Synthesis and Structure of the Smallest Cyclic Cumulene; Reaction of 1,3-Diynes with Zirconocene Complexes

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an intense band at 515 nm ($\varepsilon \approx 10000$ $M^{-1}cm^{-1}$), while **2e** absorbs only weakly in this region (490 nm, $\varepsilon \approx 1000$ $M^{-1}cm^{-1}$). The absence of ring closure in the case of the 3,5-disubstituted azobenzene derivatives **1c** and **1d** could be due to the greater spatial requirements of the substituents (R^3 = Me, Cl) in comparison to those of **1a** and **1b** (R^3 = H), which should make the formation of a planar transition state more difficult. Accordingly, only the 2,3-dihydrocinnoline derivative is formed from 3,3'-dimethylazobenzene.

Experimental Procedure

All operations were carried out under an atmosphere of nitrogen, and with anhydrous. N_2-saturated solvents.

General procedure: To a melt of two parts tolane and one part of the azo compound **1** at 85 °C was added, in portions, the appropriate amount of catalyst (in the case of **1a**, **1b**, and **1d** 0.25 equivalents, for **1c** 0.066 equivalents and for **1e** 0.33 equivalents). The mixture was then stirred for two hours at 85 °C. For **1a**, **1b**, and **1e**, the resultant material was dissolved in CH_2Cl_2, alumina added, and the mixture evaporated to dryness. The resulting powder was chromatographed on alumina (neutral, activity I. ICN) with petroleum ether/THF 10/1 (v/v). For **1c**, the reaction mixture was stirred with petroleum ether and the remaining solid extracted with ether in a Soxhlet extractor. For **1d**, dissolution in CH_2Cl_2, filtration through alumina, and evaporation to dryness gave a solid which was dissolved in a minimum amount of CH_2Cl_2 and overlayered with twice the volume of methanol to precipitate the product.

All compounds gave correct C,H,N analyses and the corresponding molecular ion peaks in their mass spectra (EI, 70 eV).

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[8] Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the deposition number CSD-400708 (**3b**), CSD-400709 (**2c**), CSD-400711 (**2e**) and CSD-380041 (**3e**).
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[14] Crystal structure analysis of **2c**: $0.6 \times 0.5 \times 0.5$ mm, triclinic, $P\bar{1}$, $a = 1224.5(2)$, $b = 1290.2(3)$, $c = 1296.6(2)$ pm, $\alpha = 103.64(2)$, $\beta = 102.82(1)$, $\gamma = 113.38(2)°$, $V = 1.708(1)$ nm^3, $\rho_{calcd} = 1.16$ gcm^{-3}, $2\theta_{max} = 54°$, $Mo_{K\alpha}$ radiation, $\lambda = 71.073$ pm, ω scan, $T = 293$ K, 7672 measured reflections, of which 7440 were independent and 2203 observed, $F > 4\sigma(F)$, SHELXTL-PLUS, direct method, full-matrix least-squares, 415 refined parameters, H atoms were taken from the difference Fourier synthesis and were not refined, $R = 0.063$, $R_w = 0.052$, refinement against $|F|$, residual electron density 0.19 $e\text{Å}^{-3}$ [8].
[15] In this case the powder diffraction diagram contains more than the calculated reflections. Possibly, **2c** crystallizes in two different modifications, only one of

which yielded crystals capable of delivering an X-ray structure. TLC, HPLC, and UV/Vis spectroscopy could not provide any evidence for the existence of isomers.

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[20] The powder diffraction diagram contains the reflections from both compounds.
[21] The possibility that traces of isomers with *cis*-stilbenyl groups exist in solution cannot be excluded.

