THE ETHENE POLYMERISATION BEHAVIOUR OF ZIRCONIUM METALLOCENES: A STERIC AND ELECTRONIC INVESTIGATION INTO THE INFLUENCE OF SUBSTITUENT EFFECTS.

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A thesis submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Doctor of Philosophy
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DECLARATION

I hereby declare that this thesis is my own, unaided work, performed under the supervision of Professor N.J. Coville and Doctor C.B. de Koning. It is being submitted for the Degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Neil Eugene Grimmer

28th Day of March 2000

ABSTRACT

A *systematic investigation* into the effect that alkyl and aryl substituents have on the ethene polymerisation behaviour of a series of MAO co-catalysed mono-substituted *bis*-(cyclopentadienyl)zirconium dichloride and *bis*-(indenyl)zirconium dichloride metallocenes was carried out. The electronic attributes of the substituents were related to the Hammett substituent functions. The sizes of the ligands were measured from the perspective of the metal using the Tolman cone angle, numerical solid angle and analytical solid angle methodologies. For the mono-substituted cyclopentadienyl metallocenes of formula $(CpR)_2ZrCl_2$ (R = Me, Et, ^{i}Pr, ^{t}Bu, $SiMe_3$, CMe_2Ph), it was found that an optimum ligand size (R = Et, ^{i}Pr) was required for high activity. These substituents protected the active polymerisation site from deactivation processes. However, if the substituent was too bulky (R = ^{t}Bu, CMe_2Ph) activity dropped drastically. Electronic factors possibly also play a role as demonstrated by the much higher activity of the $SiMe_3$ substituted catalyst over its similarly sized ^{t}Bu analogue. A series of new *bis*-(indenyl)zirconium dichloride metallocenes of formula $[2\text{–R-Ind}]_2ZrCl_2$ (R = H, Me, $SiMe_3$, Ph, Bz and 1-Naphthyl) and $[1\text{–R-Ind}]_2ZrCl_2$ (R = Me, Et, ^{i}Pr, ^{t}Bu, $SiMe_3$, Ph, Bz and 1-Naphthyl) were synthesised. Ethene polymerisation reactions with these metallocenes revealed the same electronic and steric trends observed for the $(CpR)_2ZrCl_2$ catalysts. Steric effects were found to play an important role with polymerisation activity decreasing as the size of the substituent increases. Also, the 1-substituted metallocenes had higher activities than their 2-substituted analogues, the differences in their activity increasing with the size of the substituent. By studying the conformations adopted by the indenyl ligands in the solid state, we have rationalised this phenomenon to be a result of the greater steric protection afforded to the active polymerisation site by the 1-substituted metallocenes.

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ABBREVIATIONS

An : anisidine (4-methoxyaniline), $4\text{-}CH_3\text{-}3,5\text{-}{}^tBu_2C_6H_2$

Bz : benzyl, $–CH_2(C_6H_5)$

CCD : Charge-Coupled Device (X-ray crystallography)

C_{Cp} : carbon atom in a cyclopentadienyl ring

cga : co-ordination gap aperture

COD : *cis, cis*-1,5-cyclooctadiene

Cp : cyclopentadienyl, $\eta^5–C_5H_5$

^{c}Pe : *cyclo*-pentyl

Cp^* : pentamethylcyclopentadienyl, $\eta^5–C_5Me_5$

Cp_c : the centroid of a cyclopentadienyl or indenyl ligand

CSD : Cambridge Structural Database

Cy : cyclohexyl, $–C_6H_{11}$

d : doublet (NMR spectroscopy)

dd : doublet of doublets (NMR spectroscopy)

DSC : Differential Scanning Calorimetry

EAO : ethylaluminoxane

ebmp : 2,2'-ethylenebis(6-*tert*-butyl-4-methylphenolato)

ebthi : 1,2-ethylene-1,1'-bis(η^5–tetrahydrohindenyl)

Et : ethyl, $–CH_2CH_3$

ETE : Electron Transfer Equilibria

Flu : fluorenyl, $\eta^5–C_{13}H_8$

GC : Gas Chromatography

HR-MS : High Resolution Mass Spectrometry

Ind : indenyl, $\eta^5–C_9H_7$

Ind_c : the centroid of the 5-membered ring on an indenyl ligand

$IndH_4$: tetrahydroindenyl, $\eta^5–C_9H_{11}$

^{i}Pr : *iso*-propyl, $–CH(CH_3)_2$

l.p.	:	liquid propene
m	:	multiplet (NMR spectroscopy)
Me	:	methyl, $–CH_3$
MAO	:	methylaluminoxane
mbmp	:	2,2'-methylenebis(6-*tert*-butyl-4-methylphenolato)
MW	:	molecular weight
MS	:	Mass Spectrometry
Naph	:	Naphthyl, ($C_{10}H_7$)
n.g	:	not given.
NMR	:	Nuclear Magnetic Resonance
P_{p}	:	pressure at which polymerisation reaction was carried out
PBB	:	*tris*-(2,2',2"-perfluorobiphenyl)borane
PE	:	polyethene
Ph	:	phenyl
PNB	:	*tris*-(β-perfluoronaphthyl)borane
PP	:	polypropene
^{c}Pr	:	*cyclo*-propyl
q	:	quartet (NMR spectroscopy)
r.t.	:	room temperature
sibmp	:	2,2'-sulfinylbis(6-*tert*-butyl-4-methylphenolato)
SMART	:	Small Molecule Analytical Research Tool
SSC	:	Single Site Catalyst
t	:	triplet (NMR spectroscopy)
t_{p}	:	polymerisation time
T_{p}	:	polymerisation temperature
^{t}Bu	:	*tertiary*-butyl, $-C(CH_3)_3$
tbmp	:	2,2'-thiobis(6-*tert*-butyl-4-methylphenolato)
TBS	:	*tertiary*-butyldimethylsilyl, $–SiMe_2(C(CH_3)_3)$
TCP	:	2-(tetramethylcyclopentadienyl)-4-methylphenolate
THF	:	tetrahydrofuran

TIBA	:	tri-*iso*-butylaluminium
TIPP	:	2, 4, 6-tri-(*iso*-propyl)phenyl
TIPS	:	tri-*iso*-propylsilyl, $–Si(CH(CH_3)_2)_3$
T_m	:	melting point of polymer
TMS	:	trimethylsilyl, $–Si(CH_3)_3$
TP	:	hydrotris(pyrazolyl)borate
TP^*	:	hydro-*tris*-(3,5-dimethylpyrazolyl)borate
UV	:	Ultra-Violet Spectroscopy
XRD	:	X-Ray Diffractometry
XPS	:	X-Ray Photoelectron Spectroscopy
Z-N	:	Ziegler-Natta

GLOSSARY

Co-ordination gap aperture, cga	The largest possible angle spanned by two planes through the metal centre which touch the inner van der Waals radii of the β-substituents at the C_5 ligands.
Cone (or linear) angle, θ	The angle between the vectors of right circular cone encompassing a group of atoms.
Numerical solid angle, Ω_N	The non-circular cone angle formed by subtending a vector from the point of measurement to the outer van der Waals radii of the group of atoms being measured and then tracing around these atoms. The surface of the non-circular cone traced out is then integrated.
Solid angle, Ω	The surface area of projection onto the inside of a unit sphere.
Cone angle radial profile	Plot of the cone angle, θ, as a function of distance from the point of perspective.
Numerical solid angle radial profile	Plot of the numerical solid angle, Ω_N, as a function of distance from the point of perspective.
Solid Angle radial profile	Plot of the solid angle, Ω, as a function of distance from the point of perspective.