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The evolution of the *ansa*-bridge and its effect on the scope of metallocene chemistry

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Dedicated to Professor Hans-H. Brintzinger on the occasion of his 67th birthday

Contents

Keywords: *Ansa*-bridge; Metallocene chemistry; Ferrocene

1. Introduction

Since the discovery of ferrocene [1] and the elucidation of its bis-pentahapto sandwich structure 50 years ago [2], bis-cyclopentadienyl-transition metal and -lanthanide metal compounds have been central to some of the most important developments in modern organometallic chemistry. An odd, closed ligand in the Davies–Green–Mingos classification of polyene ligands [3], the cyclopentadienyl ligand, is a relatively inert moiety that is able to function as scaffolding that both frames and defines the reaction space of the attached metal. More importantly, the cyclopentadienyl ring can be modified in a virtually limitless number of ways in order to influence the electronic properties and steric and coordination environment of the metal. A very popular modification to the metallocene ligand framework is the inclusion of a linking group between the two cyclopentadienyl rings called an interannular bridge. Complexes with this feature were originally called metallocenophanes and this term is still applied to bridged metallocene complexes of the Group 8 metals; however, the name '*ansa*-metallocene' is now more commonly used in reference to bent-metallocene complexes of the early transition metals, lanthanide and main group metals. The latin prefix *ansa* (for bent handle, attached at both ends) was introduced by Brintzinger [4], who pioneered the design and synthesis of these complexes. *Ansa*-metallocenes made a huge splash in the polymer industry with the report by Kaminsky and Brintzinger that C_2-symmetric *ansa*-zirconocene complexes activated by methylalumoxane produce highly isotactic polypropylene [5]. A plethora of *ansa*-metallocene complexes of the Group 4 metals, the Group 3 metals, and the lanthanide metals have since been developed, largely for their application as alkene polymerization catalysts and catalyst models [6–10] and also as catalysts for asymmetric synthetic organic

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transformations [11]. Numerous books and review articles on these topics have been written. Therefore, this review will focus less on the application of *ansa*-metallocene complexes toward catalysis and more on the evolution of the *ansa*-bridge in terms of the various synthetic approaches that have been used to construct the bridged ligand framework, the variety of bridges that have been introduced, and the effect of the bridge on the structure and reactivity of *ansa*-metallocene complexes as compared with their unbridged counterparts.

2. The *ansa*-effect

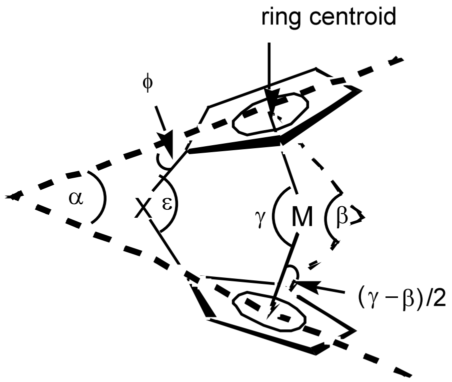
2.1. Effect of the bridge on metallocene geometry

The amount of distortion from the normal metallocene geometry that is caused by the bridge is reflected in the geometric parameters shown in Fig. 1 [12]. The degree of ring tilt is usually represented by angle α, the dihedral angle between the ring planes, and by γ, the angle between the vectors from the metal to the ring centroids. The angle β, between the vectors normal to the ring centroids, is another useful parameter, because its difference from angle γ reflects the amount of slippage of the metal from an ideal η^5 coordination to each ring [13]. Whereas a single-atom bridge can cause substantial distortions (by as much as 20°) in these angles in bent metallocene systems, the effect of two-atom-long bridges on these angles is negligible [4,14]. By contrast, *ansa*-ferrocene and -ruthenocene species are still considerably distorted by two-atom-long bridges [15], but distortion by three-atom-long bridges in these species is small [16].

The angle ϕ, the deviation of the bridge atom from the cyclopentadienyl ring plane, reflects the amount of ring strain created by the bridge. This distortion can be quite large, $\phi > 30°$, for single-atom-bridged ferrocene complexes [17–21]. It is generally smaller for normally bent metallocenes of the early transition metals but can still be sizable ($>20°$) for single-atom-bridged complexes of these metals [14,22]. As pointed out by Berenbaum et al. [20], the magnitude of ϕ is influenced not only by the length of the bridge but also by the geometric properties of the bridge. For example, the trigonal planar geometry of an sp^2-hybridized boron bridge produces a greater bending of the bridge atom to *ipso*-carbon vector away from the Cp ring plane than an sp^3-hybridized carbon or sulfur bridge [14,20]. The amount of ring slippage also affects the magnitude of ϕ. For example, ϕ values for an *ansa*-zirconocene complex with two dimethylsilylene bridges are very close to those of the singly-bridged zirconocene complex because the doubly-bridged complex exhibits more ring slippage [23]. Another parameter, D, suggested by Corey, measures how far the metal protrudes from a line connecting the centroids of its two cyclopentadienyl rings [24]. Corey proposed that the larger the distance D, the more reactive the metal center might be. This is indeed found to be case for many *ansa*-metallocene complexes. There are special exceptions however, as shown in the next section, which examines how the presence of an *ansa*-bridge alters the reactivity of the metallocene relative to its unbridged counterpart.

2.2. Effect of the bridge on metallocene reactivity

Letzner and Watts noted the effects of the bridge on the reactivity of [2] ferrocenophanes in the early 1970s [25,26]. The enforced bending of the rings by a tetramethylethylene bridge enhances the Lewis basicity of the iron center relative to Cp_2Fe but makes the ferrocenes resistant to Friedel–Crafts acetylation and to lithiation by BuLi [2]. Brintzinger has studied the effects of the interannular ethylene bridge on the reactivity of titanocene [27], zirconocene [28], and chromocene [29] complexes. Various derivatives of the *ansa*-titanocene such as the Ti(IV) dimethyl derivative, the Ti(II) ethylene adduct, and the Ti(III) chloride are unreactive under conditions in which the corresponding unbridged titanocene complexes either decompose or are transformed



$\gamma = Cp_{cent}–M–Cp_{cent}$

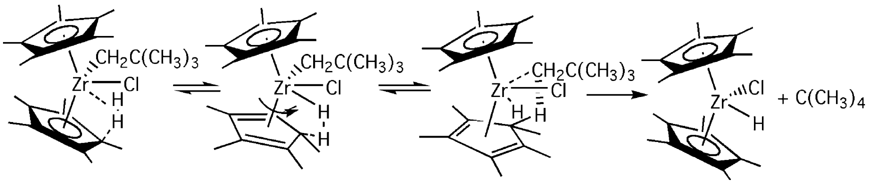
$\beta = Cp_{norm}/Cp_{norm}$

Fig. 1.

to other derivatives. This behavior was attributed to the inaccessibility of a $[(CH_2)_2(C_5H_4)_2Ti]_n$ intermediate (cf. $[(C_5H_5)Ti]_n$) [27]. Indeed, the electrochemical reduction of $(CH_2)_2(C_5H_4)_2TiCl_2$ to its Ti(II) stage requires a potential that is 0.3 V more negative than the corresponding potential for Cp_2TiCl_2 [30].

