Design of Vanadium Complex Catalysts for Olefin Coordination/Metathesis Polymerization

（オレフィンの配位・挿入やメタセシス反応に有効な
高性能バナジウム錯体触媒の設計）

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Acknowledgements

1 Introduction

Molecular catalysis plays an important role in modern synthesis. For example, asymmetric catalysts including organocatalysis opened up new strategies to synthesize fine chemicals such as drugs which usually require a defined absolute configuration.[1] Single-site olefin polymerization catalysts which were initially used as simple model compounds have provided a variety of valuable polymeric materials which are difficult to synthesize by classical heterogeneous catalysts (Ziegler-Natta catalyst, Phillips catalyst).[2,3] Recent advances in olefin metathesis have not been achieved without development of the well-defined alkylidene complexes (Schrock type alkylidene complexes) and carbene complexes (Grubbs catalysts).[4] Many improvements (e.g. efficiency, selectivity, atom economy, amount of time, cost…) have been achieved by understanding the fundamentals of catalytic cycles in organic reactions and/or polymerization reactions at the molecular level, and new process and materials have been developed by designing the molecular catalysis precisely.

In transition-metal catalyzed C-C bond forming reaction, the transition-metal species containing metal carbon bond generally are the most important key intermediates and/or act the catalytically active species. Thus, understanding the properties of those species might be a plausible way to provide new aspects for designing the catalysts.

In this introductory chapter, overviews of both olefin coordination polymerization and olefin metathesis polymerization are given.

1.1 Ziegler-Natta catalysts

Polyolefins were initially (especially till 1953) produced by radical process under high pressures and high temperatures (100-400 MPa; 150-230 °C), and polyethylenes produced under these conditions, so-called LDPE (low density polyethylene), were a low melting, highly branched polyethylene. Ziegler et al. found that ethylene could be polymerized under mild conditions (moderate temperature and pressure) by using $TiCl_4$ and alkyl aluminum

($AlEt_3$ etc.), and these catalyst systems afforded linear polyethylene with high molecular weight (HDPE; high density polyethylene) (Figure 1-1).[5] Natta then found that these catalyst systems were effective for stereospecific polymerization of propylene, yielding predominantly isotactic polypropylene.[6] Since Ziegler type titanium catalysts form heterogeneous systems which contain multiple active sites, polymer produced have broad molecular distributions (M_w/M_n = 3-7). Based on systematic research of the use of other metal salts as possible catalysts, it was revealed that the group 4, 5 and 6 metals in combination with alkyl aluminums were effective (e.g. Phillips Catalyst based on "Cr", Standard Catalyst based on "Mo").[7,8]

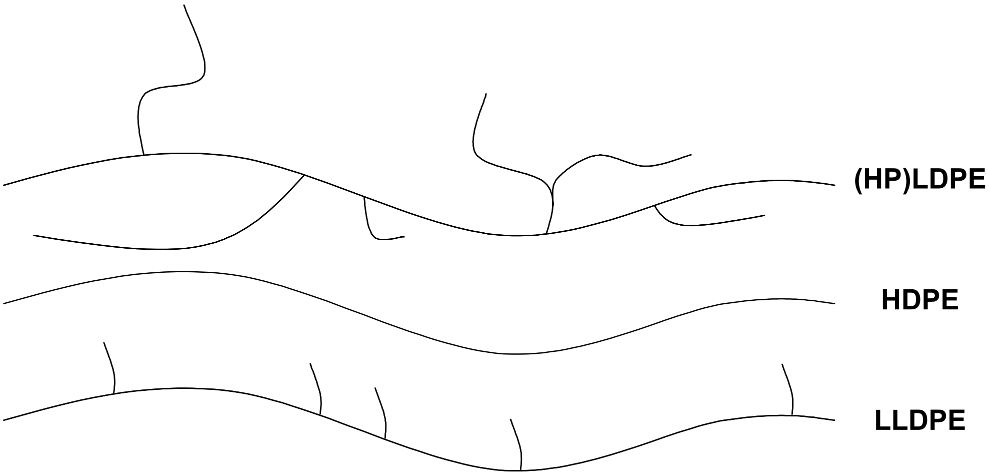


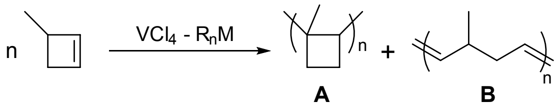
Figure 1-1. Picture of polyethylenes. [(HP)LDPE; (high pressure) low density polyethylene, HDPE; high density polyethylene, and LLDPE; linear low density polyethylene]

Another important feature of Ziegler type catalysts can be seen in polymerization of cyclic monomer such as norbornene, cyclobutene and cyclopentene.[9-11] These catalysts did not afford coordination/insertion polymerization products, but ring-opening metathesis polymerization (ROMP) products. As will be described later, the use of Ziegler type catalysts for polymerization of cyclic olefin led to the discovery of olefin metathesis.

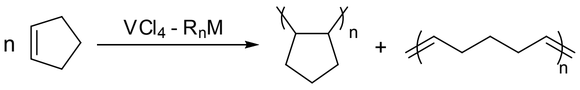
Ziegler type vanadium catalyst systems are soluble and single-site in contrast to titanium based catalysts, and displayed unique characteristics[12-15] such as (a) synthesis of a high molecular weight polymer with narrow polydispersity,[13] (b) synthesis of an ethylene/α-olefin copolymer with high α-olefin content [industrially used in production of ethylene-propylene-diene elastomers (EPDM)],[13a,14] (c) living polymerization affording propylene-methyl methacrylate diblock copolymers,[15b] and (d) others.[16]

Although the conversions were extremely low, the catalytic system derived from vanadium compounds [VCl_4, $VOCl_3$, and $V(acac)_3$ (acac = acetylacetonato)] combined with an alkylating agent with Lewis acidic properties afforded mixture of coordination/insertion polymerization products and ROMP products in polymerization of cyclic olefins (Table 1-1).[17,18]

Table 1-1. Examples for polymerization of cyclic olefins by Ziegler type vanadium catalysts.



	conv.	A	B cis-	B trans-
VCl_4/Et_3Al	37	90	0	10
VCl_4/Et_3Ga	25	90	4	6
VCl_4/Et_2Be	17	85	3	12
VCl_4/Et_2Mg	14	94	0	6
$VCl_4/{}^nBuLi$	3	0	45	55
		by Coordination -Insertion	by ROMP	



	conv.	polymer structure
VCl_4/Et_3Al	1	C_5+C_2
$VOCl_3/Et_2AlCl$	3	C_5+C_2
$V(acac)_3/Et_2AlCl$	1.5	C_5+C_2

A mixture of polymers by ROMP and Coordination-Insertion

1.2 Single-site catalysts

In the late 1950's, the first examples on homogeneous olefin polymerization catalyst have been reported.[19] Although the observed activity was lower than that of Ziegler type catalysts, ethylene was in fact polymerized in the presence of both Cp_2TiCl_2 and $AlEt_3$.

After the discovery that highly active single site catalysts could be derived from combination of titanocene (Cp_2TiCl_2) or zirconocene (Cp_2ZrCl_2) with methylaluminoxane (MAO),[12(a),20] much attention on transition-metal complexes which contained two cyclopentadienyl ligands, called metallocene, had been focused in early days and homogeneous well-defined molecular catalysts (single-site catalysts) became important class of olefin polymerization catalysts.[2] Until now, a huge number of early-to-late transition metal complexes has been reported as active molecular catalysts.[3]

Despite the increasing number of complexes have been reported as olefin polymerization catalysts, the number of vanadium complexes has been limited. Examples of vanadium complexes are shown in Figure 1-2.[21]

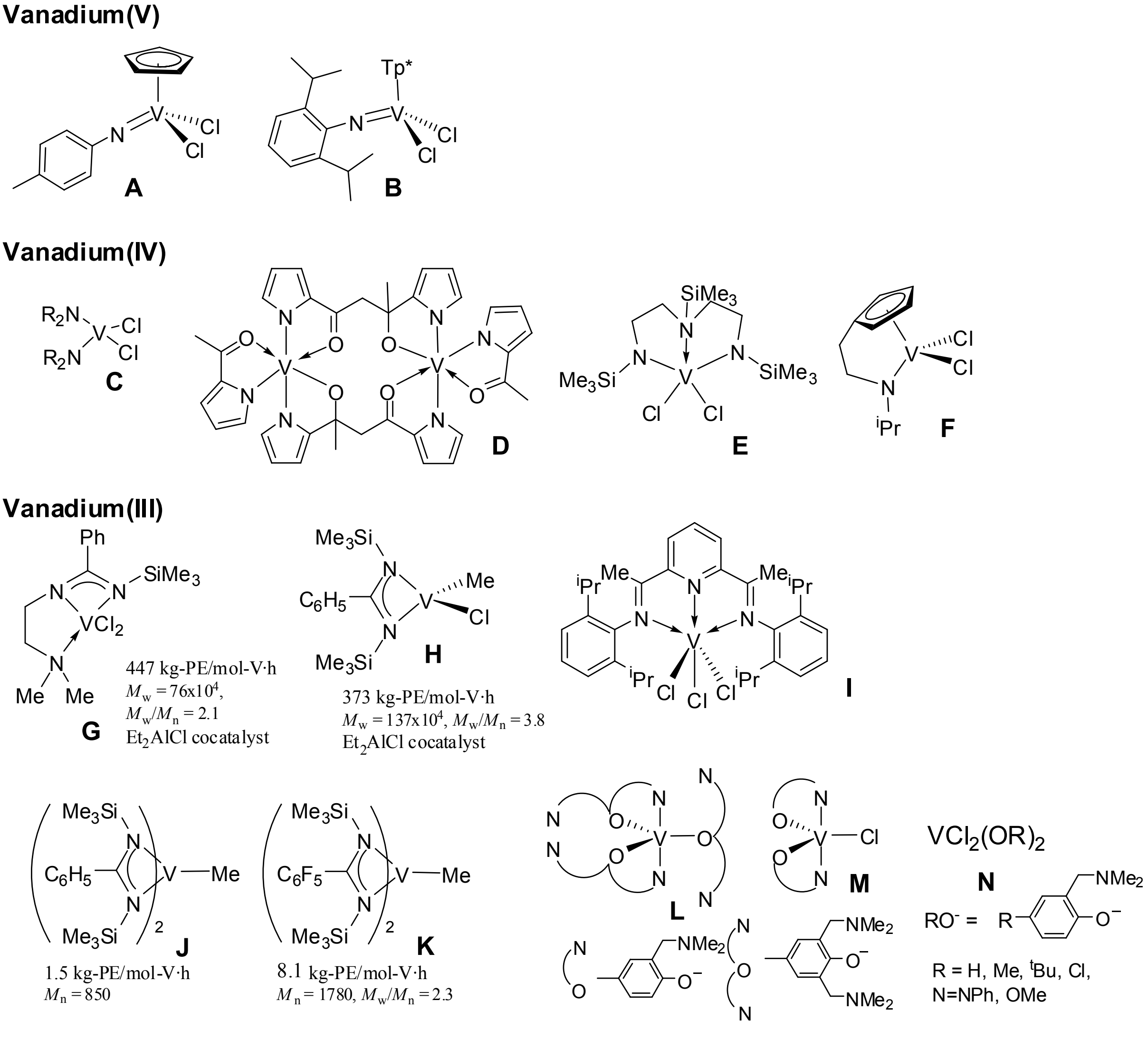


Figure 1-2. Examples of vanadium complexes for olefin polymerization.

1.3 Mechanistic aspects for olefin polymerization

It is now generally accepted that the active species for single-site catalysts are electron deficient cationic (or neutral) alkyl species. Although there are several ways to generate the active species, the similar species are believed to be produced (Figure 1-3).[22]

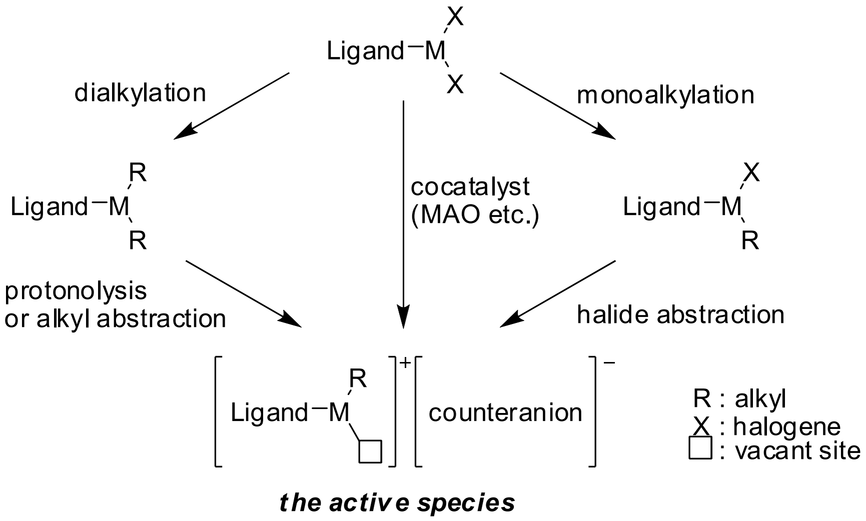
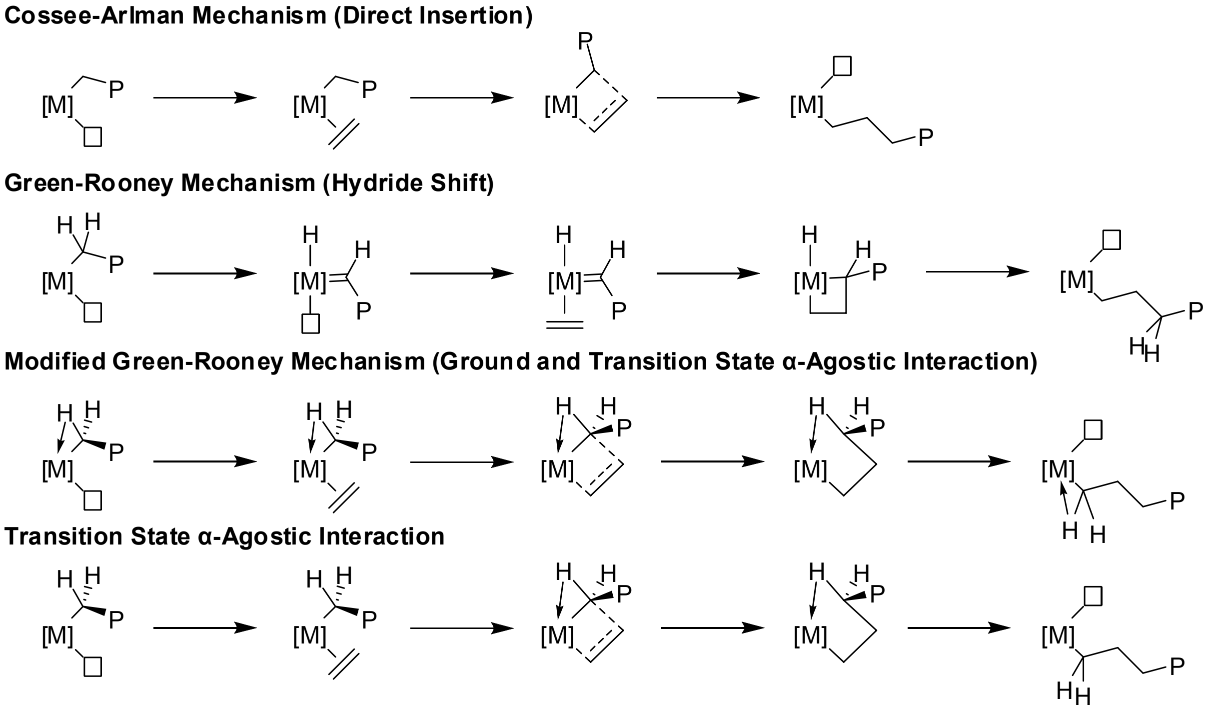


Figure 1-3. Generation of catalytically active species.

As seen in Cossee-Arlman mechanism,[23a-d] polymerization mechanism is simply stated to take place by coordination of the monomer to the vacant site of the active metal center, and subsequent migratory insertion into the metal-alkyl bond affords the similar active species (Scheme 1-1). Various modifications to this mechanism have also been reported (Scheme 1-1).[23e-j] If the agostic interactions are exist in some degree, the electron deficient metal center may be stabilized.[23k] Such interactions rigidify the transition state, and thus may play an important role in stereospecific olefin insertion.

Considering both catalytically active species and catalytic mechanism, understanding the properties of alkyl species is required to design efficient olefin polymerization catalyst.

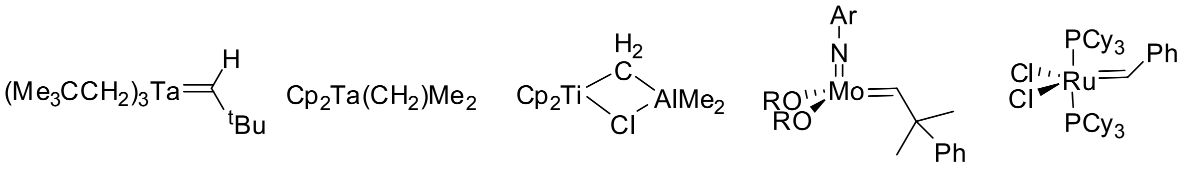
Scheme 1-1



1.4 Olefin metathesis

Olefin metathesis was historically discovered in the area of olefin polymerization.[9-11] Thus, the catalytic systems have been of the "Ziegler type", directly prepared *in-situ* by addition of an alkylating agent such as alkyl aluminum derivatives, a Grignard reagent, or alkyl lithium to a transition metal halide, usually in a high oxidation state (e.g. WCl_6, $WOCl_4$).[24] The catalytically active species were not known and the concentrations of the active species were usually less than 1% of transition metal added.

The discovery of alkylidene complexes that were stable enough to isolate led to the development in the field of olefin metathesis. The first alkylidene complexes, which had marked difference compared to the Fischer-type carbene complexes discovered in 1964,[25] was reported in 1974,[26] and the tremendous efforts to synthesize the alkylidene complexes have been done until now (Figure 1-4).[27] [Tebbe discovered that the reaction of Cp_2TiCl_2 with excess $AlMe_3$ afforded a titanium-methylene-aluminum complex (so called Tebbe reagent) around the same time, although this work was not published until late 1970's.][28]



Tantalum alkylidene Tebbe reagent Schrock type Grubbs type

Figure 1-4. Examples of alkylidene (carbene) complexes.

Although various transition metals through the periodic table including niobium and tantalum have been known, reports on well-characterized vanadium alkylidene have been limited (Figure 1-5). Although some vanadium complexes that contain metal-carbon double bond have been reported, the vanadium alkylidenes (carbenes) that exhibit notable activity olefin metathesis have never been reported so far.[29,30]

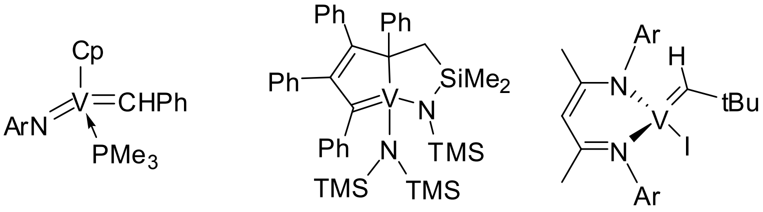
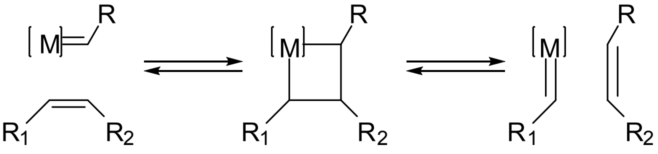


Figure 1-5. Reported vanadium alkylidene (carbene) complexes.

The olefin metathesis became a truly useful synthetic methodology after the discovery of well-defined molybdenum alkylidene complexes (e.g. Schrock type alkylidene) which are relatively functional tolerant (Figure 1-4). These developments were rapidly accelerated by the discovery of a family of ruthenium catalysts (e.g. Grubbs carbene). In general, ruthenium based catalysts are more functional-group-tolerant than earlier metal complexes, although molybdenum catalysts are effective in the presence of phosphanes[31] and thioethers[32] functional groups that readily decompose ruthenium complexes. Thus, it is difficult or not necessarily appropriate to suggest whether ruthenium based catalysts is the best, or not. It may be true that olefin metathesis are recognized one of the most powerful methods in both organic synthesis and polymer synthesis, since it can provide a variety of valuable organic compounds and/or polymeric materials difficult to synthesize by other methods.[4]

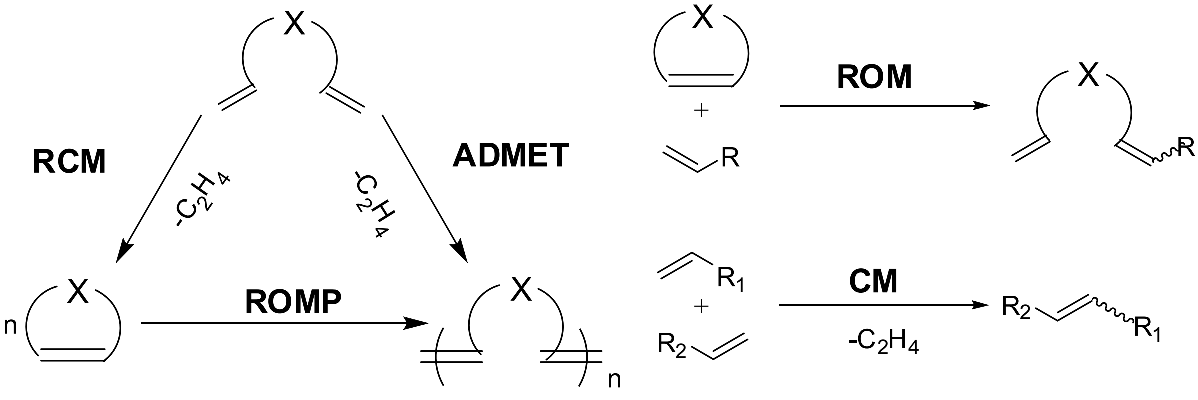
The mechanism of olefin metathesis is shown in Scheme 1-2.[33] The mechanism consists of a reaction between an alkylidene (carbene) complex and an olefin to give a metallacyclobutane intermediate, from which an olefin is lost and a new alkylidene complex formed. This fundamental reaction led a variety of olefin metathesis reactions, ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), cross metathesis (CM) reaction, ring-opening metathesis (ROM) and acyclic diene metathesis polymerization (ADMET) (Scheme 1-3).[4] Recent advances in asymmetric olefin metathesis with chiral catalysts have increased its utility.[4]

Scheme 1-2



Mechanism of Olefin Metathesis
(Chauvin's Mechanism)

Scheme 1-3



A Variety of Olefin Metathesis Reactions

1.5 Aim of the thesis

As briefly presented in previous sections, the discovery of Ziegler type catalysts led to two successful research areas, olefin polymerization and olefin metathesis. Current interest in both fields is to design and synthesis of more efficient molecular catalysts. Since the transition-metal species containing metal carbon bonds play the most important key intermediate and/or act the catalytically active species in both catalytic cycles, thus understanding the properties of those species might be a plausible way, and provide new aspects for designing the catalysts. Since Ziegler type vanadium catalysts have displayed unique characteristics, vanadium based molecular catalysts are highly expected to be effective catalysts.

The aim of the research is to explore the possibilities of vanadium complexes as effective molecular catalysts for olefin coordination/metathesis polymerization. Especially, highest oxidation state vanadium(V) complexes are focused, because olefin insertion reaction is an easy reaction especially for d^0 complexes.[34] Moreover, bridged- or *non*-bridged- group 4 half metallocenes are accepted as highly active olefin polymerization catalysts[3d,35] and Schrock type alkylidene in which metal has its highest oxidation state are one of the most active catalysts in olefin metathesis.[4,27b] Based on above facts, a series of arylimido vanadium complexes are focused. By changing the anionic donor ligand or substituents on the ligand, steric and electronic properties of the complex can easily be modified.

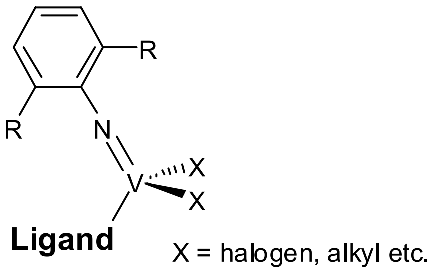


Figure 1-6. Design of arylimido vanadium(V) complex.

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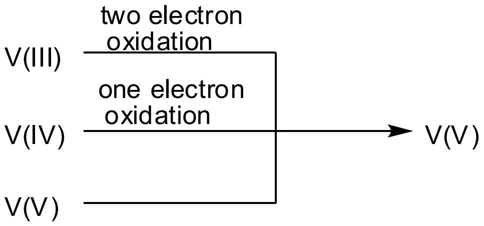
2 Syntheses of a series of arylimido vanadium complexes

Several methods have been reported to synthesize vanadium(V) complexes in addition to chemical transformation of vanadium(V) compounds. For instance, vanadium(V) alkylidene complex was synthesized by oxidation of vanadium(III) compound with Wittig reagent,[1] and vanadium(V) alkylidyne complex was synthesized by treatment of vanadium(IV) alkylidene with silver salt.[2] Although redox chemistry of vanadium complex should be of great interest, chemical transformation of vanadium(V) complexes looks the more convenient ways (Scheme 2-1).[3]

Scheme 2-1



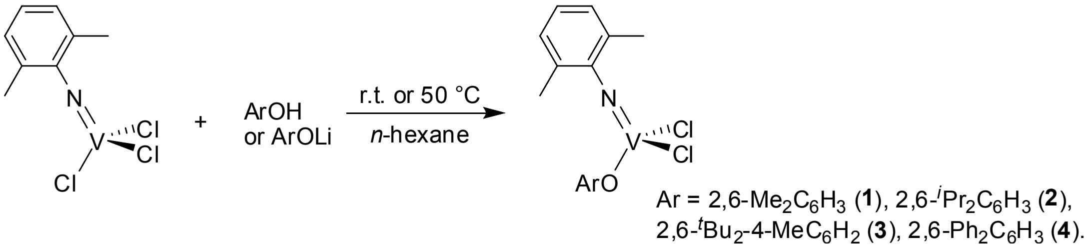
The most common problems encountered in attempting synthesis of vanadium(V) alkyls are the reductions of the metal center with organometallic reagents.[3a,4] Because of the thermal instability of several vanadium(V) alkyl complexes and the formation of oils upon alkylation, full characterization of the products and subsequent reactivity studies has often been precluded. Since bulky imido ligands are well-known as stabilizing high-oxidation-state transition-metal complexes, 2,6-disubsutituted arylimido ligand (ArN) was chosen in this study.[3,5] In addition, (arylimido)vanadium(V) trichloride analogue can easily be prepared by reacting $VOCl_3$ with one equivalent of various arylimido-isocyanate.

This chapter describes the syntheses and some coordination chemistry of a series of (arylimido)vanadium(V) complexes. Anionic donor ligands such as aryloxo and ketimide ligand are introduced by facile salt metathesis (by reacting metal-chloride group with metal salt) or HCl elimination (by reacting metal-chloride group with neutral ligand precursor).

2.1 Syntheses of (arylimido)vanadium complexes containing ancillary donor ligands

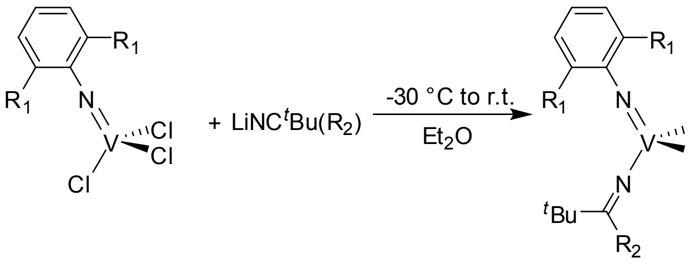
A series of (arylimido)(aryloxo)vanadium(V) complexes, of the type $VCl_2(NAr)(OAr')$ [NAr = N-2,6-$Me_2C_6H_3$; OAr' = O-2,6-$Me_2C_6H_3$ (**1**), O-2,6-$^iPr_2C_6H_3$ (**2**), O-2,6-$^tBu_2$-4-MeC_6H_2 (**3**)], have been synthesized according to literature procedure in high yields from VCl_3(N-2,6-$Me_2C_6H_3$) by treating with one equivalent of the corresponding phenol in *n*-hexane (Scheme 2-2).[3g] These complexes were also able to be prepared by adding the corresponding lithium phenoxide in place of phenol in Et_2O. VCl_2(NAr)(O-2,6-$Ph_2C_6H_3$) (**4**) could be prepared in a similar fashion except that the reaction was conducted at 50 °C. The product isolated was deep purple microcrystals and was able to be identified by ^1H, ^{13}C, and ^{51}V NMR spectra and by elemental analysis.

Scheme 2-2



The ketimide analogues (**5-7**) were also be able to be prepared by treating VCl_3(N-2,6-$Me_2C_6H_3$) or VCl_3(N-2,6-$^iPr_2C_6H_3$)$(thf)_2$ with lithium ketimide in Et_2O in high yields (84-85%, Scheme 2-3), and were identified by ^1H, ^{13}C, and ^{51}V NMR spectra and by elemental analysis (Scheme 2-3).

Scheme 2-3



R_1;R_2 = Me;^{t}Bu (**5**), ^{i}Pr;^{t}Bu (**6**), Me;CH_2SiMe_3 (**7**).

2.2 Structure determination of $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)$

The ketimide dichloro complex **5** was recrystallized from *n*-hexane to yield brown crystals suitable for X-ray structure determination (Figure 2-1). The selected bond distances and angles are summarized in Table 2-1. The structure showed that **5** folds distorted tetrahedral geometry around vanadium. The V-N(imido) bond distance (1.660 Å) was similar to those of (arylimido)vanadium(V) derivatives (1.638-1.669 Å),[3e] and slightly shorter than those of $CpV(NAr)(CHPh)PMe_3$ and $CpV(NAr)(PMe_3)_2$ (1.679 Å and 1.698 Å, respectively).[1] The V-N(C^tBu_2) bond distance (1.787 Å) was shorter than those of $V(NAr)(CH_2Ph)_2(NMePh)$ (1.866 Å)[3e] and $CpTi(NC^nBu^tBu)Cl_2$ (1.872 Å).[6] The linear geometry of the V-N(imido) and V-N(C^tBu_2), (V-N-C(Ar) = 179.2° and V-N-C(^{t}Bu) = 176.3°), were similar to those observed in $V(NAr)(CH_2Ph)_2X$ (X = NMePh, CH_2Ph, O-2,6-$^iPr_2C_6H_3$, and $OC(CF_3)_3$) and $CpTi(NC^nBu^tBu)Cl_2$, indicating the strong π-donation of the nitrogen atom lone pair to V. These results clearly suggest that **5** is a 14 electron species.

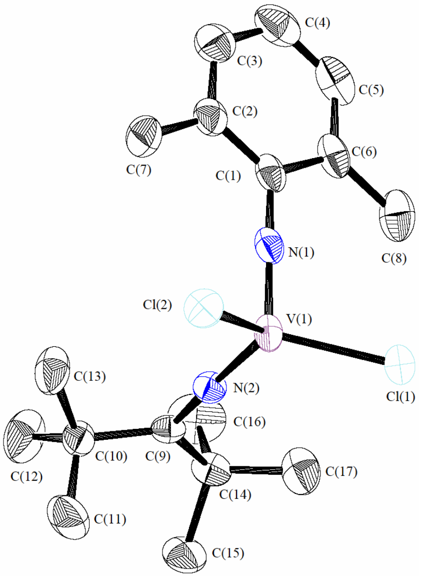


Figure 2-1. Molecular structure of $\mathrm{VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^{t}Bu_2)}$ (**5**).

Table 2-1. Selected bond distances and angles for $\mathrm{VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^{t}Bu_2)}$ (**5**).