Synthesis and Structure of the Smallest Cyclic Cumulene; Reaction of 1,3-Diynes with Zirconocene Complexes**

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For some time now we have been studying the interaction of disubstituted butadiynes with Group 4 metallocenes "Cp_2M" as a function of the metal M and the substituents of the diyne. For M = Ti the central C–C single bond of $Me_3Si-C\equiv C-C\equiv C-SiMe_3$ is cleaved, and a dimeric complex $[Cp_2Ti(\mu-\eta^1:\eta^2-C\equiv CSiMe_3)]_2$[11] containing bridged σ-π acetylide groups (type **I**) is formed. This cleavage was found to be dependent on the nature of the diyne substituents. For all other investigated disubstituted butadiynes $R^1C\equiv C-C\equiv CR^2$ ($R^1 = R^2 = Ph$, *t*Bu; $R^1 = SiMe_3$, $R^2 = Ph$, *t*Bu) the C_4 unit remains intact for M = Ti. This affords binuclear complexes with tetradehydro-*trans, trans*-butadiene moieties (μ-η(1-3), η(2-4)-*trans,trans*-butadiene or "zigzag butadiyne") between the Ti centers (type **II**).[2]

I

II
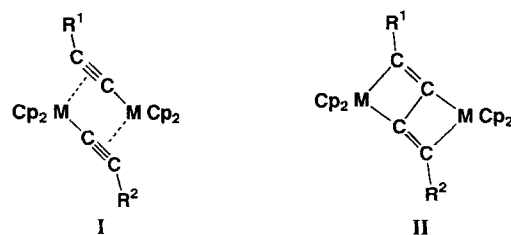
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In contrast, cleavage of the diyne appears to be favored for M = Zr. When using the zirconocene synthon $[Cp_2Zr(thf)(Me_3SiC_2SiMe_3)]$[3] all butadiynes, except $tBuC\equiv C-C\equiv CtBu$, undergo cleavage. For $R^1 = R^2 = SiMe_3$, the reaction yields the complex $[Cp_2Zr(\mu-\eta^1:\eta^2-C\equiv CSiMe_3)]_2$, which has recently also been prepared by a different route.[4] By using unsymmetrically substituted butadiynes ($R^1 = SiMe_3$, $R^2 = Ph$, tBu) we were able to prepare the first complexes of type $[Cp_2Zr(\mu-\eta^1:\eta^2-C\equiv CR^1)(\mu-\eta^1:\eta^2-C\equiv CR^2)ZrCp_2]$. Notably, the σ-π acetylide bridges connecting the two Zr centers differ in these complexes.[5] Reaction with di-tert-butyl-1,3-butadiyne yields product mixtures that are difficult to separate and do not contain any product due to cleavage.

Employing the alkyne zirconocene complex $[Cp_2Zr(py)(Me_3SiC_2SiMe_3)]$[6] (py = pyridine) as a zirconocene synthon yielded novel zirconocene complexes in a surprising array of reactions. These transformations clearly show that in treating complexes of type $[Cp_2Zr(L)(Me_3SiC_2SiMe_3)]$ (L = thf or py) with diynes the nature of the ligands L has a decisive influence on the course of the reaction.

When using $Me_3Si-C\equiv C-C\equiv C-SiMe_3$ the binuclear complex $[Cp_2Zr(\mu-\eta^1:\eta^2-C\equiv CSiMe_3)]_2$ is formed only as a byproduct. Zirconocene complex 1 is the main product, which results from the unusual coupling of two diyne molecules [Eq. (a)]. It was also recently obtained by treating the same

[Cp₂Zr(py)(Me₃SiC≡CSiMe₃)]

+

2 Me₃SiC≡C—C≡CSiMe₃

—py,
—Me₃SiC≡CSiMe₃
→

(a)

1
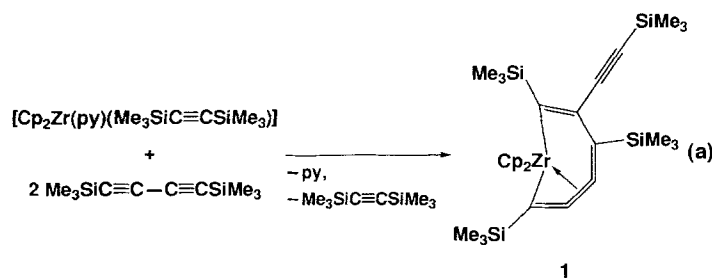
butadiyne with di-n-butylzirconocene (precursor to the Cp_2Zr synthon $[Cp_2Zr(n\text{-butene})]$[8]).[9] It crystallizes as yellow prisms that melt in an argon atmosphere at $187-188\,°C$.[7]

