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Mini Review

Carbene complexes of titanium group metals — formation and reactivity

Rüdiger Beckhaus *, Cristina Santamaría

Fachbereich Chemie, Universität Oldenburg, Postfach 2503, D-26111, Oldenburg, Germany

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Abstract

The principles in the formation of carbene complexes of titanium group metals are summarized. Characteristic examples of isolated as well as carbene complexes as intermediates are given. Selected structures and reactivity patterns are discussed. Starting from the Tebbe-type chemistry, new aspects of carbene complexes with only one or without cyclopentadienyl ligands are illustrated. In that direction, the formation of carbene complexes with N and O-donor ligands is described. Applications in co-ordination chemistry, organic syntheses and material sciences are summarized. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbene complexes; Titanium group metals; Cycoladdition reactions

1. Introduction

The formation of complexes, exhibiting transition metal–carbon σ-bonds, is of high interest in organometallic chemistry, especially in the time of increased interest in this field [1]. With the beginning of organometallic chemistry, the thermolysis of M–C bonds was used as a preparative procedure for the purification transition metals, as shown for $Ni(CO)_4$ in the *Mond* process [2]. However, first attempts to use the thermolysis of $TiMe_4$ for the preparation of pure Ti leads 'only' to titanium metal with a high carbon content [3]. These properties of the titanium alkyl bond lowered the interest in thermolytic transformations of early transition metal complexes. Additionally, first attempts to prepare zirconium carbene complexes as analogues to the tantalum derivatives, failed [4]. Therefore it took more than 30 years, to go from titanium alkyls ($TiMe_4$, 1959 solution [5], 1963 solid [6]) to structurally characterized carbene complexes of Group 4 metals (Ti 1995 [7], Zr 1993 [8], Hf 2000 [9]). During these years our understanding of the reactivity of the transition metal–carbon σ-bond has increased. In particular, the relationship between thermodynamic stability and kinetic lability of σ-organometallic compounds, together with an improved understanding of the interactions between metal, ligands and substrates, has increased the chemist's ability to plan organometallic syntheses [10]. In this area, titanium methyl complexes have been used in organic synthesis, on one hand, as reducing agents for carbonyl compounds [11] and on the other hand as kinetically controlled H elimination in carbonyl olefination reactions (Scheme 1) [12–14]. In the last sequence, a titanium carbene is the main intermediate, which is hardly ever isolated under reaction conditions. For these reasons, carbene complexes, which exist as short-living building blocks [10], are also included in the following discussion.

In this article, we want to summarize the principles of synthesis, structure and reactivity of carbene complexes of titanium group metals, particularly, the progress since the last reviews [10,15–19]. The search for new ligands, which can be used instead of the classical cyclopentadienyl moiety, has supposed advantages in

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* Corresponding author. Fax: +49-441-7983581.

E-mail address: ruediger.beckhaus@uni.oldenburg.de (R. Beckhaus).

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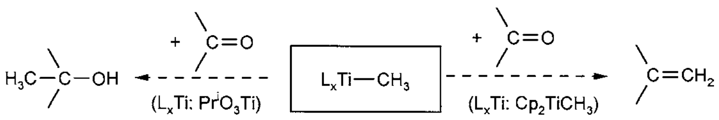


Scheme 1.

the carbene complex chemistry of early transition metals. In this way, the introduction of dentate ligands, which contain O- and/or N-donor atoms, as well as functionalized cyclopentadienyl ligands, have focused all the efforts.

2. Formation of carbene complexes of titanium group metals

2.1. *Carbene complexes of the bent-metallocene type*

2.1.1. *General routes*

The most prominent organotitanium complexes are those having two cyclopentadienyl ligands, forming the typical bent-metallocene structure. Where carbene complexes, exhibiting the titanocene fragment and a carbene ligand, are not observed in a free form, the corresponding phosphine complexes and several other adducts have been prepared [20]. The major milestone in this chemistry was the isolation of the so-called Tebbe reagent (**3**) from which a [Cp$_2$Ti=CH$_2$] (**1**) intermediate became available after the elimination of Me$_2$AlCl (Scheme 2, path b).

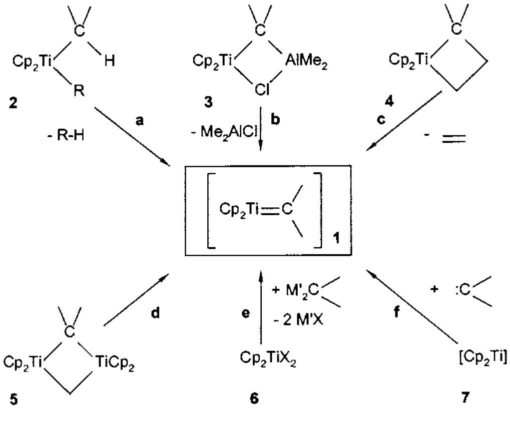
In addition to the methods described above, carbene complexes of the Fischer type are also known, which are formed by the reaction of Cp$_2$Zr(L)CO (L = CO, PMe$_3$) with Cp$^*_2$ZrH$_2$ in toluene to give, via an immediate reaction at −78°C, the corresponding zirconoxy carbenes, Cp$_2$(L)Zr=CHO–Zr(X)Cp$^*_2$ (**8**, **9**) [21] (Scheme 3, Table 1).

2.1.2. *Hydrogen elimination and generation of carbene complexes*

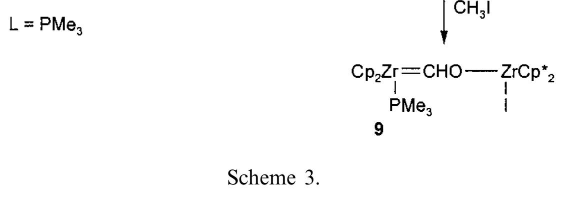
α-H eliminations proceed readily especially when there is significant steric crowding and where it is possible to transfer an α-hydrogen atom to a carbanionic acceptor ligand. The reaction is intramolecular, and first-order reaction kinetics are observed for organometallic complexes of the titanium group metals that show the C–H bond breaking in the rate determining step with a cyclic reaction path. In the case of the tetraalkyl complexes of titanium, zirconium, and hafnium, the activation energy for unimolecular methane elimination through intramolecular hydrogen abstraction increases in the order of TiMe$_4$ ≪ ZrMe$_4$ < HfMe$_4$ [42]. Unimolecular α-H abstraction for Ti(^{n}Pr)Me$_3$ and Ti(CH$_2$CMe$_3$)$_4$ is more favorable than γ-hydrogen abstraction. A comparison of activation enthalpies shows that, α-H abstractions occur more readily for neopentyl species ([Cp$_2$Ti(CH$_2$CMe$_3$)$_2$] > [Cp$_2$Ti=CHCMe$_3$], $\Delta H^{\#} = 76.2(5)$ kJ mol^{-1}, $\Delta S^{\#} = -49.8(8)$ J mol^{-1} K^{-1}) [30] than for methyl derivatives ([Cp$^*_2$Ti(CH$_3$)$_2$] > [Cp$^*_2$Ti=CH$_2$], $\Delta H^{\#} = 115.5(3)$ kJ mol^{-1}, $\Delta S^{\#} = -11.7(7)$ J mol^{-1} K^{-1}) [31]. The $\Delta S^{\#}$ values indicate a higher degree of order, corresponding to a lower mobility, for neopentyl, aryl, and vinyl derivatives than for methyl or benzyl compounds [10].

A high selectivity of methane elimination is found for the vinyl titanium complex [Cp$^*_2$Ti(CH=CH$_2$)CH$_3$] (**23**). The alternative elimination of ethylene (**23** → **14**) is not observed [39] (Scheme 4).

The spontaneous intramolecular H-transfer between the two vinyl groups in [Cp$^*_2$Ti(CH=CH$_2$)$_2$] (**24**) leads quantitatively to a methylenetitanacyclobutane (**25**) [43], the starting material of the broad titanaallene chemistry [16–18,40,44–62]. Selective α-H eliminations can also be used to generate substituted alkenylating reagents [L$_n$Ti=CHR] (R = C$_6$H$_5$ [63], ^{t}Bu [7], SiMe$_3$ [64,65]). As the reaction of bis-cyclopropyltitanocene shows [66], β-H-containing compounds of strained ring



Scheme 2.



Scheme 3.

