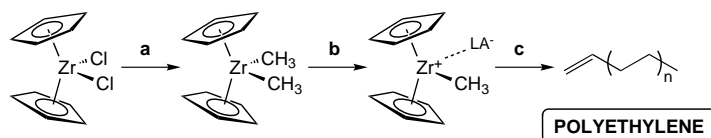# Zwitterionic Metallocenes

Warren E. Piers*

Abstract: Ion pairing in cationic metallocenes capable of the polymerization of olefins affects the activity of these catalysts. One strategy for minimizing ion–ion contacts is the preparation of zwitterionic analogues of the catalysts in which the counterion is affixed covalently to the ancillary or reactive ligand structure of the molecule. The concepts behind the varied synthetic approaches taken to three families of zwitterionic metallocenes, classified by the location of the counterion in the molecular structure, are discussed.

Keywords: homogeneous catalysis · metallocenes · olefins · polymerizations · zwitterionic states

Scheme 1. a) Alkylating agent, e.g. CH_3Li, or $-[(CH_3)Al-O]_x-$, MAO; b) strong Lewis acid, e.g. MAO, $B(C_6F_5)_3$, or $[Ph_3C][B(C_6F_5)_4]$; c) excess C_2H_4.

Introduction

Over the past 20 years, the resources devoted to research into homogeneous olefin polymerization catalysts based on organometallic compounds of the early transition metals have been substantial, and the field remains one of the most active in modern organometallic chemistry. The bulk of the research to date has been carried out using compounds in which the metal is stabilized by two anionic cyclopentadienyl-type donors, the bent metallocene family of catalysts. Although emphasis is now shifting to alternative ligand arrays, catalyst designs based on this stalwart ancillary ligand set are still receiving attention because it is still the best in terms of catalyst performance and furthermore is the most industrially relevant.

The level of knowledge concerning the chemical mode of operation of these catalyst systems is relatively sophisticated.[1] As shown (albeit simplistically) in Scheme 1, it is generally accepted that the catalyst precursors, *neutral* metallocene dichloride or dimethyl derivatives, combine with a strong Lewis acid cocatalyst (usually aluminum- or boron-based) in a chemical process which results in an active, formally 14-electron, *cationic* alkyl species. In the presence of

ethylene, this electrophilic center knits together the olefin monomers into polymer chains through successive insertions of C≡C into the metal–carbon bond.

To attain the high polymerization activity levels ($>10^6 \, g \, PE \, mol^{-1} \, Zr \, atm^{-1} \, h^{-1}$) required for an industrially viable catalyst, this metallocene cation must be as base-free as possible. While donors such as PMe_3 or THF can be excluded, such cations are never totally base-free in condensed media, and the Lewis acidity of the metal cation is quenched through intramolecular agostic interactions or ion–ion contacts with the counteranion. Thus, one of the goals in developing new catalyst systems is to minimize these interactions through the use of weakly coordinating counteranions while maintaining a stable catalyst species.[2]
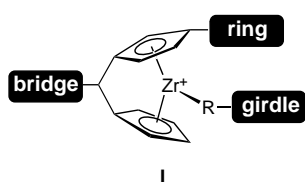
Another strategy for controlling ion pairing is through catalysts which incorporate the counterion chemically into the structure of the ligands of the metallocene, that is, zwitterionic metallocene catalysts. Sequestering the counterion covalently in some region of the molecule away from the metal center should attenuate ion pairing through enforced physical separation. Moreover, zwitterionic catalysts offer at least two other foreseeable advantages. First, such compounds might be expected to exhibit higher solubilities in the hydrocarbon media in which olefin polymerization processes are performed. Second, unlike the traditional two-component systems (Scheme 1), stable zwitterions are preactivated, well-defined single-component catalysts. In other words, an activation step is not required, offering advantages from a process engineering perspective. Although single-component catalysts based on Group 3 and lanthanide metals are available,[3] productivity levels do not approach those found in cationic Group 4 systems. Group 4 metal-based zwitterionic metallocenes offer the prospect of the advantages associated with single-component systems combined with the necessary activity levels. Offsetting these benefits are the

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significant synthetic difficulties which zwitterionic catalysts present. For synthetic chemists who enjoy such challenges this is not necessarily discouraging, but to be industrially practical, zwitterionic catalysts must also be conveniently prepared to be cost-effective in an economic sense.

