-Cl}_2\text{C}_6\text{H}_3)\text{Cl}_2(O\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)$ showed higher catalytic activity than $V(N\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2(O\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)$ for copolymerization of ethylene with NBE in the presence of Et_2AlCl .⁹ The fluorinated alkoxo analogues, $V(\text{CHSiMe}_3)(\text{NAr}')[\text{OC}(\text{CH}_3)(\text{CF}_3)_2](\text{PMe}_3)_2$ [$\text{Ar}' = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (5),

Scheme 1. Synthesis of (Imido)vanadium(V)–Alkylidene Complexes Containing Fluorinated Aryloxo/Alkoxo Ligands



2,6- $\text{Cl}_2\text{C}_6\text{H}_3$ (6)], were also prepared for comparison, not only because we reported synthesis of the dialkyl analogue, $V(N\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{SiMe}_3)_2[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]$ ^{6b} but also because the related molybdenum–alkylidene complexes, such as $\text{Mo}(\text{CHCMe}_2\text{Ph})(N\text{-}2,6\text{-Me}_2\text{C}_6\text{H}_3)[\text{OC}(\text{CH}_3)(\text{CF}_3)_2]_2$, exhibit higher activity than the *O*^tBu analogue.^{1b,c,2b,e} These complexes (2–6) were prepared from the corresponding dialkyl analogues by α -hydrogen elimination in the presence of PMe_3 (excess 3.0 equiv) in *n*-hexane (Scheme 1) and were identified by NMR spectroscopy and elemental analysis.¹⁰

Complexes (2–4) present as a mixture of *syn/anti* forms (observed as two broad resonances ascribed to protons in the vanadium–alkylidene especially in the ¹H NMR spectra),¹⁰ as observed in 1, and the ratios did not change upon addition of PMe_3 . In contrast, one resonance (and additional tiny resonance) ascribed to proton in the alkylidene was observed in 5 and 6.¹⁰ Moreover, their ¹H and ³¹P VT-NMR spectra suggest that there is fast equilibrium between coordination and dissociation in solution, as demonstrated by $V(\text{CHSiMe}_3)$ -

Received: February 27, 2015

Published: March 27, 2015

Table 1. Ring-Opening Metathesis Polymerization of Norbornene by 1–6^a

run	cat. (μmol)	temp/ $^{\circ}\text{C}$	time/min	TON ^b	TOF/h ⁻¹	$M_n^c \times 10^{-4}$	M_w/M_n^c	<i>cis</i> ^d /%
1	1 (0.5)	25	5	4110 ^e	49300	51.9	1.36	39
2	1 (0.3)	25	3	4950	99000	79.8	1.15	
3	2 (0.5)	25	5	4150 ^e	49800	92.0	1.41	47
4	2 (0.3)	25	1	5650	339000	117	1.22	
5	2 (0.3) ^f	25	3	6930 ^e	138000	129	1.40	
6	2 (0.1)	25	3	11500	230000	164	1.18	
7	3 (0.5)	25	5	3300	39600	59	1.41	53
8	3 (0.3)	25	3	3820	76300	122	1.08	
9	4 (0.1)	25	3	21200 ^e	424000	110	1.27	45
10	5 (5.0) ^f	-20	60	108	108	6.4	1.49	96
11	5 (5.0) ^g	25	20	337	1010	80.0	1.29	85
						7.0	1.20	
12	6 (1.0) ^f	-20	20	445	1340	27.4	1.38	96
13	6 (1.0)	25	20	1000	3000	52.5	1.38	92
14	6 (1.0) + PMe_3 (3.0)	25	20	2090 ^e	6270	95.0	1.15	97
15	6 (1.0) + PMe_3 (33.0)	50	10	2120 ^e	12700	83.0	1.37	96
16	6 (0.5) + PMe_3 (33.0)	80	5	3920	47000	54.6	1.36	86

^aReaction conditions: NBE 200 mg, 2.12 mmol; initial NBE concn, 0.44 mmol/mL. ^bTON (turnovers) = NBE reacted (mmol)/V (mmol); TOF = TON/time. ^cGPC data in THF vs polystyrene standards. ^dCis percentage (%) estimated by ¹H NMR spectra. ^eConversion of NBE >98%. ^fIn toluene. ^gTwo peaks were observed on GPC trace.