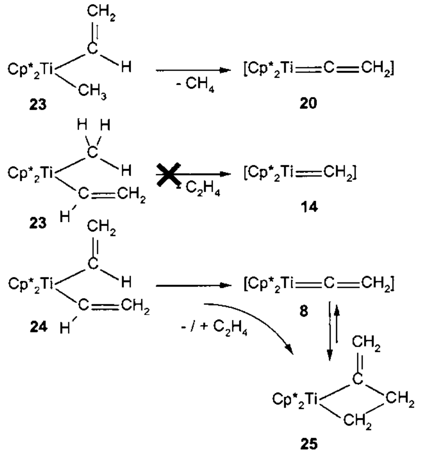
Table 1
Selected carbene complexes of Group 4 metals of the bent-metallocene type

	Complex	Starting material/method		Conditions	Comment	Reference
1	$[Cp_2Ti{=}CH_2]$	$[Cp_2TiMe_2]$	a	60°C	Intermediate	[22]
		$[Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2]$	b	+Pyridin/–$ClAlMe_2{\cdot}py$		[23]
		$[Cp_2Ti(CH_2CH_2CH_2)\text{–}]$	c	10°C, –C_2R_2		[24]
10	$[Cp_2Ti{=}CR_2]$	$2[Cp_2Ti\{P(OR)_3\}_2]$ + PhSR/–$[Cp_2Ti(SPh)_2]$	f	20°C, THF, 3 h	Intermediate	[25–28]
11	$[Cp_2Ti{=}CH_2(PMe_3)]$	$[Cp_2Ti(\mu\text{-}CH_2)_2TiCp_2]$	d	+PMe_3, 20°C	^{1}H-NMR δ 11.83, ^{13}C-NMR 285.2 (t, $^2J_{PC} = 30.5$, $^1J_{CH} = 125.1$ Hz)	[29]
12	$[Cp_2Ti{=}CHCMe_3]$	$[Cp_2Ti(CH_2CCMe_3)_2]$	a	20°C $T_{1/2} = 20\text{–}56$ min	Intermediate	[30]
13	$[Cp_2Ti{=}CHCMe_3(PMe_3)]$	$[Cp_2Ti(CH_2CCMe_3)_2] + PMe_3$	a	20°C, pentane, +PMe_3, 72%	δ 12.32 ($J_{PH} = 7.2$ Hz) δ 312.9 ($J_{PC} = 27$, $J_{CH} = 110$ Hz)	[30]
14	$[Cp^*_2Ti{=}CH_2]$	$[Cp^*_2TiMe_2]$	a	Toluene 110°C	Intermediate	[31]
15	$[Me_2Si(\eta^5\text{-}C_5Me_4)_2Ti{=}CHR]$	$[Me_2Si(\eta^5\text{-}C_5Me_4)_2Ti(CH_2R)_2]$	a	C_6H_6, 60°C, 5 h	Intermediate	[32]
16	$[Cp^*_2Ti{=}C(H)SiMe_3]$	$[Cp^*_2Ti(\eta^2\text{-}N_2 = C(H)SiMe_3)]$	f	C_6H_6, 32°C, $T_{1/2} = 2$ h	Intermediate	[33,34]
17	$[Cp_2Ti{=}C{=}C{=}CPh_2(PR_3)]$	$[Cp_2TiCl_2] + Li_2C{=}C{=}CPh_2$	e	70%	^{13}C-NMR: δ Ti=C: 264.9 $J_{PC} = 31.4$ Hz	[35]
18	$[Cp_2Ti{=}CHCH{=}CR_2(PMe_3)]$	$[Cp_2Ti(PMe_3)_2]$ + cyclopropene	f		^{13}C-NMR: δ Ti=C 284–286	[36]
19	$[Cp_2(Me_3P)Ti{=}C{=}C{=}Ti\text{-}(PMe_3)Cp_2]$	Complex reaction			Ti=C: 2.051(2) Å, ^{13}C-NMR δ 258.1	[37]
20	$[Cp^*_2Ti{=}C{=}CH_2]$	$[Cp^*_2Ti(CH{=}CH_2)_2]$	a	−25°C	Intermediate	[38]
		$[Cp^*_2Ti(CH{=}CH_2)CH_3]$	a	0…15°C	Intermediate	[39]
		$[Cp^*_2TiC({=}CH_2)CH_2CH_2\text{–}]$	c	>60°C	Intermediate	[15]
21	$[CpCp^*Ti{=}C{=}CH_2]$	$[CpCp^*(CH{=}CH_2)Me]$	a	25°C	Intermediate	[40]
8, **9**	$Cp_2(L)Zr{=}C(H)O\text{–}Zr(X)Cp^*_2$	$Cp^*_2ZrH_2 + Cp_2Zr(CO)L$		−78°C, toluene, red crystals	**9**: Zr=C 2.117(7) Å, ^{13}C-NMR $\delta = 286.3$, **8**: H $\delta = 295.0$)	[21]
22	$[Cp_2Hf{=}CHC_6H_5]$	$[Cp_2Hf(CH_2C_6H_5)_2]$	a		Intermediate	[41]

systems can be used for ‘alkylidenecyclopropanation’ in carbonyl olefination reactions.

2.1.3. Methylene-bridged derivatives and metallacyclobutanes as sources of carbene complexes

Whereas the Tebbe reagent has already been discussed in other articles as an effective and useful methylenating agent (Scheme 2, path b) [23], homologues metal compounds or substituted alkenylating agents are not accessible directly by path b. One method to prepare alkylidene-bridged Zr–Al complexes is based on the reaction of an alkenyl zirconium compound and metal hydrides [67]. The Zr=C species are generated by splitting the bimetallic complex with strong bases [68]. The bis-titanacyclobutane (bis-methylene complex) (**5**) in path d (Scheme 2) reacts rapidly and quantitatively with PMe_3 to yield $[Cp_2Ti{=}CH_2{\cdot}PMe_3]$ (**11**) [29]. The cleavage of bis-μ-methylene complexes fails, however works for other metal–metal combinations, such as Ti–Zr, Zr–Zr, or Ti–Si [29,69–72].

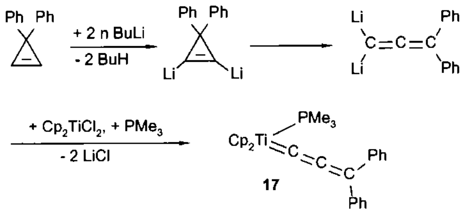


Scheme 4.

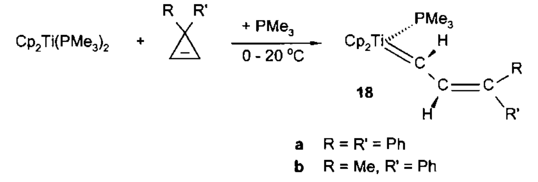
The use of titanacyclobutanes as starting materials has the advantage over the Tebbe reagent as additional Lewis acidic components, such as $[Me_2AlCl]$, are not separated after the reaction. For the synthesis of titanacyclobutanes, several procedures can be employed. While Grubbs [73], used the Tebbe reagent as the starting material, Bickelhaupt [74], preferred the 1,3-di-Grignard species [74], whereas Stryker, employed allyl complexes [75,76].

2.1.4. Synthesis of carbene complexes using carbene generating substrates

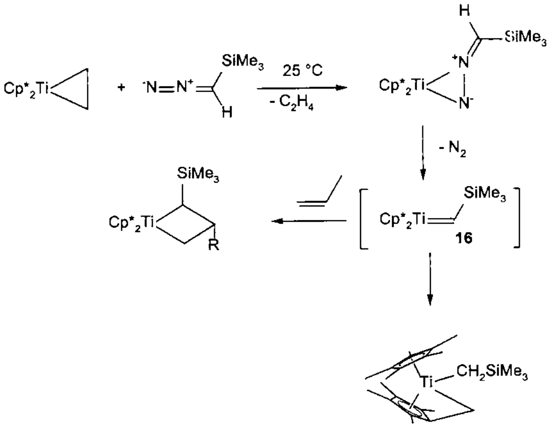
Analogous to many applications of salt metathesis reactions in organometallic chemistry, geminal M_2CR_2 species can be used to prepare carbene complexes in such a way that butyllithium reacts under mild conditions with diphenylcyclopropene to yield a 1,1′-dilithio-3,3-diphenylallene derivative, which can be reacted with



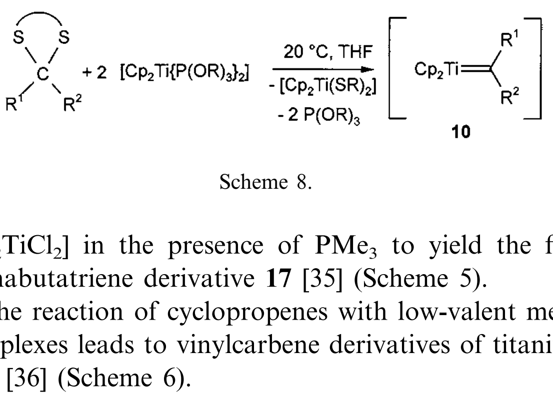
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

[Cp_2TiCl_2] in the presence of PMe_3 to yield the first titanabutatriene derivative **17** [35] (Scheme 5).

The reaction of cyclopropenes with low-valent metal complexes leads to vinylcarbene derivatives of titanium (**18**) [36] (Scheme 6).

By using a methylenecyclopropane derivative instead of cyclopropene, the bis-titanacumulene compound [$Cp_2Ti(PMe_3)=C=C=Ti(PMe_3)Cp_2$] (**19**) is formed in a complex reaction with [$Cp_2Ti(PMe_3)_2$] [37].

