DALTON
PERSPECTIVE

C_2 Building blocks in the co-ordination sphere of electron-poor transition metals. Aspects of the chemistry of early-transition-metal carbenoide complexes†

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Our understanding of the chemistry of the transition-metal–carbon σ bond is improved by investigations of the chemistry of alken-1-yl complexes of electron-poor transition metals. There is no other system known in which we can easily switch between the possible reaction pathways, depending on the nature of the metal, the ligands L and the alken-1-yl group. Only reductive elimination, α- and β-H elimination reactions give high selectivity. α-Hydrogen elimination from $Cp^*_2Ti(CH{=}CH_2)R$ ($Cp^* = \eta\text{-}C_5Me_5$) derivatives leads to the versatile titana–allene intermediate $[Cp^*_2Ti{=}C{=}CH_2]$ **8**. A wide range of cycloaddition products of high thermal stability can be prepared using **8**. In reactions of **8** with copper and gold complexes, heterodinuclear μ-vinylidene compounds, $Cp^*_2Ti(\mu\text{-}C{=}CH_2)(\mu\text{-}X)M'L$, are formed. Additionally the first examples of intermolecular carbene–carbene coupling reaction of a Fischer- and a Schrock-carbene ligand are reported by using the strong nucleophilic vinylidene fragment **8**.

The possibility of stabilising highly reactive intermediates as well as short-lived molecules is one of the great advantages of organometallic chemistry, located on the borderline between organic and inorganic chemistry.[1,2] Well known examples are illustrated in Scheme 1. The formal co-ordination of carbenes to metal fragments, was first achieved in Fischer- and Schrock-type complexes,[3] but more recently, stable carbenes in the form of imidazol-2-ylidene ligands,[4,5] have been co-ordinated to transition metals to give well characterised complexes.[6] Cyclobutadiene, vinylidene and aryne molecules can be well stabilised in the co-ordination sphere of transition metals, leading to compounds which can be handled under acceptable conditions.

This knowledge of structure and bonding relationships has developed our understanding of organometallic chemistry and led to useful applications of organometallic reagents in organic synthesis and catalysis. In many cases the actual reactive species, which participates in further reactions, must be generated in the first reaction step from the corresponding organometallic sources. In connection with this, I want to draw the attention of the reader to such complexes of titanium-group metals, which are characterised by the primary formation of an intermediate exhibiting a titanium–carbon double bond.[7] Especially starting from alken-1-yl transition-metal complexes the general reactivity of a transition-metal–carbon σ bond can be well understood.[8]

The generation of an M−C double bond in a primary reaction step can occur from quite different types of starting molecules. Some schematic drawings are given in Fig. 1. Complexes which act as primary sources of carbene complexes or intermediates, will henceforth be referred to as '*carbenoide transition metal*' complexes. Different types of titanium-group metal complexes characterised by primary carbene complex formation are known.[9] Sometimes, such carbene complexes exist in the form of isolable molecules[10–13] or occasionally in the form of intermediates.[7,14–16] Reactants which are characterised by primary titanium carbene complex formation are the Tebbe reagent **1**,[9] the Takai reagent **2**,[17,18] metallacyclobutanes **3**[19–21] or complexes exhibiting Schrock-type reactivity (**4**).[22] For the generation of Ti=C intermediates, Me_2AlCl must be removed by bases (pyridine) if **1** is used as the starting material,[19] additional reducing agents must react with **2**,[17] olefins must be thermally liberated when **3** is used,[19,23] and with **4**, α-H elimination of hydrocarbons must occur.[24–26] These reactions can be formally defined as 1,2-eliminations. Other sources of Ti=C species exist, including diazo compounds,[27] small cyclic olefins[28] and 1,1-dilithio compounds.[29]

On the other hand, carbenoide complexes of main-group metals, as investigated by Boche and co-workers (**5** and **6**), are characterised by the possibility of 1,1-elimination reactions and carbene intermediate formation thereof.[30–33] Depending on the nature of the metal, the leaving group (LG), and the reaction conditions, electrophilic as well as nucleohilic properties of the carbon centre are observed.[30,31]

For several years we have been interested in the chemistry of early-transition-metal complexes, exhibiting M−C double bonds in a cumulative unit. During the experimental work on my habilitation thesis we observed the easy transformation of vinyl complexes **7** *via* ($Cp^* = \eta\text{-}C_5Me_5$) vinylidene intermediates **8** and **9** to a metallacyclobutane **10**.[34,35] This reaction is characterised by the selective transfer of a proton from one vinyl group to the other. In contrast to the well developed chemistry of metalla–allenes of late transition metals,[36] the observation of the transformation **7**→**10** was the first discovery in the new research field of vinylidene chemistry of early transition metals.[37,38] Petasis and Bzowej[22] reported the successful use of simple Cp_2TiMe_2 ($Cp = \eta\text{-}C_5H_5$) in carbonyl olefination reactions **11**→**12**. It was the first instance of use of Ti=C intermediates in organic synthesis.[7] The greatest advantage of this method lies in the application of substituted and functionalised alkylidenes.[39–41] A detailed study of the thermolysis of $Cp^*_2TiMe_2$ *via* a $[Cp^*_2Ti{=}CH_2]$ intermediate has been published,[42] but at that time, attempts to trap the carbene intermediate were unsuccessful.

Alken-1-yl Ligands in the Co-ordination Sphere of Early Transition Metals

By comparison of the thermal stability of the vinyl, phenyl and alkyl complexes of titanium-group metals, it becomes obvious that the vinyl derivative is the most reactive one.[8] As well as α-

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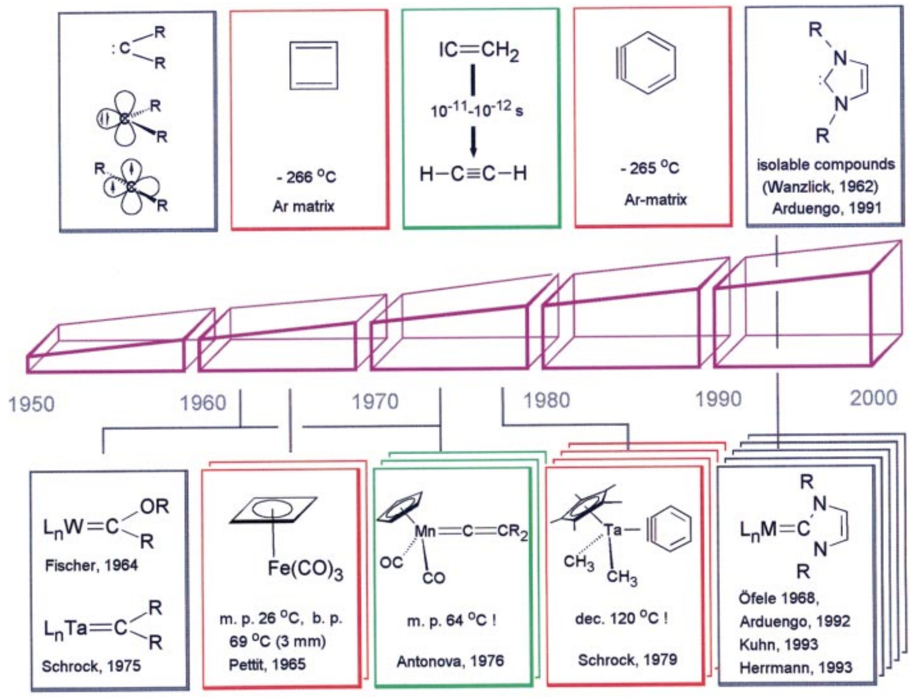
† Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday.



Scheme 1

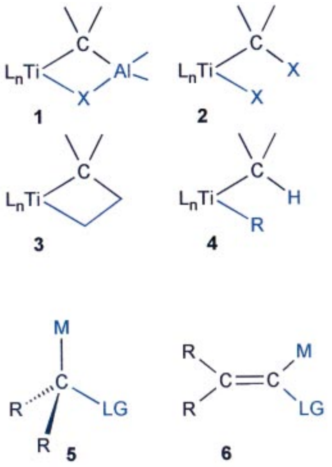
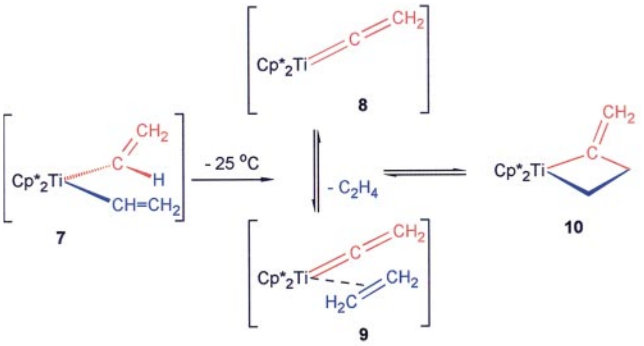


Fig. 1 Organometallic sources of Ti=C intermediates (carbenoide complexes **1**–**4**) (**1** Tebbe reagent; **2** Takai reagent; **3** metallacyclobutanes; **4** complexes of Schrock-type reactivity), and main-group metal carbenoides **5** and **6** bearing leaving groups and metal atoms on the same carbon atom



