

**Chapter 1**  
**Introduction**

## 1.0 General Introduction

This thesis is concerned with structure-reactivity relationships in metallocene chemistry. In particular new *ansa*-bridged metallocenes of Groups 5-7 have been prepared and their reactivity studied. The structure and reactivity of these *ansa*-metallocenes is compared to the well-established chemistry of analogous nonbridged metallocenes. Some pronounced differences are encountered.

This introductory chapter presents a brief review of *ansa*-metallocene chemistry. The nature of bonding in bent metallocenes is described in **Section 1.1**. The remainder of the chapter focuses on the influence imparted on the structure, reactivity and electronic properties of sandwich metallocene compounds when a bridging unit is introduced between the two cyclopentadienyl rings (**Section 1.2-1.5**).

## 1.1 Metallocenes

### 1.1.1 Historical Background

The *bis*(cyclopentadienyl)iron compound ferrocene  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$  was first obtained as a product from the attempted synthesis of fulvalene from  $[(\text{C}_5\text{H}_5)\text{MgBr}]$  and  $\text{FeCl}_3$  in 1951.<sup>1</sup> Wilkinson and Fischer independently described a sandwich structure in which the cyclopentadienyl rings are bound in a pentahapto parallel-ring conformation.<sup>2, 3</sup> Compounds containing two  $\eta\text{-C}_5\text{H}_5$  rings bonded to a transition metal are termed metallocenes.

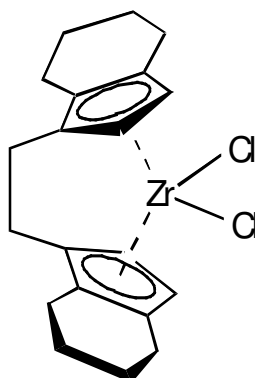
Shortly after the discovery of ferrocene it was found that metallocene species could be prepared in which the cyclopentadienyl rings are inclined at an angle to one another and that additional ligands could be bound to the metal.<sup>4</sup> The chemistry of these bent metallocenes,  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{X}_n]$ , has dominated the growth of organotransition metal chemistry, especially for the early transition metals. In general the  $\eta$ -cyclopentadienyl ligand acts as a spectator ligand, inert to both inter- and intra-molecular reactions, with reactivity being confined mainly to the X ligand positions. However appropriate substitution at the cyclopentadienyl rings is a convenient and effective method of tuning the stereochemical and electronic properties of the metallocene.

The extensive chemistry of bent metallocenes is witnessed by the abundance of such compounds of Group 3 – 6 metals reported in the literature.<sup>5</sup> Metallocenes have

been found to undergo a wide range of very interesting and important reactions, most notably C-H bond activation.<sup>6-10</sup>

Furthermore, in 1957 Breslow reported the activity of  $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$  in conjunction with diethylaluminium chloride as a homogeneous Ziegler-Natta catalyst for the polymerisation of olefins.<sup>11</sup> Activity of the catalyst could not compete with the classic heterogenous Ziegler-Natta catalysts at that time. A significant breakthrough was achieved in the early 1980's when Sinn and Kaminsky described the use of zirconocene compounds together with methylaluminoxane (MAO) as highly active catalysts giving polymers with high molecular weight.<sup>12, 13</sup> Despite the fact that these catalysts lacked control over the stereoregularity of the resulting polymer, metallocene catalysts became an area of intense research.

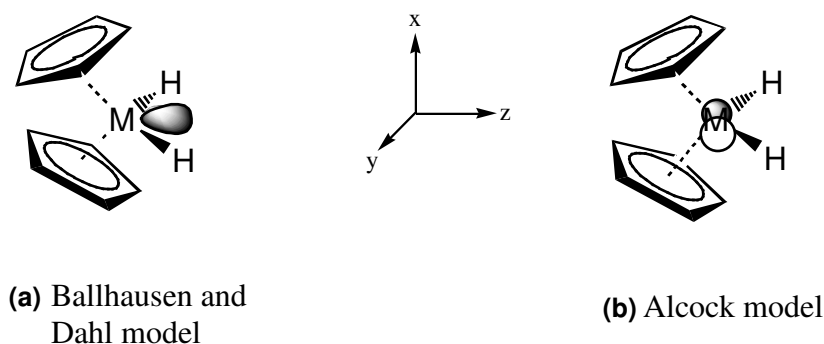
Brintzinger reported the preparation of the chiral, bridged metallocene compounds  $\text{rac-}[\text{M}\{(\eta\text{-C}_9\text{H}_6)\text{C}_2\text{H}_4(\eta\text{-C}_9\text{H}_6)\}\text{Cl}_2]$  and  $\text{rac-}[\text{M}\{(\eta\text{-C}_9\text{H}_{10})\text{C}_2\text{H}_4(\eta\text{-C}_9\text{H}_{10})\}\text{Cl}_2]$  (M = Ti, Zr) (**Figure 1.1**).<sup>14, 15</sup> The bridging unit retains the relative orientation of the two indenyl rings. Brintzinger and Kaminsky found that these bridged metallocenes, in conjunction with the co-catalyst MAO, were capable of polymerising propene and higher olefins to give highly isotactic polymers.<sup>16</sup> Ewen described the formation of stereoregular polymers from chiral catalysts as a consequence of enantiomorphous-site stereochemical control, whereby the stereochemistry of the catalyst governs the stereochemistry of the resulting polymer.<sup>17</sup> These developments have led to considerable interest in the study of bridged- or 'ansa'-metallocenes over the last 15 years.



**Figure 1.1** *Rac*-ethylenebis(4, 5, 6, 7-tetrahydro-1-indenyl)zirconium dichloride

### 1.1.2 Bonding in Bent Metallocenes

After the discovery of bent metallocenes, their molecular orbital structure was a subject of debate. In 1961 Ballhausen and Dahl proposed three metal based orbitals symmetrically disposed in the  $yz$  plane of the metallocene unit and not involved in the bonding with the  $\eta$ -cyclopentadienyl rings.<sup>18</sup> In this model the lone pair of the  $d^2$  metallocenes  $[M(\eta-C_5H_5)_2H_2]$  ( $M = Mo, W$ ) was expected to be located in the interligand wedge defined by the H-M-H fragment (**Figure 1.2(a)**).

