Inorg. Chem. **2008**, *47*, 7939−7941

Inorganic Chemistry
Communication

Unexpected Cyclopentadienyl/Alkoxo Ligand Exchange in Titano- and Zirconocene. New Opportunities

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Received May 30, 2008

A simple new route to access heterometallic alkoxo precursors for a wide range of materials is reported. This unique synthetic method comprises elimination of the cyclopentadienyl ring from Cp_2MCl_2 (M = Ti, Zr) as CpH in the presence of $M'(OR)_2$ (M′ = Ca, Mn; OR = $OCH_2CH_2OCH_3$ or OEt) in an alcohol as a source of protons. In one-pot reactions, we have prepared four different compounds with $Ti_2Ca_4(\mu_6\text{-}O)$, $Cp_2Zr_2Ca_4(\mu_4\text{-}Cl)$, $Zr_{10}Mn_{10}(\mu_3\text{-}O)_{14}$, and $Cp_3Ti_2(\mu\text{-}OEt)_2$ motifs. The compounds were characterized by single-crystal X-ray structural analysis and NMR spectroscopy.

Group 4 metal sandwich metallocenes have attracted considerable attention because of their applications in stoichiometric and catalytic reactions.[1] There are a number of books, articles, and reviews that cover the broad range of metallocene chemistry from practical aspects and synthetic strategies to theoretical investigations.[2] This rich chemistry is dominated by their applications in olefin polymerization.[3]

In most organometallic reactions of transition-metal complexes, the η^5-Cp ligand plays the role of spectator, staying tightly bound to the center throughout the reaction course.[2,4] Nevertheless, Jonas developed reactions in which cobalt, vanadium, manganese, nickel, and chromium metallocenes can be converted by Cp substitution in ether, hexane, or toluene into reactive organometallic compounds.[5] He showed that the Cp ligand could be removed from the transition-metal site by metallic potassium as CpK or exchanged with organometallic compounds or hydrides of main-group elements. Recently, Wright and co-workers[6] reported that manganese Cp_2Mn undergoes nucleophilic displacement of the Cp ligand by an organic or metalloorganic R group. On the other hand, the capability of the Cp leaving groups of Cp_2TiCl_2 and Cp_2ZrCl_2 has been neglected, and the consequent preparative applications have remained unknown.[7a] To our knowledge, there are no reported examples of reactions that remove the Cp ligand by alcohols from the titanium and zirconium coordination spheres. Although the behavior of Cp as a leaving group is rare in titanium chemistry, there are a few examples in the literature, e.g., in the synthesis of organometallic titanium−molybdenum oxides,[7b] oxosulfido,[7c] or sulfido[7d] clusters and trinuclear early−late heterobimetallic complexes.[7e]

Our studies on titanium and zirconium metallocenes showed them to be attractive precursors to an extensive range of novel molecular and supramolecular materials. Unexpectedly, the cyclopentadienyl-free colorless heterometallic compound $[Ti_2Ca_4(\mu_6\text{-}O)Cl_4(O,O')_{10}]$ (**1**) was obtained from the 1:2 stoichiometric reaction of Cp_2TiCl_2 with $Ca(O,O')_2$ in 2-methoxyethanol (O,O′H). To simplify this reaction, the metallic calcium, instead of $Ca(O,O')_2$, can be directly added to the solution of Cp_2TiCl_2 in alcohol. The appearance of free CpH in these reaction mixtures was monitored by gas chromatography/mass spectrometry (GC/MS) (Figure 1). The half-life of the ring loss for the Cp_2TiCl_2/Ca reaction is ca. 2.0 h at room temperature. After 12 h, the molar ratio CpH/

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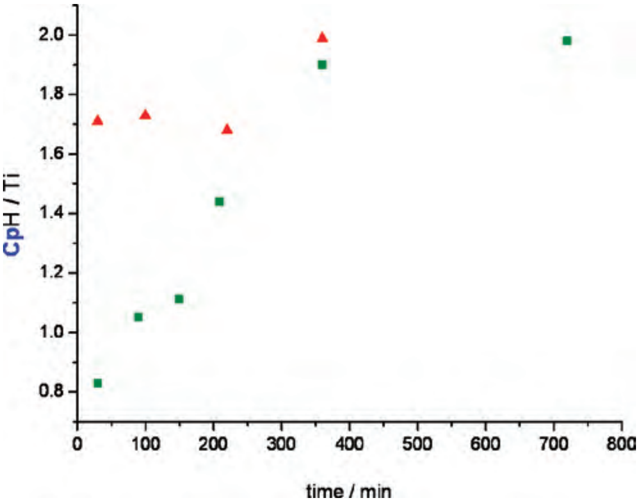

Figure 1. CpH/Ti ratio versus time plot for Cp_2TiCl_2 reactions with metallic Ca (■) and Ca(O,O′)$_2$ (▲). CpH liberation was monitored by the GC/MS technique.

