Russian Chemical Bulletin, International Edition, Vol. 53, No. 5, pp. 1007—1019, May, 2004 1007

Metallocene carbene chemistry*

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The Group IV bent metallocenes Cp_2M (M = Ti, Zr, Hf) were involved in carbene-related chemistry in various ways. Examples from four different areas are used to illustrate this. *In situ* generated Cp_2M: species exhibit some carbene-like character. They add to olefins, and their addition products can incorporate additional unsaturated organic reagents, *e.g.*, alkyne, to form five-membered metallacycles. The high oxophilicity of the Group IV metals helps the addition of alkene-, aryne-, η^2-ketone-, η^2-aldehyde-, or butadiene-containing reagents to a great variety of metal carbonyl compounds to form the Fischer-type carbene complexes. The resulting zirconoxycarbene complexes have found some application in organometallic chemistry and in organic synthesis. Reactive $[Cp_2M^{IV}R]^+$ cations can be stabilized by the addition of the Arduengo carbenes that serve as bulky two-electron donor ligands. First examples were structurally characterized. Dialkylimidazol-2-ylidenes also add to the electrophilic MX_4 compounds yielding stable *trans*-bis(imidazol-2-ylidene)MX_4 systems. Several examples are presented where ruthenium carbene complexes are used for carrying out catalytic olefin metathesis reactions at pendant olefinic substituents at the bent metallocenes. These reactions have led to the formation of novel bimetallic metallocene systems, as well as to new *ansa*-metallocenes. These catalytic reactions have helped in the current efforts to develop a functional group chemistry at the sensitive Group IV bent metallocene frameworks.

Key words: carbenes, metallocenes, catalysis, reactivity.

Introduction

The Group IV bent metallocenes have found extensive use in organometallic chemistry. Their special stereoelectronic features[1] have allowed the development of a variety of specific carbon—carbon bond forming reactions at their electrophilic central metal centers. In addition, some reactions were made to proceed even more facile by making use of the pronounced oxophilicity of the Group IV metals. A combination of such features has allowed to employ a variety of Group IV metallocene complexes as components in reaction systems relevant to carbene chemistry. Four areas of such developments will be illustrated in this account using selected examples.

Carbene-like behavior of the bis(cyclopentadienyl)zirconium(II) species

The special electronic features of the bent metallocenes[1,2] allow them to react with olefins in a "metallacarbene"-like manner. However, in many cases, the resulting "metallacyclopropane" products react further with additional olefinic (or acetylic) reagents to form stable five-membered metallacycles.

This shall be illustrated by a selected example. We have prepared *ansa*-metallocene complex **1** with pentenyl side chains at position 1 of each Me_2Si-linked η^5-indenyl ligands. Due to the planar chirality of each disubstituted (η^5-indenyl)zirconium unit, a mixture of diastereoisomers was formed, from which the major *rac*-isomer was obtained in the pure state by crystallization (Scheme 1). Reduction with sodium amalgam probably generated the corresponding zirconocene intermediate that was trapped by the two pendant olefinic groups to form the doubly bridged zirconacyclopentane complex **2** (see Scheme 1).[3]

Two views of the molecular structure of complex **2** are depicted in Fig. 1. It reveals that the metal center is very effectively shielded by the sterical bulk of its pairs of π- and σ-ligands from outside attack. This leads to some remarkable chemical behavior of complex **2**. Treatment with HCl (Scheme 2) does not lead to the formation of the expected "large metallocene"[4] but rather we observe the formation of product **4** in which one of the pendant olefinic groups of the starting compound **1** has been converted to the alkyl group. This probably indicates that metallacycle **2** is in a rapid endothermic equilibrium with

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* Materials were presented at the VII International Conference on the Chemistry of Carbenes and Related Intermediates (Kazan, 2003).

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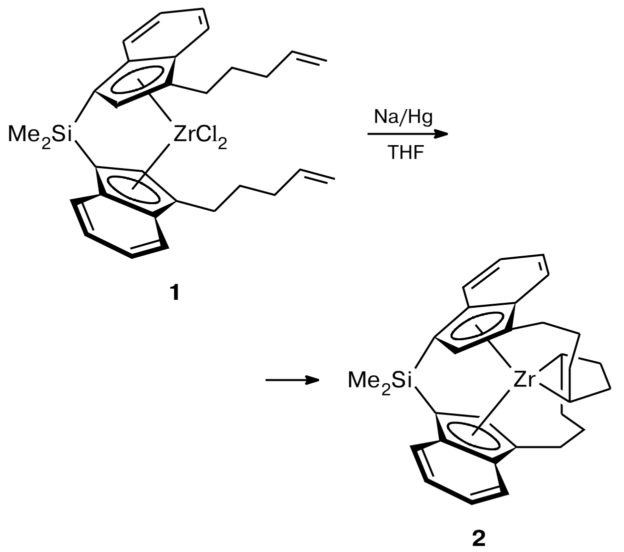
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 965—976, May, 2004.

Scheme 1



reactive monoolefin complex **3**, which is sufficiently reactive to add 2 equiv. HCl to form compound **4**. This description is supported by the fact that alleged intermediate **3** can readily be trapped by the added 2-butyne to yield unsaturated metallacycle **5** (see Scheme 2).[3]

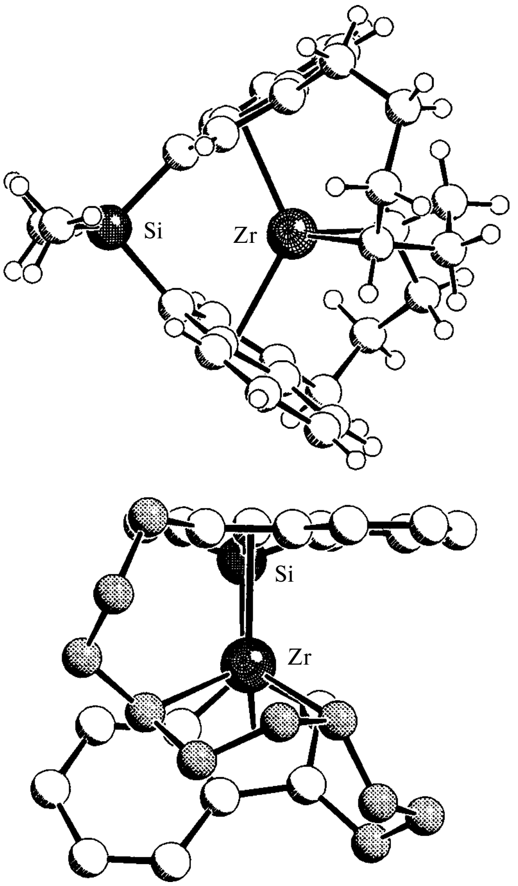
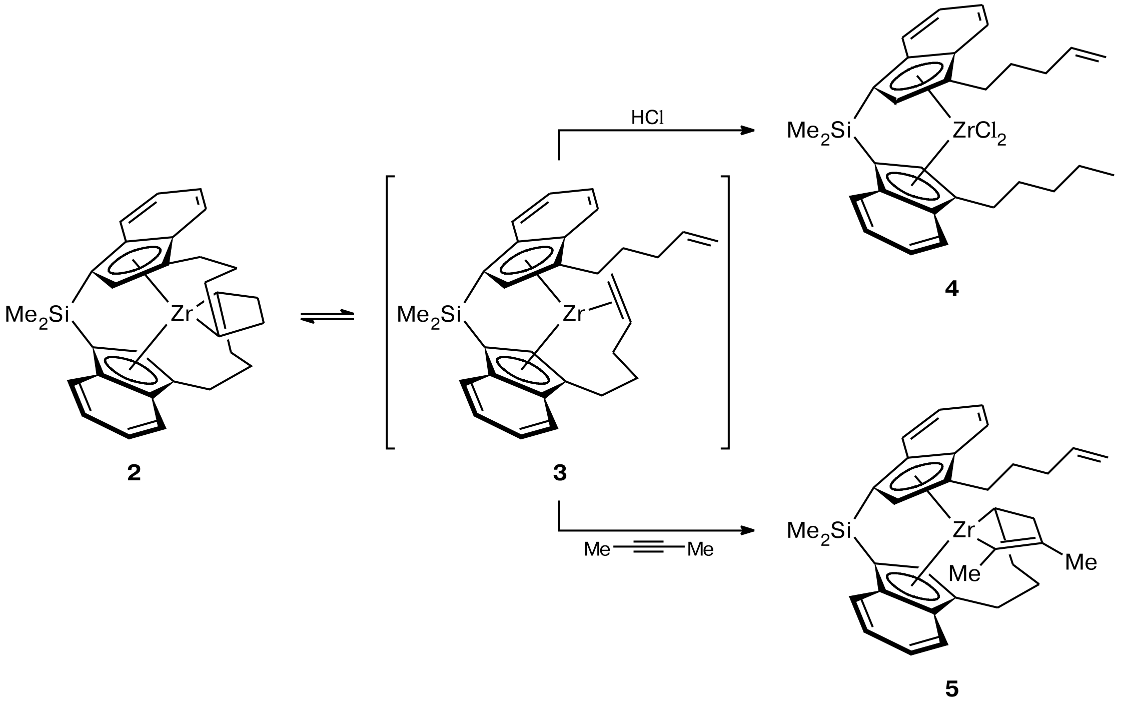


