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Highly Efficient Synthesis of *cis*-[3]Cumulenic Diols via Zirconocene-Mediated Coupling of 1,3-Butadiynes with Aldehydes

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Supporting Information

ABSTRACT: A highly efficient and convenient method for the monozirconation of silyl- or *tert*-butyl-substituted 1,3-butadiynes using the Negishi reagent has been developed. The resulting zirconium butadiyne complexes undergo two syn- S_E2' reactions with various aldehydes to yield the *cis*-[3]cumulenic diols with moderate to high diastereoselectivities. The silyl substituents at the butadiyne terminus show remarkable influence on the diastereoselectivity.



he organometallic chemistry of group 4 metal complexes with conjugated 1,3-butadiynes $R(C \equiv C)_2 R$ and polyynes $R(C \equiv C)_n R$ have attracted considerable attention, owing to their fascinating structure features, their unique M-C bonding, and their unusual capacity to induce highly selective transformations.^{1,2} Extensive studies on the reactions of 1,3butadiynes with the alkyne complexes $Cp_2M(L)(\eta^2-Me_3SiC \equiv$ $CSiMe_3$) (M = Ti, L = none; M = Zr, L = THF, pyridine) as metallocene sources have been conducted by Rosenthal's research group.¹ Unique reaction modes such as complexations, formation of metallacyclocumulenes, C-C bond cleavage, and various types of coupling reactions have been disclosed from these studies. Recently, we have investigated the cross-coupling reactions of 1,3-butadiynes with a zirconocene ethylene complex or zirconocene benzyne. The resulting α -alkynylzirconacycles/zirconacyclocumulenes were found to react with carbonyl derivatives, leading to tetrasubstituted [3]cumulenols or [3] cumulenones in a well-stereodefined manner.³ Although much progress has been achieved in this area, there have only been a limited number of reports on the direct coupling of metal butadiyne complexes with aldehydes. Two such types of coupling reactions have been reported so far (Scheme 1),⁴ which involve the addition of one molecule of aldehyde to give enynols (path a)^{2d,4a} and a Lewis acid assisted 1,3-metallotropic rearrangement to afford *cis*-[3]cumulenols (path b).^{4b} However, double addition of aldehydes to metal butadiyne complexes was not known (path c). In searching for new reaction patterns of metallacycles, we found a novel coupling reaction of 1,3-butadiynes with two molecules of aldehyde according to path c. These reactions provide a convenient and stereoselective access to cis-[3]cumulenic diols.

It has been documented that the reaction of 1,4-bis-(trimethylsilyl)buta-1,3-diyne with the Negishi reagent Cp_2ZrBu_2 leads to a homocoupling product of two diynes with the formation of a seven-membered zirconacyclocumulene.^{2e,5} Here we found, very interestingly, when SiMe₃ on the diyne terminus is replaced by Si^tBuMe₂ (TBS) group, a selective monozirconation of 1,3-butadiynes occurred in Scheme 1. Reaction Patterns of Aldehyde Addition with Metal-Butadiyne Complexes



toluene to afford, after quenching with MeOH, the (Z)-enyne 4a in 74% yield (Scheme 2). Only a trace amount of dimers was

Scheme 2. Mono-Zirconation of Conjugated 1,3-Butadiynes



observed according to ¹H NMR of the crude reaction mixture. Si^tBuPh₂- and Si(ⁱPr)₃-substituted diynes afforded results similar to those for the TBS-substituted diyne. These observations indicate that the bulkness of the alkyne substituents plays an important role in the reaction process

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with the low-valent zirconocene. Two possible zirconium intermediates, zirconacyclopropene **2** and zirconacyclopentatriene **3**, might be formed by a ligand exchange reaction, and there may exist an equilibrium between these two species.^{1a,6} To understand the organometallic intermediates, a reaction mixture of **1c** ($\mathbb{R}^1 = \text{TIPS}$) with Negishi reagent was investigated by NMR. The NMR study indicated that one major zirconium complex was formed (NMR yield ca. 77%). Although our attempts to obtain a single crystal suitable for X-ray analysis failed, this complex is suggested to be zirconacyclocumulene **3**, since the spectroscopic behavior of **3c** is very close to that of a known complex of zirconacyclocumulene, $\mathbb{Cp}^*_2\mathbb{Zr}(\eta^4-1,2,3,4-Me_3\mathrm{SiC}_4\mathrm{SiMe}_3)$.⁷

