Boron-Bridged Group-4 *ansa*-Metallocene Complexes

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Keywords: Group-4 elements / Metallocenes / Boron bridge / Lewis acids / Alkene polymerization

Boron-bridged group-4 *ansa*-metallocene complexes are newcomers to the field of metallocene-mediated olefin polymerization catalysis. Because of the Lewis acidity of the boron bridge, it is more reactive than the more common carbon and silicon bridges. It is also more vulnerable to cleavage from the ligand framework by nucleophilic agents. A primary goal of our work is to involve the boron bridge more actively in the reaction chemistry of the metallocene while keeping the bridge intact.

Introduction

Metallocenophanes and *ansa*-Metallocenes

The earliest examples of interannular-bridged metallocenes are ferrocene derivatives and are called ferrocenophanes in association with the nomenclature system for bridged, aromatic, organic compounds.[1−3] The first examples of interannular-bridged metallocene complexes of the group-4 transition metals were synthesized by Katz and by Bernal;[4,5] however, Brintzinger is responsible for popularizing these systems and for popularizing the term "*ansa*-metallocene".[6] The latin prefix *ansa* (for bent handle, attached at both ends) was also borrowed from the organic nomenclature for bridged aromatic compounds. The term *ansa*-metallocene has generally been applied to bridged, bent-metallocene complexes of main-group metals,[7−10] the early transition metals (groups 3−7)[11−22] and the lanthanide metals,[23−27] whereas the term metallocenophane continues to be used for the bridged sandwich compounds of iron and ruthenium.[28−30]

Group-4 *ansa*-metallocene complexes are currently favored for the stereocontrol that they afford in Ziegler−Natta-type olefin polymerization catalysis.[31−33] These complexes are also popular as catalysts for various asymmetric organic transformations.[34] Although a number of different bridging groups have been introduced, carbon and silicon moieties are most common and have served a primarily structural role, that of fixing the cyclopentadienyl, indenyl, or fluorenyl rings of the metallocene in a specific orientation with respect to the active site. The bridge has also been designed to direct the stereochemistry of ring addition during metallocene formation;[11] however, to date, there has been little *chemical* participation of the *ansa* moiety in the reactions occurring at the transition metal center.[25]

This chemical participation has been one of the goals of our research. To this effect we have incorporated an electrophilic borylidene moiety in the *ansa* position of the metallocene. One of our objectives is the activation of the transition metal center by the boron bridge in a manner currently accomplished by external Lewis acid coactivators. The potential to couple geometry changes at the boron bridge with chemistry occurring at the transition metal center is another attractive feature of this new class of *ansa*-metallocenes.

Although related to the boron-bridged systems described herein, group-4 metallocenes with dangling boryl groups will not be covered in this review article. Participation of the dangling boryl group in the chemistry of the transition metal has been demonstrated by Piers and co-workers.[35] Bochmann and co-workers have modeled intramolecular activation of ligands on the metal center by boron.[36] Their examples indicate that the ability of the Lewis-acidic boryl

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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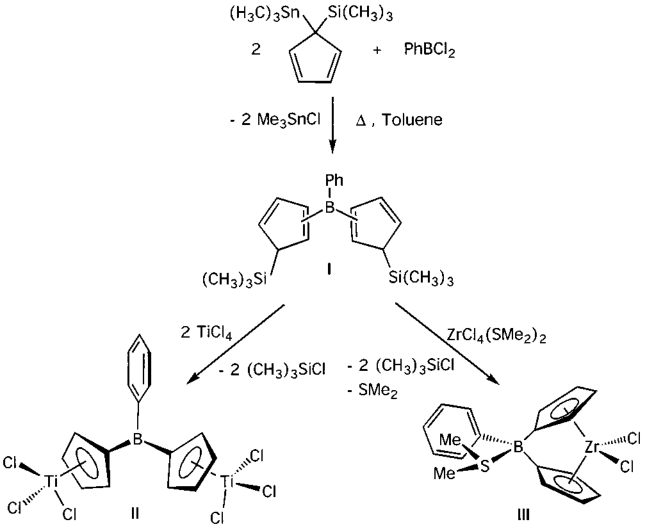
group to activate the metal complexes intramoleculary by σ-ligand abstraction is very sensitive to the proximity of the boryl group to the ligands. In this respect, dangling the boryl group over the active site of the metal center is more effective than including it within the interannular bridge of the metallocene. Nevertheless, *inter*molecular activation of the metal center of another complex by the boron bridge is still possible and does occur. Additional examples of group-4 metallocene complexes with dangling boryl groups are found in ref.[37−40,41b]

