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Review

# Developing some functional group chemistry at the Group 4 bent metallocene frameworks

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## Abstract

Four series of reactions were explored that are aimed at the development of a functional group chemistry at the sensitive bent metallocenes of the Group 4 metals. First, we have tested and employed the olefin metathesis reaction. Two $[C_5H_4–(CH_2)_n–CH{=}CH_2]_2ZrCl_2$ complexes (with $n = 4$ and $n = 1$) were treated with the $Cl_2(PCy_3)_2Ru{=}CHPh$ catalyst in dilute solution. Intramolecular metathesis took place readily with liberation of ethene to yield the corresponding *ansa*-metallocene complexes $[C_5H_4–(CH_2)_n–CH{=}CH–(CH_2)_n–C_5H_4]ZrCl_2$ that were isolated in ca. 28% ($n = 4$, *trans*-CH=CH–) or ca. 50% ($n = 1$, *cis*-CH=CH–) yield. Intermolecular olefin metathesis could also be effected using either a first or a second generation *Grubbs* catalyst to metathetically couple a variety of $(L)Cl_2M(C_5H_4–CH_2CH{=}CH_2)$-type titanium or zirconium complexes to yield the respective dimetallic products. Alkenyl substituents were attached at the ligand stage at the indenyl 2-positions by means of a nickel-catalyzed cross-coupling reaction. Transmetallation eventually gave the bis(2-alkenylindenyl)$ZrCl_2$ complexes. Photolysis of three examples of this type of complexes (with 1-alkenyl substituents being methyl, cyclohexyl, or phenyl) resulted in a very efficient intramolecular [2 + 2] cycloaddition to yield the respective substituted cyclobutylene-bridged *ansa*-metallocenes. These complexes were MAO activated to give very active homogeneous metallocene catalysts for, e.g., ethene/1-octene copolymerization. The corresponding (s-*trans*-butadiene)-*ansa*-zirconocene complexes feature a pronounced C–H/phenylene π-interaction that probably helps to stabilize the s-*trans*-diene complex relative to its s-*cis*-isomer. Deprotonation of 7-dialkylaminofulvenes provides an easy access to enamino-cyclopentadienides. Transmetallation under carefully controlled conditions gave the respective bis(enamino-$C_5H_4$)$ZrCl_2$ complexes. Their treatment with a catalytic amount of a *Lewis* acid ($TiCl_4$) or a *Brønsted*-acid ($[HNMe_2Ph^+][BPh_4^-]$) led to a rapid intramolecular *Mannich*-type carbon–carbon coupling reaction that gave novel, very rigid $C_3$-bridged, $–NR_2$ functionalized *ansa*-metallocene systems. The analogous, readily performed *Mannich*-coupling reaction starting from 1,1′-diacetylferrocene and a variety of secondary amines provided an interesting and useful novel entry to [3]ferrocenophane systems. Catalytic hydrogenation of the unsaturated bridge followed by additional functionalization opened a novel pathway to ferrocenophane-based chelate ligands (some optically active) for stereoselective catalytic transformations. Eventually, examples of direct attack of the electrophilic boranes $B(C_6F_5)_3$ or $HB(C_6F_5)_2$, respectively, to the Cp rings of bis(cyclopentadienyl)zirconacyclopentadienes are described, leading to novel types of Cp-borylated Group 4 metallocene complexes.

*Keywords:* Metallocenes; Zirconium; Photocyclization; *Mannich*-reaction; Olefin metathesis; Borylation

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## 1. Introduction

The Group 4 bent metallocenes have found widespread use as reagents in organic synthesis and especially as components for the generation of very active and often very selective homogeneous *Ziegler-Natta* catalysts. A great variety of substitution patterns at the metallocene backbone has been used to very effectively control the catalytic features of such catalyst systems [1]. In the majority of cases the substituents were introduced at the preceding ligand stage. In contrast to the metallocenes of the late metals a functional group chemistry at the metallocene frameworks especially of the Group 4 metals is not much developed. Although the presence of some reactive functional groups is clearly compatible with the general chemical features of the Group 4

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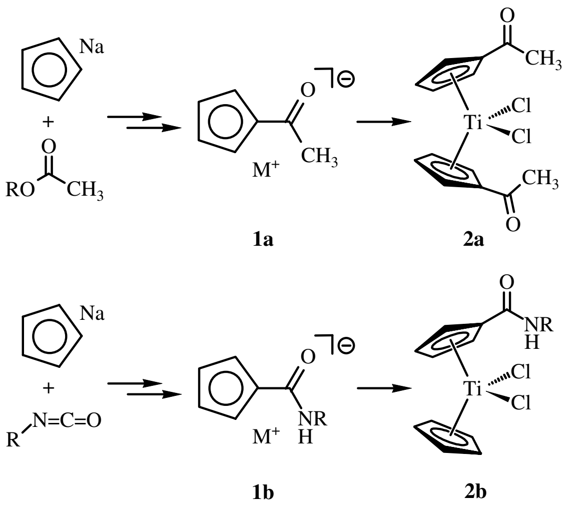


Scheme 1.

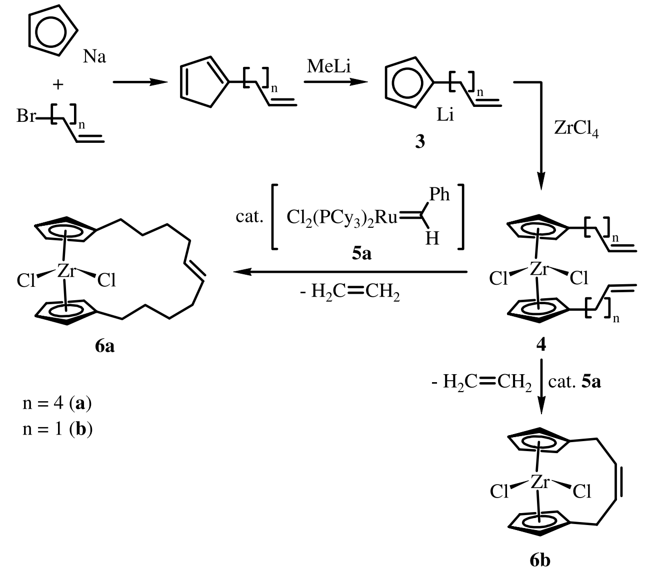
metallocenes, their introduction (or conversion) is difficult to achieve at the actual bent metallocene framework. Therefore, such reactive substituents are usually introduced at a very early stage in the Group 4 metallocene synthesis, e.g., via fulvene routes. Two typical examples are depicted in Scheme 1 [2,3].

We have searched for ways to carry out conversions of functional groups attached at the bent metallocene backbone that were compatible with the typical chemical features of the sensitive Group 4 metallocenes and would leave these organometallic systems otherwise intact. In this account, we will present and discuss typical examples from four different types of approaches to achieve this goal.

## 2. Olefin metathesis

The catalytic olefin metathesis reaction has become of increasing value in organic synthesis [4]. Because of the tolerance especially of the newly developed Ru–carbene catalysts for functional groups this reaction of the C=C double bond can be broadly applied – so why not use it for functional group interconversions at the frameworks of the sensitive Group 4 metallocenes. First examples dealt with the synthesis of *ansa*-metallocenes by metathetical ring closure of pairs of pendant alkenyl groups at non-bridged zirconocenes complexes.

