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Review

The chemistry of [1]borametallocenophanes and related compounds

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Abstract

Metallocenophanes of early and late transition metals with a variety of different main group element bridges between the two cyclopentadienyl moieties have attracted considerable interest for example as catalysts for the stereospecific generation of polyolefins or as versatile precursors for the synthesis of processable organometallic polymers. The introduction of a borylene moiety as a bridge is a very recent achievement in this area, but has already added some interesting aspects to the rich chemistry of metallocenophanes.

Keywords: Boron; Iron; Titanium; Zirconium; Metallocenophanes

1. Introduction

Since the discovery of ferrocene [1a,1b] more than five decades ago metallocenes have developed into one of the most important classes of organometallic compounds, and by now sandwich complexes are known for almost any main group [2a,2b] and transition metal [3]. The huge and ongoing interest this class of compounds has experienced is stimulated by versatile and interesting applications in important areas like catalysis and materials science [3]. As metallocenes in general show a very rich chemistry, there is almost no limit to the synthesis of complexes with special properties for specific applications. In this context, the introduction of a linkage between the two cyclopentadienyl ligands, thus leading to *ansa*-metallocenes or metallocenophanes, has proven to be a particularly successful synthetic methodology and it has long been recognised that the *ansa*-bridge has a considerable effect on both the geometry and the electronics of a given metallocene [4a,4b].

In the case of metallocenophanes of early transition metals it was shown since the 1980s particularly by Ewen and Brintzinger how the controlled stereoselective polymerisation of propene and other α-olefins may be achieved by employing catalysts of suitable symmetry and geometry [5]. Predominantly isotactic polypropylene for example, is obtained in the presence of a chiral C_2-symmetric catalyst, which can be achieved by inserting an ethanediyl bridge between the two η^5-coordinated ligands, thus preventing them from rotation with respect to the Cp_{centre}–M axis [6a,6b,6c,6d]. Subsequently, the use of *ansa*-metallocenes as catalysts for the olefin polymerisation was extended to a variety of possible bridging groups such as CR_2 [5,7,8], SiR_2 [9], and GeR_2 [10,11]. More recently, a new family of active polymerisation catalysts, the so called constrained geometry complexes (CGCs), was developed by exchanging one cyclopentadienyl ring by an amido moiety [12,13]. Dianionic bifunctional chelating ligands of the general formula $[(C_5R_4)SiR'_2(NR'')]^{2-}$ ($R = H$, alkyl; R', $R'' =$ alkyl), first employed by Bercaw for the preparation of Sc complexes [14] and subsequently utilised by Dow [15], Exxon [16], Okuda [17,18] and others [19–21] for the preparation of group IV half-sandwich complexes, yielded highly active catalysts for ethene polymerisation and co-polymerisation of ethene and higher α-olefins.

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In the case of metallocenophanes of late transition metals corresponding iron complexes in particular have attracted considerable interest. Strained ferrocenophanes with a bridging silicon atom were first reported in 1975 [22]. The elegant work of the Manners group drew attention to these compounds more recently, due to their propensity to undergo ring opening polymerisation (ROP) yielding poly(ferrocenes) [3,23a,23b,23c]. Stimulated by the interesting properties of these organometallic polymers, further [1]ferrocenophanes with the bridging main group elements Ge, Sn [24a,24b,24c,24d], P, As [25a,25b,25c,25d], S and Se [26,27] were reported more recently. Besides, a number of [*n*]ferrocenophanes ($n = 2$, 3) and [1]ferrocenophanes with bridging transition metals are also known, which, however, are not discussed in detail here. The intrinsic molecular strain of [1]ferrocenophanes, which is responsible for their successful application as precursors for ROP, is best reflected by the deviation of the two cyclopentadienyl rings from the parallel orientation known for ferrocene. Corresponding tilt angles α being reported so far for structurally characterised [1]ferrocenophanes range from 14.1° for a tin-bridged complex [24b,24c] to 31.05° for a corresponding sulfur derivative [26]. Presently, [1]silaferrocenophanes are the most widely used precursors for ROP in this area. The obtained poly(ferrocenylsilanes) represent high molecular weight organometallic polymers with weight average molecular weights (M_w) and number average molecular weights (M_n) in the order of $M_w = 10^5$–10^6 and $M_n < 10^5$, respectively. These materials can be readily processed e.g. molten into shapes and films or spun into nanoscale fibres and display interesting physical properties which make them potentially useful for various applications e.g. as conducting or semiconducting polymers, chemomechanical sensors, or precursors to magnetic ceramics [3,23c].

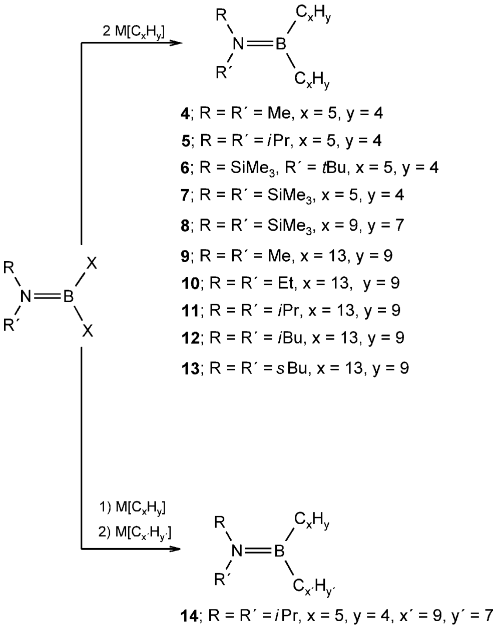
The introduction of boron bridges is among the most recent achievements in the search of metallocenophanes with new and promising properties and some aspects of the chemistry of corresponding Group 4 complexes with three- and four-coordinate boron atoms in the bridge were recently summarised [4b]. The present review will focus on *ansa*-complexes of early and late transition metals with only one three-coordinate boron centre in the bridge.