Diazoalkanes have long been used as synthons for both free carbenes and transition metal carbene complexes. In that area, Bergman et al. were able to prepare a diazoalkane complex [$Cp^*_2Ti(\eta^2\text{-}N_2CHSiMe_3)$] [34]. In subsequent reactions, the carbene intermediate **16** is formed. The latter can be trapped by olefins as well as intramolecular C–H bond activation reactions [33] (Scheme 7).

Additionally, Takeda et al. showed that thioacetales can be used by desulfurization as sources for alkylidene titanocene intermediates (**10**) [25–28] (Scheme 8).

2.2. Carbene complexes of the non-bent-metallocene type

There is considerable interest in the development of early transition metal complexes not based on metallocene derivatives. In this area, different kinds of amido [77], phosphido, and bulky alkoxides [78] become increasingly important. Selected carbene complexes of Group 4 metals exhibiting a cyclopentadienyl ligand or a functionalized cyclopentadienyl ligand as well as carbene complexes without Cp-ligands are summarized in Table 2.

2.2.1. Carbene complexes with N- and O-donor ligands

Carbene complexes are proposed as intermediates in the thermolysis of bulky alkoxy titanium alkyls (**45**) [79]. One of the first examples of a bimetallic titanium carbene complex without Cp-ligands (**46**) was prepared by Wilke et al. [80] (Table 2).

A new and unusual class of metal carbene complexes (**26**–**30**) is obtained from the reaction of bis(iminodi-(phenyl)phosphorane)methanes $CH_2(Ph_2P=NR_2)_2$ (R = Ad, $SiMe_3$) with alkyl and halides of Group 4 metals [9,81,82]. The preparation of these electron-deficient hydrocarbyl derivatives is described using different routes: (a) the metathesis reaction from the dilithio salt of the ligand with the metal tetrahalide [81], (useful for **26**, **27**); and (b) by alkane elimination in the reaction of the ligand with $ZrBz_4$ (**28**, **29**) (Scheme 9, path b) [82], as well as amine elimination from hafnium amides, forming **30** (Scheme 9, path c) [9].

The molecular structures of these complexes exhibit elongated P=N bond distances and shortened endocyclic P–C bond distances, while the exocyclic P–C bond distances are not affected. This suggests a strong π-electron delocalization in each four-membered ring, and the subsequent formulation of resonance forms with ylidic character to explain the nature of these species. In addition, these complexes show very short M=C distances (**26**: 2.008(4) Å [81]; **27**: 2.190(8) Å [81]; **28**: 2.208(3) Å [82]; **30**: 2.162(6) Å [9]) which are consistent with the multiple-bond character expected for a metal carbene.

The carbene carbon NMR resonance appears out of range to that observed for carbene complexes (**27**: $\delta = 101.7$; **28**: $\delta = 82.8$; **29**: $\delta = 84.7$ ppm) but in the region of ylide complexes. In the case of the titanium compound **26**, the same resonance ($\delta = 191.0$) lies outside of both regions. This feature, together with the

Table 2
Selected carbene complexes of Group 4 metals of the non-bent metallocene type

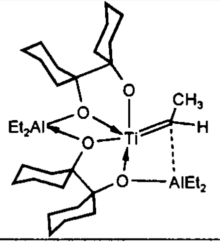
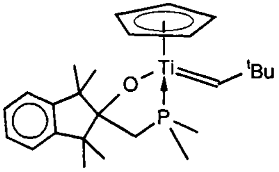
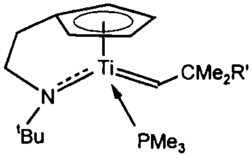
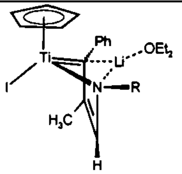
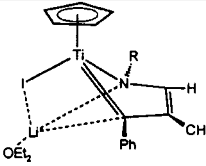
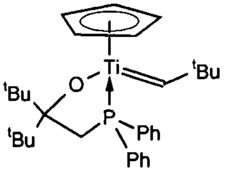
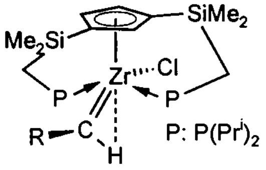
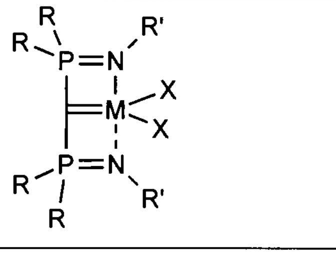
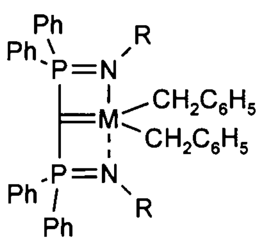
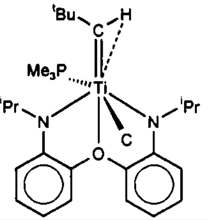
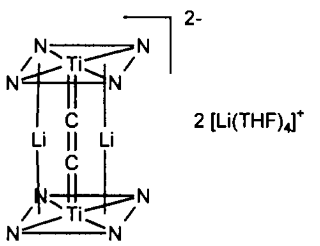
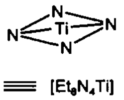
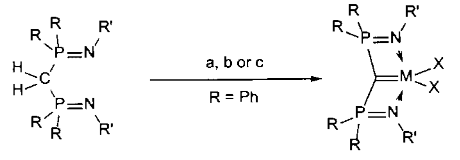
	Complex		Method	Comments	Ref
45	$[(ArO)_2Ti{=}CHC_6H_5]$		$[(ArO)_2Ti(CH_2C_6H_5)_2]$	intermediate	[79]
46			complex reaction	Ti=C 1.933(6) Å	[80]
36			$L_2Ti(CH_2CMe_3)_2$, 0°C, $-CMe_4$, dark green crystals	Ti=C 1.911(3) Å	[7]
43 **44**		R': Me, Ph	$(CpN)Ti(CH_2CMe_2R')_2$, R' = Me: 75 °C, 1.5 h, R' = Ph, 8.5 h, -RH, $+PMe_3$	**43**: δ6.39 (d, J_{PH} = 1.7 Hz), δ251.4 (dd, J_{CH} = 83.1 Hz)	[87]
33		*supine*-conformation	α-H-Elimination, red brown crystals, two different Li coordination modes in the solid state	Ti=C: 1.958(3) Å, δ244.69 (dd, J_{CH} = 83.1 Hz)	[84]
34		*prone*-conformation		Ti=C: 1.979(3) Å, δ 244.62	[84]
35			$L_2Ti(CH_2CMe_3)_2$, 0°C, $-CMe_4$, dark green crystals	δ12.4, δ287.3 (J_{CH} = 92 Hz)	[85]
38	 $[P_2Cp]Zr{=}C(H)RCl]$	R: Ph	$[P_2Cp]Zr(CH_2R)_2Cl$ -> $[P_2Cp]Zr{=}C(H)RCl$ + H_3CR (toluene, 95 °C, 6d)	**38** Zr=C 2.024(4) Å	[8]
39 **40**		R: CMe_3 R: $SiMe_3$		**40** Zr=C 2.015(9) Å	[88]
26		M: Ti	$H_2C(R_2P{=}NR')_2$ (R= Cy, Ph, R'= $SiMe_3$, Ad) a) + BuLi + $MCl_4(THF)_2$ (M: Ti, Zr)	pale yellow crystals, Ti=C 2.008(4) Å δ 191.0	[81]

Table 2 (*Continued*)

27		M: Zr		colorless crystals, Zr=C 2.190(8) Å, δ101.7	[81]
30		M: Hf	[MCl$_2${N(SiMe$_3$)$_2$}$_2$] + CH$_2$(R$_2$P=NSiMe$_3$)$_2$ (R= Cy, Ph), toluene refluxing	colorless crystals, 72-75 %, Hf=C 2.162(6) Å	[9]
28 **29**		M: Zr, R: Ad, SiMe$_3$	[Zr(CH$_2$C$_6$H$_5$)$_4$] + CH$_2$(R$_2$P=NR)$_2$ (R= Cy, Ph), toluene 70 °C, 24h	**28** yellow crystals, Zr=C 2.208(3) Å, ^{13}C NMR δ= 82.8, 84.7	[82]
32			[^{i}PrNON]Ti(CH$_2$CMe$_3$)$_2$], PMe$_3$, toluene, 45 °C, 12h	Ti=C 1.884(4) Å, δ= 3.00 δ= 229, J_{CH} 80 Hz	[83]
37		 [Et$_8$N$_4$Ti] = Octaethylporphyrine	[Et$_8$N$_4$Ti·2THF] + Li + C$_2$H$_4$	Ti=C 1.809(9), 1.757(7) Å	[86]



M: Ti, R' = SiMe$_3$; X = Cl	**26**
M: Zr, R' = SiMe$_3$; X = Cl	**27**
M: Zr, R' = SiMe$_3$, X = CH$_2$Ph	**28**
M: Zr, R' = Ad, X = CH$_2$Ph	**29**
M: Hf, R' = SiMe$_3$, X = Cl	**30**

a) + BuLi, + MCl$_4$(THF)$_2$ (M: Ti, Zr), - 2 BuH, - 2LiCl
b) + Zr(CH$_2$Ph)$_4$, - 2 H$_3$CPh
c) + HfCl$_2$[N(SiMe$_3$)$_2$]$_2$, toluene, 140 °C, - 2 HN(SiMe$_3$)$_2$

Scheme 9.

