

# Interaction of carbon dioxide with zirconocene and hafnocene dihydrides

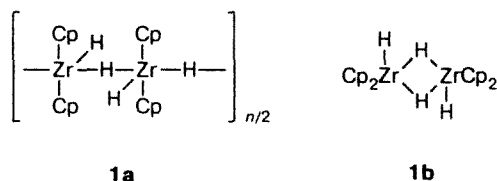
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Zirconocene and hafnocene dihydrides  $\text{Cp}_2\text{MH}_2$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) are capable of rapid absorbing carbon dioxide at room temperature and atmospheric pressure in a THF medium. In the case of  $\text{Cp}_2\text{ZrH}_2$ , the reaction results in the cleavage of the  $\text{C}=\text{O}$  bond of a  $\text{CO}_2$  molecule to form cyclic trimeric zirconocene oxide  $[\text{Cp}_2\text{ZrO}]_3$ , whose structure was confirmed by analytical and spectral methods as well as by X-ray diffraction study. Small amounts of formaldehyde and methyl formate are found in the organic products of the reaction.

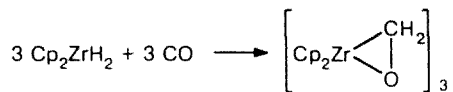
**Key words:** zirconium, hafnium, hydrides; carbon dioxide.

Zirconocene dihydride  $\text{Cp}_2\text{ZrH}_2$  (**1**) was synthesized<sup>1</sup> for the first time by the reaction of  $\text{Cp}_2\text{ZrCl}_2$  with lithium aluminum hydride in THF. According to the spectral data,<sup>1–5</sup> the solid complex has a polymeric structure  $[\text{Cp}_2\text{ZrH}_2]_n$  (**1a**) with bridging and terminal  $\text{Zr}-\text{H}$  bonds, while in solution its structure is dimeric,  $[\text{Cp}_2\text{ZrH}_2]_2$  (**1b**).



A similar polymeric structure has been suggested<sup>3,4</sup> for solid hafnocene dihydride  $\text{Cp}_2\text{HfH}_2$  (**2**).

The interaction of zirconocene dihydride **1** with  $\text{CO}$  (at 20 °C and 150 atm) has been studied,<sup>6</sup> and this reaction has been found to result in the formation of a trimeric zirconocene complex with formaldehyde  $[\text{Cp}_2\text{Zr}(\text{CH}_2\text{O})]_3$ .



In the present work, the interaction of metallocene dihydrides **1** and **2** with  $\text{CO}_2$  was investigated.

## Results and Discussion

The experiments were carried out at room temperature and atmospheric pressure in a THF medium. The absorption of  $\text{CO}_2$  was monitored using a mercury buret. A suspension of compounds **1** and **2** in THF was intro-

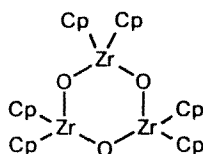
duced in the reaction with  $\text{CO}_2$  due to the poor solubility of the initial dihydrides.

The experiments performed showed that complexes **1** and **2** are capable of rapid absorbing carbon dioxide at room temperature. After 20–25 min when the reaction is practically completed, the amount of reacted  $\text{CO}_2$  is ~1 mole per mole of the initial dihydride, and 85–90% of the  $\text{CO}_2$  is absorbed in the first 5–7 min. The absorption of carbon dioxide is accompanied by fast dissolution of the dihydride, and already after 2–3 min (*i.e.*, far before the completion of  $\text{CO}_2$  absorption), the mixture becomes almost homogeneous. At this moment, the amount of absorbed  $\text{CO}_2$  is close to 0.5 moles per mole of the initial complex. This indicates that at the first stage of the process two molecules of dihydride  $\text{Cp}_2\text{MH}_2$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) are involved in a reaction with one  $\text{CO}_2$  molecule. This might mean that the dimeric form of dihydride  $[\text{Cp}_2\text{MH}_2]_2$  reacts in fact with carbon dioxide.

When the solvent is removed after the end of the reaction of complex **1** with  $\text{CO}_2$ , a slightly yellow foam-like product is formed. The  $^1\text{H}$  NMR spectrum of this product in  $\text{THF}-d_8$  is very complicated: several signals (at 6.19, 6.24, 6.25, 6.30, 6.35, 6.36, and 6.40 ppm), the most intense of which is at 6.30 ppm, are observed in the region of chemical shifts of protons of the  $\eta^5\text{-C}_5\text{H}_5$  rings. The same complicated  $^1\text{H}$  NMR spectrum is also characteristic of the foam-like substance obtained in the reaction of complex **2** with  $\text{CO}_2$ . In this case, the most intense signal in the region corresponding to the  $\eta^5\text{-cyclopentadienyl}$  protons is the signal at 6.27 ppm.

