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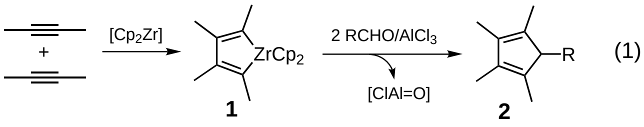
Deoxygenative Cycloaddition of Aldehydes with Alkynes Mediated by AlCl$_3$ and Zirconium: Formation of Cyclopentadiene Derivatives[**]

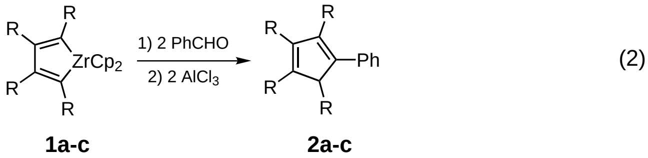
Zhenfeng Xi[*] and Pixu Li

Cleavage or deoxygenation of C–O double bonds in carbonyl compounds is of significant general interest for organic transformations.[1–4] Metal-promoted cycloaddition of unsaturated organic substrates has attracted much attention, because such reactions provide a straightforward route to useful cyclic compounds.[5] Although novel methods for constructing cyclic compounds could be developed by cycloaddition of an aldehyde with alkynes and deoxygenation of the carbonyl group, to the best of our knowledge, such reactions are unprecedented.

Although aldehydes are among the most common unsaturated substrates, transition metal-mediated cycloaddition reactions of aldehydes with alkynes are rare.[6] Tsuda, Saegusa et al. reported the first cycloadditions of diynes with aldehydes to give six-membered oxacycles such as pyrans with catalysis by Ni^0.[6a] The reaction proceeded with a formal [2+2+2] pattern. Here we report the first cyclization of two alkyne molecules with an aldehyde and deoxygenation of the C=O bond to give multiply substituted cyclopentadiene derivatives; the reactions are mediated by AlCl$_3$ and zirconocene compounds [Eq. (1); Cp = η^5-C$_5$H$_5$].



Two molecules of the same or different alkynes readily underwent cycloaddition on a low-valent zirconocene complex to afford zirconacyclopentadienes **1**.[7, 8] Addition of two equivalents of benzaldehyde and two equivalents of freshly sublimed AlCl$_3$ to a solution of **1a**, prepared in situ in toluene, led to a rapid reaction [Eq. (2)]. Gas chromatographic (GC) analysis showed that the reaction was complete within 30 min



a: R = *n*Pr 89% (65%)
b: R = Me (45%)
c: R = Ph (47%)

and **2a** was formed in 89% yield (yield of isolated product: 65%). Similarly, **2b** was isolated in 45% yield from the reaction of **1b** with benzaldehyde in the presence of AlCl$_3$. Different regioisomers of cyclopentadiene derivatives can be obtained, depending on the reaction conditions and work-up procedures, but under our reaction conditions, only the isomer shown in Equation (2) was obtained. The reaction of **1c** with benzaldehyde proceeded comparatively slowly at room temperature to give **2c** as colorless crystals in 47% yield. The NMR spectroscopic data and m.p. of **2c** are consistent with those reported earlier.[9] Reactions of metallacyclopentadienes with C$_1$ units or C$_1$ unit equivalents to form cyclopentadiene derivatives are rare.[10] Reaction (2) is the first of this kind in which an aldehyde behaves formally as a C$_1$ unit. It is noteworthy that, when zirconacyclopentadienes were prepared from [Cp$_2$ZrCl$_2$]/EtMgBr/alkynes,[11] the above reaction was not observed, even at an elevated temperature.

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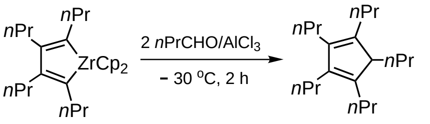
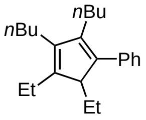
To investigate the scope of the reaction, aliphatic aldehydes were also used. Reaction of **1a** with butyraldehyde at room temperature in the presence of $AlCl_3$ resulted in a messy mixture. When the reaction was carried out at about −30 °C, **2d** was formed cleanly as a single product within 2 h in 92 % yield (GC) [Eq. (3)].

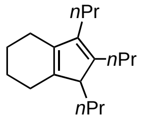


1a **2d**: 92% (86%) (3)

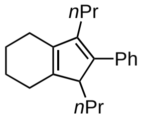
Highly selective cross-coupling between two different alkynes on Cp_2Zr^{II} species can be easily performed to afford unsymmetrically substituted zirconacyclopentadienes.[7b] The deoxygenative cycloaddition of hex-3-yne, dec-5-yne, and benzaldehyde gave the multiply substituted cyclopentadiene derivative **2e** in 80 % yield as a 1:1 mixture of two positional double-bond isomers. Tetrahydroindene derivatives **2f** and **2g** could be also prepared in good yields by the reaction of the corresponding bicyclic zirconacyclopentadienes and aliphatic (**2f**) or aromatic aldehydes (**2g**) in the presence of $AlCl_3$. Compound **2f** was obtained as a 3:1 mixture of two double-bond positional isomers. The major isomer is given.



