

Article

Ethylene Polymerization Using (Imino)vanadium(V) Dichloride Complexes Containing (Anilido)methyl-pyridine, -quinoline Ligands—Halogenated Al Alkyls Catalyst Systems

Atsushi Igarashi ¹, Wenjuan Zhang ², Wen-Hua Sun ² and Kotohiro Nomura ^{1,*}

¹ Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, Japan; E-Mail: igarashi-atsushi@ed.tmu.ac.jp

² Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun, Beijing 100190, China; E-Mails: zhangwj@iccas.ac.cn (W.Z.); whsun@iccas.ac.cn (W.-H.S.)

* Author to whom correspondence should be addressed; E-Mail: ktnomura@tmu.ac.jp; Tel./Fax: +81-42-677-2547.

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Abstract: The effect of ligand and Al cocatalysts in ethylene polymerization, using V(*N*-1-adamantyl)Cl₂(L) [L = 2-(2,6-Me₂C₆H₃)NCH₂(C₉H₆N), 8-(2,6-Me₂C₆H₃)NCH₂(C₉H₆N)] and V(*N*-2-MeC₆H₃)Cl₂[2-(2,6-R'₂C₆H₃)NCH₂(C₅H₄N)] (R' = Me, ^{*i*}Pr), has been explored. The reaction products in the presence of Et₂AlCl or Me₂AlCl cocatalyst were polyethylene whereas the reaction product of the 2-methylphenylimido analogues in the presence of MAO cocatalyst was 1-butene with high selectivity, suggesting that the catalyst/cocatalyst nuclearity effect plays a role in this catalysis.

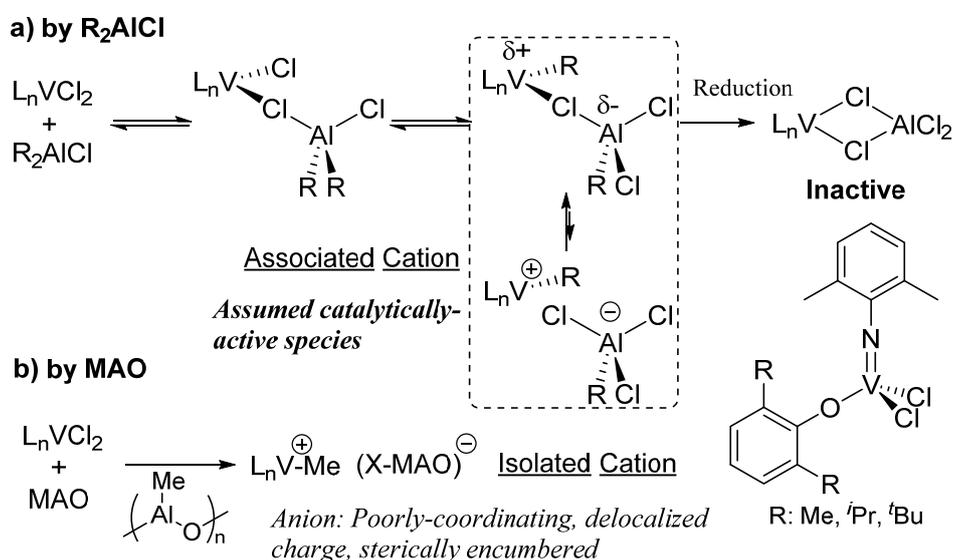
Keywords: ethylene; vanadium catalysts; polymerization; ligand effect

1. Introduction

Designing vanadium complex catalysts for olefin polymerization/oligomerization has been considered as a promising subjects, because the classical Ziegler-type catalyst systems [V(acac)₃, VOCl₃, *etc.* and Et₂AlCl, EtAlCl₂, ^{*n*}BuLi, *etc.*] display unique high reactivity toward olefins in olefin coordination/insertion polymerization [1–5]. We previously reported that (arylimido)vanadium(V) complexes, containing anionic donor ligands (L), V(*N*-2,6-Me₂C₆H₃)Cl₂(L) (L = aryloxo, ketimide, phenoxyimine *etc.*), exhibited remarkable catalytic activities for ethylene polymerization in the