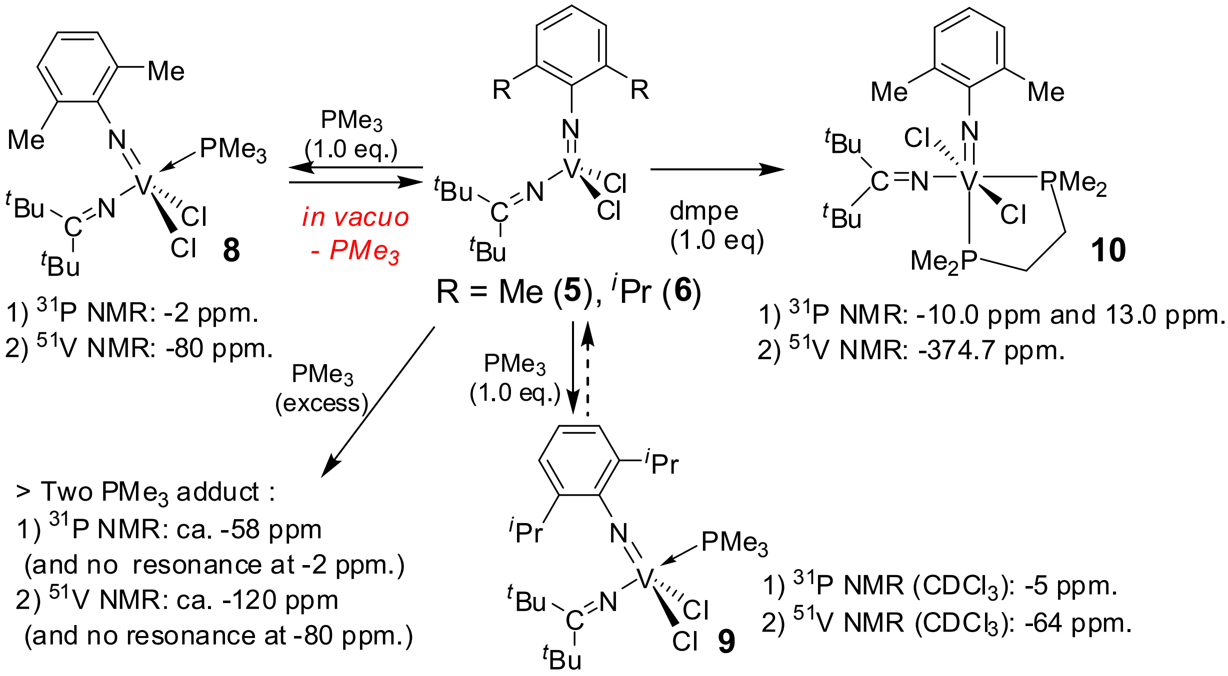
		Bond Distances in Å			
V(1)-Cl(1)	2.2710(5)	V(1)-Cl(2)	2.2338(5)		
V(1)-N(1)	1.660(2)	V(1)-N(2)	1.787(1)		
N(1)-C(1)	1.368(2)	N(2)-C(9)	1.255(2)		
		Bond Angles in °			
N(1)-V(1)-N(2)	98.42(6)	N(1)-V(1)-Cl(1)	102.62(5)	N(1)-V(1)-Cl(2)	103.95(6)
N(2)-V(1)-Cl(1)	116.27(5)	N(2)-V(1)-Cl(2)	112.79(5)		
V(1)-N(1)-C(1)	179.0(1)	V(1)-N(2)-C(9)	176.0(1)		

2.3 Coordination chemistry of ketimide complexes

Since the ketimide dichloro complexes were coordinatively unsaturated electron unsaturated complexes (14 electron counts), it was suggested that additional donor ligand might coordinate to the metal center. Thus, reaction of ketimide complex with phosphine was investigated (Scheme 2-4). The immediate formations of the phosphine adducts (**8** and

9) were confirmed by ^{1}H, ^{31}P, and ^{51}V NMR when one equivalent PMe_3 was added to the $CDCl_3$ solution of **5** and **6**. The both adducts showed an upfield shift of 142 ppm in the ^{51}V NMR compared to the dichloro complexes, respectively. Interestingly, coordination of PMe_3 was relatively weak and quantitative dissociation was observed under the vacuum condition. When excess amount of PMe_3 was used, further upfield shift of 40 ppm compared to the mono phosphine adducts **8** was observed. This suggested two phosphine molecules might coordinate to the metal center. An attempt to isolate the two phosphine adduct was successful by using chelate bisphosphine ligand, $Me_2PCH_2CH_2PMe_2$ (dmpe). The dmpe adduct **10** showed a large upfield shift of 439 ppm in ^{51}V NMR compared to **5**. Two resonances were appeared at -10 and -13 ppm in ^{31}P NMR, which indicated two different environments for each P atoms (*vide post*).

Scheme 2-4



1) ^{31}P NMR: -2 ppm.
2) ^{51}V NMR: -80 ppm.

1) ^{31}P NMR: -10.0 ppm and 13.0 ppm.
2) ^{51}V NMR: -374.7 ppm.

> Two PMe_3 adduct :
1) ^{31}P NMR: ca. -58 ppm
(and no resonance at -2 ppm.)
2) ^{51}V NMR: ca. -120 ppm
(and no resonance at -80 ppm.)

1) ^{31}P NMR ($CDCl_3$): -5 ppm.
2) ^{51}V NMR ($CDCl_3$): -64 ppm.

2.4 Structure determination of phosphine adducts $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)PMe_3$, $VCl_2(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(NC^tBu_2)PMe_3$ and $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)(dmpe)$

The single crystals suitable for X-ray analysis of phosphine adducts **8** were grown from a saturated *n*-hexane solution cooled to -30 °C. The structure, selected bond distances and angles are summarized in Figure 2-2 and Table 2-2. The crystal structure shows that **8** folds distorted trigonal bipyramidal structure around V; P atom is positioned *trans* to the N atom in the ketimide ligand [P-V-N(C^tBu_2) = 169.45°], and the V-N(C^tBu_2) distance (1.839 Å) is thus influenced by electron donation from the PMe_3. The V-P distance (2.527 Å) is longer than that of (Cp)V(NAr)(CHPh)PMe_3.[1] As suggested from the rather long V-P distance and the broad resonances of the ^{31}P NMR spectrum, the PMe_3 should be dissociated exclusively affording analytically pure **5** quantitatively when **8** was placed *in vacuo*. The both relatively short bond lengths of V-N(imido) (1.649 Å) and V-N(C^tBu_2) (1.836 Å) and linear geometry of the V-N(imido) (V-N-C(Ar) = 178.8°) and V-N(C^tBu_2) (V-N-C(^tBu) = 177.7°) were similar to those found in **5**, indicating the strong π-donation of the nitrogen atom lone pair to V. These results clearly suggested that **8** is 16 electron species.

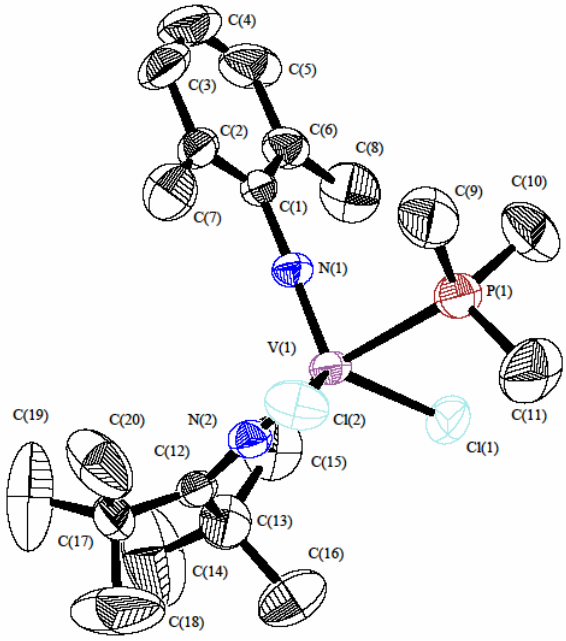


Figure 2-2. Molecular structure of $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)PMe_3$ (**8**).

Table 2-2. Selected bond distances and angles for **8**.

Bond Distances in Å					
V(1)-P	2.527(2)				
V(1)-Cl(1)	2.314(2)	V(1)-Cl(2)	2.298(2)		
V(1)-N(1)	1.652(3)	V(1)-N(2)	1.839(4)		
N(1)-C(1)	1.386(5)	N(2)-C(12)	1.260(6)		
Bond Angles in ^{o}					
P-V(1)-N(1)	89.1(3)	P-V(1)-N(2)	170.0(3)		
P-V(1)-N(1)	89.5(1)	P-V(1)-N(2)	169.4(1)		
P-V(1)-Cl(1)	78.75(5)	P-V(1)-Cl(2)	80.32(5)		
N(1)-V(1)-N(2)	100.8(2)	N(1)-V(1)-Cl(1)	116.7(1)	N(1)-V(1)-Cl(2)	112.0(1)
N(2)-V(1)-Cl(1)	94.4(1)	N(2)-V(1)-Cl(2)	97.8(1)		
V(1)-N(1)-C(1)	178.8(3)	V(1)-N(2)-C(12)	177.3(3)		

Single crystals of **9** were obtained in a similar manner. The crystal structure of **9** is analogous with **8** and **9** folds distorted trigonal bipyramidal structure around V; P atom is positioned *trans* to the N atom in the ketimide ligand [P-V-N(C^{t}Bu$_2$) = 170.0°]. The most of bond distances and angles were considerably similar to those in the corresponding PMe$_3$ adduct **8**. For example, the V-N(Ar) distances are 1.647 Å in **9** and 1.652 Å in **8**, respectively. The V-N(C^{t}Bu$_2$) distances are 1.82 Å in **9** and 1.839 Å in **8**, respectively. Thus, the complex **9** is 16 electron species.

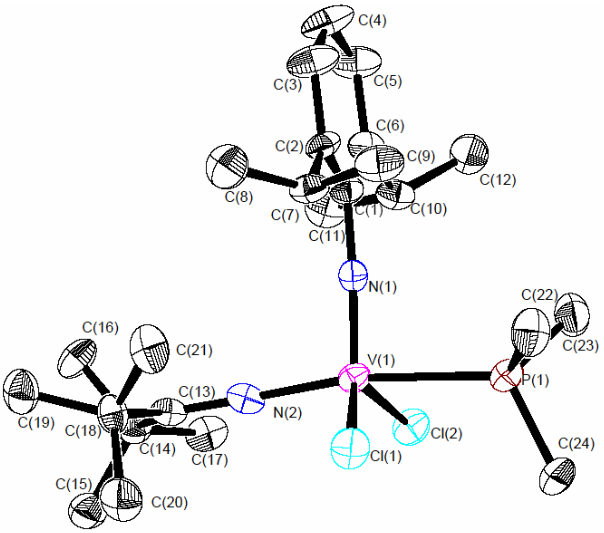


Figure 2-3. Molecular structure of VCl$_2$(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)PMe$_3$ (**9**).

Table 2-3. Selected bond distances and angles for **9**.

Bond Distances in Å

V(1)-P	2.539(4)		
V(1)-Cl(1)	2.301(4)	V(1)-Cl(2)	2.297(3)
V(1)-N(1)	1.647(8)	V(1)-N(2)	1.82(1)
N(1)-C(1)	1.39(1)	N(2)-C(13)	1.27(2)

Bond Angles in °

P-V(1)-N(1)	89.1(3)	P-V(1)-N(2)	170.0(3)		
P-V(1)-Cl(1)	79.4(1)	P-V(1)-Cl(2)	80.4(1)		
N(1)-V(1)-N(2)	100.5(4)	N(1)-V(1)-Cl(1)	117.2(3)	N(1)-V(1)-Cl(2)	112.5(3)
N(2)-V(1)-Cl(1)	93.6(3)	N(2)-V(1)-Cl(2)	98.2(3)		
V(1)-N(1)-C(1)	174.8(8)	V(1)-N(2)-C(13)	174.2(9)		

The crystal structure of **10** showed that **10** folds distorted octahedral geometry around V; one P atom is positioned *trans* to the imido-nitrogen, and the other is *trans* to the ketimide-nitrogen (Figure 2-4). The structure was quite similar to that of $VCl_3(N\text{-}2,6\text{-}{}^iPr\text{-}C_6H_3)(depe)$.[3f] Due to the *trans* influence by the dmpe and/or steric congestion around the metal, $V\text{-}N(C^tBu_2)$ distance (1.843 Å) is longer than those in both **5** and **8**. V-N(Ar) distance (1.677 Å) is slightly longer than that in **5**. Due to the intense *trans* influence of the imido ligand, V-P(trans to imido) length is about 0.1 Å longer than V-P(trans to ketimide) lengths in **8**, **9** and **10**.

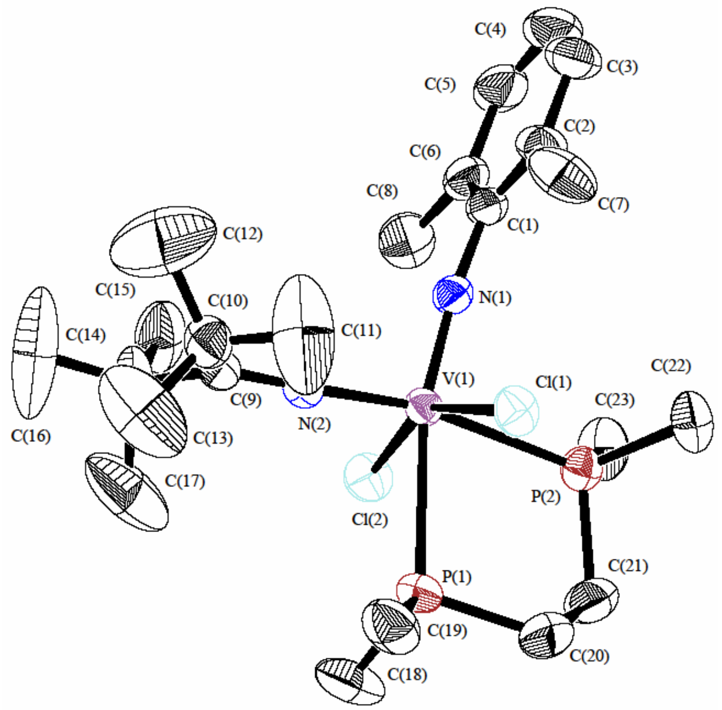


Figure 2-4. Molecular structure of $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)(dmpe)$ (**10**).

Table 2-4. Selected bond distances and angles for **10**.

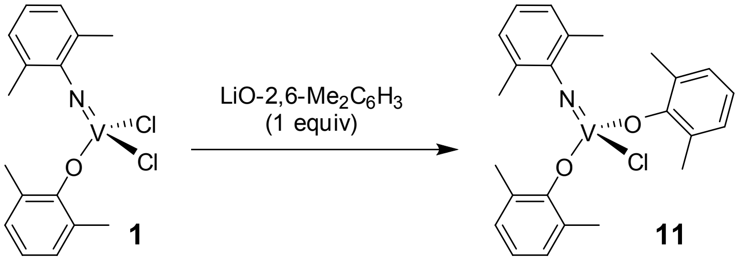
Bond Distances in Å			
V(1)-P(1)	2.648(1)	V(1)-P(2)	2.516(1)
V(1)-Cl(1)	2.3653(8)	V(1)-Cl(2)	2.3753(8)
V(1)-N(1)	1.677(2)	V(1)-N(2)	1.843(2)
N(1)-C(1)	1.373(4)	N(2)-C(9)	1.250(4)

Bond Angles in º					
P(1)-V(1)-N(1)	166.67(9)	P(1)-V(1)-N(2)	91.22(8)	P(1)-V(1)-P(2)	77.62(3)
P(1)-V(1)-Cl(1)	76.73(3)	P(1)-V(1)-Cl(2)	79.60(3)		
P(2)-V(1)-N(1)	89.27(9)	P(2)-V(1)-N(2)	168.73(8)		
P(2)-V(1)-Cl(1)	81.22(3)	P(2)-V(1)-Cl(2)	79.32(3)		
N(1)-V(1)-N(2)	101.9(1)	N(1)-V(1)-Cl(1)	99.08(8)	N(1)-V(1)-Cl(2)	100.56(8)
N(2)-V(1)-Cl(1)	97.92(7)	N(2)-V(1)-Cl(2)	97.28(7)		
V(1)-N(1)-C(1)	173.6(2)	V(1)-N(2)-C(12)	176.0(2)		

2.5 Syntheses of (arylimido)vanadium complexes containing two or three donor ligands

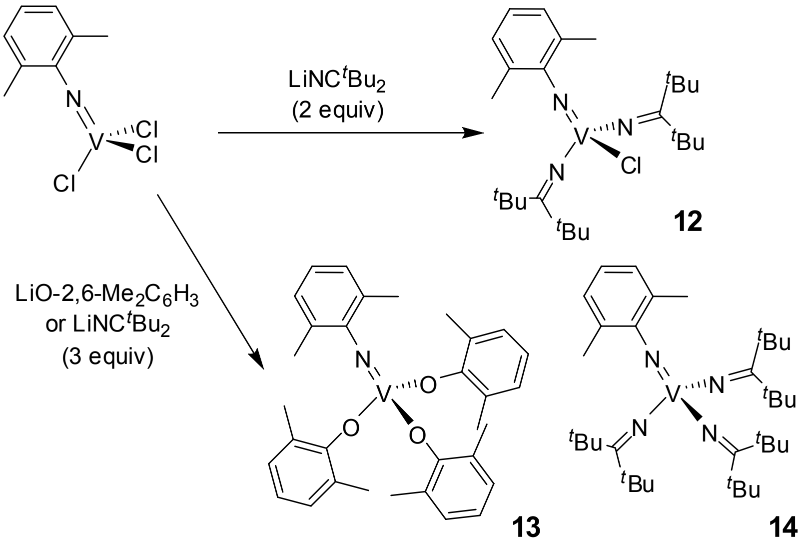
The three V-Cl bonds in the trichloro complexes, VCl$_3$(NAr), would be replaced with two or three ligands, yielding the complexes having two or three ancillary donor ligands. The bis-aryloxo complex could not be isolated from reaction of VCl$_3$(NAr) with two equivalents of LiOAr, and one probable reason was formation of several species such as mono-, bis-, and tris-aryloxo complexes. However, it was able to be isolated in good yield by reacting one equivalent of LiOAr with isolated mono-aryloxo complex (Scheme 2-5).

Scheme 2-5



In contrast, the bis-ketimide complex could easily be prepared by reacting $VCl_3(NAr)$ with two equivalents of $LiNC^tBu_2$ (Scheme 2-6). Since there were no chance to contaminate in synthesis of tris-ligated complexes when reaction of bis-ligated complex with additional lithium salt proceeds smoothly, both tris-aryloxo complex and tris-ketimide complex were thus prepared by reaction of $VCl_3(NAr)$ with three equivalents of lithium salts (Scheme 2-6).

Scheme 2-6



Introduction of an anionic ligand increases d-electron counts around the metal compared to its chloro analogue. This can be indeed observed as upfield shifts in the ^{51}V NMR spectra (Table 2-5). The bis-aryloxo complex **11** showed the upfield shift of 251 ppm in ^{51}V NMR spectrum compared to the mono-aryloxo complex **1**. The tris-aryloxo complex **13** showed the upfield shift of 166 ppm in ^{51}V NMR spectrum compared to the bis-aryloxo complex **11**. Similarly, the bis-ketimide complex **12** showed the upfield shift of 267 ppm in ^{51}V NMR spectrum compared to the mono-ketimide complex **5**, and the tris-ketimide complex **14** showed the upfield shift of 192 ppm in ^{51}V NMR spectrum compared to the bis-ketimide complex **12**.

Table 2-5. ^{51}V NMR chemical shifts (in ppm) of $V(N\text{-}2,6\text{-}Me_2C_6H_3)L_nCl_{3\text{-}n}$.

Ligand	n = 0	n = 1	n = 2	n = 3
L = O-2,6-$Me_2C_6H_3$	364	44	-207	-373
L = N=C^{t}Bu$_2$	364	72	-195	-387

2.6 Structure determination of $VCl(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_2$

The single crystals suitable for X-ray analysis of the bis-ketimide complex **12** were grown from a saturated *n*-hexane solution cooled to -30 °C. The ORTEP drawings, selected bond distances and angles are summarized in Figure 2-5 and Table 2-6. The structure showed that **12** folds distorted tetrahedral geometry around vanadium. The most of the bond distances and the angles are similar to those in the corresponding mono-ketimide **5**. For example, the V-N(Ar) distances are 1.645 Å in **12** and 1.660 Å in **5**, respectively, and the V-N(C^{t}Bu$_2$) distances are 1.805 and 1.803 Å in **12** and 1.787 Å in **5**, respectively. The linear geometry of the V-N(Ar) and V-N(C^{t}Bu$_2$), (V-N-C(Ar) = 173.0° and V-N-C(^{t}Bu) = 169.4° and 174.3°), was similar to that observed in **5** (V-N-C(Ar) = 179.2° and V-N-C(^{t}Bu) = 176.3°). Thus, the complex **12** is considered to be 16 electron species.

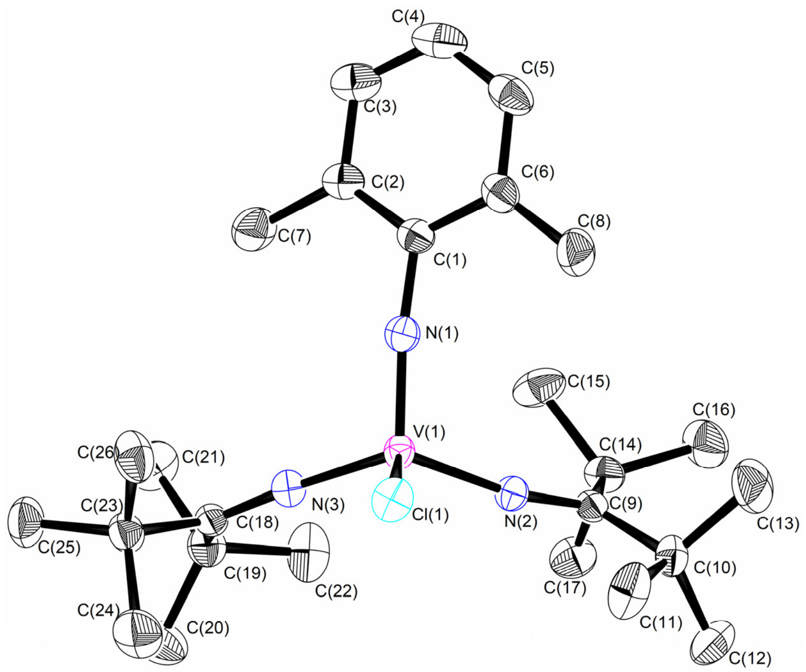


Figure 2-5. ORTEP drawing for **12**. (Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.)

Table 2-6. Selected bond distances and angles for **12**.

Bond Distances in Å

V(1)-Cl(1)	2.261(1)				
V(1)-N(1)	1.645(4)	V(1)-N(2)	1.805(3)	V(1)-N(3)	1.803(3)
N(1)-C(1)	1.377(6)	N(2)-C(9)	1.256(5)	N(3)-C(18)	1.251(5)

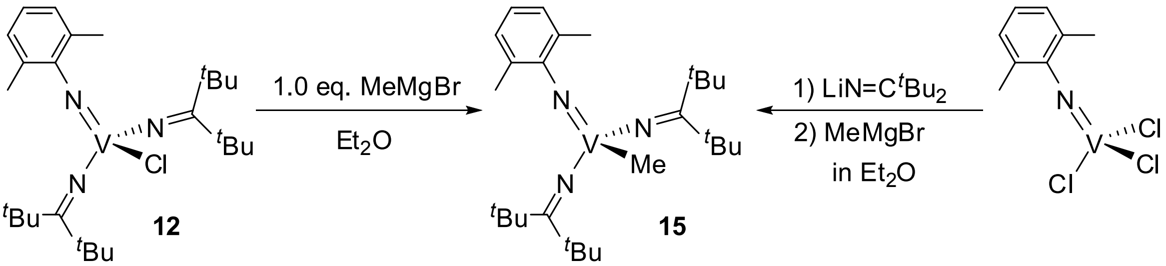
Bond Angles in ^{o}

N(1)-V(1)-Cl(1)	110.2(1)	N(2)-V(1)-Cl(1)	108.2(1)
N(3)-V(1)-Cl(1)	107.8(1)	N(2)-V(1)-N(1)	105.9(2)
N(3)-V(1)-N(1)	106.1(2)	N(3)-V(1)-N(2)	118.6(1)
V(1)-N(1)-C(1)	173.0(3)	V(1)-N(2)-C(9)	169.4(3)
V(1)-N(3)-C(18)	174.3(3)		

2.7 Synthesis and characterization of methyl complex, VMe(N-2,6-$Me_2C_6H_3$)(NC^tBu_2)$_2$

The methyl analogue of complex **12**, VMe(N-2,6-$Me_2C_6H_3$)(NC^tBu_2)$_2$ (**15**), was able to be prepared in high yield (85 %) by treating **12** with MeMgBr in Et_2O (Scheme 2-7), and was identified by ^{1}H, ^{13}C, and ^{51}V NMR spectra, elemental analysis, and X-ray crystallography. Alternatively, the methyl complex **15** was prepared directly from VCl_3(NAr) without isolation of VCl(N-2,6-$Me_2C_6H_3$)(N=C^tBu_2)$_2$ (**12**) (yield 58 %).

Scheme 2-7



The crystal structure showed that **15** folds a distorted tetrahedral geometry around V, and the V-N(C^tBu_2) distances (1.825-1.827 Å) were slightly longer than those in **12** (1.803-1.805 Å). The V-Me distance (2.064 Å) is close to V(V)-C bond lengths in (arylimido)vanadium(V)-dibenzyl analogues (2.026-2.103 Å)[3e] and Li[(^{t}Bu_3SiN)$_2$VMe_2] (2.043, 2.050 Å)[7]; the distance is very similar to some V(II-IV)-Me complexes (2.070-2.120 Å)[8a,b,c] and shorter than other V(II-IV)-Me complexes (2.206-2.222 Å)[3a,b,f,g].

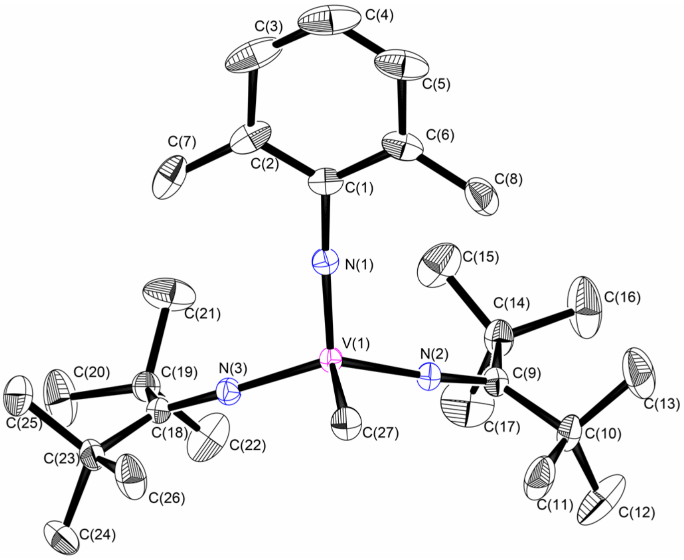


Figure 2-6. ORTEP drawing for **15**. (Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.)

Table 2-7. Selected bond distances (Å) and angles (º) for **15**.

Bond Distances in Å

V-C(27)	2.064(2)	V-N(1)	1.661(2)
V-N(2)	1.825(2)	V-N(3)	1.827(2)
N(1)-C(1)	1.387(3)	N(2)-C(9)	1.257(3)
N(3)-C(18)	1.260(2)		

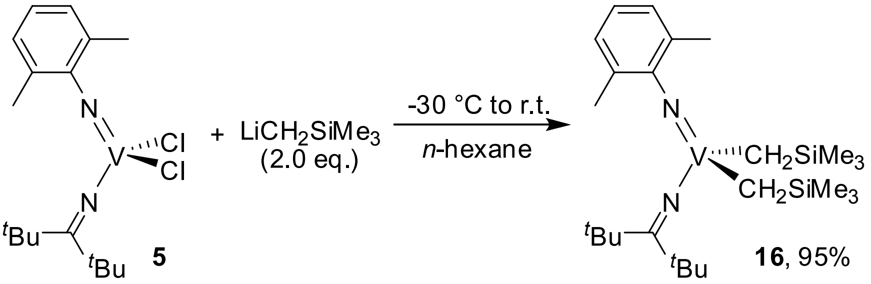
Bond Angles in º

N(1)-V-C(27)	101.2(1)	N(2)-V-C(27)	104.7(1)	N(3)-V-C(27)	105.7(1)
V-N(1)-C(1)	175.0(1)	V-N(2)-C(9)	175.1(2)	V-N(3)-C(18)	176.1(2)
N(2)-V-N(1)	110.1(1)	N(2)-V-N(3)	123.51(8)	N(3)-V-N(1)	109.10(9)

2.8 Synthesis of dialkyl complex, $V(CH_2SiMe_3)_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)$

The dialkyl complex **16** was able to be prepared by reacting $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)$ (**5**) with two equivalents of $LiCH_2SiMe_3$ in *n*-hexane (Scheme 2-8). Although the resulting product was rather sticky solid and thus could not be purified by recrystallization, the analytically pure material could be obtained by careful treatment using highly pure starting material, reagent, and solvent. The complex was identified by ^1H, ^{13}C and ^{51}V NMR spectra as well as by elemental analysis.

Scheme 2-8



Although complex **16** would be assumed as the electron deficient 14 electron species, the coordination of PMe_3 to **16** was not observed even by addition of excess amount (seven equivalents) at 25 °C, and this observation might be due to the steric hindrance of rather bulky CH_2SiMe_3 group around the V metal center (Figure 2-7).

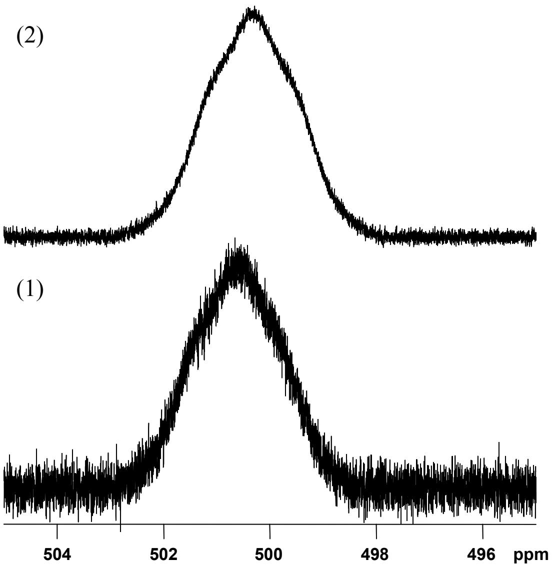


Figure 2-7. ^{51}V NMR spectra of (1) **16** and (2) **16** with PMe_3 (7.0 eq).

2.9 Conclusion

A series of arylimido vanadium complexes containing aryloxo or ketimide ligands has been synthesized in good to high yields by reacting metal-chloride group of readily accessible $(ArN)VCl_3$ with one, two, or three equivalents of lithium salts. Large upfield shifts in ^{51}V NMR spectra were always observed if chloro ligand was substituted by aryloxo or ketimide ligand. The alkyl complex **15** and dialkyl complex **16** were also isolated in high yields.

It was revealed that phosphines such as PMe_3 and dmpe was able to easily coordinate to the vanadium in dichloro complex **5** and **6** affording their phosphine adducts, whereas not to more electron deficient dialkyl analogue **16** due to steric bulkiness of $SiMe_3$ group.

2.10 Experimental section

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous-grade of solvents (benzene, diethyl ether, *n*-hexane, and THF) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2, and were passed through an alumina short column under N_2 stream prior to use. All chemicals used were of reagent grade and were purified by the standard purification procedures. $VCl_3(N\text{-}2,6\text{-}Me_2C_6H_3)$,[1] $VCl_3(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(thf)_2$,[1] and $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(OAr)$ (Ar = $2,6\text{-}Me_2C_6H_3$, $2,6\text{-}{}^iPr_2C_6H_3$, and $2,6\text{-}{}^tBu\text{-}4\text{-}MeC_6H_2$)[2] were prepared according to the published method, and syntheses of $LiNC^tBu_2$, $LiNC^tBu(CH_2SiMe_3)$ were also according to the reported procedure. Elemental analyses were performed by using PE2400II Series (Perkin-Elmer Co.). Some analysis runs were employed twice to confirm the reproducibility in the independent analysis/synthesis runs.