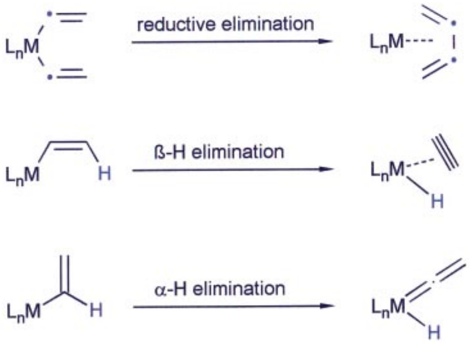


Fig. 2 Schematic drawing of possible subsequent products obtained from vinyl complexes of titanium-group metals

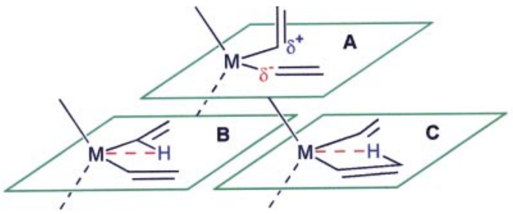
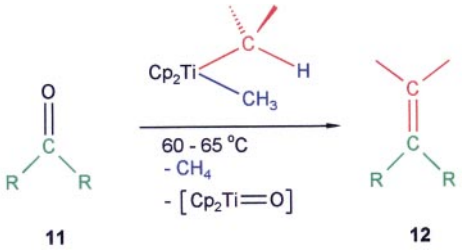
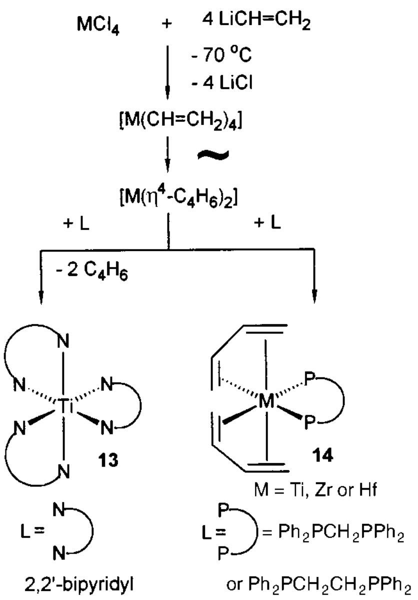


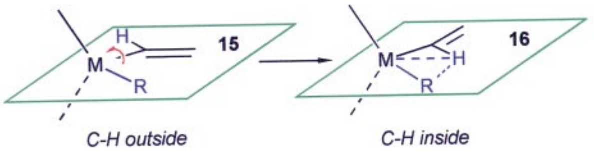
Fig. 3 Proposed transition states of reductive elimination **A**, α-H elimination **B** and β-H elimination **C** from Cp_2M alkenyl derivatives (M = Ti, Zr or Hf)



elimination processes, β- and reductive-elimination reactions are also observed. In each case, only one reaction pathway results in high selectivity.

Generally, reductive elimination reactions are the most preferred reactions of organometallic complexes from the thermodynamic point of view.[43] However, for alkyl derivatives, H-transformation reactions are kinetically preferred. In the case of alken-1-yl compounds of the titanium-group metals we find that there is a correlation between the rotational barriers of the alken-1-yl ligand around the M−C σ bond and the observed reaction pathways (Fig. 3). If free rotation is possible, reductive elimination products become dominant. Owing to the orientation of the acceptor orbitals of the bent metallocene fragment



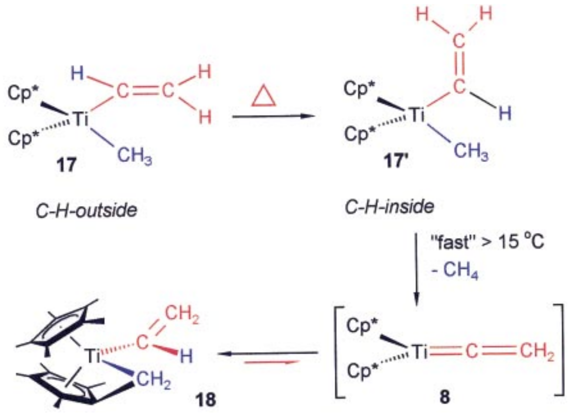


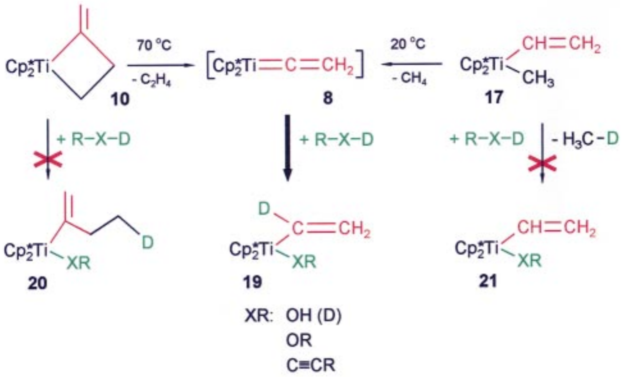
in the equatorial plane between the Cp ligands, electron transfer from the C–C double bond to the transition-metal centre in this 16 electron complex becomes possible if the vinyl group is orientated perpendicular to it (Fig. 3, **A**). This rotameric orientation leads to a suitable transition state for the reductive elimination, owing to the differences in partial charge of the α-carbon atoms, as calculated by *ab initio* methods. Generally, for d^0 systems, concerted reductive elimination reactions are forbidden by symmetry, although reductive elimination might actually be possible, especially if charge-transfer processes are involved.[44,45] On the other hand, if this rotation is hindered by using bulky ligands (Cp* instead of Cp,[46] or substituted alken-1-yl groups instead of the simple CH=CH$_2$ ligand[47]) C–H bond activation reactions become dominant (Fig. 3, **B** and **C**). Whereas the α-CH bond is activated in titanium complexes, β-CH activation occurs in zirconium complexes.[34]

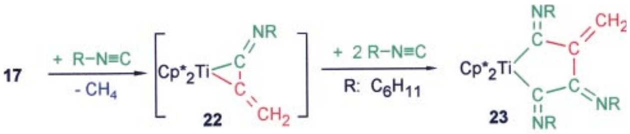
The preferred formation of dienes as the product of reductive elimination is exemplified by reaction of the tetrahalides of titanium, zirconium and hafnium with vinyllithium in a molar ratio of 1:4. In all cases, the formation of diene complexes **14** can be proved by using chelating phosphine ligands or by ligand substitution reactions, as in the case of titanium to give [Ti(bipy)$_3$] **13** (bipy = 2,2′-bipyridyl).[48]

Hydrogen elimination from carbon sp^2 centres can only occur in a mononuclear manner if the α-CH bond is directed towards the leaving group (*C–H inside* conformation **16**). This name results from the central, as opposed to the lateral (*C–H outside*) orientation of the acceptor orbitals at the metallocene fragment. However, compounds of type Cp*$_2$Ti(CH=CH$_2$)X show the *C–H outside* conformation **15** in solid-state structures and in solution [X = F,[49] OC(C$_6$H$_{11}$)CH$_2$,[50] CCPh[51] or CH$_3$[52]]. This means that the *C–H inside* conformation **16** must be realised in the first step.

The energy necessary for the rotation process in Cp*$_2$Ti-(CH=CH$_2$)$_2$, is found from MMX-force field calculations to be about 52.1 kJ mol^{-1}, compared to Cp$_2$Ti(CH=CH$_2$)$_2$ for which a value of 18.3 kJ mol^{-1} is calculated.[43] Therefore we can conclude that the rotation barrier is the main contribution to the activation energy of C–H elimination as determined by kinetic measurements for the process **17**→**8**→**18** [87.9(5) kJ mol^{-1}].[53] Selective liberation of methane occurs from complex **17** in the temperature range 5–20 °C, forming (*via* **8**) the dark green fulvene complex **18**.[53] In solution, only the *C–H outside* rotamer of **17** can be observed by NOE measurements.[52] The alternative elimination of ethylene and formation of a [Cp*$_2$Ti=CH$_2$] intermediate is not observed.