presence of Al cocatalysts [3–10]. The activity by the aryloxo analogue was strongly affected by the Al cocatalyst; the activities in the presence of halogenated Al alkyls ($i\text{Bu}_2\text{AlCl}$, EtAlCl_2 , Me_2AlCl , Et_2AlCl) were higher than those in the presence of methylaluminoxane (MAO) [7,8]. Both the activity, and the norbornene incorporation, in the ethylene/norbornene copolymerization were also affected by the Al cocatalyst employed [7,8]. We thus speculated that a reason for the observed difference would be due to a formation of the different catalytically-active species, catalyst/cocatalyst nuclearity effect (assumed in Scheme 1) [5,11–13]. The activity decreased upon addition of $\text{CCl}_3\text{CO}_2\text{Et}$ (for example, [14]), which can be commonly used as effective additives to improve the catalyst stability [8], clearly suggesting that the active species were, thus, different from those prepared from vanadium(III), (IV) complexes [1–5,14].

Scheme 1. Proposed catalytically-active species formed by different Al cocatalysts.



More recently, we demonstrated that the (adamantylimido)vanadium(V) complexes containing (2-anilidomethyl)pyridine ligand, $\text{V}(\text{NAd})\text{Cl}_2[2\text{-ArNCH}_2(\text{C}_5\text{H}_4\text{N})]$ [Ad = 1-adamantyl; Ar = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (**1a**), 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ (**1b**)], efficiently dimerize ethylene with both notable catalytic activities, and high selectivity in the presence of MAO [15,16], whereas the reaction products by **1a,b** in the presence of Me_2AlCl or Et_2AlCl cocatalyst were ultrahigh molecular weight polyethylene (PE) (runs 1–5, Table 1) [16]. Moreover, we prepared the adamantylimido complexes containing 2- or 8-(anilidomethyl)-quinoline ligands, $\text{V}(\text{NAd})\text{Cl}_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCH}_2(\text{C}_9\text{H}_6\text{N})]$ (**2a,3a**, Scheme 2), and $\text{V}(N\text{-}2\text{-MeC}_6\text{H}_4)\text{Cl}_2[2\text{-ArNCH}_2(\text{C}_5\text{H}_4\text{N})]$ complexes (**4a,b**) and explored reactions with ethylene in the presence of MAO (Table 1) [17]: remarkable effect of the imido ligand toward the selectivity (oligomer, polymer) was observed in the presence of MAO (Table 1, runs 9–12), whereas the reaction products by the quinoline analogues were a mixture of PE and oligomers. Since the reaction products by **1a,b** in presence of Et_2AlCl or Me_2AlCl were PE, in this paper, we thus explored reactions with ethylene in the presence of halogenated Al alkyls to confirm our hypothesis outlined in Scheme 1, for example in ethylene polymerization by the other vanadium complex catalysts, [18–24].

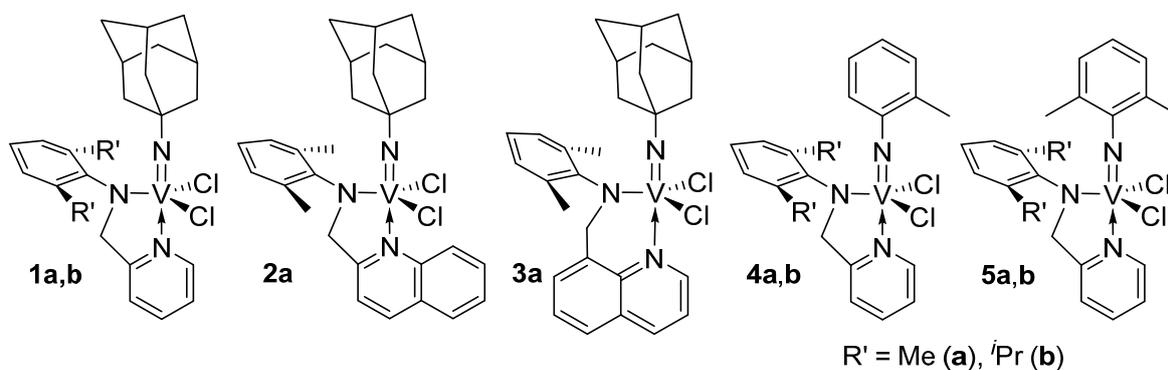
Table 1. Reaction of ethylene with $V(NR)Cl_2(L)$ [$R = Ad$, $L = 2-(2,6-R'_2C_6H_3)NCH_2(C_5H_4N)$ [$R' = Me$ (**1a**), iPr (**1b**)], $2-(2,6-Me_2C_6H_3)NCH_2(C_9H_6N)$ (**2a**), $8-(2,6-Me_2C_6H_3)NCH_2(C_9H_6N)$ (**3a**); $R = 2-MeC_6H_4$ (**4a,b**), $2,6-Me_2C_6H_3$ (**5a,b**), $L = 2-(2,6-R'_2C_6H_3)NCH_2(C_5H_4N)$]-MAO or R''_2AlCl ($R'' = Me, Et$) catalysts ^a.

