Isolation and Characterization of Zirconacyclopentane

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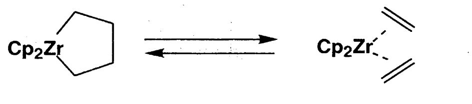
Zirconacyclopentane ($(t\text{-}Bu_2C_5H_3)_2Zr(C_4H_8)$) was isolated as stable yellow crystals and its structure was determined by X-ray analysis.

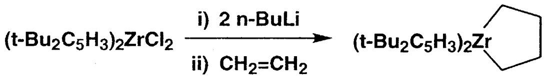
Very recently we have reported a practical and highly selective alkyne-alkyne cross coupling via zirconacyclopentane $Cp_2Zr(C_4H_8)$ **1**.[1] This process involved replacement of an ethylene moiety of **1** by an alkyne.[1-3] Similar replacement of an ethylene moiety of **1** using a phosphine,[4] an aldehyde,[5,6] has been also reported. This attractive reactivity of **1** can be formally explained by the existence of the following equilibrium (eq 1) between **1** and bis(ethylene)complex **2**.[1-7]



(1)

1 **2**

However, to the best of our knowledge, the zirconacyclopentane system $Zr(C_4H_8)$ has not been structurally characterized,[8] although the $Zr(C_4H_8)$ ring has been investigated spectroscopically.[3,7b,7d] One of the major reason is that **1** was thermally sensitive and it can be handled only in the presence of additional ethylene in solution at room temperature without decomposition.[7] In this paper we would like to report the isolation and structural characterization of a stable zirconacyclopentane compound.

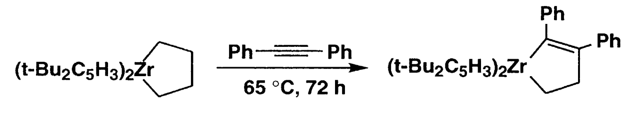


(2)

3

Introduction of an alkyl group such as Me, n-Bu and t-Bu to a cyclopentadienyl ring afforded relatively stable zirconacyclopentanes. However, crystals of these complexes were not suitable for X-ray analysis. When two t-butyl groups were introduced in each C_5H_5 ligand, $(t\text{-}Bu_2C_5H_3)_2Zr(C_4H_8)$ **3** was obtained as yellow crystals. They were stable enough and also suitable for X-ray analysis. Isolation procedure is shown as follows; To a suspension of 1.03 g (2.0 mmol) of $(t\text{-}Bu_2C_5H_3)_2ZrCl_2$ in 20 ml hexane was added 2.4 ml (1.6 M, 4.0 mmol) of n-BuLi in hexane at -78 °C. The reaction mixture was stirred for 1 h at -78 °C and then slowly warmed to 0 °C. At this temperature the stirring was continued until all the starting compound was consumed. Ethylene was slowly bubbled for 20 min in the reaction mixture at -78 °C. Then the cooling bath was removed and the bubbling was continued for two hours. The color turned from white to yellow. The precipitated LiCl was separated by a frit. From the clear filtrate **3** was crystallized at -40 °C as yellow crystals (Yield 0.38 g, 38%). Single crystals for X-ray analysis were obtained by recrystallization from hexane.

The complex **3** showed a similar reactivity towards diphenylacetylene to that of **1** and its reaction with diphenylacetylene at 65 °C for 72 h gave a zirconacyclopentene **4** in 60% yield.



3 **4: 60%**

The X-ray structure of **3** is shown in Figure 1.[9] The bond length of C(2)-C(3) (1.502(5) Å) was significantly shorter than that of C(1)-C(2) (1.542(5) Å) and C(3)-C(4) (1.547(4) Å). Similar result was reported for $Ir(C_4H_8)(PPh_3)(C_5Me_5)$ (C(1)-C(2) : 1.51(5), C(2)-C(3) : 1.32(6) Å)[10a] or $Co(C_4H_8)(PPh_3)(C_5H_5)$ (C(1)-C(2) : 1.509(9), (C(2)-C(3) : 1.454(9) Å).[10a] Structures of other metallacyclopentanes such as Rh,[10a] Mo,[10b] Re,[10c] Ta[10d] and Ti[10e] have been also reported. The bond lengths of C(1)-C(2) and C(2)-C(3) in the ring system of these complexes were almost the same.