The doubly alkenyl-substituted zirconocene dichloride complexes (**4a**,**b**) were synthesized as depicted in Scheme 2. Treatment of CpNa with hexenylbromide followed by deprotonation gave the [hexenyl-Cp]Li reagent **3a** that was transmetallated to zirconium to yield the metallocene **4a**. Its treatment with the first generation Ru-metathesis catalyst (**5a**) under high dilution conditions then led to the formation of the “large *ansa*-metallocene complex” **6a** with liberation of ethylene.



Scheme 2.

Complex **6a** was isolated in a moderate yield of 25%. It features a *trans*-C=C double bond inside the $C_{10}$-*ansa*-bridge, as was shown by X-ray diffraction (see Fig. 1) [5].

A similar synthesis starting from CpNa and allyl bromide eventually gave bis(ally-Cp)$ZrCl_2$ (**4b**) that underwent ring-closing metathesis when treated with a catalytic quantity of the Ru–carbene catalyst (**5a**). Here, the *ansa*-zirconocene product ((**6b**), isolated in ca. 50% yield) contains a *cis*-C=C double bond inside the ring. Complex **6b** was also characterized by an X-ray crystal structure analysis (see Fig. 1) [5,6].

We assume that the metathesis reactions of organometallic substrates [7] proceed in the usual fashion through reactive intermediates that contain ruthenacyclobutane moieties, which in these cases are part of heterodimetallic frameworks.

Intermolecular coupling of Group 4 metal complexes can also be achieved by means of the olefin metathesis reaction. We have treated the (Cp-allyl)$TiCl_3$ complex **7** with $Cl_2(PCy_3)_2Ru=CHPh$ (**5a**) to yield a ca. 1:3 mixture of the dimetallic Z- and E-configurated coupling products (**8a**,**b**). Treatment of **7** with a more reactive second generation *Grubbs* catalyst (**5b**), that contains an dihydroimidazol-2-ylidene ligand, selectively gave the thermodynamically favoured *trans*-product **8b** in good yield (see Scheme 3 and Fig. 2) [8]. Complex **8b** was characterized by X-ray diffraction. Related Group 4 bent metallocene complexes that contained a pendant allyl group at a Cp-ring also gave the respective dimetallic butendiyl-linked olefin metathesis coupling products when treated with the **5a** or **5b** catalysts. Some of these products gave rather active homogeneous *Ziegler-Natta* catalysts upon activation with a large excess of methylalumoxane [1,8] (see Scheme 3).

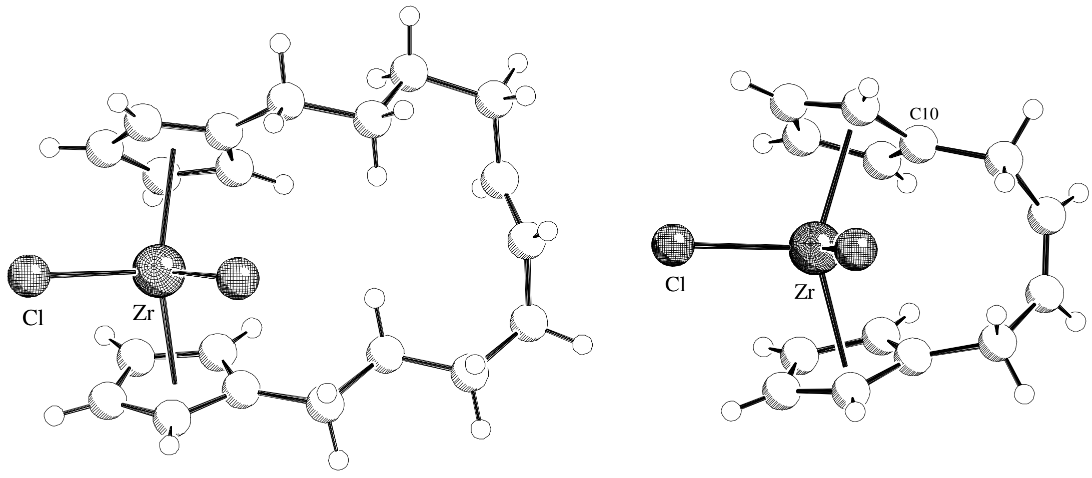
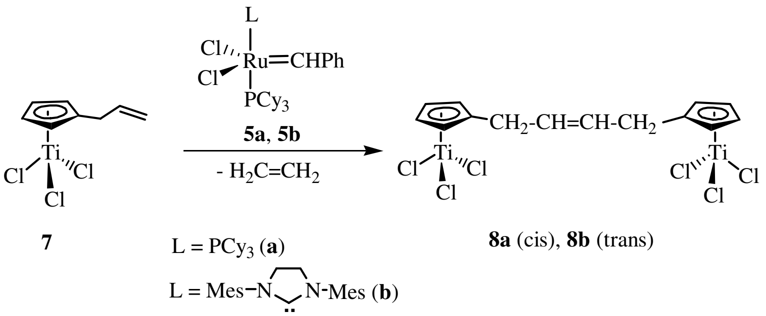


Fig. 1. Views of the molecular structures of the unsaturated *ansa*-metallocenes **6a** (left) and **6b** (right) obtained by catalytic ring-closing metathesis reactions.



Scheme 3.

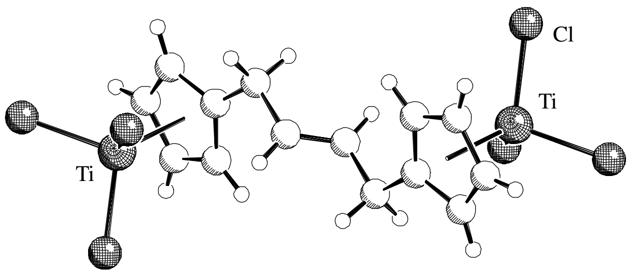


Fig. 2. A view of the molecular structure of the dimetallic olefin metathesis product **8b**.

## 3. Photochemical [2 + 2] cycloaddition reactions

We next placed the olefinic functional group into conjugation of indenyl ligands. The syntheses of the 2-alkenylindenyl ligand systems were carried out by means of a nickel-catalyzed cross-coupling reaction of 2-bromoindene with the respective alkenyl *Grignard* reagent ($R = CH_3$, Ph). In one case (R = cyclohexyl) we had to make use of the synthetic alternative, starting with 2-lithioindene addition to cyclohexylmethylketone, followed by acid-catalyzed dehydration. Deprotonation of the 2-alkenylindenes (**9**) followed by transmetallation gave the bis(2-alkenylindenyl)$ZrCl_2$ complexes (**10**). The complexes **10** undergo a very efficient photochemical [2 + 2] cycloaddition [9]. Irradiation with a high pressure mercury lamp (Pyrex filter) rapidly converted the bis(2-alkenylindenyl)zirconium complexes to the cyclobutylene-bridged *ansa*-metallocenes (**11**). Fig. 3 illustrates the efficiency of the photochemical cycloaddition. Irradiation of a sample of **10c** (R = cyclohexyl) in $d_8$-toluene solution in a NMR tube for ca. 30 min led to an almost quantitative conversion to its *ansa*-zirconocene isomer (**11c**) (see Scheme 4).

The *ansa*-metallocene complexes (**11**) give very active homogeneous *Ziegler-Natta* catalysts at elevated temperatures after treatment with methylalumoxane. A 5:1 ethene/1-octene copolymer was formed at the **11a**/MAO catalyst system at 60 °C with a high catalyst activity (ca. 2300 g copolymer/mmol[Zr] bar h), although the product had a rather low molecular weight ($M_w \approx 4300$) [9a].

