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【論文の内容の要旨】

Olefin metathesis is one of the most important methods in carbon-carbon bond formation in organic synthesis as well as polymer synthesis. High-oxidation-state early transition metal alkylidene complexes attract considerable attention,¹⁻³ because they play essential roles as catalysts in olefin metathesis, which has been known as one of the most efficient carbon-carbon bond formation methods in synthesis of organic compounds, polymers, and advanced materials, as demonstrated especially by molybdenum. Since classical Ziegler type vanadium catalyst systems [$\text{VOCl}_3 - \text{Et}_2\text{AlCl}$ etc.] demonstrate unique characteristics (notable reactivity toward olefins),³ design of the vanadium complex catalysts, especially chemistry of the alkylidene complexes thus attracts considerable attention in terms not only of better catalyst design, but also of better understanding in organometallic chemistry.³ Synthesis and reaction chemistry of (imido)- vanadium(V)-alkylidene complexes,⁴⁻⁶ reported examples so far,³⁻⁶ have been considered of fundamental importance and of their promising applications in catalysis. On the basis of these backgrounds, in this thesis, (i) synthesis of a series of (imido)vanadium(V)- alkylidene complexes containing fluorinated aryloxo or alkoxo ligand, (ii) ligand effect in ring-opening metathesis polymerization (ROMP) of norbornene, and (iii) controlled synthesis of ring-opened polymers by olefin metathesis,^{7,8} have been studied.

Results and Discussion

1. Synthesis of (imido)vanadium(V)-alkylidene complexes containing fluorinated aryloxo, alkoxo ligands.

A series of (imido)vanadium(V)-alkylidene complexes, $V(\text{CHSiMe}_3)(\text{NR})(\text{OAr})(\text{PMe}_3)_2$ [$\text{Ar} = \text{C}_6\text{F}_5$, $\text{R} = 1\text{-adamantyl (Ad, 1)}$, $2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**2**), $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ (**5**), $2,6\text{-Cl}_2\text{C}_6\text{H}_3$ (**6**); $\text{Ar} = 2,6\text{-F}_2\text{C}_6\text{H}_3$, $\text{R} = \text{Ad}$ (**3**), $2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**4**)] or $V(\text{CHSiMe}_3)(\text{NR})(\text{OR}')(\text{PMe}_3)_2$ [$\text{R}' = \text{OCH}(\text{CF}_3)_2$, $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**7**); $\text{R}' = \text{OC}(\text{CH}_3)(\text{CF}_3)_2$, $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**8**), $2,6\text{-Cl}_2\text{C}_6\text{H}_3$ (**9**)],⁸ were prepared according to our published procedure for synthesis of $V(\text{CHSiMe}_3)(\text{NAd})(\text{OC}_6\text{F}_5)(\text{PMe}_3)_2$ (**1**),^{3a,5} from the (imido)vanadium(V)-dialkyl analogues by α -hydrogen elimination in the presence of PMe_3 in *n*-hexane. The resultant complexes (**2-9**) were purified by recrystallization and were identified by ^1H , ^{51}V , ^{19}F , ^{31}P , ^{13}C NMR spectra, elemental analysis; structure of **7** was determined by X-ray crystallography. The $2,6\text{-Cl}_2\text{C}_6\text{H}_3$ analogue were chosen, because $V(\text{N-}2,6\text{-Cl}_2\text{C}_6\text{H}_3)\text{Cl}_2(\text{OAr}')$ ($\text{Ar}' = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) showed higher activity than $V(\text{N-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2(\text{OAr}')$ for ethylene/norbornene copolymerization in the presence of Et_2AlCl .⁷

Most of these alkylidene complexes were found to exist as a mixture of *syn/anti* isomers which could be proved especially by the ^1H NMR spectra (observed as two broad resonances ascribed to protons in the vanadium-alkylidene), 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 **8-9**. Moreover, their ^1H and ^{31}P VT-NMR spectra suggest that there is fast equilibrium between coordination and dissociation in solution, as demonstrated by **1**; resonances in the NMR spectrum in the OC_6F_5 analogues (**1,2,5,6**) were broad but became rather sharp at low temperature. Moreover, resonance ascribed to proton in PMe_3 was not observed in the spectra of **8,9** at $25\text{ }^\circ\text{C}$, but clearly observed below $-20\text{ }^\circ\text{C}$. These results also suggest the presence of above mentioned fast equilibrium.