^1H NMR of **3**[11] indicated that there were two signals at 1.33 ppm and 2.21 ppm assigned to α-protons and β-protons in the ring system, respectively, which showed low field shift compared with **1** (0.89 (H_α) and 1.66 (H_β))[7d] or $(C_5Me_5)_2Zr(C_4H_8)$ (0.50 (H_α) and 1.95 (H_β) ppm).[7b,12] Its ^{13}C NMR revealed that C_α and C_β signals appeared at 42.3 and 32.9 ppm, respectively. They are in or close to the range of those of **1** (39.2 (C_α) and 28.1 (C_β) ppm)[7d] and $(C_5Me_5)_2Zr(C_4H_8)$ (49.5 (C_α) and 29.8 (C_β) ppm).[7b] J(C-H) values of **3** were 122 and 124 Hz for C_α and C_β, respectively. These numbers were almost the same as those for other metallacyclopentanes $M(C_4H_8)$ (119-

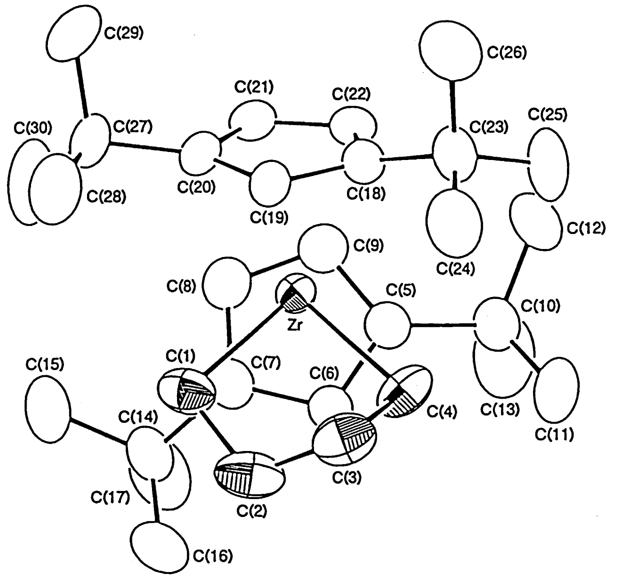


Figure 1. The structure of **3**. Selected bond angles; C(1)-C(2)-C(3): 110.8(2)°, C(2)-C(3)-C(4): 109.8(2)°, Zr-C(1)-C(2): 104.6(2)°, C(1)-Zr-C(4): 81.2(1)°.

124 Hz for C_α and 124-125 for C_β).[13]

References and Notes

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9 Crystallographic data of **3**: fw = 501.95, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 10.774(1)$ Å, $b = 11.836(1)$ Å, $c = 12.930(1)$ Å, $\alpha = 84.776(7)°$, $\beta = 68.487(7)°$, $\gamma = 69.995(8)°$, V = 1440.4(2) Å^3, and $\mu = 3.87$ cm^{-1} for Mo Kα ($\lambda = 0.71073$ Å). Intensity measurements were carried out for $2\theta < 60°$ on an Enraf-Nonius CAD4 diffractometer at 293 K. Among 9060 reflections measured (8708 were unique ($R_{int} = 0.0935$)), those of 6850 had $|Fo| > 3\sigma(|Fo|)$. Refinement by the full-matrix least-squares method led to a convergence with R = 0.041, $R_w = 0.047$ ($w = [\sigma^2(Fo)+\{0.015(Fo)\}^2]^{-1}$), $(\Delta/\sigma)_{max} = 0.225$, $(\Delta\rho)_{min} = -0.85$ eÅ^{-3} and $(\Delta\rho)_{max} = 1.04$ eÅ^{-3}.

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11 NMR data for **3**; ^{1}H NMR (C_6D_6, Me_4Si) δ 1.23 (s, 36 H), 1.33 (m, 4 H) 2,21 (q, $J = 4$ Hz); 5.28 (d, $J = 2.6$ Hz, 4 H); 6.88 (t, $J = 2.6$ Hz, 2 H). ^{13}C NMR (C_6D_6, Me_4Si) δ 31.7, 32.9, 34.0, 42.3, 103.3, 109.8, 141.7.

12 $Cp_2Ti(C_4H_8)$: 1.14 (H_α) and 1.52 (H_β) ppm;[7a,d] $Cp_2Hf(C_4H_8)$: 0.89 (H_α) and 2.23 (H_β) ppm.[3]

13 $Cp_2Ti(C_4H_8)$: $J(C_\alpha\text{-H}) = 124$ Hz, $J(C_\beta\text{-H}) = 124$ Hz;[7a,d] $Cp_2Zr(C_4H_8)$: $J(C_\alpha\text{-H}) = 124$, $J(C_\beta\text{-H}) = 125$ Hz;[7d] $(C_5Me_5)_2Zr(C_4H_8)$: $J(C_\alpha\text{-H}) = 119$, $J(C_\beta\text{-H}) = 124$ Hz;[7b] $Cp_2Hf(C_4H_8)$: $J(C_\alpha\text{-H}) = 119$, $J(C_\beta\text{-H}) = 125$ Hz.[3]