Whereas Cp^*_2ZrRX (R = neopentyl; X = halide) is readily hydrogenolyzed, the ethylene bridged species are unreactive toward hydrogen. In this case the effect of the bridge on reactivity was attributed to its restrictions on the rotation of the cyclopentadienyl ring, which was proposed to mediate the hydrogenolysis of the alkyl ligand by shuttling a hydrogen atom over to the alkyl group (Eqns 1 & 2).

Introduction of an ethylene [29] or a silylene [31] bridge between the rings has a dramatic effect on the properties of the chromocene system. Whereas Cp_2CrCO is not isolable due to the weak, reversible binding of CO by Cp_2Cr [32] a variety of *ansa*-chromocene carbonyl complexes [29,31,33] have been isolated and crystallographically characterized. DFT calculations by Jennifer Green indicate that the stabilization of the *ansa*-chromocene carbonyl derivative results from the destabilization of the uncomplexed metallocene fragment, which is prevented by the bridge from relaxing to a non-bent geometry [34]. This same effect is responsible for the greater thermal stability of *ansa*-tungstenocene methyl hydrides relative to the



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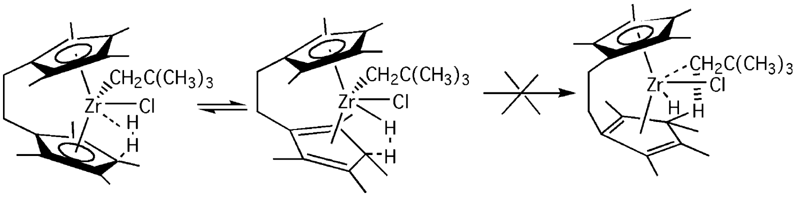

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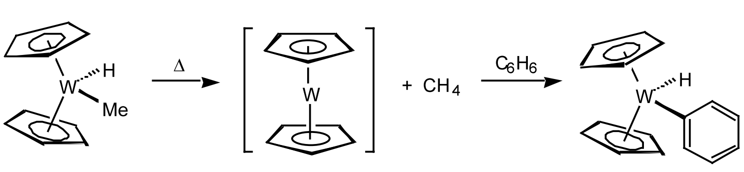

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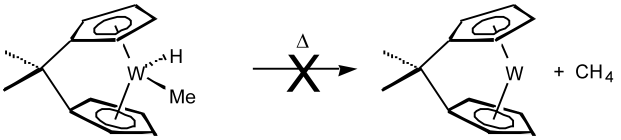

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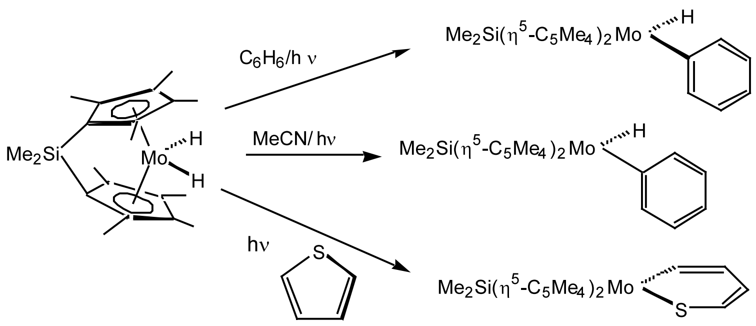


Scheme 1.

unbridged systems [12,35]. Whereas the unbridged species loses methane at 48 °C [36] to form a parallel-ring 16e tungstenocene intermediate, which undergoes further reactions, the *ansa*-species is stable up to 120 °C [37] (Eqns 3 & 4). The silylene bridge is also responsible for the greater thermal stability of $Me_2Si(C_5H_4)_2Re(Me)H^+$ [38] relative to its non-bridged counterpart [39].

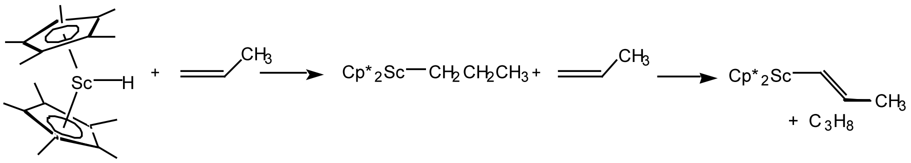
Although in the aforementioned examples the effect of the *ansa*-bridge is to make the bent-metallocene derivatives less labile and, hence, less reactive, there are many instances in which pinning the rings farther back on the metal with an *ansa*-bridge enhances the reactivity of the metallocene system. In contrast to Cp^*_2ScH, which inserts only a single α-olefin followed by a σ-bond metathesis reaction with additional α-olefin due to space restrictions on the orientation of the olefin within the equatorial wedge, $(Me_2Si)(C_5Me_4)_2Sc(PMe_3)H$ catalyzes the dimerization of α-olefins and the cyclization of α,ω-diolefins [40] (Eqns 5 & 6). Similarly, the complexes $[Me_2Si(C_5Me_4)_2MH]_2$ (M = Lu, Nd, Sm) are more active than their unbridged $[Cp^*MH]_2$ counterparts toward sterically sensitive reactions such as the oligomerization of propylene and 1-hexene [41] and the cyclization of amino olefins [42].

Parkin showed that the introduction of an interannular silylene bridge between the rings of permethylated metallocene complexes of Zr, Mo, and Ta has a dramatic effect on the reactivities of these systems relative to the unbridged bis-Cp* complexes. Unlike $Cp^*_2MoH_2$, $[Me_2Si(C_5Me_4)_2]MoH_2$ activates C–H bonds, C–C bonds, and C–S bonds (Scheme 1) [43,44]. Unlike $Cp^*_2ZrH_2$, $[Me_2Si(C_5Me_4)_2]ZrH_2$ activates the C–H bond of benzene to form $[Me_2Si(C_5Me_4)_2]Zr(Ph)H$ [45]. Finally, the *ansa*-tantalocene species $[Me_2Si(C_5Me_4)_2TaH_3$ and $[Me_2Si(C_5Me_4)_2Ta(\eta^2\text{-}C_2H_4)H$ undergo their respective reactions, the reductive elimination of H_2 and ethylene insertim8on, more rapidly than $Cp^*_2TaH_3$ and $Cp^*_2Ta(\eta^2\text{-}C_2H_4)H$ [46].