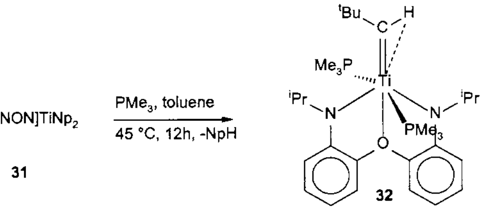
short Ti–C bond distance, suggests that the titanium species possesses more carbene character than the zirconium analogous, which displays a significant zwitterionic Zr$^{\delta+}$–C$^{\delta-}$ character.

Another example of a carbene complex that contains a tridentate ligand was isolated and characterized by Schrock et al. from the decomposition reaction of the titanium dialkyl complex, [^{i}PrNO]Ti(CHCMe$_3$)$_2$ (**31**). In the presence of an excess of PMe$_3$, this species generates the neopentylidene derivative, [^{i}PrNO]Ti(CHCMe$_3$)(PMe$_3$)$_2$ (**32**) [83] (Scheme 10).

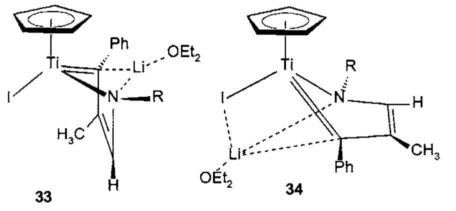
Complex **32** consists of a distorted alkylidene with a significant CH$_\alpha$ agostic interaction. The X-ray structure reveals a linear neopentylidene ligand (Ti–C–C = 179.3(3)°) with a short Ti–C bond distance (1.884(4) Å), due to the agostic interaction. The NMR data for **32**

(^{1}H: $\delta = 3.00$, ^{13}C $\delta = 230$, $J_{CH} = 80$ Hz) confirms this feature.

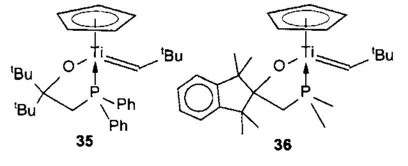
The chemistry of 1-aza-1,3-diene complexes, prepared from the reaction of $CpTiCl_3$ and magnesium in the presence of 1-aza-diene and subsequent reactions with MeLi/LiI, produces the five-membered ring complexes **33** and **34**. These complexes represent titanium alkylidenes, stabilized by conjugation with the C=C bond of the 1-aza-1,3-dien ligand. Both complexes exhibit in solution similar chemical shifts with values of $\delta = 244.69$ (**33**) and $\delta = 244.62$ (**34**) for the resonance of the alkylidene carbons [84]. However, these two complexes are significantly different in the solid state. X-ray structural studies show an overall geometry, best described as a five-membered-ring titanacycle CpTi(=C–C=C–N) with a prone conformation for **34** ($\theta = 68.2(2)°$) and a supine conformation for **33** ($\theta = 62.3(2)°$). The more important structural data are the short Ti=C bonds (**33**: 1.958(3) Å; **34**: 1.973(4) Å) (Scheme 11).



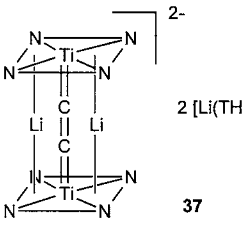
Scheme 10.



Scheme 11.



Scheme 12.



Scheme 13.

Carbene complexes with chelating P–O ligands are formed from the corresponding bis-alkyl derivatives [7,85]. The carbene complex **35** is obtained at temperatures below 5°C (^{1}H-NMR: $\delta = 12.4$; ^{13}C-NMR: $\delta = 287.3$) [85]. The phenyl group is metalated in solution. By using the ligand system of **36**, this metalation reaction can be avoided, and dark green crystals of the carbene complex **36** are obtained [7]. The Ti=C bond length (1.911(3) Å) is significantly shorter than that in the bisneopentyl starting material. The Ti=C–C angle of 158.7(2)° and the Ti=C–H angle of 85(3)°, in combination with a Ti–H distance of 2.05(5) Å, indicate also an α-agostic interaction in **36** (Scheme 12).

During the search for linear carbon chains between metal centers, Floriani et al. discovered a one-pot synthesis of a binuclear complex containing a C_2 bridge, starting from ethylene and an octaethylporphyrine derivative of titanium [86] (Scheme 13).

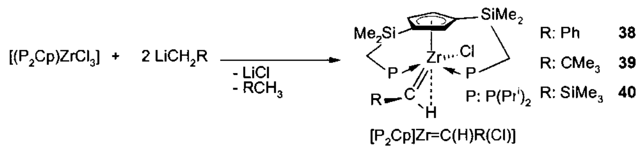
This paramagnetic ($\mu_{eff} = 1.80$ μ_B per Ti at 290 K) metallacumulene **37** forms red crystals exhibiting a linear Ti–C–C–Ti frame. The Ti=C distances (1.809(9), 1.757(7) Å) are significantly shorter than those of other [L_2Ti=C] derivatives (Tables 1 and 2).

2.2.2. Carbene complexes with functionalized cyclopentadienyl ligands

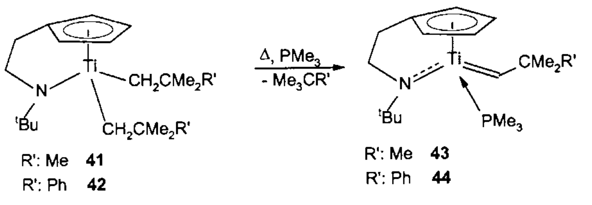
In view of the versatility showed by the [P_2Cp] ligand in the stabilization of the zirconium carbene complex [(P_2Cp)Zr=CHPh(Cl)] (**38**) [8], Fryzuk et al. tried to extend this syntheses to another alkylidene complex of zirconium, choosing two classical alkyl groups: neopentyl (CH_2CMe_3) and neosilyl (CH_2SiMe_3) [89,88].

The reaction of the starting complex [P_2Cp]$ZrCl_3$ with two equivalents of $LiCH_2R$ (R = CMe_3, $SiMe_3$) at − 78°C, and the subsequent thermolysis at 95°C generates the corresponding alkylidene complexes [P_2Cp]Zr=CHR(Cl) (R = CMe_3 (**39**), R = $SiMe_3$ (**40**)). The neopentylidene complex **39**, contaminated with side-products, shows in the ^{1}H-NMR spectrum, a singlet at $\delta = 8.56$ and in the ^{13}C-NMR spectrum, a triplet at $\delta = 209$ for the alkylidene group (Zr=*CH*CMe_3). The silyl analogue **40** could be determined by X-ray diffraction. The X-ray study of **40** reveals more significant features, such as a very short Zr–C bond distance (2.015(9) Å) and a *syn* orientation of the alkylidene fragment. In this way, the hydrogen atom lies below the metal center to form an agostic C–H interaction (Zr···H 2.28(8) Å). This situation is similar to that found in the alkylidene complex **38** reported previously. The spectroscopic data for **40** displays a singlet at $\delta = 8.99$ in the ^{1}H-NMR and a triplet at $\delta = 225$ in the ^{13}C-NMR for the alkylidene group (Zr=*CH*$SiMe_3$) (Scheme 14).

Mechanistic studies made for these complexes reveal that the fast rate-determining α-abstraction of the alkyl groups follow the order of benzyl > neosily > neopentyl, which is inverse to that that appears in the litera-



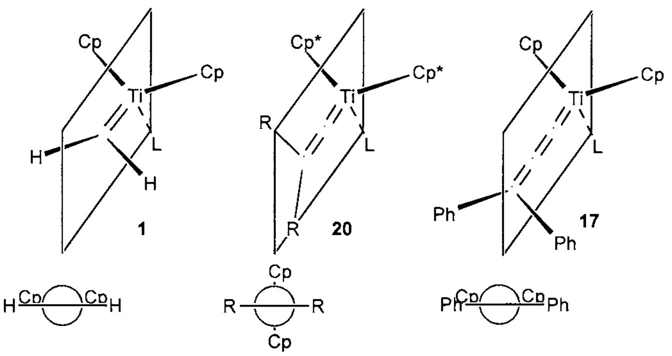
Scheme 14.



Scheme 15.

ture. This fact is explained by the steric crowding imposed by the alkyl ligands together with the sidearm phosphines in the ancillary ligand.

Teuben et al. reported that the thermal decomposition of the amido-functionalized cyclopentadienyltitanium bis(alkyl) complexes (**41**, **42**) in the presence of PMe_3, results in the formation of neopentane and the neopentylidene complex $\{\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2N\text{-}^tBu\}Ti{=}C(H)CMe_2R'{\cdot}PMe_3$ (R′: Me **43**, Ph **44**) [87] (Scheme 15).



