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Titanocene and zirconocene σ-alkynyl complexes in C–C single bond coupling and cleavage reactions

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Abstract

Group 4 metallocene mono- and bis-σ-alkynyl complexes of the type $L_2M(\sigma\text{-}C{\equiv}CR)$ and $L_2M(\sigma\text{-}C{\equiv}CR)_2$ with M = titanium and zirconium in the oxidation states +3 and +4 and L = Cp (η^5-cyclopentadienyl) and Cp* (η^5-pentamethylcyclopentadienyl) are important compounds for stoichiometric and catalytic C–C single bond coupling and cleavage reactions. Detailed investigations show five-membered metallacyclocumulenes $L_2M(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ as the key intermediates in both reactions of a C–C single bond cleavage of different 1,4-substituted 1,3-butadiynes RC≡C–C≡CR to alkynyl groups and the opposite reaction of C–C single bond formation starting from alkynyl groups under the formation of 1,4-substituted 1,3-butadiynes. Depending on different metals M and ligands L, coupling or cleavage is favoured. Combination of both reactions offered the first C–C single bond metathesis in homogeneous solution, which is photocatalyzed and titanocene-mediated. It proceeds via titanocene–mono-alkynyl complexes, which are interesting species also for other stoichiometric and catalytic C–C coupling reactions. Some similarities regarding the σ-to-π conversion exist between the coupling of the alkynyl groups at titano- and zirconocenes to complexed 1,3-butadiynes on one side and the coupling of phenyl groups at chromium to complexed diphenyl on the other side.

Keywords: Titanocene; Zirconocene; Alkynyl; C–C coupling; C–C cleavage

1. Introduction

In general, compounds with σ-bonds between transition metal and carbon are well suited to realize C–C coupling reactions by reductive elimination at one or between two metals. Two very early examples for this are the Glaser reaction from 1869 for coupling of alkynyl groups to 1,3-butadiynes by copper salts [1] and the coupling of phenyl groups to diphenyl by chromium compounds (Scheme 1; [2]).

The latter reaction of $CrCl_3$ with PhMgBr in ether was investigated by Hein [3] in 1919 giving the first arene-π-complexes, although he did not recognize the real structure at that time. In 1954, Zeiss and Tsutsui [4] were inspired by an idea of Onsager and described these compounds as arene sandwich complexes, but the mechanism of σ-to-π conversion in their formation is not clear in detail up to now. Seyferth [5] described this fascinating story of organometallic chemistry in two excellent essays.

The σ-phenyl-*ate*-complex $Ph_6Cr(Li\cdot Et_2O)_3$ [6] forms by the elimination of three equivalents of LiPh the σ-phenyl complex $Ph_3Cr(THF)_3$ [7] and, after dissociation of THF, mixtures of π-(arene)-chromium compounds, containing π-complexed diphenyl (Scheme 2).

One of the authors (U.R.) studied a long time ago the elimination reaction of LiPh from $Ph_6Cr(Li\cdot Et_2O)_3$ in the presence of the phosphonium salt $[Me_4P]Cl$, giving instead of π-(arene)-complexes, in the first step the tris-

$$n\ [\mathrm{Cu}]\ (\sigma\text{-}\mathrm{C{\equiv}CR}) \longrightarrow \mathrm{RC{\equiv}C{-}C{\equiv}CR} + [\mathrm{Cu}]$$

$$n\ [\mathrm{Cr}]\ (\sigma\text{-}\mathrm{Ph}) \longrightarrow (\pi\text{-}\mathrm{Ph{-}Ph})\ [\mathrm{Cr}]$$

Scheme 1.

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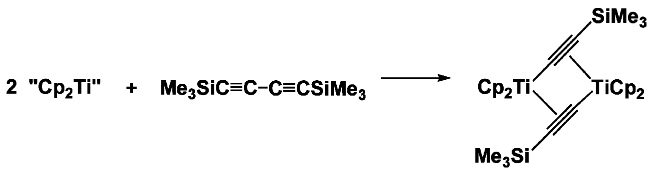
ylide complex $Ph_3Cr(CH_2{-}PMe_3)_3$ [8a]. Under elimination of benzene and metalation of three methyl groups, the hexacoordinated inner-phosphonium-*ate* complex with six Cr–C-σ bonds $Cr[(CH_2)_2PMe_2]_3$ was formed (Scheme 2; [8b,c]).

Interestingly this reaction is reversible, if phenylacetylene as a more C–H acidic substrate (compared with benzene or methane) was reacted with this complex (Scheme 3).

The formed tris-alkynyl-chromium(III) complex $(PhC{\equiv}C)_3Cr(CH_2{-}PMe_3)_3$ [8a] yields in the acidolysis with hydrogen chloride only $PhC{\equiv}CH$ and no 1,3-butadiyne, but in the mass spectra, probably as a result of thermal decomposition, small amounts of $PhC{\equiv}C{-}C{\equiv}CPh$ were detected.

Later, we came back to σ-alkynyl complexes when we started to investigate the reaction of "Cp_2Ti" with $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$. Here, an unexpected C–C single bond cleavage and the formation of the double σ,π-alkynyl-bridged complex $[Cp_2Ti(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)]_2$ was found (Scheme 4; [9]).



Scheme 4.

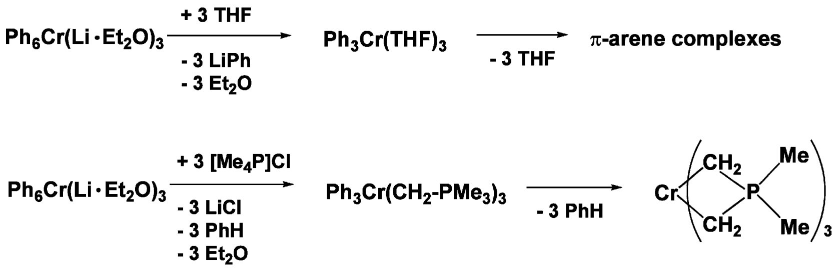
In this paper, on the basis of material selected from excellent reviews [10] and own data [11], a brief overview is given on special aspects of C–C coupling and cleavage reactions in syntheses and reactivity of Group 4 metallocene mono- and bis-σ-alkynyl complexes. Here, compounds of the type $L_2M(\sigma\text{-}C{\equiv}CR)$ and $L_2M(\sigma\text{-}C{\equiv}CR)_2$ with M = titanium and zirconium in the oxidation states +3 and +4 and L = Cp (η^5-cyclopentadienyl) and Cp* (η^5-pentamethylcyclopentadienyl) were considered. Because there is such a large amount of material present [10], the given examples are restricted to the transition metals Ti and Zr as well as to the ligands Cp and Cp* and no compounds with partially substituted Cp ligands or heterobimetallic combinations of these with other metals shall be considered here. These examples are listed in many reviews [10].

Eventually some similarities of the two examples of σ-to-π conversion will be discussed: (i) coupling of the σ-alkynyl groups at metallocenes to π-complexed 1,3-butadiyne and (ii) coupling of σ-phenyl groups at chromium to π-complexed diphenyl.