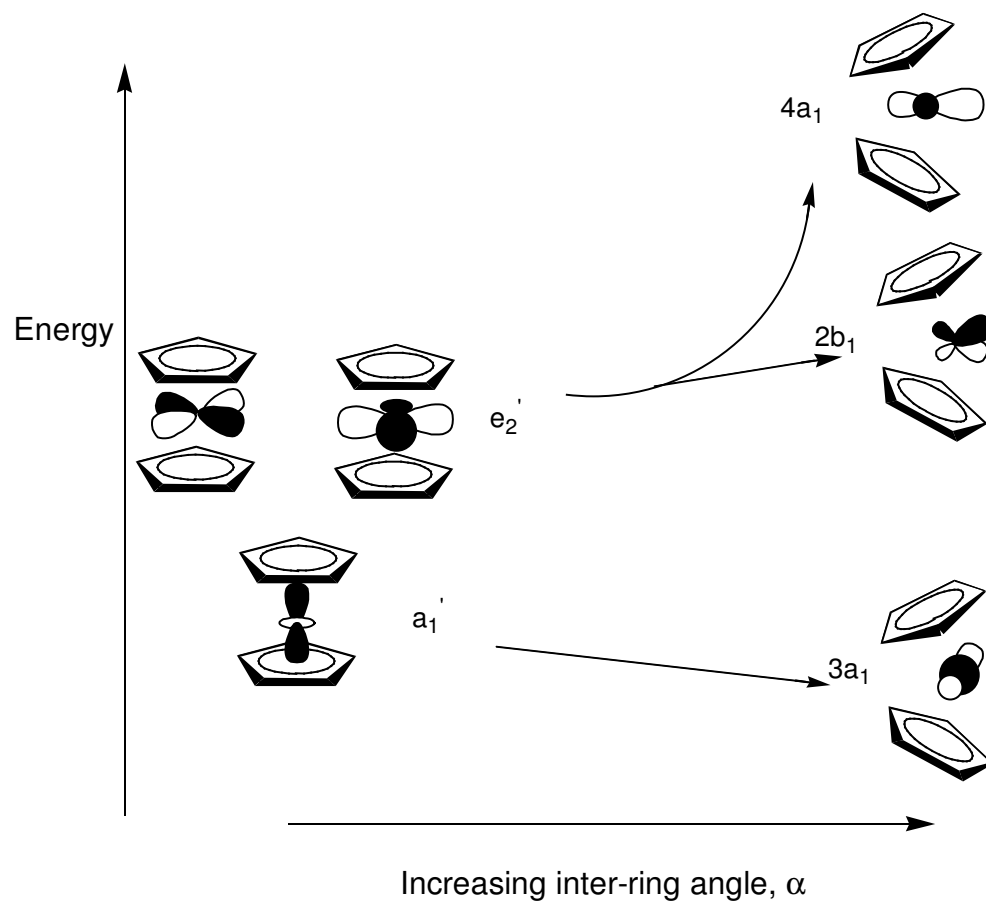


**Figure 1.2** Early models for the orientation of the nonbonding orbital in a bent metallocene  $[M(\eta-C_5H_5)_2H_2]$

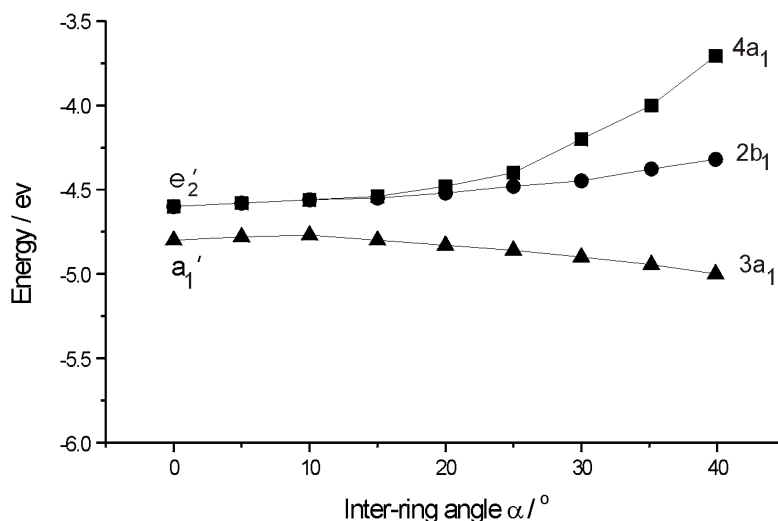
When the molecular structure of  $[Re(\eta-C_5H_5)(\eta-C_5H_4Me)Me_2]$  was determined by Alcock it was observed that the Me-Re-Me angle was too small to accommodate the lone pair electrons in the orbital predicted by the Ballhausen-Dahl model.<sup>19</sup> Alcock thus modified the Ballhausen-Dahl model proposing that the lone-pair lies in the same plane but at  $90^\circ$  to the position originally proposed (**Figure 1.2 (b)**). Subsequent developments served to support Alcock's model. The molecular structures of the series  $[M(\eta-C_5H_5)_2Cl_2]$  ( $M = Zr, Nb, Mo$ ) show that as the  $d$  electron configuration increases for Zr ( $d^0$ ) to Nb ( $d^1$ ) to Mo ( $d^2$ ) the Cl-M-Cl angle decreases along the series;  $97.1^\circ$  (Zr),  $85.6^\circ$  (Nb) and  $82.0^\circ$  (Mo).<sup>20</sup>

In the early 1970's Green *et al.* considered the molecular orbital structure of a bent metallocene unit by bending the rings of the parallel-ring structured ( $D_{5h}$ ) ferrocene.<sup>20, 21</sup> The three highest occupied molecular orbitals of  $D_{5h}$  ferrocene are shown in **Figure 1.3**. Lowering the symmetry from  $D_{5h}$  to  $C_{2v}$  causes two of the three occupied orbitals to become the same symmetry,  $a_1$ . As the inter-ring angle  $\alpha$  (see **Figure 1.13**) is increased

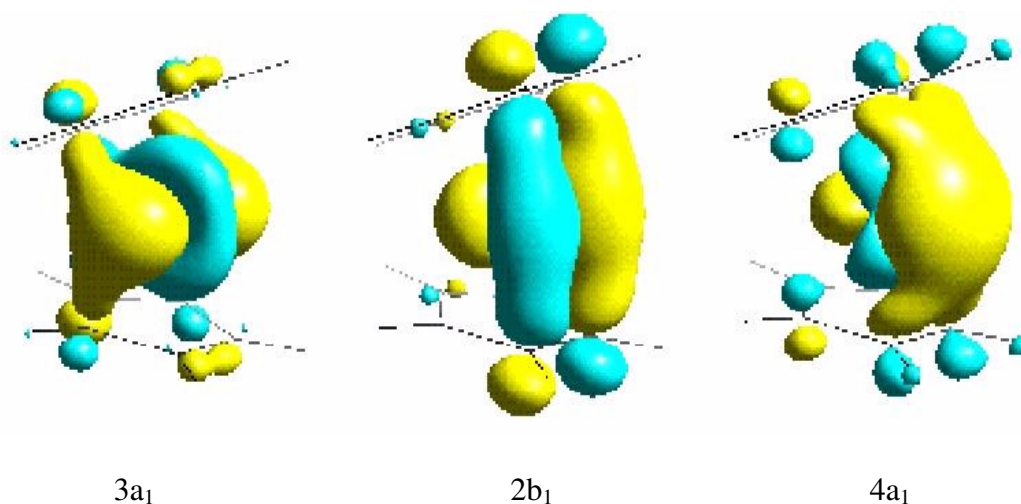
the two  $a_1$  orbitals move apart in energy with the upper  $4a_1$  orbital considerably destabilised and the  $3a_1$  orbital falling slightly in energy. The third d orbital, which becomes  $b_1$  in symmetry on bending, is increased in energy with increasing inter-ring angle  $\alpha$ , although the effect is not as marked as for  $4a_1$  (**Figure 1.4**). Three-dimensional representations of the three frontier orbitals of a bent metallocene unit calculated using density functional theory are depicted in **Figure 1.5**.<sup>22</sup>



**Figure 1.3** The three highest occupied frontier orbitals of ferrocene as a function of inter-ring angle  $\alpha$



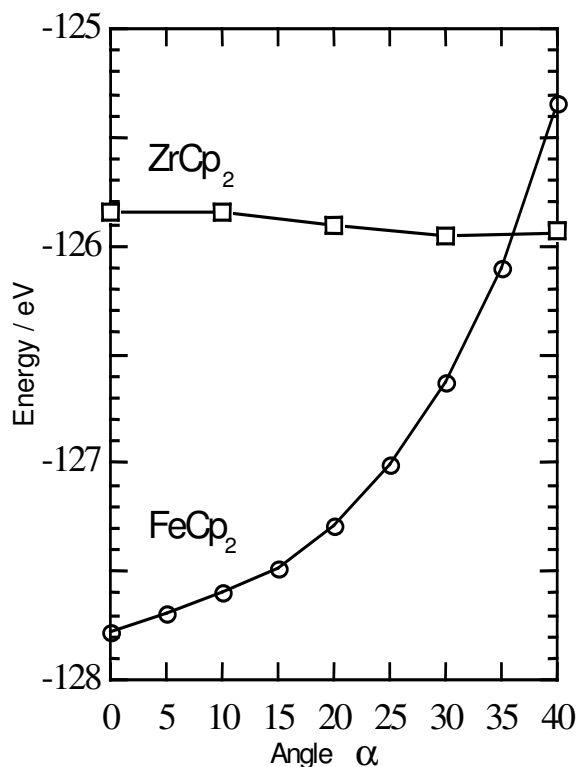
**Figure 1.4** Variation of one electron energies of ferrocene as a function of inter-ring angle  $\alpha$



**Figure 1.5** Isosurfaces for the frontier orbitals of a bent metallocene unit ( $\alpha = 35^\circ$ ).  
(Generated using the Cerius<sup>2</sup> package of Molecular Simulations Inc.)

Due to the changes in energy of the molecular orbitals on bending the metallocene unit the angle between the rings of a metallocene is controlled by the d orbital occupancy. Density functional calculations have been employed to study the effect of varying the inter-ring  $\alpha$  on the total energy of  $d^6$  ferrocene and the hypothetical triplet  $d^2$  zirconocene (**Figure 1.6**).<sup>22</sup> The total energy of the molecule is raised significantly on bending of the rings for ferrocene where the  $4a_1$  orbital is occupied. However in the case of the

hypothetical triplet zirconocene with a  $3a_1^1 2b_1^1$  configuration and an unoccupied  $4a_1$  orbital the total energy is largely insensitive to bending of the rings.



**Figure 1.6** Variation of total energy of ferrocene and triplet zirconocene as a function of bending angle  $\alpha$

## 1.2 *ansa*-Metallocenes

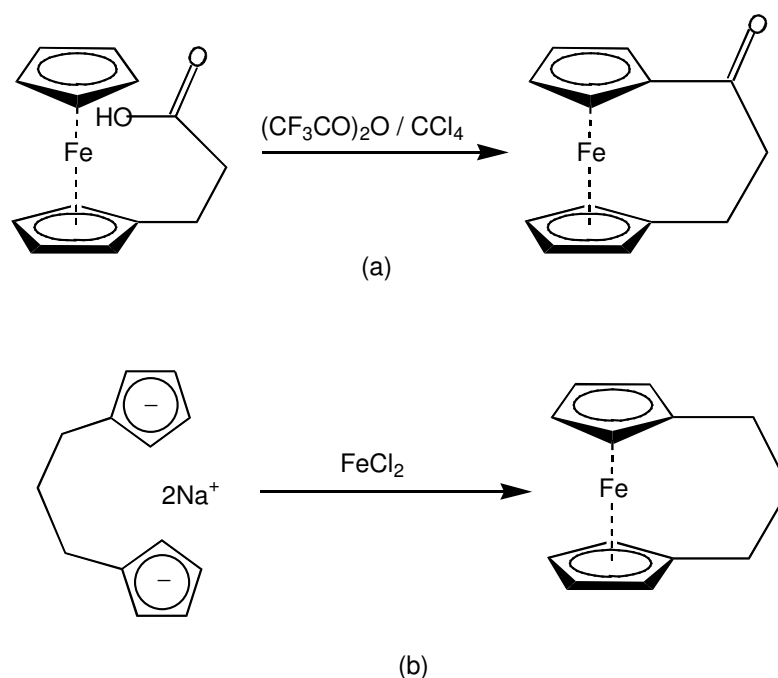
### 1.2.1 Historical Background

Prior to the discovery of bridged *bis*(indenyl) complexes acting as highly stereospecific polymerisation co-catalysts, little attention had been given to the chemistry of *ansa*-metallocenes. The first appearance of the term '*ansa*' in a chemical context was provided by Luttringhaus in 1942 when it was used to describe bridged aromatic compounds.<sup>23</sup> The following footnote was added:

*ansa* (Latin) = der Henkel.