3. C_n- and Si_n-bridged *ansa*-metallocenes

3.1. Single atom bridges

A single sp^3 hybridized carbon is the smallest bridging unit that has been introduced between the rings of an *ansa*-metallocene. The synthesis of a methylene bridged *ansa*-metallocene was first described by Katz with the synthesis of $CH_2(C_5H_4)_2TiCl_2$ [47]. The ligand frame-



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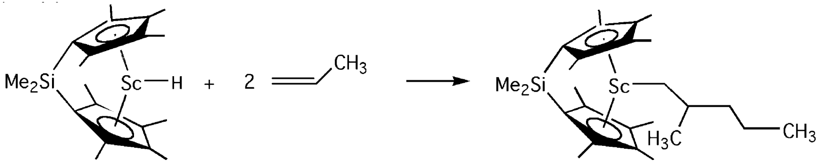
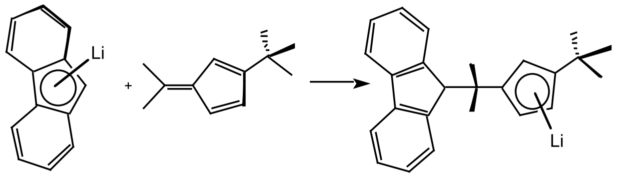


(6)

work, was prepared by allowing two equivalents of sodium cyclopentadienide to react with methylene chloride [48]. Yields of carbon-bridged metallocene ligands from the reaction of a cyclopentadienide salt with a gem-dihaloalkane are generally low [48,49]. A higher yielding method for incorporating a more substituted sp^3 carbon bridge between two rings entails reaction of a lithium cyclopentadienide salt with the appropriate fulvene (Eqn 7) [50–54]. By tethering the cyclopentadienide anion to the fulvene so that the nucleophilic attack was intermolecular, Erker developed the chiral, rigid C_1-bridged ligand framework shown in Eqn 8 [55,56]. A very similar, rigid C_1-bridged ligand is prepared via the NaCp catalyzed dimerization of 6,6-dimethylfulvene [57]. If linking two identical cyclopentadienyl or indenyl rings is the goal, it is more convenient to condense the two cyclopentadienyl or indenyl rings under basic conditions with acetone, to form a propylidene-bridged ligand [58–60], or formaldehyde, to form a methylidene bridged ligand (Eqn 9) [61].



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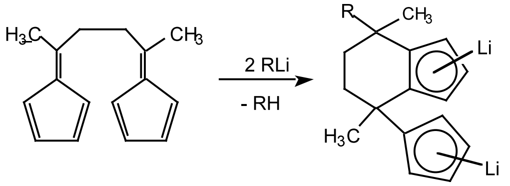

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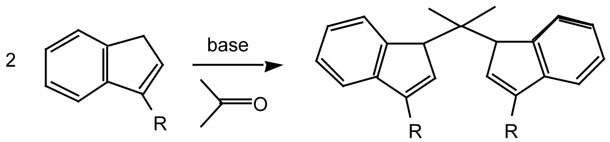
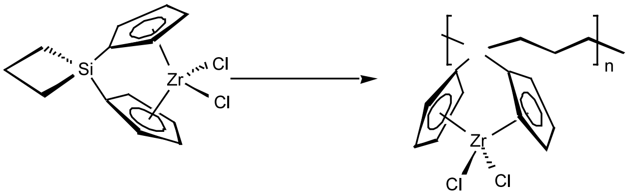


(9)

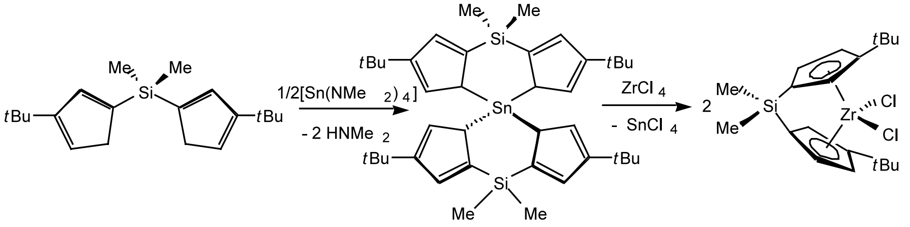
Silylene-bridged metallocene ligands are very popular because they are, in general, easily prepared by the reaction of two equivalents a lithium or sodium cyclopentadienide salt with a dichlorosilane [49,62]. A wide variety of ring systems can be attached to the silicon bridge in this manner [63]. Also, the rings can be attached to the silicon sequentially, offering a simple route to mixed ring systems [64–66]. Different types of substituents have been attached to the silylene bridge [67–69]. Manners and coworkers prepared the sila-cyclobutane bridged metallocene $(CH_2)_3Si(\eta^5\text{-}C_5H_4)_2ZrCl_2$ shown in equation 10 and successfully ring-open polymerized the sila-cyclobutane ring to afford polymer supported zirconocene complexes [70].



(10)

Incorporation of spiro-germylene or spiro-silyene bridges between indenyl and unsymmetrically substituted cyclopentadienyl rings promotes the stereoselective formation of C_2-symmetric *ansa*-metallocenes and suppresses the formation of the undesired *meso* isomers [71,72]. A clever synthesis of a C_2-symmetric silicon-bridged *ansa*-zirconocene species from a S_4-symmetric spiro-bis(silastannaindacene) compound takes advantage of the stereospecific nature of the transmetalation of the cyclopentadienyl ring from tin to zirconium (Eqn 11) [73]. Functionalized alkyl substituents have also been attached to the silylene bridge. For example, Marks tethered methoxyalkyl chains to the silicon bridge that were of sufficient length to chelate the metal center [74].