| Run | V complex (μmol) | Al cocat. | Al/V ^b | C_4',C_6' | | | Polyethylene (PE) | | |
|-----|----------------------------------|------------|-------------------|-----------------------|------------------------|------------------------|-----------------------|--------------------|------------------------|
| | | | | Activity ^c | $C_4'/\%$ ^d | $C_6'/\%$ ^d | Activity ^e | M_w ^f | M_w/M_n ^f |
| 1 | 1a (0.2) ^g | MAO | 500 | 57800 | 96.8 | 3.2 | | | |
| 2 | 1a (0.1) ^g | MAO | 1500 | 76500 | 97.0 | 3.0 | | | |
| 3 | 1b (0.5) ^g | MAO | 1000 | 35700 | 92.1 | 7.9 | | | |
| 4 | 1a (5.0) ^h | Et_2AlCl | 100 | | | | 137 | 5.92 ⁱ | |
| 5 | 1a (5.0) ^h | Me_2AlCl | 200 | | | | 704 | 6.76 ⁱ | |
| 6 | 2a (5.0) ^j | MAO | 1000 | 43 | 71.6 | 28.4 | 53 | | |
| 7 | 3a (2.0) ^j | MAO | 1000 | 201 | 92.4 | 7.6 | 30 | | |
| 8 | 3a (2.0) ^j | MAO | 1500 | 249 | 92 | 8 | 45 | | |
| 9 | 4a (0.2) ^j | MAO | 600 | 50300 | 95.2 | 4.8 | | | |
| 10 | 4b (0.2) ^j | MAO | 700 | 41500 | 97.1 | 2.9 | | | |
| 11 | 5a (2.0) ^k | MAO | 3000 | | | | 78 | 2.98 | 2.0 |
| 12 | 5b (2.0) ^k | MAO | 3000 | | | | 189 | 2.93 | 2.6 |

^a Conditions: toluene 30 mL, ethylene 8 atm., 25 °C, 10 min MAO or R''_2AlCl ($R'' = Me, Et$). ^b Al/V molar ratio.

^c Activity in (kg of ethylene reacted)/mol-V·h. ^d Determined by GC analysis. ^e Activity in kg-PE/mol-V·h. ^f GPC data in *O*-dichlorobenzene versus polystyrene standards. ^g Data cited from reference [15]. ^h Data cited from reference [16] and 0 °C. ⁱ M_v value measured by viscosity. ^j Data cited from reference [17]. ^k Data cited from reference [10].

Scheme 2. List of complexes employed in this study.



2. Results and Discussion

2.1. Ethylene Polymerization Using $V(NAd)Cl_2[2-ArNCH_2(C_9H_6N)]$, $V(NAd)Cl_2[8-ArNCH_2(C_9H_6N)]$ - Me_2AlCl Catalyst Systems

Reactions of ethylene with $V(NAd)Cl_2[2-(2,6-Me_2C_6H_3)NCH_2(C_9H_6N)]$ (**2a**), $V(NAd)Cl_2[8-(2,6-Me_2C_6H_3)NCH_2(C_9H_6N)]$ (**3a**) in the presence of Me_2AlCl were conducted in toluene and the results are summarized in Table 2. The results with $V(NAd)Cl_2[2-(2,6-Me_2C_6H_3)NCH_2(C_5H_4N)]$ (**1a**) [16], are also shown for comparison. Me_2AlCl was chosen, because Me_2AlCl showed higher catalytic activity than Et_2AlCl in ethylene polymerization using **1a,b** [16].