The reactions of metallacycles with aldehydes have been utilized for side chain extension and introduction of functional groups.⁸ To highlight the synthetic potential of these zirconium intermediates, we proceeded to examine the aldehyde addition reactions. Treatment of zirconium species 2a/3a generated from 1,4-bis(tert-butyldimethylsilyl)buta-1,3-diyne (1a) with 3 equiv of benzaldehyde at 80 °C for 3 h afforded the cis-[3] cumulenic diol 5a in 71% yield (Table 1, entry 1).⁹ The results indicated that two molecules of aldehyde insert into the metallacycles. It is interesting to note that 5a was obtained as two diastereomers with good diastereoselectivity. The two diastereomers can be separated from each other by column chromatography in this case. In order to make clear the configuration of these two isomers, the single-crystal X-ray analyses of the major isomers of cumulenic diols 5b,n were performed.¹⁰ The results unambiguously supported the syn stereochemistry (with respect to two OH groups) of the major isomer.¹¹ As shown in Table 1, a wide variety of aldehydes could be used in this reaction, furnishing the corresponding diols 5 in moderate to good yields. In most cases, moderate to high diastereoselectivity has been observed. Aromatic aldehydes bearing electron-withdrawing (-Cl, -Br) or electron-donating (-OMe) substituents were all compatible with this reaction to give **5b**-**d** in 63–72% yields (Table 1, entries 2–4). Heteroaryl aldehydes such as 2-thienyl aldehyde or 2-pyridyl aldehyde could also be incorporated successfully into the sequence, although low stereocontrol was observed in the latter case, possibly due to the competitive coordination of the pyridyl group to the metal center, interfering with the stereochemical course (entries 6 and 7). The use of alkynyl aldehyde afforded 5h in 55% yield, in which the alkyne moiety remained intact (entry 8). It is noted that the configuration of the major and minor isomers in 5g,h was not fixed, due to the poor stereoselectivities (entries 7 and 8). Alkyl aldehydes were also effective in affording the corresponding diols 5i-k in 62-76% yield (entries 9-11). Interestingly, when TBS is replaced by TBDPS or TIPS in butadiyne substrates, high stereoselectivity up to 20:1 has been observed (entries 12-15). The results show that the bulkiness of the silvl substituents has a remarkable influence on the stereoselectivity of the reaction. It is worthy to note that such 1,6-stereoinduction is quite rare.¹² [3]Cumulenes are important substances, since they have potential applications in antitumor drug design and as advanced materials, as well as in organic synthesis.¹³ However, the stereoselective synthesis of cumulenes with reasonable generality is still rare.^{14'}Our method provides an efficient and one-pot procedure for the stereoselective synthesis of cumulenes with multiple functionalities.

The reaction of the zirconocene complex derived from **1a** with paraformaldehyde led to the formation of the coordination