The attempts to reveal the nature of the organohafnium compounds formed in the reaction of dihydride **2** with carbon dioxide failed. However, we were able to isolate from the products of the reaction of complex **1** with  $\text{CO}_2$  a white fine-crystalline substance, which is easily soluble in THF, less soluble in benzene and

toluene, and insoluble in aliphatic hydrocarbons. The study of this compound showed that it is cyclic trimeric zirconocene oxide  $[\text{Cp}_2\text{ZrO}]_3$  (**3**).



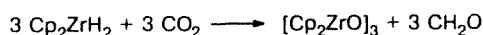
**3**

The structure of trimer **3** was confirmed by analytical and spectral methods as well as by X-ray diffraction study.<sup>7</sup> The  $^1\text{H}$  NMR spectrum of compound **3** in  $\text{THF-d}_8$  displays a sole singlet of the  $\eta^5$ -cyclopentadienyl protons at 6.30 ppm. The same signal is the most intense in the spectrum of the product obtained after removal of THF from the reaction mixture (see above). The IR spectrum of compound **3**, along with the bands assigned to the vibrations of the  $\eta^5$ - $\text{C}_5\text{H}_5$  ligands (3087, 1444, 1364, 1130, 1015, and 794  $\text{cm}^{-1}$ ), contains an intense absorption band at 729  $\text{cm}^{-1}$ , which can be assigned to the stretching vibrations of the zirconoxane  $\text{Zr}-\text{O}-\text{Zr}$  group.

According to the X-ray diffraction data,<sup>7</sup> the complex contains an almost planar six-membered  $\text{Zr}_3\text{O}_3$  cycle with alternating Zr and O atoms. The  $\text{Zr}-\text{O}$  distances in the complex are shortened (1.959–1.976 Å) probably due to the interaction of lone electron pairs of the O atoms with vacant d-orbitals of Zr. This evidences that the  $\text{Zr}-\text{O}$  bonds in the molecule of complex **3** are probably partially double. The three  $\text{Zr}-\text{O}-\text{Zr}$  bond angles in the cycle are nearly equal to each other: 142.6°, 142.4°, and 142.1°.

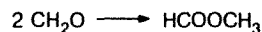
Complex **3** has been previously synthesized<sup>8</sup> by another method, viz., the reaction of  $\text{CO}_2$  with  $\text{Cp}_2\text{Zr}(\text{CO})_2$ . The spectral and structural parameters of the substance described<sup>8</sup> are very close to those of the compound obtained in our work.

Thus, the reaction of dihydride **1** with carbon dioxide results in the cleavage of the  $\text{C}=\text{O}$  bond of the  $\text{CO}_2$  molecule to form cyclic trimeric zirconocene oxide **3**. According to the scheme presented below, formaldehyde could be an organic product of this reaction. Therefore, we carried out special experiments to find formaldehyde in the products of the reaction of complex **1** with  $\text{CO}_2$ . With this purpose, after the end of the absorption of  $\text{CO}_2$ , THF was frozen from the reaction mixture into a trap cooled with liquid nitrogen and analyzed for the content of formaldehyde. The same analyses were performed for the products of the reaction of complex **2** with  $\text{CO}_2$ .



Indeed, it turned out that in both cases the THF distillates contain formaldehyde but only in very small

amounts (yield not higher than 2–3%). An additional amount of formaldehyde (~4–5%) was obtained by heating the solid residue (formed after the removal of THF) with 40%  $\text{H}_2\text{SO}_4$  at 65 °C. A small amount of methyl formate, which can be considered to be the product of the dimerization of formaldehyde by the Tishchenko reaction, was detected by GLC along with formaldehyde in the products of the reaction of dihydride **1** with  $\text{CO}_2$ .



Similar cleavage of the  $\text{C}=\text{O}$  bond in the  $\text{CO}_2$  molecule was previously observed in the interaction of carbon dioxide with the Schwarz reagent  $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ .<sup>9,10</sup> The reaction resulted in the formation of zirconoxane  $[\text{Cp}_2\text{ZrCl}]_2\text{O}$ . Formaldehyde was also found in the organic products, but its yield was not determined.