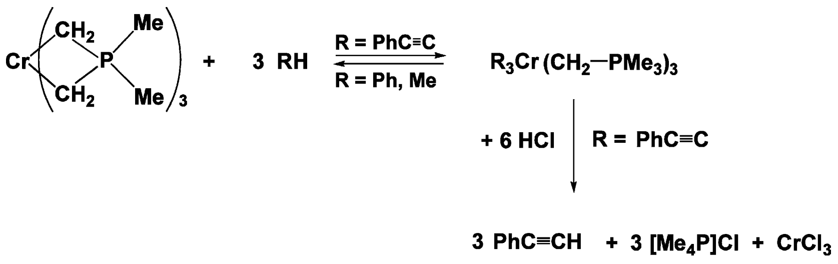
2. σ-Alkynyl complexes

2.1. *Titanocene(IV)–bis-σ-alkynyl complexes $Cp_2Ti(\sigma\text{-}C{\equiv}CR)_2$*

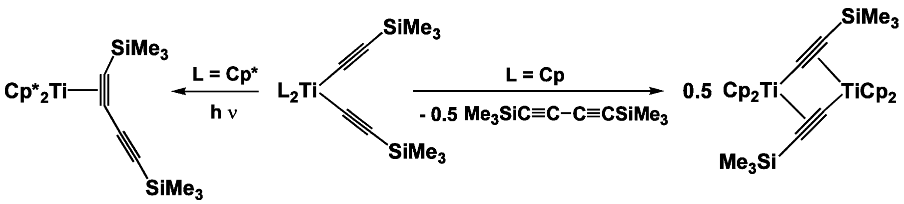
Titanocene(IV)–bis-σ-alkynyl complexes of type $Cp_2Ti(\sigma\text{-}C{\equiv}CR)_2$ have been well known in literature for quite a long time. The same applies to the respective zirconium and hafnium species. These complexes are the most typical examples for Group 4 metallocene σ-alkynyl complexes, which were listed and discussed in detail in many reviews [10]. They are prepared typically by lithium salt elimination starting from the dichlorides Cp_2TiCl_2 and the corresponding lithium acetylides $LiC{\equiv}CR$ [10]. These complexes are mostly very stable and were often used by Lang and others as tweezer-like



Scheme 2.



Scheme 3.



Scheme 5.

organometallic molecules, which can complex a lot of different salts, organometallics, alkali metals, etc. [10].

One very special case in this series of complexes is $Cp_2Ti(\sigma\text{-}C{\equiv}CSiMe_3)_2$ [12] showing the formation of the double σ,π-alkynyl-bridged titanocene(III) complex $[Cp_2Ti(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)]_2$ under reductive elimination of the butadiyne $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ (Scheme 5; [9,12]).

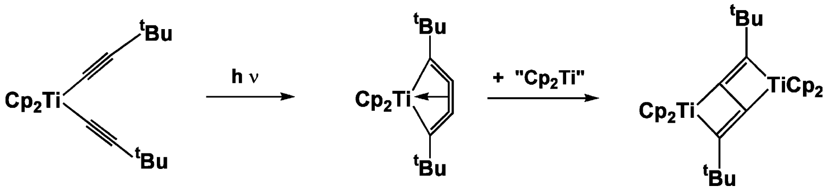
With Cp* under irradiation, a C–C coupling of the alkynyl groups to the 1,3-butadiyne occurred and a titanacyclopropene $Cp_2^*Ti(\eta^2\text{-}1,2)\text{-}Me_3SiC_2{-}C{\equiv}CSiMe_3]$ was formed (see Scheme 5 and chapter concerning $Cp_2^*Ti(\sigma\text{-}C{\equiv}CR)_2$) [20,21,25].

Irradiation of the earlier described $Cp_2Ti(\sigma\text{-}C{\equiv}C^tBu)_2$ [13c] produces the five-membered titanacyclocumulene $Cp_2Ti(\eta^4\text{-}1,2,3,4\text{-}^tBuC_4^tBu)$ [13a] which was detected by NMR as an intermediate [14] reacting with titanocene "Cp_2Ti" to the complex with an intact bridging 1,3-butadiyne $[Cp_2Ti]_2[\mu\text{-}\eta^2(1,3),\eta^2(2,4)\text{-}^tBuC_2C_2^tBu]$ (Scheme 6; [15]).

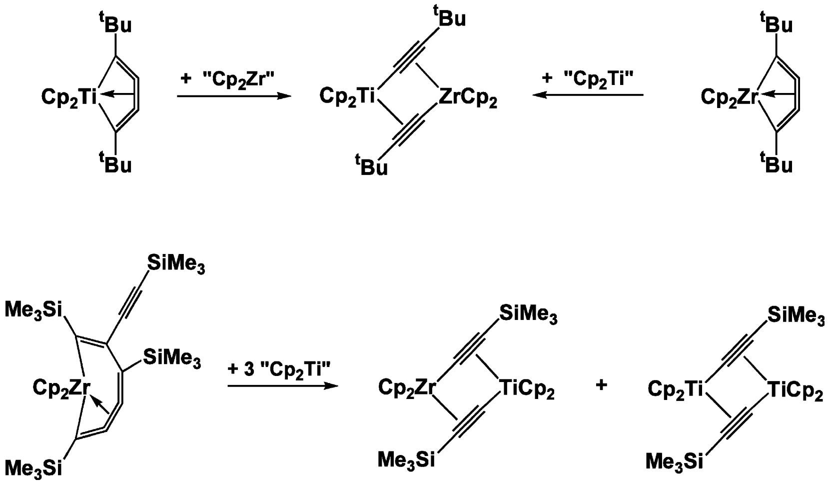
Cleavage of the diyne was found in the reaction of titanacycle $Cp_2Ti(\eta^4\text{-}1,2,3,4\text{-}^tBuC_4^tBu)$ with "Cp_2Zr" or the zirconacycle $Cp_2Zr(\eta^4\text{-}1,2,3,4\text{-}^tBuC_4^tBu)$ [16] with "Cp_2Ti", giving a heterobinuclear complex $Cp_2Ti(\mu\text{-}\sigma,\pi\text{-}C{\equiv}C^tBu)_2ZrCp_2$ ([13a]; Scheme 7).

A similar product with Me_3Si substituents $Cp_2Ti(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2ZrCp_2$ [13b] was found in the reaction of a seven-membered zirconacycle [13d] with "Cp_2Ti" (Scheme 7).

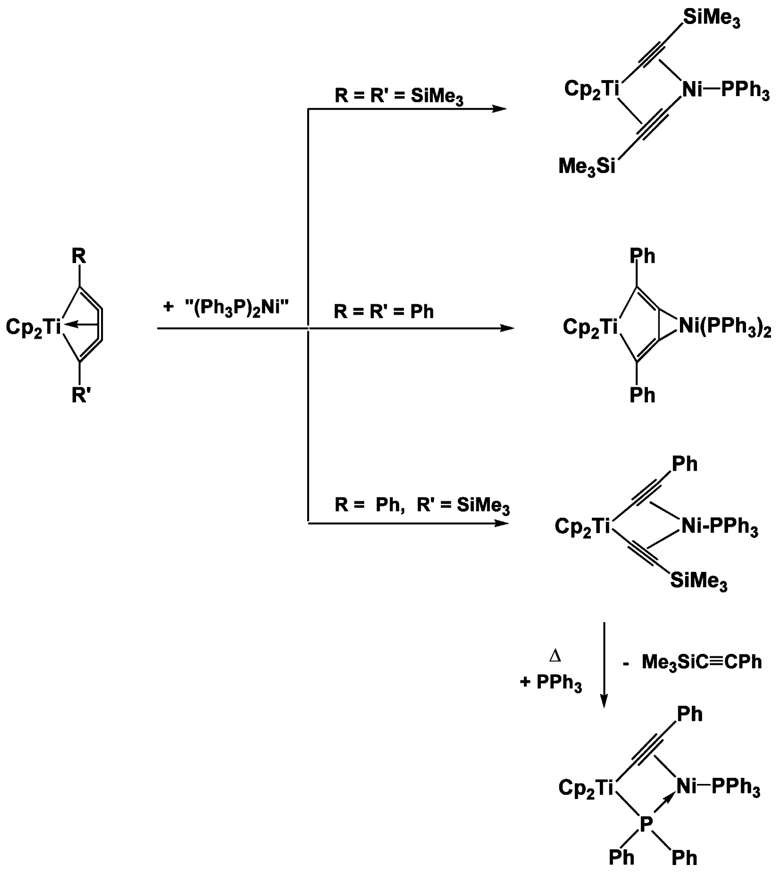
By an external complexation of "$Ni(PPh_3)_2$" at the 2,3-double bond of the cyclocumulenes $Cp_2Ti(\eta^4\text{-}1,2,3,4\text{-}PhC_4Ph)$ [17], the heterobimetallic complex $Cp_2Ti[\mu\text{-}\eta^2\text{-}(1,4)\text{-}PhC_4Ph]Ni(PPh_3)_2$ [14] with an intact bridging diyne was formed, stable only if two Ph substituents were used. With two Me_3Si groups, the early–late heterodinuclear σ,π-alkynyl bridged complex $Cp_2Ti(\sigma,\pi\text{-}C{\equiv}CSiMe_3)Ni(\sigma,\pi\text{-}C{\equiv}CSiMe_3)(PPh_3)$ and with one Ph- and one Me_3Si group the tweezer-like complex $Cp_2Ti(\sigma,\pi\text{-}C{\equiv}CSiMe_3)(\sigma,\pi\text{-}C{\equiv}CPh)Ni(PPh_3)$ [18] is formed, the latter reacting with PPh_3 under P–C bond cleavage and the formation of $Cp_2Ti(\mu\text{-}PPh_2)(\sigma,\pi\text{-}C{\equiv}CPh)Ni(PPh_3)$ [19]. In this reaction, the phenyl and $C{\equiv}CSiMe_3$ groups combine to $Ph{-}C{\equiv}CSiMe_3$ (Scheme 8).