There are fewer examples of stannylene and germylene-bridged metallocenes than silylene-bridged metallocenes, although the heavier atom bridges are introduced in a similar manner as the silicon. Herrmann et al. prepared a mononuclear dimethylstannylene-bridged zirconocene complex and a spirocyclic bis(*ansa*-zirconocene) species by metalating $(CH_3)_2Sn(C_5H_5)_2$ and $Sn(C_5H_5)_4$ with one and two equivalents of $(Me_2NH)_4Zr$, respectively [75]. These complexes are active in the polymerization of ethylene upon activation with MAO. Although the polymerization activity of the



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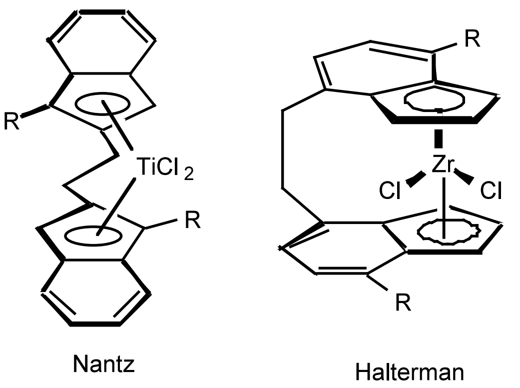
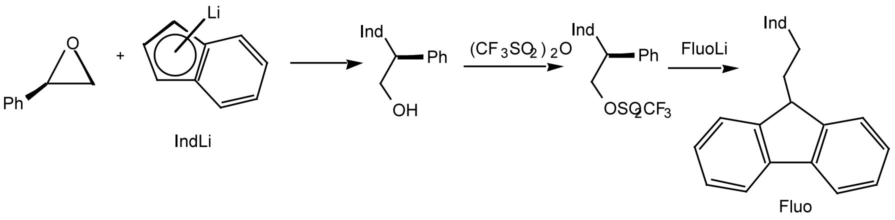


Fig. 2.



(12)

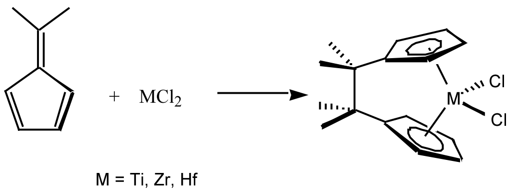
mononuclear tin-bridged complex is comparable to its silicon-bridged analog, the molecular weight of the polyethylene produced by the tin-bridged complex is much higher, indicating that the chain termination rate for the complex is lower. Suzuki et al. prepared a series of dimethyl-, diethyl-, and divinyl-silylene bridged and dimethylgermylene bridged permethylmetallocene complexes of Zr and Hf [76]. Schumann et al. have also prepared a series of dimethylstannylene- and dimethylgermylene-bridged permethylmetallocene complexes of the lanthanides Nd, Sm, Ho, and Lu [77].

3.2. Two atom bridges

An unsubstituted ethylene bridge is commonly introduced between cyclopentadienyl and indenyl rings by a salt elimination reaction between 1,2-dibromoethane and two equivalents of an alkali metal cyclopentadienide or indenide salt [78,79]. Since intramolecular cyclization of the 1-cyclopentadienyl-2-bromoethane intermediate to form spiro[2.4]hepta-4,6-diene can occur in competition with and sometimes to the exclusion of the attachment of the second cyclopentadienyl ring to the bridge [25], alternate synthetic routes to ethylene-bridged ring systems have been devised. For example, Wochner et al. based their synthesis of bis(2,3,4,5-tetramethyl-1-cyclopentadienylethane) [80] on the method developed by Threlkel and Bercaw [81] for the synthesis of alkyl- and aryl-tetramethylcyclopentadienes. In this case, the tetramethylcyclopentadienyl rings were assembled on the diethyl ester of succinic acid. By using epoxide building blocks for the bridge, Rieger developed a procedure for introducing the rings sequentially onto the ethano bridge, thereby allowing the formation of mixed ring systems (Eqn 12) [82–86].

More elaborate methods are required to introduce an ethylene bridge at positions on the indenyl rings other than C1. Nantz et al. used a multistep, disulfone-based approach to prepare the ligand 1,2-bis(2-indenyl)ethane in 41% overall yield from 1,4-bis(phenylsulfonyl)butane (Fig. 2) [87]. Nantz later prepared the ethylene bis(2-indenyl) *ansa*-ligands via the reductive coupling of 2-(hydroxymethyl)indenes with low-valent titanium (Fig. 2) [88]. Another unusual position for the ethylene bridge is at C7, on the arene portions of indene. An ethylene bridged ligand framework of this sort, as well as the methylidene-bridged analog, was prepared by Haltermann using a multistep synthetic approach (Fig. 2) [89].

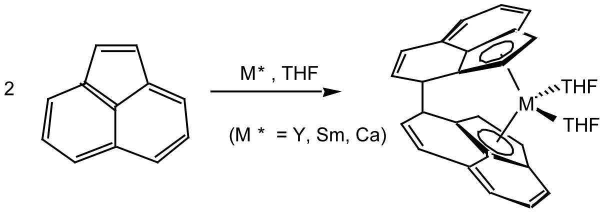
The reductive coupling of fulvenes is a convenient method for generating *ansa*-metallocene complexes with substituted ethylene bridges. A wide range of activated metals accomplish this coupling including alkaline earth metals (Mg [90–92], Ca [93–98], Sr [93]), lanthanide metals (Sm, Yb) [99–101], iron vapor [102], and Group 4 transition metal dihalides [103] (Eqn 13).



(13)

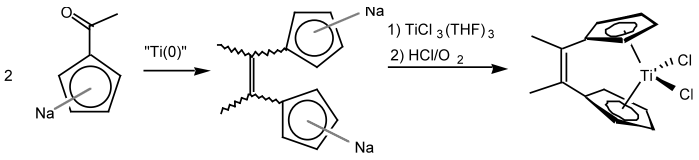
The reductive coupling of fulvenes with abstractable hydrogens β to C6 can lead to unbridged ligand side products which must be separated from the desired bridged ligands [96]. When magnesium is used to reductively couple the fulvene, a di Grignard of the bridged ligand is obtained which can be used to prepare a variety of early transition metal *ansa*-metallocene complexes [90,91,104,105]. For the other metals, *ansa*-

metallocenes are formed directly during the reductive coupling. *Ansa*-calcocene complexes formed in this manner have been used as ligand sources for *ansa*-zirconocene, -ferrocene, and -chromocene complexes [33,94,95,106]. One of the attractive features of this method is the easy access to a wide range of fulvenes with different patterns of substitution. Stereoselective coupling of unsymmetrically substituted fulvenes to form C_2-symmetric metallocenes has been achieved for fulvenes in which the exo C=C bond is included within an annulated ring, as in the reductive coupling of acenaphthylene (Eqn 14) [92,98,101]. The coupling of sterically-hindered 6-arylfulvenes with homogeneous Group 4 metal dihalides occurs with high diastereoselectivity for the *rac* over the *meso ansa*-metallocene [103]. By contrast, the coupling of sterically-hindered asymmetrically-substituted fulvenes on activated calcium offers poor to no selectivity [97].