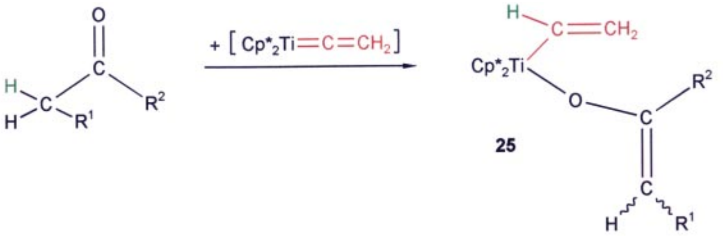


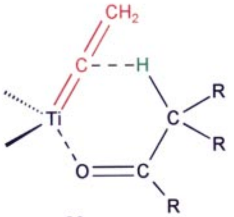
The Titana–Allene Building Block [Cp*$_2$Ti=C=CH$_2$]

The existence of the titana–allene **8** as a real intermediate, generated from **17** by methane elimination (5–20 °C)[53] or from **10** by ethylene liberation (70–100 °C),[37,38] can be proved by several trapping experiments (see later). Substrates such as ketones, alcohols, cumulenes and heterocumulenes do not react directly with **17** or **10**. Generally the formation of **8** is the rate-determining step in reactions of **10** and **17**. Substitution products **21** or ring-opened derivatives **20** could not be detected in reactions of **10** and **17** with acidic substrates. However, strong acidic substrates, *e.g.* thiophenol lead to formation of products of type **20**.[49] Several attempts were made to stabilise the vinylidene intermediate **8** itself by using electron-donating ligands like phosphines, pyridines or by using the Jutzi ligand C$_5$(CH$_3$)$_4$CH$_2$CH$_2$NMe$_2$ instead of one Cp*.[54] In all of these experiments C–H bond activation, forming the fulvene complex **18**, is dominant.

Owing to its electronic structure, the vinylidene intermediate **8** is very useful in cycloaddition reactions.[37,43] By using isocyanides an azabutatriene complex **22** is formed in the first reaction step in a [2 + 1] cycloaddition.[55,56] Owing to the high reactivity of the intermediate **22** subsequent reactions occur, forming the five-membered metallacycle **23**, which exhibits a heteroradialene substructure.[56]

The metallacyclic four-membered ring compounds **24** are synthesised in high yields by [2 + 2] cycloaddition reactions. All

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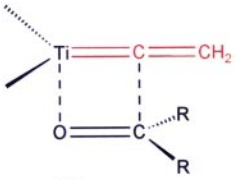
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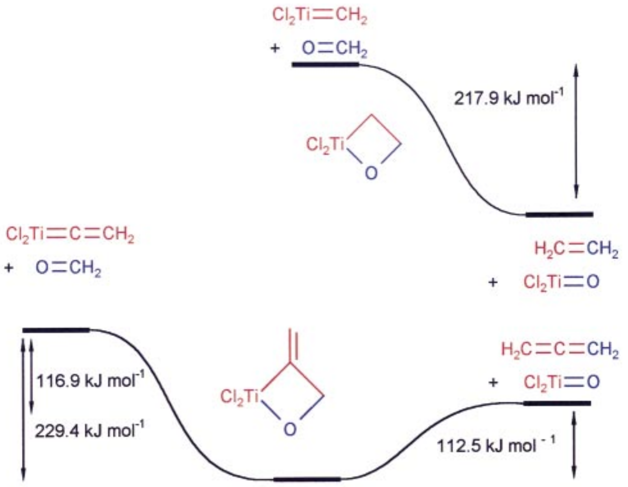
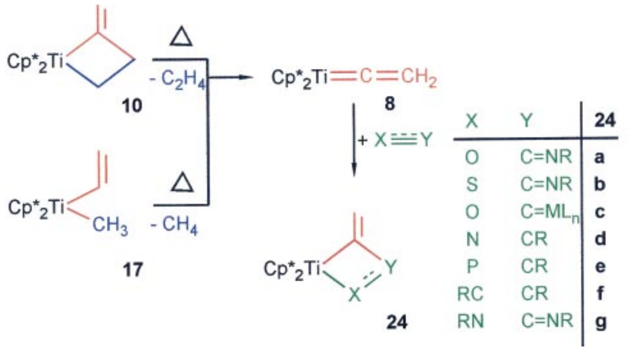
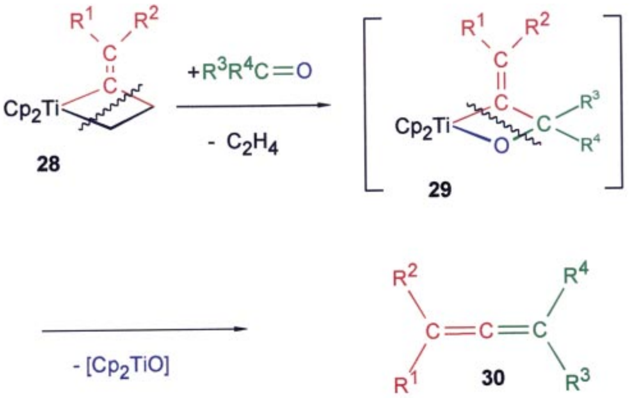


Fig. 4 Comparison of the energies of products derived from $Cl_2Ti{=}CH_2$ or $Cl_2Ti{=}C{=}CH_2$ and $O{=}CH_2$, results of *ab initio* calculations



X	Y	24
O	C=NR	a
S	C=NR	b
O	C=ML$_n$	c
N	CR	d
P	CR	e
RC	CR	f
RN	C=NR	g

these complexes were isolated as crystalline solids of high thermal stability, which allowed an extensive investigation of the reactivity of these molecules.[57–63] Oxatitanacyclobutanes[64] and azatitanacyclobutenes[65–67] are discussed as intermediates in reactions of carbenoide titanium complexes with carbonyl compounds or nitriles, but could not be isolated because of the generally high electrophilicity of the metal centre. Spontaneous ring-opening reactions afford carbonyl olefination,[19] or products of vinylimido intermediates.[66,68] Metallaoxetanes, such as $Cp_2\overline{TiCH_2CR_2O}$, have been proposed as intermediates in various transition-metal catalysed oxygen-transfer reactions.[64,69,70] Only a few metallaoxetanes, formed in the reaction of transition-metal carbenes with carbonyl compounds‡[71] or by the reaction of a terminal metal oxide fragment ($Cp^*_2Ti{=}O$)



with an allene,[74] have been characterised by X-ray diffraction methods.

The striking characteristic of the metallacycles **24** is their high thermal stability compared to products derived from a titanium methylene intermediate. From *ab initio* calculations on $Cl_2Ti{=}C{=}CH_2$ model complexes and derivatives thereof it can be shown that the formation of the carbonyl olefination products from $Cl_2Ti{=}C{=}CH_2$ and $H_2C{=}O$ is 101 kJ mol^{-1} less exothermic than the model system $Cl_2Ti{=}CH_2 + O{=}CH_2$ (Fig. 4).[43]

Our attempts to obtain titanaoxetanes from **8** and ketones have so far failed. In all cases, the formation of enolates **25** is observed. Due to the preferred six-membered transition state **26** compared to the *side-on* geometry **27**, the reaction leads in a stereo- and regio-selective manner to Δ^1 and *E*-configured products.[50] The crystal structure ($R^1 = H$, $R^2 = C_6H_{11}$) and reactivity of the enolates **25** show typical alkoxide character instead of nucleophilic properties on the β-C atom.[50] A similar behaviour is observed for enolates derived from a $Cp^*_2Ti{=}CH_2$ intermediate.[75]

However, under less sterically crowded conditions, the formation of oxetanes **29** by reaction of **28** with ketones is proposed from the formation of the carbonyl olefination products **30**.[76] This reaction is very useful for the formation of substituted allenes. The higher electrophilicity of the Cp_2Ti fragment compared to the permethylated Cp^*_2Ti in **8** prohibited the isolation or even the spectroscopic characterisation of **29**.

Remarkably, depending on the nature of the heteroatom, different subsequent reactions of the titanacycles **24** are observed. In the case of the titanacyclobutane **10**, cycloreversion reactions are dominant, forming the vinylidene intermediate **8**. In the case of the oxetanes **24a**, metathesis reactions are observed in the mass spectrometer, whereas the bimetallic oxetanes **24c** fragment to give the starting materials. These characteristics lead into the classification of *classical* and *non-classical* reaction behaviour of titanaoxetanes. *Classical* behaviour means that the formation of Ti=O metathesis products dominates, whereas

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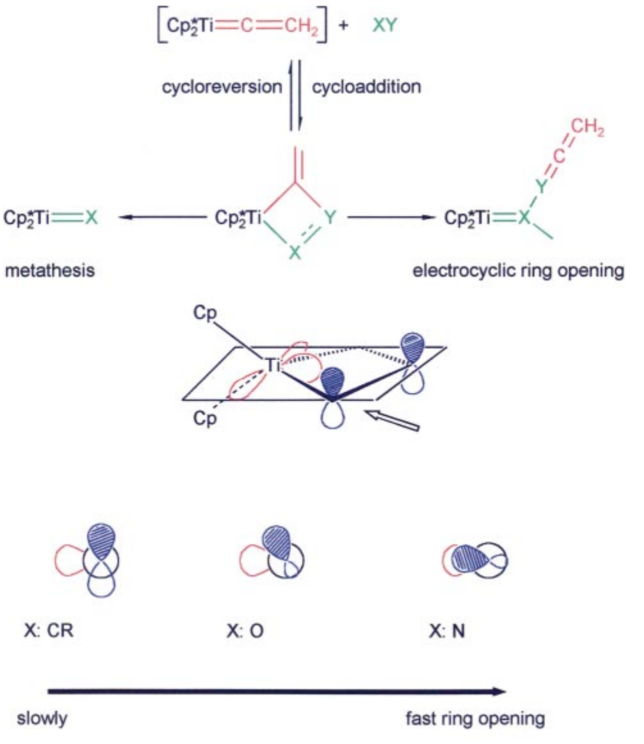
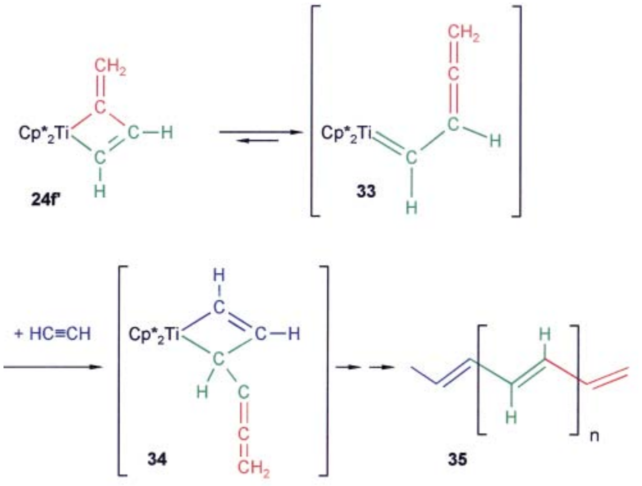
‡ Known structurally characterised metallaoxetanes comprise Ta,[71] Mo,[72] Ti[63,57] and Cr.[73]

