**Cumulene Synthesis**

# Highly Stereoselective Synthesis of TMS-, Alkyl-, or Aryl-Substituted *cis*-[3]Cumulenols via α-Alkynylated Zirconacyclopentenes**

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[3]Cumulenes have attracted much attention in recent years because they have potential applications in antitumor-drug design[1] and as advanced materials with unique electronic and photonic properties, for example, as molecular wires, non-linear optical systems, ferromagnets, conjugated polymers, etc.[2] They also serve as useful building blocks for two-dimensional carbon networks such as radialenes.[3] Although a number of methods are available for the construction of cumulenes,[1,4] most of them lead to a mixture of *E* and *Z* isomers.

Surprisingly, the stereoselective synthesis of cumulenes with reasonable generality is quite rare.[5] The *cis*-selective synthesis of acyclic cumulenes has been achieved either by Ru- or Ir-catalyzed dimerization[5a–c] of terminal alkynes with $[Ru(CO)(PPh_3)_3H_2]$ or $[\{Ir(cod)Cl\}_2]$ (cod = cycloocta-1,5-diene) as the catalyst precursor, a method that was restricted to *tert*-butyl or trimethylsilyl acetylenes, or by alkylation of alkylthiovinyl–copper(I) compounds by starting from specific substituted α-(methylthio)vinyl cuprates.[5d,e] These methods are useful for the synthesis of disubstituted *cis*-[3]cumulenes. However, there has been no example of the stereoselevtive formation of fully substituted [3]cumulenes. We report herein the first stereoselective preparation of tetrasubstituted cumulene derivatives through Zr-mediated coupling reactions of 1,3-butadiynes with aldehydes or ketones to afford *cis*-[3]cumulenols [Eq. (1)].[6]

$$\left. \begin{array}{c} R^1 \!=\!=\!=\! R^1 \\ + \\ =\!= \\ + \\ R^2R^3C\!=\!O \end{array} \right\} \xrightarrow[\text{selective coupling}]{\text{"Zr"}} \begin{array}{c} R^1 \quad\quad R^1 \\ R^2\!\!-\!\!\!\diagdown\!\!=\!=\!=\!\diagup\!\!-\!R \\ R^3 \;\; OH \end{array} \quad (1)$$

R=Et or $R^2R^3C(OH)$  *cis*-[3]cumulenes

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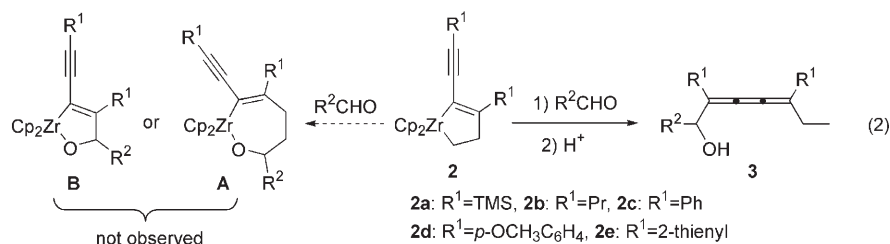Fax: (+86) 21-6416-6128
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Takahashi et al. have reported that the reaction of conjugated diynes R(C≡C)$_2$R, **1**, with [Cp$_2$Zr-(H$_2$C≡CH$_2$)] (Cp = cyclopentadienyl), prepared from [Cp$_2$ZrEt$_2$] in situ, gave α-alkynylzirconacyclopentenes **2**,[7] which afforded dideuterated enynes after deuteriolysis and α-alkynylcyclopentenones by treatment with CO/I$_2$.[7b] It has also been demonstrated that the strong interaction of a triple bond in the α position of the zirconacyclopentene with the Cp$_2$Zr moiety prevented the zirconacyclopentene from reacting with a second alkyne, such as another molecule of the diyne.[7a,b]

We now found that simple treatment of zirconacycles **2** with 1 equivalent of aldehyde at room temperature for 1–6 h readily afforded *cis*-[3]cumulenols **3** in good yields after hydrolysis [Eq. (2)]. To our surprise, the C–C bond formation occurred exclusively at the alkynylic carbon atom substituted with the R$^1$ group, whereas the expected products derived from direct insertion into a Zr–C(sp$^3$) bond [Eq. (2), complex **A**] or from **B** through a β,β′ C–C bond cleavage reaction were not detected. The chemoselectivity in this case is in marked contrast to that observed with alkyl- or aryl-substituted zirconacyclopentenes, since only insertion of aldehydes into the alkyl–zirconium bond to afford the seven-membered oxazirconacycles has been reported[8] in these zirconacyclopentenes so far.