All ^1H, ^{13}C, ^{31}P and ^{51}V NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for ^1H, 100.40 MHz for ^{13}C, 161.70 MHz for ^{31}P and 105.31 MHz for ^{51}V). All spectra were obtained in the solvent indicated at 25 ºC unless otherwise noted. Chemical shifts were given in ppm with references of $SiMe_4$ (δ 0.00, ^1H, ^{13}C), H_3PO_4 (δ 0.00, ^{31}P), and $VOCl_3$ (δ 0.00, ^{51}V). Coupling constants and half-width values, $\Delta\nu_{1/2}$, were described in Hz.

Synthesis of $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}Ph_2C_6H_3)$ (4). To a *n*-hexane solution (60 mL) containing $VCl_3(N\text{-}2,6\text{-}Me_2C_6H_3)$ (3.04 g, 11 mmol), 2,6-diphenylphenol (2.71 g, 11 mmol) was added at room temperature. The reaction mixture was allowed to heat to 50 ºC, and the mixture was stirred overnight. The mixture was then passed through Celite pad. Concentration of the solution and followed by cooling to -30 ºC gave a brown solid. Yield 4.29 g (80%). ^1H NMR ($CDCl_3$): δ 1.99 (s, 6H), 6.72 (d, 2H), 6.80 (t, 1H), 7.27 and 7.28 (s, 13H). ^{13}C NMR ($CDCl_3$): δ 17.6, 18.2, 126.1, 127.0, 127.4, 128.4, 129.6, 129.8, 129.9, 130.9, 136.9, 139.5, 165.5. Anal. Calcd for $C_{26}H_{22}Cl_2NOV$: C, 64.21; H, 4.56; N, 2.88%. Found: C; 64.71; H, 4.66; N, 2.78%.

Synthesis of $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)$ (5). To an Et_2O solution (100 mL) containing $VCl_3(N\text{-}2,6\text{-}Me_2C_6H_3)$ (4.15 g, 15 mmol), $LiNC^tBu_2$ (2.21 g, 15 mmol) was added at -30 ºC. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for additional 4 hours. The solvent was removed *in vacuo*, and the resultant brown tan residue was extracted with hot *n*-hexane (ca. 200 mL). The *n*-hexane extract was then dried *in vacuo*, and the resulting brown tan residue was treated by *n*-hexane (ca. 50 mL) at -30 ºC. The chilled solution placed in the freezer gave a brown solid. Yield 4.82 g (84%). ^1H NMR ($CDCl_3$): δ 1.35 (s, 18H, $(CH_3)_3C$-), 2.69 (s, 6H, CH_3), 6.94 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 18.9, 30.2, 47.1, 127.4, 128.2, 138.4, 169.3, 210.1. ^{51}V NMR ($CDCl_3$): δ 72.4 ($\Delta\nu_{1/2}$ = 237 Hz). Anal. Calcd for $C_{17}H_{27}N_2Cl_2V$: C, 53.55; H, 7.14; N, 7.35%. Found (1): C, 53.78; H, 7.26; N, 7.30%. Found (2): C, 53.71; H, 7.14; N, 7.26%.

Synthesis of $VCl_2(N\text{-}2,6\text{-}^iPr_2C_6H_3)(NC^tBu_2)$ (6). Synthesis of **6** was carried out by the same procedure as that in **5** except that $VCl_3(N\text{-}2,6\text{-}^iPr_2C_6H_3)(thf)_2$ (2.38 g, 5.0 mmol) and $LiNC^tBu_2$ (736 mg, 5.0 mmol) were used. Yield 1.83 g (85%). ^1H NMR ($CDCl_3$): δ 1.29 (d, 12H, $(CH_3)_2CH$-), 1.35 (s, 18H, $(CH_3)_3C$-), 4.18 (hep, 2H, $(CH_3)_2CH$-), 7.06 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 23.9, 28.3, 30.2, 31.5, 47.2, 122.4, 128.8, 148.8, 166.6, 209.9. ^{51}V NMR ($CDCl_3$): δ 87.4 ($\Delta\nu_{1/2}$ = 266 Hz). Anal. Calcd for $C_{21}H_{35}N_2Cl_2V$: C, 57.67; H, 8.07; N, 6.41%. Found: C, 57.94; H, 8.31; N, 6.20%.

Synthesis of $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)[NC(^tBu)CH_2SiMe_3]$ (7). Synthesis of **7** was carried out by the same procedure as that in **5** except that $VCl_3(N\text{-}2,6\text{-}MeC_2C_6H_3)$ (1.40 g, 5.0 mmol) and $LiNC^tBu(CH_2SiMe_3)$ (886 mg, 5.0 mmol) was used. Yield 1.73 g (84%). ^1H NMR ($CDCl_3$): δ 0.17 (s, 9H, $(CH_3)_3Si$-), 1.23 (s, 18H, $(CH_3)_3C$-), 2.12 (br, 2H), 2.67 (s, 6H), 6.90 (m, 2H). ^{13}C NMR ($CDCl_3$): δ -0.20, 18.7, 18.9, 28.1, 45.6, 126.9, 127.5, 137.6, 168.1, 204.4. ^{51}V NMR ($CDCl_3$): δ 23.4 ($\Delta\nu_{1/2}$ = 427 Hz). Anal. Calcd for $C_{17}H_{29}N_2SiCl_2V$: C, 49.63; H, 7.11; N, 6.81%. Found: C, 49.95; H, 7.00; N, 6.90%.

Synthesis of $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)(PMe_3)$ (8). To a $CDCl_3$ solution (ca. 0.5 mL) of **5** (76 mg, 0.20 mmol), PMe_3 (15 mg, 0.20 mmol) was added. All ^1H, ^{13}C, ^{31}P and ^{51}V

NMR spectra showed quantitative formation of the product. After removal of all volatiles, **5** was recovered quantitatively. The chilled solution (-30 °C) placed in the freezer afforded brown prism shape microcrystals suitable for crystal structure analysis. ^{1}H NMR (CDCl$_3$): δ 1.27 (d, 9H, P(C*H*$_3$)$_3$), 1.39 (s, 18H, (C*H*$_3$)$_3$C-), 2.51 (s, 6H, (C*H*$_3$)$_2$), 6.81 (t, 1H), 6.89 (d, 2H). ^{13}C NMR (CDCl$_3$): δ 13.9, 18.9, 30.9, 47.4, 126.6, 127.4, 138.6, 164.2, 190.0. ^{31}P NMR (CDCl$_3$): broad resonance at c.a. -1.8 ppm. The broad resonance in ^{31}P NMR spectrum indicated the equilibrium between PMe$_3$ coordinated and dissociated species in the solution. ^{51}V NMR (CDCl$_3$): δ -76.7 ($\Delta\nu_{1/2}$ = 900 Hz).

Synthesis of VCl$_2$(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(PMe$_3$) (9). To an Et$_2$O solution (50 mL) containing VCl$_3$(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(thf)$_2$ (2.39 g, 5.0 mmol), LiNC^{t}Bu$_2$ (736 mg, 5.0 mmol) was added at -30 ºC. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for additional 4 hours. The solution was removed *in vacuo*, and the resultant brown tan residue was extracted with hot *n*-hexane (ca. 200 mL). The *n*-hexane extract was concentrated *in vacuo*, and PMe$_3$ (380 mg, 5.0 mmol) was added. The chilled solution (-30 ºC) yielded 1.365 g (53%) of the product as the red crystals. ^{1}H NMR (CDCl$_3$): δ 1.17 (d, 12H, (C*H*$_3$)$_2$CH-), 1.25 (d, 9H, P(C*H*$_3$)$_3$), 1.41 (s, 18H, (C*H*$_3$)$_3$C-), 4.08 (hep, 2H, (CH$_3$)$_2$C*H*-), 7.00 (3H). ^{31}P NMR (CDCl$_3$): broad resonance at ca. -4.6 ppm. ^{51}V NMR (CDCl$_3$): δ -63.6 ($\Delta\nu_{1/2}$ = 914 Hz). Broad resonance in ^{31}P NMR spectrum would be due to the equilibrium between PMe$_3$ coordinated and dissociated species in the solution. Anal. Calcd for $C_{24}H_{44}Cl_2N_2PV$: C, 56.14; H, 8.64; N, 5.46%. Found ; C, 56.93; H, 8.67; N, 5.26%.

Synthesis of VCl$_2$(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(dmpe) (10). To an *n*-hexane solution (ca. 5 mL) of **5** (114 mg, 0.30 mmol), dmpe (46 mg, 0.305 mmol) was added. Cooling of the solution to -25 ºC yielded 80 mg (0.15 mmol, 50%) of red block microcrystals suitable for crystal structure analysis. ^{1}H NMR (CDCl$_3$): δ 1.28 (d, 6H, (C*H*$_3$)$_2$PCH$_2$-), 1.38 (s, 18H, (C*H*$_3$)$_3$C-), 1.49 (d, 6H, (C*H*$_3$)$_2$PCH$_2$-), 1.82 (br, 4H, Me$_2$PC$_2$*H*$_4$PMe$_3$), 2.70 (s, 6H, (C*H*$_3$)$_2$), 6.73 (t, 1H), 6.83 (d, 2H). ^{13}C NMR (CDCl$_3$): δ 10.9, 13.0, 20.3, 26.3, 31.0, 46.9, 125.1, 127.1, 140.6, 160.0, 188.4. ^{31}P NMR (CDCl$_3$): broad resonance at ca. 13, -10 ppm. ^{51}V NMR (CDCl$_3$): δ -365.2 ($\Delta\nu_{1/2}$ = 874 Hz). The broad resonances in ^{31}P NMR spectrum indicated the equilibrium between phosphine coordinated and (partially) dissociated species in the solution.

Synthesis of VCl(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-Me$_2$C$_6$H$_3$)$_2$ (11). To an Et$_2$O solution (10 mL) containing **1** (362 mg, 1.0 mmol), LiO-2,6-Me$_2$C$_6$H$_3$ (128 mg, 1.0 mmol) was added at -30 ºC. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for additional 3 hours. The solvent was removed *in vacuo*, and the resultant residue was extracted with *n*-hexane (ca. 30 mL). The hexane extract was concentrated *in vacuo*, and the chilled solution (-30 ºC) yielded 343 mg (77%) of the desired product. ^{1}H NMR (CDCl$_3$): δ 2.07 (s, 6H, Me$_2$), 2.36 (s, 12H, aryloxo-Me$_2$), 6.74 (s, 3H), 6.88 (t, 2H), 7.02 (d, 2H). ^{13}C NMR (CDCl$_3$): δ 17.4, 17.7, 123.9, 126.1, 127.2, 128.0, 128.3, 137.6, 167.0. ^{51}V NMR (CDCl$_3$): δ -207 ($\Delta\nu_{1/2}$ = 411 Hz). Anal. Calcd. for C$_{24}$H$_{27}$ClN$_3$O$_2$V: C, 64.36; H, 6.08; N, 3.13 %. Found (1): C, 64.51; H, 6.12; N, 3.07%. Found (2): C, 64.95; H, 6.07; N, 3.08%.

Synthesis of VCl(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)$_2$ (12). To an Et$_2$O solution (100 mL) containing VCl$_3$(N-2,6-Me$_2$C$_6$H$_3$) (2.76 g, 10.0 mmol), LiNC^{t}Bu$_2$ (2.94 g, 20.0 mmol) was added at -30 ºC. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for additional 7 hours. The solvent was removed *in vacuo*, and the resultant residue was extracted with hot *n*-hexane (ca. 200 mL). The extract was then placed in a rotary evaporator to remove *n*-hexane *in vacuo*, and the resultant residue was layered by *n*-hexane (ca. 50 mL) at -30 ºC. The chilled solution placed in the freezer gave a brown solid. Yield 3.54 g (73%). ^{1}H NMR (CDCl$_3$): δ 1.36 (s, 36H, (CH_3)$_3$C-), 2.52 (s, 6H, CH_3), 6.74 (t, 1H), 6.86 (d, 2H). ^{13}C NMR (CDCl$_3$): δ 19.0, 30.6, 46.0, 124.4, 126.9, 134.6, 164.9, 201.5. ^{51}V NMR (CDCl$_3$): δ -195 ($\Delta\nu_{1/2}$ = 432 Hz). Anal. Calcd. for C$_{26}$H$_{45}$N$_3$ClV: C, 64.25; H, 9.33; N, 8.65%. Found: C, 64.19; H, 9.75; N, 8.54%.

Synthesis of V(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-Me$_2$C$_6$H$_3$)$_3$ (13). Treatment of VCl$_3$(N-2,6-Me$_2$C$_6$H$_3$) (138 mg, 0.5 mmol) with three equivalents of LiO-2,6-Me$_2$C$_6$H$_3$ in

Et_2O caused precipitation of LiCl and color change of the solution from dark green to dark red. After 12 hours, all volatiles were removed under reduced pressure, and the product was extracted with hot *n*-hexane. Concentrating and cooling to room temperature afforded 241 mg (90%) of dark red crystalline. ^1H NMR ($CDCl_3$); δ 1.89 (s, 6H, C*H*$_3$), 2.33 (s, 18H, C*H*$_3$), 6.72 (s, 3H, N*Ar*), 6.82 (t, 3H, *p*-OAr), 7.00 (d, 6H, *m*-OAr). ^{13}C NMR ($CDCl_3$); δ 17.4, 17.5, 122.4, 126.6, 126.8, 127.1, 128.2, 136.2, 166.2. ^{51}V NMR ($CDCl_3$); δ -373 ($\Delta\nu_{1/2}$ = 395 Hz). Anal. Calcd. for $C_{32}H_{36}NO_3V$: C, 72.03; H, 6.80; N, 2.63%. Found: C, 72.13; H, 6.89; N, 2.58%.

Synthesis of $V(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_3$ (14). To an Et_2O solution (30 mL) containing $VCl_3(N\text{-}2,6\text{-}Me_2C_6H_3)$ (276 mg, 1.00 mmol), $LiNC^tBu_2$ (442 mg, 3.00 mmol) was added at -30 ºC. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for additional 10 hours. The solvent was removed *in vacuo*, and the resultant residue was extracted with hot *n*-hexane (ca. 40 mL). The *n*-hexane extract was placed in a rotary evaporator to remove the hexane *in vacuo*, and the resultant residue was layered by *n*-hexane (ca. 5 mL) at -30 ºC. The chilled solution placed in the freezer gave a brown solid. Yield 224 mg (38%). ^1H NMR ($CDCl_3$): δ 1.28 (s, 18H, (C*H*$_3$)$_3$C-), 2.50 (s, 6H, C*H*$_3$), 6.64 (t, 1H), 6.89 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 19.6, 30.7, 43.9, 121.0, 126.7, 133.1, 161.2, 187.9. ^{51}V NMR ($CDCl_3$): δ -387 ($\Delta\nu_{1/2}$ = 324 Hz). Anal. Calcd. for $C_{35}H_{63}N_4V$: C, 71.15 (69.11 + VC, vanadium carbide); H, 10.75; N, 9.48%. Found: C, 69.55; H, 10.58; N, 9.37%.

Synthesis of $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_2$ (15). Method 1. To an Et_2O solution (100 mL) containing **12** (2.95 g, 6.07 mmol), Et_2O solution of MeMgBr (3.0 M, 2.02 mL) was added dropwisely at -30 ºC. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for additional 4 hours. The solvent was removed *in vacuo*, and the resulting residue was extracted with hot *n*-hexane (ca. 100 mL). The *n*-hexane extract was concentrated *in vacuo*, and the chilled solution (-30 ºC) yielded 2.41 g (85%) of **15** as the red crystals. ^1H NMR ($CDCl_3$): δ 0.88 (br, 3H, V-CH_3), 1.31 (s, 18H, (C*H*$_3$)$_3$C-), 2.44 (s, 6H, C*H*$_3$), 6.67 (t, 1H), 6.86 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 19.4, 30.8, 36.7, 45.6, 122.2, 126.8, 134.1, 162.7, 199.4. ^{51}V NMR ($CDCl_3$): δ -138.8 ($\Delta\nu_{1/2}$ = 324 Hz). Anal. Calcd. for $C_{27}H_{48}N_3V$: C, 69.64; H, 10.39; N, 9.03%. Found: C, 69.16; H, 10.14; N, 9.09%.

Method 2 (one-pod synthesis). To an Et_2O solution (150 mL) containing VCl_3(N-2,6-$Me_2C_6H_3$) (1.38 g, 5.0 mmol), LiNC^tBu_2 (1.55 g, 10.5 mmol) was added at -30 ºC. The reaction mixture was warmed slowly to room temperature (25 ºC), and the mixture was stirred for additional 6 hours. An Et_2O solution of MeMgBr (3.0 M in Et_2O, 1.83 mL) was then added dropwisely into the reaction mixture pre-cooled at -30 ºC. The mixture was then warmed slowly to room temperature, and was stirred for additional 4 hours. The solution was then placed in a rotary evaporator *in vacuo* to remove solvent, and the resultant residue was extracted with hot *n*-hexane (ca. 200 mL). The *n*-hexane extract was then placed *in vacuo*, and the resultant residue was layered by *n*-hexane (ca. 20 mL) at -30 ºC. The chilled solution placed in the freezer gave red microcrystals. Yield 1.35 mg (58%).

Synthesis of V(CH_2SiMe_3)$_2$(N-2,6-$Me_2C_6H_3$)(NC^tBu_2) (16). To an *n*-hexane solution (75 mL) containing **1** (571 mg, 1.5 mmol), *n*-hexane solution of $LiCH_2SiMe_3$ (0.315 M, 10 mL) was added at 30 ºC. The mixture was then warmed slowly to room temperature, and then mixture was stirred for additional 6 hours. After the reaction, the mixture was filtered through Celite pad at -30 ºC, and the solvent was pumped off, leaving sticky dark red solid. Yield 694 mg (1.43 mmol, 95%), and the obtained solids were pure confirmed by NMR, elemental analysis. ^{1}H NMR ($CDCl_3$): δ 0.05 (s, 18H, $CH_2Si(CH_3)_3$), 1.29 (s, 18H, $(CH_3)_3C$-), 1.62 (br, 4H, CH_2SiMe_3), 2.56 (s, 6H, $(CH_3)_2$), 6.80 (t, 1H), 6.97 (d, 2H). ^{1}H NMR (C_6D_6): δ 0.27 (s, 18H, $CH_2Si(CH_3)_3$), 1.13 (s, 18H, $(CH_3)_3C$-), 1.87 (br, 4H, CH_2SiMe_3), 2.67 (s, 6H, $(CH_3)_2$), 6.74 (t, 1H), 6.91 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 1.74, 19.0, 30.1, 45.3, 71.1, 123.2, 126.6, 133.9, 163.5. 203.0. ^{51}V NMR (C_6D_6): δ 495.27 ($\Delta\nu_{1/2}$ = 216 Hz). Anal. Calcd for $C_{25}H_{49}N_2Si_2V$: C, 61.94 (59.46 + VC, vanadium carbide); H, 10.19; N, 5.78%. Found (1): C, 60.90; H, 10.19; N, 5.68%. Found (2): C, 59.87; H, 9.89; N, 5.85%.

Crystallographic analysis. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The selected crystal collection parameters are listed below (Table 2-8, 9), and the detailed results were described in the reports attached below. All structures were solved by direct method and expanded using Fourier techniques,[9] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **3a, 4a** were performed using the CrystalStructure[10,11] crystallographic software package.

Table 2-8. Crystal and Data Collection Parameters.[a]

Complex	**5**	**8**	**9**	**10**
Formula; Formula weight	$C_{17}H_{27}Cl_2N_2V$; 381.26	$C_{20}H_{36}Cl_2N_2PV$; 457.34	$C_{24}H_{44}Cl_2N_2PV$; 513.45	$C_{23}H_{43}Cl_2N_2P_2V$; 531.40
Habits	brown, prism	brown, prism	red, prism	red, block
Crystal size (mm)	0.30×0.67×0.50	0.42×0.33×0.33	0.83×0.25×0.13	0.33×0.33×0.13
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1 (#2)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	C2/c (#15)
a (Å)	9.814(4)	9.838(1)	14.586(4)	29.520(3)
b (Å)	9.861(4)	12.565(2)	10.922(2)	10.9241(5)
c (Å)	11.505(5)	20.509(3)	18.210(5)	18.578(1)
β (deg)	111.44(4)	95.857(4)	95.192(9)	109.683(3)
V (Å^3)	971.9(7)	2521.9(6)	2889(1)	5641.0(7)
Z value	2	4	6	8
D_{calcd} (g/cm^3)	1.303 g/cm^3	1.204 g/cm^3	1.771 g/cm^3	1.251 g/cm^3
F_{000}	400.00	968.00	1644.00	2256.00
Temp (K)	243	243	243	243
λ (Mo Kα) (Å)	0.71069	0.71069	0.71075	0.71069
No. of reflections measured: (R_{int})	total: 9512	total: 5592	total: 22680	total: 6789
	unique: 4443 (0.037)	unique: 5398 (0.000)	unique: 6544 (0.183)	unique: 6448 (0.000)
No. of observations ($I > -3.00\delta(I)$)	3819	2912	1253	4052
No. of variables	295	286	315	350
Residuals: R1; Rw	0.036; 0.045	0.057; 0.068	0.051; 0.059	0.043; 0.049
GOF	1.056	1.064	1.179	0.979
Max (minimum) peak in final diff. map (e-/ Å^3)	0.24 (-0.65)	0.52 (-0.33)	0.34 (-0.21)	0.63 (-0.31)

[a] Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\Sigma w(|F_o|-|F_c|)^2$ (w = Least squares weights, Chebychev polynomial). Standard deviation of an observation of unit weight: $[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$ (N_o = number of observations, N_v = number of variables).

Table 2-9. Crystal and Data Collection Parameters.[a]

Complex	**12**	**15**
Formula; Formula weight	$C_{26}H_{45}ClN_3V$; 486.06	$C_{27}H_{48}N_3V$; 465.64
Habits	brown, block	red, platelet
Crystal size (mm)	0.72×0.50×0.45	0.80×0.50×0.25
Crystal system	monolinic	triclinic
Space group	$P2_1/c$ (#14))	P-1 (#2)
a (Å)	8.908(6)	9.755(3)
b (Å)	24.61(1)	11.703(5)
c (Å)	12.78(1)	14.304(6)
β (deg)	90.70(7)	104.86(1)
V ($Å^3$)	2802(3)	1456(1)
Z value	4	2
D_{calcd} (g/cm^3)	1.152 g/cm^3	1.062 g/cm^3
F_{000}	1048.00	508.00
Temp (K)	243	243
λ (Mo Kα) (Å)	0.71065	0.71065
No. of reflections measured: (R_{int})	total: 14955	total: 13544
	unique: 5515 (0.045)	unique: 6503 (0.026)
No. of observations ($I > -3.00\delta(I)$)	3233	5233
No. of variables	325	328
Residuals: R1; Rw	0.067; 0.075	0.059; 0.071
GOF	1.064	1.036
Max (minimum) peak in final diff. map (e-/ $Å^3$)	0.37 (-0.42)	0.40 (-0.39)

[a] Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\Sigma w(|F_o|-|F_c|)^2$ (w = Least squares weights, Chebychev polynomial). Standard deviation of an observation of unit weight: $[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$ (N_o = number of observations, N_v = number of variables)

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3

Reaction of (arylimido)vanadium(V)-methyl complex with alcohols, thiols, and borates: Implications for unique reactivity toward alcohols

Transition metal-alkyl complexes are the most important reagents or intermediates in stoichiometric/catalytic organic reactions, as well as in olefin polymerization.[1,2] Synthesis and reaction chemistry of transition metal-alkyl complexes have been important in the design of efficient catalysts as well as for obtaining a better understanding of the organic reactions, especially with regard to catalytic cycles or reaction pathways. Certain classical Ziegler-type vanadium catalysts afford ultra-high-molecular-weight polymer with a relatively narrow polydispersity through rapid propagation in olefin coordination/insertion polymerization, and provide propylene-methyl methacrylate diblock copolymers by living polymerization.[2e,3,4] Therefore, synthesis and reaction chemistry of vanadium complexes, especially (cationic) alkyl complexes, have attracted considerable attention.[5-8] Some reactions concerning (cationic) vanadium-alkyl complexes that contain one or two cyclopentadienyl (Cp') ligands have been described in the literature[5a-c] with regard to titanocene (zirconocene) or half-titanocene.[9] However, there are still few examples of the synthesis of vanadium-alkyls that do not include Cp' ligand. This may be due to the fact that these vanadium-alkyls tend to be reactive and/or thermally labile and reductions to the lower oxidation states were often observed in reaction with organometallic reagents.[7]

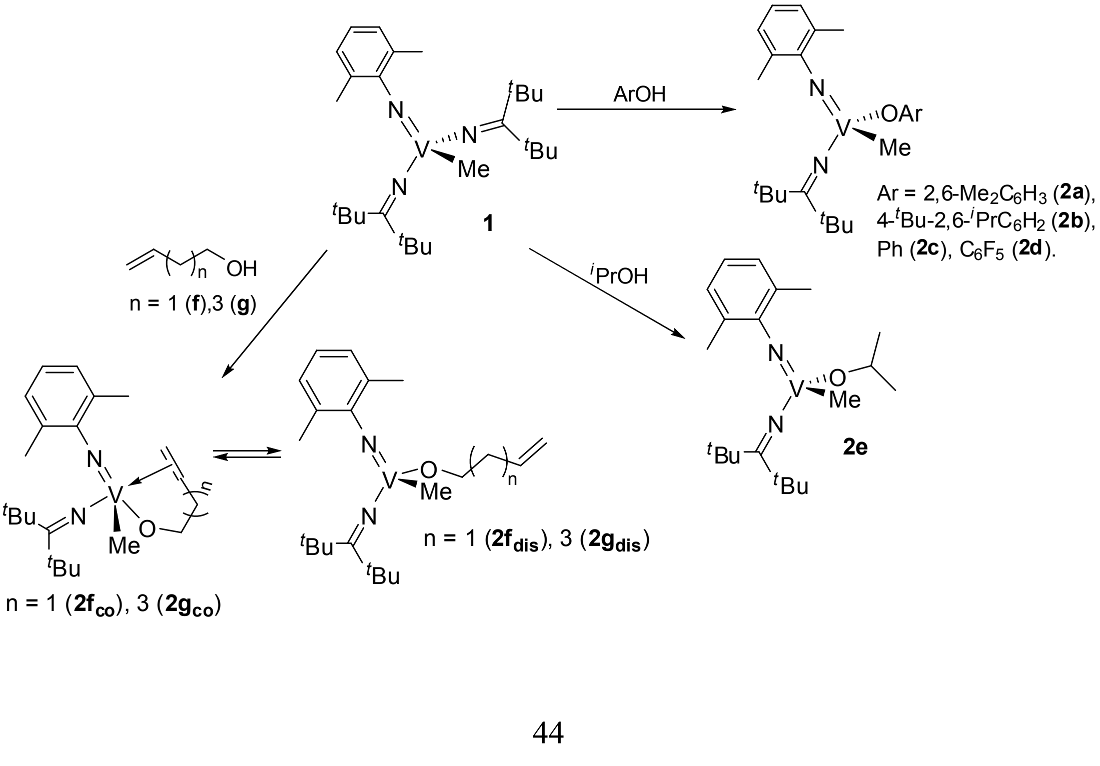
In general, metal-alkyl bonds, especially those with the early transition metals, are more nucleophilic than those with the late transition metals, and are thus highly reactive toward Brønsted/Lewis acid.[1,9,10] For instance, the cationic alkyl complexes, which have been proposed to be the catalytically active species for olefin coordination polymerization, are generated from their dialkyl analogues by reacting them with cocatalysts via facile protonolysis or alkyl abstraction.[9] Some organometallic complexes can thus be grafted onto a silica surface through the reaction of alkyl compounds with silanol groups on the surface.[9c,11,12]

This chapter describes fundamental reaction chemistry of vanadium-methyl complex of the type, $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_2$ (**1**), with various acids such as alcohols, thiols, and borates.

3.1 Reaction of $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_2$ with alcohols

Reactions of **1** with one equivalent of phenols exclusively afforded another vanadium(V)-methyl complex of the type, $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)(OAr)$ [Ar = $2,6\text{-}Me_2C_6H_3$ (**a**), $4\text{-}^tBu\text{-}2,6\text{-}^iPr_2C_6H_2$ (**b**), Ph (**c**), C_6F_5 (**d**)], by replacement with the ketimide ligand (Scheme 3-1). The reaction with the methyl group did not occur under these conditions, although **1** is a rather electron-deficient vanadium(V)-alkyl complex and no significant differences were observed in the corresponding resonances (in ^1H and ^{13}C NMR spectra) or in the V-Me bond distance (2.064 Å) from those of reported vanadium-methyl complexes.[5] It should be noted that the reaction with the methyl group did not occur even with C_6F_5OH. Treatment of **1** with ^iPrOH afforded $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)(O^iPr)$ (**2e**) and the reaction with the methyl group did not take place.

Scheme 3-1



The reaction of the ketimide with alkoxide was also observed in the reaction of **1** with 3-buten-1-ol or 5-hexen-1-ol in *n*-hexane, to give the corresponding $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)[OCH_2(CH_2)_nCH{=}CH_2]$ [n = 1 (**2f**), 3 (**2g**)] exclusively (Scheme 3-1).[13-14] Both **2f** and **2g** gave two resonances in the ^{51}V NMR spectra (-103 and -231 ppm for **2f**, -105 and -237 ppm for **2g**), and the ratios were highly dependent upon the temperature (Figure 3-1, 2). The species in the upfield was observed exclusively at 60 °C, and was identified as olefin-dissociated species (**2f**$_{\mathbf{dis}}$ and **2g**$_{\mathbf{dis}}$) based on the ^1H NMR spectra, not only because the resonances observed at 4.5-6.0 ppm were identical to those in $Cp^*TiMe(O\text{-}2,6\text{-}^iPr_2C_6H_3)[OCH_2(CH_2)_nCH{=}CH_2]$ (n = 1, 3) and $Cp^*Ti(CF_3SO_3)(O\text{-}2,6\text{-}^iPr_2C_6H_3)[OCH_2(CH_2)_nCH{=}CH_2]$,[14] but also because that the reaction of **1** with *n*-hexanol afforded a species observed at -238 ppm in ^{51}V NMR spectrum with accompanying the formation of HNC^tBu_2. In contrast, the species observed in the downfield became dominant below -40 °C, and it was assumed that this would be the olefin coordinated species (**2f**$_{\mathbf{co}}$ and **2g**$_{\mathbf{co}}$). The insertion did not take place under these conditions. ΔG values of 8.5 kcal/mol for **2f** and 8.6 kcal/mol for **2g** were thus assumed from the ^{51}V NMR spectra measured at various temperatures (-60 to 60 °C, Figure 3-3). There was no significant difference in the effect of the methylene length in alkene-1-ol (3-buten-1-ol vs 5-hexen-1-ol) on the integration ratios (equilibrium) between the coordinated and dissociated species, and these findings were somewhat different from those observed in $Cp^*Ti(CF_3SO_3)(O\text{-}2,6\text{-}^iPr_2C_6H_3)[OCH_2(CH_2)_nCH{=}CH_2]$ (n = 1,3) whereas olefin did not coordinate with the titanium.[14]

The complex **1** showed unique reactivity toward alcohols (phenols) affording various methyl complexes by the ligand exchange between the ketimide and alkoxo (aryloxo) groups exclusively without accompanying protonolysis of the methyl group with the alcohols (phenols). The results clearly indicated that the methyl group in **1** is not reactive toward alcohol under these conditions, although ordinary metal-alkyl bonds (especially in early transition metals) are readily reacted with alcohol to give alkoxide (aryloxide).[10-12]

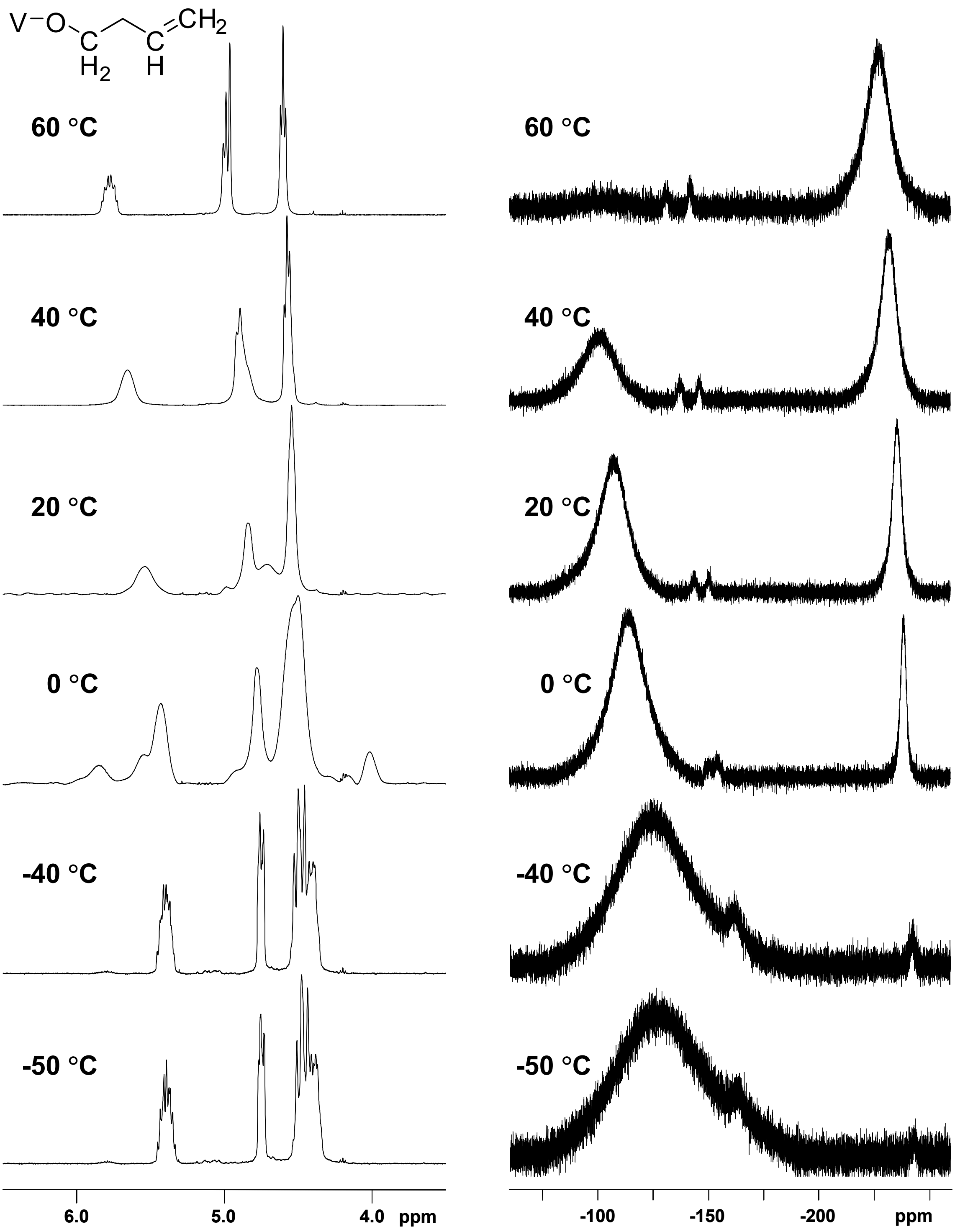


Figure 3-1. ^{1}H (3.5-6.5 ppm, left) and ^{51}V NMR spectra (right) for **2f** in $CDCl_3$.