Ti ~ 2 was achieved. The addition of Ca(O,O′)$_2$ to Cp_2TiCl_2 results in a more rapid increase in the CpH concentration in solution with ca. 1.5 equiv of cyclopentadiene per titanium at 10 min. It is worth noting that the half-life of the ring loss for Cp_2TiCl_2 in a KNO_3/D_2O solution is 57.0 ± 0.9 h at 37 °C.[8]

Similarly, Cp_2ZrCl_2 undergoes transformation involving loss of the Cp ring after treatment with Ca(O,O′)$_2$ to yield [$Cp_2Zr_2Ca_4Cl_6$(O,O′)$_8$] (**2**). On the other hand, the addition of an excess of metallic manganese, instead of calcium, to Cp_2ZrCl_2 in 2-methoxyethanol results in the formation of the Cp-free heterometallic cage [$Zr_{10}Mn_{10}(O)_{14}Cl_8$(O,O′)$_{24}$] (**3**). Moreover, changing 2-methoxyethanol to ethanol causes the formation of another compound. Stirring an ethanol solution of Cp_2TiCl_2 with 4 equiv of metallic manganese resulted in a slow color change to blue with evolution of H_2 and the formation of CpH. The reaction leads to the loss of one cyclopentadienyl ligand and the replacement of all chloride atoms by EtO groups to give neutral dark-violet crystalline [$Cp_3Ti_2(\mu\text{-OEt})_2$(OEt)] (**4**).

A solid-state X-ray crystal structure analysis for **1**−**4** is consistent with the spectroscopic data. The central $Ti_2Ca_4(\mu_6\text{-O})$ core, in **1**, has octahedral topology in which two titanium atoms occupy axial positions while four calcium atoms are in equatorial positions (Figure 2). The μ_6-O encapsulated oxygen atom resides at the center of the octahedron at an inversion center.[9] During the preparation of alkoxometal compounds, it is not uncommon for products to contain "lone" oxo groups to be formed. Such a phenomenon has abundant literature precedence.[10] The coordination sphere of the calcium ion is completed by terminal chlorine ligands; thereby, each of calcium atoms is eight-coordinate with a ClO_7 donor set. The molecular structure of **2** showed a Ca_4 calcium center, in which two symmetric [$CpZrCa_2Cl$(O,O′)$_4$] units are joined by three μ-Cl bridging chloride atoms to form a [$Cp_2Zr_2Ca_4Cl_5$(O,O′)$_8$]$^+$ cation, which encapsulates the μ_4-Cl chloride ion in the center of the array (Figure 3). While a few examples of a μ_4-Cl bridging chloride ion on late-transition-metal complexes of copper, cadmium, silver, and mercury have been reported,[11] to the best of our knowledge, this is a first unique example of a chloride μ_4-Cl ion located in a Ca_4 cage.

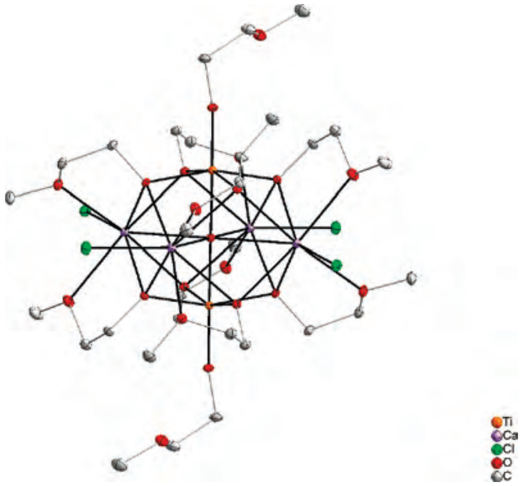

Figure 2. Structure of **1**. Hydrogen atoms are omitted for clarity.

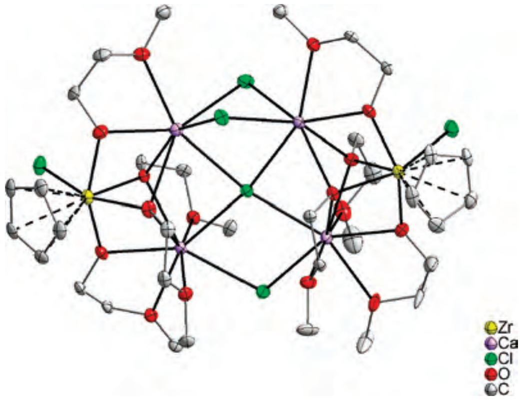

Figure 3. Structure of **2**. Disordered carbon atoms, solvent molecules, and hydrogen atoms are neglected for clarity.

