# Ethylene Polymerization and Ring-Opening Metathesis Polymerization of Norbornene Catalyzed by (Arylimido)(aryloxy)vanadium(V) Complexes of the Type,V(NAr)(OAr')$X_2$ (X = Cl, $CH_2Ph$)

Kotohiro Nomura,* Asami Sagara, and Yukio Imanishi
*Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST),*
*8916-5 Takayama, Ikoma, Nara 630-0101*

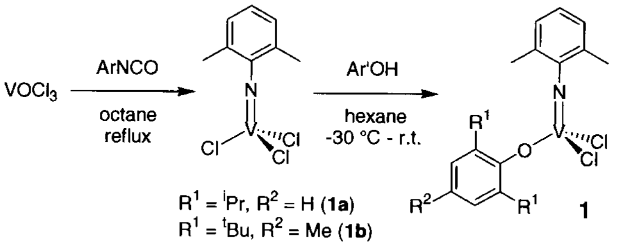
(Received October 11, 2000; CL-000924)

$VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ - methylaluminoxane catalyst has exhibited remarkable catalytic activity for ethylene polymerization. High molecular weight ring-opened poly(norbornene) has been prepared in the presence of $V(CH_2Ph)_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$.

---

Olefin polymerization by homogeneous transition metal catalysis attracts particular attention not only in the field of organometallic chemistry, but also in the field of polymer chemistry.[1] Although a lot of examples have been well-known concerning the effective catalysts with group 4B transition metal catalysts, examples with vanadium complexes have been limited[2,3] despite the fact that classical Ziegler–Natta vanadium catalyst systems have displayed a number of interesting characteristics[4] such as synthesis of high molecular weight polymers with narrow polydispersity,[5] synthesis of ethylene/α-olefin copolymer with high α-olefin content,[6] and others.[7] We thus decided to extend our chemistry to find a new-type of vanadium catalyst for olefin polymerization.

We focused (arylimido)vanadium(V) complex as the starting compounds, because synthesis of vanadium complexes with various arylimido ligand have already been established by several researchers,[8] and also because this ligand moiety should be relatively stable at high temperature.[8c] Moreover, we also focused to synthesize 14e vanadium(V) complex which should be the same electron number of our original half-metallocene type titanium catalyst.[9] In this paper, we wish to introduce our preliminary results concerning olefin polymerization by (arylimido)(aryloxy)vanadium(V) complexes.



**Scheme 1.**

(Arylimido)(aryloxy)vanadium complexes of the type, $VCl_2(NAr)(OAr')$ [NAr = $N\text{-}2,6\text{-}Me_2C_6H_3$, OAr' = $O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (**1a**), $O\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}MeC_6H_2$ (**1b**)] have been prepared in high yields from $VCl_3(NAr)$ by treating with 1 equivalent of the corresponding phenol in hexane (Scheme 1).[10] These complexes have also been prepared by adding the corresponding lithium phenoxide in $Et_2O$. The products isolated were deep purple microcrystals, and could be identified by $^1H$, $^{13}C$ NMR and repeated elemental analysis runs.[10]

Importantly, $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1a**) exhibited significant catalytic activity for ethylene polymerization in the presence of d-MAO (methylaluminoxane, white solid) which was prepared by removing toluene and excess amount of $AlMe_3$ from commercially available MAO (PMAO-S, Tosoh Akzo Co.), and the activity increased at higher reaction temperature (runs 1–3, Table 1). In addition, the resultant polymer was linear, which was confirmed by NMR spectroscopy, and has exceptionally high molecular weight with unimodal molecular weight distribution, and the polymerization results were reproducible under these conditions. The lower activity was observed if MMAO was used as cocatalyast in place of d-MAO. The activity by **1b** was lower than that by **1a**, suggesting that the steric bulk of the aryloxy ligand affects the

**Table 1.** Ethylene Polymerization Catalyzed by **1** - Cocatalyst System[a]

| Run No. | Catalyst (μmol) | Cocatalyst (Al/V)[b] | Temp. / °C | Yield / mg | Activity[c] | $M_w$[d] / x$10^{-4}$ | $M_w/M_n$[d] |
|---|---|---|---|---|---|---|---|
| 1 | **1a** (5.0) | d-MAO (1000) | 0 | 480 | 576 | 609 | 2.61 |
| 2 | **1a** (5.0) | d-MAO (1000) | 0 | 449 | 539 | 600 | 2.69 |
| 3 | **1a** (5.0) | d-MAO (1000) | 25 | 802 | 962 | 292 | 2.88 |
| 4 | **1a** (5.0) | MMAO (1000)[e] | 25 | 173 | 208 | | |
| 5 | **1b** (5.0) | d-MAO (1000) | 25 | 202 | 242 | | |
| 6 | **1b** (2.0) | d-MAO (2500) | 60 | 162 | 486 | 78.4 | 2.07 |