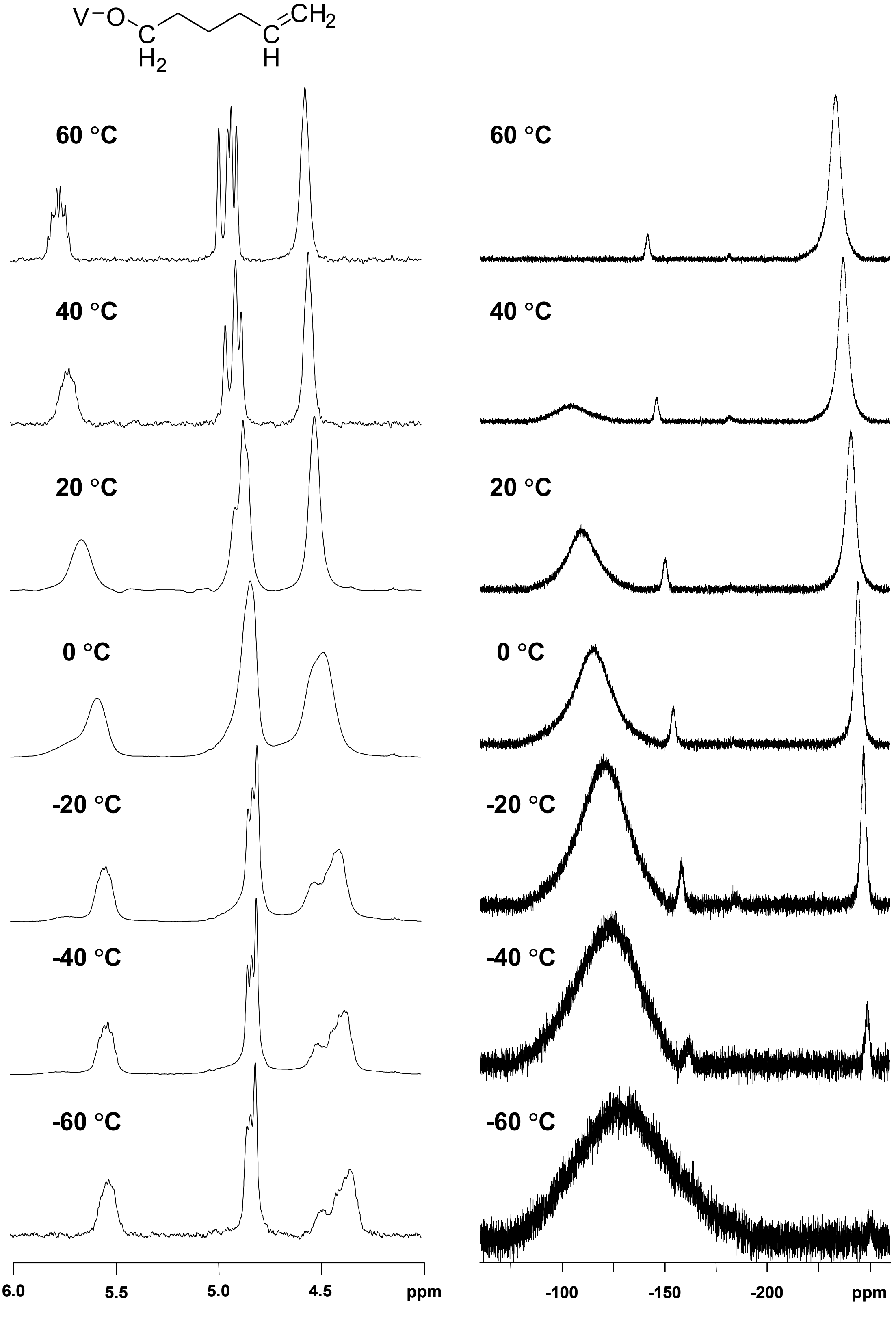
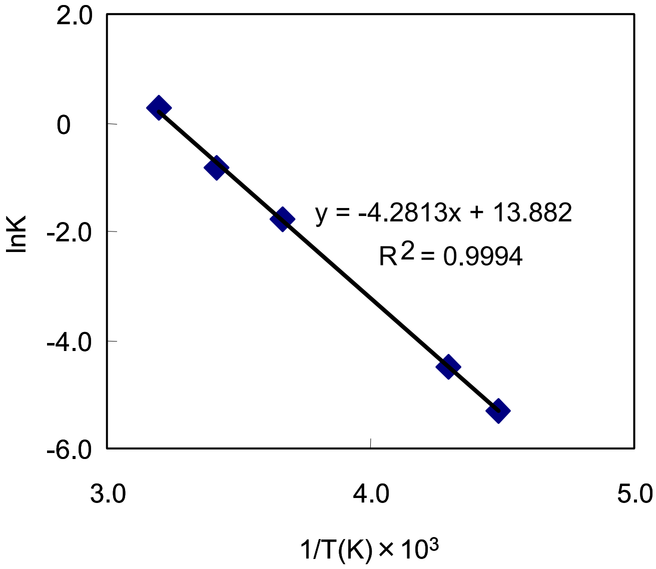


Figure 3-2. ^{1}H (4.0-6.0 ppm, left) and ^{51}V NMR spectra (right) for **2g** in $CDCl_3$.

(1) For **2f**.

Temp. / °C	Integration Ratio by ^{51}V NMR -103/-231 (ppm)
40	1.3
20	0.41
0	0.18
-40	0.011
-50	0.005

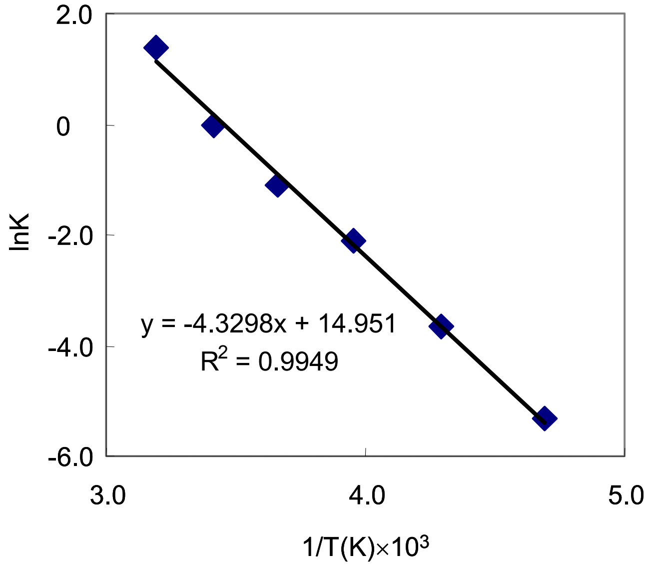


ΔG = -RTlnK, plots of lnK vs 1/T (shown above), $-\Delta G/R = -4265.5$

$\Delta G = -(-4265.5)\times 1.987 \approx$ 8.5 kcal/mol

(2) For **2g**.

Temp. / °C	Integration Ratio by ^{51}V NMR -105/-237 (ppm)
40	4
20	1
0	0.33
-20	0.12
-40	0.026
-60	0.005



ΔG = -RTlnK, plots of lnK vs 1/T (shown above), $-\Delta G/R = -4329.8$

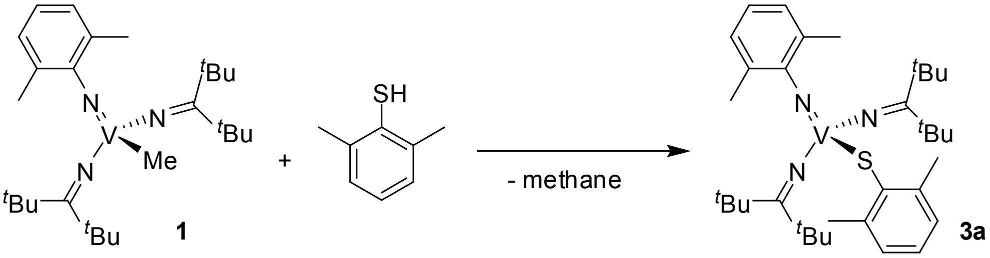
$\Delta G = -(-4329.8)\times 1.987 \approx$ 8.6 kcal/mol

Figure 3-3. Temperature dependence in the estimated ratios of two species in **2f** (1) and **2g** (2) observed in ^{51}V NMR spectra in $CDCl_3$.

3.2 Reaction of $VMe(N-2,6-Me_2C_6H_3)(NC^tBu_2)_2$ with thiols

To examine why the methyl group in **1** did not react with alcohol, the reaction of **1** with thiols were performed. The reaction of **1** with one equivalent of $2,6-Me_2C_6H_3SH$ in *n*-hexane afforded $V(N-2,6-Me_2C_6H_3)(NC^tBu_2)_2(S-2,6-Me_2C_6H_3)$ (**3a**) via cleavage of V-Me bond by facile protonolysis (75% yield, Scheme 3-2). The product was identified by ^1H, ^{13}C, and ^{51}V NMR spectra.

Scheme 3-2



The single crystal suitable for X-ray analysis of thiolate complex **3a** was obtained by cooling the *n*-hexane solution to -30 °C. The structure is shown in Figure 3-4 and the selected bond distances and angles are summarized in Table 3-1. The crystal structure showed that **3a** folds a distorted tetrahedral geometry around the vanadium metal center, and the $V-N(C^tBu_2)$ distances (1.808-1.819 Å) were intermediate in length between the chloride analogue, $VCl(N-2,6-Me_2C_6H_3)(NC^tBu_2)_2$, (1.803-1.805 Å)[8b] and the methyl analogue (**1**, 1.825-1.827). The V-S distance (2.300 Å) is slightly longer than that in $V(N-4-C_6H_4Cl)[N(CH_2CH_2S)_3]$ (2.251 Å)[15b] and $[V(CH_3CN)_6][VCl_2\{O(CH_2CH_2S)_2\}]_2$,[15c] and is close to those in five-coordinated vanadium(III) thiolate complexes, $V[P(C_6H_4-2-S)_3]$(1-methyl-imidazole), (average 2.302 Å),[16] and $V(O-2,6-^iPr_2C_6H_3)\{O(CH_2CH_2S)_2\}$(pyridine) (average 2.298 Å),[15a] and within the range expected for V–S single bonds and comparable to those in other vanadium(III) thiolate complexes.[17]

The reaction of **1** with $n-C_6H_{13}SH$ in *n*-hexane gave

$V(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_2(S\text{-}n\text{-}C_6H_{13})$ (**3b**) as the sole product, as confirmed by both ^1H and ^{13}C NMR spectra, via cleavage of the V-Me bond by facile protonolysis. These findings clearly indicate that the reaction mechanism should differ between alcohol and thiol, and the reaction with thiols favored protonolysis with V-Me bonds as seen in ordinary metal-alkyl complexes with early transition metals.[1,9,10]

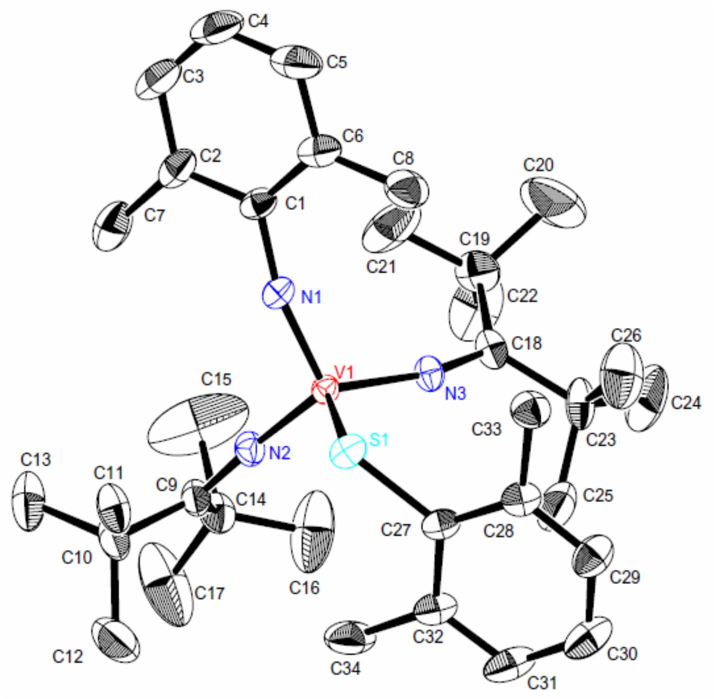


Figure 3-4. ORTEP drawing (30% probability ellipsoids) for **3a**. All hydrogen atoms are omitted for clarity.

Table 3-1. Selected Bond Distances (Å) and Angles (°) for **3a**.

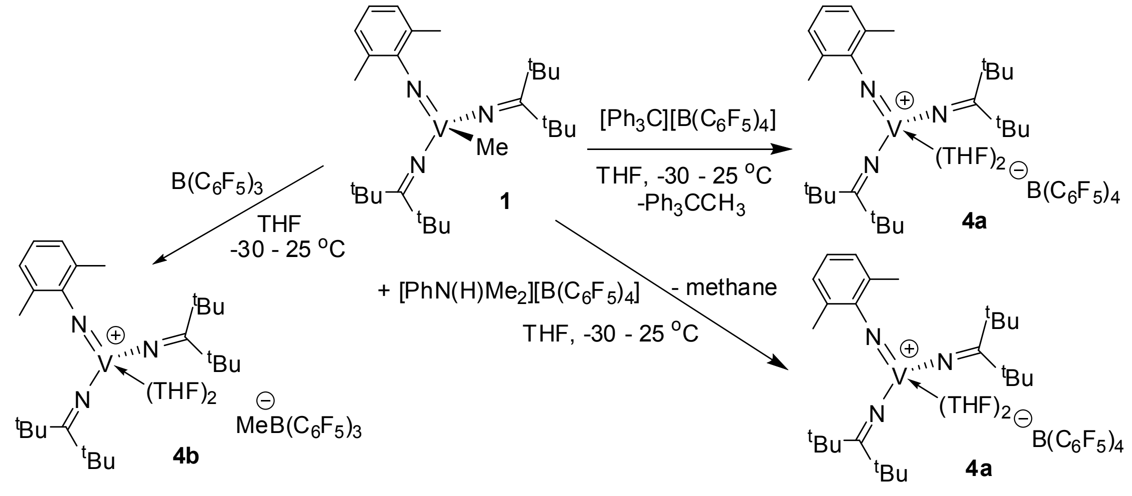
Bond Distances in Å							
V(1)-S(1)	2.300(4)	S(1)-C(27)	1.775(2)	V(1)-N(1)	1.661(4)	V(1)-N(2)	1.808(3)
V(1)-N(3)	1.819(2)	N(1)-C(1)	1.389(2)	N(2)-C(9)	1.267(2)	N(3)-C(18)	1.267(2)
Bond Angles in °							
N(1)-V(1)-S(1)	100.77(7)	N(2)-V(1)-S(1)	116.22(7)	N(3)-V(1)-S(1)	112.21(6)		
N(2)-V(1)-N(1)	107.95(9)	N(3)-V(1)-N(1)	112.09(8)	N(3)-V(1)-N(2)	107.49(8)		
V(1)-N(1)-C(1)	166.55(2)	V(1)-N(2)-C(9)	172.8(2)	V(1)-N(3)-C(18)	166.84(2)		
V(1)-S(1)-C(27)	108.14(8)						

3.3 Reactions of $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_2$ with various borates

As described above, cleavage of the V-Me bond in **1** was favored in the reaction with thiols whereas the exclusive ligand exchanges with the ketimide ligand were seen in the reaction with various alcohols. It is well known that the cationic alkyl complexes, which have been proposed to be catalytically active species for olefin coordination polymerization, are generated from its dialkyl analogues by reacting with borates.[9] To examine the detailed reactivity of the V-Me bond in **1**, reactions with borates (strong Brønsted acid) were conducted in this study.

The reaction of **1** with one equivalent of $[PhN(H)Me_2][B(C_6F_5)_4]$ in THF afforded cationic $[V(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu)_2(THF)_2][B(C_6F_5)_4]$ (**4a**) via protonolysis of the V-Me bond and free $PhNMe_2$. The exclusive formation of these compounds was confirmed by ^1H and ^{51}V NMR spectroscopy (Scheme 3-3).

Scheme 3-3



The same compound (**4a**) could be isolated by reaction of **1** with one equivalent of $[Ph_3C][B(C_6F_5)_4]$, a strong alkyl abstracting reagent, and the quantitative formations of **4a** and Ph_3CCH_3 was confirmed by ^1H and ^{51}V NMR spectra. Compound (**4a**) could be cleanly isolated (90%) and was identified by the ^1H, ^{13}C, ^{19}F, and ^{51}V NMR spectra and elemental analysis. Based on the results of both ^{1}H NMR and elemental analysis, two THF molecules per vanadium remained in the resultant red microcrystals. The reaction of **1** with $B(C_6F_5)_3$ also gave similar clean ^{1}H and ^{51}V NMR spectra in addition to the resonances ascribed to the formation of $MeB(C_6F_5)_3$ (0.48 ppm, B-Me), which strongly suggested the exclusive formation of $[V(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu)_2(THF)_2][MeB(C_6F_5)_3]$ (**4b**).

Moreover, the ^{1}H and ^{51}V NMR spectra for the reaction of **2a** with one equivalent of $[PhN(H)Me_2][B(C_6F_5)_4]$ also suggested the exclusive formation of the corresponding cationic species, of the type $[V(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)(O\text{-}2,6\text{-}Me_2C_6H_3)(THF)_2][B(C_6F_5)_4]$ (**4c**), *via* protonolysis of a V-Me group accompanied by liberation of free $PhNMe_2$. These results clearly indicate that cleavage of the V-Me bond was favored in all cases.

Red block microcrystals of **4a** suitable for X-ray crystallographic study were obtained from a chilled (-30 °C) and concentrated THF solution containing **4a** layered by *n*-hexane (Figure 3-5). Selected bond distances and angles for **4a** are summarized in Table 3-2. The crystallographic analysis of **4a** indicates that **4a** folds a pseudo-tetrahedral geometry around the vanadium center with the coordination of one THF molecule. The position of another THF molecule could not be determined probably because the THF molecule might be located among crystal lattices. The $V\text{-}N(C^tBu_2)$ distances (1.802-1.808 Å) are comparable to those found in $VCl(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_2$ (see Chapter 2) and somewhat shorter than those in **1**. The V-O distance (2.007 Å) is similar to that found in four-coordinate cationic vanadium(IV) alkylidene complex (2.000 Å), $[(Nacnac)V{=}CH^tBu(THF)](BPh_4)$ and [Nacnac = $\{ArNC(Me)CHC(Me)NAr\}^-$, Ar = $2,6\text{-}^iPr_2C_6H_3$],[18] and somewhat shorter than that found in THF-coordinated vanadium(III) complexes containing amine tris(phenolate) and triamidoamine ligands (2.107-2.152 Å).[19]

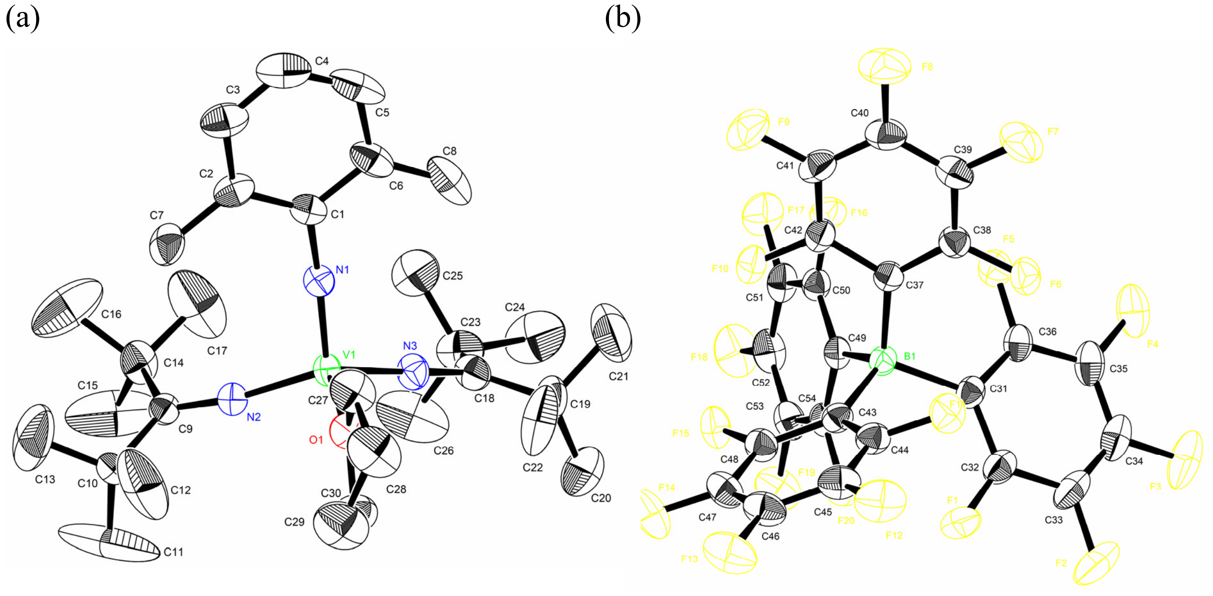


Figure 3-5. Molecular structure of **4a**. (a)The cation (left) and (b) the anion (right).

Table 3-2. Selected Bond Distances (Å) and Angles (º) for **4a.**

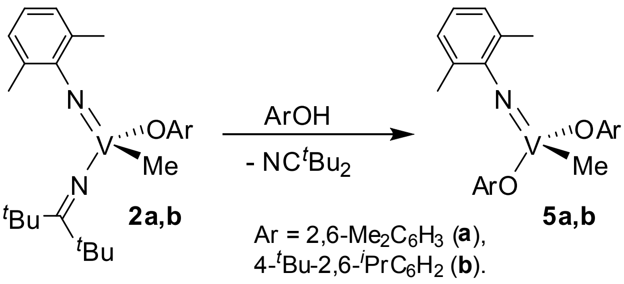
Bond Distances in Å					
V(1)-O(1)	2.007(2)				
V(1)-N(1)	1.655(2)	V(1)-N(2)	1.808(2)	V(1)-N(3)	1.802(2)
N(1)-C(1)	1.385(4)	N(2)-C(9)	1.264(4)	N(3)-C(18)	1.260(4)
Bond Angles in º					
O(1)-V(1)-N(1)	100.40(12)	O(1)-V(1)-N(2)	107.27(10)		
O(1)-V(1)-N(3)	109.02(12)	N(1)-V(1)-N(2)	108.11(13)		
N(1)-V(1)-N(3)	107.65(13)	N(2)-V(1)-N(3)	122.22(13)		
V(1)-N(1)-C(1)	174.6(2)	V(1)-N(2)-C(9)	171.6(2)		
V(1)-N(3)-C(18)	178.9(3)				

3.4 Mechanistic studies on the reaction of VMe(N-2,6-$Me_2C_6H_3$)(NC^tBu_2)$_2$ with alcohol: Examination of the unique reactivity of vanadium-methyl bonds toward alcohol

As described above, the V-Me bonds in **1** reacted with thiols and borates took place, but not with alcohols. To explain this unique reactivity of **1**, especially toward alcohol, the reaction chemistry was examined in more detail.

When one equivalent of 2,6-$Me_2C_6H_3OH$ was added to a the Teflon-sealed NMR tube containing a $CDCl_3$ solution of **2a**, the formation of HNC^tBu_2 (1.31 and 9.39 ppm) was observed in the ^1H NMR spectrum. In contrast, the generation of methane was not observed even after 24 hours. A new resonance at -64 ppm was observed in the ^{51}V NMR spectrum in addition to **2a** (-185 ppm) in the above $CDCl_3$ solution, and the conversion of **2a** reached 60% after 24 h (at 25 ºC). This result is in unique contrast to that in the reaction of **1** with 2,6-$Me_2C_6H_3OH$, since the reaction was completed within 30 minutes (starting at -30 to 25 ºC). The quantitative conversion of **2a** could be achieved when two equivalents of 2,6-$Me_2C_6H_3OH$ were added to **2a** after 24 hours (at 25 °C). The formation of methane was not observed even if two equivalents of 2,6-$Me_2C_6H_3OH$ were added to **2a**. The ^1H NMR spectra for the resultant compound showed resonances that could be assigned to the ketimide/aryloxo exchange reaction product, $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)_2$ (**5a**), according to the integration ratio of the aryloxo group and the arylimido group, in addition to a resonance at 2.11 ppm ascribed to the vanadium-methyl bond along with disappearance of the ketimide ligand (Scheme 3-4). Although the exclusive formation of **5a** could be confirmed by both ^1H and ^{51}V NMR spectra, however, an attempt for isolation of **5a** as microcrystals was unsuccessful probably due to the improved solubility in organic solvent and/or contamination of residual phenol in trace amount.

Scheme 3-4



2a,b

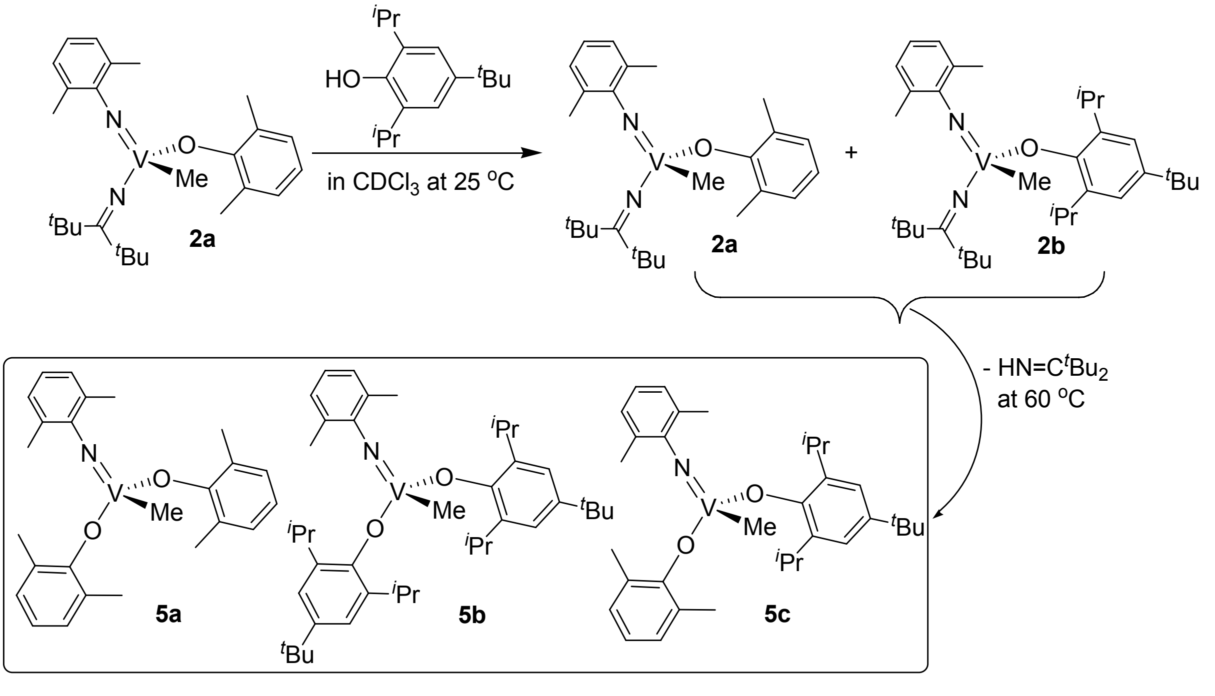
5a,b

Ar = 2,6-$Me_2C_6H_3$ (**a**), 4-^tBu-2,6-$^iPrC_6H_2$ (**b**).

The formation of **5a** could also be confirmed by a comparison of the resonances in ^{1}H and ^{51}V NMR spectra for the bis(aryloxo)-chloro analogue, $VCl(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)_2$ (**6**), and the tris(aryloxo) analogue, $V(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)_3$ (**7**) (ascribed in Chapter 2). The vanadium-methyl bond in the bis(aryloxo) analogue (**5a**) was stable even in the presence of additional two equivalents of $2,6\text{-}Me_2C_6H_3OH$, and no reaction took place upon stirring for long hours (after 24 hours at 25 °C). The formation of $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}4\text{-}{}^{t}Bu\text{-}2,6\text{-}{}^{i}Pr_2C_6H_2)_2$ (**5b**) was also confirmed by the reaction of **2b** with $4\text{-}{}^{t}Bu\text{-}2,6\text{-}{}^{i}Pr_2C_6H_2OH$ under the similar conditions (12 hours).

To examine the unique reactivity of the Me group in both **2a** and **5a** toward phenol, the reaction of **2a** with $4\text{-}{}^{t}Bu\text{-}2,6\text{-}{}^{i}Pr_2C_6H_2OH$ (and **2b** with $2,6\text{-}Me_2C_6H_3OH$) were conducted according to Scheme 3-5, and the results were shown in Figure 3-6.