Fig. 1. Two projections of the molecular structure of metallacyclic product **2**.

Formation and reactions of zirconoxycarbene complexes

(Butadiene)zirconocene was the first mononuclear metal complex for which the existence of the

Scheme 2



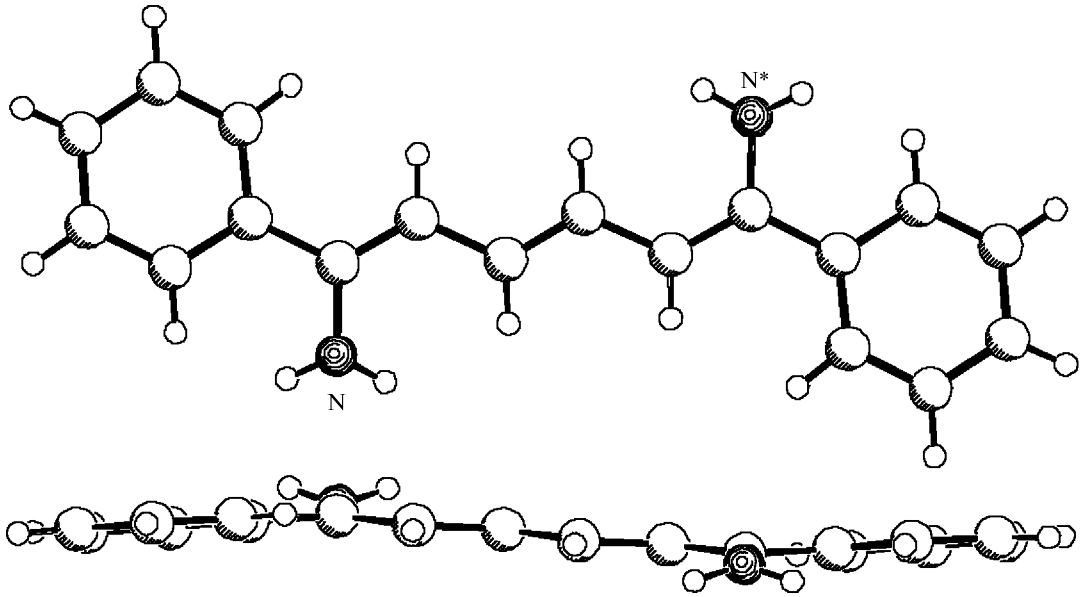
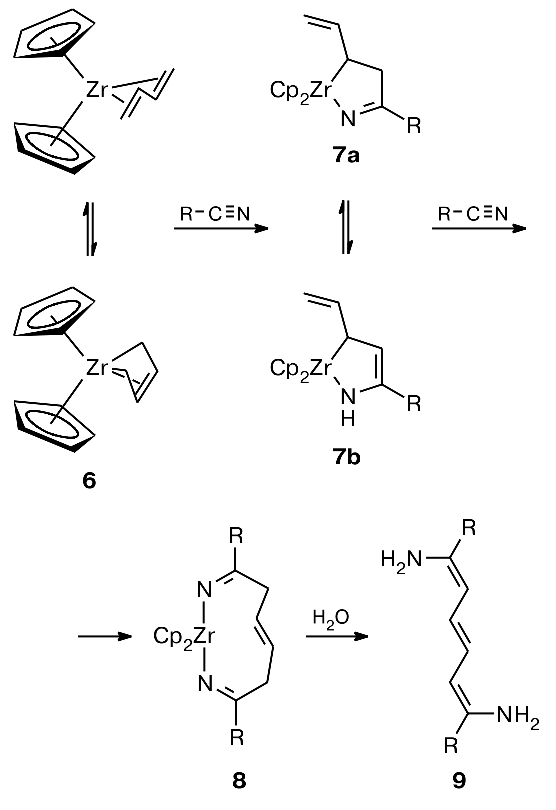


Fig. 2. Two projections of substituted 1,6-diamino-1,3,5-hexatriene (**9**) synthesized by the organometallic route depicted in Scheme 3.

η^4-*s*-*trans*-conjugated diene coordination was experimentally demonstrated.[5] Meanwhile, a number of (η^4-*s*-*trans*-1,3-diene)metal complexes has been synthesized and thoroughly characterized.[6] The parent $(C_4H_6)ZrCp_2$ complex was shown to exist as a pair of equilibrating isomeric (η^4-*s*-*trans*-butadiene)- and (η^4-*s*-*cis*-butadiene)metallocenes. In addition, the *s*-*trans*-**6** $\rightleftharpoons$ *s*-*cis*-**6** system rapidly reacts with a great variety of unsaturated reagents to form metallacyclic products. Its reactions with organic nitriles are typical examples. In a stepwise reaction, 2 equiv. R—C≡N are eventually incorporated and coupled with the terminal butadiene carbon atoms of molecule **6** (Scheme 3) to form a nine-membered metallacycle **8** that exhibits a *trans*-configured central C=C bond.[7] Subsequent hydrolysis yields a series of stable 1,6-diamino-1,3,5-hexatrienes **9**. Figure 2 shows the result of the X-ray crystal structure analysis of a typical example, featuring the close to planar arrangement of the unsaturated alternating core of this type of stable, isolable primary enamine.[8,9]

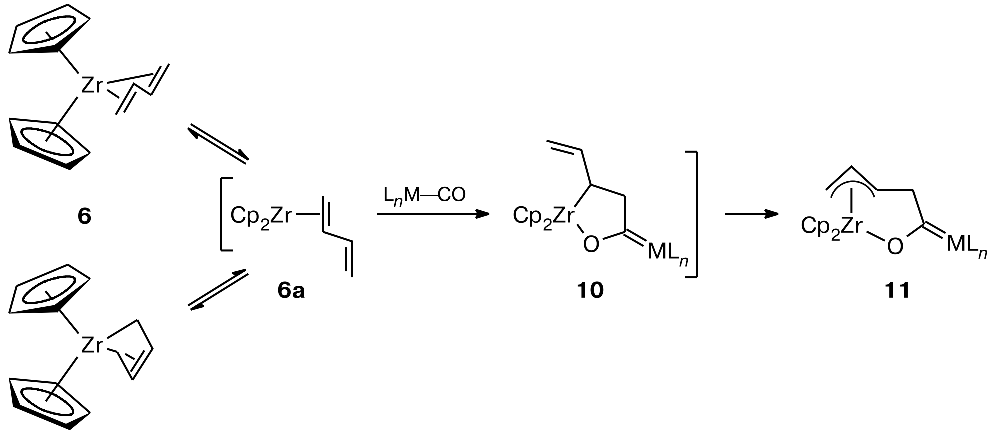
Scheme 3



A variation of this reaction was used for the preparation of a great variety of zirconoxycarbene complexes. This procedure represents a novel route to the important class of the organometallic Fischer-type carbene complexes.[10] (Butadiene)zirconocene complex **6** was treated with 1 equiv. metal carbonyl. It is probably the reactive intermediate **6a** that is trapped by the L_nM—CO reagent to form five-membered σ-allylmetaloxycarbene complex **10** (Scheme 4). In most cases, the latter then rearranges rapidly to more stable metallacyclic π-allylzirconoxycarbene complex **11**.[11]