2. [1]Borametallocenophanes of Ti, Zr, and Hf

The advantages of a bridging boron atom in Group 4 *ansa*-metallocenes are its small size and the consequential high rigidity of the ligand framework, as well as its Lewis acidic character. These properties are supposed to enhance the catalytic activity and stereoselectivity of those complexes with respect to olefin polymerisation, and hence, such [1]borametallocenophanes have recently attracted significant interest. Reetz et al. [28] and Shapiro and co-workers [29] have developed syntheses for complexes like **1** and **2**, in which the boron centre is stabilised by an additional base, thus acquiring a higher coordination number of four. First reports on base-free complexes like **3** date back to 1997 [30], but were put to doubt by other authors since the proposed structure was neither validated by X-ray data nor was the molecular weight of the compound determined and unstabilised three-coordinate boron centres are assumingly rather labile [4b,31]. Until now, the confirmed knowledge of base-free Group 4 [1]borametallocenophanes is restricted to complexes with bridging aminoborylene moieties, the chemistry of which will be discussed subsequently (Fig. 1).

2.1. Synthesis

In contrast to the synthesis of [1]boraferrocenophanes (vide infra) corresponding Group 4 complexes were obtained via ligand precursors of the type $R_2NB(C_xH_y)(C_{x'}H_{y'})$. A wide variety of the latter was reported so far for C_xH_y and $C_{x'}H_{y'}$ being cyclopentadienyl, indenyl, and fluorenyl. Although it is possible to isolate and fully characterise those aminoboranes, we and others developed a very convenient multistep one-pot synthesis for the Group 4 [1]borametallocenophanes, which starts from the aminodihaloboranes and affords the target complexes in high yields of up to 96%.



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Starting material for all ligand precursors are dialkylaminodichloroboranes $RR'N{=}BCl_2$. Solely in the case of dimethylaminoboranes we found that the more

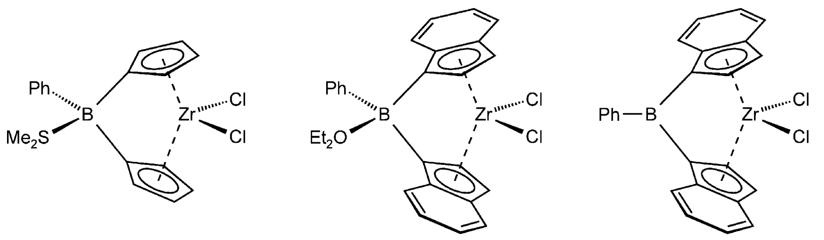

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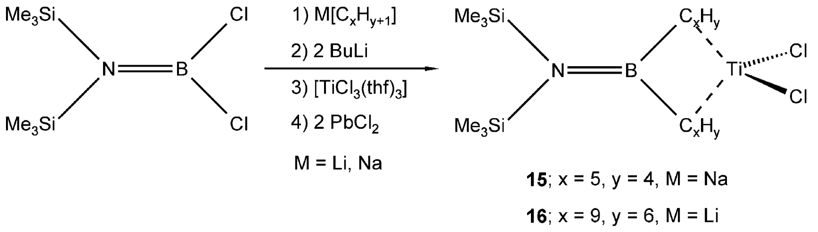
Fig. 1.

reactive dibromoborane $Me_2N{=}BBr_2$ had to be used to allow for the substitution of both halides by cyclopentadienyl [32]. The ligand precursors **4**–**9** and **14** were obtained according to Eq. (1) by salt elimination reactions employing the metallated species $M[C_xH_y]$ [32,33,35]. Already in 1989 Meller reported a series of aminodifluorenyl boranes **10**–**13**, which have been obtained by analogous methods, but have not been used for the synthesis of corresponding [1]borametallocenophanes as yet [41]. Boranes with two different organic groups e.g. cyclopentadienyl and indenyl, were afforded selectively and in high yields by addition of one equivalent of $Na[C_5H_5]$, followed by one equivalent of $Li[C_9H_7]$ [34]. Treatment of the ligand precursors with two equivalents of LiBu yields the corresponding dianions, which are expectedly highly reactive and tend to decompose readily in solution. $Li_2[(Me_3Si)_2NB(C_5H_4)_2]$, the dilithiosalt of **7** was chosen as a representative example for these compounds and fully characterised by NMR spectroscopy [33].



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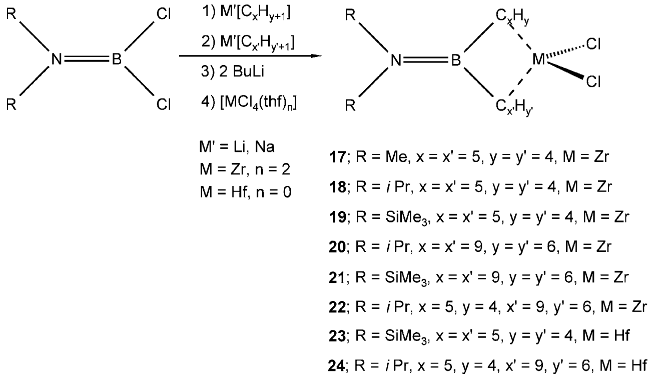
We obtained the first [1]boratitanocenophanes **15** [33] and **16** [34] according to the one-pot synthesis outlined in Eq. (2) by reacting the dilithiated ligand precursors with $[TiCl_3(thf)_3]$ and subsequent oxidation of the intermediate Ti^{III} species with $PbCl_2$.

Exploiting further this convenient route, we [34] and Ashe et al. [31] reported subsequently about the Zr complexes **17**–**22** and corresponding Hf derivatives **23**–**24** which could be obtained directly from the tetrahalides $[ZrCl_4(thf)_2]$ and $HfCl_4$, respectively (Eq. (3)).



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2.2. Structure

2.2.1. Ligand precursors

Biscyclopentadienyl(amino)boranes were synthesised as dimethyl- (**4**), di(*iso*propyl)- (**5**), *tert*-butyl-trimethylsilyl- (**6**) and bis(trimethylsilyl)- (**7**) amino derivatives by salt elimination reaction of NaCp and the respective dihalogenoaminoboranes. All ligand precursors were obtained as crude products in almost quantitative yields in the form of pale yellow oils. Analytically pure compounds were isolated after distillation at 80 °C and 10^{-2} mbar as colourless oils, but only with significantly reduced yield caused by decomposition due to thermal instability [33].