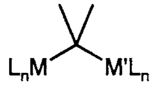
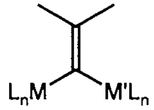
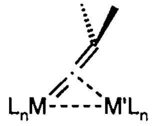
Scheme 16.

The starting alkyl complexes **41** and **42** undergo α-H-abstraction. The ^1H- and ^{13}C-NMR resonances of the alkylidene moiety in **43** are $\delta = 6.39$ and 251.4 ($J_{CH} = 83.1$ Hz), respectively.

3. Structure types of carbene complexes of titanium group metals

While alkylidene complexes are especially common for Group 5 and 6 metals, those of Group 4 have been limited to a few hafnium [9] or zirconium derivatives [8,68,81,88–90] and a handful of isolable titanium examples [7,30,36,81,83,84,87]. The majority of the latter has been generated in situ [10]. Different types of carbene complexes as well as intermediates of early transition metal carbene complexes were observed. As

Table 3
Selected data of heteronuclear carbene complexes

	Complex type	L_nM	L_nM'	Comments	Ref.
μ-Methylene complexes					
		Cp_2TiX	Rh(COD)	X-ray structure	[96-98]
		Cp_2TiCl	$Pt(PPhMe_2)Me$	X-ray structure	[99]
5		Cp_2TiCH_2	$TiCp_2$	no structure	[100, 101]
		Cp_2TiCH_2	$SiMe_2$	X-ray structure	[72]
3		Cp_2TiCl	$AlMe_2$	X-ray structure, disordered	[102]
μ-Vinylidene Complexes (1,1-dimetallaolefine)					
		Cp_2TiCl	AlR_2	intermediate, calculations	[103-105]
		Cp_2TiCl	CuR		[106]
		Cp*Ti(*μ*-O)	Cp*Ti		[107]
μ-Vinylidene Complexes (*semi*-bridged, *side-on* bridged)					
		Cp^*_2TiCl	$Au(PPh_3)$	X-ray structure	[52]
		Cp^*_2TiCl	$CuPR_3$	NMR-Data	[52]

expected from the M–C bond order, [L_nTi=C] derivatives exhibit higher bond energies than [L_nTi–C] complexes [91], which increases with the rotational barrier [92]. For [L_nM=C] complexes, a coplanar orientation of the substituents on the M–C bond was found by different calculations [93–95]. In the cumulogous complex **20**, only the C=CH_2 rotamer shown allows a TiCα π-bond (back bonding). In accordance with this, model calculations yield a rotational barrier of 134 kJ mol^{-1} [43]. For the titanaallenyliden **17**, no structural dynamics are observed, and NMR data indicate that all C atoms of the cumulene lie in the mirror plane of the molecule [35] (Scheme 16).

Detailed ab initio calculations by Cundari and Gordon show that the contributions of nucleophilic and neutral resonance structures to the description of the Ti=C bonds are dominant [92,94,95].

In a series of binuclear carbene complexes, different coordination modes of methylidene and vinylidene reagents were found. Some examples are given in Table 3. Some of the μ-methylene complexes do not only act as more or less activated [Ti=CH_2] equivalents, but can undergo a variety of different subsequent reactions [96].

4. Reactivity of carbene complexes of titanium group metals

Carbene complexes of early transition metals characterized by nucleophilic carbene carbon properties, belong to the general class of Schrock-type carbene complexes [93,108,109]. The high reactivity is well founded to the electrophilic and oxophilic nature of the transition metal center in combination with the nucleophilc α-carbon atom.

Due to the nucleophilic nature of the α-carbon atom, particularly with electrophiles, fast reactions are observed. Some examples are given for the titanaallene [Cp^*_2Ti=C=CH_2] (**20**).

As shown in Scheme 17, **20** reacts with water, alcohols [49], acidic ketones [47], and terminal acetylenes induce fruit ripening with exogenous C_2H_4 application [53,60], as well as acidic Schiff bases [61] to afford the corresponding vinyl complexes.

The most important applications of carbene complexes of titanium group metals lie in the areas of organic synthesis and catalytic reactions, such as carbonyl olefination, and the generation of cyclopropane derivatives by oxidation of metallacyclobutanes and cyclopropanation, as well as in the preparation of heterocyclic four-membered ring compounds and for ring-opening polymerization to obtain special materials [110–112], such as 'living' [113,114] or 'conducting' [115] polymers. In the following sections, some selected examples will be given to document the principles in this chemistry [10].

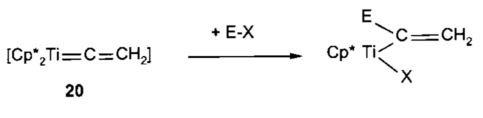
4.1. [2 + 1] Addition reactions

The titanaallene intermediate [Cp^*_2Ti=C=CH_2] (**20**), obtained via methane elimination from [Cp^*_2Ti(CH=CH_2)Me] (**23**), which reacts with 2,6-dimethylphenylisonitrile (ArNC) in a 1:2 ratio affords the first isolated and characterized azabutatriene complex of titanium, [Cp^*_2TiC(CNAr)(η^2-H_2C=C=C=NAr) (**48**). The expected symmetrically coordinated azabutatriene ligand (**47**) is not detectable [116] (Scheme 18).

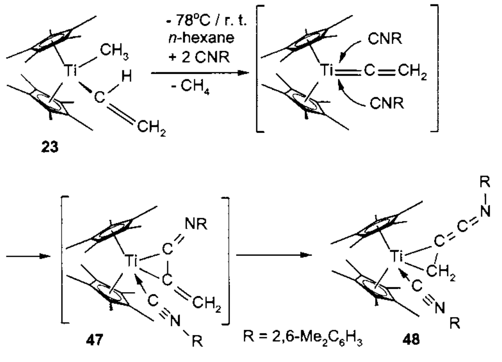
The structure of **48** (Fig. 1) exhibits a pseudo-pentacordinate geometry consisting of an isonitrile molecule and an η^2-C,C-azabutatriene moiety in the equatorial plane of the Cp^*_2Ti fragment. Consequently, the C2–Ti–C12 angle is enlarged to 108.66(8)°. The coordination of the azabutatriene fragment to the titanium centre occurs through the C_1 and C_2 atoms of the heterocumulene, exhibiting a structural situation similar to those observed in the titanium olefin complex [Cp^*_2Ti(η^2-C_2H_4)]. However, whereas the olefinic C–C bond appears shorter (**17**: Ti–C1 2.249(2), Ti–C2 2.200(2), C1–C2 1.424(3); Cp^*_2Ti(η^2-C_2H_4): Ti–C 2.160(4), C–C 1.438(5)), the Ti–C bond distances compare well with the ethylene complex. These features are consistent with a weaker back-donation in **48** due to the presence of the isonitrile as a further π-acceptor ligand [116].

The treatment of the titanaallene species **20** with three equivalents of ArNC leads to the five membered ring complex **49** (Scheme 19) [116].

The X-ray diffraction analysis of **49** displays a planar metallacyclopentane in which the titanium can be considered as pseudotetrahedric, showing Ti–Cp* distances



Scheme 17.



Scheme 18.

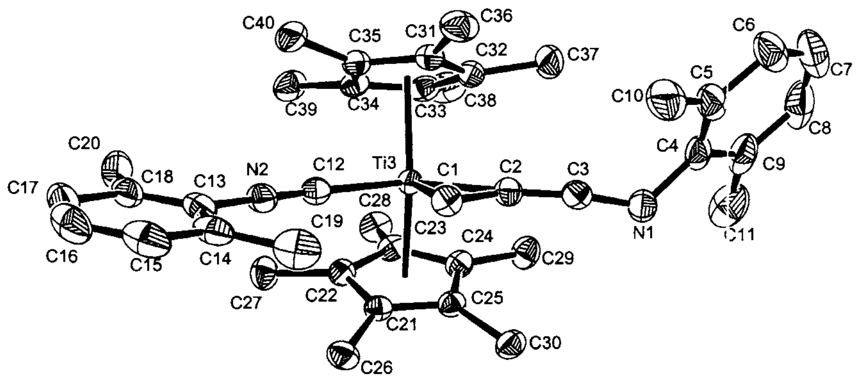


Fig. 1. Molecular structure of (**48**). Selected bond lengths (Å) and angles (°): Ti–C1 2.249(2), Ti–C2 2.200(2), Ti–C12 2.098(2), Ti–Cp$^{*}_{\text{Cent}}$ 2.149, 2.135, C2–C3 1.264(3), N1–C3 1.262(3), N2–C12 1.167(3), N1–C4 1.418(3), N2–C13 1.405(3); C12–Ti3–C2 108.66(8), C12–Ti–C1 71.37(8), C2–Ti–C1 37.31(8), N2–C12–Ti 178.24(18), C1–C2–Ti 73.2412, N1–C3–C2 170.7(3), C3–C2–Ti 138.23(19), C–C2–C1 148.1(2), C2–C1–Ti3 69.46(12), C12–N2–C13 173.7(2), C3–N1–C4 123.5(2), Cp$^{*}_{\text{Cent}}$–Ti–Cp*2$_{\text{Cent}}$ 140.2

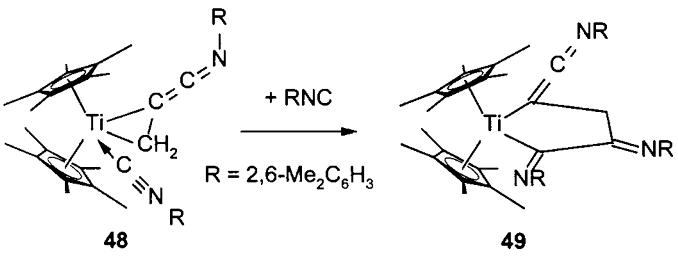
of 2.106 and 2.114 Å, and a Cp*–Ti–Cp* angle of 137.3° (Fig. 2) [116]. The Ti1–C1 and Ti1–C4 bond distances of 2.176 (2) and 2.275(2) Å, respectively, correspond to a single Ti–Csp^2 bond and compare well with other five membered ring compounds. The exocyclic double-bond lengths N1–N5 (1.241(3) Å), N2–C3 (1.258(3) Å), N3–C4 (1.278(3) Å) and C1–C5 (1.289(4) Å) lie in the expected range.