Syntheses of Boron-Bridged *ansa*-Metallocenes

Manners and co-workers reported the first example of a [1]borylidene-bridged metallocene, which was prepared by treating 1,1′-dilithioferrocene with an aminodichloroborane.[30] Unfortunately, a similar approach for introducing a boron atom between the cyclopentadienyl rings of metallocene complexes of the more reactive group-4 metals is not possible since further metallation of the cyclopentadienyl ring is unlikely in the presence of the electrophilic group-4 metal center. Instead, the boron-bridged dicyclopentadienyl ligand framework must be assembled prior to its attachment to the group-4 metal center.

In 1979, Jutzi and Seufert reported a method for the synthesis of cyclopentadienylboranes involving the reaction of haloboranes with cyclopentadienyltrimethylsilanes and -trimethylstannanes.[41a] The presence of an additional trimethylsilyl substituent on the cyclopentadienyl ring allows the further attachment of a titanium trichloride fragment by reaction with $TiCl_4$.[41b] The avoidance of salt-metathesis reactions in these synthetic steps is attractive due to the vulnerability of the boron−cyclopentadienyl linkage to cleavage by strong nucleophiles.[42] In 1995, Reetz and co-workers reported using this chemistry to form boron-substituted zirconocenes.[37] We have also employed this chemistry for the synthesis of the boron-bridged titanium homobimetallic complex **II** and the *ansa*-zirconocene complex **III** shown in Scheme 1.[43]



Scheme 1. Syntheses of boron-bridged titanium homobimetallic complex **II** and *ansa*-zirconocene complex **III**

The more labile trimethylstannyl substituents on the cyclopentadienyl rings are required for the ring borylation step. Formation of an *ansa*-metallocene was not expected from the reaction of ligand **I** with $TiCl_4$ since it has been shown that the attachment of only *one* cyclopentadienyl ligand to the titanium center is possible by this dehalodesilation route.[44] On the other hand, although zirconium tetrachloride has been shown to readily metallate two trimethylsilylcyclopentadiene rings by this route, it is completely unreactive toward ligand **I**, as are $[ZrCl_4(THF)_2]$ and $[ZrCl_4(THT)_2]$ (THT = tetrahydrothiophene). Fortunately, $[ZrCl_4(SMe_2)_2]$ does react with **I** to form the *ansa*-metallocene **III**, in which one of the dimethyl sulfide ligands is retained as an adduct on the phenylborylidene bridge. The attachment of an electropositive boron atom to the ring system apparently deactivates the silyl substituents toward electrophilic substitution by Zr^{IV} such that only a non-oligomeric, weakly solvated source of $ZrCl_4$ is suitable. Even when **I** is treated with two equivalents of $[ZrCl_4(SMe_2)_2]$, the *ansa*-metallocene is formed preferentially. We have used this same reaction to generate various other boryl-cyclopentadienylzirconium complexes, including $[\{Ph_2(SMe_2)B(C_5H_4)\}ZrCl_3]$ and $[\{(C_6F_5)_2(SMe_2)B(C_5H_4)\}ZrCl_3]$,[45] in which the boryl group is pendant to but not bridging between the cyclopentadienyl rings.