Table 1. Formation of *cis*-[3]Cumulenic diols via Reactions with Aldehydes

| | R' | R ¹ i) 3 equiv | $V = R^1 = R^1 + 80 \circ C$ | R ¹ | R ¹ |
|------------|---------------------|---------------------------------------|--|---------------------|-------------------------|
| Cp₂Zr√ | _ _ − Cp | ² Zr ii) 3 N H | \rightarrow $R^2 \rightarrow R^2 R^2$ | ≺он | |
| • | R' | R ¹ | major, syn-5 | minor, | anti-5 |
| ∠ entry | R ¹ | з aldehyde | 5 product | | yield(%) ^a |
| 1 | TBS (1a) | <i>С</i> -сно | TBS Ar OH HO | 5a Ar= Ph | 71 (6.1:1) |
| 2 | (1a) | p-CIC ₆ H ₄ CHO | Ar= p -CIC ₆ H ₄ | 5b | 66 (6.7:1) |
| 3 | (1 a) | p-BrC ₆ H ₄ CHO | $Ar = p - BrC_6H_4$ | 5c | 72 (6.2:1) |
| 4 | (1a) | <i>p</i> -MeOC ₆ H₄CHO | Ar= p -MeOC ₆ H ₄ | 5d | 63 (7.7:1) |
| 5 | (1a) | СНО | TBS OH HO | 5e | 68 (3.1:1) |
| 6 | (1a) | Сно | TBS TBS TBS TBS TBS TBS | 5f | 62 (6.5:1) |
| 7 | (1a) | Сно | | 5g | 64 (1.5:1) ^b |
| 8 | (1a) | Ph- <u></u> CHO | | 5h | 55 (1.2:1) ^b |
| 9 | (1a) | n-C₄H₃CHO | $\xrightarrow{TBS} \xrightarrow{TBS} \xrightarrow{TBS} \xrightarrow{TBS} \xrightarrow{n-C_4H_9} \xrightarrow{OH HO}$ | 5i | 67 (4.2:1) |
| 10 | (1a) | СНО | TBS TBS TBS TBS TBS 'Pr OH HO 'Pr | 5j | 76 (3.5:1) |
| 11 | (1a) | ^t BuCHO | TBS 'Bu- OH HO | 5k | 62° |
| 12 | TBDPS (1b) | СНО | TBDPS Ph | 51 | 81 (10:1) |
| 13 | TIPS (1c) | СНО | TIPS Ar OH HO | 5m Ar= Ph | 75 (20:1) |
| 14 | (1c) | p-CIC ₆ H ₄ CHO | Ar= p -CIC ₆ H ₄ | 5n | 68 (20:1) |
| 15 | (1c) | 1-naphthylaldehyd | de Ar= 1-naphthyl | 50 | 65 (20:1) |

"Combined isolated yields; the diastereomeric ratio is shown in parentheses. Unless noted, all the reactions were carried out in toluene using 3 equiv of aldehyde at 80 °C for 3-12 h. ^bThe configuration of the major and minor diastereomers was not fixed. ^cOnly the major isomer was isolated.

dimer 7 of α -alkynyloxazirconacyclopentene (Scheme 3). In this case, only monoaddition occurred. Complex 7 is stable to air and moisture, which allows a convenient separation through column chromatography on silica gel. The stability of 7 can be attributed to its dimeric structure.¹⁰ It is noted that the analogous coupling of Cp₂Zr(THF)(η^2 -Me₃SiC \equiv CSiMe₃) with formaldehyde has been described by Rosenthal et al., in which a similar dimeric oxazirconacyclopentene was obtained.¹⁵

A possible reaction mechanism for the formation of cumulenic diols is shown in Scheme 4. First of all, an





Scheme 4. Proposed Reaction Mechanism



equilibrium between zirconacyclopentatriene 3 and zirconacyclopropene 2 exists in the reaction mixture, in which 3 is likely to be the dominant species, whereas 2 is more reactive.^{3a} Addition of a carbonyl group to the less hindered propargyl zirconium moiety in complex 2 via a syn- S_F2' process takes place to deliver the oxazirconacycle 9; 9 might isomerize to the five-membered α -alkynylzirconacycle **10**, and then the addition of the second aldehyde to 10 via a similar syn- S_F2' process affords the dioxazirconacycle 12 and hydrolysis of 12 provides the cumulenol 5. To support this mechanism, we isolated the zirconium-containing intermediate 12n ($R^1 = TIPS$, $R^2 = p$ - ClC_6H_4). The X-ray crystal structure of 12n clearly shows a nine-membered dioxazirconacycle with three cumulenic double bonds, and the two aryl groups are in a cis orientation.¹⁰ The bond angles of the cumulenic moiety (C20-C19-C18 = $173.72(16)^{\circ}$ and C19-C20-C21 = $175.32(16)^{\circ}$) are near the idealized value of 180°, indicating a linear structure of the butatriene moiety. There is no coordination of the cumulene part to the metal, due to the large distances between them.