According with the spectroscopic and structural data, the formation mechanism of **49** can be explained by the insertion of two molecules of isonitrile into the Ti–CH$_2$ bond of the η^2-C,C-azabutatriene moiety in complex **48**.

4.2. *[2 + 2] Addition reactions*

The reactivity of [L$_n$Ti=C] derivatives with olefins and alkynes represents a potential way to prepare [2 + 2] cycloaddition compounds [23,24,117]. However, the ability of these species to undergo cycloreversion or electrocyclic-ring opening reactions have made the isolation of most of them unsuccessful.

The synthetic routes developed by direct interaction of the titanocene vinylidene intermediate [Cp$^{*}_{2}$Ti=C=CH$_2$] (**20**) with different unsaturated substrates (carbon dioxide, ketenes [44,45], isocyanides [116], transition-metal carbonyls [48], nitriles [50], phosphoalkanes [50], alkynes [53], carbodiimides [57], and cumulenes [118]), have allowed the preparation, isolation and characterization of a large variety of thermally stable four-membered titanacycle complexes. This stability is attributed to the reduced electrophilicity of the titanium center due to the Cp* ligands. The regiochemistry of these reactions can be explained in terms of the polarity of the unsaturated fragment employed in the cycloaddition. Large differences in the partial charge of the unsaturated substrates leads to stereochemically pure compounds, while small differences in their partial



Scheme 19.

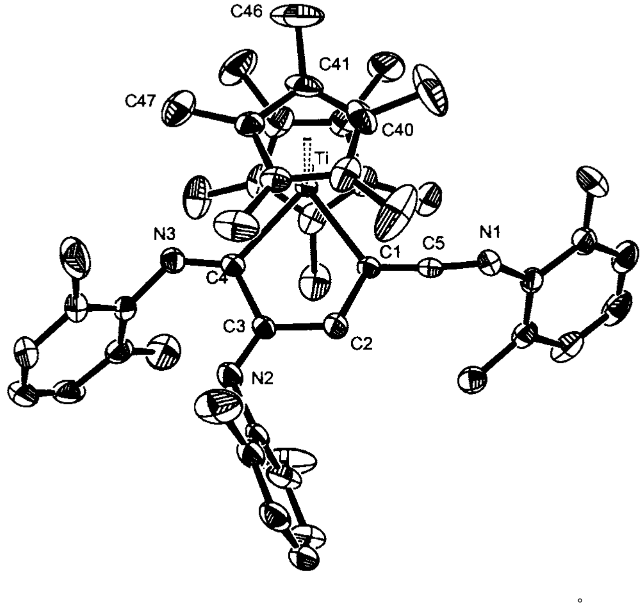
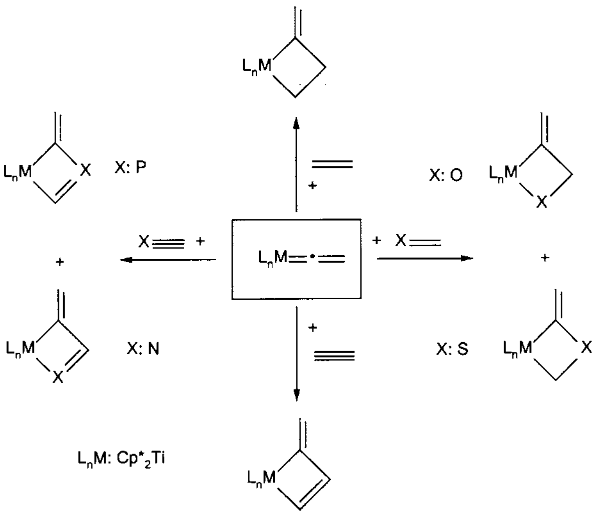


Fig. 2. Molecular structure of (**49**). Selected bond lengths (Å) and angles (°): Ti–C1 2.176(2), Ti–C4 2.275(2), Ti–Cp$^{*}_{\text{cent}}$ 2.106, 2.114, C1–C2 1.520(3), C2–C3 1.500(4), C3–C4 1.534(3, C1–C5 1.289(4), C5–N1 1.241(3), C3–N2 1.258(3), C4–N3 1.278(3), C4–Ti–C1 79.39(9), Ti–C1–C2 114.15(18), C1–C2–C3 114.9(2), C2–C3–C4 116.4(2), C3–C4–Ti 111.20(15) Cp$^{*}_{\text{cent}}$–Ti–Cp$^{*}_{\text{cent}}$ 137.3

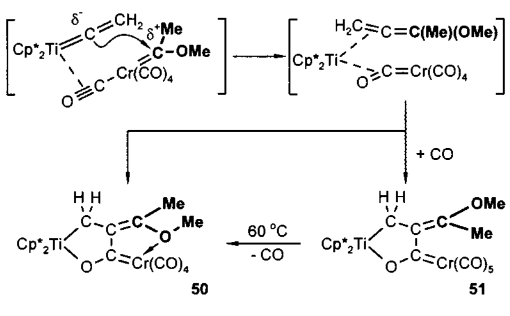


Scheme 20.

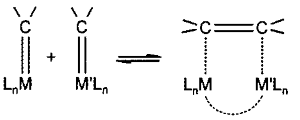
charges carry out to regioisomers, as shown for the cycloaddition of $[Cp^*_2Ti{=}C{=}CH_2]$ (**20**) with acetylenes [53]. With nitriles only one regioisomer is observed, whereas with phosphaalkynes two isomers are formed [50]. With carbonyl compounds, regioselective cycloadditions are found as expected under the formation of titanaoxetanes, whereas with RNS derivatives both isomers are observed [55]. By using CS_2, only the regioisomer with sulfur in the β-position of the four membered titanacycle is found [119], as a result of the thiophilic properties of carbanions [120,121] (Scheme 20).

Analysis of the structural data for the four-membered metallacyclic compounds shows for all α-methylentitanacycle, a planarity of the four-membered ring which is favored by the sequence of sp^2-hybridized ring atoms. A selection of the more relevant bond lengths and angles are collected in Table 4.

The reaction of the α-C-nucleophilic vinylidene complex $[Cp^*_2Ti{=}C{=}CH_2]$ (**20**) with the electrophilic methoxymethyl carbene complexes $(CO)_5Cr{=}C(OCH_3)R$ ($R = CH_3$, CH_2CH_3) leads to the heterodinuclear complexes **50** and **51**. The formation of **50** and **51** can be described by the intermolecular coupling of inversely polarized carbene ligands [54] (Scheme 21).



Scheme 21.



Scheme 22.

This intermolecular carbene–carbene metathesis can be extended to other carbene–carbene combinations [59] (Scheme 22).

4.3. Further reactions

Reactivity studies of the zirconium alkylidene complexes $[P_2Cp]Zr{=}CHR(Cl)$ ($R = Ph$ **38**, $SiMe_3$ **40**, $[P_2Cp] = \eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2P^iPr_2)_2$) with ethylene gives complex **50**, whereas with acetone the alkene $RCH{=}CMe_2$ is liberated. The expected oxo-zirconium species (**53**) could not be isolated from the solution. Carbon monoxide and isonitrile undergo insertion reactions to ketene (**51**) as well as ketenimine complexes (**52**) [89] (Scheme 23).

5. Selected application of carbene complexes of titanium group metals

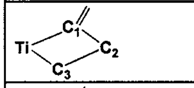
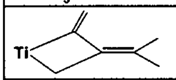
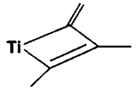
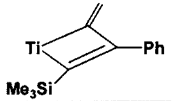
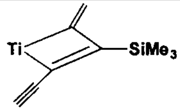
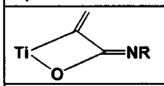
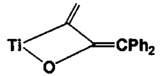
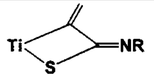
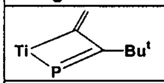
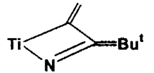
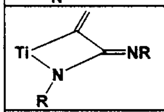
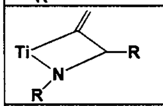
Carbene complexes of titanium group metals, especially the $[Cp_2Ti{=}CR_2]$ intermediates, represents convenient reagents which can be used for a wide variety of transformations in stoichiometric organic chemistry as well as catalytic reactions, e.g. ring opening polymerization [12–14,112,123]. In the following section, several selected examples will be given.