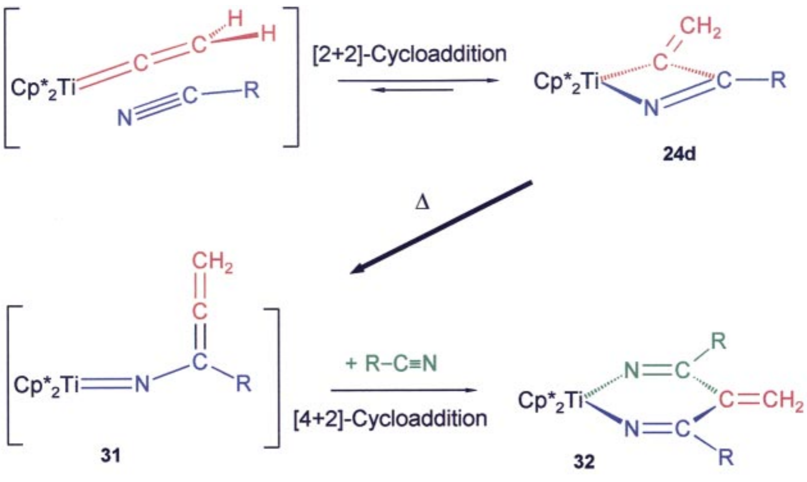
the inverse cycloreversion from the oxetane to Ti=C is observed in complexes exhibiting *non-classical* behaviour, see Scheme 2. Fast ring-opening reactions occur in the case of the azatitanacyclobutenes, leading to products of insertion into the Ti–C bond, which exhibit the *exo*-methylene group.[60] This behaviour is explained by the orientation of the lone pair on the heteroatom in **10** towards the acceptor orbitals in the equatorial plane of the metallocene Cp^*_2Ti fragment.[77] The best orbital overlap can be expected in the case of the azatitanacyclobutenes **24d**, because the lone pair at the nitrogen atom and the lateral acceptor orbital of the titanium centre are orientated in the same plane, leading to fast ring opening. The imido intermediate **31** is formed and when a further nitrile molecule is added, the formation of **32** is observed.[60] On the other hand, if the hybridisation of the nitrogen atom is changed, as in the azatitanacyclobutanes **24g**, no electrocyclic ring-opening reaction is observed. In the molecule **24g** the nitrogen lone pair is orientated perpendicular to the acceptor orbital on titanium.[78] A similar orientation of donor and acceptor orbitals is expected also in the case of titanacyclobutenes, leading to substituent controlled reactions. For titanacyclobutenes of type **24f** exhibiting large substituents (α-R = $SiMe_3$, β-R = Ph), a long internal C–C single bond of 1.502(7) Å is found by X-ray structural analysis, and the reactivity is characterised by cycloreversion processes at higher temperatures. On the other hand, with smaller substituents (R = R = Me) the internal C–C single bond is found to be shorter [1.434(4) Å] indicating a transition in the reactivity of the titanacyclobutene. Indeed, electrocyclic ring opening reactions are only observed for the non-substituted titanacyclobutene $Cp^*_2TiCH{=}CHC{=}CH_2$ **24f′** leading *via* **33** and **34** to the formation of *trans*-polyacetylene **35**.[51,79]

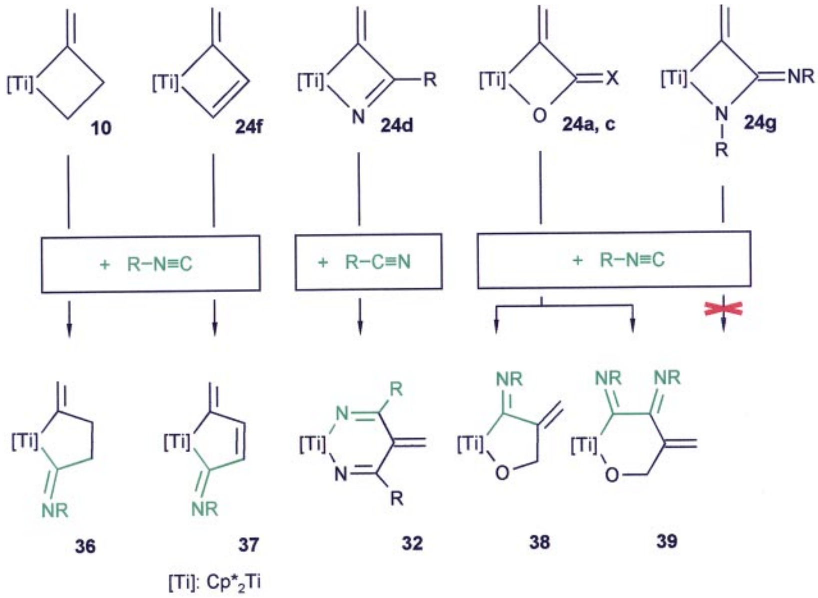
The observed reactivity of the titanacycles **24** is in accordance with the general observation, that the reactivity of bent metallocene complexes is determined by the electron deficient character of the metal centre in combination with the orientation of the acceptor orbitals in the equatorial plane of the metallocene fragment. This can be additionally illustrated by the orientation of the substituents on nitrogen atoms in $Cp^*_2TiNR'R''$ complexes. If there is no steric hindrance, the substituents on the nitrogen atom (R′ = R″ = H;[80] R′ = H, R″ = Me[81]) are rotated out of the equatorial plane of the metallocene to maximise overlap between the nitrogen lone pair (located in the p_z orbital) and the metal lowest unoccupied molecular orbital (LUMO). This effect is also found in the case of $Cp^*_2Hf(H)(NHMe)$.[82] If larger substituents are present, as in $Cp^*_2TiN(CH_3)(Ph)$ the methyl and the phenyl group are now located in the equatorial plane, and consequently a dπ–pπ interaction is no longer possible.[83] If the heteroatoms are incorporated in a planar metallacyclic ring as in **24**, such dπ–pπ interactions are the cause of the different reaction behaviour. In a similar manner, these reactivity patterns can also be observed in the insertion behaviour of the titanacycles **24** (Scheme 3). In the case of titanacyclobutane **10**[84] and cyclobutenes[51] **24f**, insertion of small molecules such as isocyanides is observed only into the Ti–C bond opposite the *exo*-methylene group. For



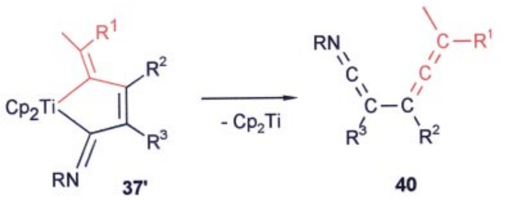
Scheme 2







Scheme 3



the titanacyclobutene **24d**, a spontaneous ring enlargement by insertion of a further nitrile molecule is observed **24d**→**32**, due to the activation of the Ti–C sp^2 bond by the lone pair on the nitrogen centre. In a similar manner the oxetanes **24a** and **24c** show insertion reactions into this Ti–C bond forming mono- (**38**) or double-insertion products (**39**).[85] On the other hand, azatitanacyclobutanes **24g** are inert to ring enlargement reactions with isocyanides even at higher temperatures.

