compounds. It would be an interesting perspective to replace the CSP at higher temperature by acid or basic catalysts such as ion exchangers, as many other classes of stereolabile compounds—for example, carbonyl compounds bearing a hydrogen-substituted, asymmetric carbon center in the α-position—could be investigated.

The chromatographic procedures summarized under the title "enantiomeric enrichment by HPLC" are a new method to convert an interconvertible racemic mixture into an excess of one enantiomer and to separate the enantiomers at the same time. Especially in cases where only one enantiomer is of interest, this may be a new approach to obtain enantiomerically pure compounds.

Experimental Section

Compounds **1** and **2** were prepared according to literature procedures.[23,24] For the chromatographic experiments the following equipment was used: pump: JASCO PU 986, degasser: JASCO DC-980-50, UV detector JASCO MD-910 multiwavelength detector and JASCO 875-UV, polarimetric detector: JASCO OR990 and JASCO Shodex OR1.

Received: February 2, 1998 [Z11421IE]
German version: *Angew. Chem.* **1998**, *110*, 2025–2028

Keywords: chiral stationary phases · enantiomeric resolution · liquid chromatography · molecular recognition

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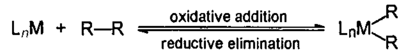
The First Metathesis of C–C Single Bonds in Homogeneous Solution: Titanocene-Mediated and Photocatalyzed Cleavage and Recombination of Disubstituted Butadiynes[**]

Siegmar Pulst, Frank G. Kirchbauer, Barbara Heller, Wolfgang Baumann, and Uwe Rosenthal[*]

Dedicated to Dr. Erhard Kurras
on the occasion of his 70th birthday

The cleavage (oxidative addition) and coupling (reductive elimination) of carbon–carbon bonds (Scheme 1) are elemental steps in many transition metal catalyzed reactions and are strongly influenced by the nature of the ligands L, metal centers M, and organic groups R. The copper-catalyzed Glaser coupling reaction (R = alkynyl) has long been known and is a well-established method for preparing 1,4-disubstituted 1,3-butadiynes.[1] In contrast, examples of the reverse reaction, the activation and cleavage of the central C–C single bond, are rare.[2]



Scheme 1.

The cleavage of the C–C single bonds of butadiynes with "Cp$_2$Ti" and "Cp$_2$Zr" (Cp = cyclopentadienyl) is influenced by the metal,[2c] the substituents,[3] and by the stoichiometry.[4] So far, all attempts to combine the cleavage reaction with a subsequent coupling reaction of the resulting alkynyl groups have failed, both with homobimetallic Ti and Zr systems and early/late heterobimetallic systems such as Ti/Ni and Zr/Ni.[2e] The high thermal stability of the intermediate metal complexes and side reactions such as diyne coupling[4, 5] and ligand cleavage[6] have until now prevented the controlled metathesis of diynes.[2c, 4] Recently, we found that the coupling reaction of the alkynyl groups in $[\mathrm{Cp_2Ti(C{\equiv}C}t\mathrm{Bu)_2}]$[7] is photo-accelerated.[8] Basset et al.[9] described the first heterogeneous "metathesis of alkanes" with silica-supported transition metal hydrides as catalysts. Here we report the first metathesis of the C–C single bonds of disubstituted butadiynes in homogeneous solution; the reaction is mediated by titanocene and photocatalyzed.