### Experimental

Experiments were carried out in an Ar atmosphere with careful exclusion of air and moisture. Solvents were purified by standard methods and distilled prior to use over metallic Na and sodium benzophenone ketyl (THF) or over Na and calcium hydride (*n*-hexane and benzene) under Ar. Carbon dioxide from a cylinder was purified by double recondensation *in vacuo* and passing through a column with  $\text{P}_2\text{O}_5$ . Initial dihydrides **1**<sup>11</sup> and **2**<sup>3</sup> were prepared by procedures described previously. IR spectra were recorded on a Bruker IFS-113v Fourier spectrometer in Nujol under Ar.  $^1\text{H}$  NMR spectra were recorded on a Bruker WH-400 spectrometer in  $\text{THF-d}_8$  using  $\text{SiMe}_4$  as the internal standard. Formaldehyde was determined quantitatively by potentiometric titration with hydrochloric hydroxylamine using a platinum electrode<sup>13</sup> as well as photometrically (after treatment of the solution analyzed with aqueous chromotropic acid in the presence of concentrated  $\text{H}_2\text{SO}_4$ ).<sup>12</sup> Methyl formate was determined by GLC on an LKhM-8MD instrument with a column packed with 15% Reoplex-400 on Chromaton NAW-HMD 8 at 30 °C.

**Trimeric zirconocene oxide  $[\text{Cp}_2\text{ZrO}]_3$ .** Complex **1** (1.11 g, 4.96 mmol) and THF (40 mL) were placed into a three-necked flask in an Ar atmosphere. Then the Ar was evacuated carefully, the flask with the suspension of complex **1** in THF was filled with pure  $\text{CO}_2$  from a mercury gas buret, and a magnetic stirrer was switched on. Fast absorption of  $\text{CO}_2$  began immediately, after 2–3 min the mixture became almost homogeneous, and after 20–25 min the absorption of  $\text{CO}_2$  ceased. At this moment, the amount of absorbed  $\text{CO}_2$  was 101 mL (under normal conditions) or 0.91 moles per mole  $\text{Cp}_2\text{ZrH}_2$ . The reaction mixture was filtered off, the colorless filtrate was concentrated *in vacuo* at 20 °C to 5 mL, and a tenfold amount of *n*-hexane was added. The white precipitate that formed was filtered, dried *in vacuo*, and extracted with hot benzene. The addition of *n*-hexane to the benzene extract filtered off gave a white precipitate (0.9 g), which was purified repeatedly according to the scheme described above. White fine-crystalline product **3** (0.28 g) was obtained. Found (%): C, 50.46; H, 4.35; Zr, 38.87.  $\text{C}_{10}\text{H}_{10}\text{OZr}$ . Calculated (%): C, 50.58; H, 4.22; Zr, 38.42. IR,  $\nu/\text{cm}^{-1}$ : 3087, 1444, 1364, 1130, 1015, 794 ( $\eta^5$ - $\text{C}_5\text{H}_5$ ); 736 ( $\text{ZrOZr}$ ).  $^1\text{H}$  NMR,  $\delta$ : 6.30 (s, 10 H,  $\eta^5$ - $\text{C}_5\text{H}_5$ ).

The reaction of complex **2** with  $\text{CO}_2$  was performed by a similar procedure.

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## Phosphorylation of dihydric phenols with amides of phosphorous acid

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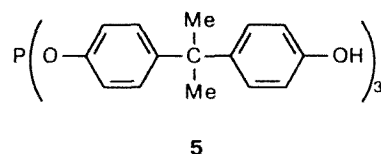
Phosphorylation of dihydric phenols with triamides of phosphorous acid was performed under different reaction conditions and using reactants taken in various ratios. The selectivity of the reaction depends on the presence of the solvent, its polarity, and, to a lesser degree, on the temperature.

**Key words:** phenol, phosphamide, phosphorylation;  $^{31}\text{P}$  NMR spectra.

Amides of trivalent phosphorus acids are convenient reagents for phosphorylating alcohols and phenols.<sup>1</sup> It is known that phenols react with phosphamides more readily in aromatic solvents due to the formation of associates.<sup>2</sup> However, the role of the polarity of the solvent in these reactions remains unclear. In this connection, we studied the reactions of 2,2-di(*p*-hydroxyphenyl)propane (**1**) with hexaethyltriamide of phosphorous acid (**2**) under different reaction conditions and taking the reagents in various ratios (Scheme 1) by  $^{31}\text{P}$  NMR spectroscopy and mass spectrometry.

The spectral characteristics of the products of the reactions studied are given in Table 1. The values of the  $^{31}\text{P}$  chemical shifts (118, 132, 141, and 128 ppm) correspond to the signals of the P atoms of compounds **2**, **3**,

and **4** (see Scheme 1) and of the triester of phosphorous acid **5**, respectively.



In the mass spectra,  $[M]^+ = 576$  and 557 for the molecular ions of **3** and **4**, respectively.

The data in Table 1 indicate that the highest selectivity of phosphorylation is observed when the reaction is performed in dioxane, which is the most polar solvent used. When other solvents were used, a polymeric com-