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A heterobimetallic Zr,Hf(μ-formaldehyde) complex from [$(CH_2O)ZrCp_2$]-dimer and hafnocene dichloride

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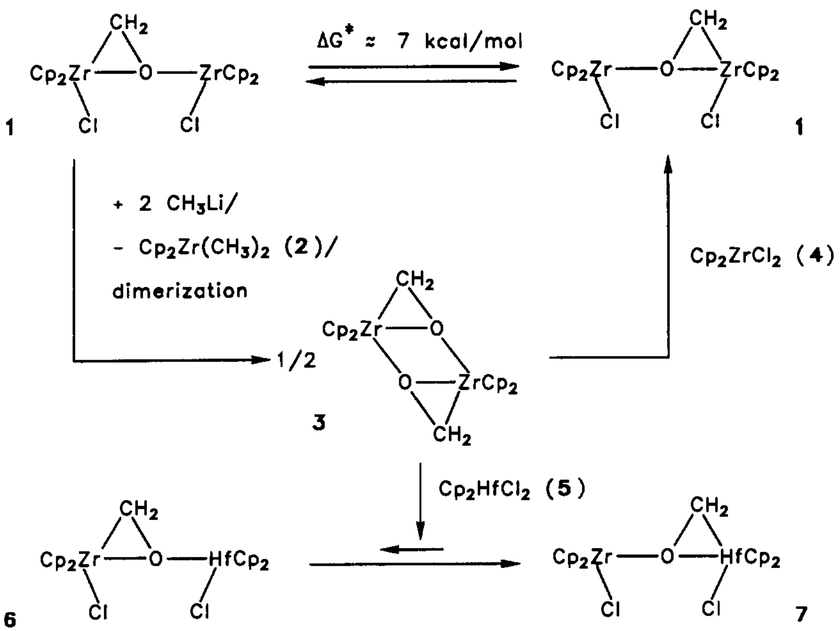
Abstract

The reaction of (η^2-formaldehyde)zirconocene dimer (3) with hafnocene dichloride (5) at room temperature gives the heterobimetallic complex [μ-(η^1-O : η^2-C,O-formaldehyde)(Cp_2ZrCl)(Cp_2HfCl)]. From thermochemical considerations it is suggested that methylene migration from zirconium to hafnium occurs during the reaction, favouring the regioisomer $Cp_2(Cl)Zr{-}\overline{O{-}CH_2{-}Hf}(Cl)Cp_2$ (7) under equilibrium conditions.

[μ-(η^1-O : η^2-C,O-aldehyde)bis(metallocene halide)] complexes, such as **1**, exhibit remarkable dynamic behavior. They undergo an alkylidene migration (of low activation energy; mechanistically a "dyotropic" rearrangement) along the metal–oxygen–metal backbone that is reminiscent of alkylidene mobility at catalyst surfaces [1]. Such complexes are usually prepared by metallocene hydride addition to (acyl)metallocene halides; the parent compound **1** is obtained in good yield by hydrozirconation of carbon monoxide [2]. We have now found an alternative means of synthezising μ(η^1-O : η^2-C,O-formaldehyde)metallocene complexes which makes use of the specific reactivity of (η^2-formaldehyde)zirconocene dimer (3). This route allows the preparation of mixed metal analogues of **1**, such as e.g. [(Cp_2ZrCl)(Cp_2HfCl)(μ-CH_2O)], that could not be obtained by the conventional method.

(η^2-Formaldehyde)zirconocene dimer was prepared, as described in the literature [3], by treating **1** with two molar equivalents of methyllithium in ether. The likely intermediate in this reaction, [$(Cp_2ZrMe)_2(\mu\text{-}CH_2O)$], is not stable under the conditions used, but rapidly cleaved to give $Cp_2Zr(CH_3)_2$ and **3**.

The [$(Cp_2ZrMe)_2(\mu\text{-}CH_2O)$] cleavage seems to be a specific example of a quite general equilibration reaction between binuclear [$(Cp_2MX)_2(\mu\text{-}CR^1R^2O)$] complexes and their mononuclear components [η^2-$(CR^1R^2O)MCp_2$] and Cp_2MX_2. Which side of this equilibrium is favoured depends on the nature of the σ-ligand coordinated to the metal. This became apparent from the outcome of the reaction of (η^2-formaldehyde)zirconocene dimer (3) with two molar equivalents of zirconocene dichloride.



Scheme 1.

The equilibrium in this case was reached only slow requiring 2 days at 40 °C in dichloromethane. ^1H NMR spectroscopy revealed that after this time there practically had been quantitative formation of $[(CH_2O)(ZrCp_2Cl)_2]$ (**1**) [δ 6.21 (s, 20H, Cp), 2.91 (s, 2H, CH_2)].