An equimolar mixture of the symmetrically substituted butadiynes **1** and **2** was irradiated with light of wavelength 390–450 nm in the presence of an excess of the titanocene ("Cp$_2$Ti") source $[\mathrm{Cp_2Ti}(\eta^2\text{-}\mathrm{Me_3SiC{\equiv}CSiMe_3})]$[10] at 100 °C in toluene. After oxidative workup with $\mathrm{AgSO_3CF_3}$, the diyne starting materials and the unsymmetrically substituted butadiyne **3** were detected by gas chromatography (Scheme 2,

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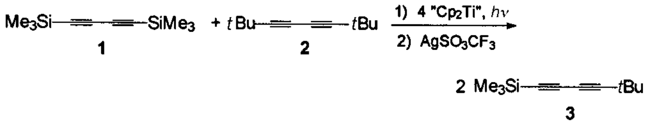
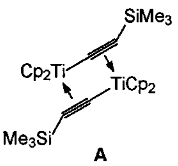
[*] Prof. Dr. U. Rosenthal, Dr. S. Pulst, Dipl.-Chem. F. G. Kirchbauer, Dr. B. Heller, Dr. W. Baumann
Institut für Organische Katalyseforschung der Universität
Buchbinderstrasse 5–6, D-18055 Rostock (Germany)
Fax: (+49) 381-466-9386
E-mail: urosen@chemie1.uni-rostock.de

[**] This work was supported by the Max-Planck-Gesellschaft, the DFG (Gz. Ro 1269/1–1), and the Fonds der Chemischen Industrie.

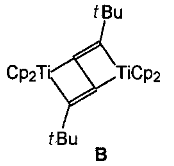


Scheme 2. “Cp_2Ti -mediated photocatalytic formation of **3** from **1** and **2**.

Experimental Section). The formation of **3** indicates a C–C single bond metathesis with cleavage of the butadiynes and subsequent recombination of the alkynyl groups. Since the workup was not optimized and is associated with a certain degree of decomposition of the three butadiynes, the yield of isolated **3** was only 4.9% with respect to the diyne starting materials. However, ^1H NMR measurements showed the presence of 71% of the diynes **1**–**3**, stabilized in the form of the complexes **A** (14%), **B** (36%), and **C** (21%). The reverse reaction, the irradiation of **3** in the presence of “Cp_2Ti”, also leads to a nearly identical mixture of the complexes **A**–**C** and of the butadiynes **1**–**3** after workup.



A



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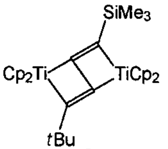


C

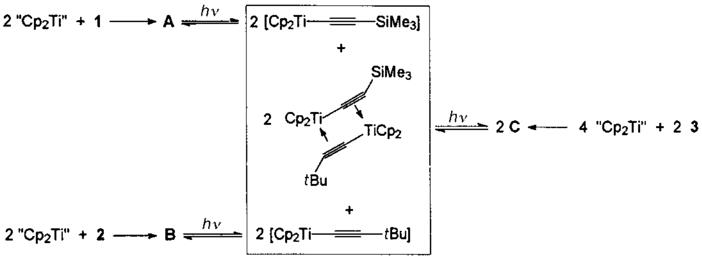
At 100 °C the titanocene source and irradiation are both essential for achieving metathesis of the butadiynes. At 140 °C and in the presence of titanocene the reaction proceeds slowly without irradiation (Table 1). Hence, the titanocene-mediated metathesis is photo-accelerated and can be regarded as a photocatalyzed reaction.[11]

Table 1. Intensities of the ^1H NMR signals of complexes **A**–**C** after various reaction times *t*.[a]

t [h]	Ratio of product		
	A	**B**	**C**
0	0.50	0.50	0
20[b]	0.38	0.50	0
7[c]	0.21	0.39	0.17
20[c]	0.14	0.36	0.21
4[d]	0.51	0.26	0
18[d]	0.44	0.21	0.18

[a] In [D_8]toluene with cyclohexane as internal reference for quantification; sealed tube. [b] Without irradiation at 100 °C. [c] With irradiation at 100 °C. [d] Without irradiation at 140 °C.