The constitution in solution was derived from multinuclear NMR data, though the proton NMR spectra

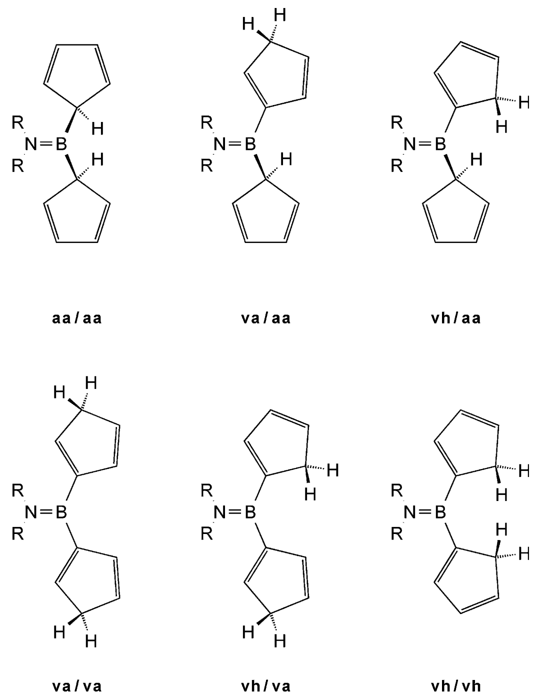


Fig. 2. Constitutional isomers of $R_2NB(\eta^1\text{-}C_5H_5)_2$.

are very complex due to the presence of several isomers. As already discussed by Jutzi and others for corresponding monocyclopentadienyl boranes [35] up to six isomers have to be expected for compounds of the type $R_2NB(\eta^1\text{-}C_5H_5)_2$, namely **aa/aa**, **aa/va**, **aa/vh**, **va/va**, **va/vh** and **vh/vh** (where each two character set represents the position of the attached boron atom with respect to the two double bonds in one of the cyclopentadienyl systems, with **a** for allylic, **v** for vinylic and **h** for homoallylic position; Fig. 2).

The first three isomers have at least one cyclopentadienyl ring bonded to the boron atom via a saturated carbon atom (**aa**). These isomers were not detected, since they rearrange at ambient temperature to the thermodynamic more stable **va** and **vh** isomers where the vinylic position of the boron atom allows π-interaction between the π-system of the ring and the vacant p_z orbital at boron [35,36a36b]. In the case of **5** we fully characterised all present isomers by assignment of all signals in the ^{1}H- and ^{13}C-NMR spectra to the respective isomers (Tables 1 and 2) [32]. The corresponding diindenyl ligand precursor $(Me_3Si)_2NB(\eta^1\text{-}C_9H_7)_2$ (**8**) is likewise obtained in almost quantitative yield as a colourless solid from the reaction of bis(trimethylsilyl)aminoborane with two equivalents of LiInd [33]. Three isomers are possible, that is with boron bonded to both ring systems in allylic position **a/a**, to both in vinylic position **v/v** or mixed **a/v** [37]. Under normal reaction conditions, only the allylic form **8 a/a**—the kinetically favoured isomer—could be detected. Quantitative rearrangement into the thermodynamically more stable isomer **8 v/v** can be achieved either by heating the **a/a** isomer or treatment with catalytic amounts of NEt_3 at ambient temperature. Similar rearrangements had been previously reported for corresponding diindenyl(organyl)boranes [28], diorganyl(indenyl)boranes [38a,38b], and 1,2-diindenyl(organyl)diboranes(4) [39]. Due to its two stereocentres, **8 a/a** is expected to form a mixture of C_2-symmetrical *rac* and C_S-symmetrical meso isomers. Indeed, a double set of signals in the ^{13}C-NMR spectrum proves the presence of both these isomers.

The crystal structure of **8 v/v** [40] reveals an almost C_2-symmetric arrangement of the compound in the solid state (Fig. 3). Both boron and nitrogen are in a trigonal planar environment, and due to the steric demand of the Me_3Si-groups the Si1–N–Si2 plane is twisted with respect to the C11–B–C21 plane by about 51°.

Di(*iso*propyl)amino(η^1-cyclopentadienyl)(η^1-indenyl)borane (**14**) was obtained in good yield in one pot from subsequent treatment of the respective dichloroborane with NaCp and LiInd as a colourless crystalline solid. Characterisation by means of multinuclear NMR spectroscopy revealed the product to be a 1:1 mixture of

Table 1
Selected data for the ligand precursors **4**–**14**

Compound	C_xH_y	$C_{x'}H_{y'}$	R	R′	Isomer(s)	Yield (%)	δ^{11}B	X-ray structure available	Reference
4	C_5H_5	C_5H_5	Me	Me	va/va va/vh vh/vh	96	37.8	No	[32]
5	C_5H_5	C_5H_5	*i*Pr	*i*Pr	va/va va/vh vh/vh	97	40.3	No	[32]
6	C_5H_5	C_5H_5	Me_3Si	Me_3C	va/va va/vh vh/vh	96	46.0	No	[32]
7	C_5H_5	C_5H_5	Me_3Si	Me_3Si	va/va va/vh vh/vh	98	49.0	No	[32]
8 a/a	C_9H_7	C_9H_7	Me_3Si	Me_3Si	a/a	96	57.6	No	[34]
8 v/v	C_9H_7	C_9H_7	Me_3Si	Me_3Si	v/v	100	50.6	Yes	[34,40]
9	$C_{13}H_9$	$C_{13}H_9$	Me	Me	–	50	42.3	Yes	[32]
10	$C_{13}H_9$	$C_{13}H_9$	Et	Et	–	51	41.6	No	[35]
11	$C_{13}H_9$	$C_{13}H_9$	*i*Pr	*i*Pr	–	39	42.1	Yes	[35]
12	$C_{13}H_9$	$C_{13}H_9$	*i*Bu	*i*Bu	–	66	42.1	No	[35]
13	$C_{13}H_9$	$C_{13}H_9$	*s*Bu	*s*Bu	–	68	42.4	Yes	[35]
14 va/a	C_5H_5	C_9H_7	*i*Pr	*i*Pr	va/a vh/a	91	41.9	Yes	[32]
14 va/v	C_5H_5	C_9H_7	*i*Pr	*i*Pr	va/v vh/v	100	40.8	No	[32]

Table 2
[1]Borametallocenophanes of the type $[\{R_2NB[\eta^5\text{-}C_xH_y)(\eta^5\text{-}C_{x'}H_{y'})\}MCl_2]$

