

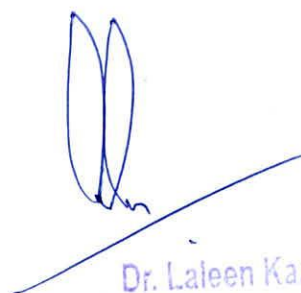
**Recent developments in the chemistry of
Vanadium complexes supported by Diimino
- Pyridine Ligand : Catalytic behaviour
towards olefin polymerization and fixation
of dinitrogen**

**By
Indu vidyaratne**

This thesis was submitted in Partial fulfillment of the requirements

**For the Master of Science in Polymer Science and Technology to
the faculty of Graduate studies of the University of Sri Jayawardenapura,
Sri Lanka.**

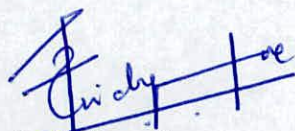
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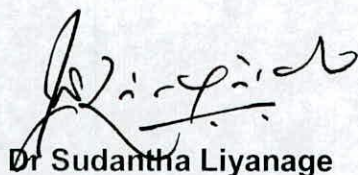
The work described in this thesis was carried out by the undersigned at the university of Sri Jayawardenapura, Sri Lanka and the University of Ottawa , Canada under the supervision of Dr Sudantha Liyanage and Professor Sandro Gambarotta and report on this has not been submitted to any university for another Degree. Also, I certify that this thesis does not include, without acknowledgement, any material previously submitted for a degree in any university and to best of my knowledge and belief it does not contain any material previously published, written or orally communicated by another person except where due reference is made in the text.



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I certify that the above statement made by the candidate is true and that this thesis is suitable for submission to the university for the purpose of evaluations .



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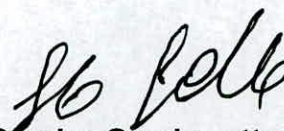
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To Gayashan, Premaratne

Kusuma and Vidyaratne

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List of Abbreviations.

<i>Acac</i>	acetylacetonato
⊕	angstrom
atm	atmosphere
°C	degrees Celsius
Calcd.	Calculated
cm ⁻¹	wave number
Cp	cyclopentadienyl
δ	chemical shift
D _{calcd}	calculated density
Et	ethyl
EP	ethylene propylene elastomers
EPDM	ethylene propylene diene elastomers
F ₀₀₀	electronic density
FTIR	Fourier transform infrared spectroscopy
F.W.	Formula weight
g	grams
G.o.F	goodness of fit
GPC	gel permeation chromatography
h	hour
<i>i</i> -Pr	isopropyl
K	Kelvin
kg	kilograms
L	ligand
μ _{calcd}	absorption coefficient
μ _{eff}	effective magnetic moment in Bohr magnetons
M	molar
MAO	methylalumoxane
mM	millimolar
Me	methyl
min	minute
ml	milliliter
mmol	millimole
m.p.	melting point
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge thermal ellipsoid program
PD	polydispersity(M_w/M_n)
Ph	phenyl
ppm	parts per million
R	alkyl group (found in reaction schemes)
R	reliability factor (ceystallographic tables)
T	temperature
THF	tetrahydrofuran
Me ₃ Al	trimethylaluminium
X	halogen
XRD	X-ray diffraction

List of Publications

1. Indu Vidyaratne, Sandro Gambarotta*, and Ilia korobkov. "*Dinitrogen Partial Reduction by Formally Zero – and Divalent Vanadium Complexes supported by the Bis-iminopyridine system.*" **Inorganic Chemistry** Vol144, 2005, 1187
2. Indu Vidyaratne Jennifer Scotte, Sudantha Liyanage, and Sandro Gambarotta* "*the ability of the diimino pyridine Ligand to sustain high Catalytic activity: New surprises from an old Ligand*" **Organometalics** Submitted.

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Abstract

The reaction schemes described below outline the different step, which lead to the polymerization of α -olefins. These mechanistic pathways are generally accepted by the scientific community for group IV catalyst. More recent studies have been focused on investigating catalyst that are not supported by group IV metal center and not supported by cyclopentadienyl ligands. Another field of research is geared towards the understanding of catalyst/co-catalyst interaction in order to optimize activity and selectivity of the catalyst. The three main features that are believed to lead to successful polymerization catalyst are (1) electron deficiency; a fourteen electron configuration seems to be the winning recipe for obtaining highly active species, (2) The possibility to vacate a coordination site adjacent to the propagating polymer chain, (3) The active catalyst should preferentially bear a positively charged metal center which increases the electrophilic properties important for enhancing the coordination of α -olefin. Some neutral alkyl-metal complexes have been reported to polymerized α -olefin¹ however the catalytic activities were typically low.