Scheme 6.



Scheme 7.



Scheme 8.

2.2. Permethyl-titanocene(IV)–bis-σ-alkynyl complexes $Cp^*_2Ti(\sigma\text{-}C{\equiv}CR)_2$

Compared with the above-mentioned Cp–, the Cp* examples of this type are relatively rare. They were also prepared by lithium salt elimination starting from the dichlorides $Cp^*_2TiCl_2$ and the corresponding lithium-acetylides LiC≡CR, e.g., for R = ^{t}Bu [20], $SiMe_3$ [21], Ph [22]. These complexes are very stable and were often used as tweezer-like organometallic molecules like the unsubstituted Cp complexes.

The complex $Cp^*_2Ti(\sigma\text{-}C{\equiv}CSiMe_3)_2$ gives under irradiation also a C–C coupling of the alkynyl groups to the 1,3-butadiyne, but no reduction as shown for the Cp case occurred, a titanacyclopropene $Cp^*_2Ti(\eta^2\text{-}1,2\text{-}Me_3SiC_2\text{–}C{\equiv}CSiMe_3)$ was obtained instead (Scheme 5; [20,21,25]).

2.3. Zirconocene(IV)–bis-σ-alkynyl complexes $Cp_2Zr(\sigma\text{-}C{\equiv}CR)_2$

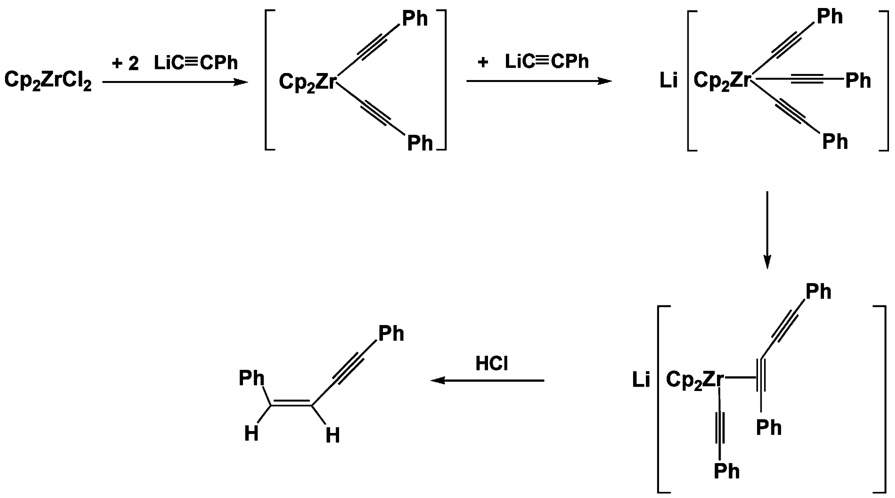
These complexes are also well known and behave very similar to the above-mentioned titanocene(IV)–bis-σ-alkynyl complexes $Cp_2Ti(\sigma\text{-}C{\equiv}CR)_2$. A series of outstanding contributions of this field are from Erker's group [23a,23b,23c,23d,23e,23f].

For example, it was described for $Cp_2Zr(\sigma\text{-}C{\equiv}CMe)_2$ that catalytic amounts of strong Lewis acids like $B(C_6F_5)_3$ catalyze, the C–C coupling reaction of the acetylide groups under the formation of 1,3-diyne complexes $Cp_2Zr(\eta^4\text{-}1,2,3,4\text{-}MeC_4Me)$ [23a,23b]. It is worth to mention that the reverse influence of $B(C_6F_5)_3$ was found in the case of permethylzirconocene systems, where the C–C bond of the complexed diyne in $Cp^*_2Zr(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ was cleaved under the formation of bis-alkynyls $Cp^*_2Zr(\sigma\text{-}C{\equiv}CR)_2$ [23g] (see also next chapter concerning $Cp^*_2Zr(\sigma\text{-}C{\equiv}CR)_2$).

One interesting question is the existence of zirconocene(IV)–tris-σ-alkynyl *ate*-complexes $[Cp_2Zr(\sigma\text{-}C{\equiv}CPh)]_3Li$ [24a] produced by the reaction of Cp_2ZrCl_2 with three equivalents of lithium acetylide LiC≡CPh, maybe formed via the zirconocene(IV)–bis-σ-alkynyl complexes $Cp_2Zr(\sigma\text{-}C{\equiv}CR)_2$. Recently it was shown that such complexes can give zirconacyclopropene-containing zirconates $[Cp_2Zr(\sigma\text{-}C{\equiv}CPh)(\eta^2\text{-}1,2\text{-}PhC_2\text{–}C{\equiv}CPh)]Li$ [24b] (Scheme 9), which after hydrolysis deliver *Z*-conjugated enynes [24a].

2.4. Permethyl-zirconocene(IV)–bis-σ-alkynyl complexes $Cp^*_2Zr(\sigma\text{-}C{\equiv}CR)_2$

Compared with the above-mentioned Cp complexes, the Cp* examples of this type are also relatively rare.



Scheme 9.

Lithium salt elimination starting from the dichloride $Cp^*_2ZrCl_2$ and the corresponding lithium-acetylides LiC≡CR is the method of preparation, e.g., for R = ^{t}Bu [20], $SiMe_3$ [25], Ph [25,26].