The rigid *ansa*-metallocene framework of **11** places the annelated phenylene moieties of the pair of indenyl subunits directly above and below the bent metallocene σ-ligand plane, as is illustrated by the top and front views of complex **11a** ($R = CH_3$) that are depicted in

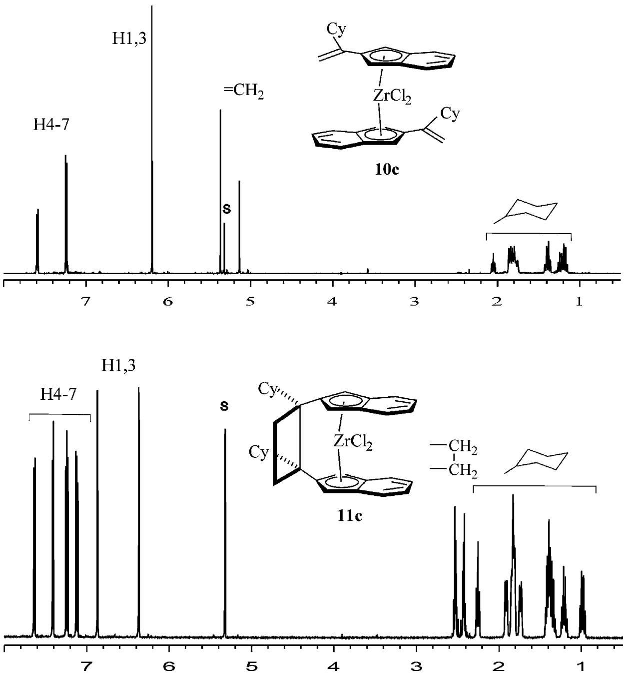


Fig. 3. $^1$H NMR spectra of a d$_8$-toluene solution of **10c** (R = cyclohexyl) (top) and its *ansa*-metallocene isomer **11c** (bottom), that was obtained by photolysis of this sample in the NMR tube (external Philips HPK 125, Pyrex filter).

Fig. 4. This special arrangement is suited to bring parts of some specific ligands into a direct influence of the phenylene π-electron systems.

Thus, treatment of the *ansa*-zirconocene dichloride (**11a**) with butadiene–magnesium results in displacement of the two chloride ligands with formation of a butadiene complex. Of the two possible isomers [10], the (s-*cis*-η$^4$-butadiene)complex is usually preferred (or exclusively formed) at many *ansa*-metallocene frameworks [11]. The reaction of **11a** with $C_4H_6Mg \cdot 2THF$ in contrast gave exclusively the corresponding (s-*trans*-η$^4$-butadiene) *ansa*-zirconocene system (**12a**) (see Scheme 5 and Fig. 5). The $^1$H NMR spectrum of complex **12a** shows the signals of six different butadiene protons. While the four 1-/4-H(*syn*/*anti*)butadiene $^1$H NMR resonances were found in the usual range, the 2-H(meso) signals were found to be upfield shifted to ca. $\delta$ −1.5 (see Fig. 5). This indicates that these butadiene meso-hydrogens are oriented towards the deshielding anisotropy area above the phenylene π-systems. It is likely that the ensuing C–H/π-in-

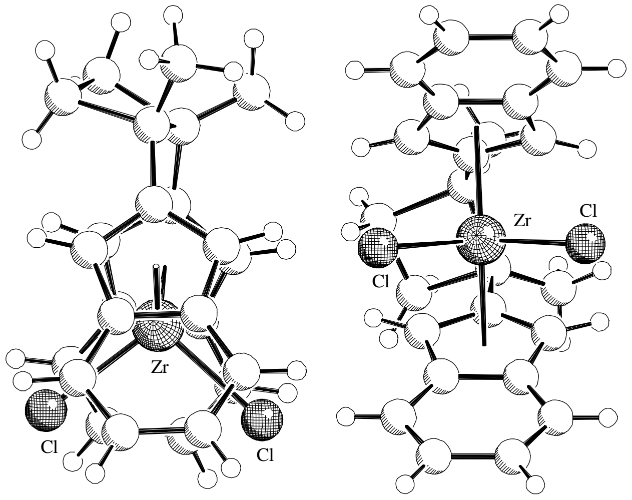
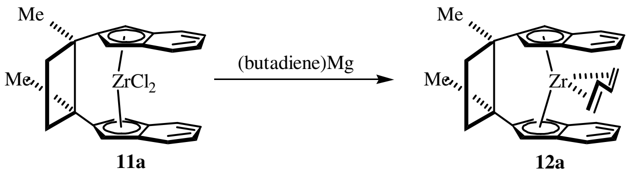


Fig. 4. Top and front side views of the *ansa*-metallocene complex **11a**.



Scheme 5.

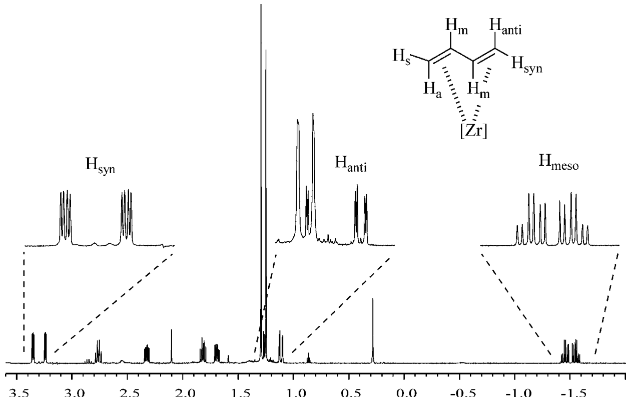
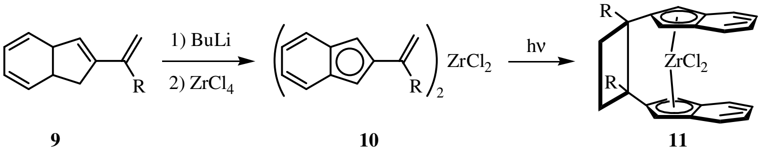


Fig. 5. $^1$H NMR spectrum of the (s-*trans*-η$^4$-butadiene)ansa-zirconocene complex **12a**, featuring the considerably high-field shifted 2-H(meso) butadiene proton resonances.



R = $CH_3$ (**a**), Ph (**b**), cyclohexyl (**c**)

Scheme 4.

teraction [12] leads to a sufficient stabilization that in this case makes the (s-*trans*-$\eta^4$-butadiene)Zr complex (**12a**) the only observed (conjugated diene) *ansa*-zirconocene isomer [9a].

## 4. Mannich-type carbon–carbon coupling reactions at metallocene frameworks

We wanted to search for realizations of reactions out of the general aldol condensation type family of functional group conversions that would be feasible to be carried out at the framework of the sensitive Group 4 bent metallocenes. That would require to maintain very specific reaction conditions in order to preserve the integrity the Group 4 bent metallocenes. It would also require the presence of functional groups to be present at the Cp-rings of the metallocenes that exhibited a “higher degree of functionality” than a simple α-olefin.

We chose enamino substituents for the purpose of our study. Enamino functionalities can very easily be introduced at a very early stage of the bent metallocene synthesis via a fulvene pathway [13]. We used a synthetic entry based on fulvene chemistry developed by Hafner et al. [2a,2b,14]. For this purpose, dimethylacetamide was activated by O-alkylation. Subsequent treatment with CpNa gave the aminofulvene (**13a**). It was deprotonated by treatment with a suitable base (e.g., methyl lithium in THF or LDA) to yield the enamino-functionalized cyclopentadienide system **14a**. Transmetallation was easily achieved by treatment of the reagent **14a** with, e.g., $CpZrCl_3$ to yield the enamino-substituted metallocene **15a** (see Scheme 6 and Fig. 6) [15].