This equilibration was found to provide the basis of a useful method for the synthesis of heterobinuclear (μ-formaldehyde)metallocene complexes. In a typical example complex **3** was treated with hafnocene dichloride (**5**, containing ca. 5% of Cp_2ZrCl_2) (1 : 2 molar ratio). Equilibration went to completion in 16 h at room temperature in tetrahydrofuran. A yellow solid was isolated (75% yield) that, according to the NMR spectroscopic analysis, consisted of a 81 : 12 : 7 mixture of $[(Cp_2ZrCl)(\mu\text{-}CH_2O)(Cp_2HfCl)]$, $[(Cp_2ZrCl)_2(\mu\text{-}CH_2O)]$, and $[(Cp_2HfCl)_2(\mu\text{-}CH_2O)]$. The mixed metal complex was also made by use of photochemical activation; thus UV-irradiation (HPK 125, Pyrex filter) of a $[(CH_2O)ZrCp_2]_2$ (**3**)/Cp_2HfCl_2 (**5**) mixture in a 1 : 2 molar ratio in tetrahydrofuran for 12 h at 0 °C gave pure $[(Cp_2ZrCl)(\mu\text{-}CH_2O)(Cp_2HfCl)]$ in 45% yield [4*].

The ^1H NMR spectrum of [μ-(η^1-O : η^2-C,O-formaldehyde)bis(zirconocene chloride] (**1**) is characterized by a single Cp-resonance at high temperature (see above) that is split into two lines of equal intensity in the low temperature limiting NMR spectra (δ 6.35 and 5.89 in $CHFCl_2/CDCl_3$ 3 : 1 at −141 °C). The position of the methylene singlet remains unchanged during the $[(Cp_2ZrCl)_2(CH_2O)]$ automerization process monitored on the NMR time scale by observation of the temperature-dependent Cp-line shape [1]. The newly formed [μ-(η^1-O : η^2-C,O-formaldehyde)(zirconocene chloride)(hafnocene chloride)] showed different NMR behavior, exhibiting

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* Reference number with asterisk indicates a note in the list of references.

an unchanged set of NMR resonances over the whole temperature range. The Zr,Hf-complex showed $^1H/^{13}C$ NMR resonances (200 MHz/50 MHz in tetrahydrofuran-d_8) at δ 6.44, 5.94 (s, 10H each, Cp)/115.0 [$^1J(CH) = 167$ Hz], 109.7 [$^1J(CH) = 173$ Hz] (Cp) and 3.09 (s, 2H, CH_2)/78.6 [$^1J(CH) = 153$ Hz] (CH_2). These ^1H NMR signals remained unchanged down to the lowest temperature used (173 K). The fact that no doubling of the Cp ^1H NMR signals was observed is probably not due to a fundamentally different kinetic behavior of the intramolecular methylene migration reaction between the (μ-CH_2O)Zr,Hf and (μ-CH_2O)Zr_2 (**1**) complexes but rather to thermodynamic factors. This raises the question which of the two possible isomers, the zirconaoxirane (**6**) or hafnaoxirane complex (**7**), is favoured under equilibrium conditions.

The answer to this question had to be sought in spite of the absence of X-ray diffraction results or the results of quantum mechanical calculations. Inspection of the two isomers **6** and **7** shows a number of subtle differences, out of which a single bonding feature is likely to dominate in determining the equilibrium state. The metallaoxirane complex **6** contains a bond between zirconium and the carbon of the bridging μ-CH_2O-ligand that probably has a pronounced σ-bond character [1,2]. Therefore, the energy difference between a Zr–C and a Hf–C single bond probably makes a major contribution in determining the energy separation of **6** and **7**. There is some experimental evidence that ordinary hafnium to carbon σ-bonds are shorter [5] and stronger (by about 3–5 kcal/mol) than their zirconium counterparts [6] [typical examples of the bond dissociation enthalpies (in kcal/mol) found for pairs of Zr(Hf) σ-hydrocarbyl complexes are as follows: $M(CH_3)_4$ 74 (79) (mean values); $Cp^\star_2M(CH_3)_2$ 67 (72) (average); $Cp^\star M(CH_3)_3$ 65 (69), 68 (71) (for first and second M–C bond cleavage, ±2 kcal/mol). If this is also the case for the metallaoxirane type complexes discussed in this paper, the equilibrium **6** $\rightleftharpoons$ **7** should lie far over to the side of the regioisomer **7**, which has the methylene carbon to metal bond at the pentacoordinated hafnium center.

We assume that use of the (η^2-formaldehyde)zirconocene moiety, generated from the readily available [(η^2-CH_2O)$ZrCp_2$]-dimer, as a building block will provide simple routes to a variety of multinuclear metal complexes, and disclose more examples of intramolecular methylene migration along a M–O–M′ metal oxide backbone.

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4 7: M.p. 178° C (DSC, exothermic decomp.). IR (KBr): ν (cm^{-1}) 3107, 1439, 1016, 831, 809, 758. Anal. Found: C, 39.62; H, 3.60. $C_{21}H_{22}OCl_2ZrHf$ (631.02) calc., corrected for the excess Zr content originating from the Cp_2MCl_2 reagent used: C, 40.40; H, 3.55%.

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