We have isolated a number of such complexes and characterized them by X-ray diffraction.[12] This cycloaddition method proved especially useful in a number of cases when the classical Fischer method of carbene complex synthesis was difficult to apply. This was the case in metal cluster carbene complexes. An interesting example

Scheme 4



is also the facile reaction of $CpV(CO)_4$ with (butadiene)zirconocene to yield zirconoxycarbene complex **11a** (Fig. 3). The X-ray crystal structure analysis revealed a V—C1 bond length of 2.102(3) Å and a C1—O distance of 1.270(4) Å. Complex **11a** was a useful intermediate for the preparation of conventional Fischer carbene complexes of vanadium,[13] which could not easily be prepared otherwise (see below). This example served to demonstrate the complementary nature of this method to the nucleophilic Fischer route to stabilized alkoxycarbene metal complexes.

This type of a zirconoxycarbene complex synthesis is not limited to the use of (butadiene)zirconocene. Other reactive zirconium reagents can be used as well. A typical example is (η^2-benzyne)zirconocene.[14] In this case, it was *in situ* generated by thermolysis of diphenylzirconocene (**12**)[15] in the presence of, *e.g.*, $W(CO)_6$. Carbon—carbon coupling with one CO ligand took place instantaneously with formation of the respective zirconoxycarbene complex **13** (Scheme 5, Fig. 4). In compound **13**, the zirconium center is sufficiently Lewis acidic to coordinate to a *trans*-CO ligand from an adjacent carbene complex entity.[16]

(η^2-Formaldehyde)zirconocene also adds metal carbonyls to form zirconoxycarbene complexes. The $[(\eta^2\text{-}CH_2O)ZrCp_2]_2$ reagent (**14**) was obtained by a hydrozirconation reaction of carbon monoxide.[17] The dimeric framework is retained in the $L_nM—C\equiv O$ addition reaction. Only one of the metallaoxirane subunits actually reacts to form carbene complexes **15** (Fig. 5).[18]

Actually, the methylene groups can be removed from the Zr_2O_2 metal oxide framework of complex **14**, forming

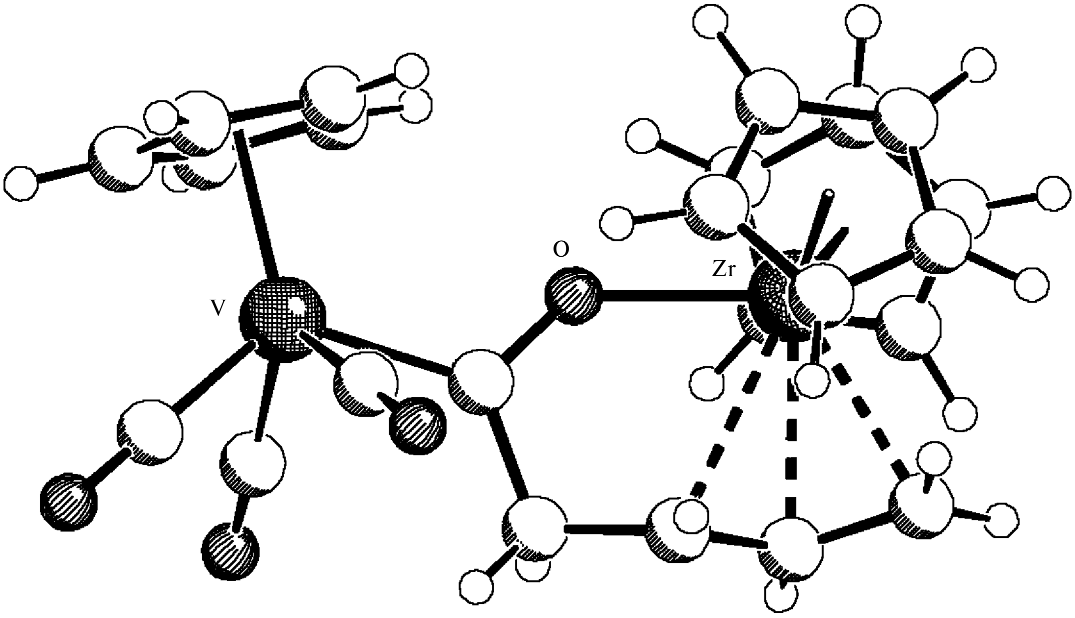


Fig. 3. Molecular structure of π-allylzirconoxycarbene vanadium complex **11a**.

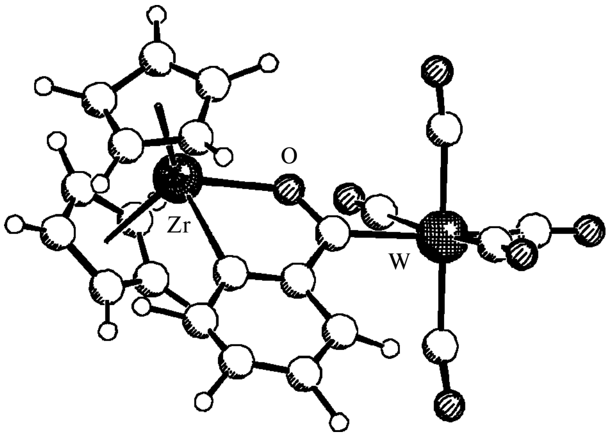
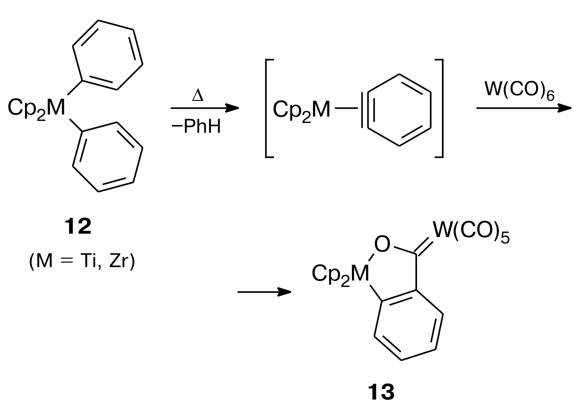


Fig. 4. Molecular structure of the monomeric subunit of complex **13**.

oligomeric alkyl chain products (**16**). Treatment with, *e.g.*, BEt_3 results in methylene transfer from zirconium to boron. Subsequent oxidative workup of the resulting borane mixture yielded a Poisson distribution of alkan-1-ols $HO(CH_2)_nEt$.[19] A tentative mechanistic description is depicted in Scheme 6 that indicates some relation to C—C coupling processes over heterogeneous Fischer—Tropsch catalysts.[20,21]

The (butadiene)zirconocene-derived metallacyclic π-allylzirconoxycarbene complex **11** contains a reactive, nucleophilic allylzircononium functional group that can be used effectively for further C—C coupling reactions.