The 2,4,7-tris(trimethylsilyl)-3-(trimethylsilylethynyl)zircona cyclohepta-2,4,5,6-tetraene 1 contains the smallest cyclic cumulene yet synthesized (seven-membered).[10] Previously only the organic cumulene cyclonona-1,2,3-triene[11] had been isolated and a cyclohexa-1,2,3-triene detected in situ.[12]

On treatment of $[Cp_2Zr(py)(Me_3SiC_2SiMe_3)]$ with $tBuC\equiv C-C\equiv CtBu$, the complex 2, in which only one diyne is complexed by zirconocene, is formed instead of the expected cleavage or coupling product [Eq. (b)].

[Cp₂Zr(py)(Me₃SiC≡CSiMe₃)]

+

tBuC≡C—C≡CtBu

—py,
—Me₃SiC≡CSiMe₃
→

(b)

2
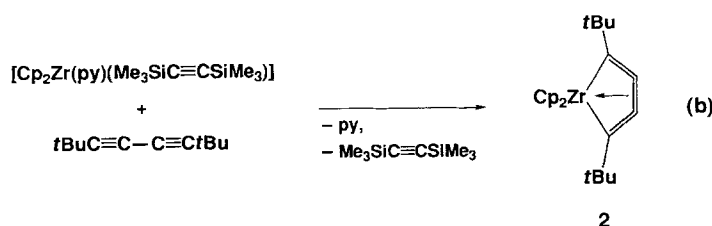
Complex 2 crystallizes as light green needles, which melt with decomposition at $190-192\,°C$. They are sensitive to oxygen and moisture. In the IR spectrum of 2, no absorption is observed in the region characteristic of the stretching vibrations for co-

ordinated ($1700-1800\ cm^{-1}$) or free C—C triple bonds ($2050-2200\ cm^{-1}$). The ^1H and ^{13}C NMR spectra of 2 confirm a highly symmetrical coordination of the butadiyne.[13] Relative to the free diyne ($\delta = 86.2$ (C≡CtBu), 65.2 (C≡CtBu), the signals for the alkyne C atoms in 2 are shifted downfield ($\delta = 186.4$ and 105.5, respectively); they are also not as prominent as those in the binuclear Ti complex of type II ($\delta = 234.4$ and 125.3, respectively).[2] The mass spectrum shows a molecular ion peak (M^+) at $m/z = 382$, indicative of a mononuclear complex.

The result of the X-ray structure analysis[14] for 2 is shown in Figure 1 and identifies the compound as a highly strained cumulene. The bond lengths for C1—C2 ($1.28(1)\ Å$), C2—C3 ($1.31(1)\ Å$), and C3—C4 ($1.29(1)\ Å$) are equivalent and confirm an identical bond order (double bond[15]). The atoms Zr, C1, C2, C3, and C4 are almost perfectly coplanar, and even the tertiary C atoms of the tBu substituents are bent out-of-plane by only $0.02(1)\ Å$. Accordingly, all four ring C atoms possess p orbitals perpendicular to the plane of cumulene; in addition, the sp-hybridized C atoms (C2, C3) also possess p orbitals lying in-plane. The C2=C3 double bond is therefore suitable for coordination by the zirconium center. This results in a shortening of the distance between the β-C atoms and the zirconium center, which reduces the deviation of the cumulene unit in 2 from linearity. Nevertheless, the cumulene remains highly strained (the bond angles C1—C2—C3 of $150.0(5)°$ and C2—C3—C4 of $147.2(5)°$ differ markedly from 180°) and is coordinated to the zirconium center by σ bonds to carbon atoms C1 and C4.

A comparison of the data listed in Table 1 supports the description of 2 as a cyclic cumulene. Distances and angles of the
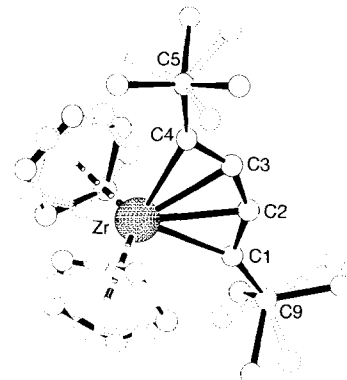

Fig. 1. Structure of 2 in the crystal.