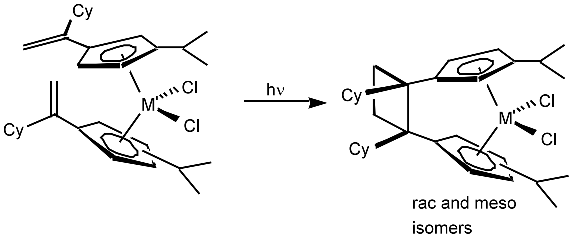
(14)

Chiral *trans*-1,2-cycloalkylene-bridged bis(indene) ligands have been prepared by allowing two equivalents of lithium indenide to react with 1,2-*trans*-dimesyl or ditosyl derivatives of cyclopentane and cyclohexane [107,108]. Metalation of the ligands produces a mixture of *meso* and *rac* metallocene diastereomers, from which the desired *rac* species must be selectively crystallized. As a result of the greater rigidity imparted by the 1,2-cycloalkane bridge to the *rac ansa*-metallocene, these complexes are more stereoselective than their ethylene bridged analogs in the polymerization of propene. Halterman has employed similar methods for preparing cyclopentane-1,3-diyl-bridged titanocene complexes [109].



(16)

Erker and coworkers designed a synthesis of 1,2-cyclobutane-bridged zirconocene complexes which involves the photochemical [2+2] coupling of 1,1′-bis(alkenyl)-zirconocene dihalides (Eqn 15) [110]. This photochemical coupling reaction has also been demonstrated with a bis(alkenyl)calcocene compound to form the corresponding *ansa*-calcocene [96].



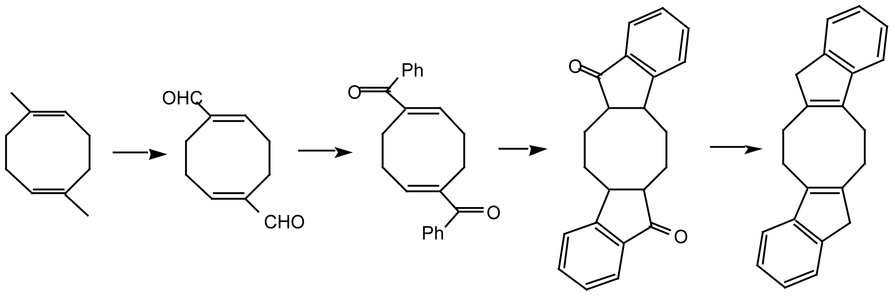
(15)

Bridges consisting of two sp^2-hybridized carbons have been incorporated between the rings of metallocenes by a few different methods. Brintzinger used a McMurry coupling of benzoyl- and acetyl-cyclopentadienyl sodium to form olefin-linked bis(cyclopentadienyl) ligands, from which *ansa*-titanocene complexes were prepared (Eqn 16) [111]. Since the McMurry coupling of 1,1′-ferrocene dicarboxaldehyde gives intermolecular coupling products in preference to the desired intramolecular coupling product, Aggarwal et al. developed a six step synthetic route to 1,2-(1,1′-ferrocenediyl)ethene starting from ferrocene [112]. 1,1′-Bis(phenylethynyl)ferrocene has been prepared via a Vollhart-type [2+2+2] cyclization reaction [113] between an acetylene–cobalt complex and 1,1′-bis(phenylethynyl)ferrocene [114].

Disilicon- and –C–Si-bridges have also been incorporated between the cyclopentadienyl and indenyl rings of metallocenes using standard salt elimination methods [115,116].

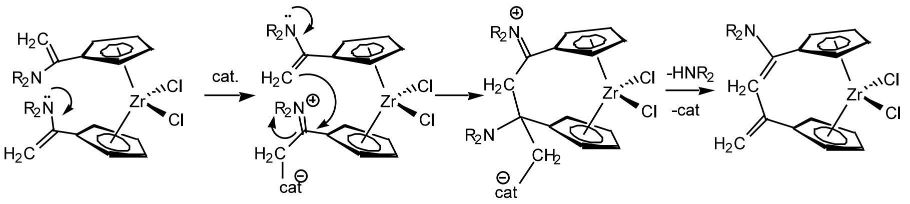
3.3. *Three atom and longer bridges*

Three atom and longer bridges have received less attention in Group 4 *ansa*-metallocene chemistry than the one and two atom bridges discussed above because these longer bridges are generally less rigid and offer less stereochemical control in alkene polymerizations and organic synthetic reactions. 1,3-Dibromopropane provides the backbone for trimethylene bridged ring



Scheme 2.

systems upon reaction with an alkali metal cyclopentadienide or indenide salt [117–119]. A more rigid C_3 bridge consisting of three sp^2-hybridized carbons was incorporated between the rings of Group 4 metallocenes by Knüppel et al. [120] and Bai et al. [121] by employing a Mannich-type carbon–carbon coupling reaction directly within the metallocene framework of a bis[(1′-dialkylaminoethenyl)cyclopentadienyl]MCl_2 (M=Ti, Hf, Zr) complexes (Eqn 17).



(17)

Si–O–Si and Si–N–Si bridges have been incorporated between the cyclopentadienyl rings of Group 4 [122–124] and Group 6 [125] metallocene complexes. *Ansa*-zirconocene complexes containing the five atom-long bridges m-$C_6H_4(CH_2)_2$-1,3, $C_5H_3N(CH_2)_2$-2,6, and $MeN(CH_2CH_2)_2$ were prepared by Qian et al. [126]. Significant intramolecular coordination of the donor containing bridge by the metal has been verified in structurally characterized examples 2,6-pyridinedimethylene-bridged metallocene complexes [127,128] and in *rac* 1,1′-(3-oxapentamethylene)-bridged bis(indenyl)lanthanide complexes [129].

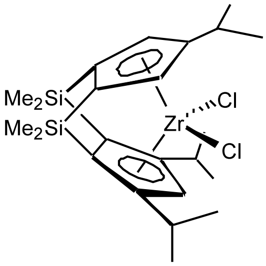


Fig. 3.