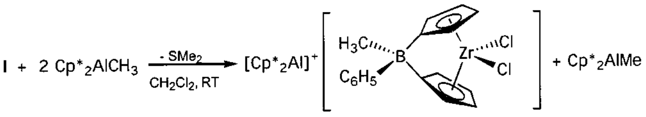
We believe that the dimethyl sulfide assists in the formation of the *ansa* complex since its coordination to the boron rehybridizes the single-atom bridge from an sp^2 to an sp^3 geometry which can better accommodate the bent-metallocene structure. As we were preparing to publish our findings, we discovered a report on the synthesis of the base-free version of **III** by Rufanov and co-workers.[46] These authors employed bis(trimethylstannyl)cyclopentadiene as the precursor to their boron-bridged ligand, forming the stannylated analog of **I**, which was treated directly with $ZrCl_4$. A mononuclear, *ansa*-metallocene structure was proposed for the base-free species, although an X-ray crystal structure was not obtained, and the molecular weight of the complex was not determined. The validity of this assignment is still in question, and we have not yet successfully prepared the base-free *ansa*-metallocene either by the Rufanov method or by complete removal the dimethyl sulfide adduct from **III**.

Lewis Aciditiy of Phenylborylidene Bridge

Efforts to abstract the Lewis base adduct from **III** with a stronger Lewis acid have been, so far, unsuccessful. Surprisingly, when either **III** or the related *tert*-butyl isocyanide complex are combined with an equimolar amount of $B(C_6F_5)_3$ in CD_2Cl_2, only partial abstraction of the Lewis base adduct (30−37%) by $B(C_6F_5)_3$ from the phenylborylidene bridge is observed by ^1H and ^{19}F NMR spectroscopy at 273 K.[47] We expected the boron atom of the phenylborylidene bridge to have an electrophilicity more comparable to that of BPh_3 based on its substitution. Indeed, ν(CN) for the *tert*-butyl isocyanide analog of **III**, $[\{(Ph)(tBuNC)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]$, is identical to that of $Ph_3B(CN-tBu)$ ($2272\ cm^{-1}$)[48] and substantially lower than that of

$(C_6F_5)_3B(CN-t\text{Bu})$ (2310 cm^{-1}).[49] Thus, we surmise that the greater affinity of **III** for its Lewis base adducts arises from the relief of the internal strain which would exist in the sp^2-hybridized boron bridge.

The reactivity of the borylidene bridge in **III** also reveals a Lewis acidity more comparable to that of $B(C_6F_5)_3$ than BPh_3, since **III** is able to accomplish methide abstraction in a manner similar to that of $B(C_6F_5)_3$. For example, reaction of **III** with Cp^*_2AlMe ($Cp^* = C_5Me_5$) affords the pentamethylaluminocenium cation $[Cp^*_2Al]^+$ with $[(Ph)(Me)B(\eta^5\text{-}C_5H_4)_2ZrCl_2]^-$ as the counteranion [Equation (1)]. $B(C_6F_5)_3$, but not BPh_3, reacts in a similar manner with Cp^*_2AlMe.[47]



IV

The formation of **IV** is important as it indicates the possibility of stabilizing a borate-bridged *ansa*-zirconocene complex as a zwitterion (Figure 1).

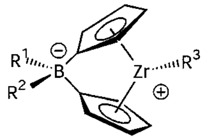


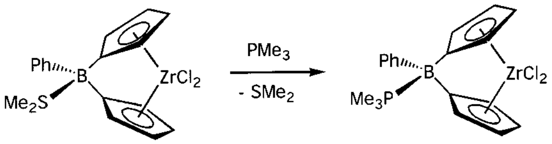
Figure 1. Hypothetical borate-bridged *ansa*-zirconocene zwitterion

