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Unraveling the Mechanism of 1,3-Diyne Cross-Metathesis Catalyzed by Silanolate-Supported Tungsten Alkylidyne Complexes

Tobias M. Schnabel, Daniel Melcher, Kai Brandhorst, Dirk Bockfeld, and Matthias Tamm*^[a]

Abstract: The benzylidyne complex $[PhC=W{OSi(OtBu)_3}]$ (1) catalyzed the cross-metathesis between 1,4-bis(trimethylsilyl)-1,3-butadiyne (2) and symmetrical 1,3-diynes (3) efficiently, which gave access to TMS-capped 1,3-divnes RC=C-C=CSiMe₃ (4). Divne cross-metathesis (DYCM) studies with ¹³C-labeled divne $PhC \equiv {}^{13}C - {}^{13}C \equiv CPh$ (3*) revealed that this reaction proceeds through reversible carbon-carbon triple-bond cleavage and formation according to the conventional mechanism of alkyne metathesis. The reaction between 1 and 3* afforded the 3phenylpropynylidyne complex PhC= $^{13}C-^{13}C=W{OSi(OtBu)_3}$] (5*), indicating that alkynylalkylidyne complexes are likely to act as catalytically active species. Attempts to isolate 5* from mixtures of 1 and 3* afforded crystals of the ditungsten 2-butyne-1,4-divlidyne complex $[(tBuO)_{3}SiO_{3}W \equiv {}^{13}C - {}^{13}C \equiv {}^{13}C = W \{OSi(OtBu)_{3}\}_{3}]$ (6*), which was additionally characterized by X-ray diffraction analysis. Depolymerization-macrocyclization of a carbazole-butadiyne polymer, obtained from 3,6-diethynyl-9-dodecylcarbazole (7) under copper-catalyzed Hay coupling conditions, was also efficiently catalyzed by 1 and afforded a mixture of mono-, diyneand triyne-containing tetrameric macrocycles, revealing that diyne disproportionation into monoynes and triynes occurs as a slow side reaction that interferes with a high diyne metathesis selectivity. Potential catalytic pathways were studied by means of quantumchemical calculations, and kinetic studies were performed to substantiate an α , α -mechanism for the catalytic diyne metathesis reaction, which involves intermediate alkynylalkylidyne and α , α 'dialkynylmetallacyclobutadiene intermediates.

Introduction

Conjugated divnes and polyynes constitute important core structures in natural products,^[1-3] supramolecular compounds,^[4–13] materials and polymers.^[14–27] Numerous methods exist for the construction of the rigid divne moiety, with metal-catalyzed oxidative homocoupling of terminal alkynes, e.g., Glaser, Eglinton and Hay coupling reactions, representing the most important method for the preparation of symmetrical 1,3-divnes (Scheme 1).^[28–32] More elaborate methods are required for the synthesis of unsymmetrical

 [a] T. Schnable, Dr. D. Melcher, Dr. K. Brandhorst, D. Bockfeld, Prof. Dr. Matthias Tamm Institut für Anorganische und Analytische Chemie Technische Universität Braunschweig Hagenring 30, 38106 Braunschweig, Germany E-mail: <u>m.tamm@tu-bs.de</u>.
 Supporting information for this article is given via a link at the end of the document. diynes,^[33-35] such as Cadiot-Chodkiewicz coupling^[36] and the Fritsch-Buttenberg-Wiechell rearrangement,[37] which usually involve the generation of reactive bromoalkynes or dibromoenyne species, respectively. These methods suffer from a limited substrate scope, and formation of bromidecontaining side products is less economical and environmentally benign. Therefore, direct metal-catalyzed cross-coupling of two terminal alkynes represents an attractive alternative;^[34,35] however, low selectivity towards the formation of the desired unsymmetrical divne will typically yield significant amounts of the corresponding homocoupled diynes as side products. Optimization was achieved by using one alkyne in large excess, e.g., 4- to 6-fold in Cu-,[38-40] Ni/Cu-[41] and Fe/Cu-catalyzed^[42] reactions. Recently, several protocols were established which display larger heteroselectivity and provide sufficient yields of the unsymmetrical diyne with application of the major alkyne in only two-fold or even lower excess.^[35] Heterogeneous^[43–45] and homogeneous^[46–48] copper and gold catalysts as well as bimetallic Pd/Cu- and Ni/Ag-based systems^[49,50] were succesfully employed for these transformations. Propargylic and homopropargylic alkohols, ethers and esters are particularly useful substrates for these heterocouplings, [46,47,50] since selective and subsequent alkyne activation is mediated by oxygen-metal interaction.[50]



Scheme 1. Synthesis of symmetrical and unsymmetrical 1,3-diynes.