Even longer and more exotic interannular bridges have been introduced between the rings of ferrocene and cobaltocene. A variety of macrocyclic bridges [16,130] have been introduced, including polyether [131], polyamine [132], and polypeptide [133] bridges that can host additional metals.

3.4. Multiple bridges

Whereas multiply-bridged ferrocenophanes containing as many as five bridges have been prepared [16], two is the maximum number of bridges that have been incorporated in Group 4 *ansa*-metallocene complexes. Group 4 metallocene complexes containing two neighboring dimethylsilylene bridges have been reported by Brintzinger [23], Royo [134], and Bercaw [135]. Brintzinger found that the greater rigidity of the double silylene-bridged ligand framework favored the diastereoselective formation of C_2-symmetric metallocenes [23]. Herzog et al. used two silylene bridges in their mixed ring zirconocene system to fix the rings of the metallocene in an arrangement that promoted syndiospecific propene polymerization (Fig. 3) [135].

The double-silylene-bridged metallocenes are considerably more strained than their single-silylene-bridged analogs. This is apparent from the substantial widening of α in these complexes (by $> 10°$) as compared with the

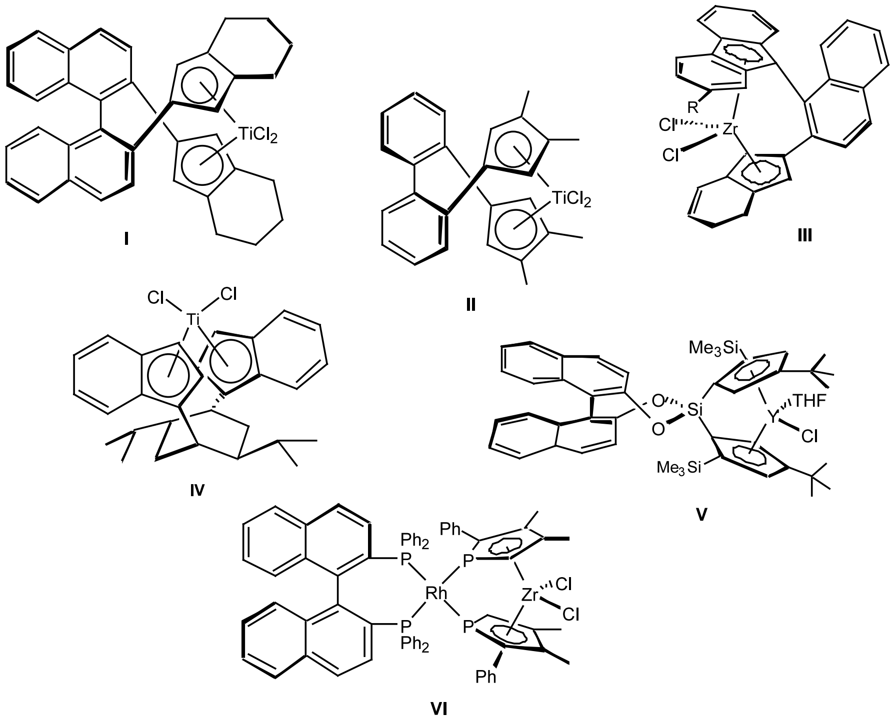
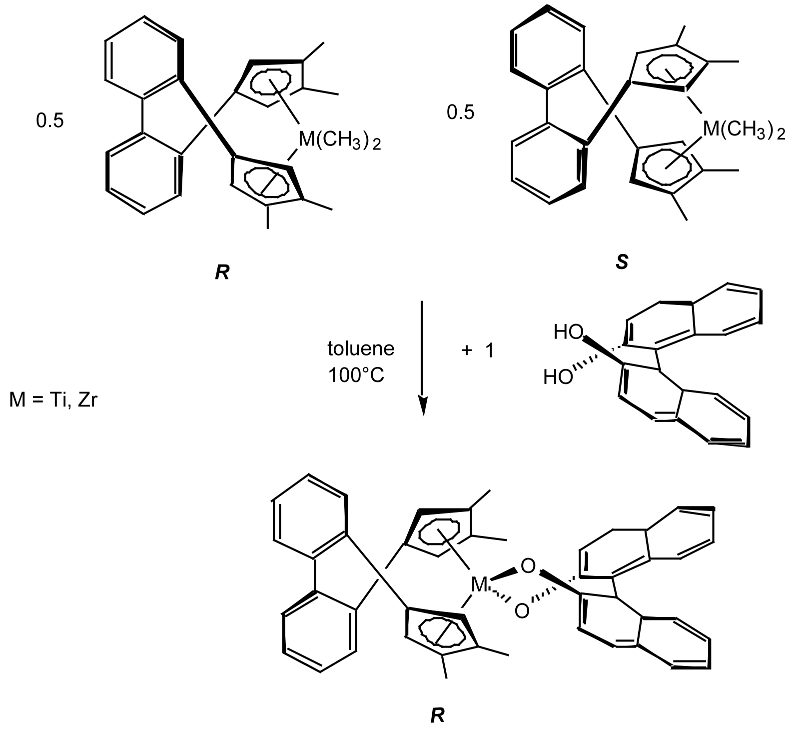


Fig. 4.

single-silylene-bridged complexes [134]. Because of this strain, the doubly bridged complexes are more vulnerable to degradation by MAO [23]. In spite of this strain, however, doubly dimethylsilylene-bridged titanocene and zirconocene dichloride complexes were not polymerizable by ring opening in the presence of Pt(0) catalysts [70].

Hafner [136] and Brintzinger [137] independently reported the synthesis of double-ethylene-bridged biscyclopentadienyl ligand frameworks. Two different

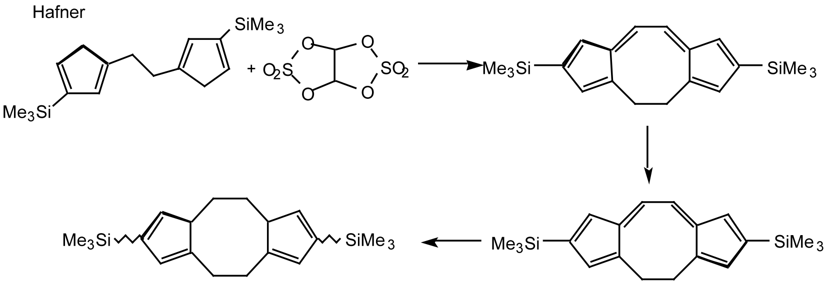


Scheme 3.