2. Ligand effect in ring-opening metathesis polymerization (ROMP) of norbornene.

Ring-opening metathesis polymerization (ROMP) of norbornene (NBE) using the alkylidene complexes containing electron withdrawing group in the aryloxo or alkoxo ligands (**1-9**). Note that the C_6F_5 (**1,2,5,6**) analogues showed the remarkable activities; the activities by the arylimido analogues were higher than those by the adamantylimido analogues. The activity increased in the order: $\text{Ar} = \text{Ad}$ (**1**) < $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ (**5**) < $2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**2**), < $2,6\text{-Cl}_2\text{C}_6\text{H}_3$ (**6**). The dichloro-phenylimido analogue (**6**) showed the highest activity, suggesting that an introduction of electron withdrawing substituent enhances reactivity of the alkylidene. The resultant polymers possessed high molecular weights ($M_n = 1.10\text{-}1.17 \times 10^6$) with low PDI (M_w/M_n) values (1.1-1.4). In contrast, the alkoxide analogues (**7-9**) showed rather low activities. It seems likely that the introduction of steric bulk leads to decrease in the activity (**8** < **7**); the activity by **9** was higher than **8**. Note that the activity by **9** increased upon addition of PMe_3 ,

whereas addition of PMe_3 led to decrease in the activity by **2**.

The resultant polymers were ring-opened structure confirmed by ^1H , ^{13}C NMR spectra. The olefinic double bonds in the polymers prepared by the aryloxo analogues (**1-6**) were a mixture of *cis* and *trans*. Importantly, the ROMP polymers prepared by the alkoxo analogues (**7,8,9**) possessed highly *cis* selectivity in the olefinic double bond, and the activity by **9** increased upon addition of PMe_3 with increasing the *cis* selectivity in the resultant ROMP polymer (92→97%), whereas the activity by **2** significantly decreased upon addition of PMe_3 . Importantly, the activity by **9** in the presence of PMe_3 (excess) increased at 50 °C with the same level of *cis* selectivity (96 %); **9** exhibited notable activity even at 80 °C affording polymer with high *cis* selectivity (86%). High *cis* specificity by **9** was also confirmed in the ROMP of norbornadiene.

Taking into account these results, it is postulated that coordination of NBE for subsequent metathesis (formation of metallocyclobutane intermediate) would be controlled in this catalysis (Scheme 2); 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 alkoxo ligands).

3. Controlled synthesis of ring-opened polymers by olefin metathesis.

It turned out that ROMP of NBE by **2** proceeded in a living manner; the M_n value increased linearly upon increasing the polymer yields (TON) with low PDI (M_w/M_n) values. The similar results were obtained in the ROMP using the aryloxo (**1-6**), alkoxo (**7-9**) analogues under optimized conditions. Moreover, a linear relationship was observed between $\ln([\text{NBE}]_t/[\text{NBE}]_0)$ and reaction time, indicating that the polymerization is first order reaction to NBE concentration and no obvious deactivation was observed under these conditions. It also turned out that these alkylidenes also showed high activity toward other NBE derivatives such as 5-vinyl-2-norbornene (VNBE) and 5-ethylidene-2-norbornene (ENBE). Molecular weights in the resultant polymers were lower than those in poly(norbornene)s (PNBE) and molecular weight distributions become rather wide. These alkylidenes are also highly active toward NBD, and the perfect stereoregularity (*cis*, *syndiotactic*, almost 100%) has been achieved by the alkoxide analogues (**9**) for the first time.

Conclusions

Through this study, a series of vanadium(V)-alkylidene complexes have been isolated and identified. These complexes are highly active for ring-opening metathesis polymerization (ROMP) of norbornene (NBE) mostly in a living manner, affording high molecular weight polymers and narrow molecular weight distributions. Remarkably high *cis* selectivity of olefinic double bonds in the ring-opened polymers has been achieved by the fluorinated alkoxide alkylidenes; the observed activities are higher than those by molybdenum, ruthenium catalysts

reported for this purpose. These alkylidenes can be used for ROMP of various NBE derivatives.

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