

# Formation of cyclooctatetraenes from zirconacyclopentadienes

Tamotsu Takahashi,<sup>\*a</sup> Wen-Hua Sun<sup>a</sup> and Kiyohiko Nakajima<sup>b</sup>

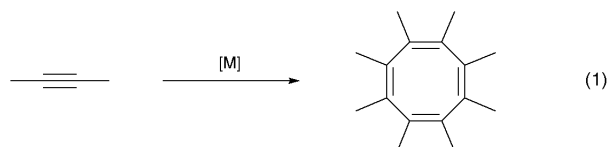
<sup>a</sup> Catalysis Research Center and Graduate School of Pharmaceutical Sciences and CREST, Science and Technology Corporation (JST) Hokkaido University, Sapporo 060-0811, Japan. E-mail: tamotsu@cat.hokudai.ac.jp

<sup>b</sup> Department of Chemistry and CREST, Science and Technology Corporation (JST), Aichi University of Education, Kariya, Aichi 448-8542, Japan

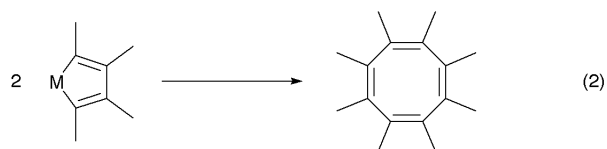
Received (in Cambridge, UK) 8th April 1999, Accepted 6th July 1999

Treatment of zirconacyclopentadienes with 2 equiv. of CuCl at room temperature and with 1 equiv. of NBS at  $-78\text{ }^{\circ}\text{C}$  selectively afforded cyclooctatetraene derivatives in good yields.

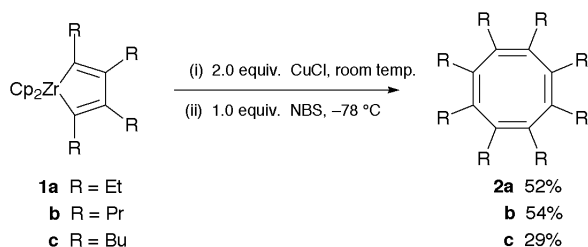
The cyclo-coupling reaction of acetylene to give cyclooctatetraene [eqn. (1)] was discovered by Reppe using the  $\text{NiBr}_2/\text{CaC}_2$  system.<sup>1</sup> For this reaction, the mechanism most generally accepted involves the coupling of two nickellacyclopentadienes for the formation of cyclooctatetraenes.<sup>2</sup>



However, to the best of our knowledge, there is no report of the formation of cyclooctatetraenes from two metallacyclopentadienes [eqn. (2)].<sup>3</sup> This prompted us to investigate the formation of cyclooctatetraene derivatives from zirconacyclopentadienes.<sup>4</sup>



Here we report the first example of cyclooctatetraene formation from metallacyclopentadienes. Sequential treatment of zirconacyclopentadiene with 2 equiv. of CuCl and 1 equiv. of NBS afforded cyclooctatetraenes as described in Scheme 1.<sup>†</sup>

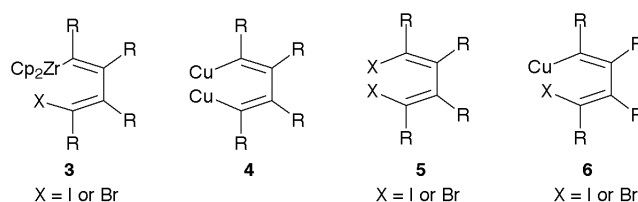


Scheme 1

A typical procedure is as follows. Tetraethylzirconacyclopentadiene **1a** in THF was treated with 2 equiv. of CuCl at room temperature for 1 h. After the mixture was cooled to  $-78\text{ }^{\circ}\text{C}$ , 1 equiv. of NBS was added, and the resulting mixture was stirred for 3 h at  $-78\text{ }^{\circ}\text{C}$ . The product, octaethylcyclooctatetraene **2a**, was obtained in 52% yield.