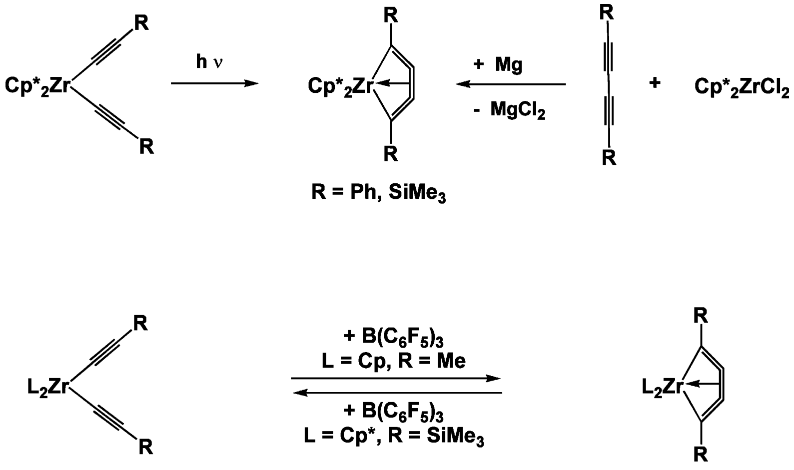
The complex $Cp^*_2Zr(\sigma\text{-}C{\equiv}CR)_2$, R = Ph, $SiMe_3$, in sunlight affords C–C coupling of the alkynyl groups to the 1,3-butadiyne, but no reduction to Ti(II) as shown for the “Cp_2Ti” case as well as a complexation to a titanacyclopropene $Cp^*_2Ti(\eta^2\text{-}1,2\text{-}Me_3SiC_2{-}C{\equiv}CSiMe_3)$ (Scheme 5) was observed. Instead, in high yields the zirconacyclocumulenes $Cp^*_2Zr(\eta^4\text{-}1,2,3,4\text{-}RC_4R)$ with R = Ph, Me and Me_3Si were formed, also prepared by the reduction of $Cp^*_2ZrCl_2$ with magnesium in the presence of the corresponding diynes (Scheme 10; [20,25]).

As mentioned above, catalytic amounts of strong Lewis acids like $B(C_6F_5)_3$ catalyze the C–C bond cleavage in the zirconacyclocumulene $Cp^*_2Zr(\eta^4\text{-}1,2,3,4\text{-}Me_3SiC_4SiMe_3)$ to form the bis-alkynyl complex $Cp^*_2Zr(\sigma\text{-}C{\equiv}CSiMe_3)_2$ [23g]. Apparently, an equilibrium between the zirconacycle and bis-alkynyl is shifted by $B(C_6F_5)_3$ for Cp–Me to the cycle and for Cp*–Me_3Si to the bis-alkynyl complex. In summary, $B(C_6F_5)_3$ catalyzes either the C–C coupling [23a,23b] or cleavage [23g] in such systems (Scheme 10).

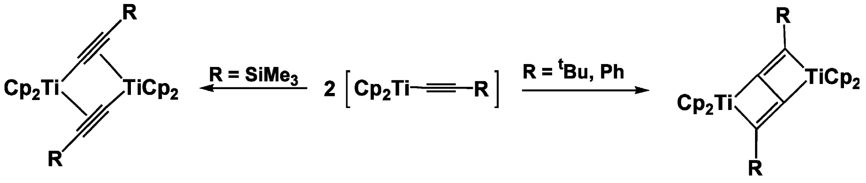
2.5. *Titanocene(III)–mono-σ-alkynyl complexes $Cp_2Ti(\sigma\text{-}C{\equiv}CR)$*

To the best of our knowledge, such complexes do not exist as stable compounds due to their strong tendency to dimerize. In a classical work, Teuben et al. [27a] investigated the reaction of $[Cp_2TiCl]_2$ with NaC≡CPh and did not obtain the expected monomeric complex [$Cp_2TiC{\equiv}CPh$] but rather a binuclear complex with a bridging butadiyne ligand $[Cp_2Ti]_2[\mu\text{-}\eta^2(1,3),\eta^2(2,4)\text{-}PhC_2C_2Ph]$ (Scheme 11). This C–C coupling reaction between two titanium atoms was investigated in detail by the Royo group [27b].

Another type of dimerization is found in the above-mentioned σ,π-alkynyl-bridged titanocene(III) complex $[Cp_2Ti(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)]_2$ [9,12].



Scheme 10.



Scheme 11.

Similar complexes [$Cp_2Ti(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSnMe_3)]_2$ were also formed starting from stannyl-substituted alkynes via π-complexes $Cp_2Ti(\eta^2\text{-}Me_3SnC_2SnMe_3)$ and elimination of $Me_3Sn{-}SnMe_3$ [28].

Upon treating $(Ph_3P)_2Ni(\eta^2\text{-}1,2\text{-}Me_3SiC_2{-}C{\equiv}C\text{-}SiMe_3)$ with "Cp_2Ti", a C–C single bond cleavage of the diyne was found and the heterobimetallic complex $Cp_2Ti(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)Ni(PPh_3)(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)$ isolated [18], which formally consists of a titanocene(III)–mono-σ-alkynyl complex [$Cp_2Ti(\sigma\text{-}C{\equiv}CSiMe_3)$], stabilized by a "nickel(I) species".

Nevertheless, the monomeric titanocene(III)–mono-σ-alkynyl complexes [$Cp_2Ti(\sigma\text{-}C{\equiv}CR)$] are very important as intermediates in many stoichiometric and catalytic reactions.

We became aware of the question of such species as [$L_2Ti(\sigma\text{-}C{\equiv}CR)$] when we considered the mechanism of our C–C single bond metathesis of 1,4-disubstituted 1,3-butadiynes (see following) [29,30].

2.6. *Permethyl-titanocene(III)–mono-σ-alkynyl complexes* $Cp_2^*Ti(\sigma\text{-}C{\equiv}CR)$

There are, to the best of our knowledge, only two examples for such monomeric species. The first is the complex $Cp_2^*Ti{-}C{\equiv}CMe$, reported as the product of the reaction of Cp_2^*TiCl with $LiC{\equiv}CMe$ without structural characterization [31]. If reacting Cp_2^*TiCl with $LiC{\equiv}C^tBu$ only in *n*-hexane, the complex $Cp_2^*Ti{-}C{\equiv}C^tBu$ was obtained and characterized by X-ray crystal structure diffraction (Scheme 12; [22a]).

In THF only the lithium tweezer compound [$Cp_2^*Ti(C{\equiv}C^tBu)_2Li(THF)$] and not the mono-σ-alkynyl titanocene(III) complex was found [22a].

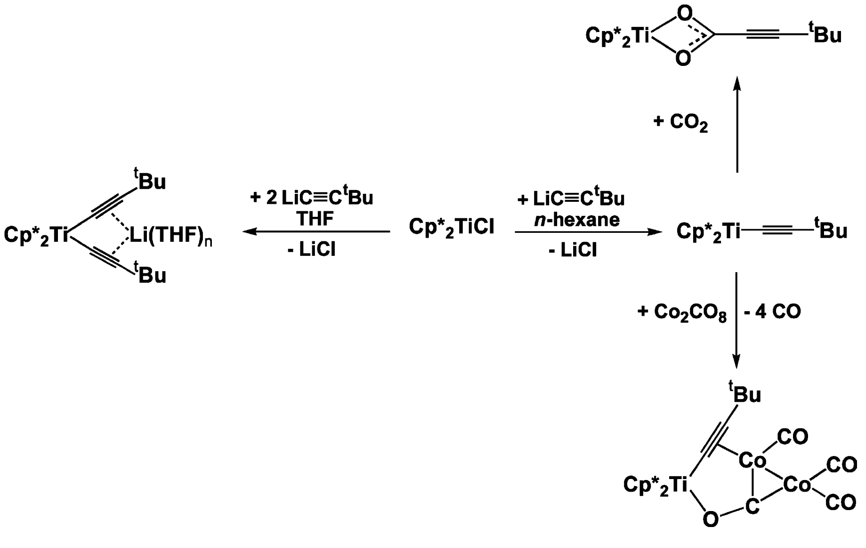
The complex $Cp_2^*Ti{-}C{\equiv}C^tBu$ reacts with $CO_2(CO)_8$ under formation of a (μ_3-(oxy-methylidin)-cyclo-(tricarbonylcobalt)(monocarbonylcobalt)-(μ_2-η2-3-trimethyl-propinyl))titanium [22b]. With carbon dioxide, the permethyltitanocene carboxylate $Cp_2^*Ti(O_2CC{\equiv}C^tBu)$ as a typical insertion product was formed (Scheme 12; [22a]).