5.1. Carbene complexes in organic syntheses

Esters, ketones, amides, and other carbonyl compounds can be methylenated using three different titanium-based reagents: the Tebbe reagent, titanacyclobutanes and dimethyltitanocene, an old reagent as shown by Petasis to be effective for olefinations [12,124]. Several different mechanisms have been proposed for olefinations with these reagents. For dimethyltitanocene, the role of the carbene intermediate $[Cp_2Ti{=}CH_2]$ was proved by detailed kinetic investigations [22].

The use of active organometallics species in catalytical reactions, in particular carbenoid complexes, has opened new perspectives in organic chemistry. In this context, we have paid attention to two of these important processes in the building of organic molecules: carbonyl olefination and vinylcyclopropanation assisted by titanium carbene complexes.

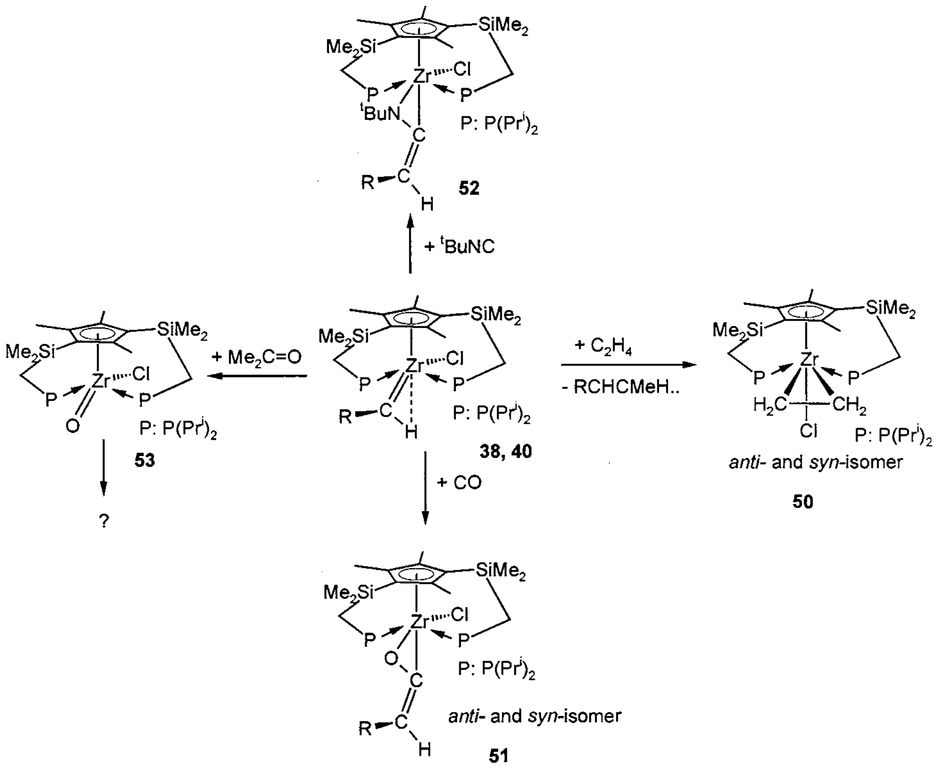
Table 4
Selected distances (Å) and angles (°) of four membered titanacycles derived from the [Cp$^*_2$Ti=C=CH$_2$] intermediate (**20**)

Compound	Ti-C$_1$	Ti-C$_3$	C$_3$-C$_2$	C$_1$-C$_2$	Ti-C$_2$	C$_1$-Ti-C$_3$	C$_1$-C$_2$-C$_3$	Ref.
	2.068(6)	2.137(7)	1.520(10)	1.521(10)	2.47	83.1(4)	115.1	[43]
	2.139(9)	2.208(8)	1.542(12)	1.439(13)	2.62	68.20(17)	109.6(3)	[118]
	2.104(3)	2.109(3)	1.365(4)	1.434(4)	2.50	68.0(1)	114.8(2)	[53]
	2.102(6)	2.173(6)	1.352(8)	1.502(7)	2.50	69.3(2)	116.7(5)	[53]
	2.110(3)	2.111(3)	1.367(4)	1.495(5)	---	68.5(1)	112.1(3)	[56]
	2.121(3)	1.983(2)	1.348(3)	1.477(4)	2.52	67.6(1)	107.9(2)	[44]
	2.119(6)	1.966(3)	1.362(7)	1.466(8)	2.53	67.5(2)	106.9(5)	[51]
	2.156(3)	2.466(1)	1.795(3)	1.484(5)	2.81	70.45(9)	109.2(2)	[55]
	2.161(5)	2.504(2)	1.701(5)	1.473(7)	2.80	68.2(1)	111.6(3)	[50]
	2.134(2)	2.017(2)	1.290(3)	1.485(3)	2.48	67.85(8)	113.2(2)	[50]
	2.129(3)	2.084(2)	1.374(4)	1.505(4)	2.64	65.8(1)	10.1(2)	[57]
	2.127(6)	2.046(4)	1.468(6)	1.554(7)	2.64	68.65(19)	102.3(4)	[122]
Ti = Cp*$_2$Ti								

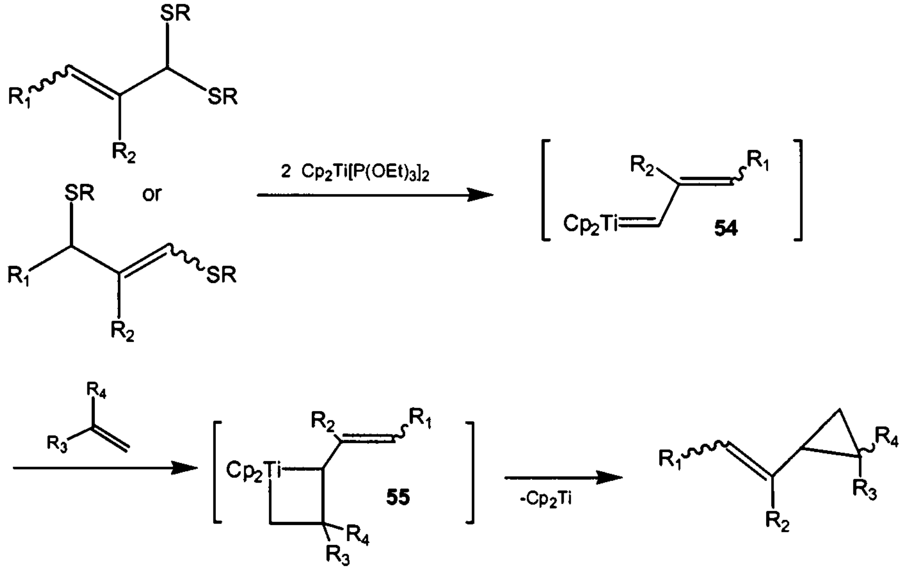
In general, the two usual routes to synthesize vinylcyclopropanes are the reaction of metal–carbene complexes or carbenes with dienes, and reacting Wittig reagents with cyclopropylketones or cyclopropanecarbaldehydes. These methods involve disadvantages (multistep reactions and limitations by the nature of the substituent on the cyclopropane ring) which can be solved by the use of organometallic reagents.

The preparation of vinylcyclopropanes, initially by treatment of unsaturated thioacetals or analogous with titanocene–olefin complex Cp$_2$Ti(π-CH$_2$=CR$_1$R$_2$), was improved by using the alkene-free titanocene Cp$_2$Ti[P(OEt)$_3$]$_2$ [28]. Results showed that the most likely intermediate formed in this reaction should be the vinylcarbene complex of titanium **54**, which then reacts with an alkane to give the vinylcyclopropane via the titanacyclobutane intermediate **55**. In addition, the yield of the vinylcyclopropane depends on the steric bulk of groups near to the double bond of the alkene [26] (Scheme 24).

The same low-valent titanium species, Cp$_2$Ti-[P(OEt)$_3$]$_2$, assists the reductive olefination of thioacetals (Scheme 25). One of the possibilities considered to explain the mechanism of this reaction involves a carbene complex of titanium **10** as a key intermediate, which reacts with a carbonyl compound to form an olefin via the oxatitanacyclobutane **55** [25].



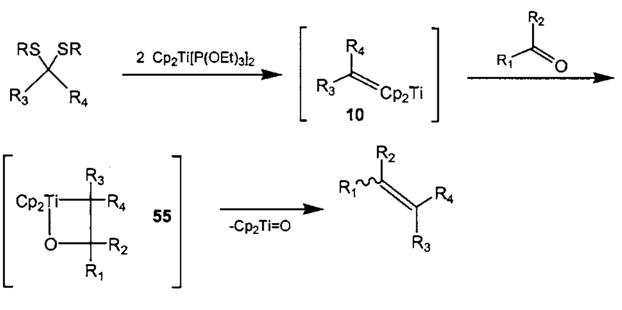
Scheme 23.