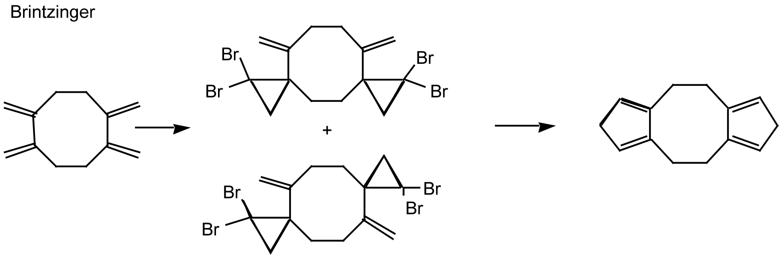
syntheses of the ligand framework were developed. The route by Hafner involved the condensation of 1,2-bis(trimethylsilylcyclopentadienyl)ethane with glyoxal sulfate to form an unsaturated precursor to the doubly bridged ligand which was subsequently reduced with $LAlH_4$ (Eqn 18). The route by Brintzinger involved a Skattebol rearrangement to annulate the cyclopentadienyl rings to the cyclooctane skeleton (Eqn 19). The double-ethylene-bridged ligand framework was used to prepare *ansa*-metallocene complexes of iron, titanium, zirconium, and vanadium. In contrast to the large distortion in metallocene geometry caused by a second silylene bridge, a second ethylene bridge has only a marginal effect.

3.5. Chiral bridges

A key function of the *ansa*-bridge is to maintain an asymmetric arrangement of substituted cyclopentadienyl rings and indenyl rings on the metal by restricting ring rotation. C_2-symmetric metallocenes have been useful as catalysts for isospecific α-olefin polymerization and as catalysts for asymmetric transformations such as the asymmetric hydrogenation of alkenes and imines. Since *meso ansa*-metallocene diastereomers are not useful for these applications it is usually desirable to suppress their formation during ring metalation. Chemists have used a variety of methods to prepare C_2-symmetric *ansa*-metallocene complexes stereoselectively.



(18)



(19)

Halterman introduced two ethylene bridges between two indene rings by constructing the indenyl rings on a 1,5-cyclooctadiene skeleton (Scheme 2) [138]. Because the indenyl rings are constrained to a C_2 arrangement by the two bridges, only the C_2-symmetric *ansa*-metallocene diastereomer can form upon metalation of the rings.

Buchwald and coworkers designed a C_2-symmetric doubly-bridged *ansa*-metallocene ligand based on a bicyclo[3.3.1]nonane skeleton, also using the Skattebøl reaction to annulate the cyclopentadienyl rings to the bridging skeleton [139]. A similar doubly bridged *ansa*-zirconocene based on the norbornadiene skeleton was proposed by Cavallo et al. [140].

The strategic placement of bulky substituents on the rings to bias the metalation toward the less sterically-hindered *rac* product is most successful when disubstituted cyclopentadienyl ligands are employed with one of the substituents at the two-position of the ring (i.e.

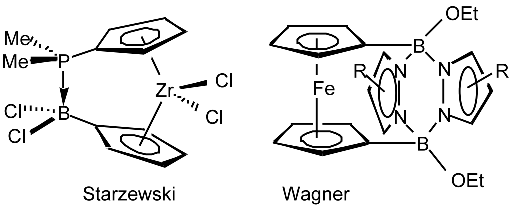
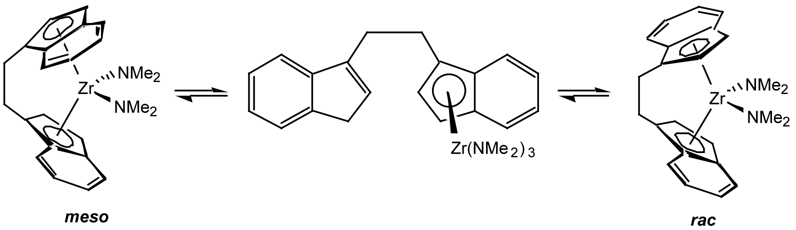


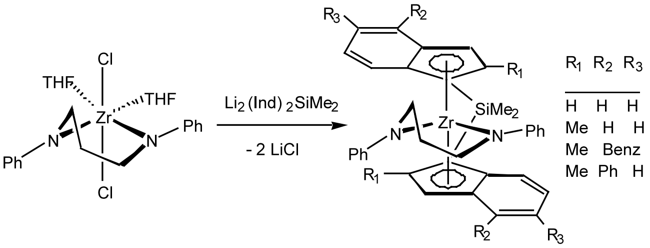
Fig. 5.

neighboring the bridge) [141–145]. In the absence of this second substituent, poor selectivity for the *rac* over the *meso* isomer is observed [90]. Jordan and coworkers demonstrated an efficient *rac*-selective synthesis of an {ethylenebis(indenyl)}zirconium complex by using an amine elimination reaction instead of a salt elimination reaction to metalate the indenyl rings, thereby rendering the metalation step reversible and allowing the buildup of the thermodynamically preferred *rac*-isomer [146,147] (Eqn 20). Eppinger et al. used a similar approach for the synthesis of silylene-bridged bis(indenyl)landthanide complexes with moderate *rac* selectivity [148].



(20)

A very clever approach used by Jordan for the *rac*-selective synthesis of a silylene-bridged bis(indenyl)zirconium derivative exploits the conformational properties of a chelating diamido ligand in the equatorial wedge of the metallocene to direct the stereochemistry of the ring attachment (Eqn 21) [149].



(21)

The incorporation of a stereogenic bridge between asymmetrically substituted rings has been used successfully to promote both the diastereoselective and enantioselective formation of chiral metallocenes [150–159]. Examples of C_2- and C_1-symmetric complexes that have been prepared by virtue of the axial chirality of their bridges are shown in Fig. 4. For examples **I**–**III** [150–153] the overall axial asymmetry of the ligand framework enforces the stereospecific formation of the chiral metallocene. For examples **IV** and **V** [155–157], the steric environment created by the axially chiral bridge promotes complete selectivity for the desired C_2-symmetric isomer.

The (*R*-Binap)Rh-bridged phosphazirconocene **VI** [158] is a rare example of a metal-bridged *ansa*-metallocene. Unlike the other *ansa*-metallocene syntheses, the rhodium bridge is introduced subsequent to attachment of the phosphole rings to the zirconium by reaction of the phosphazirconocene with [(*R*)-Binap)Rh(COD)]OTf. Rapid interconversion of the phosphazirconocene between *R*, *S*, and *meso* forms via ring slippage to an η^1-P-bound complex, allows the dynamic resolution of a single enantiomer of the *ansa*-metallocene by the stereogenic bridge.