Compound	Metal	C_xH_y	$C_{x'}H_{y'}$	R	Yield (%)	$\delta^{11}B$	X-ray structure available	Reference
15	Ti	C_5H_4	C_5H_4	Me_3Si	80	46.6	Yes	[33]
16	Ti	C_9H_6	C_9H_6	Me_3Si	71	48.6	No	[34]
17	Zr	C_5H_4	C_5H_4	Me	91	38.7	Yes	[34]
18	Zr	C_5H_4	C_5H_4	*i*Pr	38	37.6	Yes	[31]
19	Zr	C_5H_4	C_5H_4	Me_3Si	96	47.4	No	[34]
20	Zr	C_9H_6	C_9H_6	*i*Pr	33	40.8	Yes	[31]
21	Zr	C_9H_6	C_9H_6	Me_3Si	82	48.5	No	[34]
22	Zr	C_5H_4	C_9H_6	*i*Pr	82	40.0	No	[34]
23	Hf	C_5H_4	C_5H_4	Me_3Si	85	46.7	No	[34]
24	Hf	C_5H_4	C_9H_6	*i*Pr	74	39.6	No	[34]

two isomers, namely **14 va/a** and **14 vh/a**. The thermodynamic more stable isomers **14 va/v** and **14 vh/v** can be obtained as described for the diindenyl ligands.

A crystal structure was reported for **14 vh/a** (Fig. 3). Both the boron and nitrogen atom are in a trigonal planar environment, with the two planes being almost coplanar. This geometry and the short B–N distance indicate the presence of a boron–nitrogen double bond. The different distances between boron and the *ipso*-carbon atoms of the cyclopentadienyl and indenyl ring (156.6 and 161.1 pm respectively), reflect the π-interaction between the boron's empty p_z orbital and the vinylic π-system.

Apart from the aforementioned compounds the corresponding dialkylaminodi(η^1-fluorenyl)boranes with alkyl = dimethyl (**9**), diethyl (**10**), di*iso*propyl (**11**), di*iso*butyl (**12**), and di*sec*butyl (**13**) have been reported [32,35]. These molecules, however, have not been used as ligands to Group 4 metals as yet. All difluorenylboranes show markedly separated signals in the ^{1}H-NMR spectra for the two nitrogen bound alkyl groups, thus giving evidence for different anisotropic effects of the two fluorenyl substitutents towards these groups. In the case of **9** the results of the crystal structure analysis indicate a similar structure in solution as in the solid state, since one methyl group points towards the centre of one fluorenyl substitutent whereas the other methyl group faces the edge of the second fluorenyl substituent.

2.3. Complexes

A variety of *ansa*-metallocenes incorporating an aminoborylene bridge has been fully characterised so far. Their spectroscopic and structural characteristics are mainly determined by the nature of the η^5-coordinated cyclic ligand and will be discussed accordingly. The common structural feature of all compounds is the presence of a B–N double bond, documented in solution by deshielded ^{11}B-NMR resonances at about 44 ppm and in the case of non-symmetric substitution patterns double sets of signals in ^{1}H- and ^{13}C-NMR spectra due to restricted rotation. In the crystal those complexes exhibit B–N distances at about 138 pm, which is characteristic of a corresponding double bond.

Five complexes with two cyclopentadienyl rings of the type $[\{R_2NB(\eta^5\text{-}C_5H_4)_2\}MCl_2]$ have been reported, namely $[\{(Me_3Si)_2NB(\eta^5\text{-}C_5H_4)_2\}TiCl_2]$ (**15**), $[\{Me_2NB(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]$ (**17**), $[\{i\text{Pr}_2NB(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]$ (**18**), $[\{(Me_3Si)_2NB(\eta^5\text{-}C_5H_4)_2\}ZrCl_2]$ (**19**), and $[\{(Me_3Si)_2NB(\eta^5\text{-}C_5H_4)_2\}HfCl_2]$ (**23**). The structures of **15** (Fig. 4), **17**, and **18** were derived from crystal structure analyses and show the expected similarity and in all cases a slight deviation from C_{2v} symmetry. The comparison between the structures of boron-

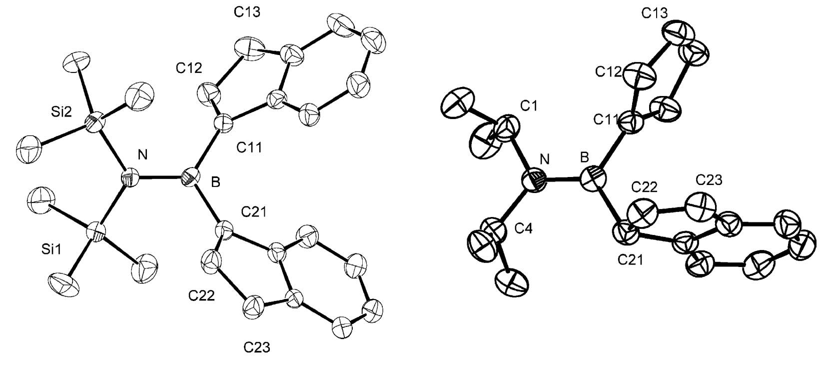


Fig. 3. Molecular structures of **8 v/v** (left) and **14 vh/a** (right).

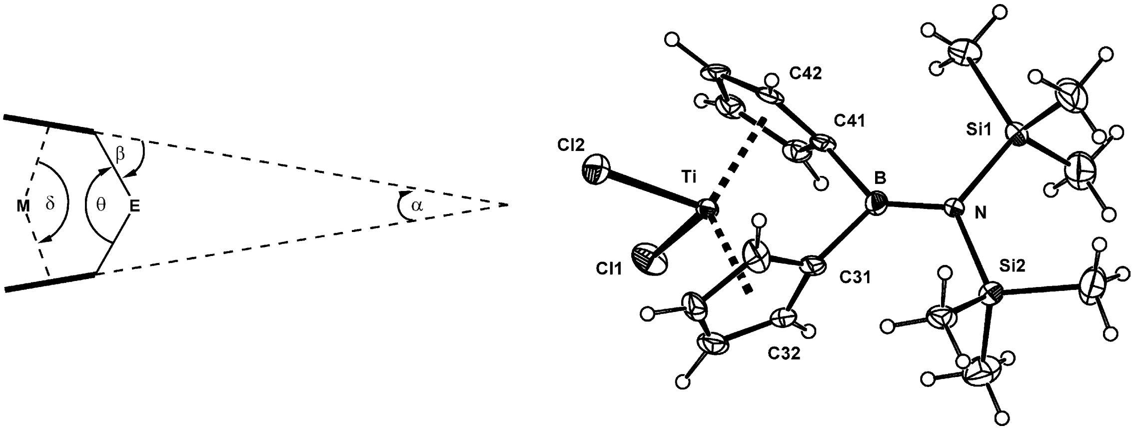


Fig. 4. Structural parameters for bent metallocenes (left) and molecular structure of **15** (right).