Despite these advances, the irreversible formation of the carbon-carbon bond in these oxidative alkyne cross-coupling reactions is still a major drawback, since the corresponding homocoupled divnes will also form inevitably and need to be discarded, if only the unsymmetrical divne is of further use. We have introduced an alternative reversible method for the synthesis of conjugated divnes that built on the recent remarkable advances in the development and application of homogeneous alkyne metathesis catalysts.^[51-62] Apart from Schrock-type^[63,64] molybdenum and tungsten alkylidyne complexes supported by fluoroalkoxides,[65-77] our group has also introduced silanolate complexes such as 1 (Scheme 1) as efficient catalysts for the metathesis and ring-closing alkynes and α, ω -diynes. metathesis of internal respectively.^[78,79] Moreover, 1 was found to promote the metathesis of methyl-capped conjugated diynes of the type RC=C-C=CMe, which was originally anticipated to afford triynes RC=C-C=C-C=CR together with 2-butvne (MeC=CMe).[80] High selectivity towards the formation of symmetrical diynes (RC=C-C=CR) was found instead; these reactions afforded stoichiometric amounts of 2,4-hexadiyne (dimethyldiacetylene, DMDA),^[81] which was removed from the equilibrium by adsorption on molecular sieves (5 Å) or by evaporation. The usefulness of this diyne homometathesis reaction should be questioned for good reason, since the loss of a C₆-building block effects poor atom economy. We concluded, however, that the reversibility of carbon-carbon triple-bond formation under thermodynamic control will potentially allow to exploit this reaction for the construction of macrocyclic or polymeric diyne materials, which was in fact demonstrated by ring-closing diyne metathesis (RCDYM).[80] Subsequently, this reactivity was also observed for silanolatesupported molybdenum alkylidyne complexes and employed in the total synthesis of naturally ocurring cyclo-1,3diynes.^[82,83]

Turning divne metathesis into a useful reaction can also be achieved by cross-metathesis of two symmetrical 1,3diynes (diyne cross-metathesis, DYCM), which are each conveniently accessible by copper-catalyzed homocoupling of the corresponding terminal alkynes (Scheme 1). Accordingly, 1 proved capable to promote the equilibrium reaction between various 1,4-diaryl- and 1,4-dialkyl-1,3-butadiynes.^[84] To increase the yield of the desired unsymmetrical diyne, one substrate is usually used in excess, e.g., 4 : 1, and the isolated yields fall in the range expected theoretically for just slightly exergonic reactions. In contrast to copper-catalyzed crosscouplings, the symmetrical diyne starting materials can be recycled and used again in the equilibrium metathesis reaction. While catalyst 1 showed remarkably high selectivity towards metathetical diyne formation, slow diyne disproportionation into the corresponding monoynes and triynes (and subsequently into polyynes) was observed after prolonged reaction times.^[84] As observed by Gross and Moore, this disproportionation is significantly faster in the presence of other alkylidyne catalyst systems, which explains the isolation of tetrameric macrocycles with yne (C₂) and diyne (C₄)

moieties from a diyne polymer under alkyne metathesis conditions.^[85]

To rationalize the high selectivity of 1 towards divne formation, we proposed a mechanism based on the conventional mechanism of alkyne metathesis via metallacyclobutadiene (MCBD) intermediates.^[86,87] Thus, divne metathesis likely involves alkynylalkylidyne intermediates (M=C-C=CR), which could reversibly undergo [2+2]-cycloaddition with the respective 1,3-diynes to afford α, α '-dialkynyl-MCBD species (α and α ' refer to the 1,3positions in the metallycycle, and β denotes the 2-position). Although this so-called α, α -mechanism was substantiated by reaction of 1 with the ¹³C-monolabeled 1,4-diphenyl-1,3butadiyne PhC=13C-C=CPh, an alternative mechanism involving alkylidyne and β-monoalkynyl-MCBD intermediates could not be excluded (β-mechanism).^[80] With both mechanistic scenarios, the selectivity towards divne metathesis is explained satisfactorily, whereas divne disproportionation can be rationalized only by deviation from the α,α -mechnism, e.g., with trivne formation via an α,β dialkynyl-MCBD. To further validate these assumptions, we would like to present in this contribution a combined experimental and theoretical study that will help to further unravel the mechanism of the 1,3-divne metathesis reaction, which we regard as an important expansion of the increasingly important field of alkyne metathesis.[51-60,62]

Results and Discussion

Diyne cross-metathesis (DYCM)

For expanding the scope of divne cross-metathesis, we investigated the equilibrium reaction between 1,4bis(trimethylsilyl)-1,3-butadiyne (2) and various symmetrical aromatic and aliphatic 1,3-divnes (3). These reactions provide access to unsymmetrical TMS-capped divnes RC=C- $C=CSiMe_3$ (4), which are useful synthetic intermediates and may serve as synthons for terminal or metalated butadiyne derivatives.^[88] As described previously for other DYCM reactions,^[84] preliminary NMR experiments were carried out for the reaction between 2 and 1,4-bis(4-methoxy)-1,3butadiyne (**3a**, R = p-MeOC₆H₄) to establish the equilibrium constant $K = [4a]^2/([2][3a])$ (Table 1, see also Table 2, Entry 1). The reaction in CH₂Cl₂ was initially followed by gas chromatography, revealing that the equilibrium for this diyne combination is established within ca. 100 minutes at room temperature in the presence of 2 mol% of catalyst 1 (see the Supporting Information, Section S8.1). The reaction was then performed under the same conditions in CD₂Cl₂ for various ratios of the starting concentrations [2]₀ : [3a]₀. Integration of the sufficiently well separated ¹H NMR signals for the OCH₃ groups in **3a** (6H, $\delta \approx 3.82$ ppm) and **4a** (3H, $\delta \approx 3.81$ ppm) allows to determine their relative concentrations and the resulting equilibrium constant K (Table 1). In accordance with Le Chatelier's principle, increasing the excess of 2 over 3a from 1:1 to 4:1 shifts the equilibrium towards the desired

unsymmetrical divne **4a** with an increasing **[4a]** : **[3a]** ratio. For all four experiments, *K* is satisfactorily well reproduced with an average value of *K* = 4.2. As expected, the corresponding Gibbs free energy ($\Delta G_{298K} < -1$ kcal mol⁻¹) indicates that the formation of the unsymmetrical 1,3-divne is only slightly exergonic. It should be noted that this experiment shall merely confirm that we are dealing with an almost thermoneutral equilibrium reaction and that the error of *K* and ΔG_{298K} must be ascribed to the limit of accuracy of integrating the respective ¹H NMR signals.