It turned out that the quinoline analogues **2a,3a** showed the higher catalytic activities than the pyridine analogue (**1a**) especially under the optimized Al/V molar ratios: the activities were affected by the Al/V molar ratios. The reaction products were polyethylene that are insoluble in hot *O*-dichlorobenzene for measurement of their molecular weight(s) by GPC in the ordinary analysis procedure, suggesting formations of ultrahigh molecular weight polymers as observed previously [8,16,17]. The activity by **2a** showed higher than **3a**, probably due to a stability of catalytically active species (formed five membered ring around vanadium and L in **2a** vs. six membered ring in **3a**). The facts observed should be promising, because the reaction products were a mixture of PE and 1-butene (major) when the reactions by **2a,3a** were conducted in the presence of MAO. Moreover, the observed activities in the presence of Me₂AlCl were higher than those in the presence of MAO.

Table 2. Ethylene polymerization with V(NAd)Cl₂(L) [L = 2-ArNCH₂(C₅H₄N) (**1a**), 2-ArNCH₂(C₉H₆N) (**2a**), 8-ArNCH₂(C₉H₆N) (**3a**), Ar = 2,6-Me₂C₆H₃]-Me₂AlCl catalysts ^a.

| Run | Vanadium complex | | Al/V ^b | Yield /mg | Activity ^c |
|-----------------|---|-------|-------------------|--------------|-----------------------|
| | L (V cat.) | /μmol | | | |
| 5 ^d | 2-ArNCH ₂ (C ₅ H ₄ N) (1a) ^e | 0.5 | 200 | 58.7 | 704 |
| 13 ^d | 2-ArNCH ₂ (C ₅ H ₄ N) (1a) ^f | 1.0 | 500 | 116 | 696 |
| 14 | 2-ArNCH ₂ (C ₉ H ₆ N) (2a) | 0.2 | 2500 | 70.2 | 2110 |
| 15 | 2-ArNCH ₂ (C ₉ H ₆ N) (2a) | 0.2 | 5000 | 122 | 3670 |
| 16 | 2-ArNCH ₂ (C ₉ H ₆ N) (2a) | 0.2 | 7500 | 152 | 4560 |
| 17 | 2-ArNCH ₂ (C ₉ H ₆ N) (2a) | 0.2 | 10000 | 120 | 3600 |
| 18 | 8-ArNCH ₂ (C ₉ H ₆ N) (3a) | 0.2 | 1000 | 79.6 | 2390 |
| 19 | 8-ArNCH ₂ (C ₉ H ₆ N) (3a) | 0.2 | 2000 | 73.6 | 2210 |
| 20 | 8-ArNCH ₂ (C ₉ H ₆ N) (3a) | 0.2 | 5000 | 58.7 | 1760 |

^a Conditions: toluene 30 mL, ethylene 8 atm, 0 °C, 10 min. ^b Molar ratio of Al/V. ^c Activity in kg-PE/mol-V·h.; ^d Data cited from reference [16]. ^e *M_n* = 6.76 × 10⁶ measured by viscosity. ^f *M_n* = 8.96 × 10⁶ measured by viscosity.

2.2. Ethylene Polymerization Using V(N-2-MeC₆H₄)Cl₂[2-(2,6-R'₂C₆H₃)NCH₂(C₅H₄N)]-Halogenated Al Alkyls Catalyst Systems

We recently reported [17] that the 2-methylphenylimido analogues, V(N-2-MeC₆H₄)Cl₂[2-(2,6-R'₂C₆H₃)NCH₂(C₅H₄N)] [R' = Me (**4a**), ^{*i*}Pr (**4b**)], exhibited remarkable catalytic activities for ethylene dimerization in the presence of MAO [17], whereas the reaction by 2,6-dimethylphenylimido analogues (**5a,b**) afforded polyethylene (Table 1, runs 11–12) [10]. Since the reaction product by the adamantylimido analogues (**1a,b**) in the presence of halogenated Al alkyls (in place of MAO) afforded ultrahigh molecular weight polyethylene, we thus conducted the reaction with ethylene in the presence of Et₂AlCl, Me₂AlCl (Table 2). The results by the 2,6-dimethylphenylimido analogues (**5a,b**) [10] are also shown for comparison.