In some cases, cycloaddition reactions involving a titana–allene intermediate are useful in organic synthesis. The preparation of allenylketenimines **40** becomes possible in high yields *via* complexes of type **37** (Cp instead of Cp*) by extrusion of 'Cp_2Ti'.[86] Additionally, the intramolecular cycloaddition of the titanocene vinylidene complex, formed by dechloroalumination of **41**,[87] with an alkene (or alkyne) affords bicyclic titanacyclobutanes and **42** (or butenes).[88] This cyclisation has proven to be possible in all such complexes. The remaining carbon–metal bond in the metallacycles **42** offers great potential for further elaboration to give organic products. This is illustrated for complex **42** in reactions with *N*-bromosuccinimide (NBS), which gave the dibromide **45**. The insertion reaction of isocyanide affords the imino complex **43** which gave the aldehyde **44** on acidic work-up; alternatively, reaction with carbon monoxide followed by acidic work-up gave the ketone **47**, presumably *via* the ene–diolate complex **46**.[88]

Regioisomers

We have demonstrated that the formation of the titanacyclobutanes and butenes **24** occur in a regioselective manner. Big differences in the partial charge of the X, Y atoms, determined *e.g.* by ^{13}C NMR measurements in the case of alkynes,[51] lead to stereochemically pure compounds with the more negative carbon bonded to titanium. α- and β-Regioisomers are obtained by using substrates with small partial charge differences. This is the case for alkynes[51] or phosphaalkynes.[60]

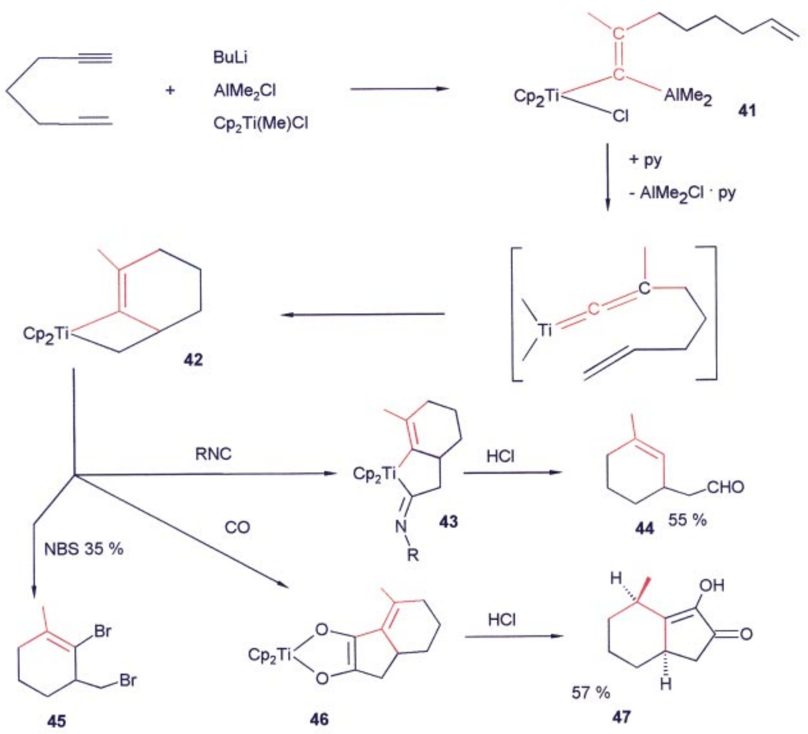
As well as the electronically controlled reactions, leading mostly to kinetic products, sterically controlled reactions are also observed. Thus from a mixture of both cycloaddition products of **8** with the phosphaalkyne Bu^{t}C≡P **24e** and **48**, only the product exhibiting the bulky *tert*-butyl group in the β position (**24e**) crystallised from the solution. In the case of mixtures of regioisomers obtained from unsymmetrical acetylenes, the more bulky group rearranged to the β position upon heating.[51]

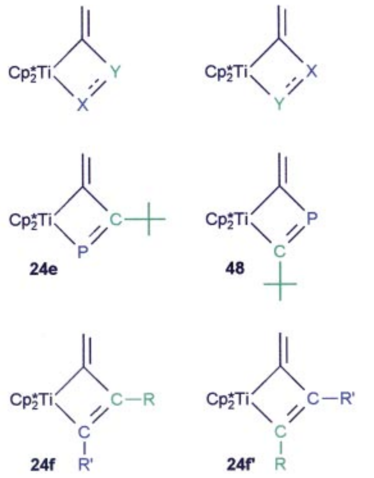
The effect of electronic and steric control can be observed in the reaction of the titanocenevinylidene intermediate $[Cp^*_2Ti{=}C{=}CH_2]$ **8** with 1,3-diynes (see Fig. 5), yielding titanacyclobutene complexes (**50**).[61] Only one regioisomer is formed, containing the acetylide group in the α position of the metallacyclic ring. The regioselectivity is in accordance with the polarities of the diynes and stereochemical conditions in the cyclobutene ring. This behaviour is in agreement with *ab initio* calculations and the results of molecular modelling. Using unsymmetric diynes, metallacyclobutenes exhibiting the larger substituent in the β position are formed, as shown for **50e**.[61]

The only primary regioisomer formed by cycloaddition of **8** with isothiocyanates is **24b**, which contains the sulfur atom in the α position of the metallacyclic ring. When heated in the presence of pyridine, **24b** can be isomerised into the other possible regioisomer **51**;[58] C=N cycloaddition products are not observed. The quantitative isomerisation **24b**→**51** shows that the lower polarity of the C=S unit in the RNCS molecule allows the formation of a second isomer. In this respect, the behaviour of titanathietanes is quite different from the behaviour of titanaoxetanes, which normally react to give Ti=O fragments (*classical* behaviour). In cycloaddition reactions of **8** with CS_2, only the regioisomer with the sulfur atom in the β-ring position is observed.[89] The inverse regiochemistry results from the difference in reactivity of a carbonyl and a thiocarbonyl group with strong carbanionic molecules and shows the thiophilic character of the nucleophilic carbene complex **8**.[90–92]

Structure Isomerisation, Vinylidene–Acetylene Rearrangement

The stabilisation of the vinylidene group $H_2C{=}C$**:**, tautomeric to acetylene, has enabled the investigation of vinylidene complexes of late transition metals. The 1,2-proton shift is a characteristic feature in the synthesis of vinylidene complexes formed from acetylenes.[93–95] Depending on the relative stability of the





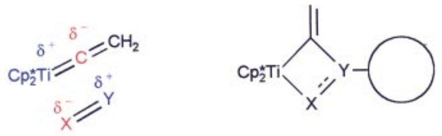
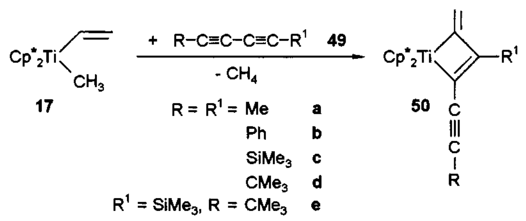


Fig. 5 Schematic drawing of electronically determined regiochemsitry (left) and sterically controlled reactions (right)



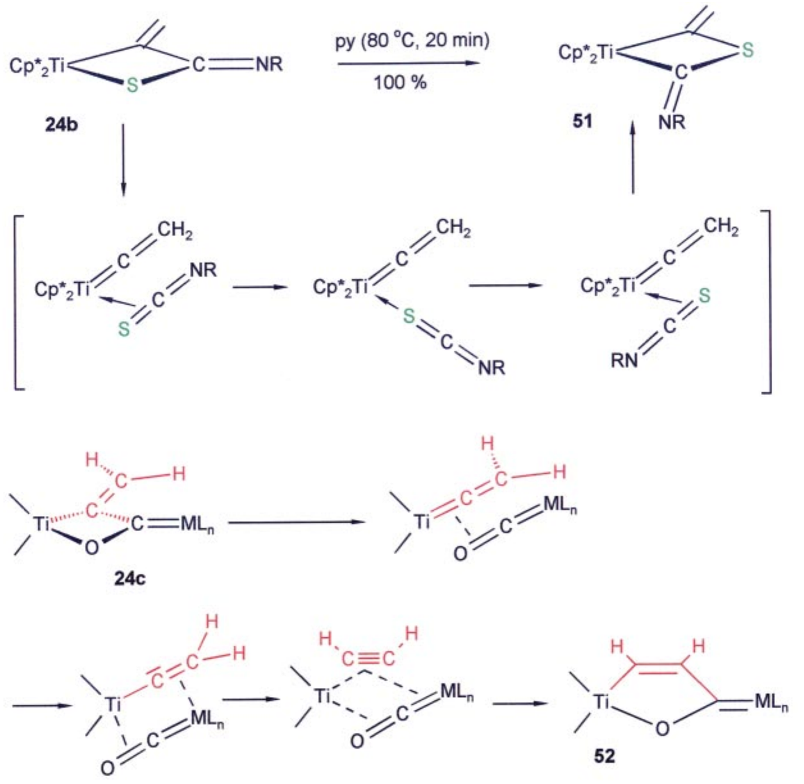
vinylidene complex compared to the acetylene derivative, the formation of vinylidene complexes is often preferred by late transition metals (Scheme 4). On the other hand, a reverse proton shift, from a vinylidene to an acetylene intermediate, is observed on heating solutions of the bimetallic oxetanes **24c**, generating the oxatitanacyclopentene complexes **52**.[38,57,59] This transformation corresponds to the behaviour of a '*free*' vinylidene $C{=}CH_2$ molecule, in the gas phase. The five-membered dinuclear complexes **52** are crystalline materials of high thermal stability (up to 220 °C).