The catalytic performances are mainly induced by the supporting ligand for many reasons, which determine selectivity, activity and polymer structure. Firstly, the ligand gives control over the coordination geometry and the number of occupied sites around the metal center. Secondly, the ligand controls and stabilizes the active oxidation state, which in turn is of the utmost importance to the high performance of the catalyst. Finally, the ligand will also play a central role in the steric protection of the active site and will have a great influence over the stereochemical properties of the transition state, which are eventually translated to the polymer structure.²

The effect of supporting ligands (i.e nitrogen donor ligands) are at the root of this study as well as an attempt to improve our understanding of the catalyst /co-catalyst interaction. The nitrogen donor based ligand systems were chosen for several reasons. These ligand systems are easily accessible, inexpensive and present a wide range of possibilities from an electronic point of view since they can be considered as either two or four electron donors. Furthermore, steric electronic properties of ligand system can also be tuned quite easily via relatively simple organic procedures. In view of these observations, nitrogen donor ligands are great candidates to synthesize the α -olefin polymerization catalyst.

Vanadium catalytic systems in α -olefin polymerization remain relatively underdeveloped mainly due to the fact that four of the five-oxidation states display paramagnetism properties. However, great efforts to surmount these obstacles have lead to the development of a handful of vanadium-based catalytic systems.³ Although the drawbacks of vanadium-based catalyst such as air sensitivity and deactivation to lower oxidation states remain rather severe, industry maintains great interest in vanadium catalyst since specific polymer properties remain unique to vanadium catalytic systems. Vanadium catalyst produce random and amorphous ethylene /propylene co-polymers with low crystallinity and furthermore they can be used in making more elaborate ter-polymers with a third monomers such as norbornylene. Studies by Ziegler's group have emphasized through theoretical calculations the high potential of the d^2 electronic configuration of vanadium (III) towards polymerization due to a low olefin insertion energy barrier and a high chain termination energy barrier.⁴

Our group had invented lot of information about vanadium polymerization mechanism. Specially we were managed to find out a possible activation pathways through a series of alkylation reactions to assess the vanadium-carbon bond stability by using a variety of nitrogen donor-based supporting ligands. Upon using alkylating agents such as the alkyaluminium co-catalysts we trapped and crystallized the active intermediate, as well as we were able to elucidate the deactivation process.⁵

In order to assess and to picture more clearly the effectiveness of the α -olefin polymerization activities of the vanadium organometallic complexes synthesized in this thesis, a table rating the catalyst has been drawn using numbers obtained from a review article from Gibson's group.² (Table 1.1)

Table 1.1 Quantifying Catalytic Activity for α -Olefin Polymerization.

Rating	Activity [$\text{g mmol}^{-1}\text{h}^{-1}\text{atm}^{-1}$]
Very low	< 1
Low	1 - 10
Moderate	10 - 100
High	100 - 1000
Very high	>1000

In contrast to group IV polymerization catalysts, the vanadium-based catalysts are capable of high activities and rapid deactivation through reduction of the metal center.⁵

In order to remedy the ligand migration to the co-catalyst a vanadium (III) complexes supported by a nitrogen donor based ligand such as bis(imino)pyridine ligand. Supporting the metal center with a nitrogen donor based ligand system has proven to be quite successful with respect to the ligand leaching problem, increasing considerably the activity of the catalyst and inducing structure in to the polymer. The bis(imino)pyridyl ligand has also opened the door to stabilizing low-valent transition metal complexes bearing alkyl groups.⁵

The bis-iminopyridine ligand when complexed to $\text{VCl}_3(\text{THF})_3$ affords a highly active catalyst for ethylene polymerization.⁵ This ligand has been deprotonated at the two methyl groups attached to the imine function forming a new dianionic ligand.⁶ The reaction of this new ligand with $\text{VCl}_3(\text{THF})_3$, resulted in the tri valent vanadium adduct which supports an extremely high level of catalytic activity for ethylene polymerization. The trivalent mono-chloro Vanadium adduct becomes even more potent catalyst upon alkylation and has been even shown ethylene trimerization activity in the absence of co-catalyst. Reduction of the mono-chloro species resulted in fixation and the two electron reduction of dinitrogen. These results will be discussed in more depth in chapter 2 and chapter 3 respectively.

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