Table 1. Distances and angles of comparable structural elements in selected cyclic cumulenes X–C(1)=C(2)=C(3)=C(4)–Y [a].

	A [b]	B [b]	C [b]	1 [9]	2
X	CH_2	CH_2	CH_2	Zr	Zr
Y	–	CH_2	CH_2CH_2	C=C	
Distances [Å]					
C1–C2	1.335	1.317	1.316	1.279(6)	1.28(1)
C2–C3	1.312	1.292	1.278	1.298(6)	1.31(1)
C3–C4	1.335	1.317	1.316	1.337(6)	1.29(1)
Angles [°]					
C1–C2–C3	116.37	132.23	145.04	148.8(5)	150.0(5)
C2–C3–C4	116.37	132.23	145.04	160.1(5)	147.2(5)

[a] A = 1,2,3-cyclopentatriene, B = 1,2,3-cyclohexatriene, C = 1,2,3-cycloheptatriene. [b] Calculated [11].

ZrC_4 unit in 2 are comparable to those reported for the cumulene unit in 1 and are also in accord with values calculated for cyclic cumulenes (A, B, and C).[11]

The cyclic structure of 2, in principal, resembles that found in metallacyclopentadienes (for example, as reported for zirconi-

um),[16] in which the ring atoms are also coplanar. However, in 2 the ring strain is increased by the central double bond.

In summary, tBuC≡C−C≡CtBu and $Me_3SiC≡C−C≡CSiMe_3$ react completely differently with zirconocene complexes. The latter cleaves[5] or couples [Eq. (a), ref. [9]] when treated with "Cp$_2$Zr". In contrast, the less reactive tBuC≡C−C≡CtBu remains intact to yield the mononuclear complex 2. One possible explanation for these differences in reactivity lies in the different electronic influences the substituents exert on the butadiyne system. For R = SiMe$_3$ a withdrawal of electron density from the central C atoms through dπ(Si)−pπ(C) interactions is conceivable; this situation is described by the limiting structure

$$\overset{(-)}{Me_3Si} = C = \overset{(+)}{C} - \overset{(+)}{C} = C = \overset{(-)}{Si}Me_3.$$

For R = tBu the central double bond (essential for coordination as a cumulene) is stabilized in the complex. Coordination is therefore favored over cleavage or coupling (as observed for R = SiMe$_3$).

Experimental Procedure

All reactions were conducted under anaerobic and anhydrous conditions.

1: To an orange solution of [Cp$_2$Zr(py)(Me$_3$SiC$_2$SiMe$_3$)] (400 mg, 0.85 mmol) in n-hexane (20 mL) was added a solution of bis(trimethylsilyl)-1,3-butadiyne (330 mg, 1.7 mmol) in n-hexane (10 mL), and the mixture was stirred for 48 h at room temperature. The solvent was removed under vacuum, the residue redissolved in n-hexane and filtered through a frit, and the filtrate was then allowed to crystallize in the cold. Yellow crystals of 1 formed and were washed with cold n-hexane and dried under vacuum. Yield: 210 mg (51 %), m.p. 187–188 °C, correct elemental analysis.

2: At room temperature, a solution of di-$tert$-butyl-1,3-butadiyne (183 mg, 1.13 mmol) in n-hexane (10 mL) was added to a stirred solution of [Cp$_2$Zr(py)(Me$_3$SiC$_2$SiMe$_3$)] (532 mg, 1.13 mmol) in n-hexane (15 mL). The solution's color changed from dark red to green. After 24 h all volatile components were removed under vacuum and n-hexane was added. Following filtration, 2 crystallized upon cooling in form of light green needles; these were washed with cold n-hexane and dried under vacuum. Yield: 281 mg (65 %, m.p. 190–192 °C (decomp.), correct elemental analysis.