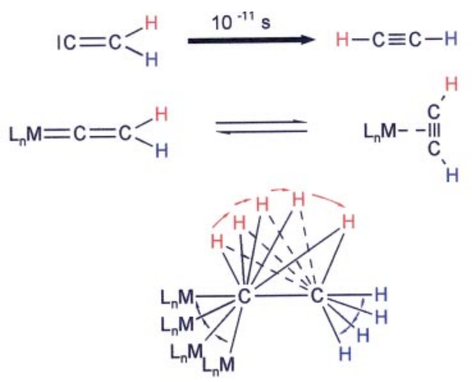
In contrast to the vinylidene–acetylene rearrangement observed for the bimetallic '*non-classical*' oxetanes **24c**, the '*classical*' oxetanes **24a** are not able to rearrange to five-membered rings. That means that there must be a destabilising effect by the second transition metal, which can be explained by a cycloreversion process in the first step and formation of an η^2-C−C bonded bridged vinylidene complex, which initiates the vinylidene–acetylene rearrangement. In this regard, the structure of heterodinuclear vinylidene bridged complexes is of general interest. Remarkably an unusual vinylidene–acetylene rearrangement is also observed for vinylidene bridged homodinuclear molybdenum complexes.[96] Using intermediate **8**, the formation of different vinylidene bridged complexes should be possible. These are the symmetrically bridged 1,1-dimetallaethylene and the unsymmetrically bridged structures, characterised by different types of dπ–pπ interaction with the Ti=C or the C=C double bond of **8** (Fig. 6).[97] These structure types are in accordance with CO- and CS-bridged binuclear complexes. The σ,σ-bridging mode is generally dominant.[36,98–102] Examples of *side-on* bridged vinylidene complexes are rare.[96,97,103–109] The semi-bridging type complexes are known for CO,[110,111] CS[112] but for vinylidene to our knowledge only one example of a Mo−Ru complex is published.[105] Indeed in reactions of **17** with copper and gold complexes, dinuclear vinylidene bridged complexes can be isolated as crystalline materials [m.p. (decomp.) 93 °C **53a**, 180 °C **53b**].[113] In the case of **53a**–**53d**, the ^{13}C NMR data are indicative of the semi-bridging structural type, due to the low field shift of the bridging α-vinylidene carbon atom in the range δ 330 (**53a**)–300 (**53d**).

Intermolecular Carbene–Carbene Coupling

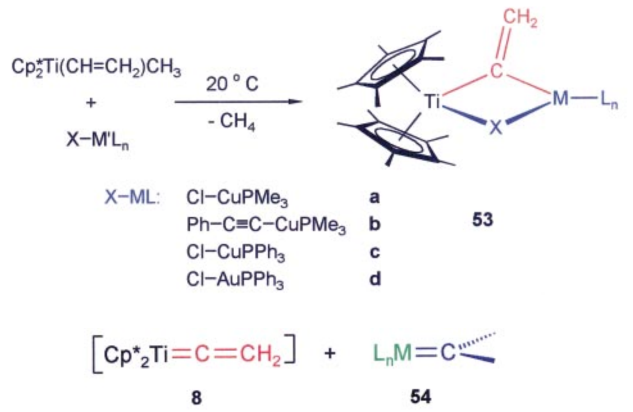
By reacting the nucleophilic Schrock-type carbene intermediate **8** with other carbene complexes **54**, the formation of the dinuclear 1,3- as well as 1,2-dimetallacyclobutanes **55** and **56** should be possible.

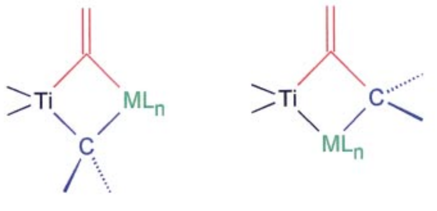
Remarkably, in reactions of thermally generated **8** from **17** with the Fischer carbene complex $(OC)_5Cr{=}C(OMe)Me$, a new type of C−C coupling reaction is found. The products **59** and **60** could be separated by chromatography. The structure of **59** was





Scheme 4





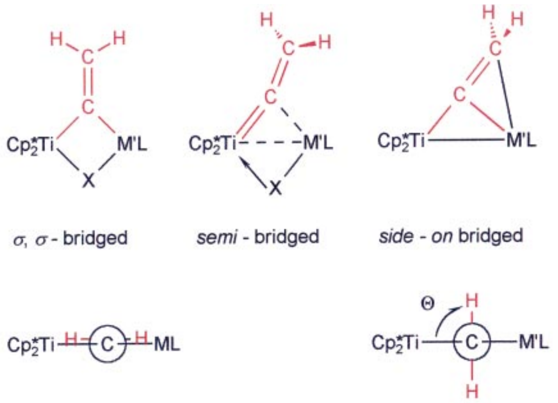
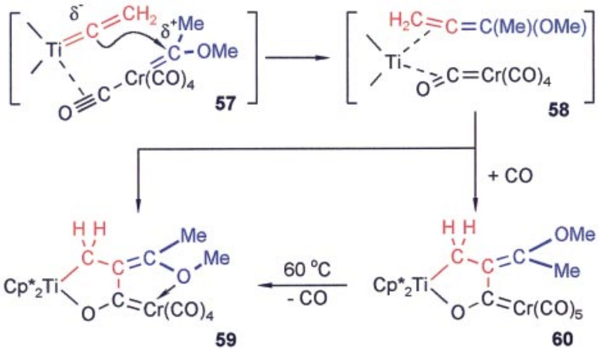
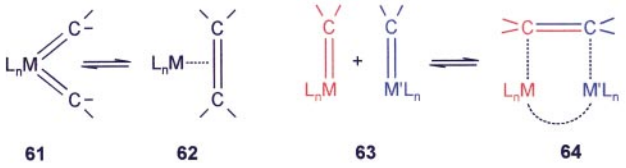


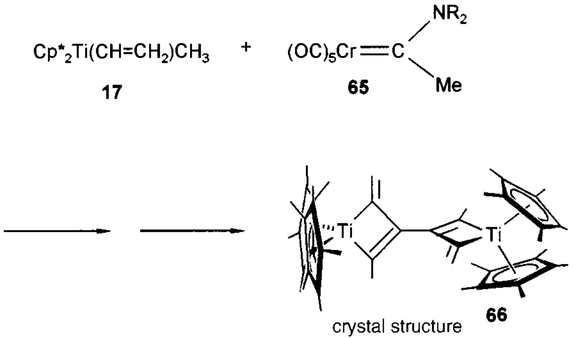
Fig. 6 Different structure types of vinylidene bridged heterodinuclear complexes

determined by X-ray diffraction.[114] In **59** the octahedral geometry at the chromium centre is realised by co-ordination of the methoxy ligand, whereas in **60** an additional carbon monoxide molecule is co-ordinated. Overall, C–C bond formation occurs between carbon atoms of a vinylidene, carbene and carbonyl ligand. The most remarkable feature of the structures of **59** and **60** is the fact that both metal atoms are bonded to different atoms than in the starting materials. The formation of **59** and **60** is in accordance with a carbene–carbene coupling *via* intermediate generation of the allene complex **58**. This reaction step becomes clear considering the primary interaction of the nucleophilic and electrophilic carbene carbon atoms, supported by CO co-ordination to the oxophilic titanium as shown in **57**. Titanium-centred cycloaddition of the allene molecule with the remaining $Cr(CO)_x$ fragment leads directly to **59** and, after fast CO addition, to **60**. The described reaction represents to our knowledge the first example of an *intermolecular* coupling of inversely polarised carbene ligands **63**→**64**, although *intramolecular* carbene–carbene coupling reactions **61**→**62** have been reported.[115]

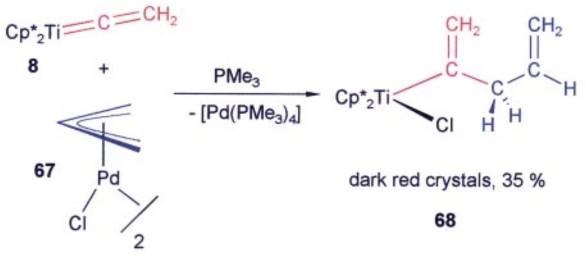
This new method of achieving metal-centred coupling of







crystal structure
dark blue crystals



dark red crystals, 35 %

several carbon atoms of different substrates can potentially be used in syntheses. With other carbon electrophiles further types of C–C coupling reactions are observed. The reaction of **17** with the aminocarbene complex **65** leads to the dinuclear titanium complex **66** after chromatographic work-up. The dimeric structure is confirmed by the mass spectrum and the crystal-structure analysis.[116] The surprising feature of **66** is its dark blue colour. In contrast, the monomeric units of the type **24f** and **50** are dark red compounds. As observed in the crystal structure of **66** there is a twist angle between the cyclobutene planes of nearly 50°. Other carbon electrophiles are also able to undergo C–C coupling reactions at the nucleophilic carbon centre of **8**. By treating allylpalladium chloride **67** with **8** in the presence of PMe_3 the formation of the coupling product **68** can be observed.[117]

Closing Remarks and Outlook

The high reactive selectivity of alken-1-yl ligands in the co-ordination sphere of electron-deficient metals has proved to be a powerful tool in the classification of organometallic reactivity. From this, we can learn what is easy and what is difficult for a transition-metal–carbon σ-bond to do.