It is clear, however, that the countercation plays a role in the stability of the borate bridge. The stability of **IV**, with its permethylaluminocenium countercation, suggests that a sterically hindered, non-intrusive countercation is desirable. This is further supported by the synthesis of a variety of stable borate-bridged *ansa*-zirconocene salts by treating **III** with $[Bu_4N]X$ (X = Cl, Br, I, BF_4, BH_4) and $[(Ph_3P)_2N]Cl$.[45] The borylidene bridge in **III**, like $B(C_6F_5)_3$, also abstracts a methyl anion from Cp_2ZrMe_2, as indicated by ^1H and ^{11}B NMR spectra of the reaction. We are currently trying to isolate and fully characterize the product of this reaction.

Alkylation of Boron-Bridged *ansa*-Zirconocene Complexes

Alkylation of the transition metal center is an essential step in forming an active catalyst center for olefin polymerization and other applications in catalysis. The vulnerability of the electrophilic boron bridge to nucleophilic attack and subsequent cleavage from the cyclopentadienyl ring is probably responsible for our unsuccessful efforts to alkylate complex **III** using conventional organometallic alkylating reagents such as alkyllithium, Grignard, alkylzinc, and alkylaluminum reagents. Such cleavage of the boryl group from the cyclopentadienyl ligand has been encountered in other cases.[43,49]

Dynamic behavior observed in the variable-temperature ^1H NMR spectra of **III** revealed that the dimethyl sulfide adduct is only weakly coordinated to the boron. It is readily replaced by more tightly coordinating ligands, such as PMe_3, to form $[\{Ph(PMe_3)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]$ (**V**) which, unlike **III**, is non-labile on the NMR time scale [Equation (2)].[43]



III **V**

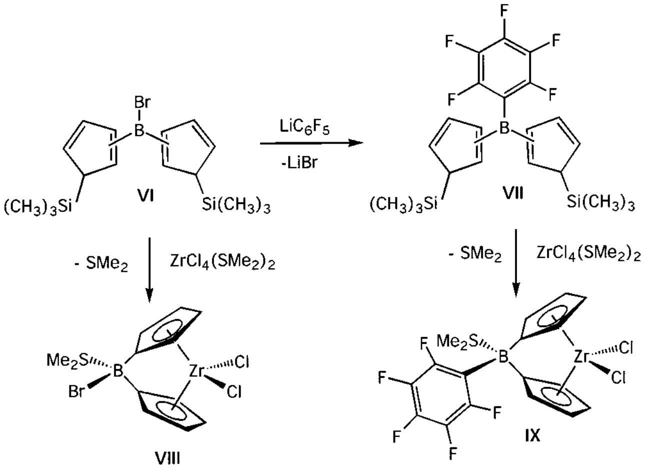
This substitution protects the boron sufficiently to allow alkylation of the zirconium center by alkyllithium and Grignard reagents to form complexes of the type $[\{Ph(PMe_3)B(\eta^5\text{-}C_5H_4)_2\}ZrR_2]$ (R = CH_2SiMe_3, $CH_2C_6H_5$), which can be activated with either $B(C_6F_5)_3$ or $[PhMeNH]^+[B(C_6F_5)_4]^-$ toward ethylene and propene polymerization.[45] A related phenylborylidene-bridged bis(indenyl)zirconium dichloride complex was recently reported by Reetz and co-workers.[50] The trimethylphosphane adduct of this complex, upon activation with MAO (MAO = methylalumoxane), was found to be a better catalyst for the polymerization of propene than the diethyl ether adduct, presumably due to stronger complexation of the boron by PMe_3. Similarly, complex **V**, with its tightly coordinating PMe_3, is activated by MAO toward olefin polymerization. Complex **III**, however, with its weakly coordinating SMe_2, is completely inactive under the same reaction conditions. Complex **IV** and other borate-bridged complexes such as $[NEt_4]^+[\{Ph(Cl)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]^-$ and $[(Ph_3P)_2N]^+[\{Ph(Cl)B(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]^-$ are also activated by MAO toward olefin polymerization, although their activities in the polymerization of ethylene were found to be lower than that of **V**.[47]