Although reaction with ethylene by **4a,b** afforded 1-butene exclusively in the presence of MAO, and the activities are similar to those by **1a,b**, the activities by **4a,b** in the presence of Me₂AlCl, Et₂AlCl were low in all cases. The reaction products were polyethylene that were insoluble in hot *O*-dichlorobenzene for measurement of their molecular weight(s) by GPC in the ordinary analysis procedure, suggesting formations of ultrahigh molecular weight polymers [8,16,17]. The activities were affected by the Al/V molar ratios employed, but the activities by **4a** showed higher than those by

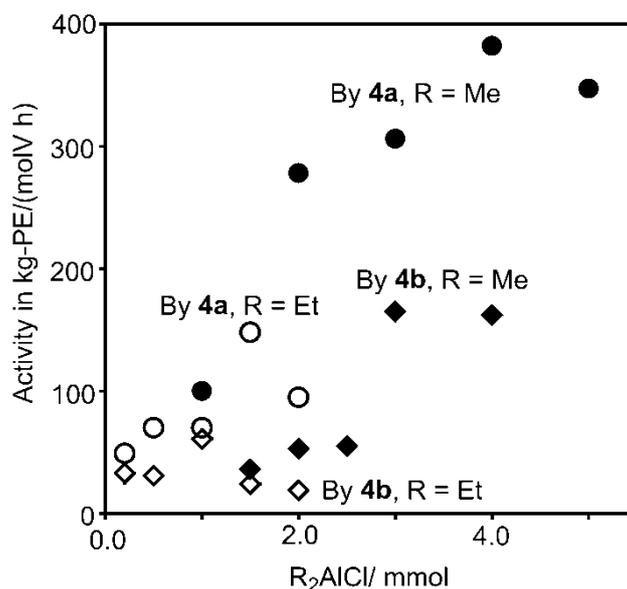
4b [ex. activity: 382 kg-PE/mol-V·h by **4a** (run 25) vs. 165 kg-PE/mol-V·h by **4b** (run 30)] and the activities in the presence of Me₂AlCl were higher than those in the presence of Et₂AlCl [ex. activity by **4a**: 382 kg-PE/mol-V·h (run 25, Me₂AlCl) vs. 148 kg-PE/mol-V·h (run 30)]. It also seems likely that the activities were affected by the amount Al employed rather than the Al/V molar ratios in this catalysis (Figure 1). Exclusive formation of polyethylene by **4a,b** should be noteworthy, because, as described above, these complexes afforded 1-butene exclusively in the reaction with ethylene in the presence of MAO [17].

Table 3. Reaction of ethylene with V(NR)Cl₂[2-ArNCH₂(C₅H₄N)] [R = 1-adamantyl (Ad, **1**), 2-MeC₆H₄ (**4**), 2,6-Me₂C₆H₃ (**5**): Ar = 2,6-Me₂C₆H₃ (**a**), 2,6-ⁱPr₂C₆H₃ (**b**)]–Me₂AlCl, Et₂AlCl catalysts ^a.