2e: 80% (56%)

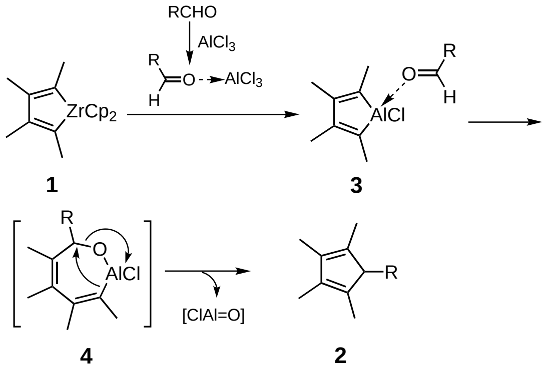


2f: 85% (65%)



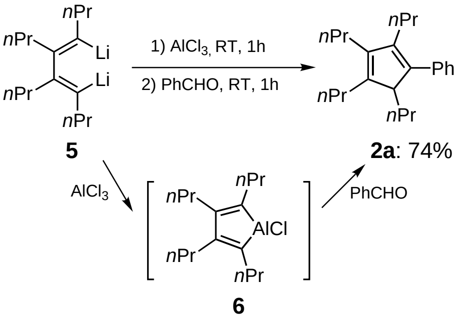
2g: 89% (70%)

A possible reaction mechanism is shown in Scheme 1. Insertion of aldehydes into zirconacyclopentenes[12] and titanacyclopentadienes[13] has been reported. However, aldehydes did not react with zirconacyclopentadienes under these reaction conditions. The ^1H NMR chemical shift of the Cp ligand in **1c** was unchanged after treatment with benzaldehyde for 1 h at room temperature. Because transmetalation of **1** with $AlCl_3$ was expected, we treated **1c** with $AlCl_3$ at room temperature for 1 h. However, no change in the chemical shift of the Cp ligand of **1c** was observed. These results indicate that transmetalation of zirconacyclopentadienes **1** with $AlCl_3$ in the absence of aldehydes is unlikely. Since interaction of aldehydes with $AlCl_3$ is well known, formation of an adduct between $AlCl_3$ and aldehyde is presumably favored.[14] Indeed, addition of $PhCHO \cdot AlCl_3$ to **1a** in toluene afforded **2a** in 85 % yield. Obviously, the adduct reacts with **1** to form aluminacyclopentadienes **3**.[15] The activated carbonyl group then inserts into an Al−C bond of **3** to afford the oxaaluminacycles **4**. We assume that formation of a cyclopentadiene ring and an oxo aluminum species is the driving force for the formation of **2** from **4**.



Scheme 1. Proposed mechanism for the $AlCl_3$-mediated reaction of zirconacyclopentadienes with aldehydes.

To further investigate the reaction mechanism, we carried out the reactions shown in Scheme 2. The 1,4-dilithio-1,3-diene compound **5** was prepared in situ by the reaction of the corresponding 1,4-diiodo compound with *t*BuLi.[16] An equimolar amount of $AlCl_3$ was then added to the reaction mixture.[15a,e,f, 17] After the mixture was stirred at room temperature for 1 h, benzaldehyde was added. The reaction was complete after 1 h at room temperature and gave **2a** in 74 % yield (GC). This indicates the formation of aluminacyclopentadiene **6** from the reaction of **5** with $AlCl_3$.[17]



Scheme 2. Investigations into the reaction mechanism.

Experimental Section

Typical procedure: oct-4-yne (2.0 mmol, 0.29 mL) was added to a solution of $[Cp_2ZrBu_2]$ (Negishi reagent),[7a] prepared in situ from $[Cp_2ZrCl_2]$ (1.0 mmol, 0.29 g) and *n*BuLi (2.0 mmol, 1.3 mL, 1.60 M in hexane) in toluene (10 mL) at −78 °C. The reaction mixture was stirred at room temperature for 1 h. Then, PhCHO (2.0 mmol, 0.21 mL) and $AlCl_3$ (2.0 mmol, 0.27 g) were added. The reaction mixture was stirred at room temperature for 1 h. Hydrolysis with 3 N HCl followed by normal work up and evaporation in vacuo gave a bright yellow oil, which was purified by column chromatography (silica gel, hexane) to afford **2a** as a colorless liquid in 65 % yield (202 mg). A yield of 89 % was determined by GC with dodecane as internal standard.

^1H NMR: 300 MHz, ^{13}C NMR: 75 MHz; $CDCl_3$, TMS, unless stated otherwise.