$\textbf{Table 1.} \ \textbf{NMR} \ \textbf{study of an quilibrium diyne cross-metathesis reaction.}^{[a]}$						
[2] ₀ : [3a] ₀ ^[b]	[4a] : [3a] ^[c]	К	∆ <i>G</i> ₂ _{98K} [kcal mol⁻¹]	Yield ^[d] [%]		
1:1	1.70	2.89	-0.63	46		
2:1	4.70	5.08	-0.96	70		
3:1	6.74	4.66	-0.91	77		
4 : 1	8.12	4.08	-0.83	80		

[a] Reaction between 1,4-bis(trimethylsilyl)-1,3-butadiyne (2) and 1,4-bis(4-methoxyphenyl)-1,3-butadiyne (3a) affording 4-(4-methoxyphenyl)-1,3-butadiyn-1-yltrimethylsilane (4a, R = 4-MeOC₆H₄; see Table 2, Entry 1); for a detailed protocol and relevant equations, see the Supporting Information (Section S5) and previous work.^[84] [b] Ratio of the starting concentrations. [c] Ratio of the equilibrium concentrations determined by integration of the OCH₃ ¹H NMR signals in 3a (6H) and 4a (3H). [d] Calculated yield based on the conversion of 3a.

DYCM with 2 was then studied for the diynes 3a-3f shown in Table 2, which were obtained from the corresponding terminal alkynes by CuCl-catalyzed homocoupling.^[89] Initially, conversion versus time diagrams were recorded for each diyne combination to establish the optimum reaction time (see the Supporting Information, Section S8). The reactions were then performed on preparative scale (2.60 mmol 2, 0.65 mmol 3, 0.065 mmol 1); after equilibration, the reaction mixtures were filtered through alumina, and the diynes were separated by column chromatography. The isolated yields of 4 are based on the conversion of the minor diyne component 3 and range from 82% (4d) to 91% (4b). In all cases, the unconverted starting material 2 could be largely recovered and used in further DYCM reactions. The isolated yield of 4a (88%) is larger than the yield determined by NMR spectroscopy for a 4:1 mixture of 2 and 3a (80%, see Table 1), which we ascribe to the error of the NMR experiment and to the different reaction conditions. Overall, our new method for the preparation TMS-capped 1,3-butadiynes is clearly able to compete with alternative procedures employing, among others, Cadiot-Chodkiewicz- or Sonogashira-type coupling reactions.[90-93]



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[a] Conditions: 2 (0.1 M), 3 (0.025 M), catalyst 1 (2 mol%), CH₂Cl₂, room temperature; see the Supporting Information (Section S6) for full details. [b] Yield of product 4 isolated after filtration through alumina and purification by column chromatography; the yields are based on the conversion of the minor substrate 3; the unconsumed starting materials 2 and 3 are largely recovered. [c] The molecular structure was determined by X-ray diffraction analysis (see Supporting Information, Section S1).

¹³C-Labeling studies

We had previously reported divne homometathesis of ¹³Cmonolabeled 1,3-pentadiyn-1-yl-2-13C-benzene (PhC=13C-C=CMe), which afforded monolabeled 1,4-diphenyl-1,3butadiyne-2-13C (PhC≡13C-C≡CPh).[80] The absence of any detectable amounts of doubly labeled 1,4-diphenyl-1,3butadiyne-2,3-13C (PhC≡13C-13C≡CPh, 3b*) confirmed that the metathesis reaction proceeds through carbon-carbon triple-bond cleavage and formation, ruling out any mechanism involving alkynyl group exchange.^[94] Here, **3b*** obtained by homocoupling copper-catalyzed of ¹³C-labeled phenylacetylene (PhC= 13 CH) was employed in DYCM with **2**. Initially, a 1: 1 mixture of both alkynes was dissolved in CD₂Cl₂ together with 2 mol% of 1. The ¹³C NMR spectrum (see the Supporting Information, Section S9.11) was recorded after 2 h reaction time, revealing the presence of the doubly labeled butadiynes $Me_3SiC\equiv^{13}C-^{13}C\equiv CSiMe_3$ (2*), $PhC\equiv^{13}C-^{13}C\equiv CPh$ (3b*) and PhC= $^{13}C-^{13}C=CSiMe_3$ (4b*), which are expected to form via the equilibrium reactions shown in Scheme 2. The ¹³C carbon atoms of the labeled positions give rise to singlets at 88.2 ppm for 2* and 74.0 ppm for 3b*, whereas two doublets at 88.0 and 74.3 ppm with ${}^{1}J_{CC} = 148$ Hz are found for asymmetric 4b*. Full experimental and simulated ¹³C NMR spectra of all the three labeled diynes with the assignment of

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all signals are presented in the Supporting Information (Section S9). Repeating the metathesis between 2 and 3b* on a preparative scale under the reaction conditions mentioned in Table 2 (four-fold excess of 2) afforded a mixture of 4b*/4b in 89% vield after chromatographic work-up. Figure 1 shows an excerpt from the resulting ¹³C NMR spectrum; the singlets at the positions marked C1, C2, C3 and C4 are assigned to unlabeled 4b, while the two doublets for the labeled positions C2 and C3 in 4b* (see above) come along with two doublets of doublets for the unlabeled carbon atoms C1 and C4, which display ${}^{1}J_{CC}/{}^{2}J_{CC}$ couplings of 147/18 Hz and 196/25 Hz, respectively. It should be noted that the DYCM protocol symmetrical access provides convenient to and unsymmetrical doubly ¹³C-labeled 1,3-butadiynes which are difficult to be obtained by other methods.^[95,96]



Scheme 2. Diyne metathesis with ¹³C-labeled diphenylbutadiyne (**3b***). The asterisks indicate labeled position; the corresponding complexes **5** and **6** are formed from unlabeled diphenylbutadiyne (**3b**).