To understand the course of the reaction, equimolar mixtures of the intermediates **A** and **B** with and without addition of **1** or **2** were irradiated in an NMR tube. In some experiments, decomposition of the silylalkyne compounds **1**, **3**, and **A** occurred. Irradiation of the mixture of complexes **A** and **B** gave the highest yield of the metathesis product **C** (and **3** after workup). Complexes **A** and **B** result from stoichiometric reactions of one equivalent of the butadiynes **1** and **2** with two equivalents of “Cp_2Ti”, and can be regarded as the initially formed intermediates.[2b, 4] In our proposed mechanism (Scheme 3), the dimeric complexes **A** and **B** (as well as **C** in the reverse reaction) decompose on irradiation to afford the monomeric σ-alkynyltitanium(III) complexes [$Cp_2Ti{-}C{\equiv}C\textit{t}Bu$] and [$Cp_2Ti{-}C{\equiv}CSiMe_3$]. These monomeric species are unstable, [12] coordinatively unsaturated 15-electron d^1 systems, and, because an equilibrium exists between the different types of complexes,[13] they recombine to give a mixture of symmetrical and unsymmetrical dimeric complexes. A similar dissociation of **A**–**C** also occurs in the mass spectrometer.[3, 14]



Scheme 3. Possible mechanism of the metathesis reaction.

Further results of the ^1H NMR investigations are summarized in Table 2. Thermal excitation or irradiation of mixtures of **1** and **2** without titanocene complex did not give **3**. The addition of the radical initiator AIBN had no effect;[15] a mechanism involving organic radicals can therefore be excluded.[16] The NMR spectra also showed that the bis(σ-alkynyl)titanium(IV) complexes [$Cp_2Ti(C{\equiv}CSiMe_3)_2$][7] and [$Cp_2Ti(C{\equiv}C\textit{t}Bu)_2$][7] are not formed. Irradiation of the silylalkynyl complex **A** in the presence of **2** or of **B** in the presence of **1** gave no **C** or **3**. Therefore, a direct reaction of the postulated monomeric σ-alkynyltitanium(III) intermediates with the butadiynes in a Ti–C/C–C metathesis reaction can be ruled out.

Table 2. Table 1: Intensities of the ^1H NMR signals of **A**–**C** and **1**–**3** after irradiation.

System (1:1)	Products	Ratio
1 + **2**[a]	**1**, **2**	1:1
A + **B**[a]	**A**–**C**	1:1.67:1
C[a]	**A**–**C**	1:1:1
1 + **2** + 4 “Cp_2Ti”[b]	**A**–**C**	3.3:2.3:1
A + **2**[b]	no **C**, no **3**	–
B + **1**[b]	no **C**, no **3**	–

[a] 2 h irradiation, 140 °C, 1,3,5-trimethylbenzene. [b] 4 h irradiation, 100 °C, toluene.

A very high titanocene concentration is essential for the success of the metathesis. An increasing butadiyne to titanocene ratio favors the formation of titanacyclopentadienes as coupling products.[4] This may explain why we have so far been unable to carry out a catalytic titanocene-mediated reaction.

Compared to titanocene complexes, the corresponding zirconocene complexes were more reactive with respect to C–C bond cleavage of butadiynes.[10b] However, the “mixed” butadiyne **3** was not observed after irradiation of mixtures of **1** and **2** in the presence of the “Cp_2Zr” source [$Cp_2Zr(py)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$] (py = pyridine). Apparently, the initially formed dimeric σ-alkynylzirconium(III) complexes are more stable toward dissociation. The above-mentioned early/late transition metal combinations Ti/Ni and Zr/Ni[2e] were also inactive.

The sp^3 orbitals of aliphatic C–C bonds are not available for interaction with transition metals. The sp orbitals of the central C–C single bond of butadiynes are better suited to this purpose and can be dramatically activated by complexation in titanacyclocumulenes.[4] Furthermore, some theoretical approaches describe free butadiynes as "dicarbenecumulenes" rather than as dialkynes.[19] The partial double bond character of the central C–C bond is more pronounced in metallacyclocumulenes and is apparent in some reactions.[8]

The novel reaction of butadiynes (Scheme 2) is the first metathesis of C–C single bonds in homogeneous solution. It can serve as a model reaction for the degradation of long-chain alkanes and polymers, which is currently of growing interest.[20] Applications in organic syntheses, analogous to known catalytic metathesis reactions of olefins and alkynes such as ring enlargement of cyclic 1,3-diynes by oligomerization and polymerization and ring-opening metathesis by combination of cyclic and acyclic 1,3-diynes, are currently under investigation.