Discussion

There are in principle three regions of the bent metallocene molecule in which the counterion might be situated (**I**). Several examples exist where the counterion is attached either to the alkyl group in the reactive girdle of the molecule or to one of the cyclopentadienyl rings. These are really two distinct classes of zwitterionic catalysts since, in principle, the girdle-type does not remain zwitterionic for long under typical polymerization conditions, while in the ring-type catalysts, the zwitterionic character should be maintained throughout the enchainment process. A third possibility is related to the ring-type in terms of zwitterion longevity and involves incorporation of the counterion into the backbone linker of an *ansa*-metallocene. There are no examples of this class of zwitterions, at least in the open literature; however, recent progress in synthetic methodology suggests that they should be accessible. Below we consider the diverse synthetic approaches which have been taken to these three types of zwitterionic catalysts.

Girdle zwitterions: The first zwitterionic metallocene catalysts reported were those discovered serendipitously by Hlatky and Turner upon reaction of [Cp*$_2$ZrMe$_2$] with [Bu$_3$NH]$^+$[B(C$_6$H$_4$R)]$^-$ (Scheme 2).[4] The initially formed
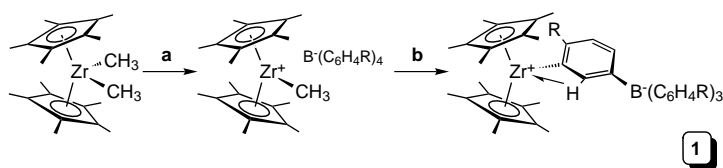
Scheme 2. Hlatky and Turner's zwitterions. a) [Bu$_3$NH]$^+$[B(C$_6$H$_4$R)$_4$]$^-$, R = H, Me, Et; −Bu$_3$N, −CH$_4$; b) −CH$_4$.

nonzwitterionic monomethyl cations are prone to sigma-bond metathesis reactions with a C$_{sp^2}$−H bond of the tetraphenylborate counterions, producing girdle zwitterions **1**. The driving force for this process, in addition to a stronger Zr−C$_{phenyl}$ bond, is the added stabilization provided by an *ortho* C−H agostic interaction. Since compounds **1** proved to be good olefin polymerization catalysts, this report stimulated others to begin thinking about similar zwitterionic catalysts and what advantages such systems could offer.

The high reactivity of aryl C−H bonds towards electrophilic organometallics and the (relatively) electron-rich nature of

aryl groups prompted an evolution away from conventional tetraarylborates towards even more weakly coordinating perfluorinated analogues. For obvious reasons, the sigma bond metathesis chemistry described above cannot be extended to include the more desirable perfluorinated borate counterions and new methodologies were required. In 1991, Marks and co-workers introduced *tris*-pentafluorophenylborane, B(C$_6$F$_5$)$_3$,[5] as a Lewis acid strong enough to abstract methide groups from dimethyl zirconocene derivatives, producing cationic complexes.[6] This prompted other groups to explore reactions of this borane with more exotic hydrocarbyl zirconocenes. For several of these precursors, particularly those which are metallacyclic in character, reaction with B(C$_6$F$_5$)$_3$ results in girdle-type zwitterionic metallocenes.