**Table 1:** Formation of *cis*-[3]cumulenes via α-alkynylated zirconacyclopentenes.[a]

| Entry | Butadiyne | Aldehyde | Product | Yield [%][b] |
|---|---|---|---|---|
| 1 | TMS—≡—≡—TMS **1a** | C$_3$H$_7$CHO | **3a** | 67 |
| 2 | **1a** | MeO-C$_6$H$_4$-CHO | **3b** | 67 |
| 3 | **1a** | Me$_2$N-C$_6$H$_4$-CHO | **3c** | 58 |
| 4 | **1a** | O$_2$N-C$_6$H$_4$-CHO | **3d** | 66 |
| 5 | **1a** | Ph-C≡C-C$_6$H$_4$-CHO | **3e** | 70 |
| 6 | Pr—≡—≡—Pr **1b** | 2-pyridyl-CHO | **3f** | 61 |
| 7 | **1b** | C$_3$H$_7$CHO | **3g** | 64 |
| 8 | **1b** | Ph-CHO | **3h** | 71 |
| 9 | Ph—≡—≡—Ph **1c** | Ph-CHO | **3i** | 65 |
| 10 | **1c** | 2-thienyl-CHO | **3j** | 62 |
| 11 | **1c** | 2-furyl-CHO | **3k** | 55 |
| 12 | Ar—≡—≡—Ar, Ar=*p*-MeOC$_6$H$_4$ | Ph-CHO | **3l** | 55 |
| 13[c] | thienyl-≡—≡-thienyl | Ph-CHO | **3m** | 35 |

[a] All the reactions were carried out at room temperature for 1–6 h. [b] Yields of isolated products. [c] Thi = 2-thienyl.

Representative results are given in Table 1. A wide range of 1,3-butadiynes, including TMS-, alkyl-, aryl-, and heteroaryl-substituted ones, participated in the cumulene formation reactions. In all cases, the cumulene products, **3a–m**, were obtained with high *cis* selectivity (> 99% by NMR spectroscopy). X-ray crystal structure analysis of **3d** provided unequivocal evidence for the stereochemical assignment (Figure 1).[9] The central C≡C bond (C(2)-C(3) = 1.258(7) Å) is significantly shorter than both terminal C≡C bonds (C(1)-C(2) = 1.334(7) Å, C(3)-C(4) = 1.315 (7) Å), a result that is indicative of electronically different bonding situations.[10]

Zirconacycles prepared from diaryldiynes are reported to undergo reductive elimination upon heating and previously reported coupling reactions of alkynes or alkenes with these zirconacycles occurred only after reductive elimination at 50 °C.[7c] In our reaction, the zirconacycles **2c–e** reacted with aldehydes at room temperature within 1 h completely, with no observation of the
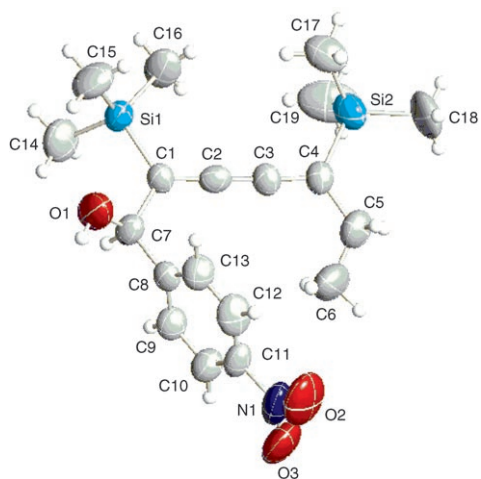
$$\text{B} \quad \text{or} \quad \text{A} \xleftarrow{R^2CHO} \text{2} \xrightarrow[\text{2) H}^+]{\text{1) R}^2\text{CHO}} \text{3} \quad (2)$$