Scheme 3-5



Rapid scrambling of **2a** and **2b** was seen when **2a** was treated with one equivalent of 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH in CDCl$_3$ at 25 ºC (Figure 3-6b), and the resultant solution eventually gave a ca. 1:1 mixture of **2a** and **2b** confirmed by ^{1}H and ^{51}V NMR spectra (within 30 minutes at 25 °C). The solution gave three species confirmed by the ^{51}V NMR spectrum (-64, -70 and -78 ppm) in approximately 1:2:1 ratio, respectively (Figure 3-6c), upon heating at 60 °C for 12 hours. The resonances observed at -64 and -78 ppm could be assigned as **5a** and **5b,** respectively, and it was estimated that the species at -70 ppm could be assigned as the mixed bis(aryloxo) complex, VMe(N-2,6-Me$_2$C$_6$H$_3$)(O-4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$)(O-2,6-Me$_2$C$_6$H$_3$) (**5c**) based on the ^{1}H NMR spectrum. Similar results were observed when **2b** was treated with 2,6-Me$_2$C$_6$H$_3$OH in CDCl$_3$, as shown in Figure 3e-h. The reaction with the Me group did not occur in both **2a-b** and **5a-b** even after 12 hours at 60 ºC.

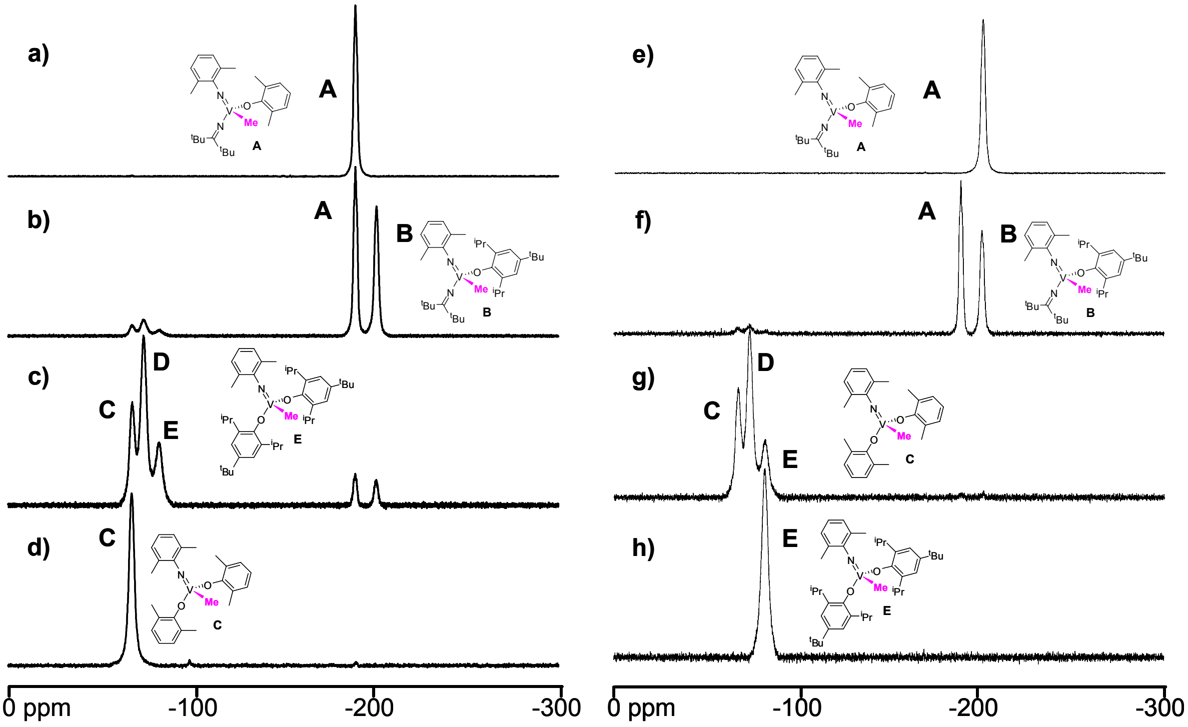
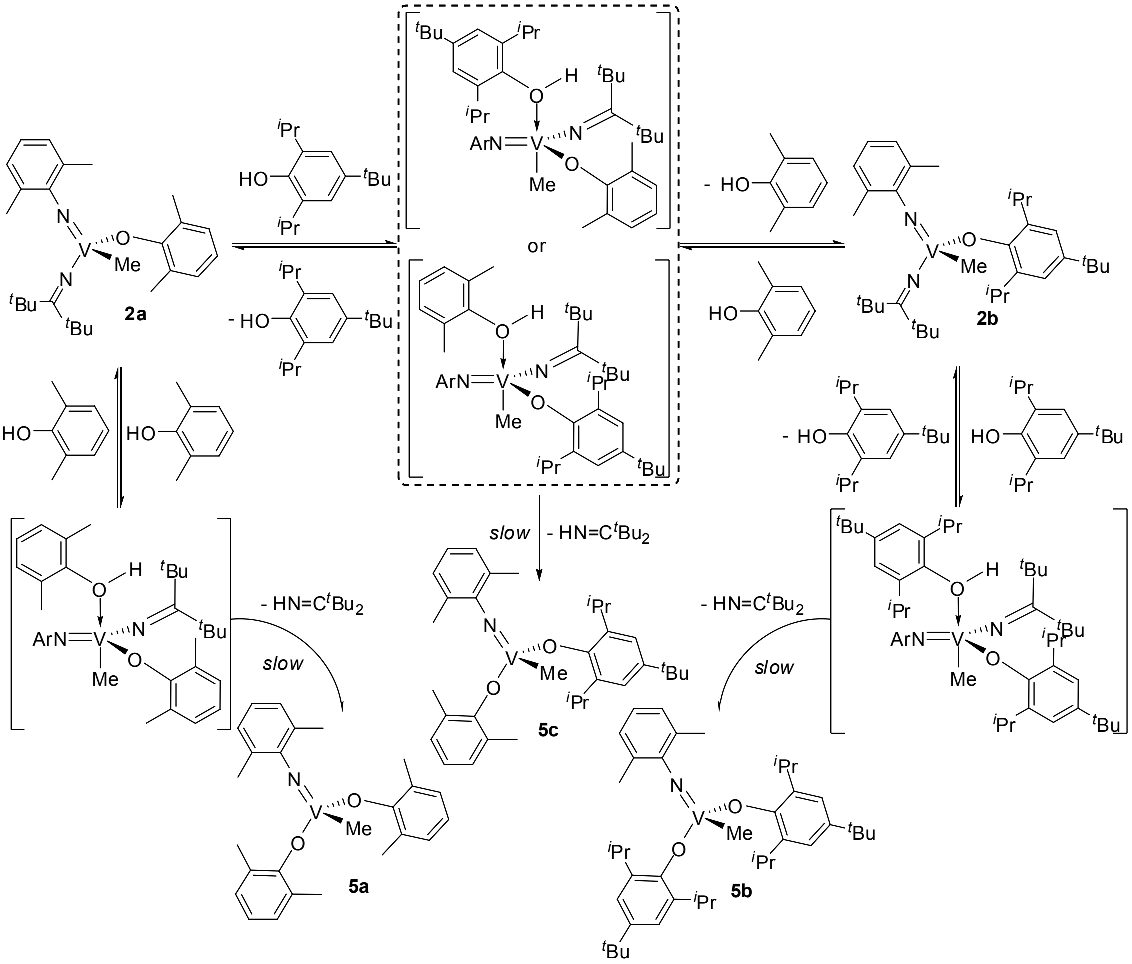


Figure 3-6. ^{51}V NMR spectra in CDCl$_3$ of the reaction of **2a** with 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH [a-d; a) **2a**, b) reaction mixture of **2a** with 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH (after 30 minutes at 25 ºC), c) reaction mixture of **2a** with 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH (at 60 ºC for additional 12 hours after b), and d) **5a**.], and **2b** with 2,6-Me$_2$C$_6$H$_3$OH [e-h; e) **2b**, f) reaction mixture of **2b** with 2,6-Me$_2$C$_6$H$_2$OH (after 30 minutes at 25 ºC), g) reaction mixture of **2b** with 2,6-Me$_2$C$_6$H$_2$OH (at 60 ºC for additional 12 hours after f), and h) **5b**.]

These results clearly indicate the unique reactivity of both **1** and **2a**,**b** toward alcohol according to a scheme shown in Scheme 3-6. Both phenol-scrambling and the phenol/ketimide exchange reaction should be preferred when the phenol approaches to the electrophilic vanadium metal center *trans* to the Me group (NNN face in **1** or NNO face in **2a**,**b**, and not the NNC faces in **1** or **2a**,**b**), to give five-coordinated trigonal bipyramidal intermediates (shown in brackets in Scheme 3-6). The reaction with the Me group would not occur if the reaction takes place via this proposed intermediate. The similar assumption was also reported by Schrock et al.[20] in the alkoxide exchange reaction of $Mo(NAr)(CH^tBu)(CH_2{}^tBu)(OAr)$ with ROH (OR = $OCMe_3$, OAd, OC_6F_5; Ad = adamantyl) and assumed the similar intermediate.

Scheme 3-6



Simple PM3 estimation also suggested that coordination of phenol into *trans* to the methyl group seemed more stable ($\Delta E_{\text{coord}} = 3.31$ kcal/mol) than the others [$\Delta E_{\text{coord}} = -1.97$ and -24.88 kcal/mol for the proposed intermediates when the phenol coordinate to *trans* to arylimido, ketimide, respectively] [$\Delta E_{\text{coord}} = E_{\text{(complex 1)}} + E_{\text{(2,6-Me2C6H3OH)}} - E_{\text{(proposed intermediate)}}$; $E_{\text{(complex 1)}}$, $E_{\text{(2,6-Me2C6H3OH)}}$, $E_{\text{(proposed intermediate)}}$ are heat of formation for complex **1**, 2,6-$Me_2C_6H_3OH$, and the proposed intermediates, respectively for three proposed intermediates in the reaction: equilibrium geometry at ground state with semi-empirical PM3, geometry optimization, RHF/PM3D Spartan ’04 for Windows (Wavefunction Inc.)]. In contrast, the same estimation suggested that the coordination of 2,6-$Me_2C_6H_3SH$ into the vanadium in **1** caused destabilization in all cases ($\Delta E_{\text{coord}} = -12.35$ to -20.88 kcal/mol). Thus, simple protonation should be favored. These results may also suggest the formation of five coordinated trigonal bipyramidal species by coordination of the phenol into **1**, although more precise geometry optimizations should be necessary for more precise evaluation.

It is thus assumed based on the Scheme 3-6 that the proton migration to the aryloxide ligand quickly occurred whereas migration to the ketimide ligand was relatively slow under these conditions.

3.5 Conclusion

The reactions of $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(NC{}^tBu_2)_2$ (**1**) with various alcohols, thiols and borates were investigated. The reaction of the V-Me bonds in **1** with thiols and borates took place exclusively, affording the corresponding thiolates and cationic complexes, respectively. In contrast, the reaction of the V-Me in **1** with alcohols did not take place and afforded the other methyl complexes via ligand substitution between the ketimide and the alkoxide/phenoxide. The reaction of $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(NC{}^tBu)(OAr)$ (**2**, Ar = 2,6-$Me_2C_6H_3$, 4-${}^tBu$-2,6-${}^iPr_2C_6H_2$) with phenols gave other methyl complexes, $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(OAr)_2$ (**5**), and the reaction with the Me group did not occur even in the presence of two equivalents of phenol. Based on these experiments, it was proposed that the reaction with alcohols proceeded in the following steps; 1) the alcohols initially approached the electron deficient metal center *trans* to the methyl group affording five coordinated trigonal bipyramidal species, 2) proton transfer onto the aryloxide/ketimide, affording the ketimine/phenol dissociation. In contrast to the reaction with alcohols, facile protonolysis took place in the reaction of **1** or **2** with thiols or borates to give the thiolate complexes or the cationic complexes, respectively. These results should be useful for the preparation of various vanadium-alkyl complexes as well as for better understanding in the basic reaction mechanism in vanadium catalyzed organic synthesis.

3.6 Experimental section

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous-grade of solvent (benzene, Et_2O, *n*-hexane, and THF) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2, and were passed through an alumina short column under N_2 stream prior to use. All chemicals used were of reagent grades and were purified by standard purification procedures. Reagent-grade $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$ and $[PhN(H)Me_2][B(C_6F_5)_4]$ (Asahi Glass Co. Ltd.) were stored in the drybox and were used as received. Synthesis of $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_2$ (**1**), $VCl(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)_2$ (**6**), and $V(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)_3$ (**7**) are described in Chapter 2 of this thesis. Synthesis of $LiNC^tBu_2$ were also according to the reported procedure.[21] Elemental analyses were performed by using PE2400II Series (Perkin-Elmer Co.). Some analytical runs were performed twice to confirm the reproducibility in independent analysis/synthesis runs.

All ^1H, ^{13}C, and ^{51}V NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for ^1H, 100.40 MHz for ^{13}C, and 105.31 MHz for ^{51}V), and ^{19}F NMR spectra were recorded on a JEOL JNM-ECP600NK spectrometer (564.69 MHz for ^{19}F). All spectra were obtained in the solvent indicated at 25 ºC unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^1H, ^{13}C), $CF_3C_6H_5$ (δ -64.0, ^{19}F) and $VOCl_3$ (δ 0.00, ^{51}V). Half-width values, $\Delta\nu_{1/2}$, is given in Hz.

Synthesis of $VMe(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)(O\text{-}2,6\text{-}Me_2C_6H_3)$ (2a). To a *n*-hexane solution (10 mL) containing **1** (372 mg, 0.80 mmol) was added $2,6\text{-}Me_2C_6H_2OH$ (98 mg, 0.80 mmol) at -30 ºC. The reaction mixture was warmed slowly to room temperature, and stirred for additional 3 hours. The solution was concentrated in vacuo, and the chilled solution (-30 ºC) yielded 335 mg (94%) of **2a** as the red crystals. ^1H NMR ($CDCl_3$): δ 1.34 (3H, V-CH_3), 1.41 (s, 18H, $(CH_3)_3C$-), 2.33 (s, 6H, CH_3), 2.47 (s, 6H, CH_3), 6.81 (m, 2H), 6.96 (d, 2H), 7.03 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 17.6, 18.9, 30.5, 38.5 (br, V-*Me*), 45.4, 120.4, 123.9, 126.8, 127.1, 128.0, 162.8, 163.87, 201.3. ^{51}V NMR (CDCl$_3$): δ -185 ($\Delta\nu_{1/2}$ = 253 Hz). Anal. Calcd. for $C_{26}H_{39}N_2OV$: C, 69.93; H, 8.80; N, 6.27%. Found: C, 70.02; H, 8.98; N, 6.20%.

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(O-4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$) (2b). Synthesis of **2b** was carried out according to the same procedure as that in **2a** except that 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH (47 mg, 0.20 mmol) was used in place of 2,6-Me$_2$C$_6$H$_2$OH. Yield 104 mg (93%). ^{1}H NMR (CDCl$_3$): δ 1.18 (d, 12H, *Me*$_2$CH-), 1.34 (s, 9H, *para*-(C*H*$_3$)$_3$C), 1.37 (s, 18H, (C*H*$_3$)$_3$C), 2.52 (s, 6H, C*H*$_3$), 3.56 (hept, 2H, Me$_2$C*H*-), 6.79 (t, 1H), 6.94 (d, 2H), 7.08 (s, 2H). The V-*Me* signal was not found due to peak overlapping with ^{t}Bu groups in both aryloxo and ketimide ligand. ^{13}C NMR (CDCl$_3$): δ 19.1, 23.2, 23.4, 26.8, 30.5, 31.7, 34.6, 38.3 (br, V-*Me*), 45.2, 119.5, 123.6, 127.0, 134.5, 136.5, 143.3, 158.1, 162.5, 200.7. ^{51}V NMR (CDCl$_3$): δ -197 ($\Delta\nu_{1/2}$ = 284 Hz). Anal. Calcd. for $C_{34}H_{55}N_2OV$: C, 73.08; H, 9.92; N, 5.01%. Found (1): C, 72.98; H, 10.14; N, 4.99%. Found (2): C, 73.14; H, 9.72; N, 5.11%.

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(OPh) (2c). Synthesis of **2c** was carried out according to the same procedure as that in **2a** except that PhOH (39 mg, 0.41 mmol) was used in place of 2,6-Me$_2$C$_6$H$_2$OH. Yield 154 mg (92%). ^{1}H NMR (CDCl$_3$): δ 1.30 (s, 18H, (C*H*$_3$)$_3$C-), 1.43 (3H, V-C*H*$_3$), 2.45 (s, 6H, C*H*$_3$), 6.77 (t, 1H), 6.89 (d, 3H), 7.04 (d, 2H), 7.19 (t, 2H). ^{13}C NMR (CDCl$_3$): δ 19.1, 30.4, 39.7 (br, V-*Me*), 45.0, 119.3, 121.0, 124.0, 127.0, 128.8, 135.8, 162.3, 165.3, 198.8. ^{51}V NMR (CDCl$_3$): δ -153 ($\Delta\nu_{1/2}$ = 1817 Hz). Anal. Calcd. for $C_{24}H_{35}N_2OV$: C, 68.88; H, 8.43; N, 6.69%. Found: C, 68.62; H, 8.36; N, 6.44%.

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(OC$_6$F$_5$) (2d). Synthesis of **2c** was carried out according to the same procedure as that in **2a** except that C_6F_5OH (92 mg, 0.50 mmol) was used in place of 2,6-Me$_2$C$_6$H$_2$OH. Yield 202 mg (79%). ^{1}H NMR (CDCl$_3$): δ 1.31 (s, 18H, (C*H*$_3$)$_3$C-), 1.49 (3H, V-C*H*$_3$), 2.42 (s, 6H, C*H*$_3$), 6.79 (t, 1H), 6.90 (d, 3H). ^{13}C NMR (CDCl$_3$): δ 18.7, 30.3, 43.1 (br, V-*Me*), 45.6, 125.1, 127.1, 133.4, 135.8, 136.6, 138.5, 139.1, 139.9, 140.9, 163.7, 203.9. ^{19}F NMR (CDCl$_3$): δ -171.64, -167.13, -160.94. ^{51}V NMR (CDCl$_3$): δ -98 ($\Delta\nu_{1/2}$ = 295 Hz).

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(O^{i}Pr) (2e). Synthesis of **2e** was carried out by the same procedure as that in **2a** except that ^{i}PrOH (48 mg, 0.80 mmol) was used in place of phenol. Yield 286 mg (93%). ^{1}H NMR (CDCl$_3$): δ 1.03 (3H, V-CH_3), 1.28 (s, 18H, (CH_3)$_3$C-), 1.28 (d, 6H, (CH_3)$_2$CH-), 2.52 (s, 6H, CH_3), 4.87 (hept, 1H, (CH$_3$)$_2$CH-), 6.70 (t, 1H), 6.92 (d, 2H). ^{13}C NMR (CDCl$_3$): δ 19.3, 26.9, 30.5, 35.0 (br. V-*Me*), 44.8, 77.6, 123.0, 127.0, 134.2, 161.8, 198.8. ^{51}V NMR (CDCl$_3$): δ -244 ($\Delta\nu_{1/2}$ = 311 Hz).

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(OCH$_2$CH$_2$CH=CH$_2$) (2f). Synthesis of **2f** was carried out according to the same procedure as that in **2a** except that 3-butene-1-ol (30 mg, 0.42 mmol) was used in place of 4-^{t}Bu-2,6-^{i}Pr$_2$C$_6$H$_2$OH. Yield 137 mg (86%). ^{1}H NMR (CDCl$_3$): δ 1.15 (s, br, 3H, V-CH_3), 1.27 (s, 18H, (CH_3)$_3$C-), 2.62 (2H, OCH$_2$CH_2), 2.62 (s, 6H, *Me*$_2$), 4.55 (2H), 4.75-4.86 (2H), 5.56 (1H), 6.76 (t, 1H), 6.93 (d, 2H). ^{13}C NMR (CDCl$_3$): δ 14.2, 19.4, 22.6, 30.6, 31.6, 39.3, 42.6, 45.0, 45.6, 75.2, 116.4, 123.5, 127.3, 134.7, 137.3, 158.1, 185.8. ^{51}V NMR (CDCl$_3$): δ -103 ($\Delta\nu_{1/2}$ = 1632 Hz), -231 ($\Delta\nu_{1/2}$ = 579 Hz). Anal. Calcd. for $C_{22}H_{37}N_2OV$: C, 66.64; H, 9.41; N, 7.07%. Found: C, 66.95; H, 9.70; N, 6.76%.

Synthesis of VMe(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(OCH$_2$CH$_2$CH$_2$CH$_2$CH=CH$_2$) (2g). Synthesis of **2g** was carried out by the same procedure as that in **2a** except that 5-hexene-1-ol (20 mg, 0.20 mmol) was used. Yield 56 mg (66%). ^{1}H NMR (CDCl$_3$ at 20 ºC): δ 1.07 (s, br, 3H, V-CH_3), 1.25 (s, 18H, (CH_3)$_3$C-), 1.41 (2H), 1.71 (2H), 1.97 (2H), 2.53 (s, 6H, CH_3), 4.52 (2H), 4.89-4.94 (2H), 5.71 (1H), 6.74 (t, 1H), 6.91 (d, 2H). ^{13}C NMR (CDCl$_3$ at 20 ºC): δ 14.1, 19.4, 22.6, 25.0, 30.5, 31.6, 33.6, 34.2, 42.2, 44.9, 76.3, 114.2, 123.4, 127.2, 134.6-137.2, 138.9, 159.7, 185.4, 198.8. ^{51}V NMR (CDCl$_3$ at 20 ºC): δ -105 ($\Delta\nu_{1/2}$ = 1685 Hz), -237 ($\Delta\nu_{1/2}$ = 527 Hz). Anal. Calcd for $C_{24}H_{41}N_2OV$: C, 67.90; H, 9.73; N, 6.60%. Found: C, 67.97; H, 9.88; N, 6.62%.

Reaction of 1 with *n*-hexanol: synthesis of V(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)[OCH$_2$(CH$_2$)$_4$CH$_3$]. The synthesis was carried out by the same procedure as that in **2a** except that *n*-hexanol (42 mg, 0.41 mmol) was used. ^{1}H NMR (CDCl$_3$): δ 0.82 (3H), 1.04 (s, br, 3H, V-CH_3), 1.23 (s, 18H, (CH_3)$_3$C-), 1.25-1.28 (m, 6H), 1.66 (2H), 2.51 (s, 6H, CH_3), 4.50 (2H), 6.73 (t, 1H), 6.90 (d, 2H). ^{51}V NMR (CDCl$_3$): δ

-238 ($\Delta\nu_{1/2}$ = 419 Hz).

Synthesis of V(N-2,6-$Me_2C_6H_3$)(NC^tBu_2)(S-2,6-$Me_2C_6H_3$) (3a). To a *n*-hexane solution (10 mL) containing **1** (186 mg, 0.40 mmol) was added 2,6-$Me_2C_6H_3SH$ (57 mg, 0.41 mmol) at -30 ºC. The reaction mixture was warmed slowly to room temperature (25 ºC), and was stirred for additional 3 hours. The solution was concentrated in vacuo, and the chilled solution (-30 ºC) yielded 176 mg (75%) of **3a** as the brown crystals. ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 36H, $(CH_3)_3C$-), 2.39 (s, 6H, CH_3), 2.51 (s, 6H, CH_3), 6.73 (t, 1H), 6.83 (t, 1H), 6.88 (d, 2H), 6.92 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 19.1, 23.9, 30.4, 45.2, 123.6, 124.4, 126.8, 126.9, 134.4, 139.5, 144.6, 163.3, 198.5. ^{51}V NMR ($CDCl_3$): δ -132 ($\Delta\nu_{1/2}$ = 341 Hz).

Reaction of 1 with *n*-$C_6H_{13}SH$ (3b). To a NMR tube equipped with Teflon (Young) valve containing C_6D_6 solution (ca. 0.5 mL) of **1** (47mg, 0.10 mmol), *n*-$C_6H_{13}SH$ (12 mg, 0.10 mmol) was added at room temperature (25 ºC). Three sets of the resonances ascribed to the product (**3b**), methane (0.15 ppm) and the starting material (**1**) (conversion 72%) were observed in the ^{1}H NMR spectrum, and two resonances ascribed to **1** and **3b** were observed in the ^{51}V NMR spectrum. ^{1}H NMR (C_6D_6): δ 0.82, 0.94, 1.15-1.45, 1.28, 1.33, 1.88, 2.68 (s, 6H, CH_3), 2.93, 3.67, 6.72 (t, 1H), 6.91 (d, 2H). ^{51}V NMR (C_6D_6): δ -153.6 ($\Delta\nu_{1/2}$ = 316 Hz).

Synthesis of [V(N-2,6-$Me_2C_6H_3$)(NC^tBu_2)$_2$(THF)$_2$][B(C_6F_5)$_4$] (4a). To a THF solution (4 mL) containing **1** (186 mg, 0.40 mmol) was added [Ph_3C][B(C_6F_5)$_4$] (369 mg, 0.40 mmol) at -30 °C. The reaction mixture was allowed to warm to room temperature (25 ºC), and was stirred for 1 hour. Removal of solvent from the mixture in vacuo gave a mixture of **4a** and Ph_3CCH_3 quantitatively. Recrystallization from THF/hexane afforded red block. Yield 460 mg (90%). ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 36H, $(CH_3)_3C$-), 1.85 (br, 8H, *thf*), 2.58 (s, 6H, CH_3), 3.73 (br, 8H, *thf*), 6.89 (t, 1H), 6.95 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 18.9, 25.5, 30.3, 45.8, 68.6, 123.8, 127.7, 135.0, 135.7, 136.9, 137.4, 139.3, 147.0, 149.4, 167.0, 207.2. ^{19}F NMR ($CDCl_3$): δ -134.4, -164.5, -168.3. ^{51}V NMR ($CDCl_3$): δ -92 ($\Delta\nu_{1/2}$ = 714 Hz). Anal. Calcd. for $C_{58}H_{61}BF_{20}N_3O_2V$: C, 54.69; H, 4.79; N, 3.30%. Found (1): C, 54.37; H, 4.79; N, 3.12 %. Found (2): C, 54.71; H, 4.82; N, 3.15%.

Synthesis of [V(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)$_2$(THF)$_2$][B(C$_6$F$_5$)$_4$] (4a) from 1 by reaction with [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$]. One equivalent of the [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] (160 mg, 0.20 mmol) was added to a solution of **1** (93 mg, 0.20 mmol) in THF at -30 °C, and the resulting mixture was warmed gradually and was continued stirring for 1hours at room temperature. Removal of solvent from the reaction mixture in vacuo gave a mixture of the product (**4a**) and PhNMe$_2$: ^{1}H NMR spectrum of the mixture was identical with that of the isolated **4a** except signals of PhNMe$_2$. ^{1}H NMR (CDCl$_3$): δ 1.35 (s, 36H, (C*H*$_3$)$_3$C-), 1.89 (br, 8H, *thf*), 2.58 (s, 6H, C*H*$_3$), 3.98 (br, 8H, *thf*), 6.89 (t, 1H), 6.95 (d, 2H). ^{51}V NMR (CDCl$_3$): δ -92 ($\Delta\nu_{1/2}$ = 704 Hz).

Synthesis of [V(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)$_2$(THF)$_2$][MeB(C$_6$F$_5$)$_3$] (4b) from 1 by reaction with [B(C$_6$F$_5$)$_3$]. To a THF solution (5.0 mL) containing **1** (186 mg, 0.40 mmol) was added B(C$_6$F$_5$)$_3$ (204 mg, 0.40 mmol) at -30 °C. The reaction mixture was warmed slowly to room temperature (25 ºC), and was stirred for 1 hours. Solvent in the mixture was then removed in vacuo, yielding analytically pure product (447 mg, quantitative) ascribed to **4b**. ^{1}H NMR (CDCl$_3$): δ 0.48 (s, 3H, B*Me*), 1.34 (s, 36H, (C*H*$_3$)$_3$C-), 1.91 (br, 8H, *thf*), 2.57 (s, 6H, C*H*$_3$), 3.82 (br, 8H, *thf*), 6.88 (t, 1H), 6.97 (d, 2H). ^{51}V NMR (CDCl$_3$): δ -94 ($\Delta\nu_{1/2}$ = 816 Hz).

Synthesis of [V(N-2,6-Me$_2$C$_6$H$_3$)(NC^{t}Bu$_2$)(O-2,6-Me$_2$C$_6$H$_3$)(THF)$_2$][B(C$_6$F$_5$)$_4$] (4c) from 2a by reaction with [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$]. One equivalent of the [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] (320 mg, 0.40 mmol) was added to a solution of **2a** (179 mg, 0.20 mmol) in THF at -30 °C. The resulting mixture was stirred for 1hours at room temperature (25 °C). After the removal of THF from the solution gave a mixture of the product (**4c**) and free PhNMe$_2$. Exclusive formation of **4c** was confirmed by ^{1}H and ^{51}V NMR spectroscopy. ^{1}H NMR (CDCl$_3$): δ 1.34 (s, 18H, (C*H*$_3$)$_3$C-), 1.97 (br, 8H, *thf*), 2.25 (s, 6H, C*H*$_3$ on aryloxo), 2.50 (s, 6H, C*H*$_3$ on arylimido), 4.00 (br, 8H, *thf*), 6.92 (t, 1H), 6.98 (s, 3H), 7.05 (d, 2H). ^{51}V NMR (CDCl$_3$): δ -77 ($\Delta\nu_{1/2}$ = 790 Hz).

Formation of VMe(N-2,6-Me$_2$C$_6$H$_3$)(O-2,6-Me$_2$C$_6$H$_3$)$_2$ (5a). To a CDCl$_3$ (c.a. 0.5 mL) solution containing **2a** (45 mg, 0.10 mmol) was added 2,6-$Me_2C_6H_3OH$ (24 mg, 0.20 mmol) at room temperature. NMR measurements were conducted after 0.5, 5.0, and 24 hours. The quantitative conversion was achieved after 24 hours. ^1H NMR ($CDCl_3$): δ 2.11 (s, 6H, C*H*$_3$), 2.29 (s, 12H, C*H*$_3$), 6.75-6.84 (m, 5H), 6.97-7.01 (m, 4H). The V-*Me* signal was not found due to overlapped by Me group in aryloxo. ^{13}C NMR ($CDCl_3$): δ 17.3, 18.0, 53.5 (br, V-*Me*), 122.0, 125.7, 126.1, 127.1, 128.1, 135.9, 164.1. ^{51}V NMR ($CDCl_3$): δ -64 ($\Delta\nu_{1/2}$ = 348 Hz).

Formation of VMe(N-2,6-$Me_2C_6H_3$)(O-4-^{t}Bu-2,6-^{i}$Pr_2C_6H_3$)$_2$ (5b). To a $CDCl_3$ (ca. 0.5 mL) solution containing **2b** (33 mg, 0.059 mmol), 4-^{t}Bu-2,6-^{i}$Pr_2C_6H_2OH$ (14 mg, 0.059 mmol) was added at room temperature. NMR measurements were conducted after 1 and 12 hours. The quantitative conversion was achieved after 12 hours. ^1H NMR ($CDCl_3$): δ 1.15 (dd, 24H, ^{i}Pr-C*H*$_3$), 1.28 (s, 18H, ^{t}Bu), 2.15 (br, 3H, V-*Me*), 2.17 (s, 6H, C*H*$_3$ on arylimido), 3.47 (hept, 4H, ^{i}Pr-C*H*), 6.74 (1H), 6.81 (4H), 7.07, (s, 4H). ^{13}C NMR ($CDCl_3$): δ 18.3, 23.1, 23.5, 27.0, 31.6, 34.6, 52.8 (br, V-*Me*), 119.6, 125.2, 127.0, 135.1, 135.9, 144.9, 160.2, 163.5. ^{51}V NMR ($CDCl_3$): δ -78 ($\Delta\nu_{1/2}$ = 458 Hz).

Typical reaction of 2a with 4-^{t}Bu-2,6-^{i}$Pr_2C_6H_2OH$ in $CDCl_3$. To a Teflon-sealed NMR tube containing $CDCl_3$ (c.a. 0.5 mL) and **2a** (45 mg, 0.10 mmol), 4-^{t}Bu-2,6-^{i}$Pr_2C_6H_2OH$ (23 mg, 0.10 mmol) was added in one portion, the resultant solution was monitored by both ^1H NMR and ^{51}V NMR (shown in Figure 3-6b), and the solution was then heated to 60 ºC and was stirred for additional 12 hours (the spectrum shown in Figure 3-6c).

Crystallographic analysis. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The selected crystal collection parameters are listed below (Table 3-3), and the detailed results were described in the reports attached below. All structures were solved by direct method and expanded using Fourier techniques,[22] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **3a, 4a** were performed using the CrystalStructure[23,24] crystallographic software package.