Scheme 3 illustrates some of the chemistry associated with a zwitterionic catalyst system derived from [Cp$_2$Zr(η^4-buta-
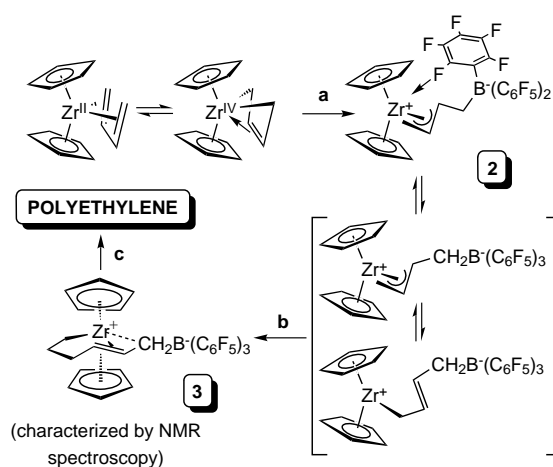
Scheme 3. Erker's [Cp$_2$Zr(butadiene)/B(C$_6$F$_5$)$_3$]-derived girdle zwitterion. a) B(C$_6$F$_5$)$_3$; b) C$_2$H$_4$, 1 equiv; c) C$_2$H$_4$, excess.

diene)] and B(C$_6$F$_5$)$_3$.[7] The butadiene complex reacts with B(C$_6$F$_5$)$_3$ through the metallacyclopentenyl Zr^{IV} σ−π resonance structure, the borane abstracting one of the terminal butadiene methylene groups. The cationic allyl product of this reaction is isolable because of a stabilizing interaction between one of the *ortho* C−F groups and the zirconium center.[7c] This is a common structural motif in metallocene-based zwitterions and is based on a weak donor interaction; such compounds readily dissociate in solution, as evidenced by the dynamic behavior often observed in their ^{19}F NMR spectra. Thus, compound **2** equilibrates in solution with coordinatively unsaturated isomers, enabling **2** to serve as an effective olefin polymerization catalyst.

The Erker group's careful study of this chemistry revealed two important features of the polymerization catalysis initiated by this family of compounds. First, through reaction of **2** with one equivalent of ethylene, an observable monoinsertion product is generated.[7b] This requires that the *next* insertion is much slower and implies, therefore, that at early stages of the polymerization the charges remain in close proximity. The data support a cation−anion contact involving the methylene group attached to the borate ion (Scheme 3). If this is a general phenomenon associated with girdle zwitterions, it

should be reflected in the molecular weight distributions of polymers produced by these catalysts. A second feature was demonstrated conclusively by an elegant laser desorption ionization MS analysis of polymer samples generated at short reaction times:[7a] girdle zwitterions are shortlived under catalytic conditions (Scheme 4). After several insertions,
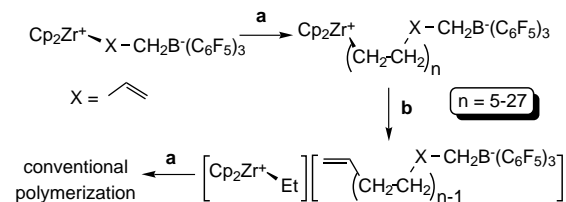
Scheme 4. The fate of girdle zwitterions. a) C_2H_4, excess; b) β-hydrogen transfer.

termination occurs to produce a conventional, nonzwitterionic active site, albeit with unusual counterions. Questions remain concerning the effects that this collection of counterions have on the catalyst system in comparison with conventional borate anions such as $H_3CB^-(C_6F_5)_3$ or $B^-(C_6F_5)_4$.

We have shown that highly electrophilic boranes also attack the coordinated olefins in phosphine-stabilized zirconocenes of general formula $[Cp_2Zr(PPh_2Me)(\eta^2\text{-}RCH=CH_2)]$ (R = H, Et, C_6H_5). For example, bis(pentafluorophenyl)borane, $HB(C_6F_5)_2$,[8] adds across a Zr–C bond of the metallacyclopropane form of the coordinated olefin to give compounds **4** (Scheme 5).[9] Charge separation in the zwitterionic products
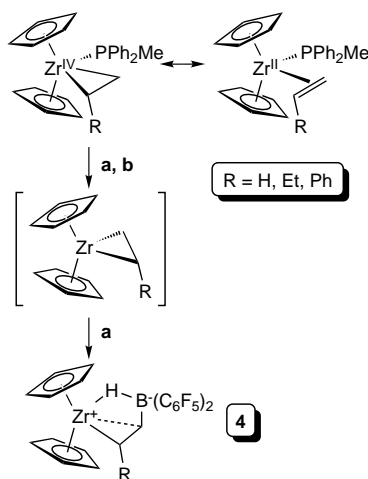
Scheme 5. Reaction of zirconocene olefin complexes with $HB(C_6F_5)_2$. a) $HB(C_6F_5)_2$; b) $Ph_2MeP \cdot BH(C_6F_5)_2$.

