Zr-promoted linear coupling of alkynes to generate bis(allene)s†‡

Xiaoyu Yan,[a] Chunbo Lai[a] and Chanjuan Xi*[ab]

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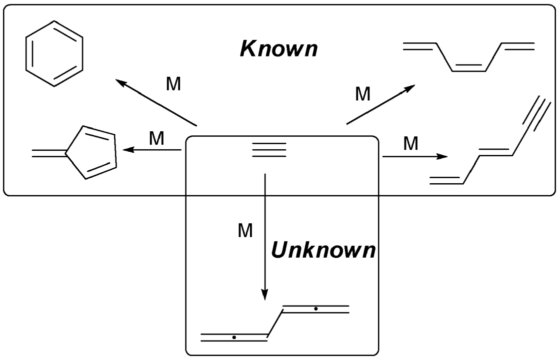
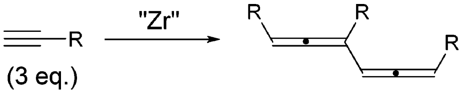
Zirconium promoted linear coupling of alkynes to generate bis(allene)s with high yields in the presence of ^{n}BuLi and chlorophosphines or trimethylsilyl trifluoromethanesulfonate.

Transition metal-mediated trimerization reactions of alkynes have been known for years.[1] Among them, the most common coupling procedure is the cycloaddition reaction of three alkynes to give arenes and fulvenes.[2,3] Recently, it has been reported that the transition metal-induced trimerization of alkynes to acyclic dieneynes,[4] endiynes,[5] and trienes after hydrolysis.[6] However, the transition metal-mediated coupling of alkynes to afford bis(allene) has not been reported (Scheme 1), to the best of our knowledge.



Scheme 1 Trimerization of alkynes.

Negishi and co-workers reported that Li[Cp$_2$Zr(C$\equiv$CR)$_3$] underwent 1,2-migration insertion to give an eneyne after hydrolysis,[7] in which two alkynes coupled. We recently reported that treatment of Li[Cp$_2$Zr(C$\equiv$CR)$_3$] with quinone afforded geminal endiynes.[5] In this case, three alkynes coupled together. During the course of our further investigation of this reaction with other reagents, we found three alkynes coupled together to afford bis(allene) as shown in eqn (1).



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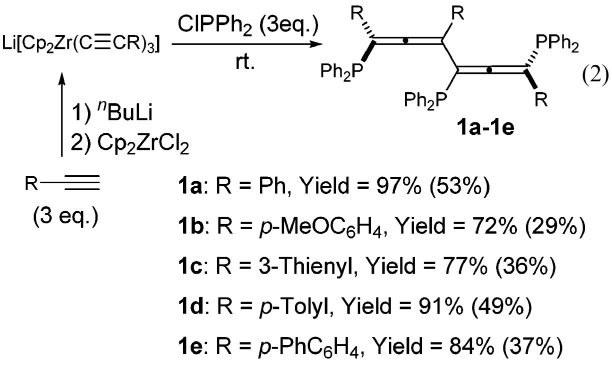
(1)

Initially, reaction of Li[Cp$_2$Zr(C$\equiv$CPh)$_3$] (1 mmol), generated *in situ* by the reaction of Cp$_2$ZrCl$_2$ with 3 equiv. of acetylide LiC$\equiv$CPh,[7] with chlorodiphenylphosphine (2 mmol) was firstly examined and 1,4,6-triphenyl-1,3,6-tris(diphenylphosphino)hexa-1,2,4,5-tetra-ene **1a** was isolated in 38% yield. In this reaction, the product **1a** contained three C–P bonds. Meanwhile, some 1,4-diphenylbut-1-en-3-yne was detected by GC-MS. When 3 equiv. of chlorodiphenylphosphine were used, the reaction proceeded smoothly, and **1a** was obtained in 97% NMR yield (eqn (2)). The product **1a** was characterized by NMR spectroscopy. In its ^{13}C NMR spectrum, the two allenic-type sp-hybridized carbon signals appeared at 209.0 and 209.9 ppm and four sp^2 carbon signals at 103.3, 105.5, 107.2, and 108.6 ppm, respectively. Its ^{31}P NMR spectrum showed three signals at −6.9, −7.9, −9.8 ppm, respectively. Under similar conditions, various terminal alkynes were examined. When aromatic 1-alkynes were used, the desired products were formed in high yields. The representative results are shown in eqn (2). However, the aliphatic 1-alkynes led to the formation of a complex, inseparable mixture. Nevertheless, a trace amount of desired product was detected by ^{31}P NMR and ESI-MS.



(2)

1a: R = Ph, Yield = 97% (53%)
1b: R = *p*-MeOC$_6$H$_4$, Yield = 72% (29%)
1c: R = 3-Thienyl, Yield = 77% (36%)
1d: R = *p*-Tolyl, Yield = 91% (49%)
1e: R = *p*-PhC$_6$H$_4$, Yield = 84% (37%)

To extend the reaction, we tried reacting Li[Cp$_2$Zr(C$\equiv$CPh)$_3$] (1 mmol) with trimethylsilyl trifluoromethanesulfonate (TMSOTf) (4 mmol) and bis(allene) **1f** was obtained in 57% isolated yield (eqn (3)). It is noteworthy that in this reaction two diastereomers were observed in 1 : 1 ratio, which was in contrast to the reaction with chlorophosphine.