Under carefully controlled reaction conditions the transmetallation of the (analogously prepared) reagent **14b** ($R = C_2H_5$) with $ZrCl_4$ gave the doubly enamino-functionalized Group 4 metallocene complex **15b**, that was also characterized by X-ray diffraction (see Fig. 7) [15].

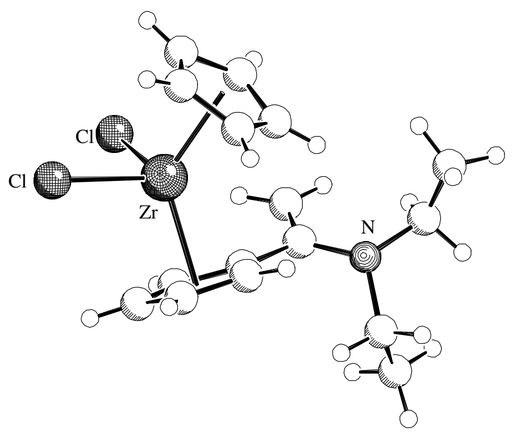


Fig. 6. A view of the enamino-substituted zirconocene complex **15a**.

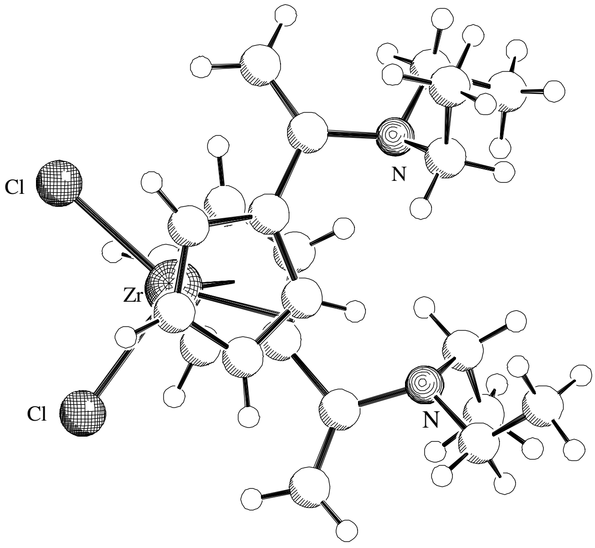
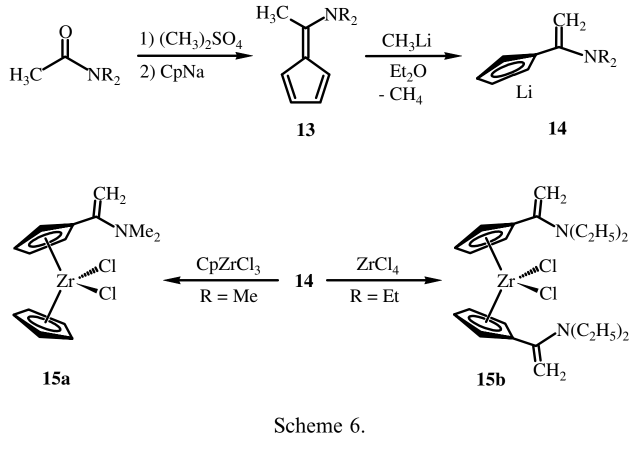


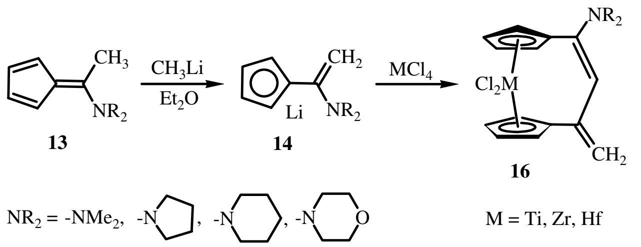
Fig. 7. Top view of complex **15b**, featuring the pair of enamino substituents in a conformational arrangement oriented toward the narrow back side of the bent metallocene wedge.



Scheme 6.

The reaction took a different course when the enamino-cyclopentadienide reagent (**14a**) was reacted with $ZrCl_4$ or $HfCl_4$ under conditions that allowed for the presence of some concentration of the *Lewis* acidic metal salt in the reaction mixture. After workup a different product (**16a**, $R = CH_3$) was isolated in good yield that obviously resulted from a condensation reaction [16,17]. The product contains a completely unsaturated three carbon *ansa*-bridge that fits between the pair of Cp-rings at, e.g., zirconium without causing a considerable strain (see Scheme 7 and Fig. 8).

The same reaction type was observed starting from a variety of amino-fulvene-derived enamino-cyclopentadienides. In each case, apparently a condensation reaction had taken place in the course of which two enamino units were CC-coupled with loss of one equivalent of the corresponding secondary amine. The observed reaction is a variant of the *Mannich* reaction [18] that takes place at the framework of the Group 4 bent metallocene



Scheme 7.

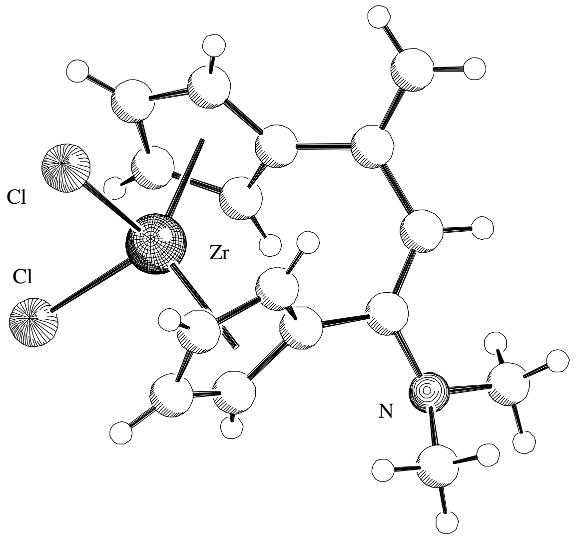


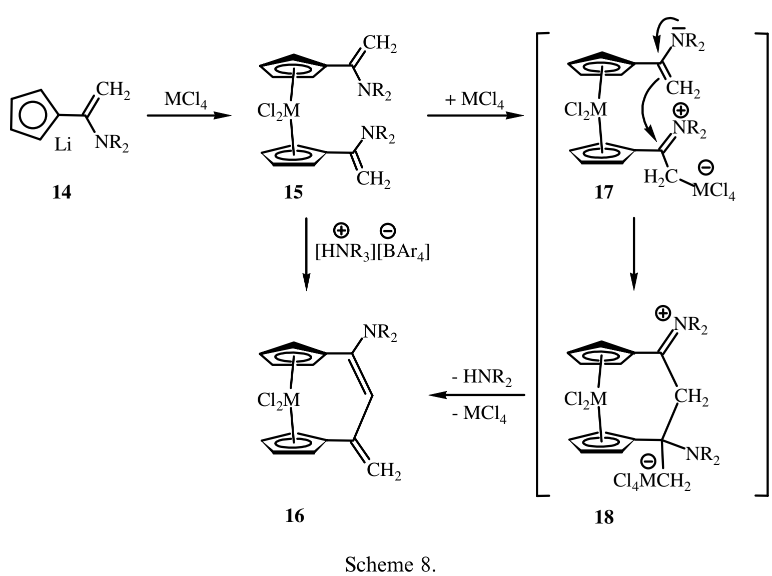
Fig. 8. A view of the molecular structure of the unsaturated *ansa*-metallocene complex **16a**.

framework. This interpretation was supported by the observation that a separately generated open bis(enamino-Cp)$ZrCl_2$ complex (**15a**) reacted rapidly when exposed to a catalytic quantity of, e.g., $ZrCl_4$ (or $TiCl_4$) to yield the condensation product **16a**. The intramolecular *Mannich* reaction of the complexes **15** can alternatively be catalyzed by a suitable *Brønsted* acid. Thus treatment of the enamino-functionalized zirconocene complex **15a** with a catalytic quantity of $[HNMe_2Ph^+]$ $[BPh_4^-]$ also resulted in the formation of the *Mannich*-coupling product **16a** (see Scheme 8).