Before the term '*ansa*' was adopted in bridged metallocene chemistry, Rinehart and Curby described the first example of such a species in 1957. 1, 1'-( $\alpha$ -ketomethylene) ferrocene  $[\text{Fe}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{H}_4\text{C}(\text{O})(\eta\text{-C}_5\text{H}_4)\}]$  was prepared by the self-condensation

reaction of  $[\text{Fe}\{(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\}]$  (**Figure 1.7(a)**).<sup>24</sup> The following year Luttringhaus and Kullick reported a low yield synthesis of  $[\text{Fe}\{(\eta\text{-C}_5\text{H}_4)\text{C}_3\text{H}_6(\eta\text{-C}_5\text{H}_4)\}]$  from the bridged sodium derivative  $[\text{Na}_2\{(\text{C}_5\text{H}_4)\text{C}_3\text{H}_6(\text{C}_5\text{H}_4)\}]$  and  $\text{FeCl}_2$  (**Figure 1.7(b)**).<sup>25</sup>



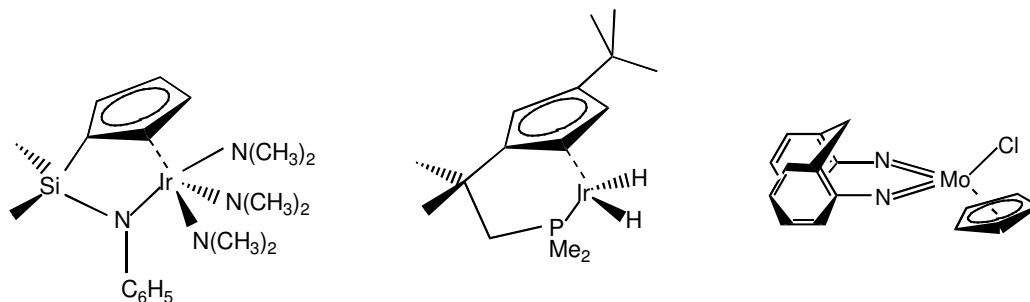
**Figure 1.7** Synthesis of the first *ansa*-metallocenes

The first Group 4 bridged metallocene compound was the methylene-bridged titanocene dichloride  $[\text{Ti}\{(\eta\text{-C}_5\text{H}_4)\text{CH}_2(\eta\text{-C}_5\text{H}_4)\}\text{Cl}_2]$  prepared by Katz and Acton in 1970 by the reaction between  $\text{TiCl}_4$  and  $[\text{Li}_2\{(\text{C}_5\text{H}_4)\text{CH}_2(\text{C}_5\text{H}_4)\}]$ .<sup>26</sup> Subsequently Hillman and Weiss described the propylene-bridged metallocene dichlorides of the Group 4 metal triad  $[\text{M}\{(\eta\text{-C}_5\text{H}_4)\text{C}_3\text{H}_6(\eta\text{-C}_5\text{H}_4)\}\text{Cl}_2]$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ).<sup>27</sup> In 1979, in the first of a large series of related papers, Brintzinger introduced the prefix ‘*ansa*’ in the context of bridged-metallocene compounds when he offered the translation:

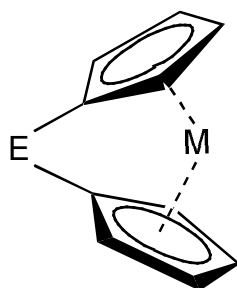
*ansa*- (Latin) = bent handle, attached at both ends.

Since then the term ‘*ansa*’ has enjoyed widespread use to describe *bis*-η-cyclopentadienyl complexes containing an interannular bridge. More recently it has been

extended to bridged  $\eta$ -cyclopentadienyl imido compounds,<sup>28, 29</sup> bridged  $\eta$ -cyclopentadienyl phosphino compounds<sup>30-32</sup> and bridged *bisimido* compounds (**Figure 1.8**).<sup>33</sup> In this thesis attention will focus on mononuclear metallocene compounds, in which the cyclopentadienyl rings are linked by a bridging unit E (**Figure 1.9**).



**Figure 1.8** Non-metallocene *ansa*-bridged organometallic compounds



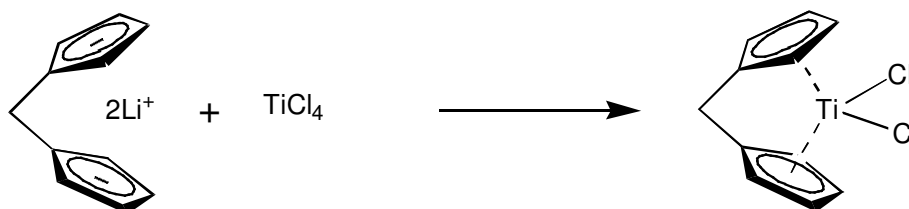
**Figure 1.9** Generic *ansa*-metallocene

## 1.2.2 Synthesis of *ansa*-Metallocenes

### 1.2.2.1 Reaction between $MCl_x$ and Dianion Ligand Reagents

*ansa*-Metallocenes are normally prepared by the chloride displacement reactions of  $MCl_x$  compounds with *ansa-bis*(cyclopentadienyl) dianion reagents (**Figure 1.10**).<sup>26</sup> Yields are at best moderate for Group 4 *ansa*-metallocenes, due to the formation of oligomeric/polymeric byproducts. Yields can be improved by using high dilution and slow mixing techniques.<sup>34</sup> The synthesis of Group 6 *ansa*-metallocenes is equally problematic. The reaction is particularly sensitive to the solvent employed, the nature of the metal chloride compound and the ligand counterion.<sup>35-37</sup> Yields have been optimised

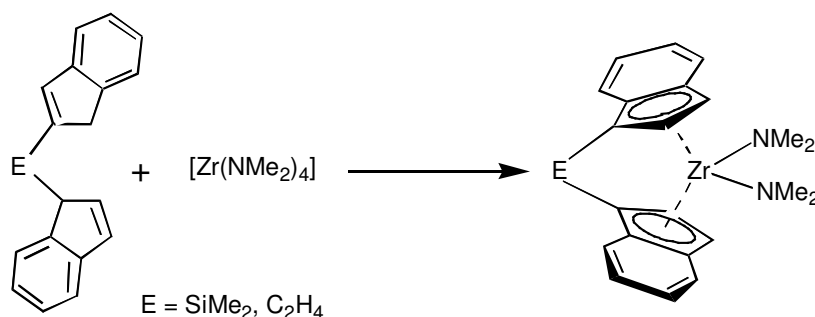
at *ca.* 30 % for the preparation of  $[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{E}(\eta\text{-C}_5\text{H}_4)\}\text{Cl}_2]$  ( $\text{E} = \text{CMe}_2, \text{C}_2\text{Me}_4, \text{SiMe}_2$ ) in a procedure analogous to that employed by Persson and Andersson for the preparation of  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$  in which the two reagents are stirred as a suspension in diethyl ether for several days.<sup>38</sup>



**Figure 1.10** Synthesis of *ansa*-metallocene *via* chloride displacement reaction

### 1.2.2.2 Reaction between $[\text{M}(\text{NMe}_2)_4]$ and Neutral *ansa*-Ligand

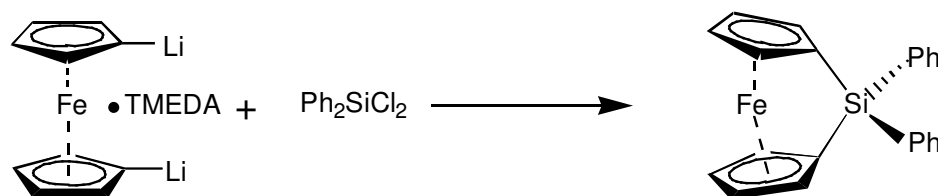
Jordan has described a promising alternative strategy to the chloride displacement synthesis *via* the amine elimination reaction of the neutral ligand  $[(\text{C}_9\text{H}_7)\text{E}(\text{C}_9\text{H}_7)]$  ( $\text{E} = \text{C}_2\text{H}_4, \text{SiMe}_2$ ) with  $[\text{Zr}(\text{NMe}_2)_4]$  to give *rac*- $[\text{Zr}\{(\eta\text{-C}_9\text{H}_6)\text{E}(\eta\text{-C}_9\text{H}_6)\}(\text{NMe}_2)_2]$  in *ca.* 70 % yield (**Figure 1.11**).<sup>39, 40</sup> The diamido compounds can be readily converted into the commonly used precursors *rac*- $[\text{Zr}\{(\eta\text{-C}_9\text{H}_6)\text{E}(\eta\text{-C}_9\text{H}_6)\}\text{Cl}_2]$  and *rac*- $[\text{Zr}\{(\eta\text{-C}_9\text{H}_6)\text{E}(\eta\text{-C}_9\text{H}_6)\}\text{Me}_2]$  by reaction with  $\text{Me}_3\text{SiCl}$  and  $\text{AlMe}_3$  respectively.