The transformation of titanium vinyl complexes to titanium vinylidene intermediates under mild thermal conditions in particular has significantly improved the access to short-lived carbene complexes of early transition metals. This has widened the spectrum of preparative and catalytic applications of [Ti=C] generating derivatives considerably. Different types of stable cycloaddition products of **8** are isolable, allowing investigation of structures and reactivity relationships. However, many questions still remain open. First, what have we learned from the easy proton elimination from vinyl groups (which does not occur in comparable alkyl ligands), and are useful H-eliminations from other substrates in the co-ordination sphere of metallocene complexes also possible under similar conditions? As well as the discussed Ti=C systems, Ti=Si,[118] M=N[119] (M = Ti[120,121] or Zr[120,122]), Zr=P,[123,124] Zr=O,[125,126] Zr=S,[125,126] and even intermediates exhibiting Ti≡C bonds,[127,128] are available. Secondly, what about axial chirality in the titana–allene building block? From the preferred C_s symmetric ground state and the calculated Ti–C rotation energy (134 kJ mol^{-1})[37] for the titana–allene compound, axial chiral complexes must be available. Thirdly, which types of further cycloaddition products are available? What about the possibility of syntheses of new types of molecules, like radialenes derived from reactions of **8** and butatrienes or from molecules of type **23**. What further types of molecules can be prepared by new C–C coupling reactions? Finally, are acetylene–vinylidene rearrangements possible in the case of electron-deficient transition-metal complexes? The fact that the polymerisation of acetylene seems to proceed *via* a vinylidene intermediate suggests that this could be the case, but up to now, there is no definitive proof of such a rearrangement.[79,129] Many reactions discussed before seem to be sterically controlled. This means that other ligand systems must also be able to realise the role of the Cp* ligand.[130,131] Let's go and find them!

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References

1 C. Elschenbroich and A. Salzer, *Organometallchemie*, B. G. Teubner, Stuttgart, 3rd edn., 1990.
2 R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, 2nd edn., 1994.
3 K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert and K. Weiss, *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, 1983.
4 M. Regitz, *Angew. Chem.*, 1996, **108**, 791; *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 725.
5 M. Regitz, *Angew. Chem.*, 1991, **103**, 691; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 674.
6 W. A. Herrmann, C. Köcher, L. J. Gooßen and G. R. J. Artus, *Chem. Eur. J.*, 1996, **2**, 1627.
7 R. Beckhaus, *Angew. Chem.*, 1997, **109**, 694; *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 687.

8 R. Beckhaus, J. Oster, J. Sang, I. Strauß and M. Wagner, *Synlett*, 1997, 241.

9 D. L. Hughes, J. F. Payack, D. Cai, T. R. Verhoeven and P. J. Reider, *Organometallics*, 1996, **15**, 663.

10 J. A. van Doorn, H. van der Heijden and A. G. Orpen, *Organometallics*, 1995, **14**, 1278.

11 S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem.*, 1995, **107**, 1200; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1092.

12 J. A. van Doorn, H. van der Heijden and A. G. Orpen, *Organometallics*, 1994, **13**, 4271.

13 M. D. Fryzuk, S. S. H. Mao, M. J. Zaworotko and L. R. MacGillivray, *J. Am. Chem. Soc.*, 1993, **115**, 5336.

14 R. K. Minhas, L. Scoles, S. Wong and S. Gambarotta, *Organometallics*, 1996, **15**, 1113.

15 H. van der Heijden and B. Hessen, *J. Chem. Soc., Chem. Commun.*, 1995, 145.

16 L. Scoles, R. Minhas, R. Duchateau, J. Jubb and S. Gambarotta, *Organometallics*, 1994, **13**, 4978.

17 K. Utimoto and K. Takai, *NATO ASI Ser., Ser. C*, 1989, **269**, 379.

18 K. Takai, T. Kakiuchi, Y. Kataoka and K. Utimoto, *J. Org. Chem.*, 1994, **59**, 2668.

19 R. H. Grubbs and R. H. Pine, *Comprehensive Organic Synthesis; Alkene Metathesis and Related Reactions*, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon, New York, 1991, vol. 5, ch. 9.3, pp. 1115–1127.

20 R. H. Grubbs, *Prog. Inorg. Chem.*, 1978, **24**, 1.

21 S. H. Pine, *Carbonyl Methylenation and Alkylidation using Titanium-Based Reagents*, in *Organic Reactions*, ed. L. A. Paquette, Wiley, New York, 1993, vol. 43, pp. 1–91.

22 N. A. Petasis and E. I. Bzowej, *J. Am. Chem. Soc.*, 1990, **112**, 6392.

23 D. A. Straus and R. H. Grubbs, *J. Mol. Catal.*, 1985, **28**, 9.

24 R. R. Schrock, *Acc. Chem. Res.*, 1979, **12**, 98.

25 J. Feldman and R. R. Schrock, *Prog. Inorg. Chem.*, 1991, **39**, 1.

26 R. R. Schrock, *Pure Appl. Chem.*, 1994, **66**, 1447.

27 J. L. Polse, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1996, **118**, 8737.

28 P. Binger, P. Müller, R. Benn and R. Mynott, *Angew. Chem.*, 1989, **101**, 647; *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 610.

29 P. Binger, P. Müller, R. Wenz and R. Mynott, *Angew. Chem.*, 1990, **102**, 1070; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1037.

30 A. Maercker, *Angew. Chem.*, 1993, **105**, 1072; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1023.

31 A. Müller, M. Marsch, K. Harms, J. C. W. Lohrenz and G. Boche, *Angew. Chem.*, 1996, **108**, 1639.

32 G. Boche, M. Marsch, A. Müller and K. Harms, *Angew. Chem.*, 1993, **105**, 1081; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1032.

33 G. Boche, K. Harms, M. Marsch and A. Müller, *J. Chem. Soc., Chem. Commun.*, 1994, 1393.

34 R. Beckhaus, K.-H. Thiele and D. Ströhl, *J. Organomet. Chem.*, 1989, **369**, 43.

35 R. Beckhaus, Habilitation Thesis, Technische Hochschule Leuna-Merseburg, 1989, RWTH Aachen, 1993.

36 M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197.

37 R. Beckhaus, S. Flatau, S. I. Troyanov and P. Hofmann, *Chem. Ber.*, 1992, **125**, 291.

38 R. Beckhaus, *Methylidentitanacyclobutane vs. Titanocene-Vinylidene-Versatile Building Blocks* in *Organic Synthesis via Organometallics*, eds. D. Enders, H.-J. Gais and W. Keim, Vieweg Verlag, Braunschweig, 1993, pp. 131–149.

39 N. A. Petasis and I. Akritopoulou, *Synlett*, 1992, 665.

40 N. A. Petasis and E. I. Bzowej, *Tetrahedron Lett.*, 1993, **34**, 943.

41 N. A. Petasis, J. P. Staszewski and D.-K. Fu, *Tetrahedron Lett.*, 1995, **36**, 3619.

42 C. McDade, J. C. Green and J. E. Bercaw, *Organometallics*, 1982, **1**, 1629.

43 R. Beckhaus and U. Böhme, unpublished work.

44 B. Akermark and A. Ljungqvist, *J. Organomet. Chem.*, 1979, **182**, 59.

45 J. M. Brown and N. A. Cooley, *Chem. Rev.*, 1988, **88**, 1031.

46 P. Courtot, V. Labed, R. Pichon and J. Y. Salaün, *J. Organomet. Chem.*, 1989, **359**, C9.

47 S. L. Buchwald and R. B. Nielsen, *Chem. Rev.*, 1988, **88**, 1047.

48 R. Beckhaus and K.-H. Thiele, *J. Organomet. Chem.*, 1986, **317**, 23.

49 R. Beckhaus, J. Sang, J. Oster and T. Wagner, *J. Organomet. Chem.*, 1994, **484**, 179.

50 R. Beckhaus, I. Strauß and T. Wagner, *J. Organomet. Chem.*, 1994, **464**, 155.

51 R. Beckhaus, J. Sang, T. Wagner and B. Ganter, *Organometallics*, 1996, **15**, 1176.

52 J. Sang, Ph.D. Thesis, RWTH Aachen, 1996.

53 G. A. Luinstra and J. H. Teuben, *Organometallics*, 1992, **11**, 1793.

54 R. Beckhaus, J. Oster and B. Ganter, unpublished work.

55 R. Beckhaus and J. Oster, *Z. Anorg. Allg. Chem.*, 1995, **621**, 359.

56 R. Beckhaus and I. Strauß, unpublished work.

57 R. Beckhaus, I. Strauß, T. Wagner and P. Kiprof, *Angew. Chem.*, 1993, **105**, 281; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 264.