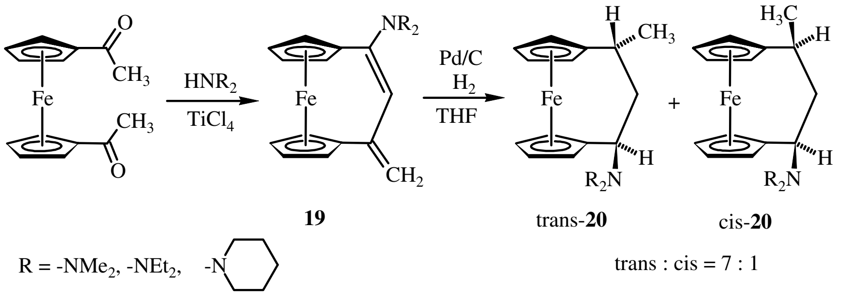
Thus it appears that the respective acid catalyst adds to the negatively polarized enamino-carbon atom of an enamino-Cp moiety of the starting material **15** to yield the activated complex **17**. Intramolecular attack of the remaining enamino-nucleophile to the in situ generated iminium salt then leads to carbon–carbon coupling with the formation of an intermediate such as **18**. Its subsequent typical stabilization pathway via cleavage of the acid catalyst and by amine elimination can then lead directly to the formation of the observed coupling product, the *ansa*-metallocene complexes **16**, with liberation of the active catalysts [16] (see Scheme 8).

In contrast to the Group 4 metallocenes, ferrocene functional group chemistry is rather well developed (see Scheme 10). Nevertheless, our new intramolecular *Mannich*-type coupling is so easily carried out that it has been found useful in the synthesis of the respective [3]ferrocenophanes as well. Thus, treatment of 1,1′-diacetylferrocene with an excess of dimethylamine in the presence of a catalytic quantity of, e.g., $TiCl_4$ rapidly resulted in the formation of the [3]ferrocenophane **19a** that exhibits an unsaturated three-carbon-containing bridge between the Cp ligands (see Scheme 9 and Fig. 9) [19].

The X-ray crystal structure analysis of the [3]ferrocenophane system **19** shows that the unsaturated three-carbon bridge fits almost perfectly into the ferrocene system. Its attachment and connection of the two Cp rings has not disturbed the central ferrocene system to any considerable extent.



Scheme 8.



Scheme 9.

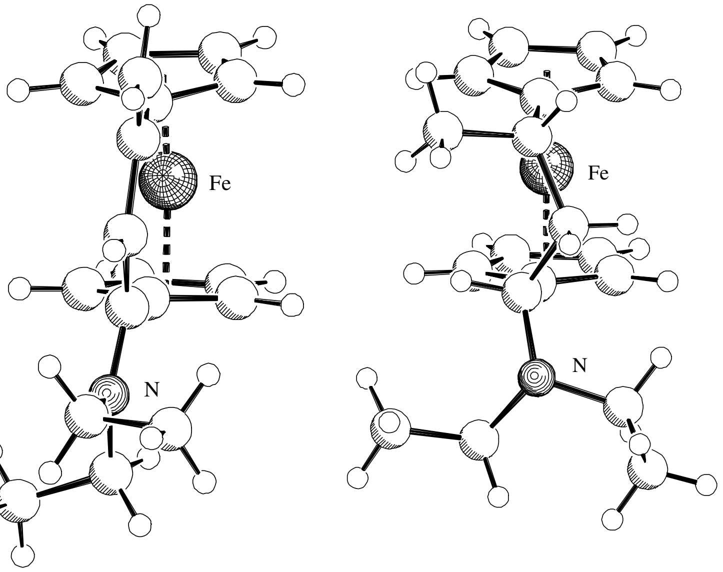
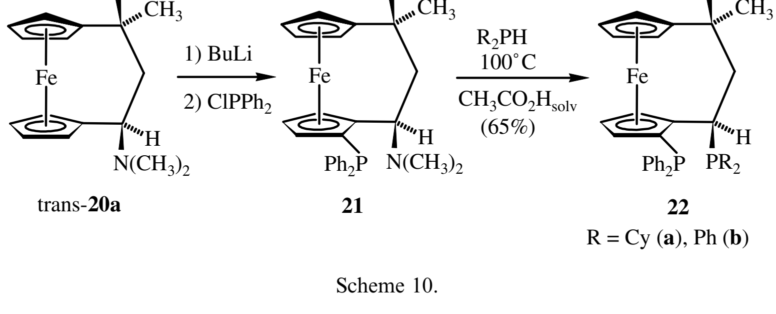


Fig. 9. A comparison of the molecular structures of the [3]ferrocenophane system **16b** (left) and its major hydrogenation product *trans*-**20b** (right).

We have employed this very convenient entry to the [3]ferrocenophane system for constructing a variety of ferrocene-based chelate ligands to be used in enantioselective catalysis. For that reason we first needed to completely hydrogenate the butadien-diyl amine bridge of the complexes **19**. The [3]ferrocenophanes **19** are readily heterogeneously hydrogenated at palladium on carbon at room temperature and ambient pressure. Both carbon–carbon double bonds of the bridging moiety are hydrogenated. This process results in the formation of two new carbon chirality centers. Therefore, in principle two diastereomeric products *cis*-**20** and *trans*-**20** could be formed. Remarkably, the catalytic hydrogenation of the systems **19** (with a variety of –$NR_2$ substituents used) seems always to proceed *trans*-selectively [20]. In all cases that we have investigated so far, *trans*-**20**/*cis*-**20** product ratios around ca. 7:1 were found. This actually means that two hydrogen atoms must be delivered from the catalyst surface to one face of the molecule while the next pair of hydrogen atoms has then been delivered to the opposite face of the formerly planar prochiral bridging unit. This is an unexpected result. Further



Scheme 10.

experimental evidence lacking at this time we must assume a two step hydrogenation pathway where the internal enamino unit is reduced first. The resulting amine intermediate may then turn around to bind itself to the catalyst surface using the $-NR_2$ functionality to account for the preferred formation of the *trans*-**20** product in the final hydrogen transfer from the catalyst surface.