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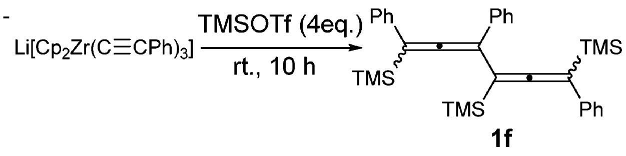
[a] *Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China. E-mail: cjxi@tsinghua.edu.cn; Tel: +86-10-62782695*
[b] *State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China*

† Dedicated to Professor John M. Birmingham on the occasion of his 80th birthday.

‡ Electronic supplementary information (ESI) available: Full experimental details, including ^{1}H and ^{13}C NMR data for new compounds. CIF file for compound **2a**. CCDC 736782. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b912175g



(3)

To confirm the structure of bis(allene) product **1**, we conducted the crystallization of compound **1a** several times but failed. When **1a** was kept in aerobic conditions for about three months, compound **2a** was obtained. Colorless crystals of **2a** suitable for X-ray analysis were obtained by diffusing *n*-hexane into the ethyl acetate solution at room temperature. The structure of compound **2a** is shown in Fig. 1.§ This result indirectly indicated that the bis(allene) had formed in the reaction.

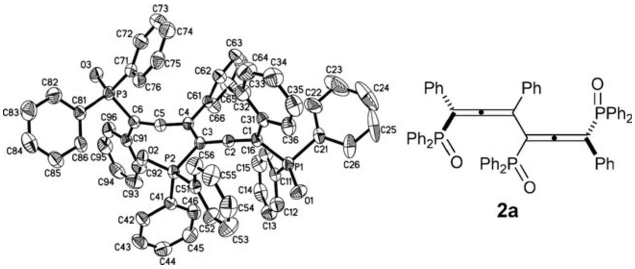


Fig. 1 X-Ray crystal structure of **2a**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms have been omitted for clarity.

On the basis of the above observations, a plausible reaction mechanism was proposed in Scheme 2. First, the zirconate complex Li[Cp$_2$Zr(C≡CR)$_3$] **3** undergoes a 1,2-migratory insertion reaction to give intermediate **4**.[7] Intermediate **4** is in equilibrium with zirconacyclocumulene **5**.[8,9] In the presence of an electrophile, **5** undergoes electrophilic attack to give intermediate **6**[10,11] with the elimination of lithium salt, in which the alkynyl group attacks the sp^2-carbon to form a new carbon–carbon bond. When chlorophosphine was used as an electrophile, the intermediate **6** rearranged to **7**, which coupled with 2 equiv. of chlorophosphine[10–12] to give compounds **1a–1e** with high stereoselectivity through isomerization of compound **8**. When TMSOTf was used as an electrophile, the intermediate **6** attacked 2 equiv. of TMSOTf to give compound **1f** as a mixture of two diastereomers. TMSOTf as an electrophile behaved differently to chlorophosphine. This may be attributed to the bulky TMS group affecting the formation of **7**.

Further investigation of the mechanism and applications is now in progress.

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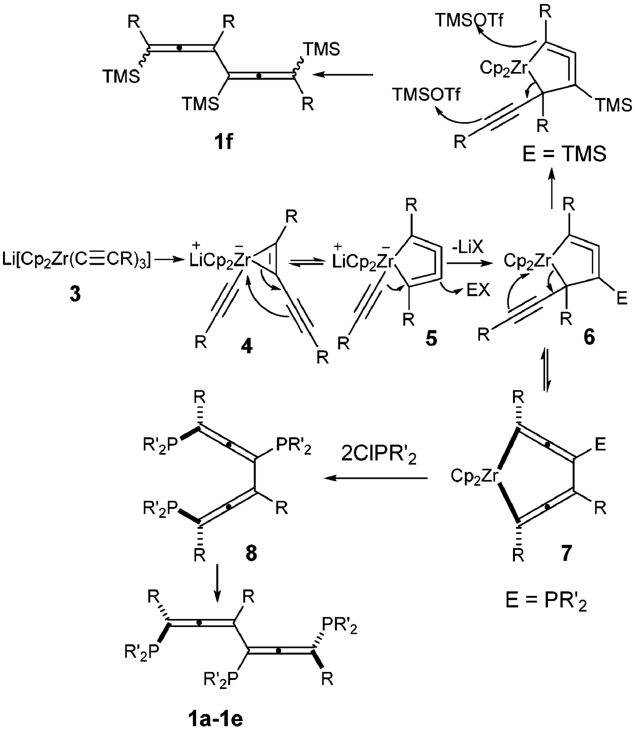

Scheme 2 Proposed mechanism.

Notes and references

§ Crystal data for **2a**: $C_{60}H_{45}O_3P_3$, M = 906.87, colorless, 0.32 × 0.23 × 0.15 mm^3, triclinic, $P\bar{1}$, a = 9.8957(4), b = 14.1576(6), c = 18.0625(8) Å, α = 82.699(3), β = 75.037(2), γ = 81.991(2)°, T = 293(2) K, V = 2409.89(18) Å^3, Z = 2, D_c = 1.250 Mg m^{-3}, μ = 0.170 mm^{-1}, Mo-Kα, 29 875 independent reflections, R_{int} = 0.0813, final R_1 [$I > 2\sigma(I)$] = 0.0897. (CCDC: 736782).

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