Scheme 5



Thus, treatment of the corresponding zirconoxycarbene vanadium complex **11a** with 1 equiv. acetone leads to the clean formation of nine-membered metallacyclic carbene complex **17** (Scheme 7, Fig. 6). As it is typical of such products (see above), complex **17** also contains a *trans*-C=C bond inside the ring system. Selective hydrolysis followed by *O*-alkylation yields the substituted Fischer-type vanadium carbene complex **18**.[22]

This reaction type has successfully been used in organic synthesis. Here is a typical example: treatment of the zirconoxycarbene tungsten complex (**11b**) with cyclopentanone (Scheme 8) gave the corresponding nine-membered metallacyclic carbene complex **17b**. This complex

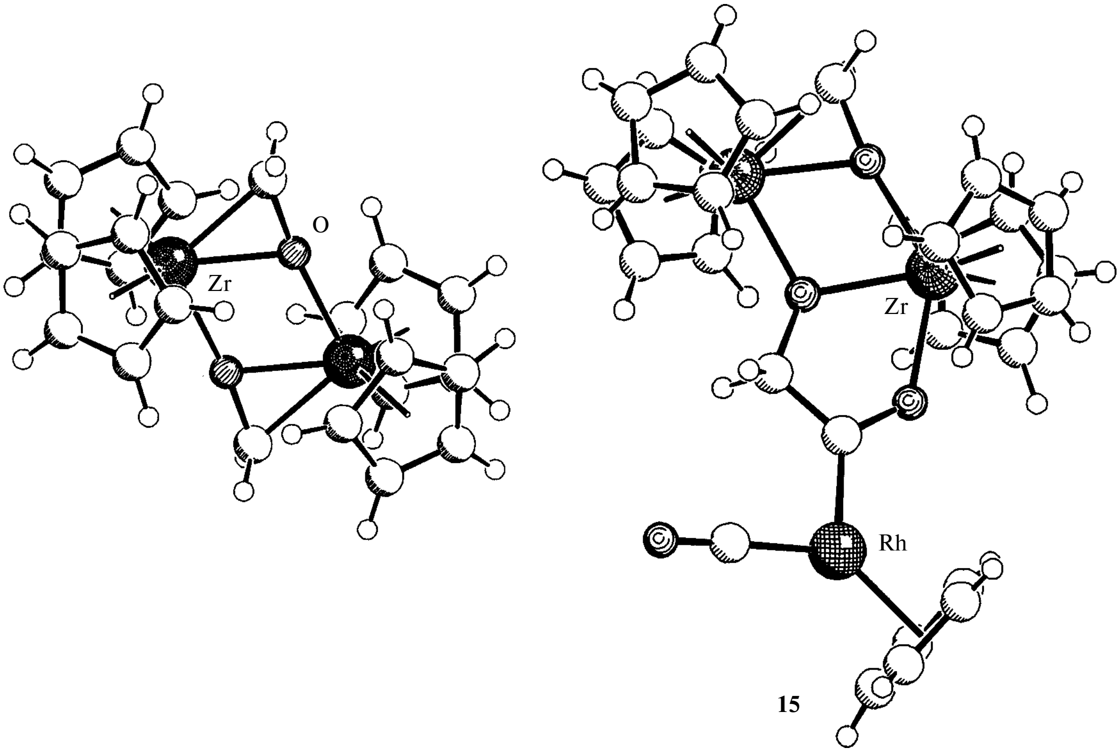
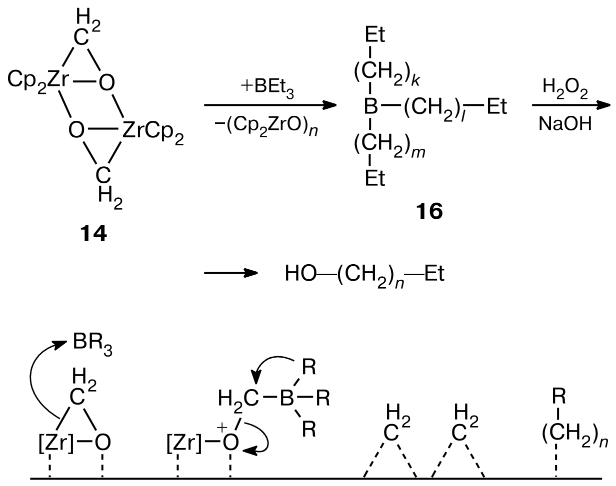


Fig. 5. Formation of zirconoxycarbene complex **15** from binuclear (η^2-formaldehyde)zirconocene.

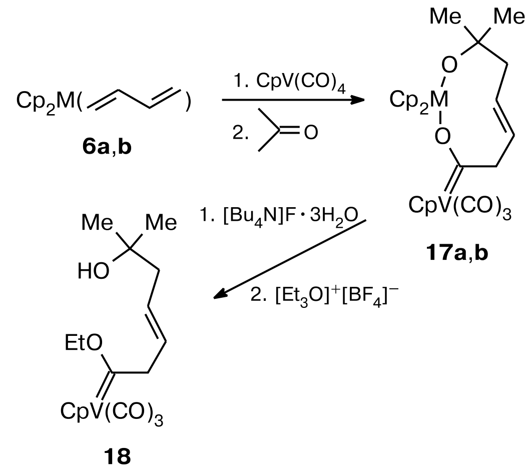
Scheme 6



did not react with the mild oxidant pyridine-*N*-oxide. However, the addition of water generated hydroxycarbene complex **19**, which was immediately oxidized to yield 6-hydroxy-*trans*-hexen-3-oic acid **20**. In the solid state, compound **20** builds up ribbon-like suprastructures (Fig. 7) in which the individual molecular building blocks are selectively connected by intermolecular hydrogen bonds between the polar functional groups. Changing the ketone component in this template reaction leads to a series of 6-hydroxy-*trans*-hexen-3-oic acids that were shown to form[23] different types of associated structures in the solid state.

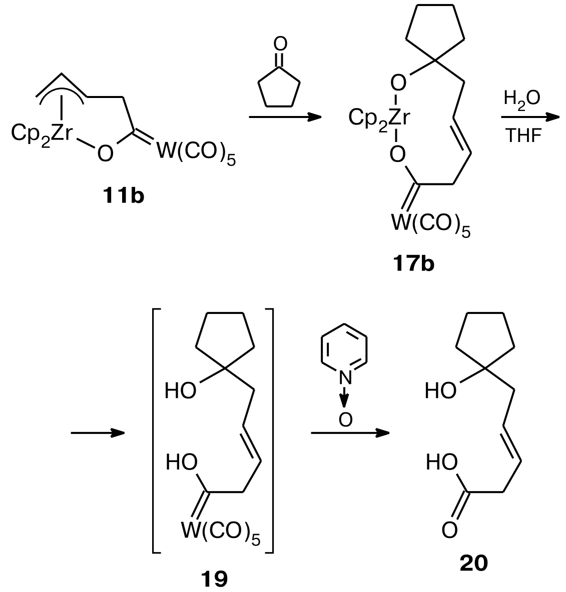
In principle, this reaction type uses the formation of the zirconoxycarbene complex, its hydrolysis, and subsequent oxidative cleavage as a synthetic equivalent of the introduction of a CO_2 group. We have used this approach, *e.g.*, for the synthesis of steroid derivatives **21** starting from the respective 17-ketosteroid precursor **22** (Scheme 9).[24] The rigid organometallic framework of the zirconoxycarbene complex intermediate (Fig. 8) allowed for α-alkylation reactions with very efficient asymmetric 1,5-induction.[24,25]

Scheme 7



M = Hf (**a**), Zr (**b**)

Scheme 8



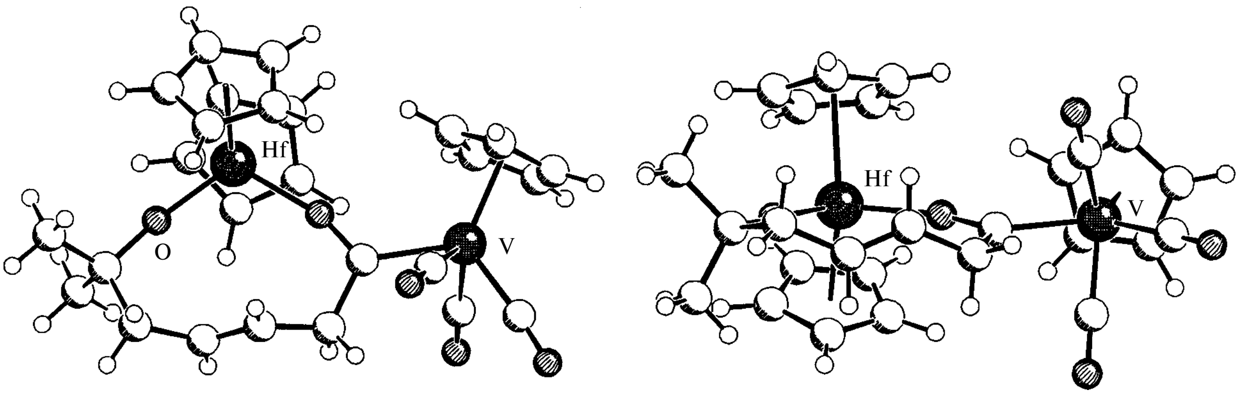


Fig. 6. Two projections of nine-membered metallacyclic vanadium carbene complex **17a**.