| Run | Vanadium complex | | Al cocat. (mmol) | Al/V ^b | Yield /mg | Activity ^c |
|-----------------|--|-------|-----------------------------|-------------------|--------------|-----------------------|
| | R (V cat.) | /μmol | | | | |
| 5 ^d | 1-adamantyl (1a) ^e | 0.5 | Me ₂ AlCl (0.10) | 200 | 58.7 | 704 |
| 13 ^d | 1-adamantyl (1a) ^f | 1.0 | Me ₂ AlCl (0.50) | 500 | 116 | 696 |
| 21 | 2-MeC ₆ H ₄ (4a) | 1.0 | Me ₂ AlCl (1.0) | 1000 | 16.7 | 100 |
| 22 | 2-MeC ₆ H ₄ (4a) | 1.0 | Me ₂ AlCl (2.0) | 2000 | 46.4 | 278 |
| 23 | 2-MeC ₆ H ₄ (4a) | 1.0 | Me ₂ AlCl (3.0) | 3000 | 51.0 | 306 |
| 25 | 2-MeC ₆ H ₄ (4a) | 1.0 | Me ₂ AlCl (4.0) | 4000 | 63.7 | 382 |
| 26 | 2-MeC ₆ H ₄ (4a) | 1.0 | Me ₂ AlCl (5.0) | 5000 | 57.8 | 347 |
| 27 | 2-MeC ₆ H ₄ (4b) | 2.0 | Me ₂ AlCl (1.5) | 750 | 11.9 | 36 |
| 28 | 2-MeC ₆ H ₄ (4b) | 2.0 | Me ₂ AlCl (2.0) | 1000 | 17.8 | 53 |
| 29 | 2-MeC ₆ H ₄ (4b) | 2.0 | Me ₂ AlCl (2.5) | 1250 | 18.2 | 55 |
| 30 | 2-MeC ₆ H ₄ (4b) | 2.0 | Me ₂ AlCl (3.0) | 1500 | 55.1 | 165 |
| 31 | 2-MeC ₆ H ₄ (4b) | 2.0 | Me ₂ AlCl (4.0) | 2000 | 54.1 | 162 |
| 32 | 2-MeC ₆ H ₄ (4a) | 1.0 | Et ₂ AlCl (0.20) | 200 | 8.1 | 49 |
| 33 | 2-MeC ₆ H ₄ (4a) | 1.0 | Et ₂ AlCl (0.50) | 500 | 11.7 | 70 |
| 34 | 2-MeC ₆ H ₄ (4a) | 1.0 | Et ₂ AlCl (1.0) | 1000 | 11.6 | 70 |
| 35 | 2-MeC ₆ H ₄ (4a) | 1.0 | Et ₂ AlCl (1.5) | 1500 | 24.6 | 148 |
| 36 | 2-MeC ₆ H ₄ (4a) | 1.0 | Et ₂ AlCl (2.0) | 2000 | 15.9 | 95 |
| 37 | 2-MeC ₆ H ₄ (4b) | 1.0 | Et ₂ AlCl (0.20) | 200 | 5.5 | 33 |
| 38 | 2-MeC ₆ H ₄ (4b) | 1.0 | Et ₂ AlCl (0.50) | 500 | 5.1 | 31 |
| 39 | 2-MeC ₆ H ₄ (4b) | 1.0 | Et ₂ AlCl (1.0) | 1000 | 10.1 | 61 |
| 40 | 2-MeC ₆ H ₄ (4b) | 1.0 | Et ₂ AlCl (1.5) | 1500 | 4.0 | 24 |
| 41 | 2-MeC ₆ H ₄ (4b) | 1.0 | Et ₂ AlCl (2.0) | 2000 | 3.2 | 19 |
| 42 | 2,6-Me ₂ C ₆ H ₃ (5a) ^g | 1.0 | Et ₂ AlCl (0.10) | 100 | 140 | 840 |
| 43 | 2,6-Me ₂ C ₆ H ₃ (5b) ^g | 0.2 | Et ₂ AlCl (0.04) | 200 | 200 | 6000 |

^a Conditions: toluene 30 mL, ethylene 8 atm., 0 °C, 10 min. ^b Molar ratio of Al/V. ^c Activity in kg-PE/mol-V·h. ^d Data cited from reference [16]. ^e $M_n = 6.76 \times 10^6$ measured by viscosity. ^f $M_n = 8.96 \times 10^6$ measured by viscosity. ^g Data cited from reference [10].

Figure 1. Effect of R_2AlCl ($R = Me, Et$) toward the activity in ethylene polymerization by $V(N-2-MeC_6H_4)Cl_2[2-(2,6-R'_2C_6H_3)NCH_2(C_5H_4N)]$ [$R' = Me$ (**4a**), iPr (**4b**)]. Details are shown in Table 3.



3. Experimental Section

3.1. General Procedure

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Anhydrous grade toluene, *n*-hexane (Kanto Kagaku Co., Ltd. Tokyo, Japan) was transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and $13 \times 1/16$) in the drybox under nitrogen stream, and were passed through an alumina short column under N_2 stream prior to use. Complexes employed here were prepared according to our previous reports [10,15–17]. Polymerization grade ethylene (purity > 99.9%, Sumitomo Seika Co. Ltd., Hyogo, Japan) was used as received. Toluene and $AlMe_3$ in the commercially available methylaluminoxane (PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co., Yamaguchi, Japan) were removed under reduced pressure (at *ca.* 50 °C for removing toluene, $AlMe_3$, and then heated at >100 °C for 1 h for completion) in the drybox to give white solids.