of these reactions is sharply attenuated by relatively strong hydrido–alkylborate interactions with the zirconium center. This is borne out in the poor performance of these compounds as olefin polymerization mediators. As might be expected by analogy to the chemistry of Scheme 3, treatment of the olefin complexes with $B(C_6F_5)_3$ results in much more active girdle zwitterions.[10]

Erker's group has also demonstrated that girdle zwitterions can be formed from nonmetallacyclic precursors. When $B(C_6F_5)_3$ abstracts an acetylide group from $[Cp_2Zr(C\equiv CCH_3)_2]$, the borate alkyne of the initial nonzwitterionic product inserts into the remaining zirconium acetylide bond, yielding the girdle zwitterion **5** (Scheme 6).[11] Although the olefin chem-
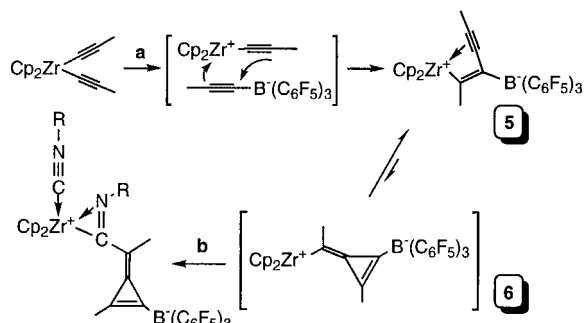
Scheme 6. Erker's $[Cp_2Zr(alkynyl)_2/B(C_6F_5)_3]$-derived girdle zwitterion. a) $B(C_6F_5)_3$; b) $2\,RN\equiv C$.

istry of this zwitterion has not been reported, it does react with nitriles[12] and isonitriles[11] (as illustrated in Scheme 6) through the less thermodynamically stable **6**, which forms by a second intramolecular insertion of the alkyne function into the zirconium–carbon bond.

As these examples have illustrated, electrophilic attack of certain zirconocene hydrocarbyl girdle ligands is a viable general strategy to attain this class of zwitterions. Given that the covalent connection between cation and anion is only a termination step away from severance, this type of zwitterionic catalyst delivers only the advantage of being a single-component olefin polymerization initiator. It would be desirable to achieve more permanent attenuation of tight ion pairing; ring-type zwitterions provide better prospects in this regard, since they should remain zwitterions throughout the polymerization process.

Ring zwitterions: Zwitterionic structures with a borate anion attached covalently to a Cp donor are accessible by a number of synthetic approaches. In fact, different routes were used for each of the handful of ring-type zwitterions that have been reported to date. It is clear from the examples known that the means by which the borate is tethered to the ring has a significant impact on the properties of the zwitterion. In particular, the length of the tether connecting the ring with the borate is crucial in determining both the stability of the compound as a zwitterion and the nature of intramolecular ion–ion contacts.

Illustrative of this notion are the results of our initial approach to ring-type zwitterions, which involved the hydroboration of allyl groups attached to a Cp ring using the reagent $HB(C_6F_5)_2$.[13] Side reactions of the borane with zirconium carbon bonds complicate the chemistry,[14] but in a case where clean hydroboration occurs, the initially formed zwitterion undergoes a rearrangement to a nonzwitterionic product **7**, presumably by the pathway depicted in Scheme 7.