In order to prepare the cyclooctatetraenes from zirconacyclopentadienes, we designed two reactions, namely, (i) a coupling reaction of **4** with **5** and (ii) a coupling reaction of two

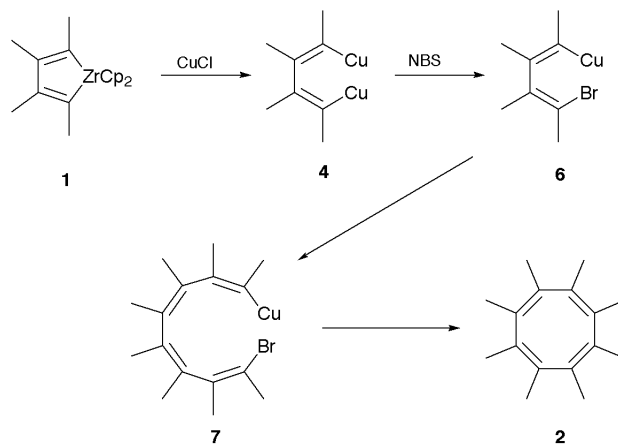
molecules of **6**. Reaction of **4** with **5** did not give **2**, and it was not a clean reaction. As already reported,<sup>5</sup> the complex **3** produced cyclobutadienes in good to high yield when it was treated with CuCl. Therefore, the formation of **6** has been



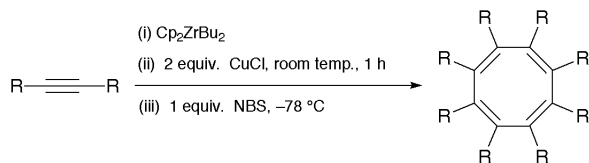
proposed although **6** was not detected. In the reaction a dimer of the cyclobutadienes, tricyclo[4.2.0.0<sup>2,5</sup>]octa-3,7-diene, was obtained as the major product at room temperature. Only a trace amount of cyclooctatetraene was detected in this reaction. This suggested that at room temperature the intramolecular coupling of **6** was faster than the intermolecular coupling. However, we expected that the reaction rate of the intramolecular coupling of **6** would be significantly decreased at low temperature due to steric crowding. In this case, the intermolecular coupling would be the major reaction. Since transmetalation of the Zr–C bond of **3** to a Zr–Cu bond requires room temperature conditions, the complex **6** could not be formed from **3** at low temperature. Therefore, we used monobromination of **4** with 1 equiv. of NBS to produce **6** at low temperature, since it proceeds at  $-78\text{ }^{\circ}\text{C}$ .

A mixture of tricyclooctadienes and cyclooctatetraenes was obtained as expected when the reaction was carried out at  $-30\text{ }^{\circ}\text{C}$ . Reflux of the mixture of the two products in THF did not change the ratio. This clearly indicates that rearrangement of tricyclooctadienes to cyclooctatetraenes did not occur. As shown in Scheme 1, cyclooctatetraenes were obtained in good yield at  $-78\text{ }^{\circ}\text{C}$  as the major product. An X-ray study was carried out to verify the structure of **2b**.<sup>‡</sup>

On the basis of these results, the following mechanism is plausible (Scheme 2). In the first step, transmetalation of



Scheme 2



Scheme 3

zirconacyclopentadiene with CuCl gives dicopper intermediate **4**. Addition of 1 equiv. of NBS to **4** leads to monobromination at  $-78\text{ }^{\circ}\text{C}$  giving **6**. The intermediate **6** undergoes intermolecular coupling to form **2** via **7**.

It is noteworthy that the formation of cyclooctatetraene derivatives can be performed in one pot from the starting acetylene as follows. For example, to a mixture of 1 mmol of  $\text{Cp}_2\text{ZrCl}_2$  and 5 ml of THF was added 2 mmol of BuLi at  $-78\text{ }^{\circ}\text{C}$ . The mixture was stirred for 1 h at  $-78\text{ }^{\circ}\text{C}$  and then 2 mmol of hex-3-yne was added. The reaction mixture was gradually warmed to room temperature and tetraethylzirconacyclopentadiene **1a** was formed. The same procedure described above for **1a** can then be used (Scheme 3).