**Figure 1.11** Synthesis of *ansa*-metallocene *via* amine elimination reaction

### 1.2.2.3 Preparation from Nonbridged Metallocenes

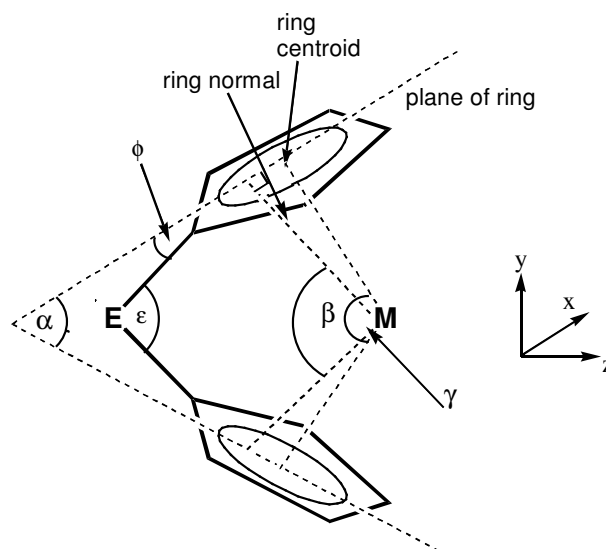
The first reported [1]-ferrocenophane compound  $[\text{Fe}\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta\text{-C}_5\text{H}_4)\}]$  was prepared from the nonbridged dilithioferrocene compound  $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{Li})_2\cdot\text{TMEDA}]$  via the reaction with  $\text{Ph}_2\text{SiCl}_2$  in hexane (**Figure 1.12**).<sup>41</sup> This general reaction has been widely employed in the synthesis of [1]-silaferrocenophanes.<sup>42</sup> Heinekey has recently extended this approach to bent metallocene chemistry with the synthesis of the first *ansa*-rhenocene compound,  $[\text{Re}\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{Me}]$  by the reaction between  $[\text{Re}\{(\eta\text{-C}_5\text{H}_4\text{Li})_2\text{Me}]$  and  $\text{Me}_2\text{SiCl}_2$  in 85 % yield.<sup>43</sup>



**Figure 1.12** Synthesis of *ansa*-metallocene from nonbridged metallocene

### 1.3 Structural Features of *ansa*-Metallocenes



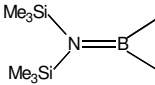
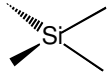


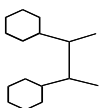
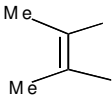
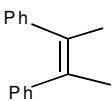
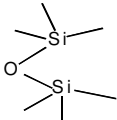
Some structural parameters of *ansa*-metallocenes which will be used in this thesis are defined in **Figure 1.13**. The orientation of the cyclopentadienyl rings with respect to the metal may be defined in three ways; either as  $\alpha$ , the angle between the ring planes, or  $\beta$ , the corresponding angle between the normals to the ring planes ( $\alpha + \beta = 180^\circ$ ) or  $\gamma$ , the angle defined by the metal and the two ring centroids. The angles  $\beta$  and  $\gamma$  are often referred to as the bending angles. If the rings are bridged by a single atom unit such as  $\text{CMe}_2$  or  $\text{SiMe}_2$ ,  $\epsilon$  is the angle defined from a bridging atom E to the *ipso*-carbons. The departure from planarity at the *ipso*-carbon is indicated by  $\phi$ , the angle between the *ipso*-carbon vector and the ring-plane. In this thesis an angle  $\phi$  below the *ipso*-carbon vector will be quoted as a positive value.



**Figure 1.13** Structural parameters of an *ansa*-metallocene

Corey has undertaken a comparison of the molecular structures of a series of Group 4 *ansa*-metallocene dichloride compounds  $[M\{(\eta\text{-C}_5\text{H}_4)\text{E}(\eta\text{-C}_5\text{H}_4)\}\text{Cl}_2]$  ( $M = \text{Ti}, \text{Zr}, \text{Hf}$ ).<sup>44</sup> This data is supplemented by more recent work and additional structural parameters in **Tables 1.1** and **1.2**. **Table 1.1** compares angles concerned with the metallocene fragment. The introduction of a single carbon bridge causes a significant reduction in the bending angle  $\beta$  by *ca.* 16-18°. This change corresponds to an increase in the inter-ring angle  $\alpha$ . The change in  $\beta$  is mirrored by that in the metal-ring centroid angle  $\gamma$ . A silicon-bridge imparts a less marked reduction in the bending angles, with  $\beta$  differing from the parent nonbridged metallocene by *ca.* 5 % as opposed to *ca.* 14 % for one carbon-bridged *ansa*-metallocenes. There is significant distortion from planarity in these single atom-bridged compounds with values of  $\phi$  in the range 15-22°.

The structural implications of the introduction of a two carbon ethylene-bridge are less pronounced. The bending angle  $\beta$  differs from analogous nonbridged metallocenes by *ca.* 2 % while there is little distortion at the *ipso*-carbon as evidenced by small values of  $\phi$ . It is noted that the inter-ring angle  $\alpha$  and bending angles  $\beta$  and  $\gamma$  of a silicon-bridge *ansa*-metallocene are much more similar to those found in ethylene-bridged species than one carbon-bridged metallocenes. This may be attributed to the larger atomic radii of a silicon atom compared to carbon.

Bridging unit E	M	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	$\Delta\beta$ (%) <sup>a</sup>	$\varepsilon$ (°)	$\phi$ (°) <sup>b</sup>	Reference
No bridge	Ti	50.9	129.1	131.0				45
	Zr	53.5	126.5	129.3				46
	Hf	52.4	127.6	127.1				47
	Ti	66.9	113.1	121.5	12.3	96.7	19.0	44
	Zr	71.4	108.6	116.6	14.2	99.8	14.9	44
	Hf	70.1	109.9	117.1	17.7	99.4	15.3	44
	Ti	68.4	111.6	122.3	13.5	95.3	22.7	48
	Ti	61.8	118.2	124.4	8.4	98.3	20.2	49
	Ti	56.3	123.7	128.7	4.2	89.4	19.8	50
	Zr	60.1	119.9	125.4	5.2	93.2	17.2	50
	Hf	57.7	122.3	126.8	4.2	93.7	19.8	51
	Ti	53.2	126.8	128.2	1.8		-1.8	48
	Ti	53.2	126.8	128.3	1.8		-2.4	52
	Ti	53.4	126.6	127.8	1.9		-2.0	53
	Ti	53.6	126.4	127.7	2.1		-1.0	53
	Ti	53.8	126.2	128.1	2.2		-2.2	53
	Ti	49.1	130.9	132.5	-1.3		-5.52	54
	Zr	51.0	129.1	130.8	-2.1		-4.54	
	Hf	47.1	126.9	132.4	0.5		-8.18	

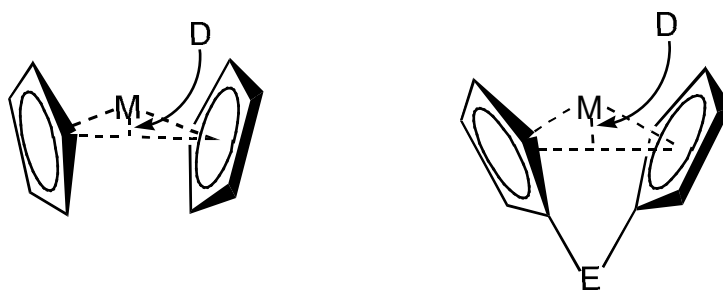
<sup>a</sup>  $\Delta\beta = [\beta (\textit{ansa}\text{-metallocene}) - \beta (\textit{parent metallocene})] / \beta (\textit{parent metallocene}) \times 100 \%$

<sup>b</sup> Average value of  $\phi$




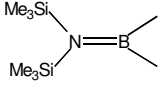


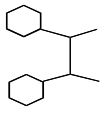
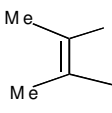
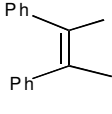
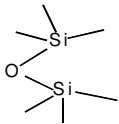
**Table 1.1** Interatomic angles and other structural features of Group 4 *ansa*-metallocene dichlorides  $[M\{(\eta\text{-C}_5\text{H}_4)E(\eta\text{-C}_5\text{H}_4)\}Cl_2]$  compared to analogous non bridged compounds  $[M(\eta\text{-C}_5\text{H}_5)_2Cl_2]$

Interatomic distances and further geometric parameters are given in **Table 1.2**. There is little variation between the average M-Cl bond distances and the average M-Cp<sub>cent</sub> distances on going from the nonbridged parent metallocene to the analogous *ansa*-bridged compounds. For the *ansa*-metallocenes the reduction in the bending angle  $\beta$  is associated with a reduction in the distance between the *ipso*-carbons.

The position of the metal relative to the rings is also affected upon the introduction of an *ansa*-bridge. **Figure 1.14** defines D, the perpendicular distance from the metal to an imaginary line connecting the two ring centroids. The distance D and the percentage change of position of the metal on going from the parent metallocene to the *ansa*-metallocene are also given **Table 1.2**. The largest change in D is seen for a single carbon-bridge (17-23 %) while the effect of a silicon- and ethylene-bridge is considerably smaller (*ca.* 5 %). The greater the extent to which the metal protrudes from the umbrella created by the cyclopentadienyl rings can be thought of as an increased contribution to bonding from an  $\eta^3$ -allyl resonance structure. This displacement of the metal centre relative to the rings is also evidenced by the difference between the bending angles  $\beta$  and  $\gamma$  in the presence of an *ansa*-bridge (**Table 1.1**). For nonbridged and ethylene-bridged metallocenes the angles  $\beta$  and  $\gamma$  are similar. However for a single carbon-bridge the ring normals angle  $\beta$  is considerably reduced compared to the metal-ring centroid angle  $\gamma$  typically by *ca.* 8-10°.