(NAd)(CH₂SiMe₃)(PMe₃)₂,^{6f} resonances in the NMR spectrum in 1–4 were broad but became rather sharp at low temperature.¹⁰ Moreover, resonance ascribed to proton in PMe_3 was not observed in the spectra of 5 and 6 at 25 $^{\circ}\text{C}$, but clearly observed below -20 $^{\circ}\text{C}$.¹⁰ These results also suggest the presence of above-mentioned fast equilibrium.

As can be seen in Table 1 (runs 1–9), the aryloxo analogues 1–4 showed remarkable catalytic activities for ROMP of NBE, and the activity under the optimized conditions increased in the order TOF (h⁻¹) = 76 300 (3) < 99 000 (1) < 339 000 (2) < 424 000 (4). It is thus clear that the activity can be tuned by modification of arylimido/aryloxo ligands. In particular, ROMP by 4 reached completion after 3 min, even under low catalyst concentration conditions (run 9, TON > 21 200), and the observed activities were much higher than those known for Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)(O^tBu)₂ (TOF = 8090 h⁻¹);^{6e} the activity by 4 is rather higher than that of known active catalyst Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)[OCMe(CF₃)₂]₂ (TON = 17 300 after 3 min, under the same conditions as for run 9).¹¹ The resultant polymers possessed high molecular weights with relatively narrow molecular weight distributions when the ROMPs were terminated before completion (runs 2, 4, 6, 8).

As exemplified in Figure 1, a good linear correlation between turnover number (TON, polymer yield on the basis of V) and M_n value along with low polydispersity index (M_w/M_n) values (after certain period, ca. 5 min) was observed in the ROMP of NBE by 2.¹¹ Similar trends were observed in the ROMP of NBE by 1 and 3 (complex 0.3–1.5 μmol , under similar conditions).^{11,12} Moreover, the reaction rate is first order with the NBE concentration, since a linear relationship between $\ln[\text{NBE}]_t/[\text{NBE}]_0$ and the polymerization time was observed (where $[\text{NBE}]_0$ and $[\text{NBE}]_t$ are the NBE concentrations initially and at a certain time, respectively).¹¹ These facts strongly suggest a possibility of living polymerization without deactivation in this catalysis, affording ultrahigh molecular

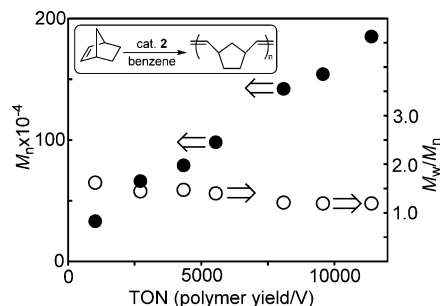


Figure 1. Plots of M_n vs turnover numbers (TON) in ROMP of NBE by 2. Conditions: 2, 0.30 μmol ; NBE, 8.48 mmol in benzene; NBE, 0.22 mmol/mL at 25 $^{\circ}\text{C}$.

weight ring-opened polymers with narrow molecular weights distributions (ex. $M_n = 1\,850\,000$, $M_w/M_n = 1.19$ for 2).¹¹ As far as we know, examples for the fast living ROMP affording ultrahigh molecular weight polymers have been limited and this is thus one of the unique characteristics in this catalysis.

In contrast, the activity by the alkoxo analogue by 5 was lower than those by the aryloxo analogues 1–4, affording polymers with bimodal molecular weight distribution (run 11). The molecular weight distribution, however, became unimodal when the ROMP was conducted at -20 $^{\circ}\text{C}$ in toluene (run 10).¹³ The activity improved by the dichlorophenylimido analogue (6), and the resultant polymer possessed unimodal molecular weight distribution, even if the ROMP was conducted at 25 $^{\circ}\text{C}$ (run 13).

It should be noted that the olefinic double bonds in the resultant polymers prepared by 5 and 6 at 25 $^{\circ}\text{C}$ possess high *cis* selectivity (92% by 6, run 13, Figure 2b), whereas the resultant polymers prepared by 1–4 possess a mixture of *cis/trans* olefinic double bonds (run 3, Figure 2a), confirmed by ¹H and ¹³C NMR spectra.¹¹ In particular, *cis* selectivity in the resultant polymers prepared at -20 $^{\circ}\text{C}$ in toluene reached 96% (runs 10, 12). Note that the activity by 6 increased upon addition