As previously described for monolabeled PhC=13C-C=CPh,[80] doubly 13C-labeled 3b* was treated with an equimolar amount of 1 in CD₂Cl₂. The ¹³C NMR spectrum indicated the formation of the 3-phenylpropynylidyne complex 5* (Scheme 2), which displays two doublets at 251.8 and 96.0 ppm (${}^{1}J_{CC} = 94 \text{ Hz}$) for the W= ${}^{13}C-{}^{13}C=CPh$ unit (Figure 2). The tungsten satellites reveal couplings with the ¹⁸³W isotope of ${}^{1}J_{CW}$ = 300 Hz and ${}^{2}J_{CW}$ = 61 Hz, which is in good agrement with the previously established values for the W=13C-C=CPh and W=C-13C=CPh congeners.[80] A similar coupling $(^{1}J_{CW} = 296 \text{ Hz})$ was reported for the quinuclidine adduct of the related complex [(tBuO)₃W=C-C=CEt], which formed in a similar fashion from [(tBuO)₃W=CMe] and 3,5octadiyne.^[97] It should be noted that other tungsten 3phenylpropynylidyne complexes, e.g., [PhC=C-C=W(CO₅X] (X = CI, Br, I),^[98–100] represent classical Fischer-type carbyne complexes and contain tungsten in the formal oxidation state +IV. Closer inspection of the full ¹³C NMR spectrum of **5*** (see the Supporting Information, Section S9.12) reveals the presence of only very minor amounts of other labeled polyyne species. A signal at 89.3 ppm is assigned to the acetylenic unit of diphenylacetylene (tolane), which must form as a side product in stoichiometric amounts. Its formation was additionally confirmed by UV/vis spectroscopy, which also indicated the absence of the starting material 1,4-diphenyl-1,3butadiyne and of the higher polyyne 1,6-diphenyl-1,3,5hexatriyne^[96,101] (see the Supporting Information, Section S10).



Figure 1. Excerpt from the ¹³C NMR spectrum of **4b*/4b** in CD₂Cl₂; the asterisk denotes an impurity of **2***.

Unfortunately, the complexes 5 and 5* could not be isolated in pure form, since all attempts to crystallize these highly soluble compounds, e.g., from hexamethyldisiloxane or toluene, afforded dark red crystals of 6 or 6* in ca. 30% yield (Scheme 2). The molecular structure of 6 was confirmed by Xray diffraction analysis, revealing the formation of a C₄-bridged ditungsten complex (Figure 3). The asymmetric unit contains two halves of two independent centrosymmetric molecules with similar geometric parameters. The W-C1-C2 and C1-C2-C2' angles are close to linearity (176°-179°), and the W-C1 bond lengths of 1.780(4) Å (molecule A) and 1.777(6) Å (molecule B) indicate the presence of tungsten-carbon triple bonds in comparison with a just slightly shorter W-C1 bond of 1.745(2) Å in 1.[78] Accordingly, the C1-C2 bonds are significantly longer than the C2-C2' bonds, revealing the presence of a bis(alkylidyne) complex with a W=C-C=C-C=W moiety. This assignment is also confirmed by the observation of two doublets of doublets for the fully labeled $W \equiv {}^{13}C ^{13}C \equiv ^{13}C - ^{13}C \equiv W$ moiety in the ^{13}C NMR spectrum of 6* (see the Supporting Information, Section S9.14), which appear at 247.0 (C_{α}) and 88.7 ppm (C_{β}) with ${}^{1}J_{CC}$ and ${}^{2}J_{CC}$ couplings of 64 and 42 Hz, respectively.

10.1002/chem.201801651

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Figure 2. Excerpt from the ¹³C NMR spectrum of a 1 : 1 mixture of 1 and 3b* in CD₂Cl₂ showing the signals of the α - and β -carbon atoms of the W=¹³C-¹³C=CPh unit in 5*.



Figure 3. Molecular structure of 6 (molecule A) with thermal displacement parameters drawn at 50% probability; methyl groups and minor components of disordered groups were omitted for clarity. The asymmetric unit contains two halves of two independent molecules; selected bond lengths [Å] and angles [°] in molecule A/B: W–C1 1.780(4)/1.777(6), C1–C2 1.361(7)/1.371(9), C2–C2' 1.238(9)/1.224(13); W–C1–C2 176.0(4)/ 178.0(5), C1–C2–C2' 176.8(6)/179.3(10).

