# Hydrogen transfer from the cyclopentadienyl rings to the 1,3-butadienyl ligand in zircona- and hafnacyclopentadienes initiated by DMF

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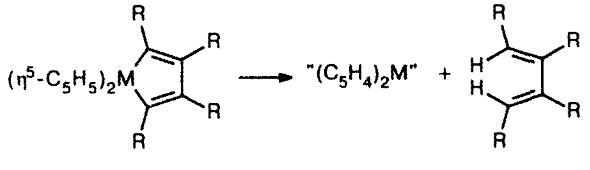
Hydrogen transfer from the $\eta^5$-$C_5H_5$ rings to another ligand or to a metal atom is one of the interesting reactions of cyclopentadienyl complexes of Group IVB metals. These reactions were described for the first time more than 20 years ago,[1—3] when it was shown that the reaction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ with magnesium and some other reducing agents yields hydride derivatives of titanium and the $\eta^5$-$C_5H_5$ rings serve as the source of hydrogen. Later it was shown (see, *e.g.*, Refs. 4—7) that hydrogen can also be transferred from $\eta^5$-$C_5H_5$ rings to σ-aryl or σ-alkyl groups bound to a metal, to the acetylene ligand, and to some other fragments.

In the present work, we report on a new reaction of this type, which spontaneously occurs at room temperature in solutions of hafna- and zirconacyclopentadiene metallacycles (**1—4**) in DMF. We found that during this reaction, hydrogen transfer occurs from the cyclopentadienyl rings in compounds **1—4** to the 1,3-butadienyl ligand to yield the corresponding 1,3-dienes.



**1—4**

M = Hf, R = Ph (**1**), Et (**2**)
M = Zr, R = Ph (**3**), Et (**4**)

When compound **1** ($[\mathbf{1}]_0 \approx 0.01$ mol $L^{-1}$) is kept in DMF in an Ar atmosphere at 20 °C, the yellow color of the initial solution of **1** gradually disappears, and in 3 h the reaction mixture becomes virtually colorless. By this time, the $^1$H NMR spectrum (400 MHz) of the reaction mixture shows that the starting compound **1** has been completely consumed and that *cis,cis*-1,2,3,4-tetraphenylbuta-1,3-diene (TPB) has appeared. This is indicated by the singlet corresponding to vinyl protons (δ 6.46) and by the multiplets due to phenyl protons (δ 6.90—6.87, 7.20—7.17, 7.48—7.46, 7.57—7.53, and 7.63—7.59) present in the spectrum; the singlet/multiplets intensity ratio is 2 : 20. In addition to the signals of TPB, the $^1$H NMR spectrum contains two complex multiplets with identical intensities at δ 6.68—6.66 and 6.58—6.56, which apparently correspond to a complex incorporating $(C_5H_4)_2Hf$ moieties. If the reaction is carried out in a saturated solution of compound **1** in DMF, the TPB formed precipitates from the reaction mixture as colorless needles. The TPB thus isolated was identified based on its melting point, $^1$H NMR spectrum (in THF-$d_8$), and mass spectrum. It is significant that when DMF is replaced by DMF-$d_7$, the TPB formed in the reaction contains virtually no deuterium (as shown by NMR spectroscopy and mass spectrometry). This indicates that it is the cyclopentadienyl rings rather than DMF that serve as the source of hydrogen for the formation of TPB.

Similar reactions involving hydrogen transfer from $\eta^5$-$C_5H_5$ rings occur in DMF solutions of compounds **2—4**. The rate of the process decreases in the order **3** > **1** ≈ **4** > **2**. In the case of metallacycle **3**, which is the most reactive, the process is completed after a period of only 15 min. The transformation of the least reactive metallacycle **2** into *cis,cis*-1,2,3,4-tetraethylbuta-1,3-diene requires as much as 20 h. In all cases, the $^1$H NMR spectra exhibit multiplets corresponding to the $(C_5H_4)_2M$ fragments, along with the signals of the diene; the chemical shifts of these multiplets vary only slightly on going from **1** and **2** to **3** and **4**.

The transformation of compounds **1—4** into dienes is accompanied by gradual precipitation of a colorless gelatinous substance, which turns yellowish with time. However, the formation of this substance is dramatically decelerated if the reaction is carried out in DMF-$d_7$. The structure of this polymeric product, which is obviously derived from DMF, is under study at present.

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