Letters to the Editor

Formation of the five-membered zirconacyclocumulene $\text{Cp}_2\text{Zr}(\eta^4\text{-Bu}^t\text{C}_4\text{Bu}^t)$ and the binuclear zirconocene butatrienyl complex $\text{Cp}_2(\text{Bu}^n)\text{Zr}(\text{Bu}^t\text{C}_4\text{Bu}^t)\text{Zr}(\text{Bu}^n)\text{Cp}_2$ in the reaction of the Negishi reagent with 1,4-di(*tert*-butyl)butadiyne

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We have recently reported^{1,2} the synthesis of di-*n*-butylhafnocene $\text{Cp}_2\text{HfBu}^n_2$ (**1**), being a hafnium analog of the Negishi reagent $\text{Cp}_2\text{ZrBu}^n_2$, which is widely used in organometallic chemistry of zirconium as a source of highly reactive "Cp₂Zr" (see Refs 3 and 4). Compound **1** was synthesized by the reaction of Cp_2HfCl_2 with *n*-butyllithium and turned out to be much more stable than $\text{Cp}_2\text{ZrBu}^n_2$. Unlike its zirconium analog, which rapidly decomposes already at low temperatures, hafnium complex **1** loses the butyl groups and generates "Cp₂Hf" only at 100 °C, which provides new potentialities for organometallic synthesis. In fact, we showed that the use of compound **1** as a source of "Cp₂Hf" in the reactions with 1,4-disubstituted butadiynes $\text{RC}\equiv\text{C}-\text{C}\equiv\text{CR}$ (R = Bu^t, Ph, and SiMe₃) makes it possible to synthesize various hafna-

cycles in good yields. Particularly, the hafnacyclocumulene complex $\text{Cp}_2\text{Hf}(\eta^4\text{-Bu}^t\text{C}_4\text{Bu}^t)$ was synthesized, which is the first example of the structurally characterized five-membered hafnacyclocumulene.^{1,2} Taking into account these data, we decided to study the reaction of the Negishi reagent with the above-mentioned diynes. The results obtained for 1,4-di(*tert*-butyl)butadiyne are presented in this work.

Experiments were carried out by mixing Cp_2ZrCl_2 and $\text{Bu}^t\text{C}\equiv\text{C}-\text{C}\equiv\text{CBu}^t$ with *n*-butyllithium in hexane at –78 °C under Ar ($\text{Bu}^n\text{Li} : \text{Cp}_2\text{ZrCl}_2 = 2 : 1$) followed by gradual (within 2–2.5 h) heating of the resulting mixture to ambient temperature. The reaction afforded a reddish-brown solution from which two products were isolated.

One product (yellow crystals stable in air) is the five-membered zirconacyclocumulene $\text{Cp}_2\text{Zr}(\eta^4\text{-Bu}^t\text{C}_4\text{Bu}^t)$ (**2**) (Scheme 1) identified by elemental analysis and NMR spectra (30% yield). This metallacycle has earlier been

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synthesized⁵ by the reaction of the zirconocene bis(trimethylsilyl)acetylene complex $\text{Cp}_2\text{Zr}(\text{Me}_3\text{SiC}_2\text{SiMe}_3)(\text{Py})$ with $\text{Bu}^t\text{C}\equiv\text{C}-\text{C}\equiv\text{CBu}^t$ in 65% yield. However, the starting bis(trimethylsilyl)acetylene complex is obtained, in turn, from Cp_2ZrCl_2 in two additional steps,^{6,7} and as a consequence, the overall yield of compound **2** based on Cp_2ZrCl_2 does not exceed 33% in this method. Thus, the described above one-step method of the synthesis of complex **2** using the Negishi reagent as a source of " Cp_2Zr " is considerably more convenient in the preparative respect.

Scheme 1

Another product of the reaction of $\text{Cp}_2\text{ZrBu}^n_2$ with $\text{Bu}^t\text{C}\equiv\text{C}-\text{C}\equiv\text{CBu}^t$, which is formed in a minor amount, is the unusual binuclear zirconocene butatrienyl complex $\text{Cp}_2(\text{Bu}^n)\text{Zr}(\text{Bu}^t\text{C}_4\text{Bu}^t)\text{Zr}(\text{Bu}^n)\text{Cp}_2$ (**3**). The complex is a red-brown crystalline solid stable in air in spite of the presence of two $\sigma\text{-Zr}-\text{Bu}$ bonds in this compound. It can be assumed that the decomposition of $\text{Cp}_2\text{ZrBu}^n_2$ gives, along with " Cp_2Zr ," small amounts of monobutylzirconocene Cp_2ZrBu^n , whose subsequent reaction with the butadiyne affords the final complex **3** (Scheme 2).

Scheme 2

The structure of compound **3** was determined by X-ray diffraction analysis (at 90 K, space group $P2_1$, $Z = 2$,

$a = 11.4581(10)$, $b = 7.9044(7)$, $c = 20.6236(16)$ Å, $\beta = 101.9730(17)^\circ$, $V = 1827.2(3)$ Å³, $\theta_{\text{max}} = 30^\circ$, $R_1 = 0.0242$ for 10 022 reflections with $I > \sigma(I)$). As can be seen from Fig. 1, complex **3** contains indeed two $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrBu}^n$ groups linked by the butatrienyl bridge and located in the *trans*-position relative to each other. The C(1)—C(2), C(2)—C(3), and C(3)—C(4) distances in the butatrienyl fragment are 1.312(3), 1.305(3), and 1.316(3) Å, respectively, being close to the length of a standard C=C double bond (1.331 Å). A remarkable structural feature of complex **3** is the coordination of the C(2) atom of the butatrienyl ligand to the Zr(1) atom, which is indicated by the considerable shortening of the Zr(1)⋯C(2) distance (2.660(2) Å) compared to the Zr(2)⋯C(3) distance (2.917(2) Å). As a result of the formation of the Zr(1)⋯C(2) coordination bond, the Zr(1)—C(1)—C(5) bond angle at the sp^2 -hybridized C(1) carbon atom increases to $141.91(14)^\circ$ and becomes by $\sim 13^\circ$ larger than the Zr(2)—C(4)—C(9) angle ($129.13(14)^\circ$), and the butatrienyl fragment deviates essentially from linearity (the C(1)—C(2)—C(3) and C(2)—C(3)—C(4) bond angles are $170.36(18)$ and $166.75(19)^\circ$). In addition, the Zr(1)—C(1) (2.297(2) Å) distance is considerably shorter than the Zr(2)—C(4) (2.326(2) Å) distance, and the Zr(1)—C(13) bond (2.339(2) Å) somewhat elongates compared to the Zr(2)—C(17) bond (2.311(2) Å).

It is most likely that the formation of the Zr(1)⋯C(2) coordination bond is due to the interaction of electrons on one of the p-orbitals of the sp -hybridized C(2) carbon atom with the vacant d-orbital of the zirconium atom. The realization of such an interaction is favored by the arrangement of this p-orbital and Zr(1) atom in the bisecting plane of the dihedral angle (49°) between the Cp rings. The C(1), C(5), and C(13) atoms lie in the same bisecting plane. The Zr(2) atom and one of the p-orbitals of the C(3) atom also lie in the bisecting plane of the corresponding dihedral angle (52.5°), but they do not interact with each other or interact but much more weakly than the C(2) and Zr(1) atoms.

Fig. 1. Molecular structure of complex **3**. The hydrogen atoms of the Cp rings and butyl groups are omitted. All non-hydrogen atoms are shown as thermal vibrational ellipsoids (50% probability).

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