2.7. *Zirconocene(III)– and permethyl-zirconocene(III)–mono-σ-alkynyl complexes* $Cp_2Zr/Cp_2^*Zr(\sigma\text{-}C{\equiv}CR)$

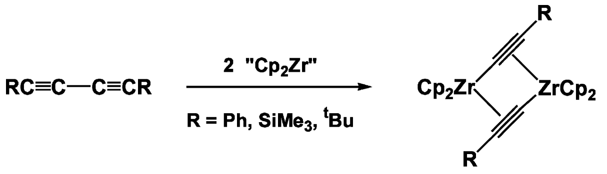
Also such complexes do not exist due to the tendency to dimerize, which is even stronger than found for the corresponding Ti compounds.

In reactions of "Cp_2Zr" with different 1,3-butadiynes $RC{\equiv}C{-}C{\equiv}CR'$ [13d,32a], the products are well-known twofold σ,π-alkynyl bridged zirconium(III) complexes (Scheme 13; [23,32]), generated by a new method.

These are thoroughly characterized and have been synthesized also by other methods (see, for example, in [10h]). The C–C single bond activation with a cleavage of that bond is favoured for zirconium as compared with



Scheme 12.



Scheme 13.

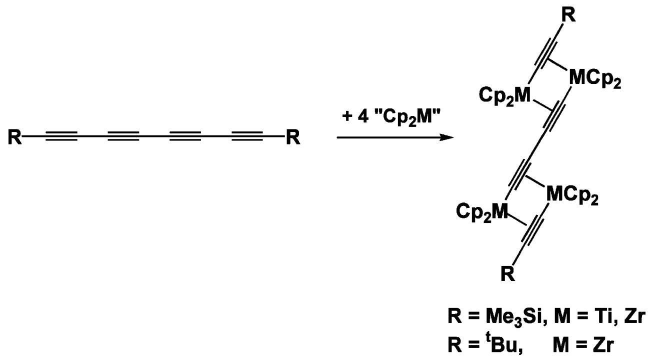
titanium [32], an observation that is backed by theoretical calculations [33,34].

The reaction of $(Ph_3P)_2Ni(\eta^2\text{-}1,2\text{-}Me_3SiC_2\text{–}C{\equiv}CSiMe_3)$ with "Cp_2Zr", like in the above-mentioned Ti case, gives a C–C single bond cleavage of the diyne and the formation of the heterobimetallic complex $Cp_2Zr(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)Ni(PPh_3)(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)$, which formally is a zirconocene(III)–mono-σ-alkynyl complex $[Cp_2Zr(\sigma\text{-}C{\equiv}CSiMe_3)]$, stabilized by a "nickel(I) species" [18].

Permethyl-zirconocene(III)–mono-σ-alkynyl complexes $Cp_2^*Zr(\sigma\text{-}C{\equiv}CR)$ till now are unknown. There are practically no data about monomeric or dimeric complexes of this type.

2.8. *Miscellaneous*

Reactions of titanocene and zirconocene towards octatetraynes RC≡C–C≡C–C≡C–C≡CR are very similar to that found for 1,3-butadiynes. Alkynyl complexes were obtained starting from RC≡C–C≡C–C≡C–C≡CR with R = Me_3Si for titanocene and zirconocene, but in the case R = ^{t}Bu only for zirconocene giving with four equivalents of the metallocene a twofold C–C single bond cleavage (Scheme 14; [35]).



Scheme 14.

If the two butadiyne moieties are separated by a *para*-phenylene unit in $RC{\equiv}C\text{–}C{\equiv}C\text{–}C_6H_4\text{–}C{\equiv}C\text{–}C{\equiv}CR$, the same type of reaction was found [36]. Tris-butadiynyl-benzenes like $1,3,5\text{-}(RC{\equiv}C\text{–}C{\equiv}C)_3C_6H_3$ give with six equivalents of zirconocene the threefold C–C cleaved product (Scheme 15; [37]).

Monosubstituted acetylenes RC≡CH, R = Ph, Me_3Si, $Me(CH_2)_3$, $Me(CH_2)_9$, react with $Cp_2^*Ti(\eta^2\text{-}Me_3SiC_2\text{-}SiMe_3)$ to form permethyltitanocene-1-alkenyl-alkynyls (Scheme 16; [38]).

The formation steps of such complexes are the substitution of $Me_3SiC{\equiv}CSiMe_3$ by RC≡CH, the oxidative addition of the formed $Cp_2^*Ti(\eta^2\text{-}RC_2H)$ to the titanocene-hydrido-alkynyl $[Cp_2^*Ti(H)(C{\equiv}CR)]$ and the subsequent insertion of a further RC≡CH to yield $Cp_2^*Ti(\sigma\text{-}(E)\text{–}CH{=}CHR)(\sigma\text{-}C{\equiv}CR)$.

In the reaction of 2-pyridyl-C≡CH with *rac*-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$, another 1-alkenyl-alkynyl complex, *rac*-(ebthi)$Zr[\sigma\text{-}(E)\text{–}C(SiMe_3){=}CH(SiMe_3)]\text{-}(\sigma\text{-}C{\equiv}C\text{-}2\text{-pyridyl})$ which is stabilized by an agostic interaction was obtained without substitution of the bis(trimethylsilyl)acetylene (Scheme 17; [39]).

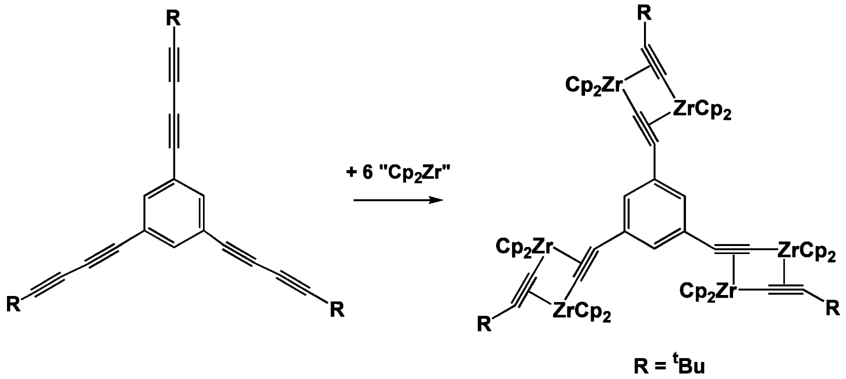
Reactions of $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with unsubstituted acetylene give beside the zirconacyclopentadiene as a coupling product a small amount of a dimeric complex with a bridging diacetylide group and agostic 1-alkenyl ligands $\{Cp_2Zr[C(SiMe_3){=}CH(SiMe_3)]\}_2[\mu\text{-}\sigma(1,2)\text{-}C{\equiv}C]$ (Scheme 18; [39]).

This complex is important in deactivation processes of catalysts for polymerization of acetylene [39].