not observed

**2a**: R$^1$=TMS, **2b**: R$^1$=Pr, **2c**: R$^1$=Ph
**2d**: R$^1$=*p*-OCH$_3$C$_6$H$_4$, **2e**: R$^1$=2-thienyl

**Figure 1.** The X-ray crystal structure of **3d**. Selected bond lengths [Å] and bond angles [°]: Si(1)-C(1) 1.875(5), C(1)-C(2) 1.334(7), C(2)-C(3) 1.258(7), C(3)-C(4) 1.315(7), C(1)-C(7) 1.521(6); C(2)-C(1)-Si(1) 120.6(4), C(3)-C(2)-C(1) 178.8(6), C(2)-C(3)-C(4) 176.4(6), C(2)-C(1)-C(7) 121.0(4).

products induced by reductive elimination. Interestingly, it was confirmed that zirconacycle **2b**, derived from an alkyl-substituted butadiyne, did not react with alkynes or alkenes; however, it readily underwent coupling reactions with aldehydes to furnish cumulenes **3 f,g,h** in 61, 64, and 71% yields (Table 1, entries 6–8), respectively.

The reaction could be applied to a wide variety of aliphatic aldehydes as well as aromatic ones bearing electron-donating or electron-withdrawing substituents. The functionalities of MeO, $NMe_2$, $NO_2$, and alkynyl groups in the aromatic ring were tolerated during the reaction, thereby affording the corresponding products **3b–e** in 58–70% yields (Table 1, entries 2–5). A number of heteroaryl aldehydes could be incorporated successfully into the sequence; for example, when 2-pyridinecarboxaldehyde or 2-thiophencarboxaldehyde were employed, the corresponding cumulenes **3 f** and **3j** were obtained in 61 and 62% yields, respectively (Table 1, entries 6 and 10). It was also found that a *cis–trans* isomerization occurred upon addition of a trace amount of iodine;[5f] for example, a 2.8:1 (*Z/E*) mixture of **3d** and its isomer was formed within 0.5 h at room temperature.

It has been demonstrated that cumulenes are generally unstable and most of the known [3]cumulenes are aryl- or *tert*-butyl-substituted because of their greater stability towards oxygen and acids. Only a limited number of procedures for the preparation of alkyl-substituted buta-1,2,3-trienes have been reported.[4e] Cumulene derivatives **3**, obtained by this new method, were sufficiently stable to allow purification by chromatography on alumina or silica gel; this eventually led to the successful isolation of the products. Their ${}^1$H and ${}^{13}$C NMR spectra were consistent with the proposed structures. The ${}^{13}$C NMR spectra displayed two characteristic resonances at $\delta = 169$–173 (TMS-substituted cumulenes), 152–155 (phenyl-substituted cumulenes), or 153–158 ppm (alkyl-substituted cumulenes), which could be assigned to the allenic-type sp-hybridized carbon atoms of **3**. An attractive advantage of this strategy is the single-pot construction of

cumulenes and also the flexibility possible in the assembly of the products by using appropriate combinations of butadiynes and carbonyl derivatives.

More interestingly, we found that the reaction of **2a** with 4 equivalents of ketones[11] afforded [3]cumulenic diols **4** in reasonable yields after hydrolysis [Eq. (3)]. The products **4** were obtained with high *Z* stereoselectivity. The tetraethyl-substituted product **4a** formed good single crystals for X-ray crystallography,[12] which clearly showed the cumulenic skeleton [see Eq. (3)]. Unsymmetrical ketones afforded (*Z*)-**4** as a mixture of diastereomers (Table 2). However, the reaction of

**Table 2:** Formation of (*Z*)-[3]cumulenic diols **4**.

| $R^1$ | $R^2$ | Product | Yield [%][a] | d.r.[b] |
|-------|-------|---------|-----------|-----|
| Et | Et | **4a** | 60 | – |
| Me | Et | **4b** | 55 | 1.2:1 |
| Me | Hex | **4c** | 42 | 1.1:1 |
| Me | *i*Pr | **4d** | 55 | 1.1:1 |
| Me | *i*Bu | **4e** | 45 | 1.1:1 |
| Me | Pr | **4f** | 44 | 1.6:1 |
| Me | isopentyl | **4g** | 46 | 1.2:1 |

[a] Yields of isolated products. [b] Diastereomeric ratio.