Experimental Section

Representative experimental procedure: A solution of [Cp$_2$Ti(η^2-Me$_3$SiC≡CSiMe$_3$)] (38 mg, 0.108 mmol), **1** (5.4 mg, 0.027 mmol), and **2**(4.5 mg, 0.027 mmol) in toluene (20 mL) under argon was irradiated with light of wavelength 390–430 nm (two 460 W Philips HPM 12 lamps) at 100 °C for 4 h. The solvent was removed at 60 °C under vacuum, and AgSO$_3$CF$_3$ (19 mg, 0.076 mmol) and THF (2.5 mL) were added. The mixture was stirred at 50 °C for 2 h and then filtered over silica gel. The yields of the butadiynes were determined by gas chromatography: 18.3 % **1**, 19.5 % **2**, 4.9 % **3**; same procedure, starting with **A** and **B**: 15.4 % **1**, 17.9 % **2** and 5.1 % **3**. Yields without irradiation after 18 h at 140 °C: 10.8 % **1**, 18.7 % **2** and 6.5 % **3**; starting from **A** and **B**: 16.9 % **1**, 15.4 % **2** and 8.5 % **3**.

NMR investigation: A solution of **A** (0.027 mmol) and of **B** (0.027 mmol) in [D$_8$]toluene (0.5 mL; cyclohexane as reference) was irradiated at 100 °C with light of the wavelength 390–430 nm (two 460 W Philips HPM 12 lamps) for 20 h in a sealed NMR tube (or allowed to react for 30 h in 1,3,5-trimethylbenzene at 140 °C without irradiation). The reaction was monitored by means of the ^{1}H NMR signals of the Cp and Me groups. Alternatively, the irradiation was carried out in an open tube under argon, the solvents were removed under vacuum, and the residue dissolved in [D$_8$]toluene (0.8 mL) for recording the ^{1}H NMR spectra.

Received: January 13, 1998
Revised version: March 25, 1998 [Z 11364 IE]
German version: *Angew. Chem.* **1998**, *110*, 2029–2031

Keywords: C–C activation · diynes · metathesis · photochemistry · titanium

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[16] In contrast, in the irradiation of equimolar mixtures of the bis(σ-alkynyl)titanium(IV) complexes [Cp$_2$Ti(C≡CSiMe$_3$)$_2$] (**D**)[7] and [Cp$_2$Ti(C≡C*t*Bu)$_2$] (**E**),[7] formation of radicals, which was demonstrated for the analogous bis-σ-aryl- and bis-σ-alkyltitanium(IV) complexes of the type Cp$_2$TiAr$_2$ (Ar = C$_6$H$_5$, CH$_3$C$_6$H$_4$)[17] and Cp$_2$TiR$_2$ (R = CH$_3$)[18] under photochemical conditions, cannot be ruled out. Complexes **A**, **B**, and **C** are produced, and the formation of intermediates such as [Cp$_2$Ti], [Cp$_2$Ti(C≡CR)], and [$^•$C≡CR] is possible. It remains uncertain whether **C** results from dimerization of the titanium(III) species (Scheme 3) or by reaction of two equivalents of "Cp$_2$Ti" with **3** (formed by coupling of different $^•$CCR species.). The irradiation of the silylalkynyl complex **D** in the presence of **2** or of **E** in the presence of **1** does not lead to **C** or **3**. Therefore, a direct reaction of the postulated monomeric σ-alkynyltitanium(III) intermediates with the butadiynes in a Ti–C/C–C metathesis reaction can be ruled out here.

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