Other Boron-Bridged Group-4 Metallocene Complexes

The phenyl group on the borylidene bridge may be replaced with other substituents for the purpose of fine-tuning the electrophilicity of the boron. By using BBr_3 instead of $PhBCl_2$ in the ligand synthesis shown in Scheme 1, we are able to prepare ligand **VI**, in which the bromine is readily replaced by other moieties, such as the pentafluorophenyl group in ligand **VII**. These ligands were used to prepare complexes **VIII** and **IX** (Scheme 2). A variable-temperature ^1H NMR study shows that, in contrast to complex **III**, the dimethyl sulfide adduct in complex **IX** is non-labile on the NMR time scale.[45]

An X-ray crystal structure of complex **IX** confirmed its formulation but the structure is highly disordered with an unidentified solvent molecule. A preliminary ORTEP drawing of the molecule is shown in Figure 2.[51]

Introduction of an amido group onto the boron bridge allows the isolation of base-free group-4 *ansa*-metallocenes complexes, examples of which have been reported by Braunschweig and by Ashe (Figure 3).[52,53] π-Electron donation from the nitrogen to the boron is evident in the X-ray crystal structures of these complexes and is presumably responsible for the greater stability of the base-free boron



Scheme 2. Variations on the substitution of the boron bridge

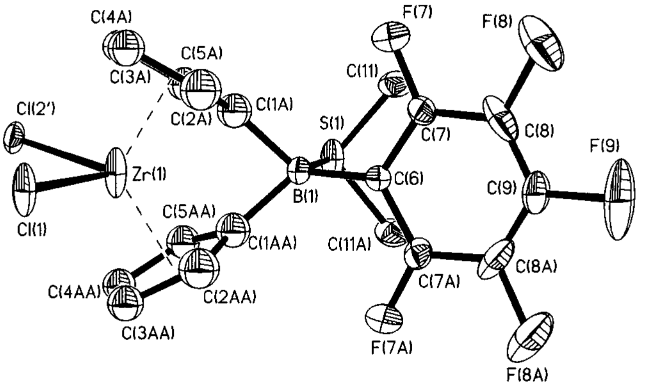


Figure 2. Preliminatry ORTEP drawing of the molecular structure of **IX**; thermal ellipsoids are drawn at 30% probability

bridges. Complex **XI**, upon activation with MAO, exhibits polymerization activities in the range exhibited by Me_2Si-bridged zirconocenes.

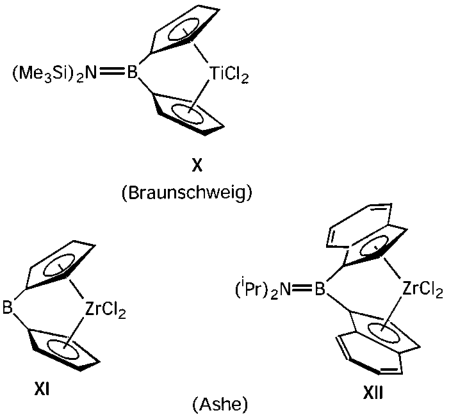


Figure 3. Amidoborylidene-bridged *ansa*-metallocene complexes of Ti^{IV} and Zr^{IV}

As mentioned above, Reetz and co-workers have recently reported the synthesis of a bis(indenyl)zirconium dichloride complex with different Lewis bases coordinated to the phenylborylidene bridge (**XIII**, Figure 4).[50] Reaction of the dianionic indenyl ligand with $ZrCl_4$ affords a 1:1 mixture of *rac*- and *meso*-metallocene isomers, from which the *rac* isomer can be selectively crystallized in 12% yield. The PMe_3 adduct of this system exhibits high propene polymerization activity as well as high selectivity for an isotactic polymer. Base-free, methylborylidene- and tris(trimethylsilyl)borylidene-bridged analogs of C_2-symmetric bis(indenyl)zirconium complexes were reported separately by Rufanov and co-workers, although no X-ray crystallographic data confirming the structures are available.[54]