To rationalize the reaction mechanism and the stereoselectivity of zirconacycle 2/3 (R¹ = TIPS) with aldehyde, density functional theory (DFT) studies have been performed. The equilibrium of 2 and 3 and the insertion of the first aldehyde (from 8 to 10), as well as the transition states for the second aldehyde insertion into the zirconacycle 10 were calculated with 1c and benzaldehyde.¹⁶ The calculated results are quite consistent with the mechanism shown in Scheme 4. The transition states for the second aldehyde insertion into the zirconacycle 10 are shown in Figure 1. The calculated results for stereoselectivity are quite consistent with the experimental observations: the cis transition state TS-cis is 2.7 kcal/mol more stable than the trans transition state TS-trans: thus, the cis product is the main product. In TS-cis, the two TIPS groups lean to the same side (left) with small distortion to the cumulenic backbone. The carbon atoms C1-C4 are approximately on a plane, and the dihedral angle Si-C4-C1-Si is 5.8°. However, in TS-trans the two TIPS groups are pushed to



Figure 1. Optimized transition states **TS**-*cis* and **TS**-*trans* for the second aldehyde insertion, calculated at the M06/(6-31+G** and 6-31G*)/Lanl2DZ level. The relative free energies including solvent effects, $\Delta G_{sol}(298 \text{ K})$, are in kcal mol⁻¹. The dihedral angle Si–C4–C1–Si is 5.8 and 53.2° in **TS**-*cis* and **TS**-*trans*, respectively.

different sides by the phenyl groups, and the cumulenic backbone is staggered. The dihedral angle Si-C4-C1-Si increases to 53.2°. Subsequently, in **TS**-*trans* the conjugation of the cumulenic backbone is partially destroyed, which decreases the stability. Thus the 1,6-interaction transfers via the steric hindrance among the TIPS, Ph, and the Cp rings. On the other hand, in comparison with **TS**-*cis*, **TS**-*trans* is more congested, which causes an entropy loss of -2.756 cal mol⁻¹ K⁻¹. This entropy loss is equivalent to 1.0 kcal mol⁻¹ destabilization under 80 °C.

As suggested by one reviewer, we also carried out the reaction of ${}^{t}BuC \equiv CC \equiv C{}^{t}Bu$ with Negishi reagent. To our delight, zirconacyclocumulene 13 was formed in 91% yield, which was inert toward water and air during the isolation process (Scheme 5). Zirconium complex 13 was also





characterized by X-ray diffraction, which shows a highly strained structure of zirconacyclocumulene.¹⁰ The crystallographic data are in agreement with those previously reported for **13**, obtained by treating the same butadiyne with $Cp_2Zr(py)(Me_3SiC\equiv CSiMe_3)$.¹⁷ The reaction of **13** generated in situ with 4-chlorobenzaldehyde in toluene at 80 °C for 17 h afforded the [3]cumulenic diol **14** (Figure 2) in 26% yield as a



Figure 2. Structure of compound 14.

single isomer; the stereochemistry of 14 has not yet been defined.

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In conclusion, we have succeeded in developing zirconocenemediated coupling reactions of silyl- or *tert*-butyl-substituted 1,3-butadiynes with aldehydes under mild reaction conditions, which provides an efficient and general route to *cis*-[3]cumulenic diols with moderate to high stereoselectivity. The silyl substituents at the butadiyne terminus show remarkable influence on the stereoselectivity. This is the first report on addition of two molecules of aldehyde to metalcoordinated butadiyne complexes. Further studies to elucidate the reaction mechanism and to extend the scope of synthetic utility are in progress in our laboratory.

ASSOCIATED CONTENT

S Supporting Information

Text, figures, tables, and CIF files giving experimental details, NMR spectra of all new products, crystallographic data of *syn*-**5b** (ethanol adduct), *syn*-**5n**, **6**, **7**, **12n**, and **13**, DFT calculations, and the calculated total energies and geometrical coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) (a) For the formation of *cis*-[3]cumulenic diols via the reactions of α -alkynylzirconacyclopentenes with ketones, see ref 4b. (b) For insertion of two molecules of CO₂ into zirconacyclopentatriene with Cp* as the ligand, see ref 7.

(10) The X-ray crystal structures of compounds *syn-***5b** (ethanol adduct), *syn-***5n**, **6**, **7**, **12n**, and **13** are shown in the Supporting Information.

(11) Reduction of cumulenone **6** prepared by DMP oxidation of *syn*-**5b** gave the two diastereomers in 61% and 26% yields, respectively. These isomers are identical with *syn*- or *anti*-**5b** formed in Zr-mediated reactions, indicating that the minor isomer is the alcohol epimer.

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