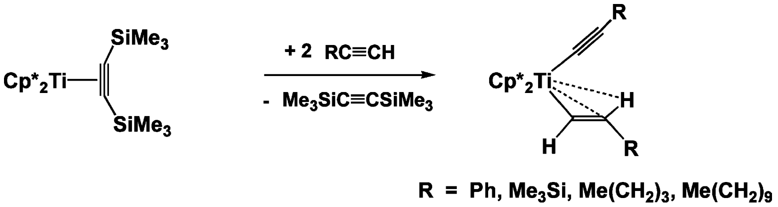
3. Reactions of σ-alkynyl complexes

3.1. *Dimerization of 1-alkynes*

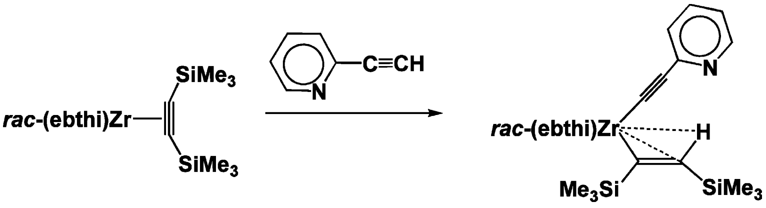
Mach [40] has shown recently that the above-mentioned complexes like $Cp_2^*Ti(\sigma\text{–}(E)\text{–}CH{=}CHR)(\sigma\text{-}C{\equiv}$



Scheme 15.



Scheme 16.

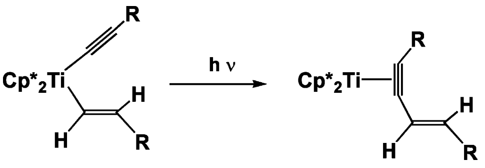


Scheme 17.

CR) show a photochemical coupling reaction of the alkenyl and the acetylide group and give titanocene complexes of 1,4-disubstituted but-1-ene-3-ynes $Cp^*_2Ti(3,4\text{-}\eta^2\text{-}RC_2CH{=}CHR)$ (Scheme 19) This reaction is in principle the same as described before for acetylide groups in permethyl-zirconocene(IV)–bis-σ-alkynyl complexes $Cp^*_2Zr(\sigma\text{-}C{\equiv}CR)_2$ (see as described in Section 4). These complexes catalyze rapid dimerization of terminal acetylenes to 2,4-disubstituted but-1-ene-3-ynes (head-to-tail dimers).

3.2. Oligomerization of 1-alkynes

Species such as $Cp^*_2Ti(C{\equiv}CR)$ could also be important in catalytic oligomerization reactions of 1-alkynes [41]. Cleavage of $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ by using an excess of the system Cp_2TiCl_2–magnesium gives the dimeric titanium(III) complex $[Cp_2Ti(C{\equiv}CSiMe_3)]_2$ [9]. The same system $Cp^*_2TiCl_2$–magnesium with an excess of $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ yields under analogous conditions, via cleavage of the central C–C single bond of the diyne and coupling of the acetylide with another diyne, the complex $Cp^*_2Ti[\eta^3\text{-}Me_3SiC_3{=}C(C{\equiv}CSiMe_3)SiMe_3]$ displaying a hex-3-ene-1,5-diyne-3-yl ligand [42]. The initial formation of a mono-alkynyl-titanium(III) complex $L_2Ti(C{\equiv}CSiMe_3)$ in both systems is assumed, which for L = Cp dimerizes quickly to $[Cp_2Ti(C{\equiv}CSiMe_3)]_2$. Alternatively for R = Cp*, it is more stable and can react with a diyne to yield the complex $Cp^*_2Ti[\eta^3\text{-}Me_3SiC_3{=}C(C{\equiv}CSiMe_3)SiMe_3]$ (Scheme 20).



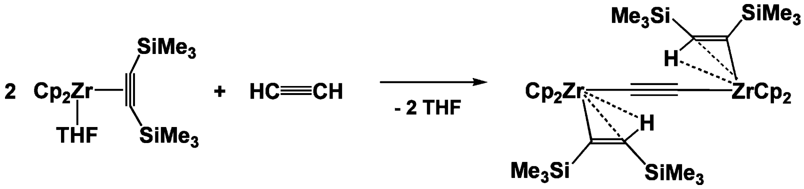
Scheme 19.

The Cp* ligands prevent dimerization of the mono-alkynyl complexes. That is why Cp^*_2Ti catalysts are better catalysts in oligomerization reactions of 1-alkynes, compared with the corresponding Cp systems.

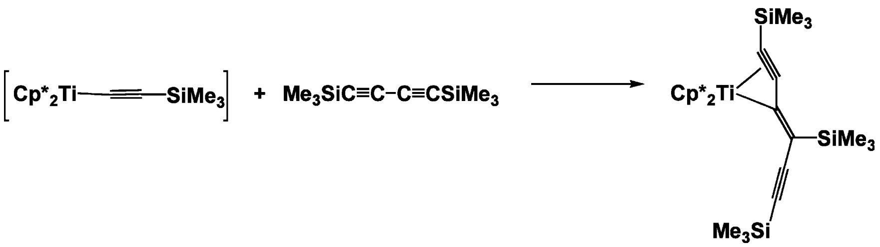
3.3. Polymerization of acetylene

On the basis of $Cp^*_2Ti(\sigma\text{-}(E)\text{-}CH{=}CHR)(\sigma\text{-}C{\equiv}CR)$ an alternative mechanism (Scheme 21) for the polymerization of acetylene [43] is assumed, which differs from the mechanism proposed by Alt et al. [44].

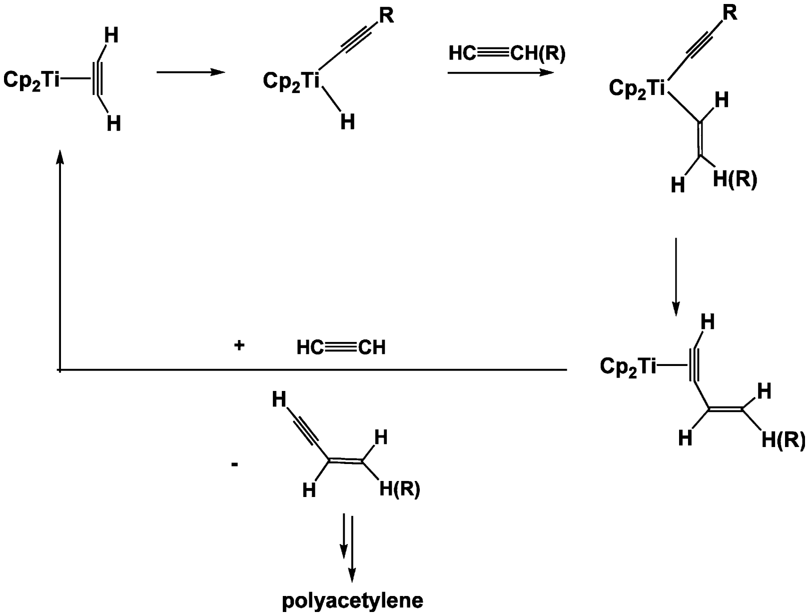
The steps could be π-complexation of acetylene to $Cp_2Ti(\eta^2\text{-}HC_2H)$, oxidative addition to the hydrido-acetylide $Cp_2Ti(H)(C{\equiv}CH)$, insertion of a further $HC{\equiv}CH$ to yield $Cp_2Ti({-}CH{=}CH_2)({-}C{\equiv}CH)$ and coupling to $Cp_2Ti(3,4\text{-}\eta^2\text{-}HC_2{-}CH{=}CH_2)$. The substitution of vinylacetylene $HC_2{-}CH{=}CH_2$ opens a new catalytic cycle, again via $Cp_2Ti(\eta^2\text{-}HC_2H)$, $Cp_2Ti(H)(C{\equiv}CH)$, insertion of $HC_2{-}CH{=}CH_2$ to yield $Cp_2Ti({-}CH{=}CH{-}CH{=}CH_2)({-}C{\equiv}CH)$, coupling to $Cp_2Ti(3,4\text{-}\eta^2\text{-}HC_2{-}$



Scheme 18.