bridged metallocenophanes and their corresponding non-bridged metallocenes [(η^5-$C_5H_5)_2MCl_2$] (M = Ti, Zr, Hf) reveals some characteristic differences. The cyclopentadienyl rings in the *ansa*-metallocenes are eclipsed due to rigidity introduced by the bridge, whereas the rings in the parent compounds are arranged in a staggered fashion. For the boron-bridged titanocene **15** the tilt angle α as well as the Cl–Ti–Cl angle are both greater by about 3° than in [Cp_2TiCl_2] [42]. The deformation angle δ—the angle between the centroids of the cyclopentadienyl rings and the metal centre—for **15** is smaller by 13° and gives evidence for an albeit small molecular strain (Fig. 4).

The differences between bridged and non-bridged species become less dominant for the Zr species which becomes clear from the Zr–Cp(centroid) distances of about 220 pm and the value for δ of 120.8° which match the corresponding data of the parent compound [(η^5-$C_5H_5)_2ZrCl_2$] [43].

Complexes with two indenyl ligands are realized in three cases so far, [{$(Me_3Si)_2NB(\eta^5$-$C_9H_6)_2$}$TiCl_2$] (**16**), [{$i Pr_2NB(\eta^5$-$C_9H_6)_2$}$ZrCl_2$] (**20**), and [{$(Me_3Si)_2NB(\eta^5$-$C_9H_6)_2$}$ZrCl_2$] (**21**). The constitutions in solution for **16**, **20**, and **21** were deduced from multinuclear NMR spectra. Interestingly, **20** was obtained as an isomeric mixture of C_2 symmetric *rac* and C_s symmetric *meso* forms, whereas the NMR spectra of **16** and **21** showed single sets of signals indicating the presence of only one of each isomer. The constitution of **21** was verified by methylation of the metal centre with LiMe yielding [{$(Me_3Si)_2NB(\eta^5$-$C_9H_6)$}$_2ZrMe_2$] and subsequent ^1H-NMR spectroscopic characterisation of the product. A single resonance in the region for metal bonded methyl groups reveals that only the *rac* isomer is present [34].

The X-ray structure has been determined for *rac*-**21** and was compared with that of the corresponding silylene-bridged zirconocene [{$Me_3Si(\eta^5$-$C_9H_6)_2$}$ZrCl_2$]. Not surprisingly, both structures have a C_2-symmetrically bridged diindenyl system about the $ZrCl_2$ moiety. Most important is the difference in the angles between the two indenyl rings which is regarded as a measure for the accessibility of the transition metal centre in Ziegler–Natta type polymerisation and, hence, crucial for the catalyst activity. Due to the smaller size of the boron atom, this angle is remarkably greater for **20** with 67° versus 62° for the silylene-bridged zirconocene [44].

The compounds [{$i Pr_2NB(\eta^5$-$C_5H_4)(\eta^5$-$C_9H_6)$}$ZrCl_2$] (**22**) and [{$i Pr_2NB(\eta^5$-$C_5H_4)(\eta^5$-$C_9H_6)_2$}$HfCl_2$] (**24**) exhibit a non-symmetrical set of ligands having both an η^5-coordinated cyclopentadienyl and indenyl moiety. Although structural data of either compound are not available as yet, their constitution in solution was unambiguously proven by multinuclear NMR data.

3. Boron-bridged constrained geometry complexes

Formal exchange of one cyclopentadienyl fragment in metallocenophanes by an amido moiety leads to so called constrained geometry complexes (CGCs). Shortly after the initial reports by Bercaw on the use of ligands of the general formula $[(C_5R_4)SiR'_2(NR'')]^{2-}$ (R = H, alkyl; R′, R″ = alkyl) for the synthesis of Sc complexes [14], corresponding ligands containing SiR_2 [12,17,18]-[12,17,18,45a,45b,45c], C = R [46], and CR_2 [47] bridges were reportedly applied for the formation of complexes of various transition metals. CGCs of Group 4 metals have attracted considerable interest as polymerisation catalyst precursors, since in comparison with metallocenphanes they exhibit a tendency to favour the copolymerisation of higher α-olefins when activated with MAO and are more stable under polymerisation conditions even at elevated temperatures [48].

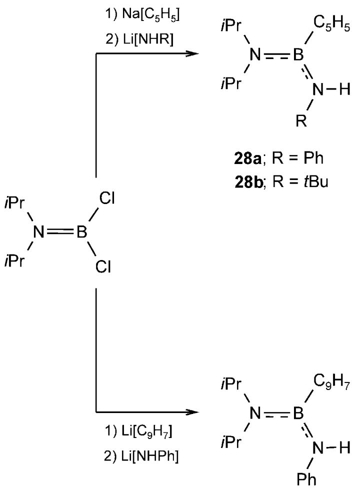
Following the reasoning previously outlined for [1]borametallocenophanes, synthesis of the corresponding boron-bridged CGC type ligands and their Group 4 complexes to combine the advantages of CGCs with the short, Lewis acidic boron bridge is an obvious step. In this context, we reported recently the synthesis and structure of the classical boron-bridged Ti CGCs [Ti(η^5-

C_5H_4-BN*i*Pr_2-NPh-κN)(NMe_2)$_2$] (**25**) and [Ti(η^5-C_5H_4-BN*i*Pr_2-NPh-κN)Cl_2] (**26**) [49] as well as the zirconocene [Zr(η^5-C_9H_6-BN*i*Pr_2-NPh-κN)$_2$] (**27**) [50] incorporating two boron-bridged CGC type ligands.

Compounds utilising boron-bridged cyclopentadienyl carboranyl ligands that can be formally derived from [1]borametallocenophanes by replacing one cyclopentadienyl fragment by a carboranyl moiety [51a,51b], as well as complexes incorporating diamido borane ligands that formally drive the concept of replacing cyclopentadienyl by amido fragments a step further [52a,52b,52c], will not be discussed in detail here.