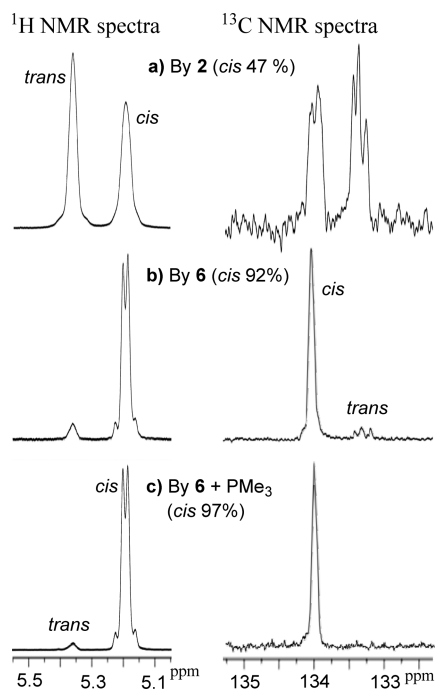
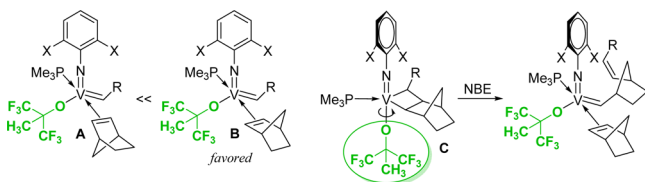


Figure 2. NMR spectra of poly(NBE) prepared from (a) **2** (run 3), (b) **6** (run 13), and (c) **6** + PMe_3 (run 14). Detailed polymerization conditions and data are shown in Table 1.

of PMe_3 with increasing the *cis* selectivity in the resultant ROMP polymer (92 \rightarrow 97%, run 13 vs run 14), whereas the activity by **2** significantly decreased upon addition of PMe_3 [TON = 1210 by **2** after 3 min under the same conditions in run 4 (TON = 5650 after 1 min) upon addition of 0.1 equiv of PMe_3].¹¹ Importantly, the activity in the presence of PMe_3 (excess) increased at 50 °C with the same level of *cis* selectivity (runs 15, 96%); **6** exhibited notable activity even at 80 °C, affording polymer with high *cis* selectivity (run 16, 86%). Although examples of *cis*-specific ROMP (olefin metathesis) catalysts^{14–16} have been shown recently by molybdenum¹⁴ and ruthenium,¹⁵ as far as we know, this is one of the most active catalysts with promising thermal stability (because most of *cis* specific ROMP were conducted at room temperature). We also confirmed that the ROMP by **6** at 25 °C proceeded in a living manner without deactivation (as observed with **1–3**).¹¹

On the basis of the above polymerization results with **5** and **6** (increase in *cis* selectivity upon addition of PMe_3 or low temperature) and the fact that fast coordination/dissociation exchange was seen in complexes **1–6**, especially evident in the ³¹P and ¹H NMR spectra (where the resonance became rather sharp at low temperatures),¹⁰ we thus speculate that coordination of NBE for subsequent metathesis (formation of metallacyclobutane intermediate **C** in Scheme 2) would be

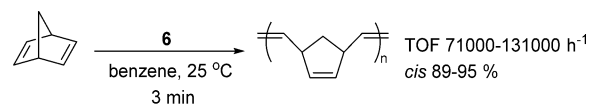
Scheme 2. Plausible Scheme for Highly *Cis*-Specific ROMP by **6** in the Presence of PMe_3



controlled in this catalysis; NBE would coordinate to *V trans* (opposite) to PMe_3 , and high *cis* selectivity would be thus achieved due to a proposed intermediate (due to a steric bulk of small arylimido and large alkoxy ligands). Although one resonance corresponding to an olefinic double bond was observed in the ¹³C NMR spectrum (Figure 2c), we speculate that the resultant polymer possesses a rather syndiotactic rich stereoregularity on the basis of glass transition temperature (T_g) determined from the DSC thermogram (67 °C) and ¹³C NMR spectrum of the polymer sample after hydrogenation.¹⁷

Complexes **1** and **2** were also effective for ROMP of NBE derivatives such as vinylnorbornene and ethylidene-2-norbornene, affording polymers with uniform molecular weight distributions.^{11,16} Moreover, importantly, **6** showed remarkable activity for ROMP of norbornadiene (NBD), affording the ring-opened polymer with high *cis* selectivity (87–95%, TOF = 52 100–131 000 h⁻¹, Scheme 3); the activity also increased

Scheme 3. *Cis*-Specific ROMP of Norbornadiene by **6**



upon addition of PMe_3 .¹¹ These facts thus clearly demonstrate that the present catalyst **6** is effective for *cis*-specific ROMP of these strained cyclic olefins.