The ditungsten complex **6** represents a new carbon-rich transition metal complex, in which sp carbon chains terminate with carbon-metal bonds.^[18,102–104] For C₄-bridged systems, complexes with an even number of electrons may exist in three conjugated forms, *i.e.* M–C=C–C=C–M (1,3-butadiyne-1,4-diyl), M=C=C=C=C=M (1,2,3-butatriene-1,4-diylidene) and M=C–C=C–C=M (2-butyne-1,4-diylidyne). The 1,3-butadiyne-1,4-diyl form is most common, and two- and four-electron oxidation would formally afford the 1,2,3-butatriene-1,4-diylidene and 2-butyne-1,4-diylidyne species.^[104–106] The dicarbyne form as realized in **6** has been stabilized only in a few ditungsten and dirhenium complexes, e.g., with M = W(CO)₂Tp' (Tp'= hydridotris(3,5-dimethylpyrazolyl)borate),^[107]

I_c(agab)W bis(diphenylphosphino)ethane), (dppe = I),^[108,109] W(CO)₂(dppe)X (X = CI. and [Re(PMe₃)₄(C=CSiMe₃)]^{+.[110]} It should be noted, however, that 6 exhibits significantly shorter metal-carbon bonds than the previous ditungsten complexes, in which the formal oxidation state +IV is assigned to the metal atoms. Therefore, 6 represents the first example of a 2-butyne-1,4-diylidyne complex terminated by two tungsten(VI) metal atoms.

The formation of 6 from 1 and 1.4-diphenyl-1.3-butadivne (3b) can be rationalized by initial formation of alkynylalkylidyne complex 5 (as evidenced by ¹³C NMR spectroscopy for 5*) with release of one equivalent of diphenylacetylene (tolane). Reaction of 5 with additional divne could then furnish 1,6diphenyl-1,3,5-hexatriyne and 1, which will further form 6 and and additional tolane, presumably via a 5-phenyl-2,4pentadiynylidyne species (W=C-C=C-C=C-Ph). Accordingly, a 1:1 reaction between 1 and 1,4-diphenyl-1,3-butadiyne furnishes 1.5 equivalents of tolane, which was the only side product that could be identified unambiguously, e.g., by UV/vis spectroscopy. It should be noted that the observed fast formation of 5/5* supports the prevalence of the α, α mechanism of diyne metathesis, whereas the subsequent slow disproportionation must proceed through an α , β -MCBD, in which the alkylidyne and alkynyl moieties reside in neighboring positions. The final formation of 6 may then quickly proceed according to the α, α -mechanism, which explains our inability to monitor the intermediate formation of $PhC \equiv {}^{13}C - {}^{13}C \equiv {}^{13}C - {}^{13}C \equiv C - Ph$ and $W \equiv {}^{13}C - {}^{13}C \equiv {}^{13}C - {}^{13}C \equiv C - Ph$ species, if labeled diphenylbutadiyne (3b*) is employed. The observation of all labeled carbon atoms in the C4 bridge of 6* rules out any other mechanistic scenario that does not involve the cleavage and formation of carbon-carbon triple bonds.

Diyne depolymerization-macrocyclization

Despite the high selectivity of catalyst 1 in diyne metathesis, the isolation of 6/6* confirmed the possibility of slow diyne (and disproportionation into monoynes and triynes subsequently into polyynes) as reported previously.^[84] This side reaction is also responsible for the formation of tetrameric macrocycles with yne (C_2) and diyne (C_4) moieties from a carbazole-butadiyne polymer in the presence of [EtC=Mo{N(Ar)*t*Bu}₃]/Ph₃SiOH. With this catalyst system, the compound with four 1,3-butadiyne-1,4-diyl units was detected only as a minor product by MALDI-TOF mass spectrometry, which also revealed the formation of a mixture of tetramers with varying amounts of C2 and C4 units incorporated in the macrocycle.[85] Since we expected a higher selectivity of catalyst 1 towards diyne formation, we studied its performance in the depolymerization of a related polycarbazole system. Therefore, 3,6-diethynyl-9-dodecylcarbazole $(7)^{[111,112]}$ was prepared and subjected to polymerization under coppercatalyzed Hay coupling conditions (Scheme 3).[85] According to gel permeation chromatography (GPC), the resulting polymer 8 had a Mn of 27 kDa, a polydispersity index (PDI) of 1.7 and a degree of polymerization of 51 (Table 3).

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Table 3. Gel permeation chromatography data. ^[a,b]					
Compound	<i>M</i> ₀ [kDa]	<i>M</i> _w [kDa]	M _w /M _n	Pn ^[c]	
Monomer 7	0.55	0.55	1.0	-	
Polymer 8	27.9	47.8	1.7	51	
Tetramers 9 ^d	2.5	2.5	1.0	- -	

[a] Reactions conditions: toluene, 10 wt% **1**, 22 h, rt. [b] Based on polystyrene standards, see the Supporting Information (Section S11) for details. [c] Degree of polymerization $P_n = M_n(\text{polymer})/M_n(\text{monomer})$. [d] Mixture of tetramers **9** with all distributions shown in Scheme 3.

A toluene solution of the diyne-bridged polycarbazole **8** was treated with a catalytic amount of **1** (10 wt%) and stirred at room temperature for 22 h (Scheme 3). The resulting crude reaction mixture was passed through a short pad of neutral aluminium oxide to remove the catalyst. Recrystallization from THF solution at -30 °C afforded a white powder in 75% yield;

the GPC trace indicates the conversion of polycarbazole 8 to a (quasi-)monodisperse lower molecular weight oligomer (Figure 4, Table 3). Analysis of this product by MALDI-MS (Figure 5) revealed that the depolymerization-macrocyclization reaction did not exclusively produce the expected tetramer 9 (m/z = 1525), but also afforded the tetrameric species $9+C_2$ (m/z = 1549), $9-C_2$ (m/z = 1501), $9-C_4$ (m/z = 1477). Again, the formation of **9** with four divide units as the main product confirms the ability of 1 to act as a rather selective diyne-metathesis catalyst. However, the prolonged reaction times required for complete depolymerization lead to substantial divne disproportionation as an undesired side reaction, which also furnishes the tetrameric species with one C_6 and three C_4 units (9+ C_2), one C_2 and three C_4 units (9- C_2) as well as two C2 and two C4 units (9-C4). In principle, the latter compound should exist as a mixture of two structural isomers (Scheme 3). It is obvious that diyne disproportionation constitutes an unavoidable, albeit slow side-reaction, and in future experiments, further adjustment regarding the degree of polymerization, catalyst loading, and reaction time is required to apply this catalytic diyne metathesis methodology efficiently in supramolecular chemistry.