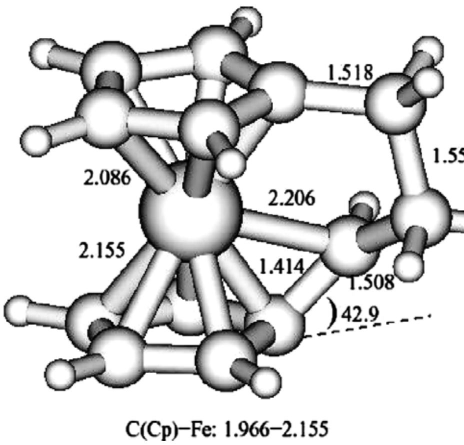
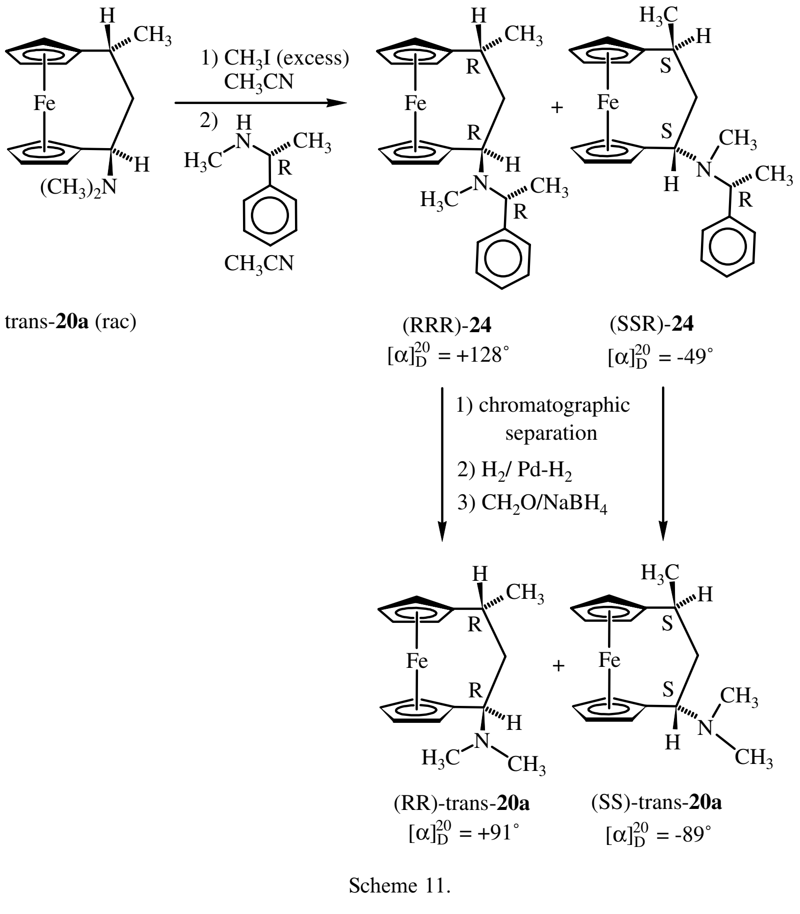


Fig. 10. A view of the DFT-calculated reactive intermediate **23** of the Fe-assisted stereochemical double inversion process that converts **21** to **22**.

Several examples of the complexes *trans*-**20** were analyzed by X-ray diffraction. In each case, the methyl substituent at the carbon atom C3 of the bridge was found to attain a pseudo-axial orientation at the chair shaped saturated [3]ferrocenophane framework, whereas the more bulky $-NR_2$ groups always were found to be placed pseudo-equatorially. Fig. 9 shows a comparison of the molecular geometries of the pair of [3]ferrocenophane complexes **16b** and *trans*-**20b** (both containing a $-NEt_2$ substituent) [20].

Complex *trans*-**20a** ($-NMe_2$) was selected as the starting material for the synthesis of bis(phosphine) chelate ligands [21]. For that purpose, the complex was treated with *n*-butyl lithium to effect a directed "ortho-lithiation" at the adjacent Cp ring. Quenching with $ClPPh_2$ then gave **21**. The amino group was then exchanged for, e.g., $-PCy_2$ with overall retention of configuration [22,23] by treatment with HOAc followed by the reaction with $HPCy_2$ to give **22** (see Scheme 10). The substitution process utilizes the strong neighboring group participation of the Fe atom [21,22] to effect overall stereochemical retention by means of a double inversion process. The reactive intermediate **23** was identified by a DFT-calculation (see Fig. 10) [23b].

Complex **22** reacts readily with a variety of palladium(II) systems to yield the corresponding chelate



Scheme 11.

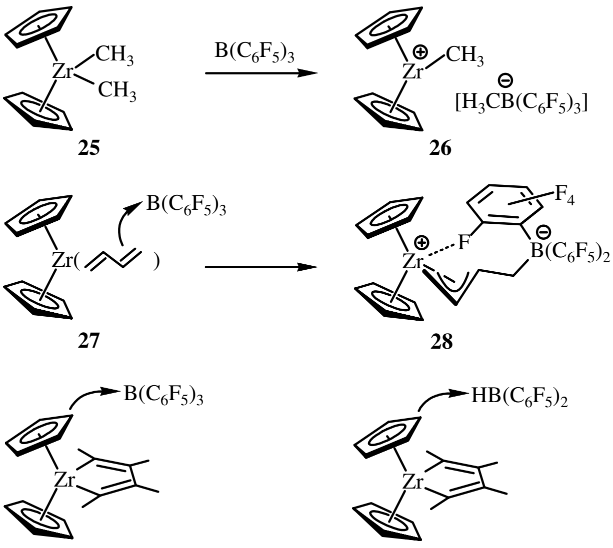
compounds. In situ generated, some such systems turned out to be very efficient homogeneous catalysts for the alternating carbon monoxide/1-alkene copolymerization [21,24].

We have separated the enantiomers of *trans*-**20a** by the route outlined in Scheme 11 [25]. The pure R,R-*trans*-**20a** enantiomer was then converted to the corresponding chelate ligand **22a** in optically active form. Its in situ generated Pd(II) complex turned out to be a very active catalyst for the alternating CO/propene copolymerization. The obtained polyketone exhibits main chain chirality and was obtained optically active [26] $\{[\alpha]_D^{20} = -30°\}$ [27].

## 5. Electrophilic borylation at the Group 4 metallocene Cp-ligands

The reaction of the strong *Lewis* acid $B(C_6F_5)_3$ is very often used for abstracting a σ-ligand from, e.g., dimethylzirconocene complexes to generate active $[^{R}Cp_2Zr{-}CH_3^+]$ $[CH_3B(C_6F_5)_3^-]$ homogeneous *Ziegler-Natta* catalyst systems [28]. The $B(C_6F_5)_3$ reagent can also add to π-ligands that are attached at Group 4 metal centers. A typical example is the reaction of (butadiene)zirconocene that adds this boron *Lewis* acid at the even-numbered π-ligand to form a zwitterionic complex (**28**) that is also an active metallocene polymerization catalyst [29] (see Scheme 12). In addition we have found first examples where the $B(C_6F_5)_3$ electrophile attacks the cyclopentadienyl π-ligand, even in the presence of σ-ligands, to eventually yield Cp-borylated complexes. Two typical examples will briefly be discussed in this concluding section of our account.

In the first example we reacted $B(C_6F_5)_3$ with the zirconacycle **29a** [30]. The boron *Lewis* acid did not react with the σ-ligand system. Instead, the product **31** was formed (as a mixture of two equilibrating stereoisomers) which contains the $-B(C_6F_5)_3$ borate group attached at a cyclopentadienide ligand (see Scheme 13 and Fig. 11) [31]. We must assume that the bulky borane electrophile would not reach at the hindered Zr-σ-alkenyl system and, therefore, the alternative reaction pathway was followed that involved electrophilic attack at the Cp-π-ligand. We assume that $B(C_6F_5)_3$ addition from the outside has led to the reactive intermediate **30**



Scheme 12.