Table 3-3. Crystal Data and Collection Parameters of Complexes **3a** and **4a**.[a]

	3a	**4a**
formula	$C_{34}H_{54}N_3SV$	$C_{54}H_{53}BF_{20}N_3OV$
formula weight	587.82	1201.75
crystal color, habit	brown, prism	red, block
crystal size (mm)	0.80×0.60×0.20	0.80×0.80×0.44
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	12.086(3)	15.606(5)
b (Å)	16.246(4)	15.262(4)
c (Å)	17.986(7)	24.342(6)
β (deg)	84.449(14)	93.897(13)
V (Å^3)	3515.1(18)	5784.3(27)
Z value	4	4
D_{calcd} (g/cm^3)	1.111 g/cm^3	1.380 g/cm^3
F_{000}	1272.00	2456.0
Temp (K)	243	243
μ(MoKα) (cm^{-1})	3.658	2.752
2θ range (deg)	6.05-54.97	6.01-54.97
no. of reflections measured	33359	53601
no. of observations ($I > 2.00\sigma(I)$)	11424	7733
no. of variables	406	802
R1	0.0627	0.0565
wR2	0.1220	0.1632
goodness of fit	1.002	1.004

[a] Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\sum w(|F_o|-|F_c|)^2$ (w = Least squares weights). Standard deviation of an observation of unit weight: $[\sum w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$ (N_o = number of observations, N_v = number of variables).

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4

Ethylene polymerization with (arylimido)vanadium complexes containing aryloxo or ketimide ligand

Topics concerning precise synthesis of polyolefins by new generation of transition metal catalysis attract considerable attention,[1] because the evolution of new polyolefins that can not be prepared by ordinary catalysts is highly expected. Moreover, precise control of the catalyst properties (e.g. catalyst structure-property relationships and details of the polymerization process) that can not be achieved by the practical heterogeneous catalysts, are possible by the modification of both centered metal and ligand with well-defined molecular catalysts.[2] Since the classical Ziegler type vanadium catalyst systems displayed unique characteristics[3-6] such as (a) synthesis of a high molecular weight polymer with a narrow polydispersity,[4] (b) synthesis of an ethylene/α-olefin copolymer with high α-olefin content,[4a,5] (c) living polymerization[6] affording propylene-methyl methacrylate diblock copolymers,[6b] and (d) others,[7] therefore, design and synthesis of new vanadium complex catalysts directed toward controlled olefin polymerization have been the most attractive goals.

Nomura et al. reported that (arylimido)(aryloxo)vanadium(V) complexes exhibited high catalytic activity for ethylene polymerization in the presence of MAO, and the activity in the presence of Et_2AlCl was higher than that in the presence of MAO.[8] These catalyst systems also showed the notable catalytic activities for ethylene/norbornene (NBE) copolymerization, and afforded ultrahigh molecular weight poly(ethylene-co-NBE)s with unimodal, narrow molecular weight distributions.[8e]

The (arylimido)vanadium(V) complexes display the following tremendous aspects; (1) Imido ligands are often used in vanadium(V) chemistry, since the good π-donating capabilities of these ligands stabilize the high oxidation state of the metal center. Indeed, syntheses of a series of (arylimido)vanadium(V) complexes have already been established by several researchers.[8b,8c,9,10] (2) The (arylimido)vanadium(V) complexes containing mono anionic donor ligaind, of the type $(ArN)VCl_2(L)$, should have the same electron counts as the Cp-Ti moieties of bridged- or *non*-bridged- group 4 half metallocenes which are accepted as highly active olefin polymerization catalysts.[2d,11] (3) Ligand introduction can be easily achieved by facile salt metathesis (by reacting metal-chloride group with metal salt) or HCl elimination (by reacting metal-chloride group with neutral ligand precursor).[8b,8c] A variety of ligand is available, and subsutituents on ligand can be easily modified.

This chapter focuses on results of ethylene polymerization with a series of (arylimido)vanadium(V) dichloro complexes containing aryloxo or ketimide ligands (**1**-**7**, Chart 4-1). Synthesis of these dichloro complexes was already described in chapter 2 of this thesis.

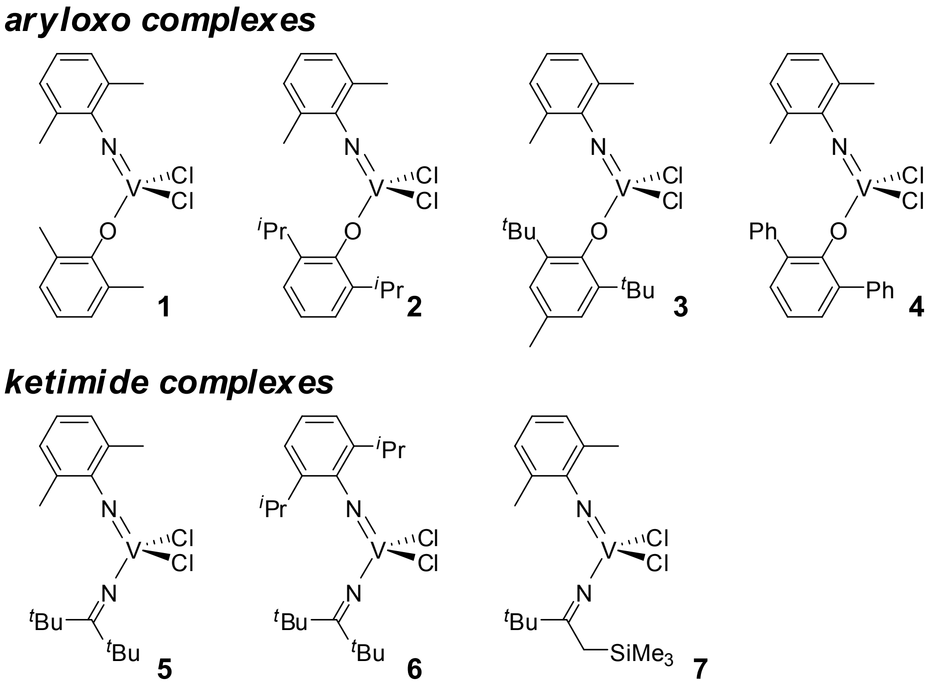


Chart 4-1

4.1 Ethylene polymerization using a series of (arylimido)(aryloxo)vanadium complexes - MAO catalyst systems: Effect of Al/V molar ratio

Ethylene polymerization using four aryloxo complexes (**1**-**4**) was conducted for exploring effect of substituents on the aryloxo ligand. Methylaluminoxane (MAO) white solid was also chosen as the cocatalyst because the use of MAO is quite effective due to the fact that the observed activities were highly reproducible by removing an excess amount of $AlMe_3$ contaminated in the commercially available MAO.

Table 4-1 summarizes results for ethylene polymerization with various Al/V molar ratios using a series of (arylimido)(aryloxo)vanadium complexes (at 25 ºC, ethylene 8 atm). It was revealed that **1** showed the highest catalytic activity, and the observed activities were highly dependent upon Al/V molar ratios. As shown in Figure 4-1, the optimized Al/V molar ratio was dependent upon aryloxo ligand employed. The optimized value was 1000 for **1**, and the activity decreased with both lower and higher Al/V molar ratios. The observed activity was, on the other hand, relatively high even at low Al/V molar ratio (run 2, 1130 kg-PE/mol-V·h, Al/V = 250), and the moderate activity was still observed even at lower Al/V molar ratio of 50 (415kg-PE/mol-V·h under the same conditions as run 1). These results suggest that the reaction of **1** with MAO generating the catalytically-active species took place predominantly even at low Al/V molar ratios, and these are somewhat different from those observed using some group 4 transition metal catalysts.[11] The similar trend was also seen in the polymerization using **2** although the observed activity was somewhat low compared to those by **1**. The complex **4** showed the lowest activity, and the effect of steric bulk may be considered. Resultant polymer was linear polyethylene confirmed by ^{13}C NMR with very high molecular weight with unimodal molecular weight distributions as reported previously with **2**.[8a,b] No marked differences were also observed for M_w values of resultant polymers prepared by **1**-**4** (Figure 4-2, typical GPC traces).

Table 4-1. Effect of Al/V molar ratios - Ethylene polymerization by **1-4** - d-MAO catalyst systems.[a]

Run No.	Cat.	Al/V[b]	Polymer Yield /mg	Activity / kg-PE/mol-V·h	M_w[c,d]	M_w/M_n[c]
1	**1**	50	173	415		
2	**1**	250	473	1130		
3	**1**	500	543	1300		
4	**1**	1000	740	1780	$9.49x10^5$	4.61
5	**1**	1000	737	1770	$1.27x10^6$	4.65
6	**1**	2000	660	1600		
7	**1**	3000	614	1470	$1.71x10^6$	4.91
8	**2**	50	73	175		
9	**2**	100	245	588		
10	**2**	250	288	691		
11	**2**	500	387	928		
12	**2**	1000	439	1050	$1.17x10^6$	4.92
13	**2**	1000	436	1050	$1.37x10^6$	
14	**2**	1500	388	932		
15	**2**	2000	353	847	$2.93x10^6$	11.06
16	**2**	2000	352	846		
17	**2**	3000	320	768		
18	**3**	250	39	93		
19	**3**	500	70	169		
20	**3**	1000	105	252		
21	**3**	1500	154	370	$3.06x10^6$	10.2
22	**3**	2000	161	386		
23	**3**	3000	146	349		
24	**4**	250	369	910	$6.75x10^5$	8.31
25	**4**	500	479	1150		
26	**4**	1000	453	1090	$1.03x10^6$	3.89
27	**4**	2000	369	886		
28	**4**	3000	236	566		

[a] Reaction conditions: **1-4** 2.5 μmol, toluene 30 mL, ethylene 8 atm, 25 ºC, 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] GPC data in *o*-dichlorobenzene vs polystyrene standard; [d] Extremely trace amount of low molecular weight polymer was observed in GPC traces.

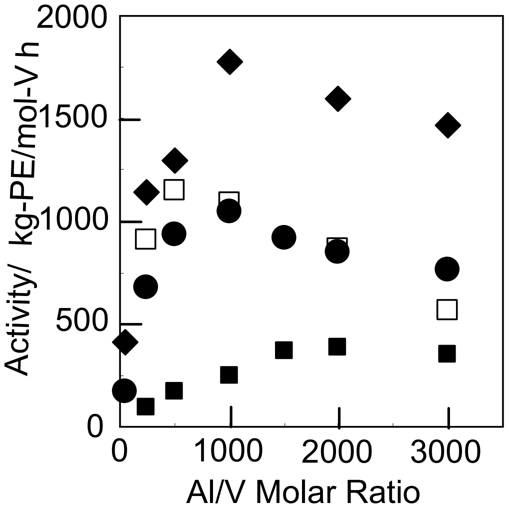


Figure 4-1. Effect of Al/V molar ratio for the catalytic activity in ethylene polymerization [cat. = **1**(♦), **2**(●), **3**(■), and **4**(□)]. Detailed conditions are summarized in Table 4-1.

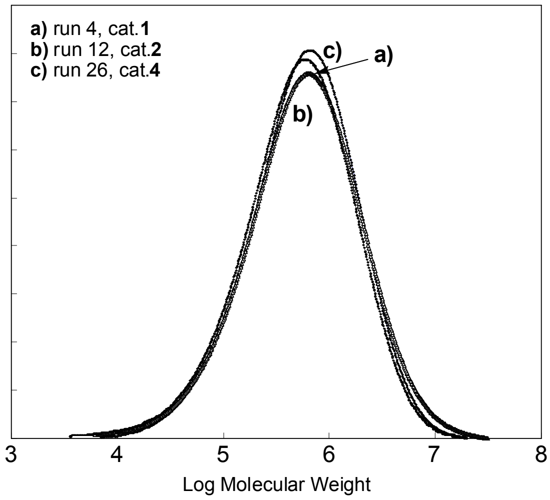


Figure 4-2. GPC traces for polyethylenes prepared by **1**,**2** and **4** - MAO catalysts. a) by **1** (run 4), b) by **2** (run 12), c) by **4** (run 26).

Figure 4-3 summarizes effect of ethylene pressure for the catalytic activity. It is clear that linear first order dependence was observed in all cases. The result is important for considering the catalytically-active species, and the proposed catalytically active species, [VR(NAr)(OAr')(ethylene)]$^+$ (R = alkyl), coordinate one ethylene molecule in spite of its electronically unsaturated 14e nature that may coordinate more ethylene at the same time.

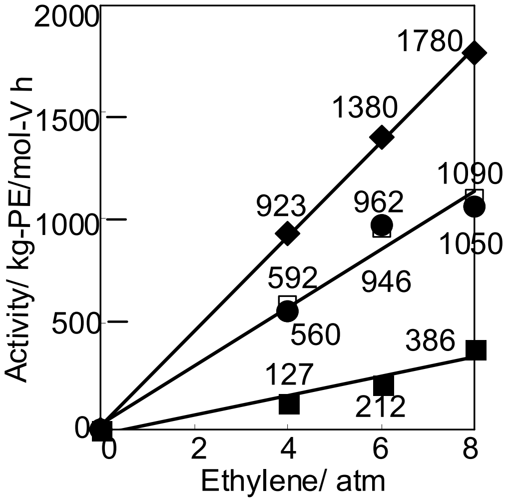


Figure 4-3. Effect of ethylene pressure for the catalytic activity in ethylene polymerization [cat. = **1**(♦), **2**(●), **3**(■), and **4**(□)]. Conditions are the same as those in runs 4, 12, 22, and 26 except the ethylene pressure. Numbers in each plots are the activities (kg-PE/mol-V·h) under the polymerization conditions

The optimized Al/V molar ratios for **3** (2000) and **4** (500) were somewhat different from those for **1** and **2** (1000). Relatively high catalytic activity was observed at low Al/V molar ratio of 250 when **4** was chosen as the catalyst. Since these catalysts exhibited relatively high catalytic activities at the low molar ratios, the observed difference in the optimized values might be due to the degree for generating catalytically-active species.

4.2 Results of ethylene polymerization using a series of (arylimido)(aryloxo)vanadium complexes - MAO catalyst systems: Temperature dependence

Table 4-2 summarizes the polymerization results at various temperatures under various ethylene pressures. The observed activity decreased at lower ethylene pressure and/or lower polymerization temperature of 0 ºC when **1** was used as the catalyst (runs 4, 29, and 32-33). The activity also decreased at higher temperature (runs 30-31). The similar trend could be seen in **2** (runs 12 and 34-35), as reported previously.[8b]

Table 4-2. Effect of ethylene pressure and polymerization temperature - Ethylene polymerization by **1-4** - d-MAO catalyst systems.[a]

Run No.	Cat.	Al/V[b]	Ethylene / atm	Temp. / ºC	Time / min	Polymer Yield /mg	Activity / kg-PE/mol-V·h
29	**1**	1000	8	0	10	184	441
4	**1**	1000	8	25	10	740	1780
30	**1**	1000	8	40	10	347	834
31	**1**	1000	8	60	10	239	573[c]
4	**1**	1000	8	25	10	740	1780
32	**1**	1000	6	25	10	573	1380
33	**1**	1000	4	25	10	385	923
34	**2**	1000	8	0	10	316	758
12	**2**	1000	8	25	10	439	1050
35	**2**	1000	8	40	10	161	387
36	**2**	1000	8	60	10	114	274
37	**3**	2000	8	0	10	71.2	171
20	**3**	1000	8	25	10	105	252
22	**3**	2000	8	25	10	161	386
38	**4**	500	8	0	10	559	1340
25	**4**	500	8	25	10	479	1150
39	**4**	1000	8	0	10	572	1370
40	**4**	1000	8	0	10	568	1360
46	**4**	1000	8	25	10	453	1090
41	**4**	1000	8	40	10	266	638
42	**4**	1000	8	60	10	132	318

[a] Reaction conditions: **1-4** 2.5 μmol, toluene 30 mL, 100 mL scale autoclave, d-MAO (prepared by removing $AlMe_3$ and toluene from commercially available MAO). [b] Molar ratio of Al/V. [c] $M_w = 3.14 \times 10^5$, $M_w/M_n = 5.09$.

It should be noted that the high catalytic activity of **4** was observed at 0 ºC (runs 38-40), and the observed temperature dependence was thus different from those using other complexes. It is assumed that the observed difference would be due to that the catalytically active species may not be stable even at 25 ºC for longer hours, because the activity decreased at 40 ºC. Although the reason for the observed difference is not clear at this moment, one plausible explanation is due to decomposition of aryloxo ligand by a reaction between vanadium-alkyl and H on phenyl (2 or 6 position) because the H atoms are relatively close to the centered metal. In this sense, it is thus suggested that alkyl substituent on aryloxo ligand would be suited rather than phenyl substituent.

4.3 Ethylene polymerization using a series of (arylimido)(ketimide)vanadium complexes - MAO catalyst systems

Table 4-3 shows the results of ethylene polymerizations by ketimide complexes and the results by the aryloxide analogues **1-2** under the similar conditions are also cited for comparison. It was revealed that **5-7** showed high catalytic activities and the activities were dependent upon the Al/V molar ratios; the activities with the molar ratios of 3000 for **5**, **6** and 2000 for **7** seemed to be the optimum (runs 43-45 for **5**, 48-50 for **6**, and 52-55 for **7**). The resultant polymers prepared by **5-7** were linear polyethylene confirmed by ^{1}H and ^{13}C NMR spectra, and the attempts for GPC measurement were not successful due to that these polymer samples were hardly soluble even in hot *o*-dichlorobenzene for GPC analysis, as seen in the ethylene polymerization by **1** (Table 4-1). The activities at 25 °C under the optimized conditions increased in the order: **1** > **2** > **7** > **5**, **6**. The aryloxide analogues **1-2** showed higher the activities than the ketimide analogues **5-7**, and the remarkable difference in the activity between **5** and **6** was not seen (runs 45 and 49). In contrast, **7** showed higher activities than **5**, suggesting that the effect of substituent in the ketimide ligand is more dominant than the arylimido ligand for the activity under these conditions (runs 45 and 53). The activities were also dependent upon ethylene pressure, and the activities increased at higher ethylene pressure.

Table 4-3. Ethylene polymerization using (arylimido)(ketimide)vanadium complexes (**5**-**7**) - d-MAO catalyst systems.[a]

Run No.	Cat.	Al/V[b]	Ethylene / atm	Temp. / ºC	Polymer Yield /mg	Activity / kg-PE/mol-V·h
43	**5**	1000	8	25	64	384
44	**5**	2000	8	25	65	389
45	**5**	3000	8	25	111	666
46	**5**	3000	8	50	124	743
47	**5**	3000	8	80	88	526
48	**6**	1000	8	25	110	661
49	**6**	3000	8	25	120	715
50	**6**	3000	8	25	119.5	715
51	**6**	1000	8	50	122	730
52	**7**	1000	8	25	121	728
53	**7**	2000	8	25	164	985
54	**7**	2500	8	25	149	892
55	**7**	3000	8	25	128	767
56	**7**	2000	6	25	113	677
57	**7**	2000	4	25	61	368
58	**7**	2000	8	0	74	444
59	**7**	2000	8	50	91	543
60	**7**	2000	8	80	30	178
55	**7**	3000	8	25	128	767
4	**1**	1000	8	25	740	1780
30	**1**	1000	8	40	347	834
31	**1**	1000	8	60	239	573
12	**2**	1000	8	25	436	1050
35	**2**	1000	8	40	161	387

[a]Reaction conditions: **1**-**2** 2.5 μmol, **5**-**7** 1.0 μmol, toluene 30 mL, 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.

As mentioned in section 4-2, the catalytic activities by **1**-**2** decreased upon increasing the polymerization temperature probably due to the decomposition of the catalytically active species. The optimized temperature by the aryloxide analogues (**1**, **2**) was ca. 25 °C, and the activity also decreased at 0 °C. In contrast, the activities by **5** and **6** at 50 °C were higher than those at 25 °C, but the activities decreased at 80 °C. These results should be a unique contrast that the thermal stability could be improved by using the ketimide analogue in place of the aryloxide analogues. Moreover, the activity by **7** at 50 °C was lower than that at 25 °C, clearly suggesting that two ^{t}Bu groups play an important key role to improve the thermal stability under the polymerization conditions.

4.4 Effect of cocatalysts for ethylene polymerization

In previous section, MAO white solid was used as the cocatalyst because the use of this MAO is quite effective due to the fact that the observed activities were highly reproducible by removing excess amount of $AlMe_3$ contaminated in the commercially available MAO. Since the catalytically active species are assumed as cationic alkyl complex (Scheme 4-1), the activities often depend on both Al cocatalyst and solvent employed. Thus, the effect of both Al cocatalysts and solvents in ethylene polymerization by the aryloxo complex (**1**,**2**) and the ketimide analogues (**5**-**7**) were studied, and the results are summarized in Table 4-4.

Scheme 4-1. Assumed catalytically active species.

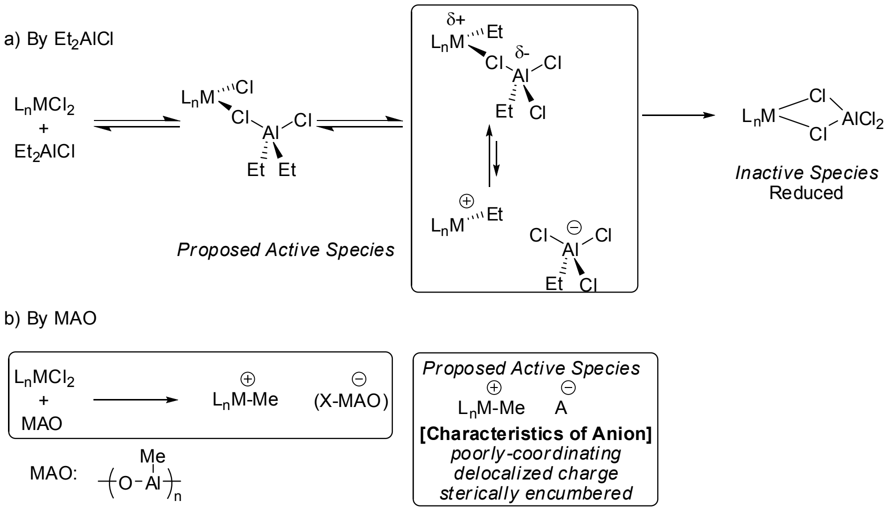


Table 4-4. Effects of cocatalysts and solvents.[a]

Run No.	Cat. (μmol)	Al/V[b]	Temp. / ºC	Polymer Yield /mg	Activity / kg-PE/mol-V·h
4	**1**(2.5)	1000 (MAO)	25	740	1780
61[c]	**1**(0.05)	250	0	97	11700
62[c]	**1**(0.05)[d]	250	0	23	2760
63[c]	**1**(0.05)[e]	250	0	158	19000
64[c]	**1**(0.05)[f]	250	0	110	13200
65[c]	**1**(0.05)[g]	250	0	9	1080
12	**2**(2.5)	1000 (MAO)	25	439	1050
66[c]	**2**(0.05)	250	0	79	9490
26	**4**(2.5)	1000(MAO)	25	453	1090
67[c]	**4**(0.05)	250	0	115	13700
45	**5**(1.0)	3000 (MAO)	25	111	666
68	**5**(1.0)	250	0	86.9	521
69	**5**(1.0)[d]	250	0	105.5	633
70	**5**(1.0)	250	25	42.2	253
49	**6**(1.0)	3000 (MAO)	25	120	715
71	**6**(1.0)	250	0	53	318
72	**6**(1.0)	250	25	17.5	105
53	**7**(1.0)	2000 (MAO)	25	164	985
73	**7**(1.0)	250	0	116.5	699
74	**7**(1.0)	250	25	137.4	824

[a] Reaction conditions: catalyst, Et_2AlCl or MAO, solvent 30 mL, 100 mL scale autoclave.
[b] Molar ratio of Al/V. [c] Cited from ref. 8e. [d] *n*-hexane solvent. [e] C_6H_5Cl solvent.
[f] CH_2Cl_2 solvent. [g] Polymerization in the co-presence of CCl_3CO_2Et (10.0 equiv to V).

As reported previously,[8e] Et_2AlCl was effective as the cocatalyst for ethylene polymerization using the aryloxide analogues (**1**, **2**, and **4**). The observed activities were also highly dependent upon solvent employed. When **1** was used as the catalyst precursor, the activity in *n*-hexane was lower than those in other solvent such as toluene, chlorobenzene, dichloromethane under the same conditions (runs 61-65). In contrast, the observed catalytic activities by **5**-**7** in the presence of Et_2AlCl were lower than those in the presence of MAO (runs 45 and 70 for **5**, 49 and 72 for **6**, and 53 and 74 for **7**). The activities by **5**, **6** in the presence of Et_2AlCl increased at 0 °C, and no distinct differences in the activities were observed when *n*-hexane was used as solvent in place of toluene (run 69). It might be considered that more electron deficient nature of the metal in aryloxo complex caused bigger cocatalysts and solvents effect than ketimide analogue.

It should be noted that the polymerization by **1** in the co-presence of CCl_3CO_2Et (10.0 eq. to V), which has been known as a mild oxidizing reagent to restart the catalytic cycle from the deactivated state in the polymerization using vanadium(III) and/or vanadium(IV) complexes - halogenated aluminum alkyls catalyst systems, showed the significant decrease in the catalytic activity, and the activity decreased upon further addition (run 65). The results clearly suggest that the catalytically-active species were thus apparently different from those prepared from vanadium(III), (IV) complexes. Taking into account these facts, the catalytically-active species should be derived from vanadium(V) containing both arylimido and anionic donor ligand (aryloxide, ketimide) in this catalysis.

4.5 Attempts for styrene polymerization using (arylimido)(aryloxo)vanadium complex

Because **1**-**4** exhibited high catalytic activities for ethylene polymerization, and a series of *non*-bridged (cyclopentadienyl)(aryloxo)titanium complexes exhibited high catalytic activities for both ethylene and styrene polymerizations,[11,12,13] styrene polymerization by using **2**-MAO catalyst system were thus attempted (Table 4-5). However, *2 showed extremely low (or no) catalytic activities for the polymerization*. The polymer isolated from the reaction mixture was atactic polystyrene that is produced by MAO, and the yield for atactic polystyrene was lower than that performed without vanadium catalyst under the

Table 4-5. Attempted polymerization of styrene by **2** - MAO catalyst system.[a]

run no.	cat.**2** / µmol	Al / mmol	Al/V[b]	yield[c] / mg
75	20	10.0	500	179
76	5.0	3.0	600	117
77	---	3.0	---	156

[a] Polymerization conditions: styrene 10 mL, 25 ºC, 30 min; [b] Molar ratio of Al/V; [c] Resultant polymer was soluble in acetone, atactic.

same conditions. Although our attempt was not successful, this fact clearly indicates that the catalytically active species for styrene polymerization cannot be generated under these conditions.

Copolymerizations of ethylene with styrene by **2** - MAO catalyst system were also carried out, although complex **2** exhibited no catalytic activities for styrene polymerization. The results are summarized in Table 4-6.

Table 4-6. Attempted copolymerization of ethylene with styrene by **2** - d-MAO catalyst system.[a]

run no.	cat.**2** / µmol	Al/V[b]	ethylene / atm	styrene / mL	time / min	yield[c] / mg	activity[d]	M_w[e] $\times 10^{-4}$	M_w/M_n[e]
12	2.5	1000	8	---	10	439	1050	117	4.92
78	10	500	8	2.5	30	75.2	15.0	17.7	1.65
79	10	500	8	5.0	30	52.4	10.5	5.41	1.23
								0.29	1.65
80	10	500	8	10	30	51.0	10.2	5.71	2.99[f]
81	40	300	8	2.5	30	188	9.4	11.3	1.58
82	40	300	8	5.0	30	141	7.1	7.67	1.59

[a] Polymerization conditions: toluene+styrene total 30 mL, 25 °C, d-MAO. [b] Molar ratio of Al/V. [c] Yield of acetone insoluble fraction. [d] Activity in kg-polymer/mol-V·h. [e] GPC data in *o*-dichlorobenzene *vs* polystyrene standards. [f] Small amount of low molecular weight polymer was observed in GPC trace.

Significant decrease in the catalytic activity was observed in the presence of styrene, and the activity decreased at higher styrene concentration. Resultant polymers possessed unimodal molecular weight distribution in most cases, and the M_w value was lower than that by ethylene polymerization. However, resulting acetone insoluble polymer was linear polyethylene in all cases confirmed by ^{13}C NMR spectra, and these results clearly indicate that **2** is not effective for copolymerization of ethylene with styrene. Since **2** did not show any catalytic activities for styrene polymerization, it is thus suggested that reaction of **2** with styrene would afford catalytically inactive (dormant) species. The results presented here would be very important for designing efficient catalyst for precise olefin polymerization.

4.6 Conclusion

Ethylene polymerization with a series of (arylimido)vanadium(V) dichloro complexes was investigated in various conditions (cocatalyst, temperature, solvent). It was revealed that both anionic ancillary donor ligand and subsutituents on the anionic ligand played key roles especially for exhibiting the high catalytic activities. The aryloxo complexes seemed to exhibit higher catalytic activities than the ketimide complexes, and the activities at 25 °C under the optimized conditions increased in the order: **1** > **2**, **4** > **7** > **5**, **6** > **3**. The sustituents at 2,6-positions on aryloxo ligand affected both catalytic activities and thermal stabilities during polymerization runs. For example, the activity by **4** increased upon lowering polymerization temperature, whereas the activities by **1** and **2** decreased at 0 °C. Most drastic changes in the catalytic activity could be observed, when ^{t}Bu groups were placed on the 2,6-positions, probably due to the steric hindrance around the metal. Substituents on ketimide ligand also affected the catalysts behavior (**5**, **6** versus **7**), and substituents on imido ligand had a little effect in the polymerization.

4.7 Experimental section

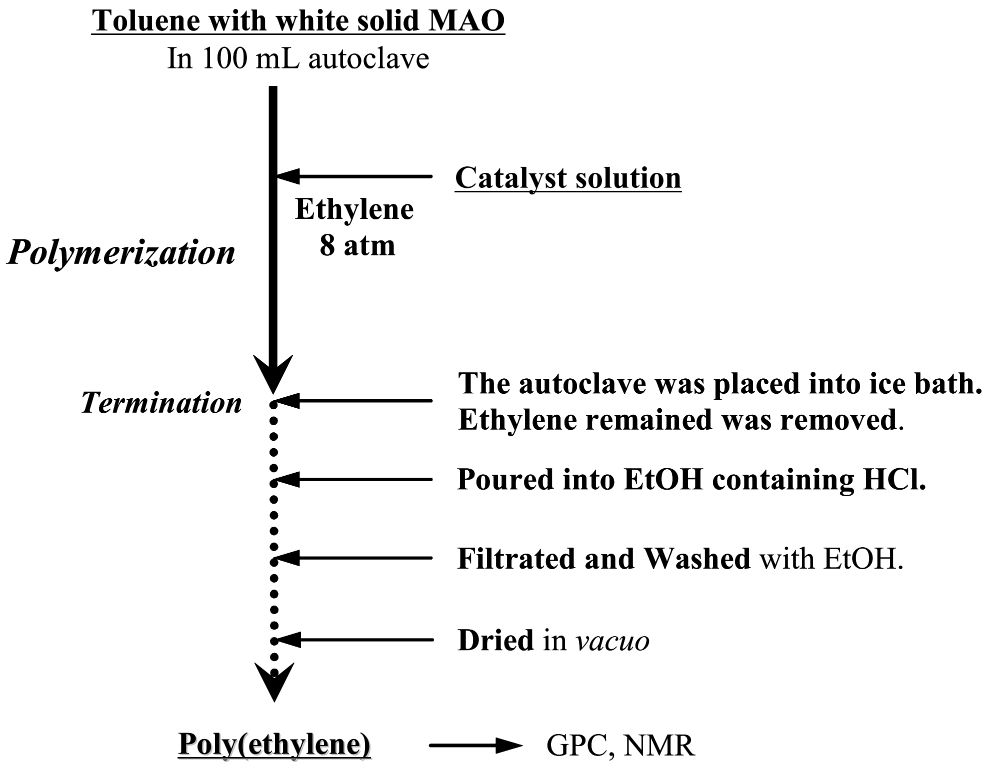
All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous-grade of solvent (toluene, *n*-hexane, C_6H_5Cl and CH_2Cl_2) were stored in a Schlenk tube in the drybox in the presence of molecular sieves and were used without further purification. Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co. Ltd.) and was used as received. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were removed and dried in vacuo in the drybox and used as the white solid.