We have herein demonstrated highly active (living) ROMP catalysts (**2**, **4**) and *cis*-specific ROMP catalysts (**5**, **6**) that can be tuned by ligand modification in (imido)vanadium(V)-alkylidene complexes. A unique increase in the activity upon addition of PMe_3 at higher temperature was observed in **6**. The results here should present and emphasize promising characteristics that are different from those of ROMP catalysts with ruthenium and molybdenum. We are exploring additional details, including scope and limitations of this catalysis.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details for the synthesis of (arylimido)vanadium(V)-alkylidene complexes **2–6**, along with NMR spectra (measured at various temperatures upon addition of PMe_3), additional polymerization results, selected ¹H and ¹³C NMR spectra for poly(NBE) and poly(NBD), and DSC thermogram for poly(NBE). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*ktnomura@tmu.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was partly supported by a Grant-in-Aid for Scientific Research on Innovative Areas (“3D Active-Site Science”, No. 26105003) from The Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. X.H. acknowledges the Tokyo Metropolitan government (Asian Human Resources Fund) for a predoctoral fellowship. The authors express their thanks to Profs. S. Komiya, A. Inagaki, and K. Tsutsumi (Tokyo Metropolitan University) for discussions.

K.N. also thanks Prof. D. Mendiola (University of Pennsylvania) for helpful comments, and Dr. S. Hayano (Nippon Zeon Co.) for analysis of poly(NBE) samples and comments.