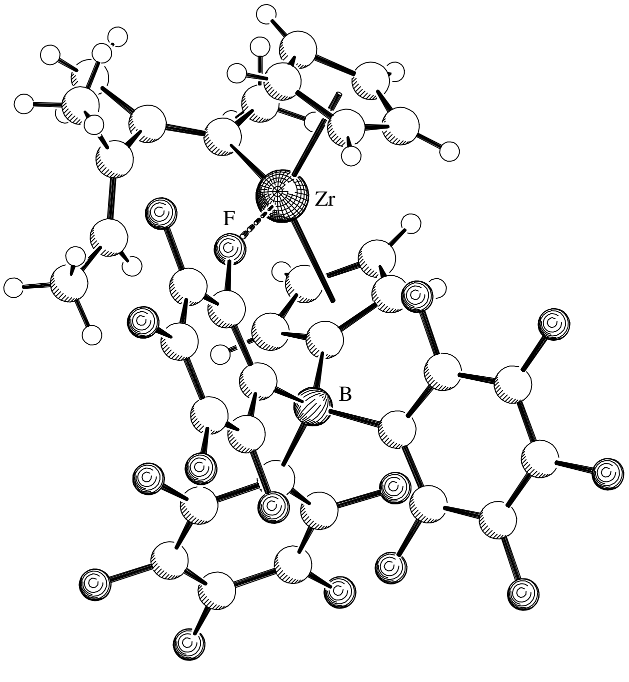
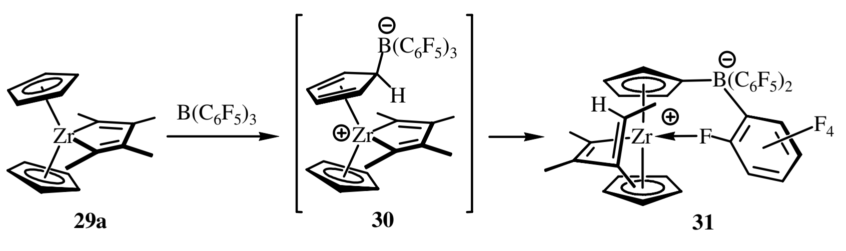
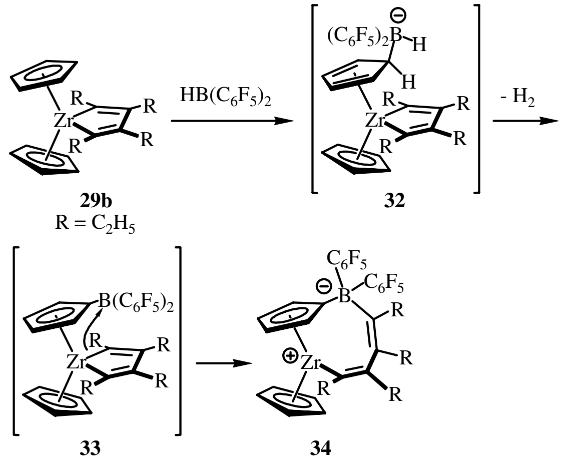


Fig. 11. A view of the molecular structure of complex **31**.



Scheme 13.



Scheme 14.

which was subsequently stabilized by internal proton transfer to the basic σ-ligand system to yield **31** [31].

The reaction of the metallacycle **29b** (R = Et) with the much smaller $HB(C_6F_5)_2$ reagent [32] actually takes a similar course. Again, a Cp-borylated product (**34**) is formed. We assume that the borane $HB(C_6F_5)_2$ also preferentially attacks a Cp-ligand at zirconium. The resulting reactive intermediate (**32**) may in this case eliminate $H_2$ to form **33**. In complex **33** the very electrophilic $–B(C_6F_5)_2$ residue at the Cp-ligand is probably not compatible with an adjacent Zr–C σ-ligand. Thus, intramolecular σ-ligand abstraction may now be favourable to eventually yield the observed product **34** [33] (see Scheme 14).

It thus appears that suitable electrophiles can well attach and bind to the Cp-rings of the sensitive Group 4 bent metallocenes, even in cases where σ-ligands are present. It may actually turn out that such electrophilic attack may be governed by specific selectivity rules, similar as they where found and described some time ago for nucleophilic attack at various π-ligands of positively charged electrophilic metal complexes (the "*Davies–Green–Mingos* rules") [34]. The presented manifold of examples of selective functional group interconversions (see above) together with the emerging examples of selective direct substitution reactions at the Cp-rings of the bent metallocenes lets us hope for a rapid further development of a rich functional group chemistry at the Group 4 bent metallocenes to take place and become a valuable tool in this area of Organometallic Chemistry.

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## References

[1] H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. 107 (1995) 1255;
Angew. Chem. Int., Ed. Engl. 34 (1995) 1143.

[2] (a) K. Hafner, G. Schulz, A. Wagner, Lieb. Ann. Chem. 678 (1964) 39;
(b) K. Hafner, K.H. Völpel, G. Ploss, C. König, Org. Synth. 47 (1967) 52;
(c) W.P. Hart, D.W. Macomber, M.D. Rausch, J. Am. Chem. Soc. 102 (1980) 1196;
(d) W.P. Hart, D. Shihua, M.D. Rausch, J. Organomet. Chem. 282 (1985) 111;
(e) M.D. Rausch, J.F. Lewison, W.P. Hart, J. Organomet. Chem. 358 (1988) 161;
(f) S.S. Jones, M.D. Rausch, T.E. Bitterwolf, J. Organomet. Chem. 396 (1990) 279;
(g) M. Ogasa, D.T. Mallin, D.W. Macomber, M.D. Rausch, R.D. Rogers, A.N. Rollins, J. Organomet. Chem. 405 (1991) 41;
(h) S.S. Jones, M.D. Rausch, T.E. Bitterwolf, J. Organomet. Chem. 450 (1993) 27;
Reviews: (a) D.W. Macomber, W.P. Hart, M.D. Rausch, Adv. Organomet. Chem. 21 (1982) 1;
(b) N.J. Coville, W. Pickl, Coord. Chem. Rev. 116 (1992) 1.

[3] M. Oberhoff, L. Duda, J. Karl, R. Mohr, G. Erker, R. Fröhlich, M. Grehl, Organometallics 15 (1996) 4005;
See also: D. Hüerländer, R. Fröhlich, G. Erker, J. Chem. Soc., Dalton Trans. (2002) 1513.

[4] (a) M. Schuster, S. Blechert, Angew. Chem. 109 (1997) 2124;
Angew. Chem. Int., Ed. Engl. 109 (1997) 2036;
(b) R.H. Grubbs, S. Chang, Tetrahedron 54 (1998) 4413;
(c) A. Fürstner, Angew. Chem. 112 (2000) 3140;
Angew. Chem., Int. Ed. Engl. 39 (2000) 3013;
(d) T. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18.

[5] D. Hüerländer, N. Kleigrewe, G. Kehr, G. Erker, R. Fröhlich, Eur. J. Inorg. Chem. (2002) 2633.

[6] M. Ogasawara, T. Nagano, T. Hayashi, J. Am. Chem. Soc. 124 (2002) 9068.

[7] (a) A.J. Locke, C. Jones, C.J. Richards, J. Organomet. Chem. 637–639 (2001) 669;
(b) J. Ruwwe, J.M. Martín-Alvarez, C.R. Horn, E.B. Bauer, S. Szafert, T. Lis, F. Hampel, P.C. Cagle, J.A. Gladysz, Chem. Eur. J. 7 (2001) 3931;
(c) C.R. Horn, J.M. Martín-Alvarez, J.A. Gladysz, Organometallics 21 (2002) 5386.