Molecular weights and molecular weight distributions for the resultant polyethylenes were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel column (TSK gel GMH_{HR}-H HT x 2) at 140 ºC using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with polystyrene standards.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^1H), and all spectra were obtained in the solvent indicated at 25 ºC unless otherwise noted. ^{13}C NMR spectrum for polyethylene was recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, ^{13}C) with proton decoupling. The pulse interval was 5.2 sec, the acquisition time was 0.8 sec, the pulse angle was 90º, and the number of transients accumulated was ca. 10000. The analysis samples were prepared by dissolving polymers in a mixed solution of 1,2,4-trichlorobenzene/benzene-d_6 (90/10 wt/wt), and the spectrum was measured at 130 ºC.

General procedure for ethylene polymerization. Ethylene polymerizations were conducted in a 100 mL scale stainless steel autoclave. The typical reaction procedure (run 4, Table 4-1) was as follows. Toluene (29.5 mL) and MAO solid (145 mg) were added into the autoclave in the drybox. The reaction apparatus was then filled with ethylene (1 atm), toluene solution (0.5 mL) containing **1** (2.5 μmol) was added into the autoclave, the reaction apparatus was then immediately pressurized to 8 atm. and the mixture was magnetically stirred for 10 min in a water bath of 25 ºC (water-ice bath in case of 0 ºC and oil-bath in case of higher temperature). The mixture was then poured into acidified ethanol. The resultant polymer was collected, washed with EtOH and water, and then dried in vacuo at 50 °C for several hours. Polymerization of ethylene in the presence of styrene was carried out in the similar manner, and resultant polymer was separated by an extraction with acetone to remove atactic polystyrene formed by MAO itself according to the reported procedure.[13a]

Scheme 3-2.



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5 Syntheses of vanadium alkylidene complexes and their use as catalysts for ring-opening metathesis polymerization (ROMP)

High oxidation state transition metal-alkylidene complexes attract considerable attention because of their promising possibility as catalyst (initiator) for olefin metathesis such as ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM) and cross metathesis (CM) reaction etc.[1-3] Such metathesis is recognized one of the most powerful methods in both organic synthesis and polymer synthesis, since it can provide a variety of valuable organic compounds and/or polymeric materials which is hard to synthesize by other methods.[2] Since the first "high oxidation state" transition metal alkylidene complex containing a metal-carbon double bond was discovered in the form of $(Me_3CCH_2)_3Ta(CHCMe_3)$[4] and $(\eta^5\text{-}C_5H_5)_2Ta(CH_2)(CH_3)$,[5] a number of alkylidene has been reported.[1] Successful examples of metathesis have already been demonstrated by molybdenum (e.g. Schrock type alkylidene).[1b-d,2] The carbene complexes, in which the metal-carbon bond is not as a dianion $[M(\delta^+)=C(\delta^-)]$ as it is in an early transition metal complex and the metal is not in its highest possible oxidation state, have also been reported as olefin metathesis catalysts. In particular, Grubbs carbene complexes have been widely used as relatively oxygen-, water-, and functionality-tolerant olefin metathesis catalysts.[2-3]

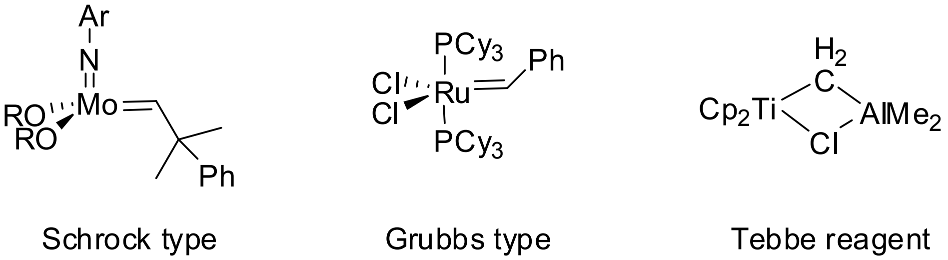
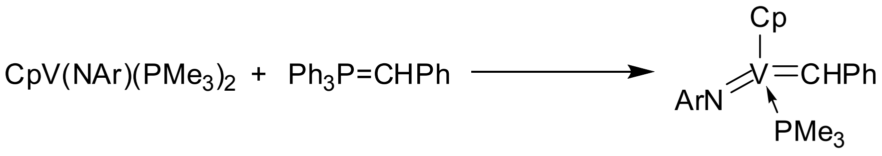


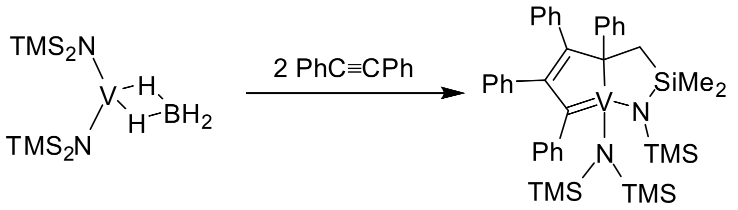
Figure 5-1. Several transition metal alkylidene (carbene) complexes.

Although various transition metals through the periodic table including niobium and tantalum have been adopted, reports on well-characterized vanadium alkylidene have been limited in followings; The first vanadium alkylidene, of the type $VCp(CHPh)(NAr)PMe_3$ (Ar = $2,6\text{-}{}^{i}PrC_6H_3$), has been reported by Teuben et al. in 1994 and synthesized via transfer of a benzylidene from phosphorus to vanadium(III) (eq 1).[6a]



(1)

The second has happened to be prepared by the reaction between the V(III) borohydride complex and diphenylacetylene and the mechanism for the reaction remained to be elucidated (eq 2).[6b]

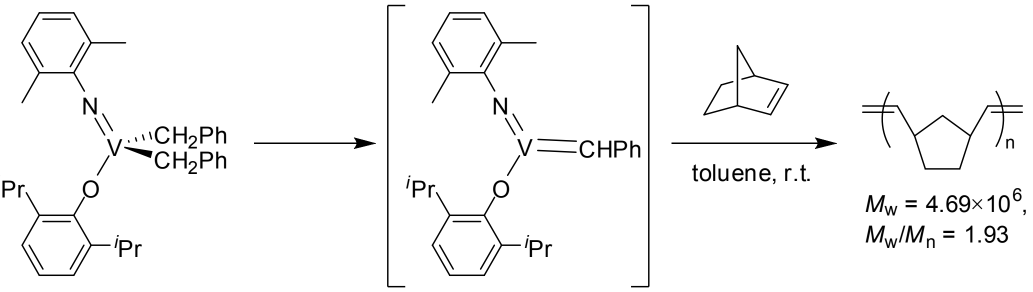


(2)

Recently, Mindiola et al. reported that vanadium(IV) carbene complex could be prepared through one-electron oxidation of vanadium(III) complex containing β-diketiminate ligand by silver salt.[7c,d,e] Although some vanadium complexes that contain metal-carbon double bond have been reported, the vanadium alkylidenes (carbenes) that exhibit notable activity olefin metathesis have never been reported so far.[7,8]

In 2002, Nomura et al. reported the first example that dibenzyl complex, $V(CH_2Ph)_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)$, could initiate ring-opening metathesis polymerization (ROMP) of norbornene (NBE) without cocatalyst although the activity was low (turn over number = 37) and they could not succeed in isolation of the active species (eq

3).[9] This result suggested that vanadium alkylidene is responsible for olefin metathesis catalyst.

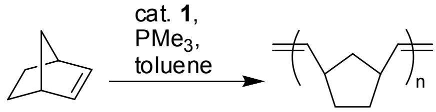


(3)

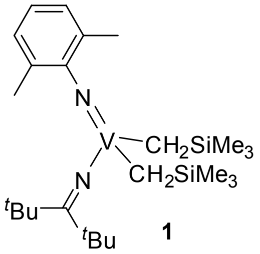
This chapter will focus on syntheses of (arylimido)vanadium(V) alkylidene complexes. The results of ROMP using the alkylidene will also be discussed.

5.1 Evidence of formation of vanadium alkylidene *in situ*

The ROMP of NBE as a model reaction of olefin metathesis (eq 4) was investigated using dialkyl complex, of the type $V(CH_2SiMe_3)_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)$ (**1**), and results are summarized in Table 5-1.



(4)



1

Table 5-1. ROMP of NBE with $V(CH_2SiMe_3)_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)$ (**1**).[a]

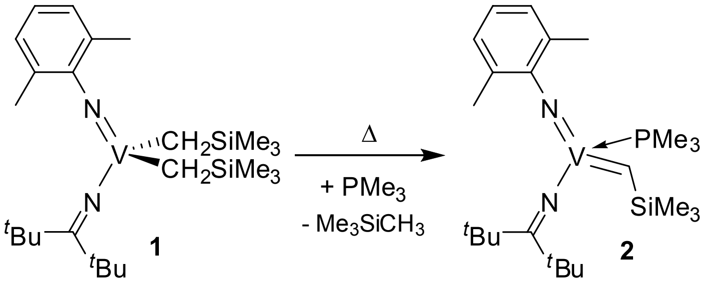
Run	Complex (μmol)	NBE / mmol	NBE conc.[b]	P/V[c]	Temp. / °C	Time / h	TON[d]	M_w[e] $\times 10^{-4}$	M_w/M_n[e]
1	**1** (10.0)	2.12	0.89	---	25	6	3		
2	**1** (10.0)	2.12	0.89	3	25	6	1.6		
3	**1** (20.0)	4.24	0.89	---	50	6	6.5		
4	**1** (20.0)	4.24	0.89	3	50	3	61		
5	**1** (10.0)	4.24	0.89	3	50	6	140	26.1	5.4
6	**1** (10.0)	4.24	0.89	3	50	6	150		
7	**1** (10.0)	4.24	0.89	5	50	6	66	48.1	4.0
8	**1** (20.0)	4.24	0.89	---	80	6	6.8		
9	**1** (20.0)	4.24	0.89	3	80	1	61		
10	**1** (10.0)	4.24	0.89	3	80	3	378	60.3	5.4
11	**1** (10.0)	2.12	0.44	3	80	3	212[f]	87	3.2
12	**1** (10.0)	1.06	0.22	3	80	3	101	97	3.0
13	**1** (10.0)	2.12	0.44	5	80	3	40	47	3.0
14	**1** (10.0)	4.24	0.89	5	80	3	183	69	3.7
15	**1** (10.0)	4.24	0.89	5	80	6	285		

[a] Conditions: catalyst, NBE 1.06-4.24 mmol, PMe_3, toluene. [b] Initial NBE concentration in mmol/mL. [c] Molar ratio of PMe_3/V. [d] TON = NBE consumed (mmol)/V (mmol). [e] GPC data vs polystyrene standards. [f] Completion of polymerization.

The complex **1** initiated ROMP of NBE without cocatalyst in some degree (runs 1, 3 and 8). The activity increased upon addition of PMe_3 (runs 3-6), and this might be due to the more efficient formation of the vanadium-alkylidene in the mixture. However, the activity decreased upon further addition (run 7), and this can be assumed that the coordination of PMe_3 into the vanadium metal center retards the propagation (coordination of NBE), leading to the lower activities. Note that the observed catalytic activity (in the presence of PMe_3) notably increased at higher temperature, and the higher activity was observed even at 80 °C. The activity was also affected by the NBE concentration (runs 10-12), and the resultant polymer possessed unimodal, but wide molecular weight distributions probably due to the rapid propagation compared to the slow initiation. Resultant polymer contained ring-opened structure which is a mixture of *cis*- and *trans*- olefinic double bonds (*cis*/*trans* = 5.7, run 6) confirmed by ^1H and ^{13}C NMR spectra, and the fact was somewhat different from those observed in the ROMP by $(ArN)VCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ - $AlMe_3$ catalyst system (*trans*/*cis* = 10).[9] This would be assumed as due to the degree of *syn*/*anti* rotamer (rotational isomer or rotamer) and/or the mode of NBE coordination into the vanadium metal center proposed by the molybdenum-alkylidene catalyst.[1]

The above result clearly indicated that olefin metathesis active vanadium alkylidene efficiently generated *in situ* under polymerization conditions. It is thus obvious that both PMe_3 and reaction temperature play important roles for exhibiting the high catalytic activity. The formation of alkylidene could be confirmed by NMR experiment (Scheme 5-1). The time-course ^1H NMR spectra upon heating the C_6D_6 solution of dialkyl complex **1** at 80 °C in the presence of excess amount of PMe_3 are shown in Figure 5-2. The peaks of dialkyl complex **1** disappeared over the time-course, and new peaks appeared (indicated by arrowheads), although no reaction occurred at 25 °C (see Chapter 2). Especially appearance of α-proton of alkylidene (ca. 16 ppm) and tetramethylsilane (0 ppm) clearly indicated the formation of vanadium alkylidene species.

Scheme 5-1.



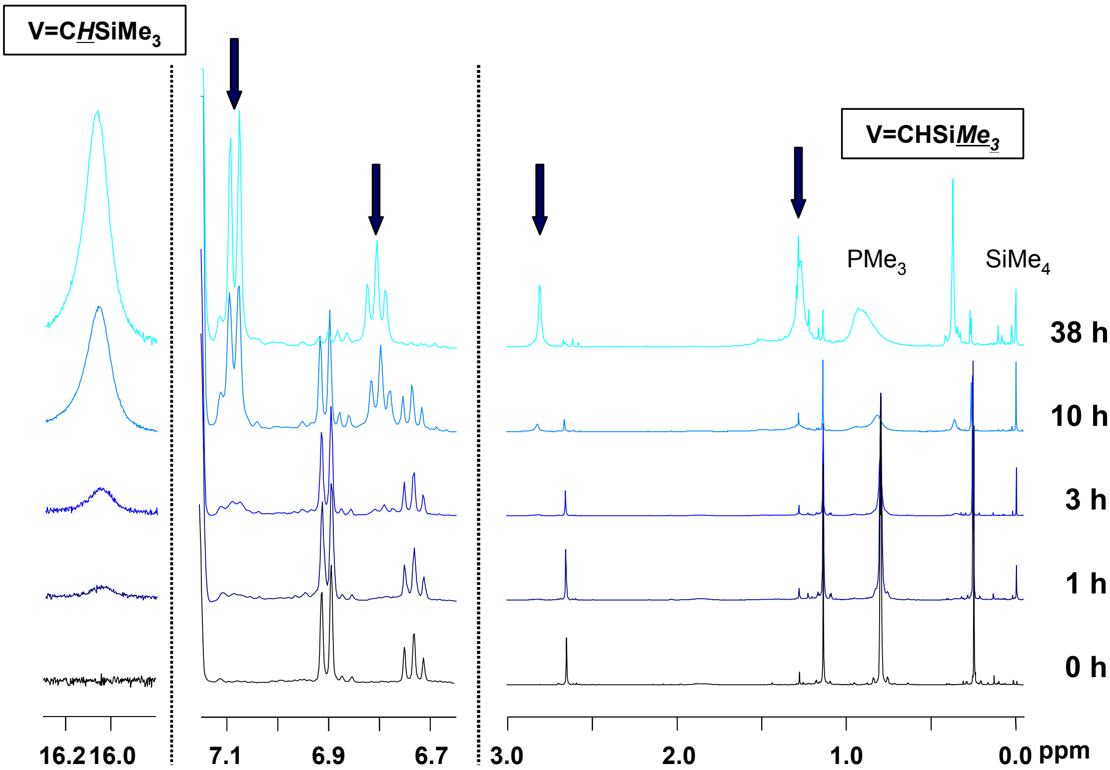


Figure 5-2. ^{1}H NMR spectra (C_6D_6) of dialkyl-complex **1** with PMe_3 (7.0 eq) upon heating.

5.2 Synthesis and isolation of vanadium alkylidene containing ketimide ligand

Thermolysis of dialkyl complex **1** in the presence of excess amount of PMe_3 was thus conducted on preparative scale (6.5 mmol scale). Recrystallization from *n*-hexane afforded the alkylidene **2** and the product was identified by ^1H, ^{13}C NMR and elemental analysis. The α-proton ($V{=}C\mathit{H}SiMe_3$) resonance appeared at 14.5 ppm in C_6D_6, and α-carbon ($V{=}\mathit{C}HSiMe_3$) appeared at 302.0 ppm in C_6D_6. It was revealed that one equivalent of PMe_3 was coordinated to the metal center.

Red prism microcrystals of **2** suitable for X-ray crystallography were grown from a saturated *n*-hexane solution cooled to -30 °C (Figure 5-3). The selected bond distances and angles for **2** are summarized in Table 5-2.

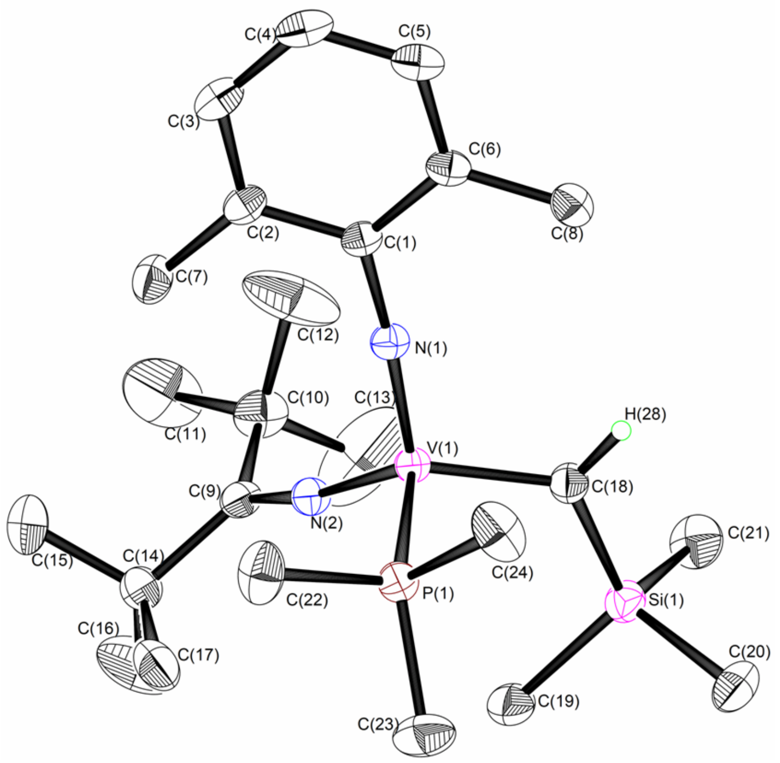


Figure 5-3. ORTEP drawing for **2**. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 5-2. Selected bond distances (Å) and angles (°)
for $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_2PMe_3$ (**2**).

Bond Distances in Å

V-C(18)	1.860(2)	V-P(1)	2.4331(7)
V-N(1)	1.679(2)	N(1)-C(1)	1.383(2)
V-N(2)	1.847(2)	N(2)-C(9)	1.267(3)
Si(1)-C(18)	1.847(2)		

Bond Angles in °

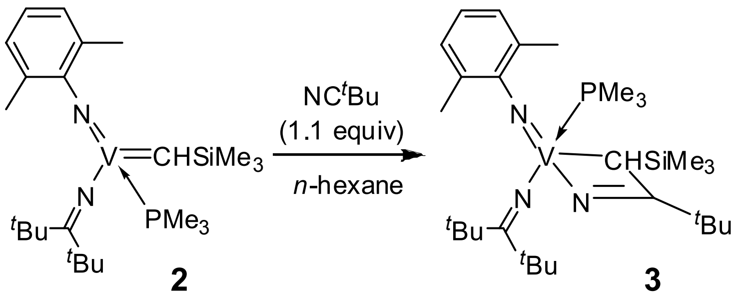
C(18)-V-N(1)	109.14(9)	C(18)-V-N(2)	119.8(1)	C(18)-V-P(1)	97.45(8)
N(1)-V-N(2)	115.60(9)	N(1)-V-P(1)	93.46(7)	N(2)-V-P(1)	117.03(6)
V-C(18)-Si(1)	121.4(1)	V-N(1)-C(1)	174.4(2)	V-N(2)-C(9)	169.9(2)

The alkylidene **2** folds distorted tetrahedral geometry around vanadium metal center, and the V-$CHSiMe_3$ bond distance (1.860 Å) is close to that in the bicyclic carbene-amide complex (1.876 Å)[6b] and is shorter than that in the benzylidene complex (1.922 Å);[6a] the distance is longer than those in V(III)-CH^tBu (1.809 Å),[4a-b] neutral and cationic V(IV)-CH^tBu complexes (1.787-1.795 Å).[4c-d] The V-C-Si bond angle is 121.4° suggesting that almost no α agnostic interaction was present. (For comparison, the V=C-C angles in $CpV(CHPh)(NAr)PMe_3$ and $CpV(CHCMe_3)(dmpe)$ were found to be 136.9(4)° and 173.3(3)°, respectively.) The V-P bond distance (2.433 Å) is shorter than those in $VCl_2(NAr)(NC^tBu_2)PMe_3$ and $VCl_2(NAr)(NC^tBu_2)(dmpe)$ (2.515-2.646 Å, see Chapter 2). These results clearly indicate that **2** is 16 electron vanadium(V)-alkylidene complex.

5.3 Reaction of $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_2PMe_3$ with nitrile

Reaction of ketimide-alkylidene **2** with 1 equiv of pivalonitrile was investigated (Scheme 5-2). The reaction proceeded smoothly affording nitrile adduct, $V(N\text{-}2,6\text{-}Me_2C_6H_3)(NC(^tBu)CHSiMe_3)(NC^tBu_2)(PMe_3)$ (**3**, 80% isolated yield), and the product was characterized by ^1H, ^{13}C, ^{51}V NMR spectra and elemental analysis. It was confirmed by ^1H, and ^{13}C NMR spectra and elemental analysis that PMe_3 was remained in the adduct. The ^{51}V NMR spectrum showed resonance at - 466 ppm and large upfield shift was observed compared to other 18 electrons complexes in Chapter 2 [$VCl_2(NAr)(NC^tBu_2)(dmpe)$ at -365, V(NAr) (O-2,6-$Me_2C_6H_3)_3$ at -373, and $V(NAr)(NC^tBu_2)_3$ at -387]. Furthermore, two resonances characteristic to NCR_2 were appeared in the ^{13}C NMR spectra. These results strongly suggested that the nitrile adduct **3** was 18 electrons compound and contained azametallacyclobutene ring. The result also suggested that the V=CHSiMe$_3$ bond in **2** might be polarized δ+ on V and δ– on C as it is common feature in high oxidation state transition metal alkylidene.

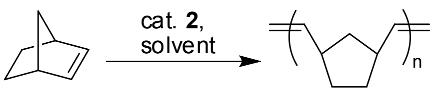
Scheme 5-2



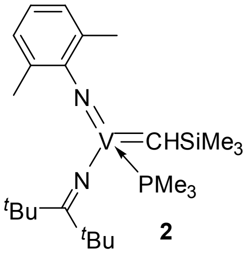
Similar investigation was reported by Hessen et al. using vanadium(III) carbene, of the type VCp(CH^{t}Bu) (dmpe) (dmpe = 1,2-bis(dimethylphosphino)ethane),[7b] and Mashima et al. using tantalum(V) alkylidene, of the type TaCp*(CHPh)(η^4-DMBD) (DMBD = 2,3-dimethyl-1,3-butadiene).[10] In both cases, the reaction of tantalum benzylidene with one equivalent of pivalonitrile afforded the corresponding imido complex via azametallacyclobutene intermediate.

5.4 Results of ROMP of NBE catalyzed ketimide-alkylidene, $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)_2PMe_3$

The ROMP of NBE as a model reaction of olefin metathesis was investigated using vanadium alkylidene **2** (eq 5), and results are summarized in Table 5-3.



(5)



2

Table 5-3. ROMP of NBE with $V(CHSiMe_3)(NAr)(NC^{t}Bu_2)PMe_3$ (**2**) and $Ru(CHPh)Cl_2(PCy_3)_2$ (**Ru**).[a]

Run	Complex	Solvent	NBE / mmol	NBE conc.[b]	Temp. / °C	Time / h	TON[d]	M_w[e] $\times 10^{-4}$	M_w/M_n[e]
16	**2**	benzene	2.12	0.22	25	6	267	46	2.3
17	**2**	toluene	1.06	0.44	25	6	82		
18	**Ru**	toluene	2.12	0.22	25	1	1306	54	1.7
19	**2**	benzene	2.12	0.22	50	3	1275	49	1.6
20	**2**	toluene	2.12	0.22	50	3	166		
21	**2**	toluene	2.12	0.22	50	6	320		
22	**2**	benzene	2.12	0.22	80	0.5	967	140	1.3
23	**2**	benzene	2.12	0.22	80	1	1583	133	1.4
24	**2**	benzene	2.12	0.22	80	2	2071[f]	115	1.6
25	**2**	toluene	2.12	0.22	80	1	1244	32	2.8
26	**Ru**	toluene	2.12	0.22	80	1	350		

[a] Conditions: catalyst 1.0 μmol, NBE 1.06 or 2.12 mmol, benzene or toluene. [b] Initial NBE conc. in mmol/mL, [c] Molar ratio of PMe_3/V. [d] TON = NBE consumed (mmol)/V (mmol). [e] GPC data vs polystyrene standards. [f] Yield 98%.

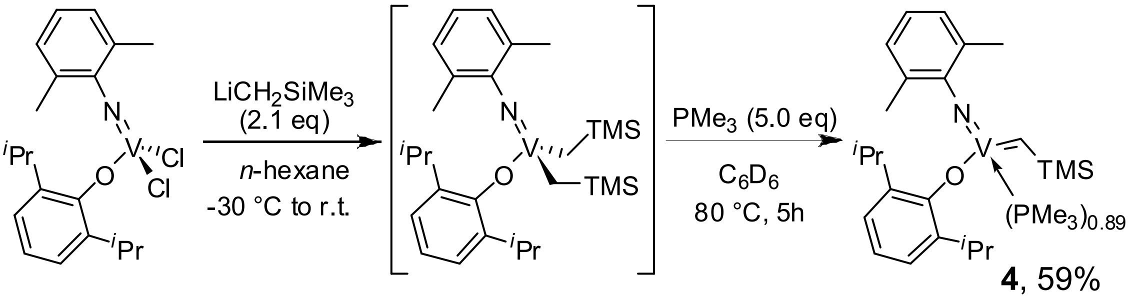
It should be noted that **2** initiated ROMP of NBE with remarkable catalytic activity affording high molecular weight ring-opened polymer with unimodal molecular weight distributions (run 24, 98% yield, $M_n = 1.15\times10^6$, $M_w/M_n = 1.6$). It should be noted that the activity markedly increased in benzene at higher temperature of 80 °C (runs 16, 19, and 24), and the observed activity was higher than that by the known $Ru(CHPh)Cl_2(PCy)_2$ under the same conditions, due to the improved thermal stability at 80 °C (runs 23, 25 *vs* 26). The solvent also affected the activities, and the activities in benzene were higher than those in toluene (runs 16 *vs* 17, 19 *vs* 20, and 23 *vs* 25).

Since the molecular weights for resultant poly(NBE)s were higher than those estimated based on NBE/V molar ratios, the catalyst (initiation) efficiency of **2** was not perfect. This is probably because the dissociation of PMe_3 is necessary for the formation of catalytically-active species [e.g. estimated catalyst efficiency = number of polymer (mmol)/initial catalyst (mmol) was 27% for run 24], since the observed catalytic activity decreased at higher PMe_3/V molar ratio in the ROMP by **1** (see section 5.1 in this chapter).

5.5 Synthesis and isolation of vanadium alkylidene containing aryloxo ligand

Based on the above findings on the synthesis of ketimide-alkylidene, synthesis of vanadium alkylidene containing aryloxo ligand in place of ketimide ligand was thus attempted (Scheme 5-4).

Scheme 5-4



Reaction of $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPrC_6H_3)$ with two equivalent of $LiCH_2SiMe_3$ afforded mixture of dialkyl complex (>92%) and tiny amount of unidentified byproduct. Since the product was highly soluble even in *n*-hexane and thus could not be purified by recrystallization, the mixture was used as was obtained. The aryloxo alkylidene **4** could be isolated as micro crystals by heating the C_6D_6 solution of the crude mixture at 80 °C in the presence of excess amount of PMe_3 and be identified by ^1H, ^{13}C, ^{31}P, and ^{51}V NMR spectra, and by elemental analysis. Due to bulky ^{i}Pr-group on aryloxo ligand, some of PMe_3 were dissociated from the metal center during purification. Thus, molar ratio of PMe_3 to V atom in the isolated alkylidene **4** was less than one (P/V = 0.89).

5.6 Results of ROMP of NBE catalyzed by aryloxo-alkylidene, $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)(PMe_3)_{0.89}$

The results of ROMP of NBE by aryloxo-alkylidene **4** are summarized in Table 5-4, and the results by ketimide-alkylidene **2** are also cited for comparison. The aryloxo-alkylidene also could initiate the ROMP, and the aryloxo-alkylidene showed higher activities at 25 °C than the ketimide-alkylidene (runs 28 *vs* 16). The resultant polymers obtained at 25 °C possessed quite narrow polydispersity (runs 27 and 28), and possibility of living polymerization was thus expected. To confirm this hypothesis, polymerization was conducted in a flask, and prescribed amount of the reaction mixture was removed via a syringe from the polymerization solution to monitor the time course (run 29). The time-course plots [plots of M_n and M_w/M_n versus conversion] were shown in Figure 5-3. It turned out that the M_n value was increased upon increasing the TON value. Additionally, the observed polydispersities (PDIs, M_w/M_n) kept relatively narrow (< 1.2) during polymerization. These results indicated that ROMP of norbornene by aryloxo-alkylidene proceeded in a living manner at 25 °C. In contrast, the polydispersity of the resultant polymer was broad when polymerization was conducted at 50 °C (run 30). This was probably due to the catalyst decomposition. As was seen in ethylene polymerization, the thermal stability of aryloxo-alkylidene was somewhat lower than that of ketimide analogue. Because the catalytically active species are of electron deficient in both ethylene polymerization and metathesis reaction, the less electron donating feature of aryloxo ligand may be one reason for the thermal instability.

Table 5-4. ROMP of NBE with $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^iPrC_6H_3)(PMe_3)_{0.89}$ (**4**).[a]

Run	Complex	Solvent	NBE / mmol	NBE conc.[b]	Temp. / °C	Time / h	TON[d]	M_w[e] ×10^{-4}	M_w/M_n[e]
27	**4**	benzene	2.12	0.22	25	3	297	3.6	1.1
28	**4**	benzene	2.12	0.22	25	6	478	6.7	1.1
16	**2**	benzene	2.12	0.22	25	6	267	46	2.3
29[f]	**4**	benzene	4.24	0.89	25	1	149	3.1	1.1
						2	255	4.8	1.1
						3	393	6.7	1.1
						6	701	11	1.2
						10	1338	17	1.2
30	**4**	benzene	2.12	0.22	50	3	860	73	4.5
19	**2**	benzene	2.12	0.22	50	3	1275	49	1.6
25	**2**	benzene	2.12	0.22	80	2	2071	115	1.6

[a] Conditions: catalyst 1.0 μmol, NBE 2.12-4.24 mmol, benzene or toluene. [b] Initial NBE conc. in mmol/mL. [c] Molar ratio of PMe_3/V. [d] TON = NBE consumed (mmol)/V (mmol). [e] GPC data vs polystyrene standards. [f] Polymerization was conducted in a flask. A prescribed amount of the reaction mixture was removed via a syringe from the polymerization solution to monitor the time course.