REFERENCES

- (1) For examples, see: (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (b) Schrock, R. R. In *Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Springer: Berlin, Germany, 1998; p 1. (c) Schrock, R. R. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 1, p 8. (d) Pietraszuk, C. In *Olefin Metathesis: Theory and Practice*; Grela, K., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2014; p 371. (e) Schrock, R. R. *Acc. Chem. Res.* **2014**, *47*, 2457.
- (2) For examples, see: (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (c) Mendiola, D. *Acc. Chem. Res.* **2006**, *39*, 813. (d) Mendiola, D.; Bailey, B.; Basuli, F. *Eur. J. Inorg. Chem.* **2006**, *16*, 3135. (e) Schrock, R. R. *Chem. Rev.* **2009**, *109*, 3211. (f) Nomura, K.; Zhang, W. *Chem. Sci.* **2010**, *1*, 161.
- (3) (a) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012. (b) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (c) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592. (d) Samojzowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev.* **2009**, *109*, 3708. (e) Vougioukalakis, G.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746.
- (4) Examples for metathesis polymerization, see: (a) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565. (b) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003; Vol. 3. (c) Buchmeiser, M., Eds. *Metathesis Polymerization*; Springer-Verlag: Berlin/Heidelberg, Germany, 2005. (d) Nomura, K.; Abdellatif, M. M. *Polymer* **2010**, *51*, 1861. (e) Leitgeb, A.; Wappel, J.; Slugovc, C. *Polymer* **2010**, *51*, 2927. (f) Buchmeiser, M. R. *Macromol. Symp.* **2010**, *298*, 17. (g) Mutlu, H.; de Espinosa, L. M.; Meier, M. A. R. *Chem. Soc. Rev.* **2011**, *40*, 1404. (h) Atallah, P.; Wagener, K. B.; Schulz, M. D. *Macromolecules* **2013**, *46*, 4735. (i) Schulz, M. D.; Wagener, K. B. *Macromol. Chem. Phys.* **2014**, *215*, 1936.
- (5) Related reviews for olefin polymerization catalysts including vanadium complexes: (a) Gambarotta, S. *Coord. Chem. Rev.* **2003**, *237*, 229. (b) Hagen, H.; Boersma, J.; van Koten, G. *Chem. Soc. Rev.* **2002**, *31*, 357. (c) Redshaw, C. *Dalton Trans.* **2010**, *39*, 5595. (d) Nomura, K.; Zhang, S. *Chem. Rev.* **2011**, *111*, 2342 and related references cited therein.
- (6) (a) Yamada, J.; Nomura, K. *Organometallics* **2005**, *24*, 2248. (b) Nomura, K.; Onishi, Y.; Fujiki, M.; Yamada, J. *Organometallics* **2008**, *27*, 3818. (c) Zhang, W.; Nomura, K. *Organometallics* **2008**, *27*, 6400. (d) Zhang, S.; Tamm, M.; Nomura, K. *Organometallics* **2011**, *30*, 2712. (e) Nomura, K.; Suzuki, K.; Katao, S.; Matsumoto, Y. *Organometallics* **2012**, *31*, 5114. (f) Hatagami, K.; Nomura, K. *Organometallics* **2014**, *33*, 6585. (g) Nomura, K.; Bahuleyan, B. K.; Tsutsumi, K.; Igarashi, A. *Organometallics* **2014**, *33*, 6682.
- (7) Part of these data (especially using 1–3) were presented at the International Symposium on Catalysis and Fine Chemicals, Beijing, China, December, 2013, and International Conference on Organometallic Chemistry, Sapporo, Japan, July, 2014.
- (8) Suzuki, K.; Matsumoto, Y.; Nomura, K. *J. Organomet. Chem.* **2011**, *696*, 4057.
- (9) Diteepeng, N.; Tang, X.; Hou, X.; Li, Y.-S.; Phomphrai, K.; Nomura, K. *Dalton Trans.* **2015**, DOI: 10.1039/c4dt04026k.
- (10) Typical synthetic procedures for synthesis of 2–6, and their NMR spectral data including the measurement at various temperatures (upon addition of PMe_3), are shown in the Supporting Information.
- (11) Additional polymerization data for the resultant polymers in the ROMP of NBE, vinyl-NBE, ethylidene-2-NBE, and NBD, and selected ^1H and ^{13}C NMR spectra for poly(NBE) and poly(NBD), are shown in the Supporting Information.
- (12) At this moment, it seems difficult to explore the time course in the ROMP by 4 because of exceptionally remarkable activity; an optimization of conditions (including setup of conditions with further removal of impurities) is under investigation.
- (13) We assume that there are two catalytically active species (one or two PMe_3 dissociated species) for explanation of these facts (NMR data and ROMP data upon addition of PMe_3) shown in this text and the Supporting Information.
- (14) (a) Ibrahim, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844. (b) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962. (c) Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16630. (d) Torker, S.; Müller, A.; Chen, P. *Angew. Chem., Int. Ed.* **2010**, *49*, 3762. (e) Flook, M. M.; Gerber, L. C. H.; Debelouchina, G. T.; Schrock, R. R. *Macromolecules* **2010**, *43*, 7515. (f) Flook, M. M.; Ng, V. W. L.; Schrock, R. R. *J. Am. Chem. Soc.* **2011**, *132*, 1784. (g) Marinescu, S. C.; Schrock, R. R.; Müller, P.; Takase, M. K.; Hoveyda, A. H. *Organometallics* **2011**, *30*, 1780. (h) Meek, S. J.; O'Brien, R. V.; Llaveria, J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, *471*, 461.
- (15) (a) Endo, K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 8525. (b) Keitz, B. K.; Endo, K.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 9686. (c) Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 693. (d) Keitz, B. K.; Fedorov, A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 2040. (e) Marx, V. M.; Herbert, M. B.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 94. (f) Rosebrugh, L. E.; Herbert, M. B.; Marx, V. M.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 1276. (g) Occhipinti, G.; Hansen, F. R.; Törnroos, K. W.; Jensen, V. R. *J. Am. Chem. Soc.* **2013**, *135*, 3331. (h) Cannon, J. S.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2013**, *52*, 9001. (i) Khan, R. K. M.; Torker, S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2013**, *135*, 10258. (j) Hartung, J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 10183. (k) Khan, R. K. M.; Torker, S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2014**, *136*, 14337. (l) Koh, M. J.; Khan, R. K. M.; Torker, S.; Yu, M.; Mikus, M. S.; Hoveyda, A. H. *Nature* **2015**, *517*, 181.
- (16) (a) Gottumukkala, A. L.; Madduri, A. V. R.; Minnaard, A. J. *ChemCatChem* **2012**, *4*, 462. (b) Shahane, S.; Bruneau, C.; Fischmeister, C. *ChemCatChem* **2013**, *5*, 3436.
- (17) We acknowledge Dr. S. Hayano (Nippon Zeon Co.) for NMR analysis of our typical poly(NBE) for comparison of samples with different tacticity. Although the resultant polymer after hydrogenation was poorly soluble in CDCl_3 , two resonances were observed. On the basis of the spectra and DSC thermograms (T_g), we assumed that the polymer resulting from 6 is syndiotactic-rich. Control of the tacticity should be our next goal. For stimulation of tacticity in the hydrogenated poly(NBE), see: Hayano, S.; Nakama, Y. *Macromolecules* **2014**, *47*, 7797.