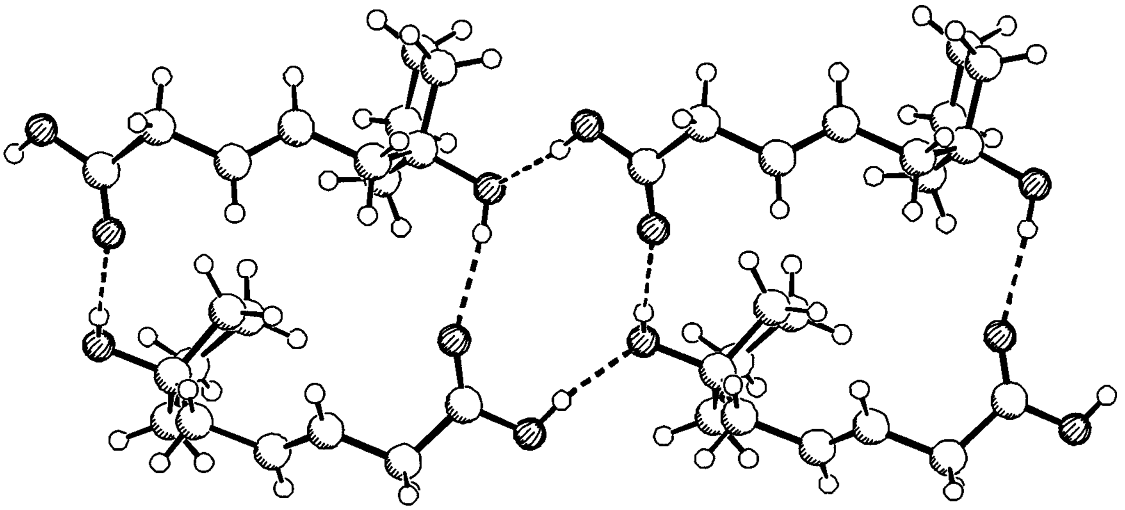


Fig. 7. Projection of the associated ribbon-like suprastructure of compound **20** in the solid state.

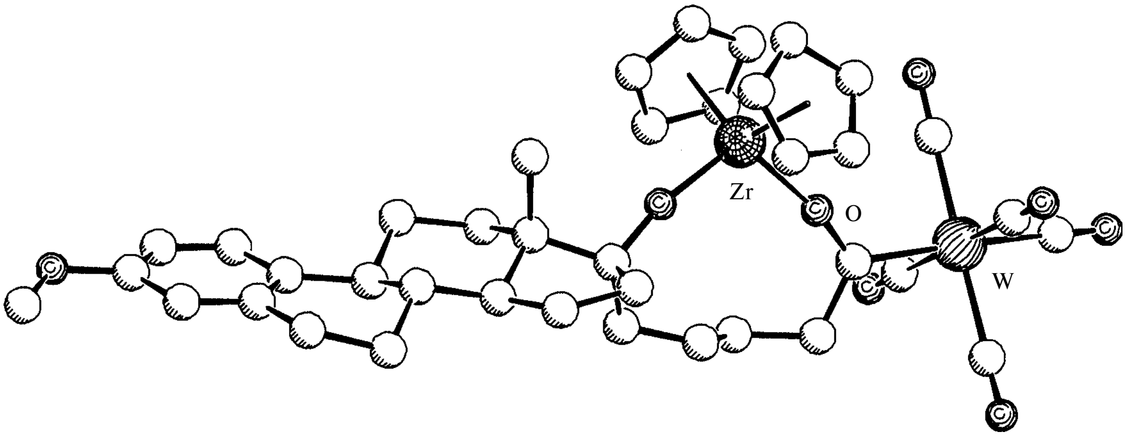
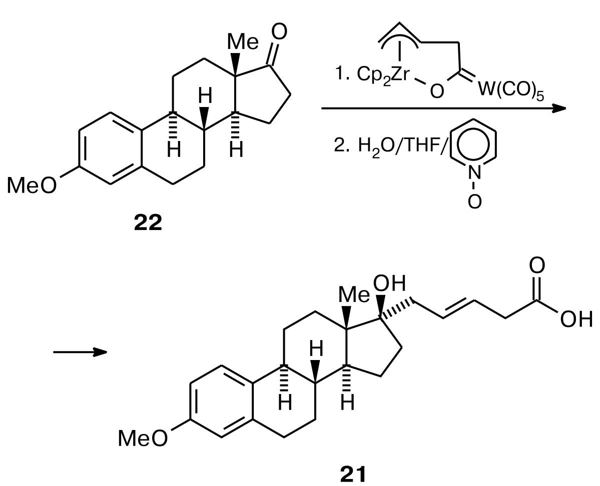


Fig. 8. Molecular structure of a steroid-derived zirconoxycarbene tungsten complex.

Scheme 9

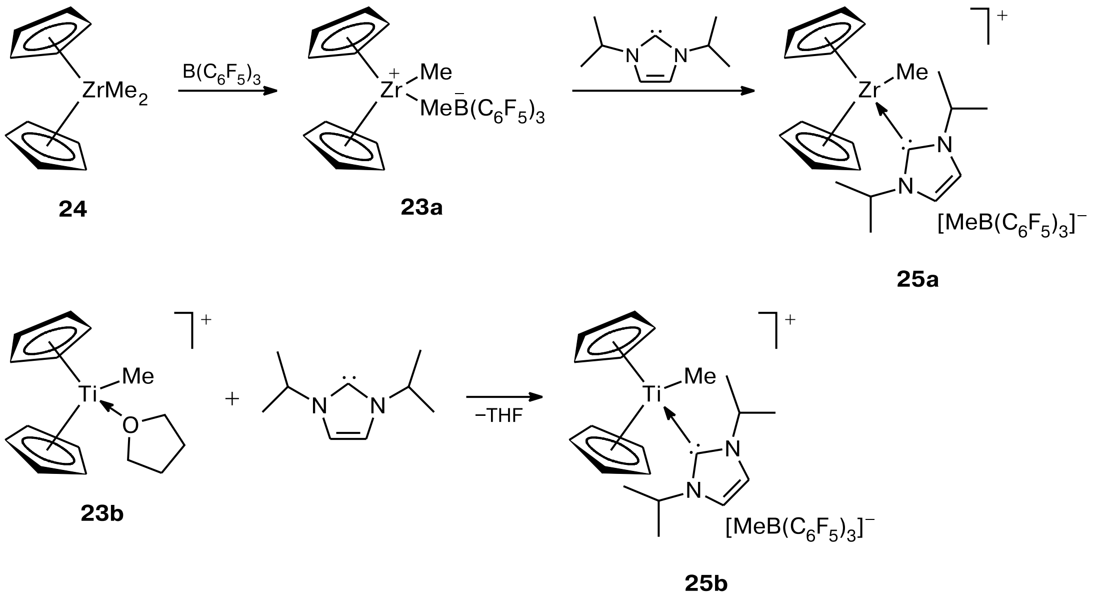


Group IV metal Arduengo carbene complexes

Subsequent to the pioneering works,[26,27] imidazol-2-ylidenes have found some use as stabilizing σ-donor carbene ligands in organometallic chemistry and catalysis.[28] Imidazol-2-ylidene complexes of a great variety of transition metals have become known. However, surprisingly only rather few examples of such carbene complexes of the Group IV metals had been described so far.[29] We have synthesized several new examples and characterized them with regard to their specific structural features.