The crystal structure of **3** consists of a $Zr_{10}Mn_{10}$ core held together by 14 μ_3-O$_{oxo}$ and 22 μ-O$_{alkoxo}$ oxygen atoms and two μ-Cl chloride atoms (Figure 4). This complex can be divided into two subunits. An internal zirconium moiety (A) is formed by two fused corner-shared Zr_6O_8 units in which adamantane skeletons can be distinguished.[12] The external moiety (B) is formed by 10 Mn^{2+} outer-perimeter ions that are linked with zirconium atoms by 8 μ_4-O$_{oxo}$, 2 μ_3-O$_{alkoxo}$, and 16 μ-O$_{alkoxo}$ oxygen atoms.

Complex **4** is an unsymmetrical dimer containing two types of titanium centers: Cp_2Ti and CpTi(OEt), which are linked by a double μ-OEt bridge (Figure 5).

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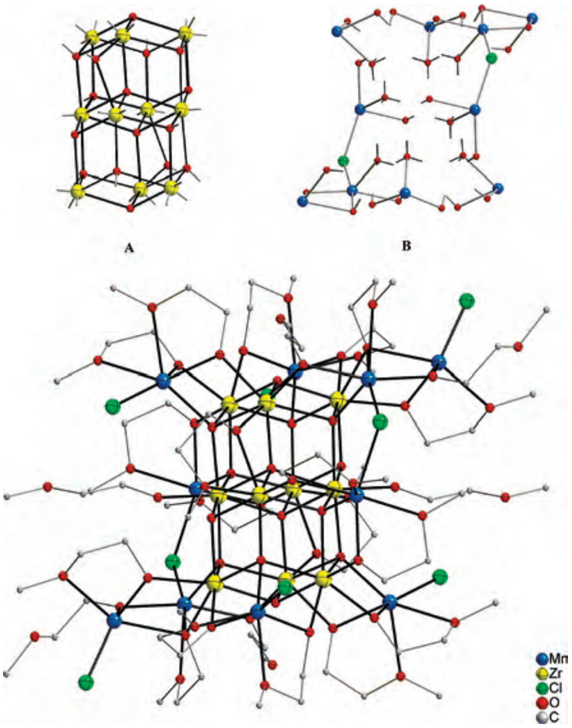

Figure 4. Structure of **3**, its zirconium−oxygen core (A), and its manganese−oxygen−chloride core (B). Hydrogen atoms are omitted for clarity.

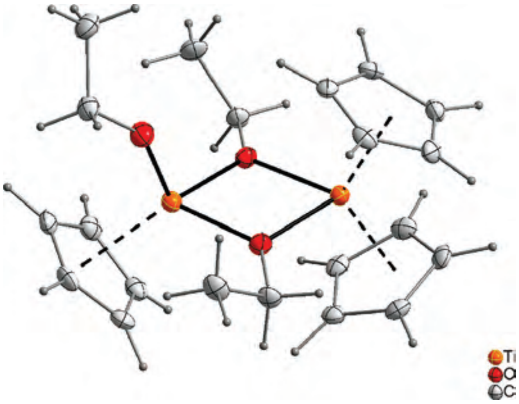

Figure 5. Structure of **4**.

The presented results clearly demonstrate that in all reactions an important transformation of the titanium and zirconium metal coordination sphere takes place and that the Cp ligands are partially or totally exchanged by alkoxo groups in alcohol, providing in return proton functionalities necessary for CpH liberation. Whether only one or both Cp ligands are exchanged or whether both processes take place side by side strongly depends upon the reactants involved, their stoichiometric ratio, the nature of the alcohol, and to a great extent the nature of the metal M. These results open new opportunities for application of the new metallocenes **2** and **4** as precursors for olefin polymerization catalysts[4,13] and the nonmetallocene precursor **3** for highly pure oxide ceramics,[14] which have not been prepared yet by other routes.[15] Investigations along these lines are currently underway.

Acknowledgment. This work was supported by Polish State Committee for Scientific Research under Grants PBZ-KBN-118/T09/19 and N205 4036 33.

Supporting Information Available: Complete synthetic, spectroscopic, and structural data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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