

**Structure-Reactivity Relationships  
in Metallocene Chemistry:  
The *ansa*-Effect**

by

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The work described in this thesis was carried out in the Inorganic Chemistry Laboratory, Oxford, from September 1997 to April 2000 under the supervision of Professor M. L. H. Green F. R. S. All the work is my own unless stated to the contrary and has not been submitted previously for any other degree at this, or any other, university.

To Victoria

## Abstract

# Structure Reactivity Relationships in Metallocene Chemistry: The *ansa*-Effect

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This thesis is concerned with structure-reactivity relationships in metallocene chemistry. In particular new *ansa*-metallocenes of Groups 5-7 have been prepared. The structure and reactivity of these *ansa*-metallocenes is compared to the corresponding nonbridged metallocenes.

**Chapter 1** presents a brief review of *ansa*-metallocene chemistry, focussing on the changes in structure, reactivity and electronic properties imparted by the introduction of a bridging unit between the cyclopentadienyl rings of a metallocene.

**Chapter 2** describes the synthesis and characterisation of new Group 5 *ansa*-metallocenes. A systematic study of the effect of variation of the bridging unit E on bridge-terminal hydrogen exchange in the BH<sub>4</sub> ligand of the tetrahydroborate derivatives [M{(η-C<sub>5</sub>H<sub>4</sub>)E(η-C<sub>5</sub>H<sub>4</sub>)}(η<sup>2</sup>-BH<sub>4</sub>)] (M = Nb, E = CMe<sub>2</sub>, CEt<sub>2</sub>, C(C<sub>5</sub>H<sub>10</sub>), SiMe<sub>2</sub>, C<sub>2</sub>Me<sub>4</sub>; M = V, E = C<sub>2</sub>Me<sub>4</sub>) has been undertaken. The free energy barrier ΔG<sup>‡</sup> to bridge-terminal hydrogen exchange is considerably reduced when the *ansa*-bridge imposes significant structural changes in the metallocene unit. A possible exchange pathway has been identified by density functional calculations.

**Chapter 3** describes the synthesis of the higher n-alkyl hydride species [W{(η-C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>(η-C<sub>5</sub>H<sub>4</sub>)}{(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>}H] (n = 2-4). The isotopically labelled compounds [W{(η-C<sub>5</sub>D<sub>4</sub>)C(CD<sub>3</sub>)<sub>2</sub>(η-C<sub>5</sub>D<sub>4</sub>)}{(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>}D] (n = 1-4) and [W{(η-C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>(η-C<sub>5</sub>H<sub>4</sub>)}{CD<sub>2</sub>CD<sub>3</sub>}H] have been prepared and are found to exhibit intramolecular hydrogen scrambling between alkyl ligand and hydride sites under thermal conditions. The results are consistent with an exchange pathway involving an alkane σ-complex as either a transition state or an intermediate.

**Chapter 4** is divided into two parts. The first part of the chapter describes a study of quantum mechanical exchange coupling in *ansa*-metallocene trihydrides. The compound [W{(η-C<sub>5</sub>H<sub>4</sub>)C(C<sub>5</sub>H<sub>10</sub>)(η-C<sub>5</sub>H<sub>4</sub>)}H<sub>3</sub>][BF<sub>4</sub>] exhibits a very large, temperature dependent H-H coupling constant in the <sup>1</sup>H NMR spectra. In the second part of the chapter a preliminary investigation into *ansa*-rhenocene chemistry is described. A theoretical study provides an explanation for the unexpected molecular structure of the compound [Re{(η-C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>(η-C<sub>5</sub>H<sub>4</sub>)}Cl].

**Chapter 5** outlines the experimental details for the preceding chapters.

**Chapter 6** presents the characterising data for the new compounds described in this thesis.

**Appendices A-H** contain details of the crystallographic data for the structurally characterised compounds described in this thesis.

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## List of Abbreviations

### *General abbreviations*

$a_{\text{iso}}$	hyperfine splitting parameter (ESR spectroscopy)
Ar	aryl group
b. p.	boiling point
bpy	2,2-bipyridyl
<sup>t</sup> Bu	<i>tertiary</i> -butyl
calc.	calculated
$C_{\text{ipso}}$	<i>ipso</i> -carbon
Cp	cyclopentadienyl
$Cp^*$	pentamethylcyclopentadienyl
$Cp_{\text{cent}}$	cyclopentadienyl ring centroid
$Cp_{\text{norm}}$	normal to the plane of cyclopentadienyl ring
Cy	cyclohexyl
DFT	density functional theory
DME	1,2-dimethoxyethane
DMSO	dimethylsulphoxide
DMPM	<i>bis</i> (dimethylphosphino) methane
DPPH	1,1-diphenyl-2-picrylhydrazyl
E	general <i>ansa</i> -bridge
EI	electron impact (mass spectrometry)
ESR	electron spin resonance
Et	ethyl
FAB	fast atom bombardment (mass spectrometry)
FTIR	fourier transformed infra-red
$g_{\text{iso}}$	isotropic <i>g</i> value (ESR spectroscopy)
HOMO	highest occupied molecular orbital
HOMO-1	second highest occupied molecular orbital
h $\nu$	irradiation
IE	ionisation energy
IR	infra-red
L	general two electron donor ligand
LUMO	lowest unoccupied molecular orbital
LUMO-1	second lowest unoccupied molecular orbital
M	metal atom

M <sup>+</sup>	molecular ion (mass spectrometry)
MAO	methylaluminumoxane
Me	methyl
MO	molecular orbital
<i>m/z</i>	atomic mass units per unit charge
NMR	nuclear magnetic resonance
p-	para-position of an aryl ring
Ph	phenyl
R	general alkyl or aryl group
RT	room temperature
SCF	self consistent field
T <sub>c</sub>	coalescence temperature
THF	tetrahydrofuran
TMEDA	N, N, N', N'-tetramethylethylenediamine
UV	ultra-violet
X	generic ligand

*NMR spectroscopic abbreviations*

br	broad
COSY	correlated spectroscopy
δ	chemical shift
d	doublet
EXSY	exchange spectroscopy
fwhh	full width at half height
{ <sup>1</sup> H}	proton decoupled
HMQC	heteronuclear multiple quantum coherence
I	nuclear spin quantum number
<sup>n</sup> J <sub>AB</sub>	n bond coupling constant between A and B
J <sub>ex</sub>	quantum mechanical exchange coupling constant
m	multiplet
NOE	nuclear Overhauser effect
ppm	parts per million
q	quartet
qn	quintet
s	singlet