We first reacted the metallocene salt $[Cp_2ZrMe]^+[MeB(C_6F_5)_3]^-$ (**23a**) (which was prepared by treatment of dimethylzirconocene (**24**) with the strong Lewis acid $B(C_6F_5)_3$) with 1,3-diisopropylimidazol-2-ylidene.[30] The stable Arduengo carbene cleanly adds to the methylzirconocene cation. The NMR spectrum of

Scheme 10



adduct **25a** shows signals of a nonequivalent pair of isopropyl groups, which indicates that the heterocyclic carbene is oriented coplanarly with the metallocene σ-ligand plane.

Tetrahydrofuran-stabilized methyltitanocene cation **23b** reacts with 1,3-diisopropylimidazol-2-ylidene by replacement of the THF ligand. The NMR spectrum of the resulting carbene adduct **25b** (Scheme 10, Fig. 9) again shows the resonances of a pair of symmetry-nonequivalent isopropyl groups (doublets of Me groups at $\delta_{^1\mathrm{H}}$ 3.05 and 3.05, 6 H each) and a signal of the carbene C atom at $\delta_{^{13}\mathrm{C}}$ 178.2.[31]

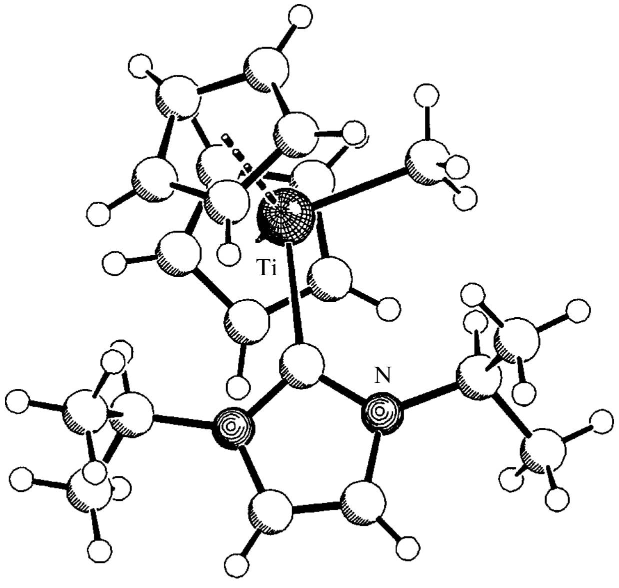
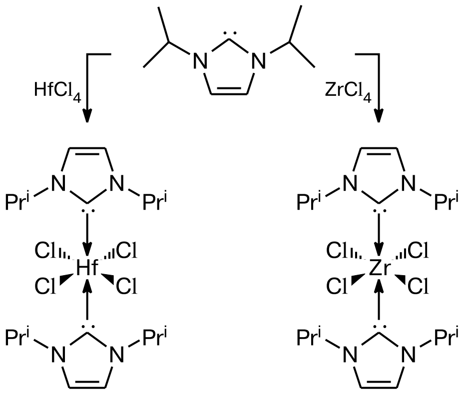


Fig. 9. Molecular structure of **25b** (cation only).

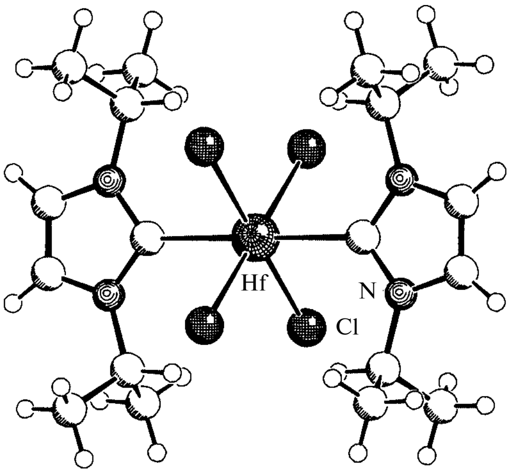
The X-ray crystal structure analysis confirms the coplanar arrangement of the heterocyclic core of the carbene with the titanocene σ-ligand plane (Ti—C_{Cb} 2.289(2) Å, Ti—CH_3 2.178(3) Å, where Cb is carbene). A theoretical analysis of the system revealed that the hindered rotation around the M^{IV}—C_{Cb} vector is simply steric in origin[31]: the Arduengo carbenes serve almost as pure σ-donor ligands, as it is often observed in other metal complexes with imidazol-2-ylidenes.[32]

1,3-Diisopropylimidazol-2-ylidene ($\delta_{^{13}\mathrm{C}}$ 210.5, C(2)) reacts with $HfCl_4$ (Scheme 11) to form the corresponding bis-adduct **26a** ($\delta_{^{13}\mathrm{C}}$ 181.8, C(2)). In the crystalline state, complex **26a** shows a pseudo-octahedral coordination geometry with the coplanar imidazol-2-ylidene ligands in *trans*-positions. The related Zr-containing complex **26b**

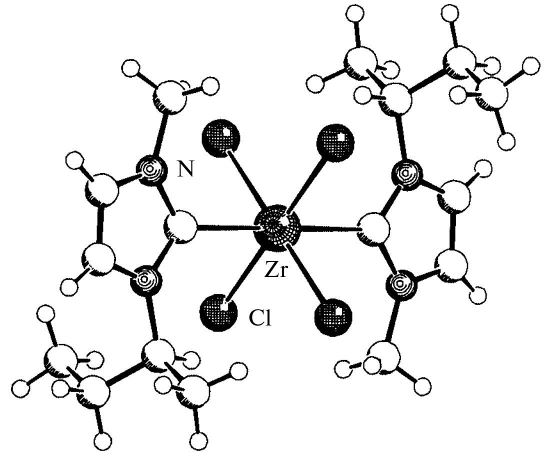
Scheme 11



26a **26b**



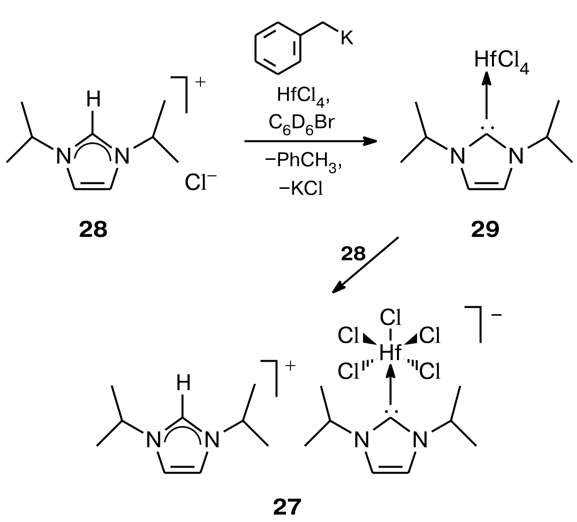
26a



26b

Fig. 10. Molecular structures of complexes **26a**,**b**.

