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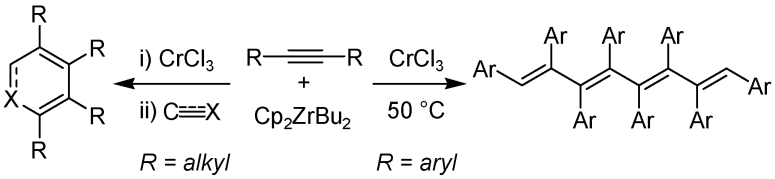

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Formation of Linear Tetramers of Diarylalkynes by the Zr/Cr System

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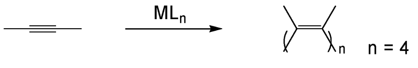
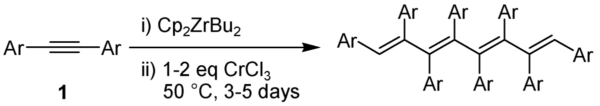
Oligomerization of alkynes catalyzed or mediated by transition metal complexes is of great interest since it can be an efficient way to construct new π-conjugated compounds, which attract much attention in the area of organic functional materials.[1] Although dimerization and cyclic trimerization of alkynes are well-known, selective formation of higher linear oligomers of alkynes is rare.[2]

The formation of linear tetramers of internal alkynes with high stereoselectivity still remains challenging. In this paper, we would like to report a novel Zr/Cr system for linear tetramer formation of diarylalkynes. We also report that the alkyl-substituted alkynes were converted into cyclized products in the Zr/Cr system.[3]



Linear tetramer

Internal alkynes readily couple with Cp_2ZrBu_2 (Negishi reagent) to form zirconacyclopentadienes.[4] During the course of our study on the C−C bond and the C-heteroatom bond formation of the zirconacyclopentadienes, we found here that addition of $CrCl_3$ to the mixture of diarylalkynes and Cp_2ZrBu_2 at 50 °C led to the formation of tetraenes **2** as shown in eq 1.



2a (Ar = Ph, 82%)
2b (Ar = m-Tol, 35%)
2c (Ar = 2-Thienyl, 71%)
2d (Ar = 3-Thienyl, 59%)

Without a Cr salt, no tetraene was formed under the same conditions, and the intermediate of zirconacyclopentadiene **3** totally remained. The reactions usually required 3−5 days to consume zirconacyclopentadienes. THF was selected as the solvent to obtain clean transformation, whereas reactions in acetonitrile and DMF were sluggish.

Trivalent chromium species, such as Cp^*CrCl_2, $MeCrCl_2$, and $PhCrCl_2$, afforded the same product **2a** in 73, 58, and 45% NMR yields, respectively, while $CrCl_2$ did not react with zirconacyclopentadienes. Other metals, such as $NiCl_2(PPh_3)_2$, CuCl, $FeCl_3$, and Ph_2SnCl_2, did not afford the desired product **2a**. To our surprise, the single-crystal X-ray analysis of **2a**[5] and **2c** indicated that the stereochemistry of these compounds was (1*E*,3*E*,5*E*,7*E*)-octatetraene, which means the geometry of the inner double bonds in **2** changed from cis to trans during the reaction. Determination of the stereochemistry of **2b** was done by comparison of the spectral data of its isomer (1*E*,3*Z*,5*Z*,7*E*)-octatetraene **4b**, prepared by the coupling reaction of iododiene with dienyl copper compounds.[6]

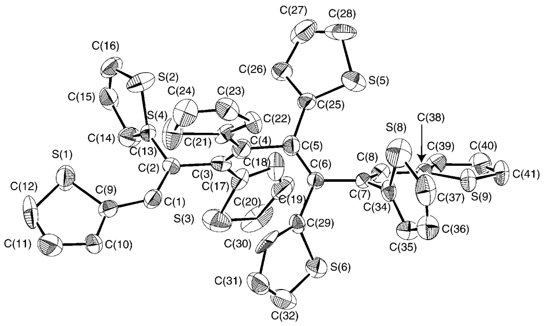
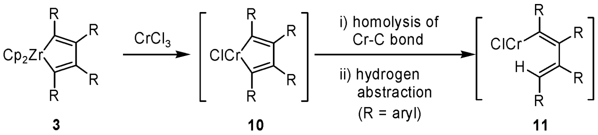


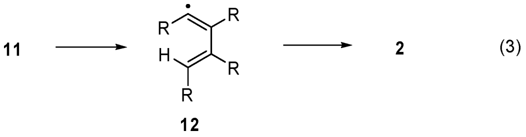
Figure 1. Linear tetramer of dithienylacetylene **2c**.