3.1. Synthesis

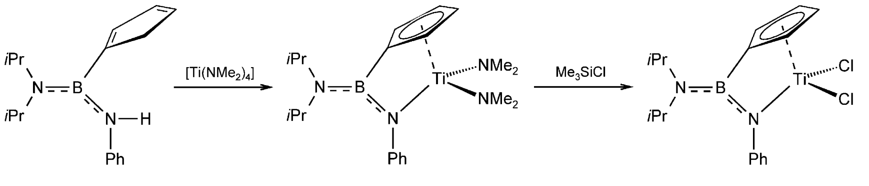
The synthesis of the ligand precursors is straightforward and follows a salt elimination procedure similar to the one described for bis(cyclopentadienyl)amino boranes. Starting from the dialkylaminodihaloborane, both halogen atoms are stepwise replaced firstly by a cyclopentadienyl fragment and secondly by an amido moiety (Eq. (4)). It is essential to follow the sequence in the given order since twofold amination of the borane distinctly lowers the activity towards further substitution on the boron atom.



28c

(4)

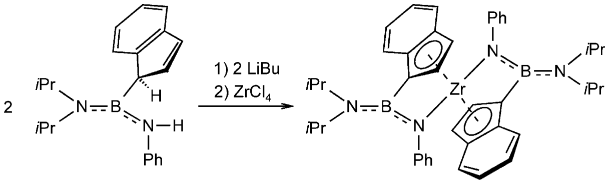
The preparation of complexes applies standard protocols for the synthesis of CGCs and related compounds. Titanium complex **25** could be obtained in high yields by amine elimination reaction using the ligand precursor **28a** and [Ti(NMe_2)$_4$] (Eq. (5)). Treatment of **25** with Me_3SiCl then leads to the corresponding dichloro complex **26** that may be used as a catalyst precursor for the Ziegler–Natta type polymerisation of olefins (Eq. (5)) [49].



28a **25** **26**

(5)

Dilithiation of the ligand precursor **28c** and subsequent reaction with $ZrCl_4$ gave the metallocene complex **27** that incorporates two boron-bridged ligands in a chelating fashion (Eq. (6)) [50]. Formation of such complexes bearing two bridged amino cyclopentadienyl ligands is well-known in CGC chemistry and particularly occurs for the higher Group 4 homologues [46,47,53a,53b,53c,53d]. Successful synthetic routes for typical boron-bridged CGC of zirconium and hafnium remain elusive at this stage.



28c **27**

(6)

3.2. Structure

3.2.1. Ligand precursors

A few boron-bridged amido cyclopentadienyl ligands (**28a**–**c**) have been reported [40,49,50]. They exhibit the expected isomer distributions in close analogy to the aforementioned aminobis(cyclopentadienyl) boranes and aminodiindenyl boranes, respectively. The CGC type ligand precursors **28a** and **28b** bearing a cyclopentadienyl moiety are obtained as 1:1 mixtures of vinyl–allyl and vinyl–homoallyl isomers as was demonstrated by ^{1}H-NMR spectroscopy [40]. The diaminoindenyl borane **28c** can be obtained as the kinetically favoured allylic isomer. Isomerisation of the final product to the thermodynamically more stable vinylic isomer at elevated temperature or in the presence of bases such as NEt_3 does not occur, probably due to a decreased Lewis acidity of the boron centre. However, the vinylic isomer is accessible if the isomerisation is performed before introducing the second amino moiety [50].

The structure of the ligand precursor **28c** in solution as well as in the solid state was thoroughly studied by multinuclear NMR spectroscopy and X-ray diffraction [50]. At ambient temperature, the *iso*propyl groups bonded to nitrogen show coalescence indicating a rapid rotation of the di*iso*propylamino group around the B–N axis on the NMR time scale. This observation is obviously due to the decreased π-character of both B–N bonds in the molecule that becomes equally apparent in the X-ray structure. The B–N distances of 143.0(6) resp. 141.3(6) pm indicate some π-interaction between the two atoms, but are slightly elongated compared to other B–N double bonds on trigonal planar coordinated boron [54].

3.3. Complexes

Boron-bridged titanium CGCs **25** and **26** were both characterised by multinuclear NMR spectroscopy and the former additionally by X-ray diffraction methods [49]. For both complexes double sets of signals for the *iso*propyl groups in the ^{1}H- and ^{13}C-NMR spectra at ambient temperature indicate a hindered rotation with respect to the B–N2 bond due to a comparably strong π-donation from the nitrogen atom. The X-ray structure of **25** (Fig. 5) reveals that both the boron and the nitrogen atom N2 are in a trigonal planar environment and are indeed almost coplanar with respect to each other showing only a slight deviation by 2.2(3)°. The Cp(centroid)–Ti–N1 angle in **25** that can be used to estimate the strain in the complex is with 99.2° significantly smaller than in the corresponding silicon-bridged compound [Ti(η^5-C_5H_4-$SiMe_2$-N*t*Bu-κN)-$(NMe_2)_2$] (105.5°) [55] but less acute than in the sp^3-carbon-bridged complex [Ti(η^5-C_5H_4-CHMe-NPh-κN)$(NMe_2)_2$] (95.6°) [47]. Zirconium compound **27**, which incorporates two boron-bridged CGC type ligands and is formally a 20-electron complex, is best described as a zirconocene with two additional amino donor moieties. Both ^{1}H- and ^{13}C-NMR spectra indicate the presence of four non-equivalent *iso*propyl groups. N–B distances in the solid state are unobtrusive, whereas the Zr–N distances of 215.7(0) pm are remarkably elongated [50] (Fig. 6).

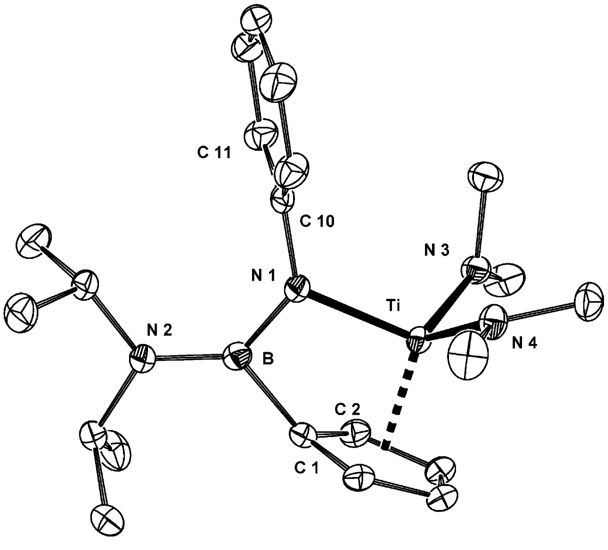


Fig. 5. Molecular structure of **25**.