Scheme 12



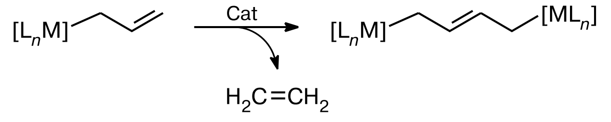
shows a similar structure with the bulky isobutyl substituents in an *anti*-orientation (Fig. 10).[33]

Salt **27** was obtained by treatment of 1,3-diisopropylimidazolium chloride (**28**) with $HfCl_4$ and benzylpotassium in a ratio of 2 : 1 : 1. It is likely that coordinatively unsaturated complex **29** (Scheme 12) is formed as a reactive intermediate in this reaction. Addition of the chloride then results in the formation of compound **27** (Fig. 11).[34]

Olefin metathesis reactions

The olefin metathesis reaction (Scheme 13) has become a very powerful tool in organic synthesis. It allows the construction of carbon frameworks by selectively using olefinic reagents in the presence of a great variety of other functional groups that remain untouched by this catalytic process.[28] The use of the olefin metathesis reaction as a synthetic tool in organometallic chemistry is emerging from the literature.[35]

Scheme 13



Cat is catalyst

We have prepared a variety of mono- and bis(cyclopentadienyl)titanium and -zirconium complexes that were bearing allyl side chains at their Cp ligands (*e.g.*, **30** and **31**, Scheme 14). All these systems readily undergo olefin metathesis reactions to yield the respective bimetallic ($Cp—CH_2—CH=CH—CH_2—Cp$)-bridged systems (with liberation of ethylene when treated with a catalytic amount of the [Ru]=CHPh carbene complex).[36] Using the $Cl_2(PCy_3)_2Ru=CHPh$ catalyst converted complex **30** to a mixture of dinuclear complexes *cis*-**33** and *trans*-**33** in a ratio of ~1 : 3, whereas almost a selective formation of the latter was observed when the more reactive second generation Grubbs catalyst **34** was employed (complex *trans*-**33** was characterized by X-ray diffraction analysis, Fig. 12). A similar result was obtained in the metathesis reaction of metallocene derivative **31**, which gives *cis*- and *trans*-isomers of compound **35** (see Scheme 14).[36]

It was tempting to try out the catalytic olefin metathesis reaction for intramolecular coupling at pendant alkenyl units attached to Group IV metallocenes that would lead to *ansa*-metallocene products. A suitable starting material was prepared as outlined in Scheme 15. Catalytic intramolecular olefin metathesis of the $[CH_2=CH(CH_2)_4Cp]_2ZrCl_2$ complex (**36**) was carried out under high dilution conditions using the

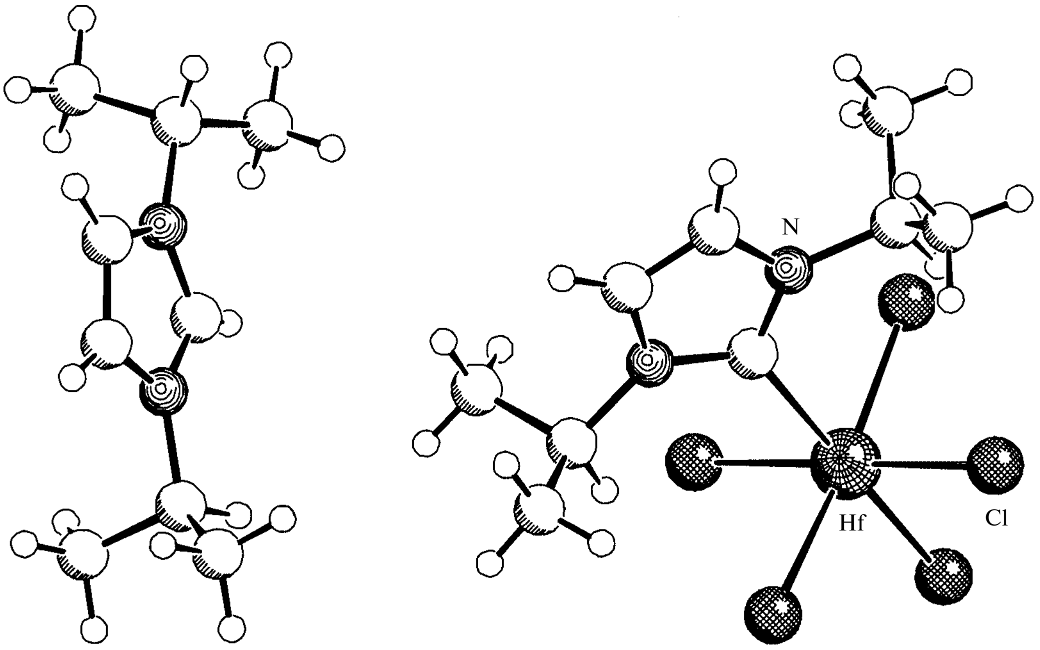
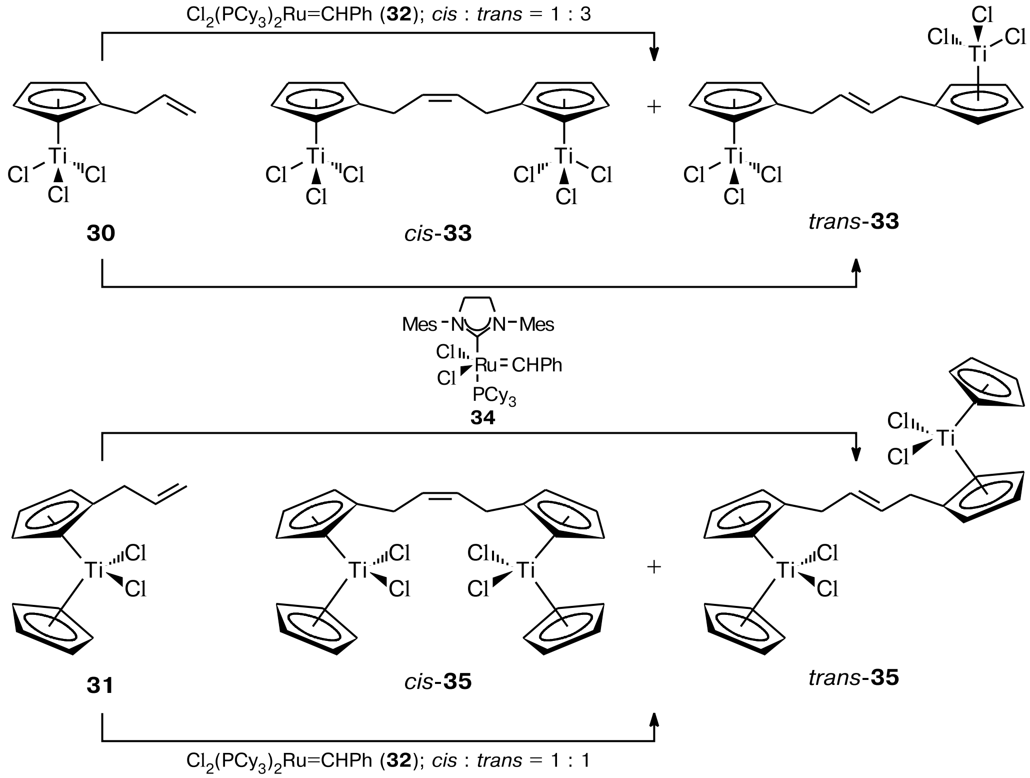


Fig. 11. Molecular structure of salt **27** in the crystal.