It was known that transmetalation of zirconacyclopentadiene to Cu, Ni, Li, Bi, etc. was performed, and in situ formed new metalacyclopentadienes showed their characteristic reactions.[8] When tetraethylzirconacyclopentadiene reacted with $CrCl_3(THF)_3$ at 50 °C for 12 h, the formation of Cp_2ZrCl_2 was observed in 39% yield. Although the yield was not high, this fact suggests that transmetalation from zirconacyclopentadienes to Cr proceeded. Chromacyclopentadiene has been prepared by the reaction of Cp^*CrCl_2 with Mg and 2-butyne by Wilke et al.[9]

Deuteriolysis of the resulting mixture did not give any deuterated product of **2a**. The protons at the terminal carbons of the diene moiety came from abstraction during the reaction but not from hydrolysis after the reaction. There is no direct evidence for the mechanism, but this result suggests that the chromacyclopentadiene **10** formed by transmetalation from zirconacyclopentadienes opens the ring to give a dienylchromium compound **11**.



Homolytic cleavage of the Cr−C bond of **11** to afford a dienyl radical compound **12** shows the isomerization from cis to trans of the internal double bond moiety in **12**.



To verify this ring opening and isomerization, the following reaction was carried out. A ring-opened linear dienylzirconocene

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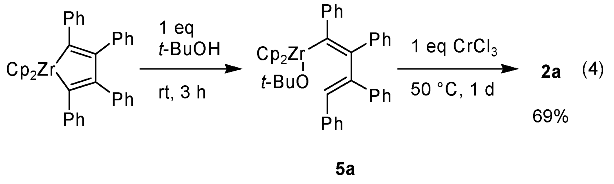
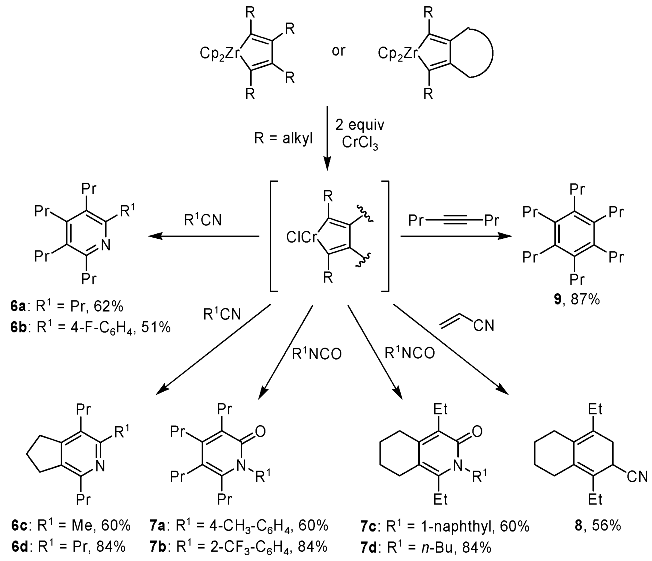
complex **5a** was prepared by the treatment of tetraphenylzirconacyclopentadiene with *t*-BuOH. Selective monoprotonation proceeded to afford **5a** cleanly. To the ring-opened linear zirconocene compound **5a**, 1 equiv of $CrCl_3$ was added. The mixture was heated to 50 °C and stirred. As expected, the desired tetraene **2a** was formed in 69% yield within 1 day. This result indicates that the reaction from **11** to **2** is relatively fast. Rate-determining step is the transmetalation or the ring-opening step.

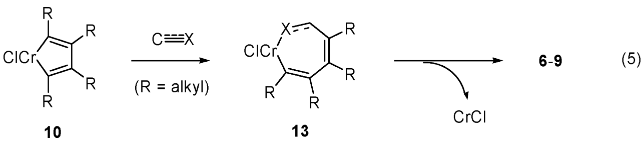


This prompted us to use the chromacyclopentadienes formed in situ. Recently, we have reported the preparation of pyridines and pyridones from azazirconacyclopentadienes in the presence of Ni(II) complexes.[7] However, it is well-known that zirconacyclopentadienes do not directly react with usual nitriles[8d] or even after transmetalation to Ni or Cu. Pyridines were not formed with Ni or Cu. It is interesting to note that when the reaction mixture of tetrapropylzirconacyclopentadiene with $CrCl_3$ was treated with butyronitrile, pentapropylpyridine **6a** was obtained in 62% yield at 50 °C. Similarly, bicyclic zirconacyclopentadiene prepared from 4,9-tridecadiyne reacted with butyronitrile after treatment with $CrCl_3$ to afford bicyclic pyridine derivative **6d** in 84% yield. The reaction of tetrapropylzirconacyclopentadiene with isocyanates gave pyridine derivatives **7a** and **7b** in 60 and 84% yields, respectively. Thus, the combination of zirconacyclopentadienes and $CrCl_3$ showed new reactivity toward nitriles or isocyanates. When the mixture of tetrapropylzirconacyclopentadiene and $CrCl_3$was treated with the 4-octyne, hexapropylbenzene **9** was obtained in 87% yield. This reaction is similar to the Ni-mediated reaction of zirconacyclopentadienes with alkynes.[8f] The reaction with an olefin having an electron-withdrawing group, such as acrylonitrile, proceeded to give cyanocyclohexadiene derivative **8** in 56% yield. The results are shown in Scheme 1.