**2a** with methylphenylketone or diphenylketone failed to produce any detectable products due to the lower reactivity of aryl ketones. This reaction is of interest when related to the results of a reaction reported by Rosenthal and co-workers between a five-membered zirconacyclocumulene and carbon dioxide, in which a double insertion occurred to give the cumulenic dicarboxylate [Cp*Zr{O(C=O)C(SiMe₃)=C=C=C-(SiMe₃)C(=O)O}] (Cp* = pentamethylcyclopentadienyl).[13] This strongly suggests that a similar intermediate of oxazirconacycle with a cyclic cumulene moiety may exist in our system.
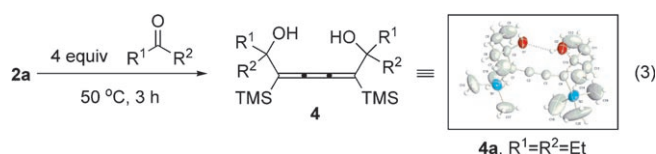


On the basis of the above observations, a possible reaction mechanism is proposed in Scheme 1. The interaction of an aldehyde with zirconacycle **2**, presumably via intermediate **5**, gives a nine-membered oxazirconacycle **6** with a cyclic cumulene structure. Hydrolysis of **6** affords the desired products **3**. The stereoselectivity might be induced by strong coordination of the aldehyde to the zirconium center. An NMR study of the reaction of **2a** with *p*-methoxybenzaldehyde indicated the formation of **6b** ($R^1 = $ TMS, $R^2 = p$-MeOC₆H₄) in 75% yield. The ${}^1$H NMR spectrum of **6b** in C₆D₆/THF (2:1) showed two sets of singlets at $\delta = 5.60$ and 5.81 ppm, and the ${}^{13}$C NMR spectrum revealed two singlets at $\delta = 110.5$ and 111.1 ppm, which were assigned to Cp ligands. The signals at $\delta = 38.1$ and 41.8 ppm are assignable to a (CH₂)₂ unit attached to the zirconium atom, and the low-field
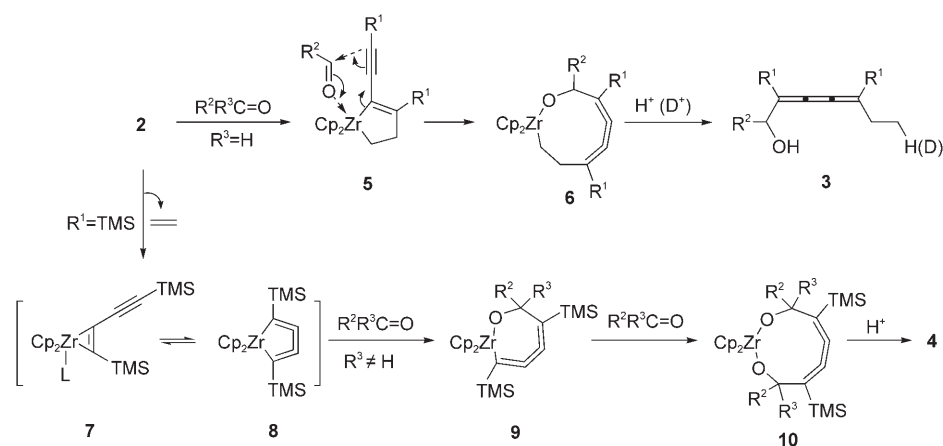
**Scheme 1.** Proposed mechanism for the formation of *cis* cumulenes.

signals ($\delta = 173.7$ and $175.4$ ppm) are characteristic for sp carbon atoms in cumulenic skeletons.

