# 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 $BH_4$ ligand of the tetrahydroborate derivatives $[M\{(\eta\text{-}C_5H_4)E(\eta\text{-}C_5H_4)\}(\eta^2\text{-}BH_4)]$ (M = Nb, E = $CMe_2$, $CEt_2$, $C(C_5H_{10})$, $SiMe_2$, $C_2Me_4$; M = V, E = $C_2Me_4$) has been undertaken. The free energy barrier $\Delta G^{\ddagger}$ 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 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_nCH_3\}H]$ (n = 2-4). The isotopically labelled compounds $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\{(CH_2)_nCH_3\}D]$ (n = 1–4) and $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{CD_2CD_3\}H]$ 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 $[W\{(\eta\text{-}C_5H_4)C(C_5H_{10})(\eta\text{-}C_5H_4)\}H_3][BF_4]$ exhibits a very large, temperature dependent H-H coupling constant in the $^1H$ 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 $[Re\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl]$.

**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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For most of the time I have braved the eccentricities of *ansa*-metallocenes alone. I am, however, grateful to Dr. Adam Stephens (gone, but not forgotten) and Dr. Nigel Bailey for their help in the early days. I am particularly grateful to Adam for his contribution to the rhenocene chemistry. Outside of Oxford, collaborations have been to initiated with Dr. Sean McGrady of King's College, London and Professor Michael Heinekey of the University of Washington, Seattle, whom I thank for helpful discussions, particularly Sean who has taken a keen interest in my work throughout. Whilst the results of these collaborations have not made the pages of this thesis they promise to be of great interest.

As this is a study of structure-reactivity relationships I am indebted to those who have solved my crystal structures and put up with my ignorance of crystallography, namely Drs. Linda Doerrer, Michael Leech, Leigh Rees and David Watkin. Also worthy of thanks are Drs. Daniel Haüßinger and Cliff Williams, for help with NMR and Dr. Steve Barlow for showing me around the not so state of the art ESR spectrometer. Ino Vei, Dr. Karl Coleman, Neale Jones, Gerry Clancy and Malcolm have proof-read parts or all of this thesis and I admire and thank you all.

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## Contents

## Appendices

## List of Abbreviations

*General abbreviations*

| | |
|---|---|
| $a_{iso}$ | hyperfine splitting parameter (ESR spectroscopy) |
| Ar | aryl group |
| b. p. | boiling point |
| bpy | 2,2–bipyrridyl |
| $^{t}$Bu | *tertiary*-butyl |
| calc. | calculated |
| $C_{ipso}$ | *ipso*-carbon |
| Cp | cyclopentadienyl |
| $Cp^{*}$ | pentamethylcyclopentadienyl |
| $Cp_{cent}$ | cyclopentadienyl ring centroid |
| $Cp_{norm}$ | normal to the plane of cyclopentadienyl ring |
| Cy | cyclohexyl |
| DFT | density functional theory |
| DME | 1,2-dimethoxyethane |
| DMSO | dimethylsulphoxide |
| DMPM | *bis*(dimethylphosphino) methane |
| DPPH | 1,1-diphenyl-2-picryhydrazyl |
| E | general *ansa*-bridge |
| EI | electron impact (mass spectrometry) |
| ESR | electron spin resonance |
| Et | ethyl |
| FAB | fast atom bombardment (mass spectrometry) |
| FTIR | fourier transformed infra-red |
| $g_{iso}$ | isotropic g value (ESR spectroscopy) |
| HOMO | highest occupied molecular orbital |
| HOMO-1 | second highest occupied molecular orbital |
| hν | 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 |

| | |
|---|---|
| $M^+$ | molecular ion (mass spectrometry) |
| MAO | methylaluminoxane |
| Me | methyl |
| MO | molecular orbital |
| *m/z* | 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 |
| $T_c$ | coalescence temperature |
| THF | tetrahydrofuran |
| TMEDA | N, N, N', N'-tetramethylethylenediamine |
| UV | ultra-violet |
| X | generic ligand |

*NMR spectroscopic abbreviations*

| | |
|---|---|
| br | broad |
| COSY | correlated spectroscopy |
| $\delta$ | chemical shift |
| d | doublet |
| EXSY | exchange spectroscopy |
| fwhh | full width at half height |
| $\{^1H\}$ | proton decoupled |
| HMQC | heteronuclear multiple quantum coherence |
| I | nuclear spin quantum number |
| $^nJ_{AB}$ | n bond coupling constant between A and B |
| $J_{ex}$ | quantum mechanical exchange coupling constant |
| m | multiplet |
| NOE | nuclear Overhauser effect |
| ppm | parts per million |
| q | quartet |
| qn | quintet |
| s | singlet |