**Figure 1.14** Position of metal in a metallocene and an *ansa*-metallocene

Bridging unit E	M	M-Cp <sub>cent</sub> (Å) <sup>a</sup>	M-Cl (Å) <sup>b</sup>	D(Å)	% change	C <sub>ipso</sub> -C <sub>ipso</sub> (Å)	Ref.
No bridge	Ti	2.059	2.364(1)	0.853			45
	Zr	2.203	2.447(1)	0.933			46
	Hf	2.18	2.423(2)	0.971			47
	Ti	2.056	2.340(10)	1.005	18	2.276	44
	Zr	2.192	2.432(6)	1.152	23	2.327	44
	Hf	2.174	2.409(5)	1.135	17	2.331	44
	Ti	2.045	2.338	0.986	16	2.264	48
	Ti	2.075	2.356(1)	0.898	5	2.636	50
	Zr	2.197	2.435(1)	1.008	8	2.712	50
	Hf	2.191	2.424(2)	1.020	5	2.742	51
	Ti	2.048	2.336	0.954	12	2.421	49
	Ti	2.053	2.354	0.897	5	2.683	48
	Ti	2.051	2.365	0.896	5	2.675	52
	Ti	2.042	2.355	0.898	5	2.672	53
	Ti	2.061	2.358	0.042	5	2.674	53
	Ti	2.067	2.375	0.051	6	2.709	53
	Ti	2.069	2.355	0.833	-2	3.379	54
		2.210	2.442	0.919	-2	3.543	
		2.176	2.416	0.878	10	3.519	

<sup>a</sup> Average M-Cp<sub>cent</sub> <sup>b</sup> Average M-Cl

**Table 1.2** Geometric parameters of Group 4  
*ansa*-metallocene dichlorides [M{(η-C<sub>5</sub>H<sub>4</sub>)E(η-C<sub>5</sub>H<sub>4</sub>)}Cl<sub>2</sub>]  
 compared to analogous non bridged compounds [M(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>]

## 1.4 *ansa*-Metallocenes as a Tool to Study Structure-Reactivity Relationships

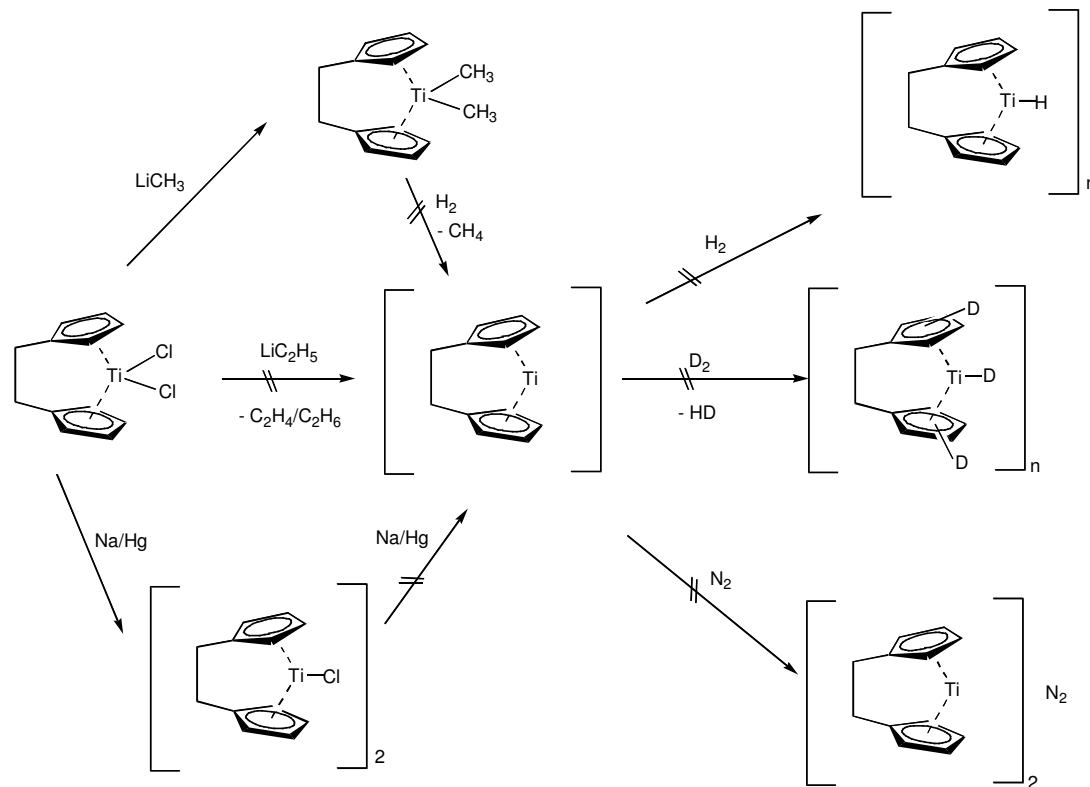
A wide variety of bridging units can be introduced between the cyclopentadienyl rings of a metallocene (**Table 1.1-1.2**). The number of bridging atoms can be changed while the nature of the bridging atom has been successfully varied from carbon and silicon to other main group atoms, such as boron and phosphorus, or to heteroatomic bridges, such as  $\text{Me}_2\text{SiOSiMe}_2$ . Thus the structure of a metallocene can be systematically and subtly varied and subsequent changes in reactivity of the metallocene can be correlated to these structural variations. The wealth of known metallocene chemistry particularly of the early transition metals provides vast scope for studying relationships between structure and reactivity in metallocene chemistry.

## 1.5 The *ansa*-Effect in Metallocene Chemistry

There is now a considerable body of evidence to show that the presence of an *ansa*-bridge can have a significant effect on the electronic properties and hence reactivity of metallocene compounds. A variety of examples are described below to illustrate these *ansa*-effects. Attention has already been drawn to the importance of *ansa*-bridges in Group 4 metallocenes and their isospecific catalytic reactions.<sup>55-58</sup> Since this thesis is not directly concerned with catalytic reactions of *ansa*-metallocene compounds this area will not be discussed further.

### 1.5.1 Reactivity of *ansa*-Titanocene Compounds

In 1981 Brintzinger reported the influence of an interannular ethylene-bridge on the reactivity of titanocene derivatives, namely that several transformations involving  $\text{Ti}^{\text{IV}}$  and  $\text{Ti}^{\text{III}}$  oxidation states do not follow reaction paths previously observed for unbridged titanocene complexes where the reaction is believed to occur *via* the free titanocene  $\text{Ti}^{\text{II}}$  intermediate, namely  $[\text{Ti}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{H}_4(\eta\text{-C}_5\text{H}_4)\}]$  (**Figure 1.15**).<sup>59</sup>

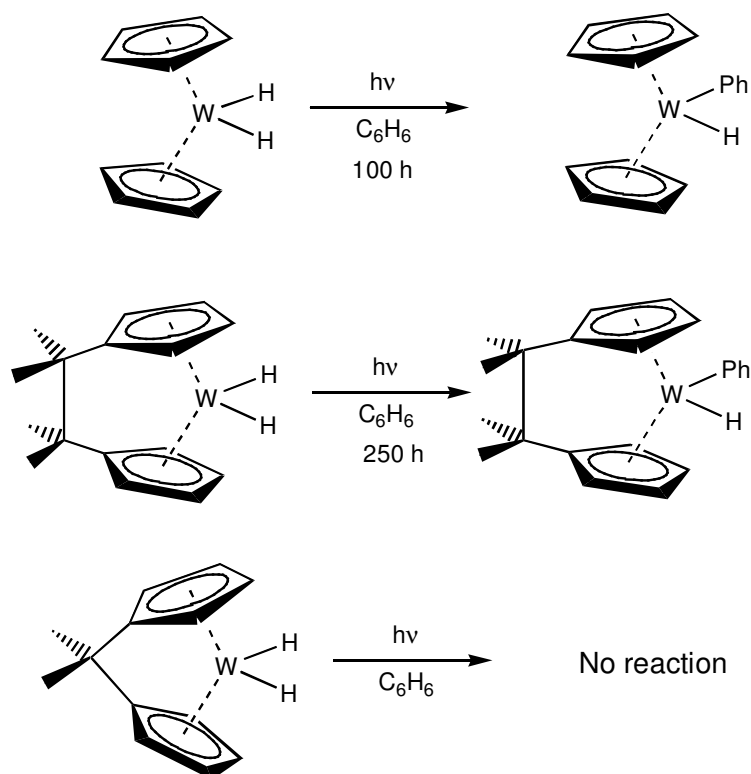


**Figure 1.15** Some typical titanocene reactions unavailable to the ethylene-bridged *ansa*-titanocene compound  $[\text{Ti}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{H}_4(\eta\text{-C}_5\text{H}_4)\}\text{Cl}_2]$

### 1.5.2 Stability to Reductive Elimination in Group 6 *ansa*-Metallocenes

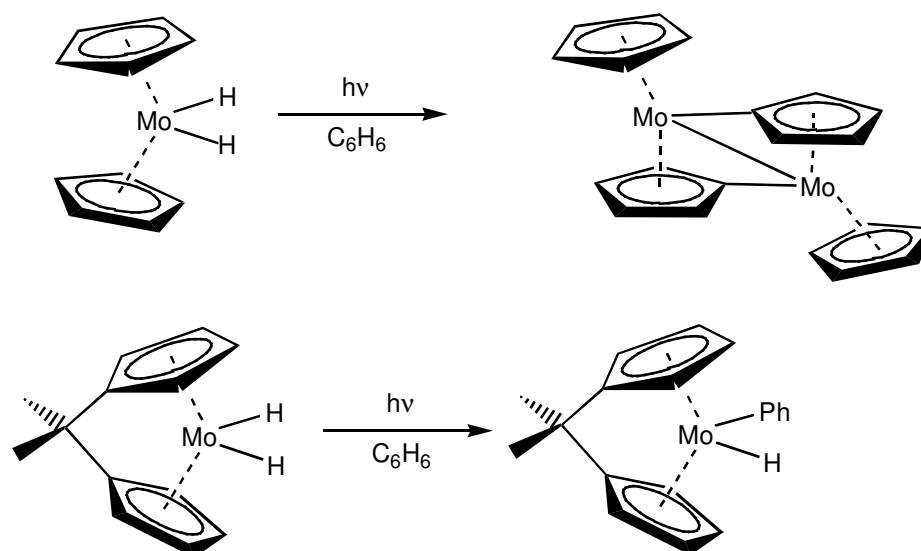
Pronounced differences in the reactivity of Group 6 *ansa*-metallocenes compared to the corresponding nonbridged derivatives have been identified by Green *et al.*<sup>35-37, 60</sup> Whereas the nonbridged dihydride complex  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$  undergoes reductive elimination of dihydrogen under photolytic conditions, readily activating the C-H bonds of the solvent benzene to form the phenyl hydride complex  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{Ph})\text{H}]$ , the corresponding *ansa*-bridged compound  $[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{H}_2]$  is inert under identical conditions (**Figure 1.16**). The geometrically less strained compound  $[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{Me}_4(\eta\text{-C}_5\text{H}_4)\}\text{H}_2]$  is found to be reactive under such conditions, though more slowly than for the nonbridged compound  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ . Reductive elimination has been shown in some cases to generate the highly reactive 16-electron tungstenocene intermediate  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2]$ , which adopts a parallel-ring structure in its triplet ground state.<sup>61</sup> The increased stability of these *ansa*-metallocene compounds was attributed to the

constraining effect of the *ansa*-bridge preventing the *ansa*-tungstenocene intermediate  $[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}]$  adopting a parallel-ring structure.