In a deuteration experiment with benzaldehyde and **2a**, the monodeuterated compound [D]**3n** was obtained in 60% yield with high deuterium incorporation (D = 90%). To account for the formation of cumulenic diols **4**, a zirconocene–butadiyne complex **7** (an $\eta^2$ complex)[14] formed through a $\beta,\beta'$ C–C bond cleavage reaction was suggested; this complex might form an equilibrium with zirconacyclocumulene **8** (an $\eta^4$ complex). A double insertion of a ketone into **8** would lead to the formation of (Z)-**4** after hydrolysis. In this reaction, the $\eta^2$ and $\eta^4$ complexes of Cp$_2$Zr with 1,4-bis(trimethylsilyl)-1,3-butadiyne were formed in situ from complex **2** by using the ethylene unit in the zirconacyclopentene as a spectator ligand. With Cp*$_2$Zr, such complexes do exist, but the reactivity of these complexes is restricted to only small molecules (for example, carbon dioxide) due to steric reasons.[13,14]

In summary, we have shown that zirconium-mediated coupling of 1,3-butadiynes with aldehydes or ketones provides access to an efficient, general, and one-pot method for the *cis*-selective synthesis of tetrasubstituted [3]cumulenols. Remarkably, the reaction occurs with complete chemoselectivity with respect to the $\alpha$-alkynylated zirconacyclopentenes, which is different to that of the reactions with alkyl- or aryl-substituted zirconacyclopentenes reported so far. Clarification of the reaction mechanism and further application of this chemistry are in progress.

## Experimental Section

Typical procedure for the cross-coupling reaction of $\alpha$-alkynylated zirconacyclopentenes with aldehydes: EtMgBr (1.0 M THF solution, 2.5 mmol) was added to a solution of [Cp$_2$ZrCl$_2$] (0.365 g, 1.25 mmol) in THF (5 mL) at $-50\,°C$. After the reaction mixture was stirred for 1 h at the same temperature, 1,4-bis(trimethylsilyl)buta-1,3-diyne (0.19 g, 1 mmol) was added and the reaction mixture was warmed to room temperature and stirred for 2 h. *p*-Methoxybenzaldehyde (0.12 mL, 1 mmol) was added and the mixture was stirred for 6 h. The reaction mixture was quenched with 5% HCl and extracted with ethyl acetate. The extract was washed with water and brine, then dried over Na$_2$SO$_4$. The solvent was evaporated in vacuo and the residue

was purified by chromatography over silica gel (petroleum ether (60–90 °C)/ethyl acetate 20:1). The (Z)-[3]cumulenol derivative (Z)-1-(4-methoxyphenyl)-2,5-bis(trimethylsilyl)-hepta-2,3,4-trien-1-ol **3b** (241 mg, 67%) was obtained as a light-yellow oil: $^1$H NMR (CDCl$_3$, Me$_4$Si): $\delta = 0.20$ (s, 9H), 0.37 (s, 9H), 1.30 (t, $J = 6.9$ Hz, 3H), 2.54 (q, $J = 7.2$ Hz, 2H), 3.11 (s, 1H), 3.96 (s, 3H), 5.50 (s, 1H), 7.03 (m, 2H), 7.45 ppm (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): $\delta = -1.42$, $-0.82$, 13.28, 28.78, 55.16, 75.60, 113.65, 128.67, 130.05, 133.79, 135.02, 159.18, 169.62, 170.51 ppm; HRMS (MALDI/DHB): calcd for C$_{20}$H$_{32}$O$_2$Si$_2$Na $[M+\text{Na}]^+$: 383.1839; found: 383.1828. DHB = 2,5-dihydroxybenzoic acid.

General procedure for the cross-coupling reaction of $\alpha$-alkynylated zirconacyclopentenes with ketones: In the procedure described above, *p*-methoxybenzaldehyde was replaced by a ketone (4 mmol), the mixture was stirred for 3 h at 50 °C, and chromatography was over alumina. (Z)-[3]cumulenic diol derivatives **4a–g** were obtained as white solids or light-yellow oils. Data for 3,8-diethyl-4,7-bis(trimethylsilyl)-deca-4,5,6-triene-3,8-diol (**4a**): Column chromatography afford it as a white solid (220 mg, 60%); $^1$H NMR (CDCl$_3$, Me$_4$Si): $\delta = 0.20$ (s, 18H), 0.83 (t, $J = 7.4$ Hz, 12H), 1.61–1.71 (m, 8H), 2.37 ppm (br s, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si): $\delta = 0.71$, 8.06, 34.22, 81.74, 135.26, 171.66 ppm; HRMS (MALDI/DHB): calcd for C$_{20}$H$_{40}$O$_2$Si$_2$Na $[M+\text{Na}]^+$: 391.2465; found: 391.2457.

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