Figure 5. Partial MALDI-TOF mass spectrum of the mixture containing the tetramers $9-C_4$ (m/z = 1477), $9-C_2$ (m/z = 1501), 9 (m/z = 1525) and $9+C_2$ (m/z = 1549) shown in Scheme 3.

9 after 22 h.

FULL PAPER



Scheme 4. Possible catalytic cycles for the metathesis of conjugated diynes. Microscopic reversibility is expected for all reaction steps; the direction of arrows shall indicate constructive reaction paths towards the cross-metathesis of two symmetrical diynes $R^1C=C-C=CR^1$ and $R^2C=C-C=CR^2$.

Quantum chemical modeling of diyne metathesis reactions

The divne metathesis studies employing the ¹³C-labeled divnes $PhC \equiv {}^{13}C - C \equiv CMe$, $PhC \equiv {}^{13}C - C \equiv CPh$, ${}^{[80]}$ and $PhC \equiv {}^{13}C - {}^{13}C \equiv CPh$ (vide supra) rule out any mechanistic scenario that does not involve the cleavage and formation of carbon-carbon triple bonds according to the established mechanism of the alkyne metathesis reaction, which involves intermediate metallacyclobutadiene (MCBD) species.^[86] It is therefore reasonable to assume that the metathesis of conjugated diynes also proceeds through a combination of reversible [2+2] cycloaddition and cycloreversion steps. However, the situation is less clear-cut, since two alternative catalytic cycles can be entered from a pre-catalyst (like 1 in this paper), which involve different catalytically active species. As shown in Scheme 4, initiation by cycloaddition of a diyne to the pre-catalyst can afford either an α - or a β -MCBD, which differ in the position of the alkynyl group. Subsequent cycloreversion will lead to alkynylalkylidyne (Scheme 4, left) or alkylidyne complexes (Scheme 4, right), which each appear as intermediates in one of the two catalytic cycles. On the left, catalytic turnover proceeds further via α, α '-dialkynyl-MCBDs (" α, α -mechanism"), whereas β monoalkynyl-MCBDs ("
ß-mechanism") are exclusively involved on the right-hand side. As previously stated,^[80] both mechanisms allow to rationalize the selectivity towards the formation of 1,3divnes during their homo- and cross-metathesis, whereas the observed side reaction, slow divne disproportionation into monoand trivnes (and subsequently into polyvnes).^[84,85] is explained by deviation from the two alternative mechanistic pathways and by the occurrence of α,β -dialkynyl-MCBDs. Overall, the α,α mechanism is more likely, since the formation of the latter species does also require alkynylalkylidyne intermediates, which were identified unambiguously by NMR spectroscopy as ¹³C-labeled $W \equiv {}^{13}C - C \equiv CPh$, $W \equiv C - {}^{13}C \equiv CPh$ and $W \equiv {}^{13}C - {}^{13}C \equiv CPh$ units (vide supra). It must be emphasized, however, that their observation under the reaction conditions in the NMR tube cannot be regarded as conclusive proof, and therefore, we tried to disclose the mechanism of divne metathesis by density functional theory (DFT) calculations.

Since the tungsten complex **1** is currently the only alkylidyne complex that is capable to promote the metathesis of diynes efficiently, the ancillary silanolate ligands seem to be crucial for the observed catalytic activity and selectivity and need to be fully included in the quantum chemical calculations. Because of the enormous size and nature of the silanolate ligands in complex **1**,

FULL PAPER

appropriate consideration of dispersion effects are of particular importance to predict the catalytic activity, and therefore, we decided to employ the PW6B95-D3 functional together with the def2-TZVP basis for the calculation of all reported electronic energies.^[113–117] Unfortunately this level of theory turned out to be too demanding for running geometry optimizations and frequency calculations, and we had to resort to the M06^[118] functional and the rather small double-zeta basis set 6-31G(d,p) for this task. Therefore, all reported values correspond to pure electronic energies computed at the PW6B95-D3/def2-TZVP level of theory at the geometries optimized at the M06/6-31G(d,p) level of theory. For details see Supporting Information (Section S15).

In line with previous studies,[65-67,72,87] we have computed all relevant intermediates and transition states for the two considered catalytic cycles for a model reaction of the tungsten ethylidyne complex $[MeC=W{OSi(OtBu)_3}]$ with 2,4-hexadiyne as the substrate (Scheme 4, $R^1 = R^2 = Me$). In addition, alternative reaction pathways for divne disproportionation were studied computationally. Figure 6 shows the calculated potential-energy profiles for the two alternative initiation steps via α - and β -MCBDs (Scheme 4, upper part), which indicates that the formation of an alkynylalkylidyne complex is favored by 4.9 kcal mol⁻¹. Furthermore, the transition states for the cycloaddition and cycloreversion via the α -MCBD are much lower in energy than the respective transition states for the β -addition. Overall, the α addition of the divne is predicted to be kinetically preferred over the β -addition, and the formation of the alkynylalkylidyne intermediate is kinetically and thermodynamically preferred.