Scheme 1



Interestingly, zirconacyclopentadienes prepared from diarylalkynes did not react with nitriles nor with isocyanates in the presence of $CrCl_3$. This is probably due to the low reactivity toward insertion of nitriles or isocyanates. To the contrary, alkyl-substituted zirconacyclopentadienes did not give tetramers of dialkylacetylenes by the Zr/Cr system. This is probably because the ring opening is not favorable in the case of tetraalkyl-substituted chromacyclopentadienes.



Further investigation on the mechanism and new applications is now in progress.

Supporting Information Available: Experimental details and spectroscopic characterization of new compounds, and X-ray data for **2a** and **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, pp 753−770. (b) Shore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 1152−1162. (c) Mashima, K.; Nakayama, Y.; Nakamura, A. *Catalyst & Catalysis* **1997**, *39*, 645−653. (d) Eisch, J. J.; Ma, X.; Han, K. I.; Gitua, J. N.; Krüger, C. *Eur. J. Inorg. Chem.* **2001**, 77−88.

(2) (a) Bruce, M. I.; Hall, B. C.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Chem. Soc., Dalton Trans*. **2000**, 2279. (b) Haskel, A.; Straub, T.; Dash, A. K.; Eisen, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 3014. (c) Haskel, A.; Wang, J.; Straub, T.; Neyround, T. G.; Eisen, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 3025. (d) Burrows, A. D.; Green, M.; Jeffery, J. C.; Lynam, J. M.; Mahon, M. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3043. (e) Biagini, P.; Caporusso, A. M.; Funaioli, T.; Fachinetti, G. *Angew. Chem*. **1989**, *101*, 1079.

(3) A part of this work has been orally reported at the 227 ACS National Meeting in Anaheim, CA, March 28, 2004.

(4) For dimerization of internal alkynes with a zirconocenedibutyl complex, see: (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett*. **1986**, *27*, 2829. (b) Takahashi, T.; Swanson, R. D.; Negishi, E. *Chem. Lett*. **1987**, 623−626. (c) Negishi, E.; Holmes, S. J.; Tour, J.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336−3346. (d) Xi, Z.; Hara, R.; Takahashi, T. *J. Org. Chem.* **1995**, *60*, 4444−4448.

(5) Compound **2a** has been obtained as a byproduct, and its X-ray structure has been reported. However, there is no procedure for the formation of **2a**. See: Rheingold, A. L.; Staley, D. L.; Heck, R. F.; Silverberg, L. *Acta Crystallogr*. **1990**, *C46*, 144−146.

(6) Compounds **4** were synthesized by the following procedure: To a solution of a zirconacyclopentadiene (1 mmol) were added 1-iodo-1,2,3,4-tetraaryl-(1*Z*,3*E*)-butadiene (1 mmol), CuCl (1 mmol), and $Pd(PPh_3)_4$ (0.05 mmol). After stirring the mixture at 50 °C for 24 h, **4** was obtained.

(7) (a) Takahashi, T.; Tsai, F. Y.; Kotora, M. *J. Am. Chem. Soc.* **2000**, *122*, 4994. (b) Takahashi, T.; Tsai, F. Y.; Li, Y. Z.; Wang, H.; Kondo, Y.; Yamanaka, M.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 5059.

(8) For the transmetalation of zirconacyclopentadienes to Cu, see: (a) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672−1680. (b) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154−5155. To Bi: (c) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310−2312. (d) Takahashi, T.; Li, Y. Z.; Ito, T.; Xu, F.; Nakajima, K.; Liu, Y. H. *J. Am. Chem. Soc*. **2002**, *124*, 1144−1145. To Li: (e) Takahashi, T.; Huo, S.; Hara, R.; Noguchi, Y.; Nakajima, K.; Sun, W.-H. *J. Am. Chem. Soc.* **1999**, *121*, 1094−1095. To Ni: (f) Takahashi, T.; Tsai, F. Y.; Li, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1999**, *121*, 11093−11100.

(9) Wilke, G.; Benn, H.; Goddards, R.; Kruger, A. C.; Pfeil, B. *Inorg. Chim. Acta* **1992**, *198−200*, 741−748.

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