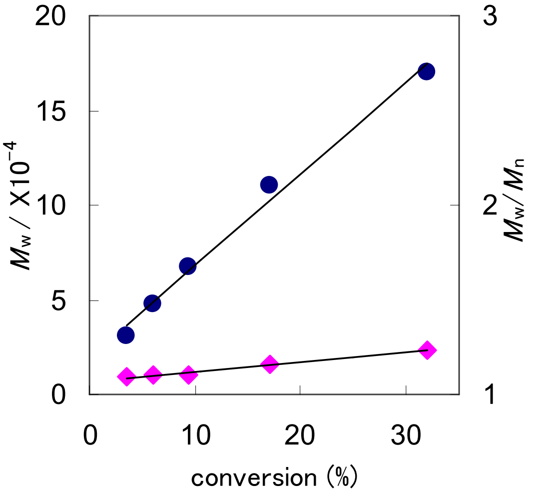
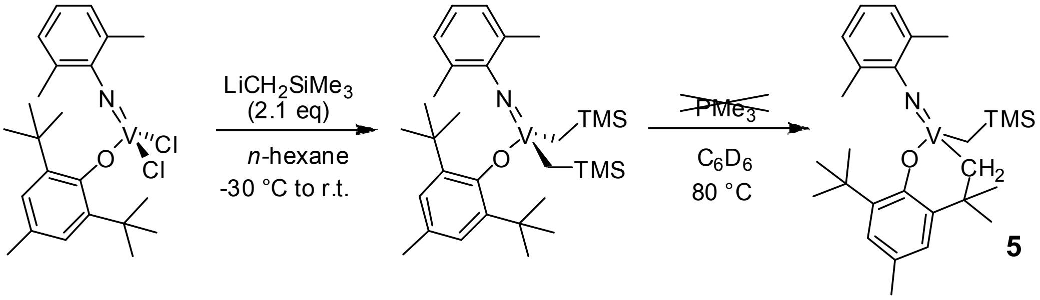


Figure 5-3. Plots of conversion vs. M_n (●) and M_w/M_n (◆) for ROMP of NBE with **4** (run 29).

5.7 Attempt to isolate vanadium alkylidene without using PMe_3

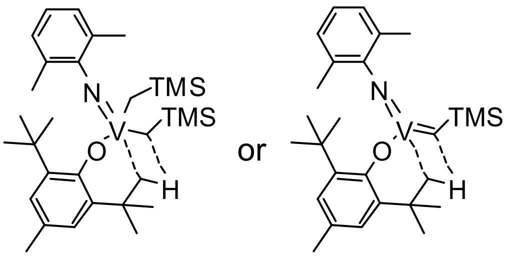
Based on the results shown in previous sessions, it was speculated that steric congestion around the metal was required for α-hydrogen abstraction and the catalytically active species were phosphine free 14 electrons compound. Furthermore, PMe_3 was easily dissociated in aryloxo alkylidene compared to ketimide alkylidene. Taking into account these things, isolation of vanadium alkylidene without PMe_3 was attempted. The aryloxo ligand having bulky ^{t}Bu group on 2,6-positions was shown in Scheme 5-5. The dialkyl complex, of the type $V(CH_2SiMe_3)_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}MeC_6H_3)$, was prepared by reaction of $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}MeC_6H_3)$ with two equivalents of $LiCH_2SiMe_3$.

Scheme 5-5



Thermolysis of the dialkyl complex in the absence of PMe_3 was monitored by ^1H and ^{51}V NMR spectra. The formation of unexpected complex **5** was confirmed after heating the C_6D_6 solution at 80 °C for 3 hours. The complex **5** was probably formed via facile σ -bond metathesis (Scheme 5-6).

Scheme 5-6



5.8 Conclusion

The vanadium alkylidene complexes containing ketimide ligand and aryloxo ligand were successfully synthesized. As a model of olefin metathesis, ROMP of norbornene was investigated using these complexes. It was found that both alkylidene complexes could initiate the ROMP reaction, and this was the first example of olefin metathesis active vanadium alkylidene. The ketimide alkylidene **2** is the rare example of “thermally stable” olefin metathesis active transition metal alkylidene. By changing anionic donor ligand from ketimide to aryloxo, living ROMP could also be achieved. Various applications such as ROMP, acyclic diene metathesis (ADMET) polymerization, CM, RCM with vanadium alkylidene can be thus highly expected.

5.9 Experimental section

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All chemicals used were reagent grade and were purified by the standard purification procedure. Anhydrous-grade of solvent (benzene, *n*-hexane and toluene) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2, and were then passed through an alumina short column before use.

The syntheses of $V(CH_2SiMe_3)_2(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)$ (**1**), $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}^iPr_2C_6H_3)$, and $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}MeC_6H_3)$ are described in Chapter 2 of this thesis. Elemental analyses were performed by using PE2400II Series (Perkin-Elmer Co.).

^1H, ^{13}C, ^{31}P and ^{51}V NMR spectra were acquired at room temperature (unless otherwise noted) using JEOL JNM-LA400 spectrometer (399.65 MHz for ^1H, 100.40 MHz for ^{13}C, 161.70 MHz for ^{31}P, and 105.31 MHz for ^{51}V), and all spectra were obtained in the solvent indicated at 25 ºC unless otherwise noted. Chemical shifts are in ppm, downfield (or upfield) from TMS (δ 0.00, ^1H, ^{13}C), H_3PO_4 (δ 0.00, ^{31}P), and $VOCl_3$ (δ 0.00, ^{51}V). Half-width values, $\Delta\nu_{1/2}$, are reported in Hz.

Synthesis of $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)PMe_3$ (2). A C_6D_6 solution (60 mL) containing **1** (3.15 g, 6.50 mmol) and PMe_3 (3.46 g, 45.5 mmol) was allowed to heat at 80 ºC. The mixture was stirred for 40 hours, and the solution was filtered through Celite pad. The filtrate was concentrated *in vacuo*, and the resultant tan residue was dissolved in minimum amount of *n*-hexane. The concentrated solution was placed in the freezer at -30 ºC, yielding 1.05 g (2.22 mmol, 34%) of red prism shape microcrystals suitable for crystal structure analysis. The reason for the low yield may be due to the difficulty to isolate as the microcrystals (because of high solubility in *n*-hexane), because the ^1H NMR spectrum for the reaction mixture showed formation of **2** exclusively. ^1H NMR (C_6D_6): δ 0.38 (s, 9H, $CHSi(CH_3)_3$), 0.93 (d, 9H, PMe_3), 1.25 (s, 18H, $(CH_3)_3C$-), 2.78 (s, 6H, $(CH_3)_2$), 6.82 (t, 1H), 7.09 (d, 2H), 14.52 (br, 1H, C*H*Si(CH_3)$_3$). ^{13}C NMR ($CDCl_3$): δ 2.8, 17.4, 17.7, 20.2, 31.0, 42.4, 121.9, 127.6, 134.5, 161.7, 193.8, 302.0. Anal. Calcd for $C_{24}H_{46}N_2PSiV$: C, 60.99 (58.68 + VC, vanadium carbide); H, 9.81; N, 5.93%. Found: C, 58.68; H, 9.72; N, 5.73%.

Synthesis of V(N-2,6-$Me_2C_6H_3$)(NC(^{t}Bu)CHSiMe_3)(NC^{t}Bu$_2$)PMe_3 (3). To a *n*-hexane solution (5 mL) containing **2** (236 mg, 0.50 mmol), ^{t}BuCN (50 mg, 0.50 mmol) was added at room temperature. Cooling the solution to -30 ºC gave titled product. Yield 224 mg (81%). ^{1}H NMR (C_6D_6): δ 0.47 (s, 9H, $CH_2Si(CH_3)_3$), 1.13 (9H, PMe_3), 1.34 (d, 18H, NC(CMe_3)$_2$), 1.62 (s, 9H, NC(CMe_3)CHSi), 2.75 (s, 6H, (CH_3)$_2$), 4.86 (s, 1H, VCHSi), 6.88 (t, 1H), 7.15 (d, 2H). ^{13}C NMR (C_6D_6): δ 1.6, 16.0, 20.6, 30.8, 31.2, 40.3, 41.8, 42.2, 101.1, 121.7, 127.7, 133.5, 160.0, 183.0, 189.5. ^{51}V NMR (C_6D_6): δ -466 ($\Delta\nu_{1/2}$ = 1356 Hz). Anal. Calcd for $C_{29}H_{55}N_3PSiV$: C, 62.67; H, 9.97; N, 7.56%. Found: C, 62.40; H, 10.22; N, 7.57%.

Synthesis of V(CHSiMe_3)(N-2,6-$Me_2C_6H_3$)(O-2,6-^{i}Pr$_2C_6H_3$)(PMe_3)$_{0.89}$ (4). To a *n*-hexane solution (100 mL) containing VCl_2(N-2,6-$Me_2C_6H_3$)(O-2,6-^{i}Pr$_2C_6H_3$) (560 mg, 1.18 mmol), LiCH_2SiMe_3 (234g, 2.48 mmol) was added at -30 ºC. The mixture was then warmed slowly to room temperature, and then mixture was stirred for additional 4 hours. After the reaction, the mixture was filtered through Celite pad, and the solvent was pumped off, leaving sticky dark red solid. Yield 610 mg [as 1:0.08 mixture of dialkyl complex and unidentified compound (confirmed by ^{51}V NMR)], and the obtained solids were used without further purification. ^{1}H NMR (C_6H_6): δ 0.25 (s, 18H, (C*H*$_3$)$_3$Si-), 1.15 (d, 12H, (C*H*$_3$)$_2$CH-), 1.83 (br, 2H), 2.42 (s, 6H, C*H*$_3$), 2.54 (br, 2H), 3.38 (m, 2H, (CH_3)C*H*-), 6.66 (t, 1H), 6.76 (d, 2H), 6.91 (t, 1H), 6.99 (d, 2H). ^{51}V NMR (C_6H_6): δ 507 ($\Delta\nu_{1/2}$ = 337 Hz).

The solid was dissolved in 10 mL of C_6D_6, and PMe_3 (449 mg, 5.9 mmol) was added. The solution was heated for 5 hours at 80 ºC. All volatiles were removed under reduced pressure, and the resultant solid was dissolved in minimum amount of *n*-hexane. Cooling the solution to -30 ºC afforded the product. Yield 348 mg (59% total yield). The ^{1}H NMR spectrum of isolated alkylidene at room temperature showed two alkylidene resonances around 16 ppm, while the ^{51}V NMR spectrum showed two resonances (60 and -100 ppm). On the basis of the Schrock type alkylidene, they can be assumed as syn/anti isomer. However, the ^{1}H NMR spectra at various temperatures did not show any differences. On the other hand, the resonances of one of the alkylidene disappeared by addition of excess PMe_3. These facts clearly indicate that the major is PMe_3 adduct and the other is PMe_3 free species (8.15:1). ^{1}H NMR (C_6H_6): δ 0.27 and 0.40 (9H, $(C\mathit{H}_3)_3$Si-), 0.76 (br, P*Me*$_3$), 1.24 and 1.26 (12H, $(C\mathit{H}_3)_2$CH-), 2.74 and 2.83 (6H, $C\mathit{H}_3$), 3.35-3.97 (m, 2H, $(CH_3)C\mathit{H}$-), 6.79 (t, 1H), 6.97 (t, 1H), 7.06 (d, 2H), 7.24 (d, 2H), 16.08 and 16.37 (1H, V=C*H*-). ^{13}C NMR (C6H6): δ 3.1, 16.1, 20.5, 24.1, 26.8, 117.3, 122.7, 123.2, 134.6, 135.8, 163.7, 322.8. ^{31}P NMR (C_6H_6): δ -13.9. ^{51}V NMR (C_6H_6): δ -110 ($\Delta\nu_{1/2}$ = 1050 Hz), 54 ($\Delta\nu_{1/2}$ = 1106 Hz). Anal. Calcd. for $C_{26.67}H_{44.01}NOP_{0.89}V$: C, 63.90 (61.50 + VC, vanadium carbide); H, 8.85; N, 2.79%. Found: C, 61.34; H, 8.69; N, 2.66%.

Thermolysis of $V(CH_2SiMe_3)_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^t\!Bu\text{-}4\text{-}MeC_6H_2)$ (5). To a *n*-hexane solution (150 mL) containing $VCl_2(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}{}^t\!Bu_2\text{-}4\text{-}MeC_6H_3)$ (730 mg, 1.59 mmol), $LiCH_2SiMe_3$ (314g, 3.34 mmol) was added at -30 ºC. The mixture was then warmed slowly to room temperature, and then mixture was stirred for additional 4 hours. After the reaction finished, the mixture was filtered through Celite pad, and the solvent was pumped off, leaving sticky dark red solid. Yield 640 mg, and the obtained solids (dialkyl complex) were analytically pure used without further purification. ^{1}H NMR (C_6H_6): δ 0.29 (s, 18H, $(C\mathit{H}_3)_3$Si-), 1.45 (s, 18H, $(C\mathit{H}_3)_3$C-), 2.11 (d, 1H), 2.18 (s, 3H), 2.31 (d, 2H), 2.57 (6H, $C\mathit{H}_3$), 6.69 (t, 1H), 6.81 (d, 2H), 7.08 (s, 2H). ^{51}V NMR (C_6D_6): δ 583 ($\Delta\nu_{1/2}$ = 497 Hz)

The dialkyl complex (56 mg) was dissolved in 0.5 mL of C_6D_6. The ^{1}H and ^{51}V NMR spectra were taken after heating the solution for 3 h at 80 ºC. Quantitative conversion was confirmed by ^{1}H and ^{51}V NMR spectra. ^{1}H NMR ($CDCl_3$): δ 0.18 (s, 9H, $(CH_3)_3$Si-), 1.24 (s, 3H, CH_3), 1.49 (s, 9H, $(CH_3)_3$-), 1.66 (s, 3H, CH_3), 2.24 (3H, para-CH_3), 2.54 (6H, $(CH_3)_2$), 2.92 (d, 1H, VCHH-), 3.63 (d, 1H, VCHH), 6.75 (t, 1H), 6.89 (d, 2H), 7.00 (s, 1H), 7.14 (s, 1H). ^{51}V NMR (C_6D_6): δ 799 ($\Delta\nu_{1/2}$ = 1316 Hz).

Crystallographic analysis. All measurements were made on a Rigaku RAXIS-RAPID

Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The selected crystal collection parameters are listed below (Table 5-5), and the detailed results were described in the reports attached below. All structures were solved by direct method and expanded using Fourier techniques,[11] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **2** were performed using the CrystalStructure[12,13] crystallographic software package.

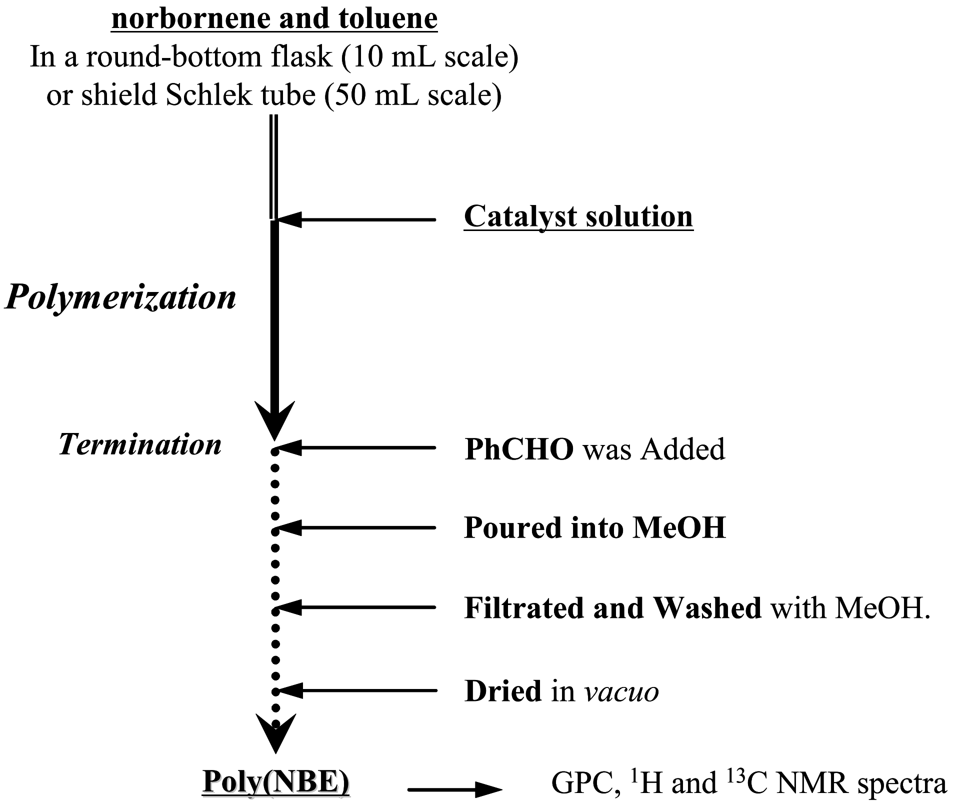
Table 5-5. Crystal and Data Collection Parameters for $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)PMe_3$ (**2**).[a]

Complex	**2**
Formula; Formula weight	$C_{24}H_{46}N_2PSiV$; 472.64
Habits; Crystal size (mm)	red, prism; 0.80×0.50×0.25
Crystal system	triclinic
Space group	P-1 (#2)
a (Å); b (Å); c (Å)	10.554(2); 10.944(2); 13.145(3)
β (deg); V (Å^3)	92.067(9); 1482.2(5)
Z value	2
D_{calcd} (g/cm^3)	1.059 g/cm^3
F_{000}	512.00
Temp (K)	243
λ (Mo Kα) (Å)	0.71075
No. of reflections measured: (R_{int})	total: 14565, unique: 6743 (0.034)
No. of observations (I > 3.00σ(I))	5284
No. of variables	308
Residuals: R1 ; Rw	0.054; 0.67
GOF	1.020
Max (minimum) peak in final diff. map (e-/ Å^3)	0.31 (-0.36)

[a] Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\Sigma w(|F_o|-|F_c|)^2$ (w = Least squares weights, Chebychev polynomial with 3, 13.3898, 7.2647, 9.6689). Standard deviation of an observation of unit weight: $[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$ (N_o = number of observations, N_v = number of variables).

General procedure for ROMP of norbornene with 2. The typical reaction procedure (Table 5-3, run 24) is as follows (Scheme 5-7). Into a sealed Schlenk tube (50 mL scale) containing norbornene (2.12 mmol) dissolved in benzene (9.1 mL), 0.5 mL of a 2.0 μM solution **2** (1.0 μmol) in benzene was added in one portion at -30 °C. The reaction vessel was then immediately placed into an oil bath preheated at 80 °C. The mixture was stirred for prescribed time. The polymerization was then quenched by the addition of excess PhCHO, and the solution was stirred for additional 1 hour at room temperature. The mixture was then poured into methanol (ca. 100 mL). The resultant solid was collected by filtration, washed with methanol, and then dried *in vacuo*. ^{1}H NMR ($CDCl_3$): δ1.02 and 1.84 (m, 2H), 1.33 and 1.77 (m, 4H), 2.42 and 2.77 (br, s, 2H), 5.19 and 5.33 (br, m, 2H olefinic). ^{13}C NMR ($CDCl_3$): δ 32.2, 32.3, 32.9, 33.1, 38.4, 38.6, 41.3, 42.1, 42.7, 43.1, 43.4, 132.8 and 133.0 (olefinic), 133.8, 133.9.

Scheme 5-7.



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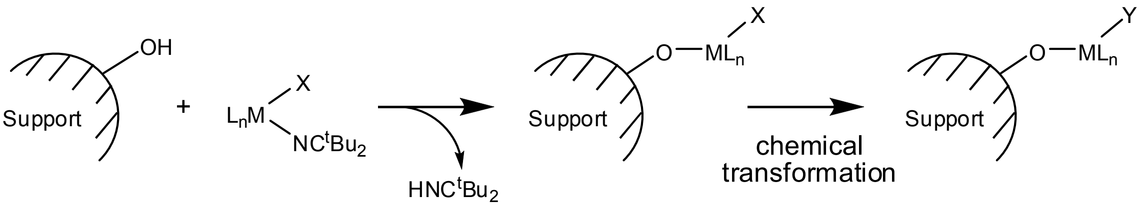
6

Concluding remarks

In the present work, the possibilities of vanadium(V) complexes as effective molecular catalysts for both olefin coordination polymerization and olefin metathesis polymerization were explored. Especially synthesis and reaction chemistry of vanadium(V) complexes containing metal carbon bonds were focused, because they should play roles as the most important key intermediates and/or the catalytically active species in both catalysis cycles.

In chapter 2, a series of (arylimido)vanadium(V) complexes containing aryloxo or ketimide ligands were synthesized in high yields by reacting metal-chloride group of readily accessible VCl_3(N-2,6-$Me_2C_6H_3$) with one, two, or three equivalents of lithium salts. The syntheses of mono-alkyl complex, VMe(N-2,6-$Me_2C_6H_3$)(NC^tBu_2)$_2$, and dialkyl complex, V(CH_2SiMe_3)$_2$(N-2,6-$Me_2C_6H_3$)(NC^tBu_2), were also described.

In chapter 3, the reaction of VMe(N-2,6-$Me_2C_6H_3$)(NC^tBu)$_2$ with various alcohols, thiols and borates were investigated. It was found that the reaction of V-Me in VMe(N-2,6-$Me_2C_6H_3$)(NC^tBu)$_2$ with alcohols did not take place and afforded the other methyl complexes via ligand substitution between the ketimide and the alkoxide/phenoxide. In contrast, facile protonolysis took place in the reaction of the methyl complex with thiols or borates to give the thiolate complexes or the cationic complexes, respectively. These results should be promising for preparation of various vanadium-methyl complexes as well as for better understanding in the basic reaction mechanism in vanadium catalyzed organic synthesis. As another application, the ligand substitution between the ketimide and the alkoxide can be applied for grafting the complex onto silica surface (Figure 6-1).



M = transition metal, L_n = ligand, X and Y = reactive site

Figure 6-1. Schematic drawing for grafting the complex onto silica surface.

In chapter 4, ethylene polymerization with a series of (arylimido)vanadium(V) dichloro complexes were investigated in various conditions (cocatalyst, temperature, solvent). Although the catalytically active species were not isolated, it was suggested the catalytically active species should be derived from vanadium(V) containing both arylimido and anionic donor ligand (aryloxide, ketimide) in this catalysis. Thus, both ancillary donor ligand and subsutituents on the anionic ligand affected the activities and the thermal stabilities. Further information about steric and electronic effects on catalytic activities are required to design more active catalysts. For example, introduction of electron donating and/or electron withdrawing group at *para* position on aryloxo ligand will give additional insight about electronic effects.

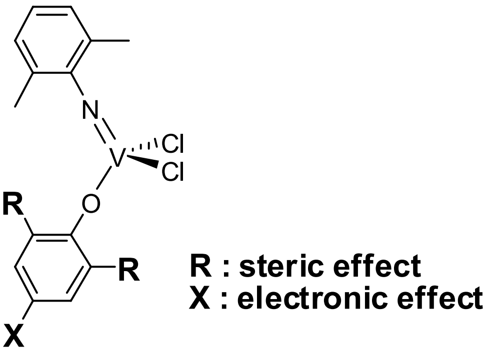
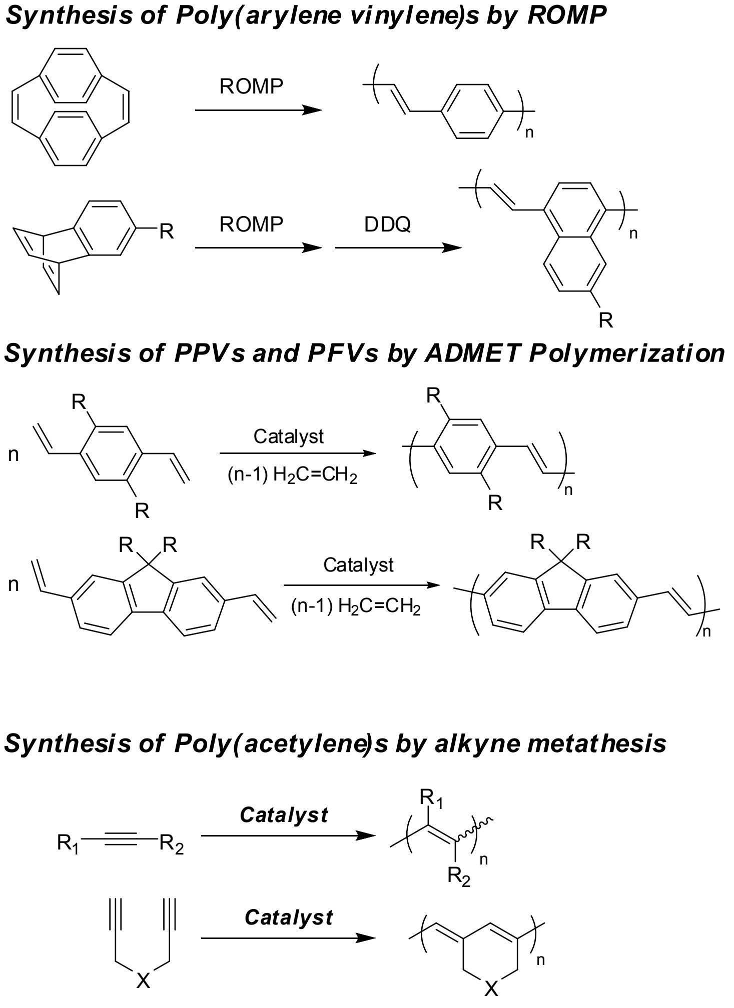


Figure 6-2. Design of new aryloxo complex.

In chapter 5, the syntheses of vanadium alkylidene complexes were discussed. The vanadium alkylidene complexes containing ketimide ligand, $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(NC^tBu_2)PMe_3$, and aryloxo ligand, $V(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)(O\text{-}2,6\text{-}^iPr_2C_6H_3)(PMe_3)_{0.89}$, were successfully synthesized. Both alkylidene complexes could initiate the ROMP reaction, and this was the first example of olefin metathesis highly active vanadium alkylidene. Various applications such as ROMP, acyclic diene metathesis (ADMET) polymerization, CM, RCM, alkyne metathesis with vanadium alkylidene can be thus highly expected. Especially, synthesis of poly(arylene-vinylene)s and poly(acetylene) by metathesis are promising targets, since more active catalysts which afford high molecular weight polymer are expected in such field and ketimide alkylidene afforded high molecular weight ROMP polymer.

Scheme 6-1


Synthesis of Poly(arylene vinylene)s by ROMP

Synthesis of PPVs and PFVs by ADMET Polymerization

Synthesis of Poly(acetylene)s by alkyne metathesis

Through this thesis, I am confident to demonstrate that the vanadium complex catalysts will be a truly useful if it provides a valuable organic compounds and/or polymeric materials that are difficult to synthesize or can not be produced by other known catalysts.

As one the promising targets as the olefin coordination polymerization, copolymerization of ethylene with cyclic olefins using a series of (arylimido)vanadium(V) dichloro complexes would be considered, because various examples were known concerning copolymerization of ethylene with bicyclic and multicyclic olefins using the classical Ziegler type catalyst systems consisting of $VOCl_3$, $VCl_2(OEt)$, and $Et_3Al_2Cl_3$, and because some cyclic olefin copolymers are known to be amorphous materials with a promising combination of high transparency in the UV-vis region along with humidity- and heat-resistance. Some results concerning copolymerization of ethylene with norbornene have already reported from our group.

The scope and limitation of the vanadium alkylidene complexes, including the ligand effects and functional group tolerances, should be clarified to demonstrate the unique characteristics in olefin metathesis with vanadium. These will be the subject in this topic.

List of Publications

学位論文の主たる部分を公表した論文

1) “Effect of aryloxo ligand for ethylene polymerization by (arylimido)(aryloxo)vanadium(V) complexes - MAO catalyst systems.　Attempt for polymerization of styrene”
W. Wang, J. Yamada, M. Fujiki, and K. Nomura
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2) “Vanadium(V)-alkylidene complex exhibiting remarkable catalytic activity for ring-opening metathesis polymerization (ROMP)”
J. Yamada, M. Fujiki, and K. Nomura
Organometallics, 24, 2248-2250 (2005).

3) “A stable vanadium(V)-methyl complex containing arylimido and bis(ketimide) ligands that exhibits unique reactivity with alcohol”
J. Yamada, and K. Nomura
Organometallics, 24, 3621-3623 (2005).

4) “Effect of anionic ancillary ligand in ethylene polymerization catalyzed by (arylimido)vanadium complexes containing aryloxide, ketimide ligand”
K. Nomura, W. Wang, and J. Yamada
Studies in Surface Science and Catalysis, 161, 123-128 (2006).

5) “Ring opening metathesis polymerization of norbornene catalyzed by V(CH2SiMe3)2(N-2,6-Me2C6H3)(N=CtBu2). In situ generation of the vanadium-alkylidene”
K. Nomura, and J. Yamada
Studies in Surface Science and Catalysis, 161, 175-178 (2006).

6) “Synthesis of various (arylimido)vanadium(V)-methyl complexes containing ketimide ligands and reactions with alcohols, thiols, borates: Implications for unique reactivity toward alcohols”
J. Yamada, M. Fujiki, and K. Nomura
submitted for publication.

Book and symposium issue

1) “Ethylene polymerization catalyzed by various (aryloimido)(aryloxo)vanadium(V) complexes - MAO catalyst systems, and attempted styrene (co)polymerization”
W. Wang, J. Yamada, M. Fujiki, and K. Nomura,
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2) “オレフィンの精密重合を指向したバナジウム錯体触媒の設計”
山田純司、野村琴広
月刊ファインケミカル特集企画、小宮三四郎監修、株式会社シーエムシー出版、東京、2007 年 6 月.（依頼投稿）.

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J. Yamada, M. Fujiki, and K. Nomura
15th International symposium on olefin metathesis and related chemistry (ISOMXV), P04, Kyoto, 7/’03.

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K. Nomura, A. Sagara, J. Yamada, M. Fujiki, and W. Wang, 15th International Symposium on Olefin Metathesis and Related Chemistry (ISOMXV), P05, Kyoto, 7/’03.

2) “Olefin polymerization by (arylimido)vanadium(V) complexes - cocatalyst systems - Remarkable role of aluminum cocatalyst -”

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4) “In situ generation of olefin metathesis active vanadium alkylidene”

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厚見尚志、野村琴広、藤木道也、山田純司

第36回石油・石油化学討論会, 2D02, 鹿児島, 2006年12月.

Acknowledgements

The present research has been done at the Polymer Science Laboratory, Graduate School of Materials Science, Nara Institute of Science and Technology. The present research was partly supported by Tokuyama Science Foundation. The present research was also supported by a predoctoral fellowship (No. 5042) of JSPS.

The author would like to express his sincere gratitude to Professor Michiya Fujiki of the Advanced Polymer Science Laboratory, Graduate School of Materials Science, Nara Institute of Science and Technology, for his kind advice, continuous supporting, encouragement and supervision throughout the course of this research.

The author is deeply indebted to Associate Professor Kotohiro Nomura of the Advanced Polymer Science Laboratory, Graduate School of Materials Science, Nara Institute of Science and Technology, for his constant guidance, insightful opinions, supervision and heartwarming encouragement throughout the course of this research, and for his comments on the preparation of this thesis.

The author wishes to express his sincere gratitude to Professor Kiyomi Kakiuchi of the Laboratory of Synthetic Organic Chemistry, Graduate School of Materials Science, Nara Institute of Science and Technology, for his instructive discussion as well as critical reading of this thesis.

The author is sincerely grateful to Visiting Associate Professor Takahiro Honda of the Laboratory of Functional Surface Science, Graduate School of Materials Science, Nara Institute of Science and Technology, for his valuable discussion as well as critical reading of this thesis.

The author expresses his thanks to Professor Bart Hessen of Stratingh Institute for Chemistry and Chemical Engineering, University of Groningen, for

helpful advice and giving the opportunity to study in his group for 3 months beginning July, 2005.

The author expresses his thanks to Professor Tamio Hayashi of Department of Chemistry, Graduate School of Science, Kyoto University, for teaching the basics of organic synthesis. The author spent a worthwhile year in his group in the final year at the university.

The author expresses his thanks to Mr. Fumio Asanoma for help in NMR analysis and Mr. Shohei Katao for help in crystallographic analysis.

The author is sincerely grateful to Dr. Masanobu Naito and Dr. Hisanari Onouchi of the Advanced Polymer Science Laboratory, Graduate School of Materials Science, Nara Institute of Science and Technology, and Dr. Giseop Kwak of Department of Polymer Science, Kyungpook National University, for their valuable discussion.

The author would like to thank all of his colleagues in the Advanced Polymer Science Laboratory, Graduate School of Materials Science, Nara Institute of Science and Technology, for not only sharing nice time for research work and useful discussion but also having fun during the years in the laboratory.

Finally, the author would like to express his thanks to his parents, Harugi and Chieko Yamada, for their understanding, warm support, and heartfelt encouragement.

March, 2007
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