[a]Reaction Conditions: toluene (30 mL), ethylene 8 atm, 10 min, 100 mL scale autoclave, d-MAO (prepared by removing $AlMe_3$ and toluene from commercially available MAO). [b]Molar ratio of Al/V. [c]Activity = kg-PE/mol-V·h. [d]GPC data in *o*-dichlorobenzene vs polystyrene standard. [e]*n*-Hexane was used in place of toluene, and MMAO (methyl isobutyl aluminoxane) was used in place of MAO.

activity. We assume that the reason for the higher activity than those previously reported using a series of (arylimido)vanadium(V) complexes[2b,c] would be due to the low coordinate (14e) vanadium species as the starting catalyst precursor.

Attempt to isolate dibenzyl complex from **1a** by treating with $\mathrm{PhCH_2MgCl}$ was not successful, probably due to the difficulty for isolating from the reaction mixture. However, the desired complex $\mathrm{V(CH_2Ph)_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)}$ (**2**) could be synthesized from its tribenzyl analogue, $\mathrm{V(CH_2Ph)_3(N\text{-}2,6\text{-}Me_2C_6H_3)}$,[11] by treating with 1 equivalent of $\mathrm{2,6\text{-}{}^iPr_2C_6H_3OH}$ in $\mathrm{CH_2Cl_2}$.[12]

It should be noted that ring-opened poly(norbornene) could be isolated if norbornene and **2** were dissolved in toluene.[13] This is, as far as we know, the first example of the ring-opening metathesis polymerization (ROMP) initiated by the vanadium complex without cocatalyst. Moreover, this is also the rare example affording exceptionally high molecular weight polymer with unimodal molecular weight distribution ($M_\mathrm{w} = 4.69 \times 10^6$, $M_\mathrm{w}/M_\mathrm{n} = 1.93$).[14] Since the polymerization would proceed via metathesis mechanism, we assume that the vanadium-alkylidene complex would be the active species in this catalysis.[15]

We are now exploring the effect of substituents for the activity in ethylene polymerization, and attempting isolation of vanadium–alkylidene complex which should be the proposed active species for the ROMP. These results will be introduced in the future.

**References and Notes**

1 For example (Review), a) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, **34**, 1143 (1995). b) W. Kaminsky, *Macromol. Chem. Phys.*, **197**, 3903 (1996). c) W. Kaminsky and M. Arndt, *Adv. Polym. Sci.*, **127**, 143 (1997). d) J. Suhm, J. Heinemann, C. Wörner, P. Müller, F. Stricker, J. Kressler, J. Okuda, and R. Mülhaupt, *Macromol. Symp.*, **129**, 1 (1998). e) A. L. McKnight and R.M. Waymouth, *Chem. Rev.*, **98**, 2587 (1998). f) G. J. P. Britovsek, V. C. Gibson, and D. F. Wass, *Angew. Chem. Int. Ed.*, **38**, 429 (1999).

2 a) F. J. Feher and R. L. Blanski, *Organometallics*, **12**, 958 (1993). b) S. Scheuner, J. Fischer, and J. Kress, *Organometallics*, **14**, 2627 (2995). c) M. P. Coles and V. C. Gibson, *Polym. Bull.*, **33**, 529 (1994). d) P. T. Witte, A. Meetsma, and B. Hessen, *Organometallics*, **18**, 2944 (1999). e) D. Ricardon, F. Conan, S. Gambarotta, G. Yap, and Q. Wang, *J. Am. Chem. Soc.*, **121**, 9318 (1999).