[8] J. Cano Sierra, D. Hüerländer, M. Hill, G. Kehr, G. Erker, R. Fröhlich, Chem. Eur. J. 9 (2003) 3618.

[9] (a) W.-L. Nie, G. Erker, G. Kehr, R. Fröhlich, Angew. Chem. 116 (2004) 313;
Angew. Chem. Int., Ed. Engl. 43 (2004) 310;
(b) See also: G. Erker, S. Wilker, C. Krüger, R. Goddard, J. Am. Chem. Soc. 114 (1992) 10983;
(c) G. Erker, S. Wilker, C. Krüger, M. Nolte, Organometallics 12 (1993) 2140.

[10] (a) G. Erker, C. Krüger, G. Müller, Adv. Organomet. Chem. 24 (1985) 1;
(b) H. Yasuda, K. Tatsumi, A. Nakamura, Acc. Chem. Res. 18 (1985) 120;
(c) G. Erker, G. Kehr, R. Fröhlich, Adv. Organomet. Chem., in press.

[11] (a) M. Dahlmann, G. Erker, R. Fröhlich, O. Meyer, Organometallics 19 (2000) 2956;
(b) M. Dahlmann, G. Erker, R. Fröhlich, O. Meyer, Organometallics 18 (1999) 4459.

[12] The CH/π-Interaction; Evidence, Nature, and Consequences M. Nishio, M. Hirota, Y. Umezawa, in: A.P. Marchand (Ed.), Methods in Stereochemical Analysis, Wiley/VCH, NY, 1998.

[13] (a) P. Renaut, G. Tainturier, B. Gautheron, J. Organomet. Chem. 148 (1978) 35;
(b) G. Erker, R. Nolte, R. Aul, S. Wilker, C. Krüger, R. Noe, J. Am. Chem. Soc. 113 (1991) 7594.

[14] (a) K. Kunz, G. Erker, S. Döring, S. Bredeau, G. Kehr, R. Fröhlich, Organometallics 21 (2002) 1031;
(b) K. Kunz, J. Pflug, A. Bertuleit, R. Fröhlich, E. Wegelius, G. Erker, E.-U. Würthwein, Organometallics 19 (2000) 4208, and references cited therein.

[15] S. Venne-Dunker, G. Kehr, R. Fröhlich, G. Erker, Organometallics 22 (2003) 948.

[16] S. Knüppel, G. Erker, R. Fröhlich, Angew. Chem. 111 (1999) 2048;
Angew. Chem. Int., Ed. Engl. 38 (1999) 1923.

[17] S.-D. Bai, X.-H. Wei, J.-P. Guo, D.-S. Liu, Z.-Y. Zhou, Angew. Chem. 111 (1999) 2051;
Angew. Chem. Int., Ed. Engl. 38 (1999) 1926.

[18] M. Tramontini, Synthesis (1973) 703.

[19] S. Knüppel, R. Fröhlich, G. Erker, J. Organomet. Chem. 586 (1999) 218;
J. Organomet. Chem. 595 (2000) 307.

[20] P. Liptau, S. Knüppel, G. Kehr, O. Kataeva, R. Fröhlich, G. Erker, J. Organomet. Chem. 637–639 (2001) 621.

[21] P. Liptau, T. Seki, G. Kehr, A. Abele, R. Fröhlich, G. Erker, S. Grimme, Organometallics 22 (2003) 2226.

[22] (a) D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, I. Ugi, J. Am. Chem. Soc. 92 (1970) 5389;
(b) G. Gokel, D. Marquarding, I. Ugi, J. Org. Chem. 37 (1972) 3052;
(c) T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, M. Kumada, Bull. Chem. Soc. Jpn. 53 (1980) 1138;
(d) R. Gleiter, R. Seeger, Helv. Chim. Acta 54 (1971) 1217;
(e) R. Gleiter, R. Seeger, H. Binder, E. Fluck, M. Cais, Angew. Chem. 84 (1972) 1107;
Angew. Chem. Int., Ed. Engl. 11 (1972) 1028;
(f) Reviews: W.E. Watts, J. Organomet. Chem. Library 7 (1979) 399;
A.J. Pearson, Metallo-Organic Chemistry, Wiley, New York, 1985, p. 319.

[23] (a) G. Tainturier, K. Chhor y Sok, B. Gautheron, C. R. Acad. Sci. Paris C (1973) 1269;
(b) K. Chhor y Sok, G. Tainturier, B. Gautheron, Tetrahedron Lett. 25 (1974) 2207;
(c) K. Chhor y Sok, G. Tainturier, B. Gautheron, J. Organomet. Chem. 132 (1977) 173;
(d) E.M. Caynela, L. Xiao, T. Sturm, B.R. Manzano, F.A. Jalón, W. Weissensteiner, Tetrahedron: Asymmetry 11 (2000) 861;
(e) T. Sturm, W. Weissensteiner, F. Spindler, K. Mereiter, A.M. López-Agenjo, B.R. Manzano, F.A. Jalón, Organometallics 21 (2002) 1766, and references cited therein;
(f) P. Liptau, M. Neumann, G. Erker, G. Kehr, R. Fröhlich, S. Grimme, Organometallics 23 (2004) 21.

[24] (a) Reviews: E. Drent, P.H.M. Budzelaar, Chem. Rev. 96 (1996) 663;
(b) C. Bianchini, A. Meli, Coord. Chem. Rev. 225 (2002) 35.

[25] P. Liptau, L. Tebben, G. Kehr, B. Wibbeling, R. Fröhlich, G. Erker, Eur. J. Inorg. Chem. (2003) 3590; 4261.

[26] G. Erker, L. Tebben, G. Kehr, B. Rieger, unpublished results.

[27] See for a comparison: C. Gambs, S. Chaloupka, G. Consiglio, A. Togni, Angew. Chem. 112 (2000) 2602;
Angew. Chem. Int., Ed. Engl. 39 (2000) 2486.

[28] (a) X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10015;
(b) Review: E.Y.-X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391.

[29] (a) B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich, S. Kotila, Angew. Chem. 107 (1995) 1867;
Angew. Chem. Int., Ed. Engl. 34 (1995) 1755;
(b) Reviews: G. Erker, Acc. Chem. Res. 34 (2001) 309;
(c) G. Erker, Chem. Commun. (2003) 1469.

[30] (a) E. Negishi, F.E. Cederbaum, T. Takahashi, Tetrahedron Lett. 27 (1986) 2829;
(b) D.R. Swanson, E. Negishi, Organometallics 10 (1991) 825.

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

[32] (a) D.J. Parks, R.E.V.H. Spence, W.E. Piers, Angew. Chem. 107 (1995) 895;
Angew. Chem. Int., Ed. Engl. 34 (1995) 809;
R.E.V.H. Spence, D.J. Parks, W.E. Piers, M.A. MacDonald, M.J. Zaworotko, S.J. Rettig, Angew. Chem. 107 (1995) 1337;
Angew. Chem. Int., Ed. Engl. 34 (1995) 1230;
(b) Y. Sun, W.E. Piers, S.J. Rettig, Organometallics 15 (1996) 4110;
(c) W.E. Piers, T. Chivers, Chem. Soc. Rev. 26 (1997) 345.

[33] W.-H. Sun, G. Kehr, N. Kleigrewe, G. Erker, unpublished results.

[34] S.G. Davies, M.L.H. Green, D.M.P. Mingos, Tetrahedron Report no. 57, Tetrahedron 34 (1978) 3047.