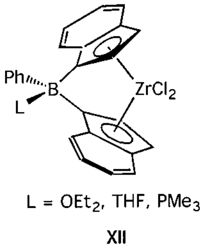


Figure 4. Phenylborylidene-bridged *rac*-bis(indenyl)zirconium complex prepared by Reetz and co-workers

A new paradigm for the synthesis of interannularly bridged metallocenes involving the formation of a donor/acceptor linkage between a Lewis-acidic boryl substituent on one ring of the metallocene and a Lewis-basic substituent on the opposite ring was introduced by Starzewski and co-workers (**XIV**, Figure 5).[55] This self-assembly approach to bridge formation affords enormous synthetic control and versatility in the design of the *ansa*-metallocene complexes since the electronic and steric properties of the donor and acceptor components are easily varied and the final stereochemistry of the metallocene, i.e. the relative orienation of asymmetrically substituted cyclopentadienyl rings or indenyl rings, is more easily controlled.

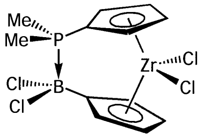


Figure 5. Donor/acceptor *ansa*-zirconocene complex introduced by Starzewski and co-workers

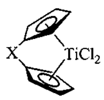
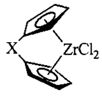
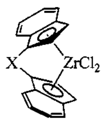
Structural Features of Boron-Bridged *ansa*-Zirconocene and -Titanocene Complexes

Table 1 lists selected geometric features of crystallographically characterized boron-, silicon-, and 1-, 2-, and 3-carbon-bridged metallocenes. The bite angle ε of the bridge, the dihedral angle α between the ring planes, and the angle γ formed by the metal center and the ring centroids are defined in Figure 6.

The narrowing of γ and the widening of α relative to the two-carbon- and three-carbon-bridged complexes reflects the distortion of the *ansa*-metallocenes from a "normal" geometry. The degree of distortion caused by a boron bridge is much larger than that of a silicon bridge but not quite as large as the distortion in a carbon-bridged *ansa*-metallocene.

Large changes in the size of the bridge bite angle ε produce relatively small changes in γ and α. For instance, despite a difference of over 5° in the bridge bite angles for the

Table 1. Selected angles [°] for various C-, Si-, and B-bridged *ansa*-metallocene complexes

Complex	X	Bridge angle ε	Ring-ring dihedral α	Ct–M–Ct γ	Ref.
	–(CH$_2$)$_3$–	—	53.3	130.2	65
	–(CH$_2$)$_2$–	—	53	128	6
	Me$_2$Si<	89.5(1)	51.2	128.7(1)	65
	H$_2$C<	97	63, 68	121, 122	6
	(Me$_3$Si)$_2$NB<	98.3(6)	61.8	124.4	53
	–(CH$_2$)$_3$–	—	50.2	129	65
	Me$_2$Si<	93.2(2)	56.8	125.4(3)	65
	Me$_2$C<	99.8	71.4	116.6	66
	Ph(SMe$_2$)B<	101.1(2)	65.9	121.3(2)	44
	Ph(PMe$_3$)B<	100.1(3)	68.5	121.1(6)	44
	Ph(Me)B$^{\ominus}$<	97.2	65.2	120.5	48
	Ph(Cl)B$^{\ominus}$<	99.4	65.9	120.9	48
	(iPr)$_2$NB<	103.9(3)	65.5	119.6	54
	–(CH$_2$)$_2$–[a]	—	60.4	125.3	67
	Me$_2$C<	100.3(3)	70.8	118.3	68
	Me$_2$Si<	94.57(6)	61.94	119.04	62
	(THF)PhB<	101.5(2)	67.2	122.3(8)	51
	Ph(PMe$_3$)B<	99.4(2)	66.7	121.5(7)	51
	(iPr)$_2$NB<	104.9	66.8	121.6	54

[a] This complex contains tetrahydroindenyl ligands.