3 Catalytic activity for ethylene polymerization in the previous reports, 14 kg-PE/mol-V·h (ethylene 1 atm, in toluene, MAO cocatalyst, r.t. 105 min, $M_\mathrm{w} = 4.7 \times 10^4$, $M_\mathrm{w}/M_\mathrm{n} = 3.0$) by $\mathrm{Tp^{*}V(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2}$ [Tp* = hydrotris(3,5-dimethylpyrazolyl)borato],[2b] 27 kg-PE/mol-V·h (ethylene 1 atm, in toluene, MAO cocatalyst, 25 °C, 1 h) by $\mathrm{CpV(N\text{-}4\text{-}MeC_6H_4)Cl_2}$,[2c] 627 kg-PE/mol-V·h (ethylene 3 atm, in toluene, MAO cocatalyst, 50 °C, 30 min, $M_\mathrm{w} = 1.49 \times 10^4$, $M_\mathrm{w}/M_\mathrm{n} = 3.0$) by $\mathrm{[Et(C_5Me_4)(N^iPr)]VCl_2}$,[2d] 2243 kg-PE/mol-V·h (ethylene 6.8 atm, in toluene, MAO cocatalyst, 50 °C, 30 min, $M_\mathrm{w} = 17.42 \times 10^4$, $M_\mathrm{w}/M_\mathrm{n} = 50.79$) by $\mathrm{\{2,6\text{-}bis[2,6\text{-}({}^iPr)_2PhN{=}C(Me)]_2(C_5H_3N)\}VCl_3 \cdot 1.3(CH_2Cl_2)}$.[2e]

4 For example, H. Sinn and W. Kaminsky, in "Advances in Organometallic Chemistry," ed. by F. G. A. Stone and R. West, Academic Press, New York (1980), Vol. 18, p. 99.

5 For examples, a) W. L. Carrick, *J. Am. Chem. Soc.*, **80**, 6455 (1958). b) W. L. Carrick, R. W. Kluiber, E. F. Bonner, L. H. Wartman, F. M. Rugg, and J. J. Smith, *J. Am. Chem. Soc.*, **82**, 3883 (1960). c) D. L. Christman, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 471 (1972). d) M. H. Lehr and C. J. Carmen, *Macromolecules*, **2**, 217 (1969). e) E.W. Duck, D. Grant, J. R. Horder, D. K. Jenkins, A. E. Marlow, S. R. Wallis, A. G. Doughty, J. M. Marandon, and G. A. Skinner, *Eur. Polym. J.*, **10**, 481 (1974).

6 For example (synthesis of syndiotactic polypropylene), Y. Doi, N. Tokuhiro, M. Nunomura, H. Miyake, S. Suuki, and K. Soga, in "Transition Metals and Organometallic as Catalysts for Olefin Polymerization," ed. by W. Kaminsky and H. Sinn, Springer-Verlag, Berlin (1988), p. 379.

7 For example, A. Zambelli, A. Proto, and P. Longo, in "Ziegler Catalysts," ed. by G. Fink, R. Mulhaupt, and K. H. Brintzinger, Springer-Verlag, Berlin (1995), p. 217.

8 a) D. D. Devore, J. D. Lichtenhan, F. Takusagawa, and E. A. Maata, *J. Am. Chem. Soc.*, **109**, 7408 (1987). b) J. -K. F. Buijink, J. H. Teubin, H. Kooijman, and A. L. Spek, *Organometallics*, **13**, 2922 (1994). c) K. Nomura, R. R. Schrock, and W. M. Davis, *Inorg. Chem.*, **35**, 3695 (1996).

9 For example, a) K. Nomura, N. Naga, M. Miki, K. Yanagi, and A. Imai, *Organometallics*, **17**, 2152 (1998). b) K. Nomura, K. Oya, T. Komatsu, and Y. Imanishi, *Macromolecules*, **33**, 3187 (2000).