2a: ^1H NMR: $\delta = 0.77-1.02$ (m, 14 H), 1.30–1.62 (m, 8 H), 2.02–2.44 (m, 6 H), 3.61 (t, $J = 6.4$ Hz, 1 H), 7.10–7.38 (m, 5 H); ^{13}C NMR: $\delta = 14.50$ ($3CH_3$), 14.58 (CH_3), 16.18 (CH_2), 23.70, 23.96, 24.05, 27.86, 28.69, 29.12, 30.57, 52.69 (CH), 125.38, 128.02, 128.46, 137.96, 140.61, 141.76, 142.45, 144.33; HRMS calcd for $C_{23}H_{34}$: 310.2661; found: 310.2656.

2b: Colorless liquid, 45 % yield (89 mg); ^1H NMR: $\delta = 1.02$ (d, $J = 7.4$ Hz, 3 H), 1.82 (s, 3 H), 1.94 (s, 3 H), 2.04 (s, 3 H), 3.20 (m, 1 H), 7.15–7.50 (m, 5 H); ^{13}C NMR: $\delta = 11.10$, 11.89, 12.68, 14.75, 50.05 (CH), 125.37, 128.07, 128.35, 134.99, 137.09, 140.67, 142.68; HRMS calcd for $C_{15}H_{18}$: 198.1409; found: 198.1410.

2c:[9] Colorless crystals, 47 % yield (210 mg); m.p. 255–257 °C; ^1H NMR: $\delta = 5.0$ (s, 1 H), 6.82–7.20 (m, 25 H); ^{13}C NMR (C_6D_6): $\delta = 63.15$ (CH), 126.56, 126.73, 126.86, 127.64, 127.85, 128.57, 128.65, 129.26, 130.30, 136.08, 136.43, 144.16, 147.03.

2d: Colorless liquid, 86% yield (237 mg); ^{1}H NMR: $\delta = 0.79-0.94$ (m, 17H), 1.29–1.59 (m, 10H), 2.03–2.30 (m, 8H), 2.86 (t, $J = 6.6$ Hz, 1H); ^{13}C NMR: $\delta = 14.32$, 14.41, 14.68, 16.41, 23.87, 24.10, 27.93, 29.01, 30.46, 50.95 (CH), 139.73, 141.43; HRMS calcd for $C_{20}H_{36}$: 276.2817; found: 276.2820.

2e: 1:1 mixture of positional double-bond isomers, combined yield 56% (347 mg, 2.0-mmol scale); ^{1}H NMR of the mixture: $\delta = 0.62-1.80$ (m, 20H), 1.96–2.62 (m, 8H), 3.34–3.52 (m, 1H), 7.02–7.40 (m, 5H); ^{13}C NMR of the mixture: $\delta = 13.92$, 14.05, 15.35, 19.82, 20.70, 22.81, 22.92, 23.07, 25.43, 26.33, 32.76, 33.15, 52.34 (CH), 52.49 (CH), 125.41, 127.76, 128.04, 128.07, 128.25, 128.32, 128.37, 137.76, 140.59, 140.85, 143.04, 145.12; HRMS calcd for $C_{23}H_{34}$: 310.2661; found: 310.2663.

2f: 3:1 mixture of positional double-bond isomers, combined yield 65% (320 mg, 2.0-mmol scale); ^{13}C NMR of the major isomer: $\delta = 14.28$, 14.37, 14.42, 15.01, 24.08, 24.14, 24.20, 27.53, 27.90, 28.47, 28.72, 30.43, 52.48, 138.16, 139.03, 139.55, 141.27; HRMS calcd for $C_{18}H_{30}$: 246.2348; found 246.2354.

2g: Colorless liquid, 70% yield (392 mg, 2.0-mmol scale); ^{1}H NMR: $\delta = 0.64-0.94$ (m, 8H), 1.44–1.62 (m, 8H), 2.27–2.35 (m, 6H), 3.31 (t, $J = 5.2$ Hz, 1H), 7.14–7.34 (m, 5H); ^{13}C NMR: $\delta = 14.38$, 14.45, 16.98, 23.21 (2 CH_2), 23.25, 23.36, 24.34, 28.48, 30.62, 54.08 (CH), 125.41, 128.04, 128.44, 137.71, 138.91, 141.47, 141.85, 142.32; HRMS calcd for $C_{21}H_{28}$: 280.2191; found: 280.2187.

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Synthesis and Structure of an Anionic $Ga_{26}R_8$ Cluster with a Metalloid Core**

Alexander Rodig and Gerald Linti*

In anionic partial structures of compounds of gallium with more electropositive metals, gallium clusters are found, for example the Ga_8 dodecahedron in $RbGa_3$,[1] the Ga_{12} icosahedron in $RbGa_7$,[2] and the Ga_{11} octadecahedron in K_3Ga_{13}.[3] Up to now, the nonagallane **1**[4] and the two Ga_{22} clusters **2a, b**[5, 6] have been the only examples of metalloid[7] gallium cluster compounds (Scheme 1). All the other gallium cluster compounds such as the tetragallane R_4Ga_4[8, 9] and **4**[4] have a

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1433-7851/00/3916-2952 $ 17.50+.50/0