Scheme 14



Cy is cyclohexyl

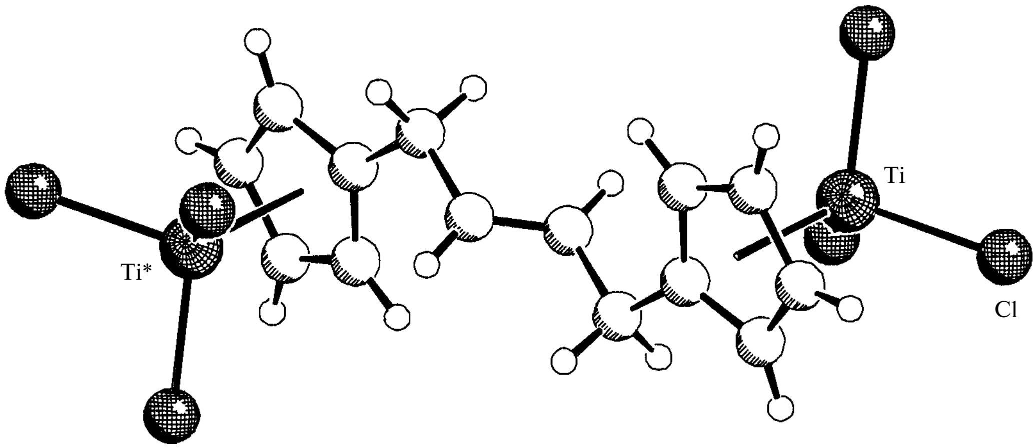
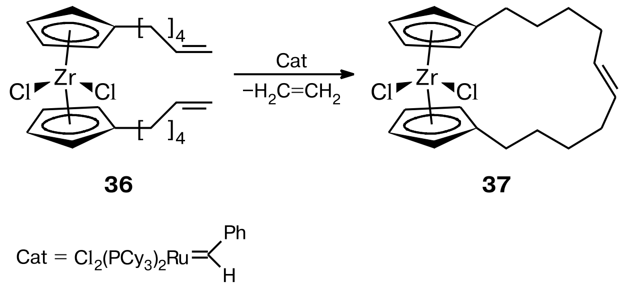


Fig. 12. Projection of the molecular structure of the organometallic metathesis product *trans*-**33**.

Scheme 15

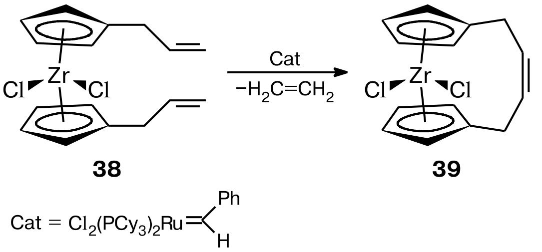


36 **37**

$Cl_2(PCy_3)_2Ru=CHPh$ catalyst to give the "large *ansa*-zirconocene dichloride" complex **37** in ~25% yield. Exclusively that product, which contains a *trans*-CH=CH unit inside the ten-membered *ansa*-bridge, was obtained (Fig. 13).[37]

The $(CH_2=CHCH_2Cp)_2ZrCl_2$ complex (**38**) also undergoes the catalytic intramolecular olefin metathesis reaction to yield an *ansa*-metallocene (Scheme 16). In this case, the —CH=CH— unit inside the C_4-*ansa*-bridge of product **39** has a *cis*-configuration (Fig. 14). Complex **39** was used as a starting material for the generation of an active homogeneous Ziegler—Natta catalyst.[37,38]

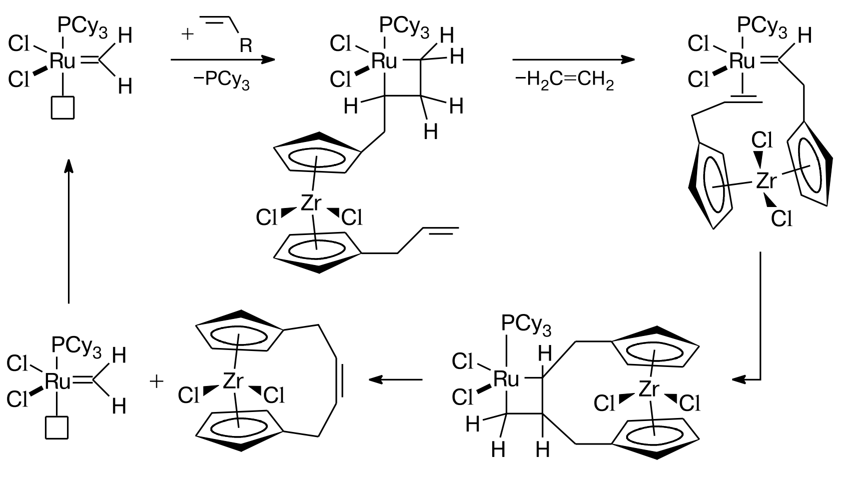
Scheme 16



38 **39**

We assume a reaction mechanism, which involves a series of bimetallic Zr/Ru complexes (Scheme 17) and

Scheme 17



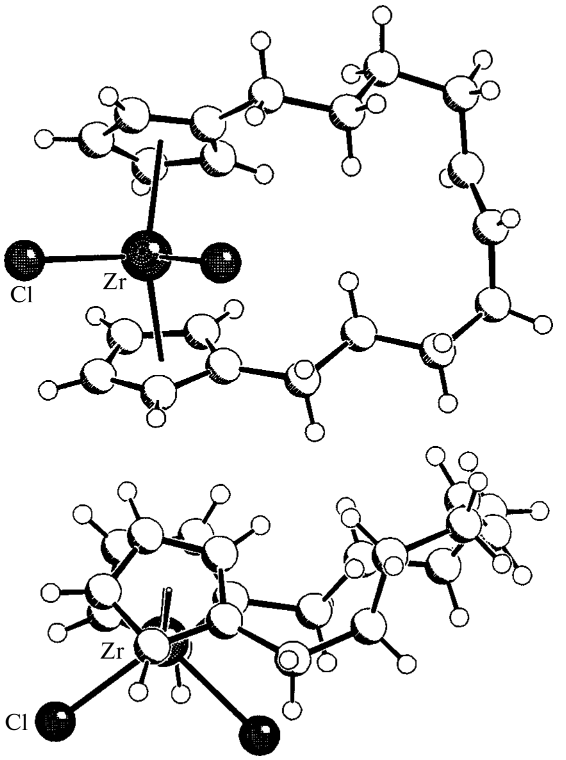


Fig. 13. Two projections of the molecular geometry of *ansa*-zirconocene complex **37**.

uses $Cl_2(PCy_3)Ru{=}CH_2$ as a chain-carrying reactive catalytic species.

G. Erker acknowledges many contributions of the members of his group and other collaborations to the chemistry described in this article. Their names are given in the references.

This work was financially supported by the Foundation of the Chemical Industry (Fond der Chemischen Industrie) and the German Research Foundation (Deutsche Forschungsgemeinschaft).

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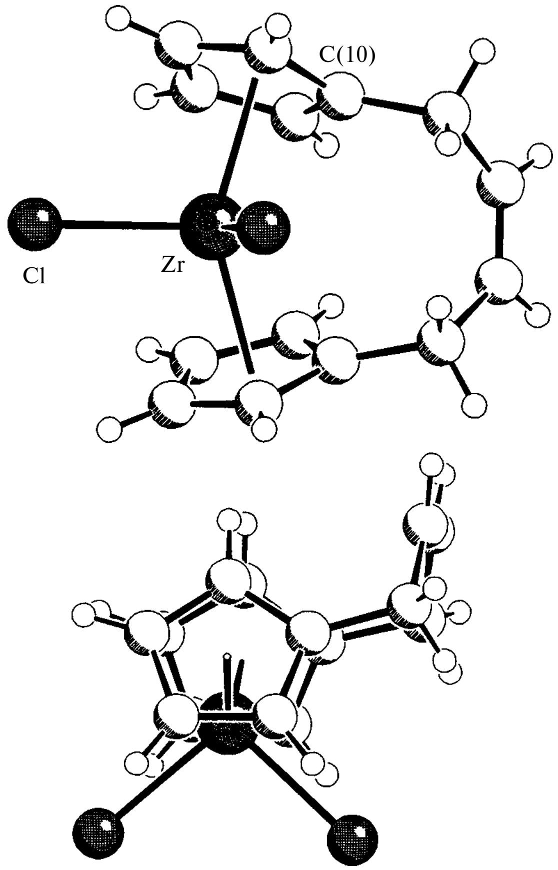

Fig. 14. Two projections of the molecular geometry of *ansa*-zirconocene dichloride complex **39**.

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Received November 12, 2003