10 General experimental procedure for synthesis of **1a**: Into a *n*-hexane solution (30 mL) containing $\mathrm{V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_3}$ (1.30 g, 4.70 mmol), $\mathrm{2,6\text{-}{}^iPr_2C_6H_3OH}$ (838 mg, 4.70 mmol) was added dropwisely at –30 °C, and the reaction mixture was warmed slowly to room temperature, and then the mixture was stirred for 10 h. The solvent was removed in vacuo, and the resultant deep brown tan residue was layered by *n*-hexane (ca. 5 mL) at –30 °C. The chilled solution gave deep brown solid, which was washed quickly with small amount of cold hexane and dried in vacuo. Yield 1.82 g (93%). $^1$H NMR ($\mathrm{CDCl_3}$): δ 1.13 (d, 12H, $(\mathrm{C}H_3)_2\mathrm{CH}$–, $J$ = 6.8 Hz), 2.38 (s, 6H, $\mathrm{CH_3}$), 3.24 (m, 2H, $\mathrm{Me_2C}H$–), 6.82 (m, 3H), 7.10 (m, 3H) . $^{13}$C NMR ($\mathrm{CDCl_3}$): δ 18.3, 23.2, 27.1, 123.3, 126.2, 127.3, 129.6, 136.2, 138.9, 166.5. Anal. Calcd for $\mathrm{C_{20}H_{26}Cl_2NOV}$: C, 57.43; H, 6.27; N, 3.35. Found (1): C, 57.46; H, 6.42; N, 3.22%. Found (2): C, 57.42, H, 6.40, N, 3.28%. For **1b**, Yield 94%. $^1$H NMR ($\mathrm{CDCl_3}$): δ 0.97 (s, 18H), 1.93 (s, 3H), 2.07 (s, 6H), 6.42 (m, 3H), 6.64 (s, 1H), 6.82 (s, 1H). $^{13}$C NMR ($\mathrm{CDCl_3}$): δ 21.5, 22.7, 31.9, 35.5, 125.5, 126.0, 127.3, 129.9, 134.4, 139.0, 139.1, 168.6 . Anal. Calcd for $\mathrm{C_{23}H_{32}Cl_2NOV}$: C, 60.01; H, 7.01; N, 3.04%. Found(1): C, 59.86; H, 7.13; N, 2.80%. Found(2): C, 60.05; H, 7.24; N, 2.91%.

11 This complex was prepared according to the analogous procedure for synthesis of $\mathrm{V(CH_2Ph)_3(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)}$, V. J. Murphy and H. Turner, *Organometallics*, **16**, 2495 (1997).

12 Experimental procedure: Into a cold $\mathrm{CH_2Cl_2}$ solution (25 mL, –30 °C) of $\mathrm{V(CH_2Ph)(N\text{-}2,6\text{-}Me_2C_6H_3)}$ (1.0 g, 2.25 mmol), 2,6-diisopropylphenol was added in several portions and the mixture was stirred for 40 h at room temperature. The reaction mixture was filtered through Celite pad, and the solvent was removed in vacuo, and the resultant solid was dissolved in small amount of hexane. The chilled solution gave deep brown microcrystals. Yield 75%. For **2**, $^1$H NMR($\mathrm{CDCl_3}$): δ 1.32 (d, 12H), 2.97 (d, 10H), 3.20 (m, 2H), 7.23 (m, 16H). $^{13}$C NMR ($\mathrm{CDCl_3}$): δ 22.7, 27.1, 37.8, 37.9, 77.2, 120.6, 123.4, 125.9, 128.3, 128.4, 133.6, 141.8, 150.0.

13 Polymerization procedure: Into a round bottom flask (10 mL scale) containing norbornene (235 mg) dissolved in toluene (2.9 g), a toluene solution (1.0 g) containing **2** (13.2 mg, 25 μmol) was added in one portion at room temperature. The mixture was stirred for 11 h, and the solution was poured into methanol (200 mL). The resultant solid was collected by filtration and was washed with methanol, and was then dried in vacuo. Yield; 87 mg (37%). Molecular weight and molecular weight distribution were measured by GPC (Shimadzu SCL-10A with RID-10A detector, column: ShimPAC GPC-806, 804, and 802) in THF vs polystyrene standard. $^1$H NMR ($\mathrm{CDCl_3}$): δ 5.22 and 5.35 (br.m, 2H olefinic), 2.80 and 2.37 (br.s, 2H), 1.85 and 1.08 (m, 2H), 1.81 and 1.36 (m, 4H). $^{13}$C NMR ($\mathrm{CDCl_3}$): δ 134.0, 133.9, 133.8, 133.7, and 133.1, 133.0 and 132.8 (olefinic), 68.0, 50.8, 43.4, 43.2, 42.7, 42.1, 41.3, 38.6, 38.4, 33.1, 32.9, 32.3, 32.2, 25.6, 21.3.

14 Example concerning synthesis of high molecular weight ROMP polymers, Y. Nakayama, H. Saito, N. Ueyama, and A. Nakamura, *Organometallics*, **18**, 3149 (1999).

15 Previous report concerning synthesis of vanadium–alkylidene complex, see ref 8b.