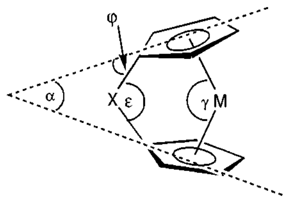


Figure 6. Illustration of *ansa*-metallocene angles listed in Table 1

final two entries of Table 1, the magnitudes of γ and α for the two complexes are nearly identical. This is due to a compensating distortion, represented by angle φ, in which the bridging atom bends away from the plane of the cyclopentadienyl or indenyl rings. The bending distortion of the bridge for the final complex (φ =18° and 20°) is greater than that of the preceding complex (φ =16° and 16.5°).

The bite angles of the base-free amidoborylidene-bridged species, complexes **II**, **XI**, and **XII**, are quite narrow for sp^2-hybridized boron atoms (cf. the 127° bridge angle for the bimetallic titanium complex **II** shown in Scheme 1[39]), illustrating the considerable strain experienced by an sp^2-hybridized boron atom in the *ansa* position.

Increasing the reaction space about the transition metal center by reducing the size of the bridge has been found to improve metallocene catalyst activity in some instances[56–58] and diminish it in others.[59][60] The effect of ring tilt on the olefin polymerization activity of metallocene catalysts is somewhat unpredictable because it depends on the type of rings comprising the ligand framework as well as on their substitution.[61–63] For example, [Me$_2$Si(Ind)$_2$ZrCl$_2$] generates a better catalyst for propene polymerization than [Me$_2$C(Ind)$_2$ZrCl$_2$] upon activation with MAO;[61] however, the reverse is true when the indenyl rings are substituted with *tert*-butyl groups at the 3-position.[63]

We have already noted from the data in Table 1 that the boron-bridged metallocenes are more distorted from a relaxed metallocene geometry than the silicon-bridged complexes but less distorted than the carbon-bridged complexes. Polymerization studies to date have shown that, with suitable protection of the boron, the activity and isospecificity of the boron-bridged complexes can be comparable to that of silicon-bridged analogs.[50,53] Furthermore, the potential to tune the electronic properties of the boron bridge, and consequently the transition metal center,[64] expands the range of ligand modification opportunities available for controlling the activity and selectivity of the metallocene catalyst.

Summary

The viability of boron-bridged goup-4 *ansa*-metallocene complexes as olefin polymerization catalysts that are competitive with the more common carbon- and silicon-bridged systems has been demonstrated. Although the boron bridge tends to be more vulnerable to nucleophilic attack and subsequent cleavage from the metallocene rings, tightly coordinating Lewis bases can protect it from this type of degradation. Furthermore, anionic borate bridges remain intact when accompanied by a suitable countercation.

Base-free, boron-bridged species have been prepared by introducing substituents that can donate additional π-electrons to the empty p orbital on the boron. In the absence of such stabilization, the sp^2-hybridized boron bridge behaves as a strong Lewis acid because of the internal strain it experiences in the *ansa* position, strain which can be somewhat relieved by rehybridization of the boron to sp^3 through the coordination of a Lewis base. This property, together with the ability of the boron to coordinate a wide variety Lewis bases, expands the potential functionality of the *ansa* bridge well beyond the structural role that it normally plays.

Acknowledgments

I thank my talented co-workers listed in the references for their contributions to this chemistry, and I am grateful to the National Science Foundation and the University of Idaho for their support. I am also grateful to Dr. Brendan Twamley (University of Idaho) for calculating many of the angles in Table 1 from the original crystal structure data and for proof-reading this manuscript.

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Received May 3, 2000
[I00177]