The facility of this entropically driven process illustrates that a three-carbon tether is too long to sustain ring-type zwitterionic structures.
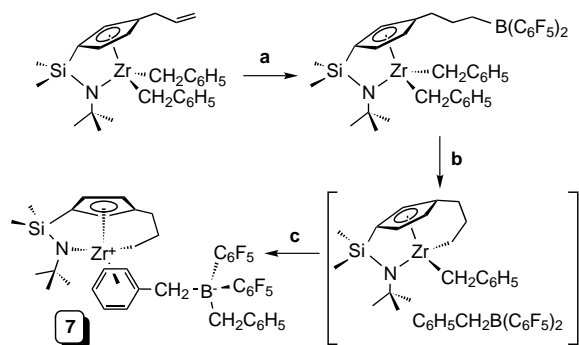
Scheme 7. Hydroboration of a pendant allyl group with $HB(C_6F_5)_2$. a) $HB(C_6F_5)_2$; b) alkyl exchange; c) benzyl abstraction.

In light of these results, we chose to explore the reactions of so-called tuck-in metallocenes with the boranes $HB(C_6F_5)_2$ and $B(C_6F_5)_3$, reactions designed to produce ring zwitterions with a short linker of only one carbon. One family of tuck-in metallocenes contain a metallated pentamethylcyclopentadienyl donor;[15] abstraction of the metallated methylene group by the aforementioned boranes leads directly to zwitterions.

We have characterized a number of these compounds extensively, several crystallographically.[16] In the solid state, two types of intramolecular ion–ion contacts occur in tuck-in/$B(C_6F_5)_3$-generated zwitterions. The factors which differentiate between the preferred mode of stabilization are subtle, as illustrated by the chemistry of the tuck-in phenyl/$B(C_6F_5)_3$ system (Scheme 8). When the two reagents are mixed
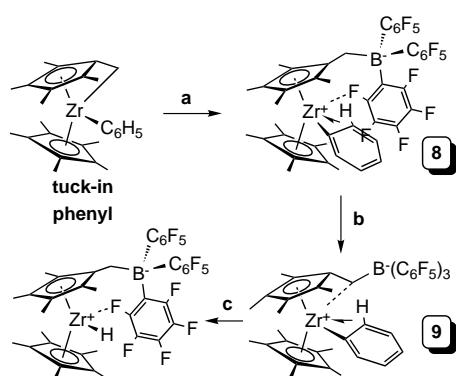
Scheme 8. Tuck-in zirconocene/$B(C_6F_5)_3$-derived zwitterions. a) $B(C_6F_5)_3$, hexanes; b) benzene or 50°C; c) H_2.

together in hexanes, a yellow kinetic product **8** precipitates from solution. In the solid-state structure of this species there is a short contact between an *ortho* fluorine atom and the cationic zirconium center, reminiscent of Erker's observations concerning girdle zwitterion **2**. This weak interaction is the most common ion–ion association in the tuck-in derived ring zwitterions; however, when the other ligand in the wedge is of

moderate steric bulk, the $Zr^+ \cdots F-C$ interaction is disfavored. Consequently, the kinetic product **8** converts under mild conditions to an orange thermodynamic product **9**, in which the zirconium center is satiated by the negative charge built up on the carbon attached to the borate boron atom. Stabilization in this manner allows the bulky trio of C_6F_5 groups to swing away from the metal center and relieve steric interaction with the phenyl ligand. Upon conversion to a zwitterionic hydrido complex, the complex reverts to the $Zr^+ \cdots F-C$ mode of stabilization, suggesting that the nature of ion–ion interactions may be variable during the course of a polymerization reaction.

Both $Zr^+ \cdots F-C$ and $Zr^+ \cdots CH_nB^-(C_6F_5)_3$ motifs have also been observed in nonzwitterionic[17] compounds. Although further quantitative work is required, there is evidence[16] that the interactions in the ring zwitterions are weaker than those measured for conventional metallocenes.[18] Zwitterion **9** is a highly active single-component ethylene polymerization catalyst, comparable to its closest nonzwitterionic analogue.[17] More sophisticated polymerization experiments are required to arrive at an absolute comparison of the two types of catalyst.