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[7] 1 (cf. ref. [9]): IR (Nujol): $\tilde{v}$ = 1650, 1874, 2122 cm^{-1}; MS: m/z = 608 (M^+); ^{1}H NMR (C$_6$D$_6$, Bruker ARX 300, 30 °C): δ = 0.31. 0.35, 0.57, 0.66 (s, 9 H, SiMe$_3$). 5.38 (s. 10 H, Cp); ^{13}C{^{1}H} NMR: δ = − 0.3. −0.1, 1.3, 3.2 (CH$_3$), 105.3 (Cp). 91.6, 161.2, 162.8, 229.3 (CCSiMe$_3$), 101.1, 110.1, 152.3. 187.9 (CCSiMe$_3$).

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[13] 2: C$_{22}$H$_{28}$Zr, M_r = 383.66 g mol^{-1}, MS: m/z = 382 (M^+); ^{1}H NMR (C$_6$D$_6$, Bruker ARX 300, 30 °C): δ = 1.52 (s, 18 H, CH$_3$), 5.23 (s, 10 H, Cp); ^{13}C{^{1}H} NMR: δ = 33.2 (CH$_3$), 37.4 (C(CH$_3$)$_3$), 103.7 (Cp), 105.5 (C = CtBu), 186.4 (C = CtBu).

[14] CAD 4 diffractometer with graphite monochromator, Mo$_{K\alpha}$-radiation, structure solution with direct methods SHELXS-86 (G. M. Sheldrick, Acta Crystallogr. Sect. A 1990, 46, 467–473), refinement with SHELXL-93 on full matrix by the least squares method for F^2 (G. M. Sheldrick, unpublished), structural drawings generated with SCHAKAL 92 (E. Keller, Universität Freiburg, 1992). Space group $P2_12_12_1$, a = 9.2279(6), b = 14.357(1), c = 15.059(2) Å, V = 1995.1(3) Å^3. Z = 4, ρ = 1.277 gcm^{-3}, 6480 measured reflections at 293 K, 3439 symmetry-independent reflections of which 2879 were observed

(I > 2σ(I)). disordered atoms isotropic, all other non-hydrogen atoms anisotropic, $R1$ = 0.040, $wR2$ = 0.101, (I > 2σ(I)) for 193 parameters and no boundary constraints. Further details of the crystal structure investigation are available upon request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.

[15] In general, double bonds between sp- and/or sp^2-hybridized carbon atoms are 1.28–1.31 Å in length (F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. 2 1987. S1–S19).

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An Antibody-Catalyzed 1,2-Rearrangement of Carbon–Carbon Bonds**

Yuanwei Chen, Jean-Louis Reymond,* and Richard A. Lerner*

Catalytic antibodies are generated by immunization with stable transition state analogues of a chemical reaction. This technique provides rapid and practical access to new protein catalysts, and has been successfully applied to a number of chemical transformations.[1] However, only a few reactions involving C−C bonds have been catalyzed by antibodies.[2] These include the Diels–Alder reaction,[3] the Claisen and the oxy-Cope rearrangements,[4] and decarboxylations.[5] Herein we report on the first antibody-catalyzed 1,2-rearrangement of C−C bonds, namely the dienone–phenol rearrangement.

Many rearrangements of C−C bonds are nucleophilic 1,2-shifts, in which an electronic sextet formed on an atom A attached to a carbon atom induces an adjacent C−C bond to move with its electron pair to that center to fill its valence shell. A carbenium ion is left behind, which is then stabilized by donation of an electron pair from one of its substituents (Scheme 1).
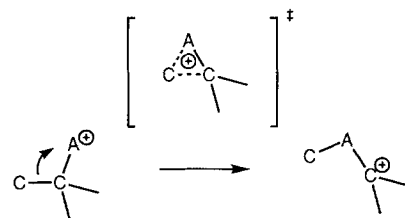
Scheme 1. Nucleophilic 1,2-shift of a C−C bond. The atom A has an electronic sextet and may be positively charged (A = carbon, oxygen) or neutral (A = nitrogen).

This mechanism is of extremely broad scope and encompasses many important synthetic transformations.[6] When A is oxygen or nitrogen, the reaction is an oxidation. Examples of this are the Baeyer–Villiger and Beckmann rearrangements of ketones and oximes, or the Curtius and Hofmann degradations of carboxylic acids. When A is carbon, the reaction is a rearrangement, as is the case in the pinacol, dienone–phenol, or Wagner–Meerwein reactions.

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