## Notes and references

† Selected data for **2a**:  $\delta_{\text{H}}(\text{CDCl}_3, \text{Me}_4\text{Si})$  0.94 (t,  $J$  7.5, 24H), 1.99–2.10 (m, 16H);  $\delta_{\text{C}}(\text{CDCl}_3, \text{Me}_4\text{Si})$  14.24, 23.58, 138.39. HRMS for  $\text{C}_{24}\text{H}_{40}$ : calc. 328.3128, found 328.3132. For **2b**:  $\delta_{\text{H}}(\text{CDCl}_3, \text{Me}_4\text{Si})$  0.87 (t,  $J$  7.3, 24H), 1.17–1.29 (m, 8H), 1.30–1.44 (m, 8H), 1.85–2.00 (m, 16H);  $\delta_{\text{C}}(\text{CDCl}_3, \text{Me}_4\text{Si})$  14.88, 22.86, 33.58, 137.68. HRMS for  $\text{C}_{32}\text{H}_{56}$ : calc. 440.4379,

found 440.4391. For **2c**:  $\delta_{\text{H}}(\text{CDCl}_3, \text{Me}_4\text{Si})$  0.89 (t,  $J$  7.0, 24H), 1.21–1.37 (m, 32H), 1.94–1.98 (m, 16H);  $\delta_{\text{C}}(\text{CDCl}_3, \text{Me}_4\text{Si})$  14.01, 23.44, 30.94, 31.93, 137.71. HRMS for  $\text{C}_{40}\text{H}_{72}$ : calc. 552.5630, found 552.5638.

‡ Crystal data for **2b**:  $\text{C}_{32}\text{H}_{56}$ ,  $M = 440.80$ , triclinic, space group  $P\bar{1}$  (No. 2),  $a = 9.5552(2)$ ,  $b = 9.5131(3)$ ,  $c = 17.1505(9)$  Å,  $\alpha = 88.553(4)$ ,  $\beta = 83.021(3)$ ,  $\gamma = 87.903(2)^{\circ}$ ,  $U = 1546.0(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{c}} = 0.95$  g cm<sup>-3</sup>,  $\mu(\text{Cu-K}\alpha) = 3.53$  cm<sup>-1</sup>, 6676 measured reflections, 3160 reflections with  $I > 3\sigma(I)$ ,  $R = 0.053$ . CCDC 182/1315. See <http://www.rsc.org/suppdata/cc/1999/1595/> for crystallographic data in .cif format.

- 1 W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Justus Liebigs Ann. Chem.*, 1948, **560**, 1.
- 2 G. Wilke, *Pure Appl. Chem.*, 1978, **50**, 677; R. E. Colborn and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1986, **108**, 5470; C. J. Lawrie, K. P. Gable and B. K. Carpenter, *Organometallics*, 1989, **8**, 2274; J. J. Eisch, J. E. Galle, A. A. Aradi and M. P. Boleslawski, *J. Organomet. Chem.*, 1986, **312**, 399.
- 3 D. Lloyd, *The Chemistry of Conjugated Cyclic Compounds*, Wiley, Chichester, 1990, p. 21; P. Aucher-Krummel and K. Muellen, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1003; D. B. Grotjahn, in *Comprehensive Organometallic Chemistry II*, ed. W. Edard, E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 12, p. 747; P. W. Jolly, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, London, 1982, vol. **8**, p. 649; M. Lautens, W. Klute and W. Tam, *Chem. Rev.*, 1996, **96**, 49; P. M. Maitlis, *J. Organomet. Chem.*, 1980, **200**, 161.
- 4 For a recent review on the preparation and reactions of zirconacyclopentadienes, see T. Takahashi, Z. Xi and M. Kotora, *Res. Dev. Pure Appl. Chem.*, 1998, 2 and references therein.
- 5 H. Ubayama, W.-H. Sun, Z. Xi and T. Takahashi, *Chem Commun.*, 1998, 1931.

Communication 9/02788B