Figure 6. Potential-energy profiles for the α - (black) and β -addition (red) of 2,4hexadiyne to the tungsten ethylidyne complex [MeC=W{OSi(OtBu)}_3]; the red profile corresponds to the β -mechanism shown in Scheme 4 for R¹ = R² = Me. All reported values are electronic energies computed at the PW6B95-D3/def2-TZVP level of theory.

For the alkynylalkylidyne complex to be catalytically active the subsequent reaction with 2,4-hexadiyne must be considered, too. As shown in Figure 7, the cycloaddition reaction can either afford α, α - or α, β -MCBDs, and cycloreversion of the latter will then lead to the formation of triynes. Again, the α -addition is kinetically preferred over the β -addition, and divne metathesis via α, α -

MCBD is kinetically and thermodynamically preferred compared to triyne and monoyne formation via an α , β -MCBD, In conclusion, our computations predict that alkynylalkylidyne complexes represent the catalytically active species and that diyne metathesis follows the α , α -mechanism, whereas the formation of higher polyynes is disfavoured.



Figure 7. Potential-energy profiles for the α - (black) and β -addition (red) of 2,4hexadiyne to the tungsten 2-butynylidyne complex [MeC=C-C=W{OSi(OfBu)_3}_3]; the black profile corresponds to the α, α -mechanism shown in Scheme 4 for R¹ = R² = Me. All reported values are electronic energies computed at the PW6B95-D3/def2-TZVP level of theory.



Figure 8. Ball-and-stick presentation of relevant stationary points for the α , α -MCBD formation by using the M06 density functional; methyl groups were omitted for clarity. Selected bond lengths [Å] in TS/ α , α -MCBD: W–O1 2.212/2.027, W–O2 2.199/2.578.

Finally, it should be mentioned that an appropriate consideration of dispersion interactions seems to be of utmost importance, since inspection of the calculated structures reveals secondary interactions for various stationary points, which involve the coordination of the silanolate ligand in a chelating fashion through an additional oxygen atom of one of the SiO*t*Bu groups. This is illustrated in Figure 8 for the three relevant stationary points for the formation of the α , α -MCBD from the alkynylalkylidyne complex and 2,4-hexadiyne (Figure 7, left part). The alkynylalkylidyne complex does not show secondary

FULL PAPER

tungsten–oxygen interactions, and the calculated W–O bond lengths of 1.899 Å are in perfect agreement with those established for **1** experimentally by X-ray diffraction analysis, *i.e.* 1.8809(14)–1.8882(14) Å.^[78] In contrast, both the transition state (TS) and the α, α -MCBD contain one silanolate ligand bound in a chelating OSi{OSi(OtBU)_3}-\kappa^2O fashion. Surprisingly, the two W–O distances are almost identical in the TS structure (2.212 and 2.199 Å), whereas the MCBD features a shorter W–O1 (2.199 Å) and a longer W–O2 bond (2.578 Å), which resembles the situation found in the complex [MesC=W{OSi(OtBU)_3}{OC(CF_3)_3}].^[73] These findings indicate that secondary interactions with the silanolate ligand play a crucial role in the stabilization of transition states and intermediates and are potentially a key factor for the understanding of the observed high diyne metathesis selectivity of catalyst **1**.

Kinetic study of diyne metathesis

Although the DFT calculations predict a preference for the α . α over the ß-mechanism, we finally devised a kinetic study of the divne cross-metathesis (DYCM) reaction between 1.4bis(trimethylsilyl)-1,3-butadiyne (2) and 1,4-diphenyl-1,3butadiyne (3b). Since the ¹³C-labeling experiments clearly indicated the fast formation of the 3-phenylpropynylidyne complex 5 upon mixing the pre-catalyst 1 and 3b (Scheme 2), we monitored the progress of the DYCM reaction by gas chromatography (GC) for two different experimental procedures: The standard procedure is identical to that described in Table 2 with addition of 2 mol% of 1 to the reaction mixture, while the alternative procedure involved pre-mixing of equimolar amounts of 1 and substrate 3b in dichloromethane for 10 min, followed by addition of this pre-mixed or active catalyst solution to the reaction mixture. Thus, the reaction mixtures contain either the alkylidyne or predominantly the alkynylalkylidyne species at the beginning of the DYCM reaction (t = 0), which will afford different kinetic profiles, if only one of the tungsten compounds is catalytically active.

Comparison of the respective concentration-time diagrams recorded for a catalyst loading of 2 mol% (Figure 9) reveals that the premix protocol (pre) effects a significantly faster conversion than the standard protocol (std) employing the pristine alkylidyne catalyst solution. The respective rate constants $k_{pre} = 2.0 \ 10^{-3} \ s^{-1}$ and $k_{\text{std}} = 6.3 \ 10^{-4} \ \text{s}^{-1}$ have been obtained by an exponential fit corresponding to an observed first-order kinetic, indicating that "premixing" leads to an accelaration by a factor of ca. 3.2 compared to the "standard" reaction. Since both catalytic experiments only differ in the initial concentration of the 3phenylpropynylidyne complex 5, this species is responsible for the observed higher catalytic activity, corroborating that the DYCM reactions proceeds most likely through the α, α mechanism and involves alkynylalkylidyne intermediates (Scheme 4, left side). This result is consistent with the DFT calculations and all experiments reported above.