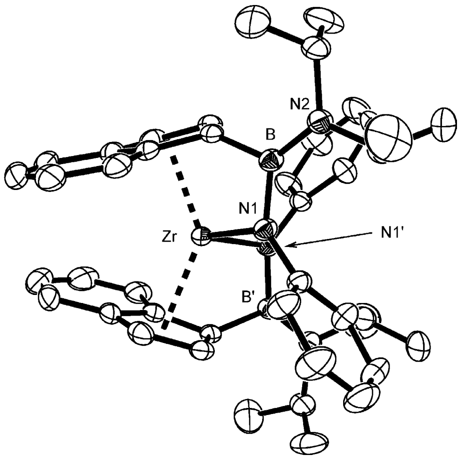


Fig. 6. Molecular structure of **27**.

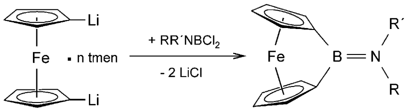
4. [1]Boraferrocenophanes

As introduced in Section 1, strained [1]ferrocenophanes are the most widely studied class of middle and late transition metal-based [1]metallocenophanes, mainly investigated by Manners [3,23a,23b,23c,24a,-24b,24c,24d,25,25b,25c,25d,26,27]. Many of these compounds, especially those with silylene bridges, have been studied in detail, and their reactivity explored, using a wide range of physical techniques. The organometallic polymers obtained by ROP of such complexes possess a very high potential for applicability due to their special mechanical, electronic and magnetic properties. While the silicon-bridged [1]ferrocenophanes are those which provided the highest abundance of results, their borylene-bridged analogues represent the most recent results in this field. The general interest and the applicability of [1]ferrocenophanes arises doubtlessly from their intrinsic molecular strain. In this respect, the change from spacers such as sulfur or silicon to a boron atom represents an important testbed of investigation, not only because of the reduced size and the highly electron-deficient nature of boron, but also because of the change in angular geometry at the bridging element associated with such transition.

The structurally related [*n*]Boraferrocenophanes ($n =$ 2, 3) which, however, are beyond the scope of this article, are an obvious term of comparison for [1]boraferrocenophanes. Amongst them, the first complexes in which the boron atom is directly linked to the Cp moiety were prepared in the late 1990s and belong to two types: 1,3-dibora-2E[3]ferrocenophanes (E = N, O, S, Se, Te) and 1,2-dibora[2]ferrocenophanes, mainly studied by Wagner [56a,56b,56c] and Herberhold [57a,57b].

4.1. Synthesis and structure

We in collaboration with Manners obtained the first [1]boraferrocenophanes by salt elimination reaction between dilithioferrocene n tmen and aminodihalo boranes $RR'NBCl_2$ (R, R′ = alkyl) according to Eq. (7) in yields around 40% [58,59]. The choice of organic groups R and R′ used as N-substituents appears to be of crucial importance, since only boranes with bulky substituents (i.e. R = R′ = $SiMe_3$, R = R′ = *i*Pr, and R = $SiMe_3$, R′ = *t*Bu) led to successful synthesis of [1]boraferrocenophanes, whereas the use, in combination, of smaller groups such as Me, Ph and Bu as N-substituents yielded only products insoluble in common organic solvents.



28; R = R′ = *i*Pr
29; R = R′ = $SiMe_3$
30; R = *t*Bu, R′ = $SiMe_3$

(7)

The constrained ring structure of **28**–**30** is clearly revealed by NMR spectroscopy. For example, the resonances of α and β hydrogens in the C_5H_4 units show a characteristic separation in the ^{1}H-NMR spectra. The X-ray molecular structure of **28** and **29** reveals an unprecedented high strain [58,59]. Fig. 4 shows the main structural parameters used as a measure of ring strain in bent metallocenophanes, namely the tilt angle α between the planes of the Cp rings, the angle β between the Cp ring planes and the E–C axis, the centroid angle δ (equal to 180° in ferrocene molecule), and the C–E–C angle θ.

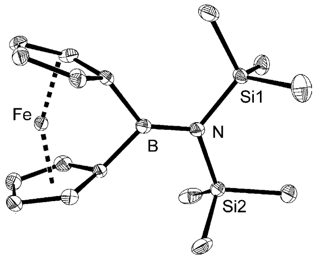


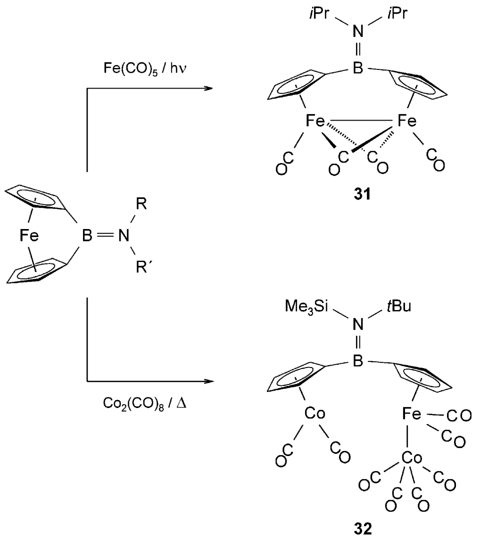
Fig. 7. Molecular structure of **28**.