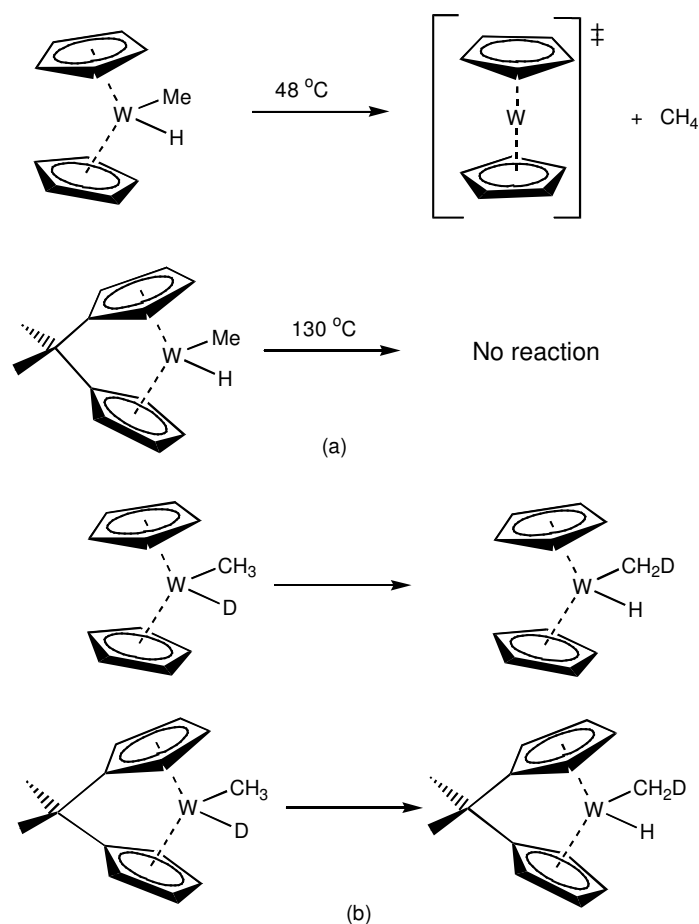
**Figure 1.16** Differences in reactivity for  $[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{E}(\eta\text{-C}_5\text{H}_4)\}\text{H}_2]$  ( $\text{E} = \text{C}_2\text{Me}_4, \text{CMe}_2$ ) compared to  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$

Furthermore whereas the photolysis of  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$  in benzene yields the dimer  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\mu\text{-}\kappa, \eta\text{-C}_5\text{H}_4)_2]$  photolysis of the corresponding *ansa*-molybdocene dihydride gives the phenyl hydride compound  $[\text{Mo}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}(\text{Ph})\text{H}]$  (**Figure 1.17**).



**Figure 1.17** Differences in reactivity for  $[\text{Mo}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{H}_2]$  compared to  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$

The increased stability towards reductive elimination imparted by an *ansa*-bridge, particularly a single carbon bridge, is also observed in the thermolysis of tungstenocene alkyl hydride complexes (**Figure 1.18(a)**). The nonbridged compound  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{Me})\text{H}]$  undergoes reductive elimination of methane above 48 °C.<sup>62</sup> In contrast the corresponding *ansa*-bridged compound  $[\text{W}\{(\eta\text{-C}_5\text{H}_4)_2\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}(\text{Me})\text{H}]$  displays remarkable thermal stability up to 130 °C.<sup>36</sup> Heinekey has also noted the increased thermal stability of the isoelectronic rhenocene alkyl hydride compound  $[\text{Re}\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta\text{-C}_5\text{H}_4)\}(\text{Me})\text{H}][\text{BAr}'_4]$  ( $\text{Ar}' = 3, 5\text{-(CF}_3)_2\text{C}_6\text{H}_3$ ) relative to the nonbridged analogues.<sup>43</sup>

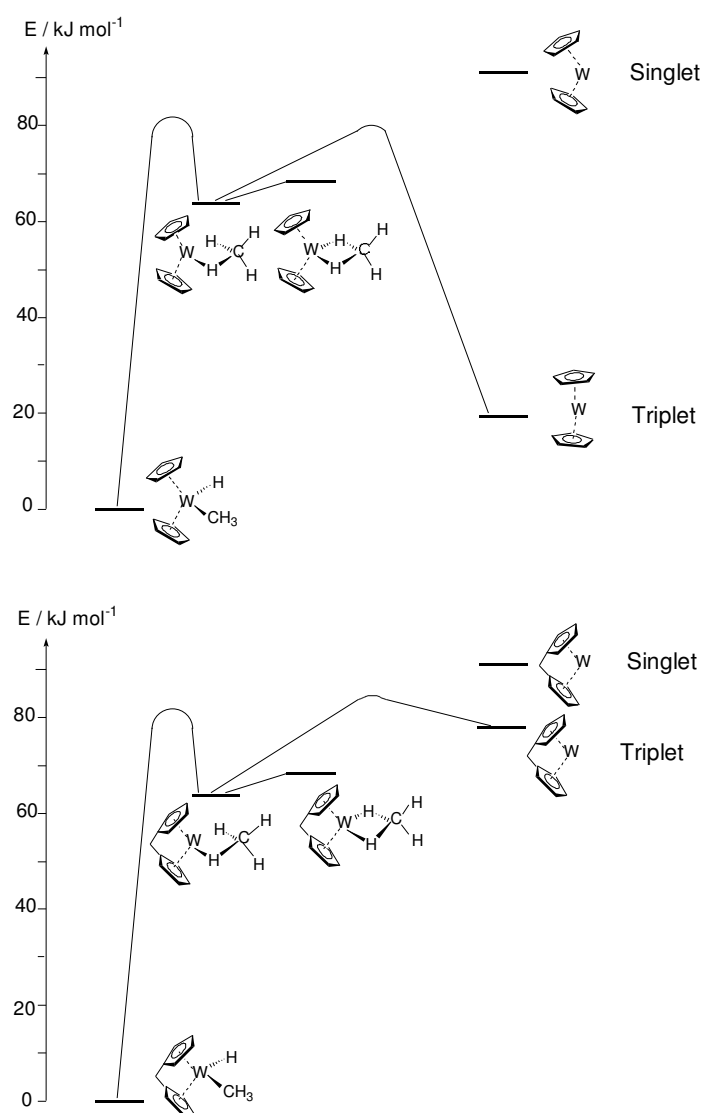


**Figure 1.18** Methane elimination (a) and intramolecular hydrogen scrambling (b) in nonbridged and *ansa*-tungstenocene methyl hydride.

The observation of increased thermal stability of the compound  $[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}(\text{Me})\text{H}]$  relative to compound  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{Me})\text{H}]$  is of particular significance since both complexes display intramolecular hydrogen exchange between alkyl ligand and hydride sites (**Figure 1.18(b)**).<sup>63-65</sup> Whereas the exchange process is only marginally faster than the reductive elimination of alkane for the nonbridged compound, hydrogen exchange can be studied more rigorously for the *ansa* compound where the competing elimination process is absent.

A density functional study by Green and Jardine of hydrogen exchange and methane elimination from  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)\text{H}]$  and  $[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}(\text{CH}_3)\text{H}]$  has examined the reaction pathway for both processes.<sup>66</sup> It is postulated that both exchange and elimination occur *via* the same pathway on which are located both singly agostic  $\eta^1\text{-H}$  and doubly agostic  $\eta^2\text{-H,H}$  methane  $\sigma$ -complexes (**Figure 1.19**). Reductive elimination of methane results in the

formation of a 16-electron ( $d^4$ ) tungstenocene species which has a triplet ground state. The minimum energy structure for such a species is one in which the rings are in a parallel arrangement with an  $e_2^3 a_1^1$  electron configuration (**Figure 1.4**). For the corresponding *ansa*-tungstenocene  $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}]$ , the constraining  $CMe_2$  bridge prevents adoption of a parallel ring configuration. In order to avoid spin pairing the high energy  $4a_1$  orbital must be partially occupied; the energy of this orbital increases sharply with increased inter-ring angle  $\alpha$  (**Section 1.1.2**). The high energy of the *ansa*-tungstenocene intermediate thus results in increased stability of the parent methyl hydride. In contrast there is considerable energy gain as the nonbridged tungstenocene undergoes geometric relaxation to a parallel ring structure and consequently reductive elimination of alkane is facile.