Knowing that the DYCM reaction rate is increased by "premixing" the alkylidyne complex with a diyne at higher concentrations prior to the actual catalysis, we repeated the kinetic study with a further reduced catalyst loading of 0.5 mol%. The resulting concentration-time diagram qualitatively shows the same behaviour, albeit with lower reaction rates (Figure 10). The ratio between the fitted rate constants $k_{pre} = 4.4 \ 10^{-4} \ s^{-1}$ and $k_{std} = 1.8 \ 10^{-4} \ s^{-1}$ show again a significant accelaration by a factor of 2.4 for the "premixed" catalyst solution, while the ratios $k_{pre,2\%}/k_{pre,0.5\%} = 4.5$ and $k_{std,2\%}/k_{std,0.5\%} = 3.5$ reflect the four times lower catalyst loading quite well. These results indicate that diyne metathesis reactions can be carried efficiently at low catalyst loading, which was additionally exemplified by the DYCM reactions between 1,4-diphenyl-1,3-butadiyne and 1,4-bis(4-methoxyphenyl)-1,3-butadiyne or dodecadiyne (see Supporting Information, Section S14).



Figure 9. Concentration-time diagram of the diyne cross-metathesis (DYCM) reaction of 1,4-bis(trimethylsilyl)-1,3-butadiyne (2) with 1,4-diphenyl-1,3-butadiyne (3b) in a 4 : 1 ratio under standard conditions (dashed line) and with a pre-mixed catalyst solution (solid line) at 2 mol% catalyst loading.



Figure 10. Concentration-time diagram of the diyne cross-metathesis (DYCM) reaction of 1,4-bis(trimethylsilyl)-1,3-butadiyne (2) with 1,4-diphenyl-1,3-butadiyne (3b) in a 4 : 1 ratio under standard conditions (dashed line) and with a pre-mixed catalyst solution (solid line) at 0.5 mol% catalyst loading.

Conclusions

The ability of the tungsten alkylidyne complex 1 to promote not only the metathesis of internal alkynes,^[78] but also the metathesis of 1,3-diynes,^[80,84] has been further exploited by diyne cross-metathesis (DYCM) between 1,4-bis(trimethylsilyl)-1,3butadiyne and symmetrical 1,3-diynes. The resulting trimethylsilane derivatives may serve as useful synthons for the preparation of terminal or functionalized 1,3-diynes, and accordingly, we regard this new diyne metathesis methodology as an important addition to the plethora of methods available in preparative acetylenic chemistry for the construction of conjugated diynes and polyynes. Furthermore, this method provides convenient access to unusual symmetrical and unsymmetrical ¹³C-labeled 1,3-diyne species. In contrast to alternative routes such as irreversible cross-coupling of terminal alkynes, the reversible divne metathesis reaction occurs under full thermodynamic control, which allows to shift the equilibrium in a favorable manner by employing one of the divne substrates in excess. Unreacted starting materials can be recovered and used again for subsequent DYCM reactions. Although catalyst 1 exhibits a remarkably high selectivity towards divne metathesis, diyne disproportionation into monoynes and triynes, and subsequently into higher polynes, occurs as a slow side reaction, which was demonstrated by catalytic depolymerizationmacrocyclization of a carbazole-butadiyne polymer, which does not only afford the desired C4-bridged tetramers, but also macrocycles with a mixture of C_2 -, C_4 - and C_6 -bridges.

Since the ¹³C-labeling studies in this and in a previous study^[80] clearly indicated fast formation of alkynylalkylidyne complexes (M=C-C=C-CR) upon mixing 1 and 1,3-diyne substrates, a mechanism was substantiated that involves alkynylalkylidyne complexes as catalytically active species and α, α -dialkynyl-MCBD intermediates (α , α -mechanism). The disproportionation into monoynes and triynes can then be rationalized by deviation from this mechanism through formation α , β -dialkynyl-MCBD, which according to our theoretical calculations is clearly kinetically and thermodynamically disfavored. The role of catalytically active alkynylalkylidyne species is also in agreement with a kinetic study that reveals significantly higher catalytic activity if pre-catalyst 1 and a 1,3-diyne substrate are premixed and then added to the reaction mixture. However, all attempts to isolate alkynylalkylidyne complexes in pure form by fractional crystallization were prevented by the high solubility owing to the presence of the OSi(OtBu)3 ligand, and only the 2-butyne-1,4divlidyne ditungsten complex 6 that is slowly formed could be isolated in crystalline from.

We fell that diyne metathesis with the level of selectivity provided by catalyst **1** is clearly competitive with other methods for the preparation of symmetrical and unsymmetrical diynes, since it allows to establish carbon-carbon triple bonds in a reversible fashion under thermodynamic control. This will be particularly useful for the construction of macrocyclic diyne and oligo(diyne) formation in view of the great recent success of catalytic alkyne metathesis in supramolecular chemistry.^[59–62]

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FULL PAPER

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FULL PAPER

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The benzylidyne complex $[PhC=W{OSi(OtBu)_3}_3]$ catalyzes the cross-metathesis between 1,4bis(trimethylsilyl)-1,3-butadiyne and symmetrical 1,3-diynes efficiently, giving access to TMS-capped 1,3diynes RC=C-C=CSiMe_3. Experimental and theoretical studies reveal a mechnism that involves reversible carbon-carbon triple-bond cleavage and formation according to the conventional mechanism of alkyne metathesis.



T. M. Schnabel, D. Melcher, K. Brandhorst, D. Bockfeld, and M. Tamm*



Unraveling the Mechanism of 1,3-Diyne Cross-Metathesis Catalyzed by Silanolate-Supported Tungsten Alkylidyne Complexes