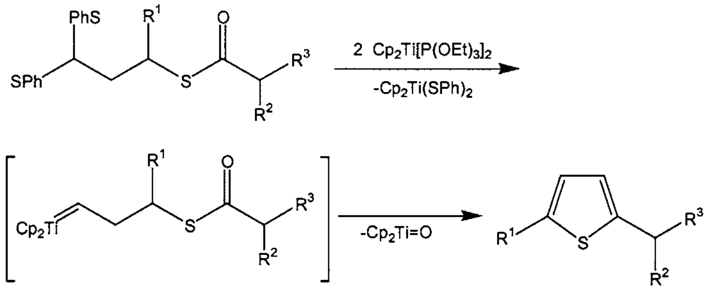
Scheme 24.

Recently, Takeda et al. have reported the preparation of 5-substituted 2,3-dihydrothiophenes by intramolecular carbonyl olefination of thioesters using the thioacetal $Cp_2Ti[P(OEt)_3]_2$ system (Scheme 26). It assumes that the key intermediate of the transformation is a titanium–carbene complex [27].

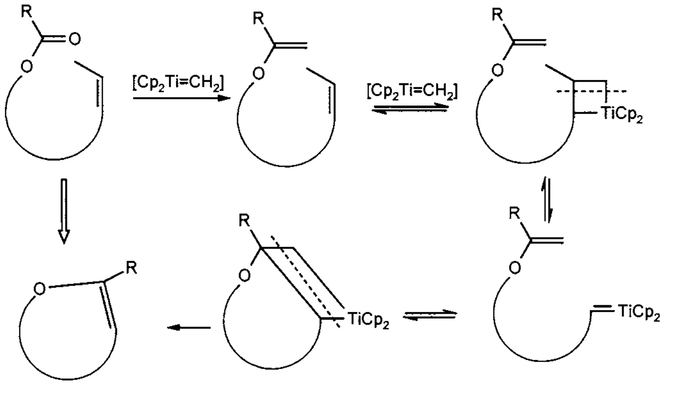
Titanium–carbene complexes are also used for the conversion of olefinic esters to cyclic enol ethers with Tebbe-type reagents [125]. This procedure can be extended to a powerful tool for the construction of com-



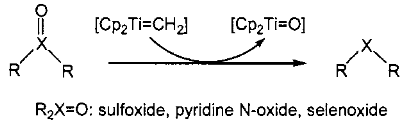
Scheme 25.



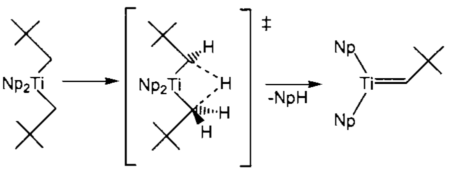
Scheme 26.



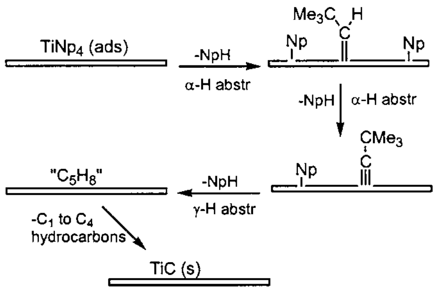
Scheme 27.



Scheme 28.



Scheme 29.



Scheme 30.

plex polycyclic frameworks and/or extended hydroxy olefins using simple functional groups as coupling partners in ring closing. Total synthesis of natural and designed molecules of the marine biotoxin family are reported (Scheme 27) [125].

The use of Tebbe and Petasis reagents as effective agents of carbonyl olefination, has lead Nicolau et al. to discover a novel synthetic method by which deoxygenated sulfoxides and selenoxides as well as 2-methylpyridines can be prepared by an unprecedented carbene-initiated deoxygenation mechanism [126]. A significant feature of these reactions is the mild conditions under which deoxygenation occurs even in the presence of numerous functional groups (Scheme 28).

5.2. Carbene complexes in material sciences

In order to study the mechanism responsible for the conversion of [Ti(Np)$_4$] into titanium carbide under CVD (chemical vapor deposition) conditions, Girolami et al. developed, in parallel the study of the thermolysis of tetraneopentyltitanium in solution [127]. The thermolysis of [TiNp$_4$] in solution points to an intramolecular α-hydrogen abstraction process to give a titanium alkylidene complex irrespective of the medium. Neopentane is the predominant organic product (Scheme 29). Afterwards, the titanium alkylidene reacts with the hydrocarbon solvent. Diverse alkylidene trapping experiments were unsuccessful, which demonstrates that these species decompose almost as fast as they are generated.

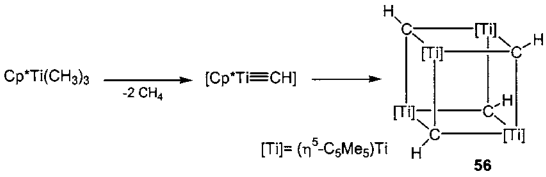
An extrapolation of these results to the growth of TiC films from TiNp$_4$ under CVD conditions at 250°C, demonstrates that the first step is the same as in solution: the α-hydrogen abstraction to form neopentane and a titanium alkylidene intermediate (Scheme 30) [128].

Recently, Wu et al. have extended the chemical vapor deposition study to neopenthylzirconium [$ZrNp_4$]. The results show that, while for [$TiNp_4$], the α-hydrogen abstraction is clearly favorable, [$ZrNp_4$] undergoes γ-hydrogen elimination [42].

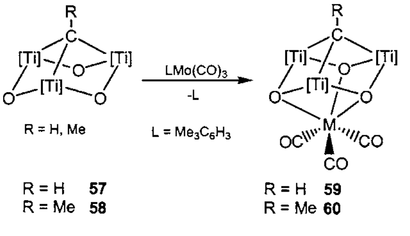
6. Miscellaneous

As shown for the thermal degradation of titanium alkyl bonds from $Ti–CH_3 > Ti{=}CH_2$, $Ti{\equiv}C–H$ as well as TiC species, molecular chemistry of titanium carbyne intermediates should be accessible. Indeed, Mena et al. showed that the thermal treatment of [$(\eta^5\text{-}C_5Me_5)TiMe_3$] (24 h, 120°C) forms a methylidyne cubane **56**, as dark brown crystals (74% yield) via a [$Cp^*Ti{\equiv}C–H$] intermediate [129]. The ^{13}C-NMR spectra of this novel compound exhibits a surprisingly downfield shift of the alkylidyne carbon signals at $\delta = 490.8$. The solid-state determination study of **56** describes the complex as a nearly perfect cube with C–Ti–C angles very closed to 90° (Scheme 31).

In further investigations the formation of μ_3-alkylidyne groups supported by a titanium oxide without a metal–metal bond, [$\{TiCp^*(\mu\text{-}O)\}_3(\mu_3\text{-}CR)$] (R = H **57**, Me **58**), is reported [130]. The μ_3-carbyne ^{13}C signals are observed at a very low field ($\delta(\mu_3\text{-}CH) = 383.2$ (**57**), $\delta(\mu_3\text{-}CMe) = 401.7$(**58**)), as well as in the heterometallic cubanes **59** and **60**, ($\delta(\mu_3\text{-}CH) = 410.3$ (**59**), $\delta(\mu_3\text{-}CMe) = 434.8$ (**60**)) [131]. The reactivity exhibited by these species against metal carbonyl hydrides [132], isonitriles, carbon monoxide [133] as well as ketones [107] with direct participation of the alkylidyne units, demonstrates the nucleophilic character of the alkylidene moiety. Such types of complexes exhibiting a pre-cubane structure, constitute potential species, e.g. for surface geometries in heterogeneous catalysis, as it is shown in the formation of the heterocubanes **59** and **60** by reaction with transition metal carbonyls [131] (Scheme 32).



Scheme 31.



Scheme 32.

7. Conclusions

Beginning with the titanium–carbon σ-bonds as chemical curiosities with the pioneering work of Herman [134,135] and Clauss [5,136,137], the formation of titanium group metal carbene complexes over the last five decades has shown us a chemistry of fascinating species which are involved in many reactions of high synthetic interest. During the last decade, our understanding of Group 4 metal carbene chemistry has improved dramatically with the syntheses of new carbene complexes and applications in other fields [138]. The first chemistry on titanium carbyne intermediates shows, that 'high temperature' organometallic chemistry has a great potential for developing new complexes and new structure types. Up to now the molecular chemistry of titanium carbides is still open.

8. Abbreviations

Cp	C_5H_5
Cp*	$C_5(CH_3)_5$
P_2Cp	$C_5H_3(SiMe_2CH_2PPr^i_2)_2$
Me	CH_3
Bz	$C_6H_5CH_2$
^{i}Pr	$(H_3C)_2CH$
^{t}Bu	$(H_3C)_3C$
Np	$(H_3C)_3CCH_2$
Ad	adamantyl

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