Scheme 20.



Scheme 21.

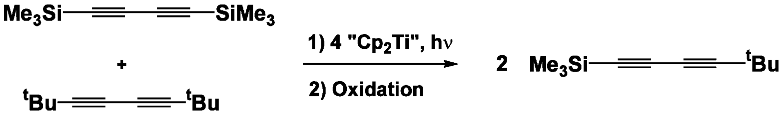
CH=CH–CH=CH$_2$). Repeated sequence: substitution, oxidative addition, coupling, etc. would lead to the *trans*-polyacetylene [11c].

3.4. Photocatalytic C–C single bond metathesis

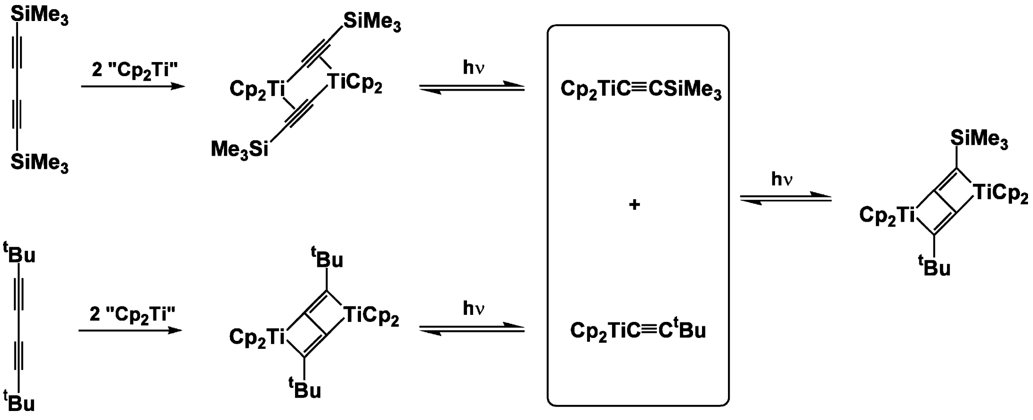
The interaction of butadiynes with titanocenes and zirconocenes can give, via metallacyclocumulenes, a cleavage of, or a coupling to butadiynes by the metallocene cores. Cleavage of symmetrically substituted butadiynes in combination with a subsequent alternating recombination of the fragments realizes a C–C single bond meta-thesis (Scheme 22; [45]).

If one-to-one mixtures of the butadiynes ^{t}BuC≡C–C≡C^{t}Bu and Me$_3$SiC≡C–C≡CSiMe$_3$ are treated with an excess of an “Cp$_2$Ti” reagent and under irradiation, the unsymmetrically substituted diyne ^{t}BuC≡C–C≡CSiMe$_3$ is afforded after an oxidative work-up, in addition to the symmetrically substituted starting diynes. This is the first titanocene-mediated, photocatalyzed C–C single bond metathesis in homogeneous solution. With regard to the metal compound, this meta-thesis cannot be conducted catalytically. The course of reaction (Scheme 23) can be formulated in such a way that the titanocene forms with ^{t}BuC≡C–C≡C^{t}Bu the binuclear complex with an intact C$_4$ backbone and with Me$_3$SiC≡C–C≡CSiMe$_3$ the σ,π-alkynyl-bridged cleavage product.

Under the influence of light, both complexes are subsequently cleaved to the extremely unstable monomeric Ti(III) complexes [Cp$_2$Ti(σ-C≡C^{t}Bu)] and [Cp$_2$Ti(σ-C≡CSiMe$_3$)], which then dimerize to either the respective starting complexes or to a differently substituted binuclear complex. The reverse reaction is realizable. This was recently supported by dynamic NMR investigations in which we could show that



Scheme 22.



Scheme 23.

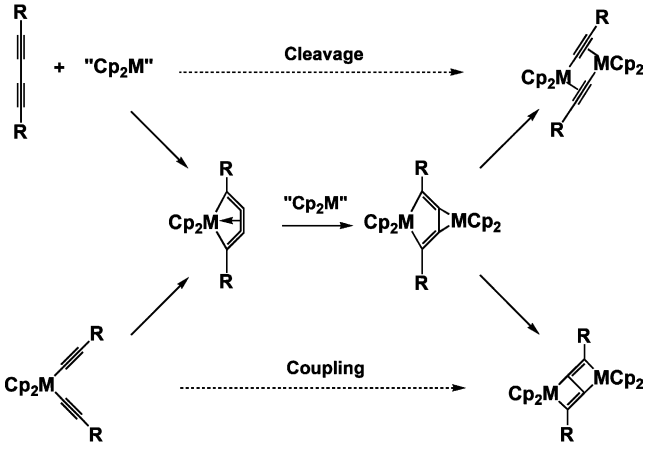
dinuclear C–C cleaved complexes, e.g., $[Cp_2Ti]_2[(\mu\text{-}C{\equiv}CSiMe_3)(\mu\text{-}C{\equiv}C^tBu)]$ very likely are present in solutions of the uncleaved complexes $[Cp_2Ti]_2[\mu\text{-}\eta^2(1,3),\eta^2(2,4)^t\text{-}BuC_2C_2SiMe_3]$ [30].

To overcome the problem of the non-catalytic reaction sequence with respect to the metal compound, sterically demanding ligands were used to avoid unintentional coupling reactions between the substrates. Using the pentamethylcyclopentadienyl ligand (Cp*) instead of the cyclopentadienyl ligand (Cp) leads to unintended coupling reactions of diynes with the Cp* ligand [20].

4. Generalization

By taking into account all above-mentioned results, a general reaction scheme is deduced, which is capable of explaining both the cleavage of and the coupling to 1,3-butadiynes in a uniform order of events (Scheme 24; [46]).

According to this scheme, the cleavage as well as the coupling progresses via metallacyclocumulenes, in which the intramolecular coordination of the inner double bond is, in the subsequent step, replaced by an intermolecular one. These intermediates then rearrange depending on the metals M and the substituents R to afford products in which either an intact or a cleaved C_4 linkage is present. The individual energy levels of these and comparable complexes as well as of the claimed intermediates have been determined by thorough calculations, and the results confirm the relative thermodynamic stabilities as observed experimentally. Thus these theoretical results emphatically support the documented concept about the reaction course [46].



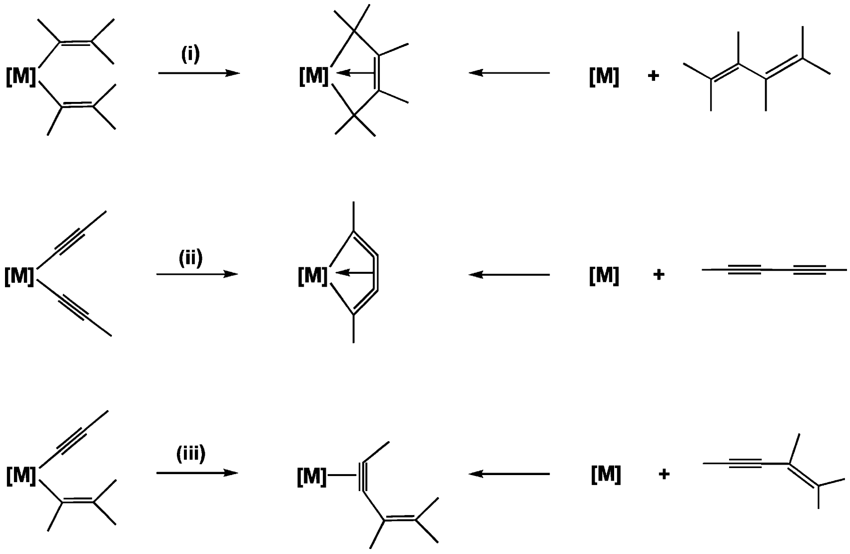
Scheme 24.