**Figure 1.19** Energy scheme for hydrogen exchange and methane elimination in  $[W(\eta-C_5H_5)_2(CH_3)H]$  and  $[W\{(\eta-C_5H_4)CH_2(\eta-C_5H_4)\}(CH_3)H]$

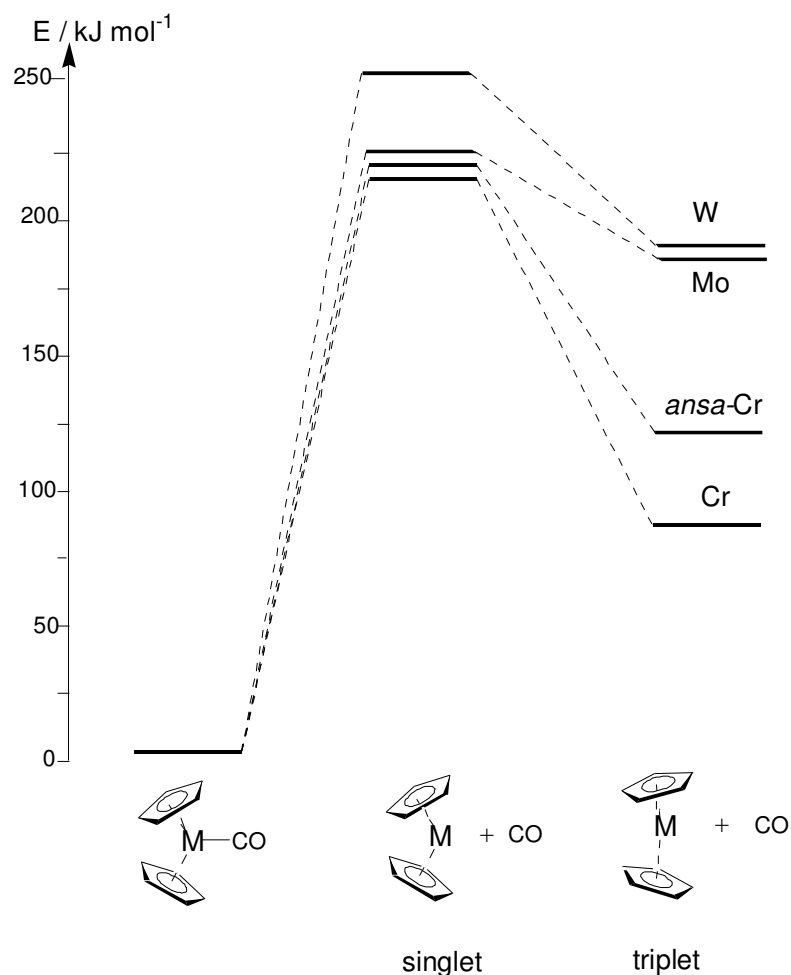
Such an explanation is also proposed to account for the differences in reactivity of ethylene-bridged titanocene compounds relative to analogous nonbridged species (**Section 1.5.1**).<sup>22</sup> For the nonbridged triplet titanocene  $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2]$  relaxation of the metallocene geometry from an inter-ring angle  $\alpha = 50^\circ$  to an optimal value of  $\alpha = 26^\circ$  results in an energy gain of 0.63 eV. Such an energy gain is not accessible to the ethylene-bridged triplet titanocene  $[\text{Ti}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{H}_4(\eta\text{-C}_5\text{H}_4)\}]$  due to the constraining influence of the interannular bridge. This may well account for the observed reactivity differences. For triplet zirconocene the magnitude of the energy gain upon relaxation of the rings is predicted to be 0.21 eV and thus less striking differences between nonbridged and *ansa*-zirconocene compounds are predicted.<sup>22</sup>

The stability of Group 6 metallocenes towards reductive elimination is found to increase in the presence of an *ansa*-bridge. Conversely, Parkin has demonstrated that for the tantalocene trihydrides a silicon-bridge strongly promotes reductive elimination.<sup>67</sup> For example  $[\text{Ta}\{(\eta\text{-C}_5\text{Me}_4)\text{SiMe}_2(\eta\text{-C}_5\text{Me}_4)\}\text{H}_3]$  reacts with ethylene *ca.* 4000 times faster than  $[\text{Ta}(\eta\text{-C}_5\text{Me}_5)_2\text{H}_3]$ . This apparent anomaly is resolved by considering the intermediate upon reductive elimination of hydrogen. For the tantalocene trihydrides elimination of dihydrogen gives a Ta(III) monohydride intermediate which is expected to have a bent sandwich structure geometry and not a parallel-ring structure encountered for the tungstenocene intermediate.

### 1.5.3 Trends in Stability of Group 6 Metallocene Carbonyl Compounds

Wong and Brintzinger investigated the reactivity patterns of the Group 6 metallocenes with CO.<sup>68</sup> The compounds  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$  ( $\text{M} = \text{Mo}, \text{W}$ ) are both stable whereas formation of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$  from  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)_2]$  and CO is reversible. However when the rings are linked by a tetramethylethylene *ansa*-bridge, as in  $[\text{Cr}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{Me}_4(\eta\text{-C}_5\text{H}_4)\}(\text{CO})]$ , thermal stability of the chromocene monocarbonyl compound is afforded.<sup>69</sup> The stability of the carbonyl compounds have again been shown by DFT to reflect the energy of the triplet metallocene intermediates  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2]$  (**Figure 1.20**).<sup>70</sup> For chromium where the d electron spin-pairing energy is greater than for molybdenum and tungsten, the formation of a triplet metallocene is particularly favoured, consistent with the reduced thermal stability of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$  compared to  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$  ( $\text{M} = \text{Mo}, \text{W}$ ). However the introduction of an *ansa*-bridge in

$[\text{Cr}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{Me}_4(\eta\text{-C}_5\text{H}_4)\}(\text{CO})]$  hinders the formation of the optimum near-parallel ring triplet state geometry of the chromocene intermediate, imparting increased thermal stability on the carbonyl complex.



**Figure 1.20** Calculated CO dissociation energies of Group 6 metallocene monocarbonyls to singlet and triplet metallocenes and CO

#### 1.5.4 Quantum Mechanical Exchange Coupling in *ansa*-Metallocene Trihydride Cations

Large, temperature dependent coupling constants have recently been noted for a number of organotransition metal trihydride complexes.<sup>71-73</sup> This phenomenon has been attributed to an exchange coupling contribution,  $J_{\text{ex}}$ , to the observed coupling constant  $J_{\text{AB}}$ . Green and Souter have reported that the cationic methylene-bridged *ansa*-tungstocene trihydride species  $[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{H}_3][\text{PF}_6]$  exhibits remarkable behaviour

in the  $^1\text{H}$  NMR spectrum with  $J_{\text{AB}} = 16000$  Hz at  $-70$  °C, decreasing to  $J_{\text{AB}} = 2900$  Hz at  $-130$  °C.<sup>36</sup> In contrast the analogous nonbridged compound  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3][\text{Cl}]$  displays a normal value of  $J_{\text{AB}} = 8.5$  Hz at all temperatures.<sup>74</sup> Cationic *ansa*-metallocene trihydrides complexes with a less geometrically constrained metallocene framework have also been prepared. Both  $[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{H}_3][\text{BF}_4]$  and  $[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{Me}_4(\eta\text{-C}_5\text{H}_4)\}\text{H}_3][\text{Cl}]$  exhibit quantum mechanical exchange coupling, although the magnitude of  $J_{\text{AB}}$  is much reduced compared to the methylene-bridged compound.<sup>37</sup>  $J_{\text{AB}}$  varies from 75 Hz at 0 °C to 8 Hz at  $-140$  °C for the silicon-bridged compound while for the analogous ethylene-bridged species,  $J_{\text{AB}}$  is found to vary from 35 Hz at  $-10$  °C to 8 Hz at  $-80$  °C.

### 1.5.5 Increased Electrophilicity of the Metal Centre in *ansa*-Metallocenes

Experimental and theoretical evidence suggests that an *ansa*-bridge reduces the electron density at the metal centre in a metallocene, thus creating a more electrophilic metal centre. As described in **Section 1.3** the molecular structure of *ansa*-metallocenes, particularly when bridged by a single carbon bridge, show a subtle shift from  $\eta^5$  towards  $\eta^3$  coordination of the ring. Density functional studies by Ziegler have shown that the electron deficiency of the Zr centre in  $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{CH}_3]^+$  is greater than in  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{CH}_3]^+$ .<sup>75</sup>

**Table 1.3** compares stretching frequencies for some *ansa*-metallocene carbonyl and dihydride compounds with their nonbridged analogues. The carbonyl stretching frequency is increased in the presence of an *ansa*-bridge for the zirconocene dicarbonyl compounds indicating a more electrophilic metal centre. In the series of Group 6 metallocene dihydrides the M-H stretching frequencies are reduced in the presence of an *ansa*-bridge, with the effect most marked for a methylene-bridge. The values of  $\nu(\text{M-H})$  illustrate the well-established trend that a silicon- and ethylene-bridge exert a similar influence and one that is intermediate between that of no bridge and a single carbon bridge.