58 R. Beckhaus, J. Sang, T. Wagner and U. Böhme, *J. Chem. Soc., Dalton Trans.*, in the press.

59 R. Beckhaus, J. Oster and T. Wagner, *Chem. Ber.*, 1994, **127**, 1003.

60 R. Beckhaus, I. Strauß and T. Wagner, *Angew. Chem.*, 1995, **107**, 738; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 688.

61 R. Beckhaus, J. Sang, U. Englert and U. Böhme, *Organometallics*, 1996, **15**, 4731.

62 M. Wagner, Diplomarbeit, RWTH Aachen, 1996.

63 R. Beckhaus, I. Strauβ and T. Wagner, *Z. Anorg. Allg. Chem.*, 1997, **623**, 654.

64 B. Schiott and K. A. Jorgensen, *J. Chem. Soc., Dalton Trans.*, 1993, 337.

65 K. M. Doxsee, J. K. M. Mouser and J. B. Farahi, *Synlett*, 1992, 13.

66 K. M. Doxsee, J. B. Farahi and H. Hope, *J. Am. Chem. Soc.*, 1991, **113**, 8889.

67 K. M. Doxsee and J. B. Farahi, *J. Am. Chem. Soc.*, 1988, **110**, 7239.

68 K. M. Doxsee and J. B. Farahi, *J. Chem. Soc., Chem. Commun.*, 1990, 1452.

69 K. A. Jorgensen and B. Schiott, *Chem. Rev.*, 1990, **90**, 1483.

70 K. A. Jorgensen, *Chem. Rev.*, 1989, **89**, 431.

71 L. L. Whinnery, jun., L. M. Henling and J. E. Bercaw, *J. Am. Chem. Soc.*, 1991, **113**, 7575.

72 G. C. Bazan, R. R. Schrock and M. B. O'Regan, *Organometallics*, 1991, **11**, 1062.

73 J. Sundermeyer, K. Weber and H. Pritzkow, *Angew. Chem.*, 1993, **105**, 751.

74 D. J. Schwartz, M. R. Smith III and R. A. Andersen, *Organometallics*, 1996, **15**, 1446.

75 C. P. Gibson and D. S. Bem, *J. Organomet. Chem.*, 1991, **414**, 23.

76 S. L. Buchwald and R. H. Grubbs, *J. Am. Chem. Soc.*, 1983, **105**, 5490.

77 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.

78 R. Beckhaus and M. Wagner, unpublished work.

79 A. Ohff, V. V. Burlakov and U. Rosenthal, *J. Mol. Catal.*, 1996, **108**, 119.

80 E. Brady, W. Lukens, J. Telford and G. Mitchell, *Acta Crystallogr., Sect. C*, 1994, **51**, 558.

81 W. W. Lukens, jun., M. R. Smith III and R. A. Andersen, *J. Am. Chem. Soc.*, 1996, **118**, 1719.

82 G. L. Hillhouse, A. R. Bulls, B. D. Santarsiero and J. E. Bercaw, *Organometallics*, 1988, **7**, 1309.

83 J. Feldman and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 1991, 1042.

84 R. Beckhaus, C. Zimmermann, T. Wagner and E. Herdtweck, *J. Organomet. Chem.*, 1993, **460**, 181.

85 R. Beckhaus and I. Strauß, unpublished work.

86 R. D. Dennehy and R. J. Whitby, *J. Chem. Soc., Chem. Commun.*, 1992, 35.

87 T. Yoshida and E. Negishi, *J. Am. Chem. Soc.*, 1981, **103**, 1276.

88 R. D. Dennehy and R. J. Whitby, *J. Chem. Soc., Chem. Commun.*, 1990, 1060.

89 R. Beckhaus and J. Sang, unpublished work.

90 J. March, *Advanced Organic Chemistry*, Wiley, New York, 1985.

91 P. Beak and J. W. Worley, *J. Am. Chem. Soc.*, 1972, **94**, 597.

92 A. Ohno, K. Nakamura, Y. Shizume and S. Oka, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1003.

93 H. Werner, *Nachr. Chem. Tech. Lab.*, 1992, **40**, 435.

94 H. Werner, *Angew. Chem.*, 1990, **102**, 1109; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1077.

95 J. Silvestre and R. Hoffmann, *Helv. Chim. Acta*, 1985, **68**, 1461.

96 S. F. T. Froom, M. Green, R. J. Mercer, K. R. Nagle, A. G. Orpen and R. A. Rodrigues, *J. Chem. Soc., Dalton Trans.*, 1991, 3171.

97 H. El Amouri and M. Gruselle, *Chem. Rev.*, 1996, **96**, 1077.

98 M. I. Bruce and A. G. Swincer, *Adv. Organomet. Chem.*, 1983, **22**, 59.

99 H. Werner, J. Wolf, G. Müller and C. Krüger, *J. Organomet. Chem.*, 1988, **342**, 381.

100 J. E. Huheey, E. A. Keiter and R. L. Keiter, *Anorganische Chemie–Prinzipien von Struktur und Reaktivität*, Walter de Gruyter, Berlin, 2nd edn., 1995.

101 C. P. Horwitz and D. F. Shriver, *Adv. Organomet. Chem.*, 1984, **23**, 219.

102 P. V. Broadhurst, *Polyhedron*, 1985, **4**, 1801.

103 U. Kern, C. G. Kreiter, S. Müller-Becker and W. Frank, *J. Organomet. Chem.*, 1993, **444**, C31.

104 M. Akita, S. Sugimoto, A. Takabuchi, M. Tanaka and Y. Moro-oka, *Organometallics*, 1993, **12**, 2925.
105 R. Boese, M. A. Huffmann and K. P. C. Vollhardt, *Angew. Chem.*, 1991, **103**, 1542.
106 F. J. G. Alonso, V. Riera, M. A. Ruiz, A. Tripicchio and M. T. Camellini, *Organometallics*, 1992, **11**, 370.
107 N. M. Doherty, C. Elschenbroich, H.-J. Kneuper and S. A. R. Knox, *J. Chem. Soc., Chem. Commun.*, 1985, 170.
108 F. A. Cotton, *Prog. Inorg. Chem.*, 1976, **21**, 1.
109 R. A. Doyle, L. M. Daniels, R. J. Angelici and F. G. A. Stone, *J. Am. Chem. Soc.*, 1989, **111**, 4995.
110 R. H. Crabtree and M. Lavin, *Inorg. Chem.*, 1986, **25**, 805.
111 M. J. Winter, *Adv. Organomet. Chem.*, 1989, **29**, 101.
112 H. P. Kim, S. Kim, R. A. Jacobson and R. J. Angelici, *J. Am. Chem. Soc.*, 1986, **108**, 5154.
113 J. Oster, Ph.D. Thesis, RWTH Aachen, 1996.
114 R. Beckhaus, J. Oster, R. Kempe and A. Spannenberg, *Angew. Chem.*, 1996, **108**, 1636; *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1565.
115 H. Kücükbay, B. Cetinkaya, S. Guesmi and P. H. Dixneuf, *Organometallics*, 1996, **15**, 2434 and refs. therein.
116 R. Beckhaus and J. Oster, unpublished work.
117 R. Beckhaus and J. Oster, unpublished work.
118 E. Hengge and M. Weinberger, *J. Organomet. Chem.*, 1993, **443**, 167.
119 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.
120 C. P. Schaller, C. C. Cummins and P. T. Wolczanski, *Organometallics*, 1996, **118**, 591.
121 C. C. Cummins, C. P. Schaller, G. D. Van Duyne, P. T. Wolczanski, A. W. E. Chan and R. Hoffmann, *J. Am. Chem. Soc.*, 1991, **113**, 2985.
122 P. J. Walsh, F. J. Hollander and R. G. Bergman, *Organometallics*, 1993, **12**, 3705.
123 J. Ho, Z. Hou, R. J. Drake and D. W. Stephan, *Organometallics*, 1993, **12**, 3145.
124 Z. Hou and D. W. Stephan, *J. Am. Chem. Soc.*, 1992, **114**, 10 088.
125 M. J. Carney, P. J. Walsh, F. J. Hollander and R. G. Bergman, *Organometallics*, 1992, **11**, 761.
126 M. J. Carney, P. J. Walsh, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1989, **111**, 8751.
127 R. Andres, P. Gomez-Sal, E. de Jesus, A. Martin, M. Mena and C. Yelamos, *Angew. Chem.*, 1997, **109**, 72; *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 115.
128 R. Andres, M. V. Galakhov, A. Martin, M. Mena and C. Santamaria, *Organometallics*, 1994, **13**, 2159.
129 H. G. Alt, H. E. Engelhardt, M. D. Rausch and L. B. Kool, *J. Organomet. Chem.*, 1987, **329**, 61.
130 See for example, R. R. Schrock, C. C. Cummins, T. Wilhelm, S. Lin, S. M. Reid, M. Kol and W. M. Davis, *Organometallics*, 1996, **15**, 1470 and refs. therein.
131 J. S. Freundlich, R. R. Schrock and W. M. Davis, *Organometallics*, 1996, **15**, 2777.

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