3.2. Ethylene Polymerization

Ethylene polymerizations were conducted in a 100 mL scale stainless steel autoclave. The typical reaction procedure is as follows. Toluene (29 mL) and a prescribed amount of Et_2AlCl or Me_2AlCl (1 M in *n*-hexane) were added into the autoclave in the drybox. The reaction apparatus was then filled with ethylene (1 atm.), and catalyst in toluene (1.0 mL) was then added into the autoclave, the reaction apparatus was then immediately pressurized to 7 atm. (total 8 atm.), and the mixture was magnetically stirred for a prescribed time. After the above procedure, ethylene that remained was purged upon cooling, and the mixture was then poured into MeOH containing HCl. The resultant polymer (white

precipitate) was collected on a filter paper through filtration, and was adequately washed with MeOH. The resultant polymer was then dried *in vacuo* at 60 °C for 2 h.

4. Conclusions

In summary, in this paper, we explored ethylene polymerization using V(NR)Cl₂(L) [R = 1-adamantyl, L = 2-(2,6-R'₂C₆H₃)NCH₂(C₅H₄N) {**1a,b**, R' = Me (**a**), ⁱPr (**b**)}, 2-(2,6-Me₂C₆H₃)NCH₂(C₉H₆N) (**2a**), 8-(2,6-Me₂C₆H₃)NCH₂(C₉H₆N) (**3a**); R = 2-MeC₆H₄ (**4a,b**), 2,6-Me₂C₆H₃ (**5a,b**), L = 2-(2,6-R'₂C₆H₃)NCH₂(C₅H₄N)] in the presence of halogenated Al alkyls. The reaction products were polyethylene that were insoluble in hot *O*-dichlorobenzene for measurement of molecular weights by GPC in ordinary analysis procedure, suggesting formation of ultrahigh molecular weight polymers as reported previously [8,16]. Moreover, we demonstrated by **1a,b**, that the anionic chelate donor ligand plays an essential role for stabilization of catalytically-active species and proposed an assumption that cationic vanadium(V) species play a key role in this catalysis, the facts observed here should be promising and important for designing efficient catalysts for olefin polymerization/dimerization, including the effect of catalyst/cocatalyst nuclearity that would play an important role in this catalysis.

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Conflict of Interest

The authors declare no conflict of interest.

References

1. Hagen, H.; Boersma, J.; van Koten, G. Homogeneous vanadium-based catalysts for the Ziegler–Natta polymerization of α -olefins. *Chem. Soc. Rev.* **2002**, *31*, 357–364.
2. Gambarotta, S. Vanadium-based Ziegler/Natta: Challenges, promises, problems. *Coord. Chem. Rev.* **2003**, *237*, 229–243.
3. Nomura, K.; Zhang, W. (Imido)vanadium(V)-alkyl, -alkylidene complexes exhibiting unique reactivity towards olefins and alcohols. *Chem. Sci.* **2010**, *1*, 161–173.
4. Redshaw, C. Vanadium procatalysts bearing chelating aryloxides: structure–activity trends in ethylene polymerisation. *Dalton Trans.* **2010**, *39*, 5595–5604.
5. Nomura, K.; Zhang, S. Design of vanadium complex catalysts for precise olefin polymerization. *Chem. Rev.* **2011**, *111*, 2342–2362.
6. Nomura, K.; Sagara, A.; Imanishi, Y. Olefin polymerization and ring-opening metathesis polymerization of norbornene by (arylimido)(aryloxo)vanadium(V) complexes of the type VX₂(NAr)(OAr ϕ). Remarkable effect of aluminum cocatalyst for the coordination and insertion and ring-opening metathesis. *Macromolecules* **2002**, *35*, 1583–1590.