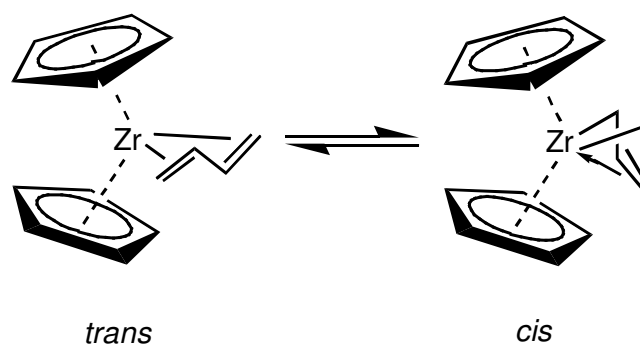
Compound	$\nu(\text{CO})/\text{cm}^{-1}$	Reference
$[\text{Zr}(\eta\text{-C}_5\text{Me}_5)_2(\text{CO})_2]$	1942, 1850	76
$[\text{Zr}\{(\eta\text{-C}_5\text{Me}_4)\text{PPh}(\eta\text{-C}_5\text{Me}_4)\}(\text{CO})_2]$	1959, 1874	77
$[\text{Zr}\{(\eta\text{-C}_5\text{Me}_4)\text{SiMe}_2(\eta\text{-C}_5\text{Me}_4)\}(\text{CO})_2]$	1947, 1861	78
$[\text{Ta}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})\text{H}]$	1868	79
$[\text{Ta}\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta\text{-C}_5\text{H}_4)\}(\text{CO})\text{H}]$	1887	67
	$\nu(\text{MH})/\text{cm}^{-1}$	
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$	1896	74
$[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{C}_2\text{Me}_4(\eta\text{-C}_5\text{H}_4)\}\text{H}_2]$	1875, 1860	37
$[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{H}_2]$	1865	37
$[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{H}_2]$	1833, 1823	35
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$	1847, 1826	80
$[\text{Mo}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{H}_2]$	1760, 1750	35

**Table 1.3** Stretching frequencies for *ansa*-metallocene complexes

Parkin has demonstrated the increased Lewis acidity of the zirconium centre of the *ansa*-system  $[\text{Zr}\{(\eta\text{-C}_5\text{Me}_4)\text{SiMe}_2(\eta\text{-C}_5\text{Me}_4)\}\text{H}_2(\text{PMe}_3)]$  compared to  $[\text{Zr}(\eta\text{-C}_5\text{Me}_5)_2\text{H}_2(\text{PMe}_3)]$  where the rate constant for phosphine dissociation is *ca.* 500 times greater for the nonbridged compound.<sup>78</sup>

### 1.5.6 (Butadiene)*ansa*-Zirconocene Compounds

(Butadiene)zirconocene  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_4\text{H}_6)]$  was the first example of a system where an  $\eta^4$ -coordination mode of a *trans* conjugated diene was shown to be present in a stable mononuclear organometallic complex. Erker and co-workers<sup>81-84</sup> and Nakamura *et al.*<sup>85</sup> reported that the *trans*- $\eta^4$ -conjugated diene complex  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\textit{trans}\text{-}\eta\text{-C}_4\text{H}_6)]$  was found in equilibrium with the *cis*- $\eta^4$ -butadiene complex  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\textit{cis}\text{-}\eta\text{-C}_4\text{H}_6)]$  in a 1:1 ratio (**Figure 1.21**). The first disorder-free *trans*- $\eta^4$ -butadiene metallocene molecular structure,  $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta\text{-C}_5\text{H}_4)\}(\textit{trans}\text{-}\eta\text{-C}_4\text{H}_6)]$ , has recently been reported.<sup>86</sup>



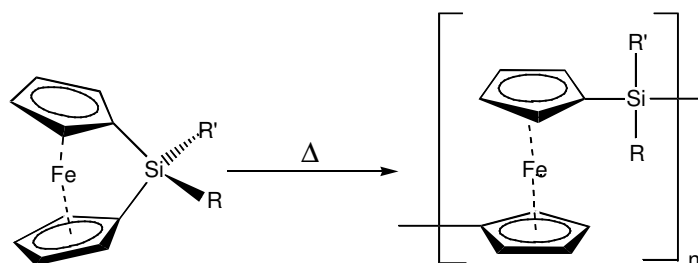
**Figure 1.21** *trans*- and *cis*-butadiene zirconocene

Green *et al.* have shown that when the metallocene fragment contains the highly constraining  $\text{CMe}_2$  *ansa*-bridge as in the fragment  $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}]$  the *cis*-butadiene isomer alone is detected by  $^1\text{H}$  NMR spectroscopy.<sup>87</sup>  $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}(\text{cis-}\eta\text{-C}_4\text{H}_6)]$  is conformationally rigid on the NMR time scale over the range  $-90$  °C to  $95$  °C, thus suggesting that the *ansa*-bridge somehow restricts the butadiene ligand from flipping between the *cis*- and *trans*-structures. DFT calculations have indicated that the energy differences between *cis*- and *trans*-forms in both the *ansa*-bridged and nonbridged compounds are both small and very similar ( $5$   $\text{kJ mol}^{-1}$  for  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_4\text{H}_6)]$  and  $7$   $\text{kJ mol}^{-1}$  for  $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}(\eta\text{-C}_4\text{H}_6)]$ ). Therefore while the equilibrium between *cis*- and *trans*-isomers found for  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_4\text{H}_6)]$  is well modelled by the calculations, they provide no clear explanation for the greater preference for the *cis*-butadiene compound in  $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}(\eta\text{-C}_4\text{H}_6)]$ .

A similar phenomenon has been reported by Erker when describing the inversion of the  $\text{M}(\eta\text{-C}_4\text{H}_6)$  envelope in a carbon-bridged (*cis*- $\eta^4$ -butadiene) *ansa*-metallocene compound.<sup>88</sup> The Gibbs activation energy  $\Delta G_{\text{inv}}$  is *ca.*  $30$   $\text{kJ mol}^{-1}$  greater than in the corresponding nonbridged compound  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{cis-}\eta\text{-C}_4\text{H}_6)]$ . The principal structural change in the two compounds is a reduction in the bending angle  $\beta$  from  $126.8^\circ$  in the nonbridged metallocene to  $107.6^\circ$  in the bridged compound. Extended Huckel calculations suggest an increase in  $\pi$ -character of the metal-butadiene bonding as the energy of the frontier orbitals are perturbed by the further bending back of the rings due to the *ansa*-bridge. This may account for the restricted butadiene inversion in the *ansa*-bridged compound.

### 1.5.7 Strained, Ring-Tilted [n]-Metallophenanes

The inherent strain in an *ansa*-metallocene unit has been utilised in late transition metal metallocene complexes. Strained, ring-tilted [n]-metalloceneophanes such as [1]-silaferrocenophane undergo quantitative, thermal ring opening polymerisation (TROP) (**Figure 1.22**).<sup>89, 90</sup> The resulting materials are rare examples of well-defined, high molecular mass, soluble polymers, in which the organometallic moieties form part of the main chain of the polymer. As described in **Section 1.1.2** the  $d^6$  ferrocene unit is reluctant to bend. **Table 1.4** presents some structural parameters (defined in **Figure 1.13**) for a series of *ansa*-silaferrocenophane complexes.



**Figure 1.22** Thermal ring-opening polymerisation (TROP) of [1]-silaferrocenophanes

Compound	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$	$\epsilon/^\circ$	$\phi/^\circ$	Reference
[Fe{(η-C <sub>5</sub> H <sub>4</sub> )SiMe <sub>2</sub> (η-C <sub>5</sub> H <sub>4</sub> )}]	20.8	159.2	164.7	95.7	37.0	90
[Fe{(η-C <sub>5</sub> H <sub>3</sub> Me)SiMe <sub>2</sub> (η-C <sub>5</sub> H <sub>3</sub> Me)}]	18.6	161.4	166.5	97.0	39.1	91
[Fe{(η-C <sub>5</sub> Me <sub>4</sub> )SiMe <sub>2</sub> (η-C <sub>5</sub> Me <sub>4</sub> )}]	16.1	163.9	168.6	98.1	40.3	91
[Fe{(η-C <sub>9</sub> Me <sub>6</sub> )SiMe <sub>2</sub> (η-C <sub>9</sub> Me <sub>6</sub> )}]	13.0	167.0	170.1	99.2	43.1	92

**Table 1.4** Selected structural parameters for [1]-silaferrocenophanes

The inter-ring or ‘ring-tilt’ angle  $\alpha$  and the bending angle  $\gamma$  shows that the introduction of a SiMe<sub>2</sub> bridge distorts the metallocene fragment from the favoured parallel-ring geometry. The strain imposed is evidenced by the large deviation from planarity at the *ipso*-carbon with values of  $\phi = 37$ - $43^\circ$ . This strain makes the ferrocenophanes susceptible to ring-opening reactions. Early transition metal

metallocenes show no tendency to rupture the bridge consistent with the energy changes involved in bending various  $d^n$  configurations. The TROP reaction has been extended to germanium-,<sup>93, 94</sup> phosphorus-<sup>95</sup> and sulphur-bridged<sup>96</sup> species, as well as to ethylene-bridged [2]-ferrocenophanes,<sup>97</sup> [2]-ruthenocenophanes<sup>98</sup> and [2]-cobaltocenophanes.<sup>99</sup> The absence of single carbon-bridge metallocenophane complexes reflects the highly constraining influence of such a bridge on metallocene geometry.

## 1.6 Aims of this Thesis

As has been outlined in this chapter, the modification of the molecular structure of a metallocene compound by the introduction of an *ansa*-bridge between the cyclopentadienyl rings can impart differences in the electronic and bonding properties and the reactivity of the metallocene. These differences can be particularly pronounced when there is significant change in the geometry of the metallocene unit.

The aims of this thesis were two-fold. Firstly, to identify new examples of, and to attempt to delineate, the '*ansa*-effect' by undertaking a systematic investigation of the effect of structural modifications on the reactivity of metallocene compounds. The second aim of this thesis was to exploit the changes in reactivity of metallocene compounds imparted by an *ansa*-bridge to explore new and previously inaccessible chemistry.

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