Examples of ring-type zwitterions in which the borate is *directly* attached to the ring (i.e., with a zero-carbon linker) have also been reported.[19] Rather than introducing the borane at a late juncture of the zwitterion synthesis, Bochmann and co-workers incorporated the counterion at the beginning of their synthetic scheme, working with anionic compounds throughout (Scheme 9).[20] This tactic cleverly
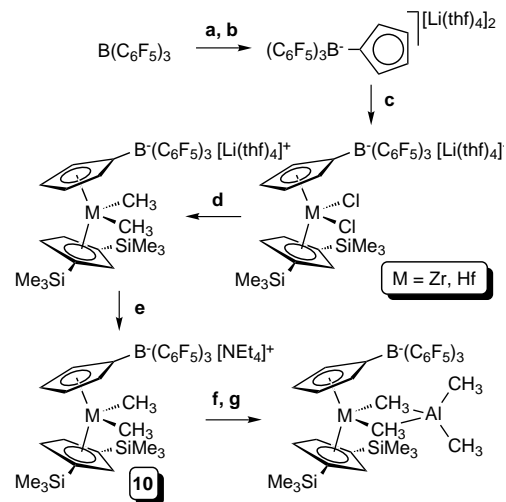

Scheme 9. Bochmann's anionic and zwitterionic metallocenes. a) C_5H_5Li; b) BuLi; c) $[\{C_5H_3(SiMe_3)_2\}MCl_3]$; d) 2MeLi; e) $[NEt_4][BF_4]$; f) M = Hf; $[Ph_3C][B(C_6F_5)_4]$, 0.5 Al_2Me_6; g) $-Ph_3CMe$, $-[NEt_4]^+[B(C_6F_5)_4]^-$.

avoids the synthetic problems associated with the presence of an electrophilic borane center by masking it as a borate. A hafnocene zwitterion is generated from the anionic dimethyl precursor **10** by treatment with the trityl activator $[Ph_3C][B(C_6F_5)_4]$ and trapping with $AlMe_3$.

No solid-state structural data was reported for the above zero-carbon linker ring-type zwitterion, so there is no information concerning the nature of the interaction, if any, between the positive and negative charges in the molecule.

Since the cationic center is complexed by a trimethylaluminum fragment, the charges are likely well separated. Without the alkyl aluminum stabilizer, the metal center is again bolstered by *ortho*-fluorine coordination, as Erker et al. found in a related zirconocene zwitterion.[21] In the reaction of 1,1-bis(cyclopentadienyl)-2,3,4,5-tetramethylzirconacyclopentadiene with $B(C_6F_5)_3$, the borane surprisingly attacks one of the Cp rings rather than a σ bond of the girdle ligand (Scheme 10). *Endo*-proton transfer from the ring to a vinylic carbon σ-bonded to zirconium yields zwitterion **11**.
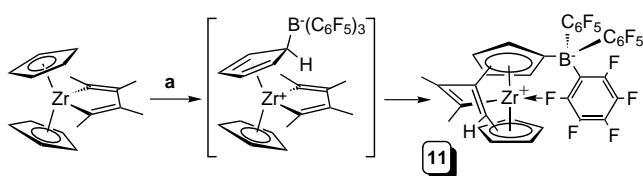
Scheme 10. Ring zwitterions from electrophilic attack on Cp by $B(C_6F_5)_3$. a) $B(C_6F_5)_3$.

Electrophilic attack of Cp may prove a general route to ring zwitterions for zirconocenes in which the Zr–C bonds in the girdle are sterically protected and difficult for the borane to access. We have observed this type of reactivity in, for example, the reaction of the alkyne complex $[Cp_2Zr(\eta^2\text{-}EtC{\equiv}CEt)(PMe_3)]$ and $HB(C_6F_5)_2$.[22] Judged by NMR spectroscopy, the product is the chelating borate zwitterion **12** shown in Scheme 11. This reaction shows promise for producing a range of intriguing zwitterionic compounds; further exploration is required.
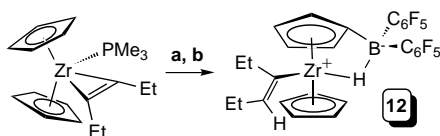
Scheme 11. Ring zwitterions from electrophilic attack on Cp by $HB(C_6F_5)_2$. a) $2\,HB(C_6F_5)_2$; b) $-Me_3P\cdot BH(C_6F_5)_2$.