7. Wang, W.; Nomura, K. Remarkable effects of aluminum cocatalyst and comonomer in ethylene copolymerizations catalyzed by (arylimido)(aryloxo)vanadium complexes: efficient synthesis of high molecular weight ethylene/norbornene copolymer. *Macromolecules* **2005**, *38*, 5905–5913.
8. Wang, W.; Nomura, K. Notable effects of aluminum alkyls and solvents for highly efficient ethylene (co)polymerizations catalyzed by (arylimido)-(aryloxo)vanadium complexes. *Adv. Synth. Catal.* **2006**, *348*, 743–750.
9. Onishi, Y.; Katao, S.; Fujiki, M.; Nomura, K. Synthesis and structural analysis of (arylimido)vanadium(V) complexes containing phenoxyimine ligands: new, efficient catalyst precursors for ethylene polymerization. *Organometallics* **2008**, *27*, 2590–2596.
10. Zhang, S.; Katao, S.; Sun, W.-H.; Nomura, K. Synthesis of (arylimido)vanadium(V) complexes containing (2-anilidomethyl)pyridine ligands and their use as the catalyst precursors for olefin polymerization. *Organometallics* **2009**, *28*, 5925–5933.
11. Macchioni, A. Ion pairing in transition-metal organometallic chemistry. *Chem. Rev.* **2005**, *105*, 2039–2073.
12. Li, H.; Marks, T.J. Nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15295–15302.
13. Bochmann, M. The chemistry of catalyst activation: the case of group 4 polymerization catalysts. *Organometallics* **2010**, *29*, 4711–4740.
14. Christman, D.L. Preparation of polyethylene in solution, *J. Polym. Sci. Part A-1* **1972**, *10*, 471–487.
15. Zhang, S.; Nomura, K. Highly efficient dimerization of ethylene by (imido)vanadium complexes containing (2-anilidomethyl)pyridine ligands: notable ligand effect toward activity and selectivity. *J. Am. Chem. Soc.* **2010**, *132*, 4960–4965.
16. Igarashi, A.; Zhang, S.; Nomura, K. Ethylene dimerization/polymerization catalyzed by (adamantylimido)vanadium(V) complexes containing (2-anilidomethyl)pyridine ligands: factors affecting the ethylene reactivity. *Organometallics* **2012**, *31*, 3575–3581.
17. Nomura, K.; Igarashi, A.; Katao, S.; Zhang, W.; Sun, W.-H. Synthesis and structural analysis of (imido)vanadium(V) complexes containing chelate (anilido)methyl-imine ligands: Ligand effect in ethylene dimerization, *Inorg. Chem.* **2013**, in press.
18. Redshaw, C.; Rowan, M.A.; Homden, D.M.; Dale, S.H.; Elsegood, M.R.J.; Matsui, S.; Matsuura, S. Vanadyl C and N-capped tris(phenolate) complexes: influence of procatalyst geometry on catalytic activity. *Chem. Commun.* **2006**, 3329–3331.
19. Wu, J.-Q.; Mu, J.-S.; Zhang, S.-W.; Li, Y.-S. Vanadium(V) complexes containing tetradentate amine trihydroxy ligands as catalysts for copolymerization of cyclic olefins. *J. Polym. Sci. Part A* **2010**, *48*, 1122–1132.
20. Redshaw, C.; Warford, L.; Dale, S.H.; Elsegood, M.R.J. Vanadyl complexes bearing bi- and triphenolate chelate ligands: highly active ethylene polymerisation procatalysts. *Chem. Commun.* **2004**, 1954–1955.
21. Arbaoui, A.; Redshaw, C.; Homden, D.M.; Wright, J.A.; Elsegood, M.R.J. Vanadium-based imido-alkoxide pro-catalysts bearing bisphenolate ligand for ethylene and ϵ -caprolactone polymerisation. *Dalton Trans.* **2009**, 8911–8922.

22. Redshaw, C.; Rowan, M.A.; Warford, L.; Homden, D.M.; Arbaoui, A.; Elsegood, M.R.J.; Dale, S.H.; Yamato, T.; Casas, C.P.; Matsui, S.; *et al.* Oxo- and imidovanadium complexes incorporating methylene- and diacetylenemethyleneoxa-bridged calix[3]- and diacetylenemethyleneoxa-bridged calix[4]arenes: synthesis, structures and ethylene polymerisation catalysis. *Chem.-Eur. J.* **2007**, *13*, 1090–1107.
23. Homden, D.; Redshaw, C.; Wright, J.A.; Hughes, D.L.; Elsegood, M.R.J. Early transition metal complexes bearing a c-capped tris(phenolate) ligand incorporating a pendant imine arm: synthesis, structure, and ethylene polymerization behavior. *Inorg. Chem.* **2008**, *47*, 5799–5814.
24. Clowes, L.; Redshaw, C.; Hughes, D.L. Vanadium-based pro-catalysts bearing depleted 1,3-calix[4]arenes for ethylene or ϵ -caprolactone polymerization. *Inorg. Chem.* **2011**, *50*, 7838–7845.

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