In the series of coupling of anionic unsaturated groups X like $CH{=}CH_2$ and $C{\equiv}CR$ at Group 4 metallocene complexes Cp_2MX_2 all possible combinations are well investigated (Scheme 25):

i) coupling of two anionic vinyl groups to 1-metallacyclopent-3-enes (formed also by complexation of 1,3-butadienes; [47,48]);
ii) coupling of two alkynyl groups to 1-metallacyclopenta-2,3,4-trienes (formed also by complexation of 1,3-butadiynes; [25,49]);
iii) mixed coupling of one alkynyl and one vinyl groups to 1-metallacyclopropenes (formed also by complexation of but-1-ene-3-ynes; [40]).

Interesting is the easy formation of 1-metallacyclopent-3-enes (1,3-butadiene complexes (i)) by coupling of two anionic vinyl groups and of the 1-metallacyclo-2,3,4-trienes (1,3-butadiyne complexes (ii)) by coupling of two anionic alkynyl groups. Also the mixed coupling of one alkynyl and one vinyl group to but-1-ene-3-ynes was observed in similar systems, but so far the complexation of such ligands was only investigated for titanocene.

It was calculated that the dianionic products 1-metallacyclopent-3-enes (i) [50] and 1-metallacyclopenta-2,3,4-trienes (ii) [46a], both formed by coupling of two anions, are thermodynamically more stable compared with the corresponding metallocene starting materials $Cp_2M(-CH{=}CHR)_2$ and $Cp_2M(C{\equiv}CR)_2$. The

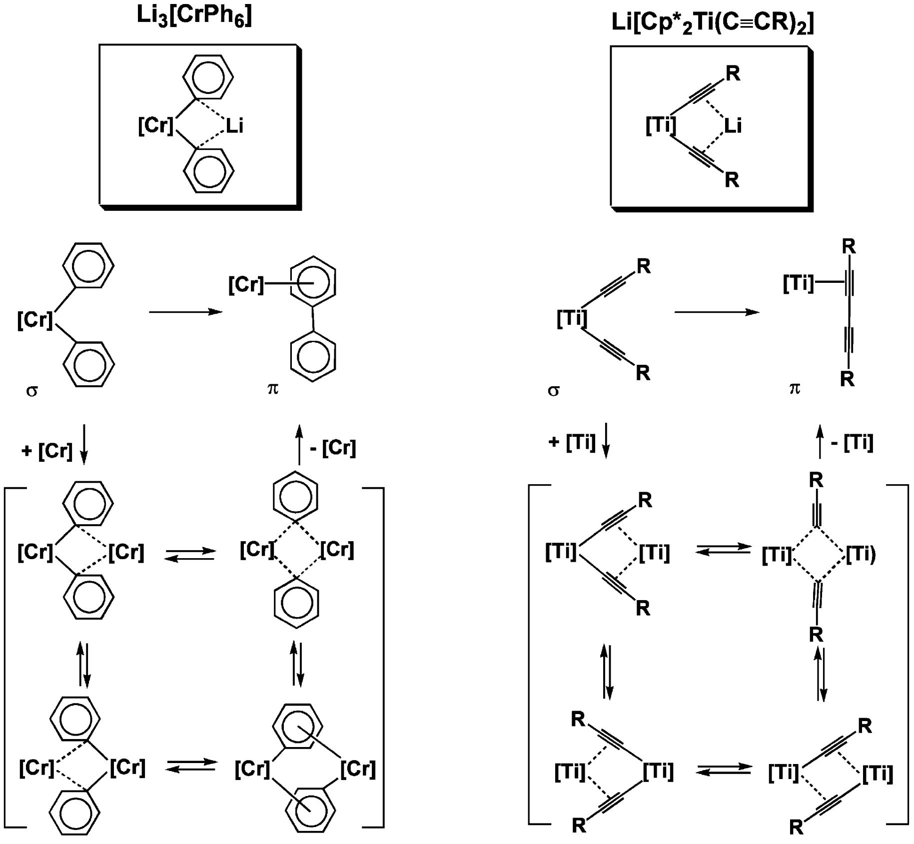


Scheme 25.

reverse C–C cleavage reaction for the product (ii) was found to be possible only under very drastic conditions or with the help of another metal, giving other thermodynamically much more stable complexes, different from the starting ones. Very recently systems such as Cp_2TiX_2 with X = saturated R were calculated also [46d].

4.1. *Similarities of the σ-to-π conversion in coupling of alkynyl groups at titanium and phenyl groups at chromium?*

In the case of Group 4 metallocene phenyl complexes $Cp_2M(\sigma\text{-}Ph)_2$ thermal activation gives aryne complexes $Cp_2M(\eta^2\text{-}C_6H_4)$ together with benzene and small



Scheme 26.

amounts of Ph–Ph [51], whereas under irradiation the formation of phenyl radicals and their combination to diphenyl was assumed [52]. On the basis of only some experiments, the formation of any aryne complexes was ruled out in the coupling of σ-bonded phenyl groups to diphenyl at chromium [53].

As mentioned in Section 1, the complex $Ph_3Cr(THF)_3$ or its LiPh-*ate*-complex $Ph_6Cr(Li\cdot Et_2O)_3$ form mixtures of π-(arene)-chromium compounds. In the structure of $Ph_6Cr(Li\cdot Et_2O)_3$ [6b], the chromium is surrounded by six phenyl groups and the phenyl groups appear to bridge the Li and Cr atoms under formation of strong Li...C...Cr three-centered two-electron bonds. Similar tweezer-like structures with bridging alkynyl groups are found in the Ti(III) *ate*-complexes like, e.g., $[Cp^*_2Ti(C\equiv C^tBu)_2Li(THF)]$ [22] formed by $Cp^*_2Ti(C\equiv C^tBu)$ and $LiC\equiv C^tBu$ (Scheme 26).

As shown above, bis-alkynyl-complexes in the oxidation state (IV) $Cp_2M(\sigma\text{-}C\equiv CR)_2$ show coupling of alkynyl groups to 1,3-butadiynes. Also monoalkynyl-complexes in the oxidation (III) $Cp_2M(\sigma\text{-}C\equiv CR)$ can dimerize to give complexed 1,3-butadiynes.

If bridging alkynyl groups between two titanium Ti...C...Ti or phenyl groups between two chromium atoms Cr...C...Cr are assumed (instead of the above-discussed combinations Li...C...Ti or Li...C...Cr), one can see some similarities for the σ-to-π conversions at titanium under coupling of alkynyl groups to diynes and at chromium of phenyl groups to diphenyl in the formed π-(arene)-chromium compounds.

For the mixed case, very recently an example of a reversible coupling and cleavage reaction of phenyl and alkynyl groups was found for Pt(0) and tolane $Ph-C\equiv C-Ph$ giving $Ph-[Pt]-C\equiv C-Ph$ [54]. Interestingly, these systems behave totally different to the above-described titanium and zirconium complexes in reaction with $Me_3SiC\equiv C-C\equiv CSiMe_3$ where a cleavage of the internal C–C single bond and the formation of double σ,π-alkynyl-bridged metallocene(III) complexes $[Cp_2M(\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)]_2$ was observed. They show a double Si–C bond cleavage to the complexes $Me_3Si-[Pt]-[\mu\text{-}\sigma(1,2)\text{-}C\equiv C-C\equiv C]-[Pt]-SiMe_3$ [55].

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