Bridge zwitterions: Incorporation of the counterion into the linker backbone of an *ansa* metallocene is the most synthetically challenging—but perhaps the most aesthetically pleasing—option of the three classes of zwitterions given in **I**. Bridge-type zwitterions elegantly achieve enforced charge separation while taking advantage of the many attractive features of *ansa*-metallocenes. Though other structural types may be envisioned, published attempts at such compounds have so far focused on metallocenes with one boron atom

bridging the two Cp ligands, generally depicted in **II**, as targets. While the requisite ligands are accessible by a couple of routes, ligand attachment reactions tend to give products in which the ligand bridges two metal centers rather than engaging in the desired chelating bonding mode of structure **II**. Bochmann
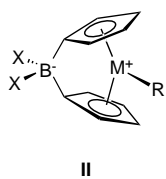
et al. found that when lithium biscyclopentadienylbispentafluorophenyl borate reacts with tetrabenzyl zirconium, toluene elimination leads to the dinuclear anionic complex **13** rather than a borylidene-bridged *ansa*-metallocene (Scheme 12).[20] Similarly, Shapiro and co-workers reported
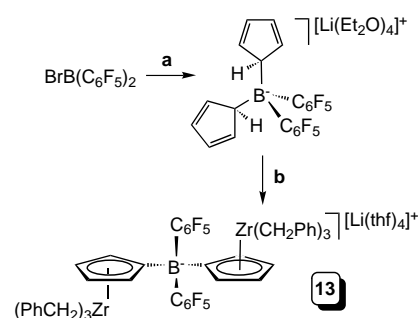

Scheme 12. Bochmann's borate-bridged dinuclear metallocene. a) $2\,C_5H_5Li$; b) $[Zr(CH_2Ph)_4]$.

that the reaction of neutral bis[(trimethylsilyl)cyclopentadienyl]phenyl borane (**14**) with $TiCl_4$ gives a binuclear complex with loss of Me_3SiCl (Scheme 13).[23]
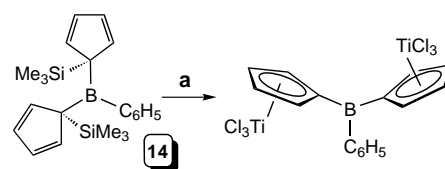
Scheme 13. Shapiro's boryl-bridged dinuclear metallocene. a) $2\,TiCl_4$, $2\,Me_3SiCl$.

This phenomenon is presumably attributable to the small size of the boron atom linker. Recently, however, Rufanov et al. showed that, under the right conditions, boron-bridged *ansa*-metallocenes can be favored. Remarkably, simply substituting the trimethylsilyl groups in Shapiro's compound **14** with trimethylstannyl substituents and using $ZrCl_4$ instead of $TiCl_4$ leads preferentially to the boron-bridged *ansa*-zirconocene **15** (Scheme 14).[24] Clearly, this compound is close to a bridge-type zwitterion, and strongly suggests that structures akin to **II** are viable synthetic targets.[25]
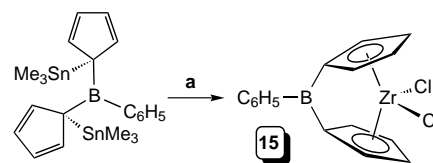
Scheme 14. Rufanov's boryl-bridged *ansa*-metallocene. a) $ZrCl_4$, $-Me_3SnCl$.

Conclusions

Progress on development of zwitterionic metallocenes has been substantial since Hlatky and Turner's seminal report.[4] Much work remains to be done to assess whether or not

zwitterions are better than their nonzwitterionic analogues in terms of the projected advantages outlined in the Introduction. Many are indeed single-component mediators of olefin polymerization, and at least rival conventional catalysts with respect to productivity; more careful studies are required to address this point. Given the broad interest in olefin polymerization catalysts, research in this chemically intriguing sub-genre of metallocene chemistry is sure to continue.

[1] Selected reviews: a) H. H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.* **1995**, *107*, 1255; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143; b) M. Bochmann, *J. Chem. Soc. Dalton Trans.* **1996**, 255; c) T. J. Marks, *Acc. Chem. Res.* **1992**, *25*, 57; d) R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325.