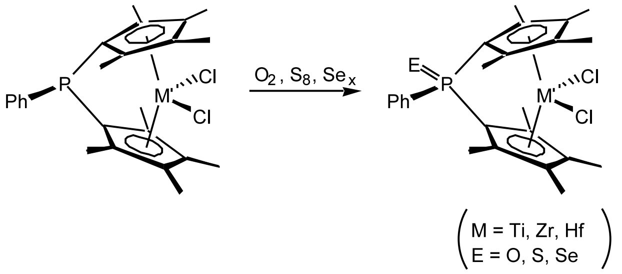
By incorporating a homochiral ligand within the equatorial wedge of the metallocene, as opposed to the *ansa* bridge, Brintzinger and coworkers have achieved the dynamic resolution of single enantiomers from racemic mixtures of C_2-symmetric Group 4 *ansa*-metallocenes. The epimerization of *ansa*-titanocene and -zirconocene complexes containing a homochiral binapholide ligand in the equatorial wedge was promoted photochemically [159] in one instance and thermally in the other (Scheme 3) [160].

4. Heteroatom-bridged *ansa*-metallocenes

Besides the Group 14 elements (C, Si, Ge, and Sn), various heteroatoms have been introduced into the *ansa* bridging position. Single heteroatom-bridged metallocenes reported to date include B, P, As, and S as the bridging atoms. Singly oxygen- or nitrogen-bridged *ansa*-metallocenes are unknown, although these elements have been included in the bridge with silicon. As with silicon [161] and germanium [162], the incorporation of heteroatoms such as phosphorus [163], arsenic [163], sulfur [19], and boron [20] between the rings of ferrocene is accomplished via a salt-elimination between 1,1′-dilithioferrocene and a suitable source of the bridging moiety. The strain in these heteroatom-bridged ferrocenophanes makes them good precursors to metallocene polymers by ring-opening polymerization [19,20]. Another method for polymerizing heteroatom-bridged ferrocenophanes that does not rely on bridge strain was introduced by Rauchfuss, who used the desulfurizing activity of *n*Bu$_3$P to polymerize ferrocenophanes containing trisulfane bridges to form ferrocene network polymers [164].

For the earlier transition metals, the heteroatom-bridged ligand framework must usually be assembled prior to its attachment to the metal. Introduction of a heteroatom between the cyclopentadienyl rings is generally accomplished via a salt elimination reaction between a heteroatom dihalide or dicarbamate compound and 2 molar equivalents of lithium cyclopentadienide or indenide. Although sulfur [165], disulfane [166], and tellurium [167] bridges have been incorporated between cyclopentadiene rings, the preparation of metallocene complexes from such ligands was not reported. Boron- [168–177], phosphorus- [13,178] and arsenic-[179] bridged bis(cyclopentadienyl) and bis(indenyl) complexes of titanium and zirconium have been prepared. Brintzinger and coworkers prepared a variety of phosphonium bridged *ansa*-metallocenes of Zr, K, and Ba starting from the phosphine bridged ligands RP(2-Me-4-*t*Bu-C$_5$H$_3$)$_2$ (R = Me, *n*Bu). These were converted to phosphonium bridge, ligands by reaction with RI, and the phosphonium salts were subsequently metalated [178]. Parkin used a similar synthetic approach to prepare the dimethylphosphonium bridged permethylmetallocene complexes $\{[Me_2P(C_5Me_4)MCl_2\}^+I^-$ (M = Zr, Hf) [180].

Chemical modification of the phosphorus bridge has been accomplished while the ligand is complexed to the transition metal. The PhP(III) bridge of the Group 4 *ansa*-metallocene complexes [PhP(C$_5$Me$_4$)$_2$MCl$_2$ (M = Ti, Zr, Hf) was oxidized to Ph(E)P(IV) (E = O, S, Se) upon reaction of the complexes with O$_2$, S$_8$, and Se$_x$ (Eqn 22) [13]. Anderson and Lin linked two phosphine-bridged zirconocenes together by inserting a Ph(Cl)Pt fragment between them [181]. They also created a platinum-bridged *ansa*-zirconocene complex by inserting a Ph(Cl)Pt fragment between the pendant phosphines on [(Ph$_2$PC$_5$H$_4$)$_2$ZrCl$_2$].



(22)

Modification of the substituents on the boron bridge has also been accomplished while it is contained within the metallocene complex [170,174,177].

The only diborane-bridged *ansa*-metallocenes reported to date are *ansa*-kalocene and -calcocene compounds containing two fluorenyl rings tethered by a (Me$_2$N)$_2$B$_2$ unit [182]. Starzewski and coworkers developed a clever *ansa*-metallocene design that involves the reversible formation of donor/acceptor bridges between a Lewis-acidic boryl substituent on one ring and a Lewis-basic phosphine or amine substituent on the opposite ring (Fig. 5) [183]. Wagner and coworkers have also used the acceptor properties boron to form self-assembling bridges between the rings of 1,1′-diboryl-ferrocene by the insertion of diazo molecules such as pyrazoles between the boryl substituents [184].

5. Conclusion

As the field of metallocene chemistry was reaching maturity, the introduction of an *ansa*-bridge brought these complexes, once again, to the forefront of academic and industrial organometallic research. The body of work concerning the synthesis and application of *ansa*-metallocene complexes is so vast that it is impossible to mention all of the contributions that have been made to this chemistry in one review article. The examples presented here were selected to illustrate the multiple functions the *ansa*-bridge has served in the chemistry of metallocenes. These functions include: (a) fixing the symmetry of the metallocene complex by preventing free rotation of the rings, (b) controlling the stereochemistry of metallocene formation by directing the orientation of the rings upon metalation, (c) influencing the reactivity of the metal by enforcing a bent-sandwich geometry between the rings, (d) increasing the electrophilicity of the metal and increasing the access of substrates to the equatorial wedge of the complex by increasing the tilt of the rings on the metal, and (e) providing a reactive site at which ring opening polymerization chemistry, ligand substitution, reversible bridge formation, and reversible metal ion binding can occur. The *ansa*-metallocene ligand design has inspired the design of related bridged ligand frameworks. These include cyclopentadienyl-type ring systems tethered to amine [185], amide [186], alkoxide [187,188], ether [189], phosphine [190], phosphide, [191] and arene ligands [192] and interannular-bridged bis(η^6-arene) [193], bis(dicarbollide) [194], and bis(boratabenzene) [195] transition metal complexes.

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