Compounds **28** and **29** display very large tilt angles compared to related compounds, the one in **28** (32.4°) being the largest ever reported (Fig. 7). Only for one compound, the [1]thiaferrocenophane $[\{S(\eta^5\text{-}C_4H_5)_2\}\text{-}Fe]$, a similar tilt angle (31.05°) was reported [26]; complexes **28** and **29**, however, display two major differences compared to $[S(\eta^5\text{-}C_4H_5)_2Fe]$, namely a larger β angle and a smaller centroid angle δ, on account of a greater strain in the borylene-bridged complexes [59]. Such observations reflect the effect of the main features accompanying the introduction of the boron atom as bridging element, i.e.: (i) the reduced size of boron compared to sulfur; (ii) the shorter B–C bonds (ca. 1.6 Å) compared to S–C bonds (ca. 1.8 Å), causing the Fe···B non-bonded distances (ca. 260 pm) to be shorter than the Fe···S non-bonded distance (ca. 280 pm); and (iii) the change in angular geometry at the bridging unit, resulting in an expected C–B–C angle of ca. 120° versus an expected C–S–C angle of ca. 109°; the molecular strain, however, reduces such angles to ca. 100 and 90°, respectively. Such differences are well reproduced by the DFT geometry optimisations of **28**–**30** and $[\{S(\eta^5\text{-}C_4H_5)_2\}Fe]$ [59]. The analysis of Fe···B distances suggests the absence of significant interactions between the central metal atom and the bridging element, even though Mossbauer data on [1]silaferrocenophanes [23c,27] showed that weak dative interactions from Fe towards the bridging atom, albeit undetectable on the basis of a structural analysis, can be present.

UV–vis spectroscopy is a useful tool for the measuring of the ring constraint in [1]metallocenophanes, since the absorbances recorded are in general sensitive to the decrease in the HOMO–LUMO gap which, due to the loss of molecular symmetry, follows to the formation of the constrained ring structure [60]. The absorbances recorded for **28**–**30** ($\lambda_{max} = 479$, 489 and 498 nm, respectively) are, in fact, significantly lower than the value found for ferrocene ($\lambda_{max} = 440$ nm); however, they are not as low as in $[\{S(\eta^5\text{-}C_4H_5)_2\}Fe]$ ($\lambda_{max} = 504$ nm) [59]. That was, supported by DFT-calculations, attributed to the fact that the HOMO–LUMO energy difference is not only sensitive to the skeletal effects of the constrained geometry, but also to other factors such as changes in the electronic surroundings of the bridging atom [60]. This is also reflected in the different values of λ_{max} for **28**–**30**, indicating the degree of electron density released by the ligands R, R′ onto the N = B bridging moiety, which should be decreasing exactly in the order: **28** > **30** > **29**, revealing, in fact, a very regular trend.

4.2. Reactivity

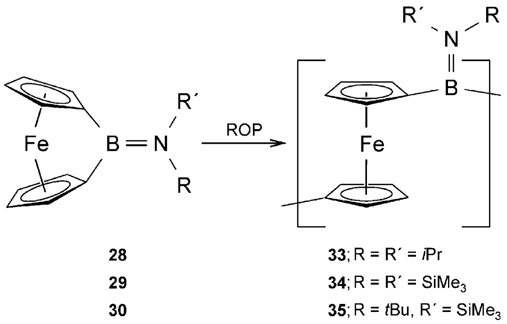
As a consequence of their pronounced intrinsic molecular strain the [1]boraferrocenophanes **28**–**30** proved to to be highly reactive and exhibit an interesting chemistry. Upon reaction with carbonyl complexes, an unprecedented cleavage of the Fe-(η^5-Cp) coordination was observed [59]. Both the photochemical reaction of **28** with [$Fe(CO)_5$] at low temperature and the ordinary thermal reaction with [$Fe_2(CO)_9$] afforded the dinuclear complex [$i Pr_2N{=}B(C_5H_4)_2Fe_2(\mu\text{-}CO)_2(CO)_2$] **31** according to Eq. (8). The thermal reaction is reported to yield **31**, which was fully characterised in solution and in the solid state, in a higher purity and a significantly higher yield.



(8)

0 An analogous reaction of **30** with [$Co_2(CO)_8$] at ambient temperature (Eq. (8)) yielded a compound with a different structure compared to **31**, although resulting again from the rupture of the Fe-(η^5-Cp) coordination and the retention of the B–C_{ipso} bonds: the product [$i Pr_2N{=}B(C_5H_4)_2FeCo_2(CO)_8$] (**32**), fully characterised by NMR and X-ray data, shows a peculiar structure seeing the *ansa* $i Pr_2N{=}B$ fragment linking a (η^5-C_5H_4)$Co(CO)_2$ and a (η^5-C_5H_4)$Fe(CO)_2$–$Co(CO)_4$ unit.

Like their silicon-bridged analogues, [1]boraferrocenophanes **28**–**30** are reported to undergo thermally induced ROP according to Eq. (9), yielding the first poly(ferrocenylboranes) [$RR'NB(\eta^5\text{-}C_5H_4)_2Fe]_n$ **33**–**35** (**33**: $R = R' = i Pr$, **34**: $R = R' = SiMe_3$, **35**: $R = SiMe_3$, $R' = t Bu$) [58,59].



(9)

ROP experiments are typically carried by heating the sample in high vacuum at the temperatures previously determined by Differential Scanning Calorimetry (DSC), in which the absorption or emission of heat by the sample is recorded as the temperature is increased slowly; typical thermograms show an early endotherm in correspondence of the melting temperature, followed by a broad exotherm at higher temperatures indicating the occurring of the polymerisation; the absence of transitions on cooling indicates the polymerisation completeness under those experimental conditions [61].

The melting temperatures of [1]boraferrocenophanes show to be strongly influenced by the substitution at the bridging unit (**28**: 185 °C, **29**: 115 °C, **30**: 150 °C), whereas the ROP occurs at similar temperatures for the three compounds (around 180–200 °C); the value of ΔH_{ROP} for **29** is equal to 95 kJ mol^{-1}. The value of ROP enthalpy can be taken as a measure of ring strain. In fact, the value found for **29** is much higher compared to the less strained [1]silaferrocenophanes (on average: $\alpha = 16–21°$, $\Delta H_{ROP} = 70–80$ kJ mol^{-1}) [62]. However, the much higher value found for the equally strained [1]thiaferrocenophane [{$S(\eta^5\text{-}C_5H_4)_2$}Fe] ($\alpha = 31.05°$, $\Delta H_{ROP} = 130$ kJ mol^{-1}) [27] indicates that the differences in ROP enthalpy can be explained not only on the basis of the tilt angle, but also, presumably, in terms of steric bulk of the bridging moieties. In this respect, the preparation of sterically unencumbered [1]boraferrocenophanes could provide quite revealing results on the basis of DSC experiments.

The ROP products **33**–**35** were characterised by NMR spectroscopy and mass spectrometry; the significantly reduced separation of the Cp hydrogen resonances with respect to the strained precursor molecule, is a typical signal of the formation of polymeric material.

Acknowledgements

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