[2] For recent examples, see Y.-X. Chen, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1997**, *119*, 2582, and references therein.

[3] J. P. Mitchell, S. Hajela, S. K. Brookhart, K. I. Hardcastle, L. M. Henling, J. E. Bercaw, *J. Am. Chem. Soc.* **1996**, *118*, 1045, and references therein.

[4] G. G. Hlatky, H. W. Turner, R. R. Eckman, *J. Am. Chem. Soc.* **1989**, *111*, 2728.

[5] A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245.

[6] X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1991**, *113*, 3623.

[7] a) B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich, S. Kotila, *Angew. Chem.* **1995**, *107*, 1867; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1755; b) B. Temme, J. Karl, G. Erker, *Chem. Eur. J.* **1996**, *2*, 919; c) J. Karl, G. Erker. R. Fröhlich, *J. Am. Chem. Soc.* **1997**, *119*, 1116.

[8] D. J. Parks, R. E. von H. Spence, W. E. Piers, *Angew. Chem.* **1995**, *107*, 895; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 809.

[9] Y. Sun, W. E. Piers, S. J. Rettig, *Organometallics* **1996**, *15*, 4110.

[10] Y. Sun, W. E. Piers, S. J. Rettig, *Chem. Commun.* **1997**, in press.

[11] a) B. Temme, G. Erker, R. Fröhlich, M. Grehl, *Angew. Chem.* **1994**, *106*, 1570; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1480; b) W. Ahlers, B. Temme, G. Erker, R. Fröhlich, T. Fox, *J. Organomet. Chem.* **1997**, *527*, 191.

[12] B. Temme, G. Erker, R. Fröhlich, M. Grehl, *J. Chem. Soc. Chem. Commun.* **1994**, 1713.

[13] R. E. von H. Spence, W. E. Piers, *Organometallics* **1995**, *14*, 4617.

[14] R. E. von H. Spence, D. J. Parks, W. E. Piers, M. MacDonald, M. J. Zaworotko, S. J. Rettig, *Angew. Chem.* **1995**, *107*, 1337; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1230.

[15] L. E. Schock, C. P. Brock, T. J. Marks, *Organometallics* **1987**, *6*, 232.

[16] Y. Sun, R. E. von H. Spence, W. E. Piers, M. Parvez, G. P. A. Yap, *J. Am. Chem. Soc.* **1997**, *119*, 5132.

[17] X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10015.

[18] P. A. Deck, T. J. Marks, *J. Am. Chem. Soc.* **1995**, *117*, 6128.

[19] Borylated zirconocenes which perhaps serve as neutral precursors to zero-carbon linker ring-type zwitterions have also been reported: M. T. Reetz, H. Bruemmer, M. Kessler, J. Kuhnigk, *Chimia* **1995**, *49*, 501.

[20] M. Bochmann, S. J. Lancaster, O. B. Robinson, *J. Chem. Soc. Chem. Commun.* **1995**, 2081.

[21] J. Ruwwe, G. Erker, R. Fröhlich, *Angew. Chem.* **1996**, *108*, 108; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 80.

[22] L. Somlai, W. E. Piers, unpublished results.

[23] S. A. Larkin, J. T. Golden, P. J. Shapiro, G. P. A. Yap, D. M. J. Foo, A. L. Rheingold, *Organometallics* **1996**, *15*, 2393.

[24] K. A. Rufanov, V. V. Kotov, N. B. Kazennova, D. A. Lemenovskii, E. V. Avtomonov, J. Lorberth, *J. Organomet. Chem.* **1996**, *525*, 287.

[25] **Note added in proof** (November 25, 1997): Shapiro and co-workers have very recently reported a more detailed account of the syntheses of compounds closely related to **15**. This work represents a significant advance in methodology towards viable bridge-type zwitterions: D. S. Stelck, P. J. Shapiro, N. Basickes, A. L. Rheingold, *Organometallics* **1997**, *16*, 4565.