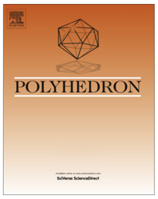
Polyhedron 58 (2013) 120–128

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Structural diversity in tris(cyclopentadienyl) complexes of the Group 4 metals: Synthesis of Cp and MeCp complexes of Zr and Hf, and crystallographic characterization of $(MeCp)_3HfCl$ and $(MeCp)_4Zr$ ($MeCp = C_5H_4CH_3$)

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ARTICLE INFO

Article history:
Received 13 July 2012
Accepted 4 March 2013
Available online 14 March 2013

Dedicated to the memory of Professor Michelle M. Millar, wonderful friend and colleague, who we miss dearly.

Keywords:
Organometallics
Zirconium
Hafnium
Tris-cyclopentadienyl
Hapticity
Synthesis
Crystallography

ABSTRACT

Previous theoretical studies have predicted structural differences between the tris(cyclopentadienyl) zirconium and hafnium complexes Cp_3MX ($Cp = C_5H_5$; M = Zr, Hf). Cp_3ZrCl can be isolated via the stoichiometric reaction of Cp_2ZrCl_2 and NaCp, but forming the analogous Hf complex is complicated by ligand redistribution. Partial crystallographic analysis of these two complexes indicates likely structural differences wherein the Zr complex has three η^5 Cp ligands ("**3-5**" structure) while the Hf complex has two η^5 Cp ligands and one η^1 Cp ligand ("**2-5**,**1-1**" structure). The use of $C_5H_4CH_3$ (MeCp) simplifies both the syntheses and the procurement of suitable crystals. The preparation of a number of MeCp complexes of Zr and Hf is reported along with crystallographic characterization of $(MeCp)_3HfCl$, which has a **2-5**,**1-1** structure and $(MeCp)_4Zr$, which has a **3-5**,**1-1** structure.

1. Introduction

The coordination of cyclopentadienyl (Cp) ligands to transition metals is arguably the cornerstone of modern organometallic chemistry [1]. We have been interested in exploring the electronic structure of tris(η^5-Cp) complexes of the actinide and transition elements, in part because of the remarkable contrast between these elemental families: prior to the development of the rich chemistry of polymethylated Cp ligands with the f-elements, the tris(η^5-Cp) structural motif was clearly the most common one in organoactinide chemistry [2], with examples spanning the early and later actinide elements. In contrast, the tris(η^5-Cp) bonding mode is very rare in transition metal chemistry, exhibited only by Zr. As discussed below, it also represents a rare instance in which the chemistry of Zr and Hf are decidedly different.

The tris(η^5-Cp) ligand set also provides an uncommon electronic structural contrast between the transition and actinide elements insofar as the three-fold symmetry of the ligands necessarily generates a filled ligand-based symmetry-adapted linear combination of a_2 symmetry (C_{3v} point group). As first pointed out by Moffitt, and expanded upon by Lauher and Hoffman, this filled orbital is unable by symmetry to interact with any orbitals of a transition metal but there is an available 5f acceptor orbital for actinide elements [3].

The first example of the tris(η^5-Cp) ligand set in a transition-metal system was afforded by the tetrakis-Cp complex $(\eta^5\text{-Cp})_3Zr(\eta^1\text{-Cp})$, which has three Cp ligands bonded in pentahapto fashion and the fourth serving as a monohapto alkyl ligand [4]. We will refer to this coordination type as "**3-5**,**1-1**", indicating three η^5 ligands and one η^1 ligand. Interestingly, both the Ti and Hf homologs show a different structure, namely $(\eta^5\text{-Cp})_2M(\eta^1\text{-Cp})_2$ (M = Ti, Hf), a "**2-5**,**2-1**" motif with only two of the Cp ligands bound in pentahapto fashion [5]. We have previously explored the structural chemistry of the tris-Cp chloro complexes Cp_3MCl (M = Zr, Hf) to see whether this structural difference persists in the absence of a fourth Cp ligand [6]. The crystal structure of Cp_3ZrCl clearly indicates that it has a **3-5** structure (Scheme 1) analogous to Cp_4Zr. Attempts to obtain X-ray quality crystals of Cp_3HfCl were less successful and only a partial structure could be obtained. That structure indicated a **2-5**,**1-1** structure (Scheme 1) for the Hf derivative, seeming to indicate again the unusual structural differences between homologous Zr and Hf complexes.

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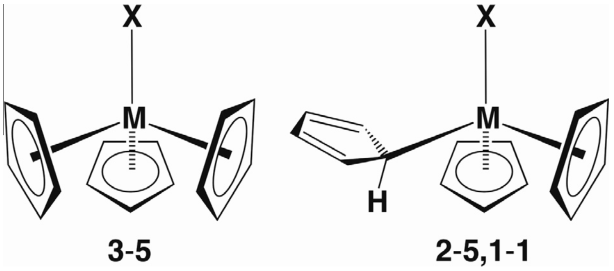
http://dx.doi.org/10.1016/j.poly.2013.03.007



Scheme 1. The **3**-**5** (three η^5-Cp ligands) and **2**-**5**,**1**-**1** (two η^5- and one η^1-Cp) bonding motifs for Cp_3MX complexes.

We have used relativistic density functional theory to explore the preferred structures of Cp_3MX complexes (M = Zr, Hf; X = H, CH_3, OR, NR_2) [7]. On the basis of these calculations, we concluded that the preferred structure (**3**-**5** or **2**-**5**,**1**-**1**) will depend on the π-donor ability of the ligand X. Thus, we predict that the simple hydride and methyl complexes should show the structural differences between Zr and Hf noted above, namely that the Zr complexes prefer a **3**-**5** structure whereas the Hf complexes prefer the **2**-**5**,**1**-**1** motif. As the π-donor ability of the X ligand increases, we propose an ultimate preference for the **2**-**5**,**1**-**1** structure as the competition between π-donation from the X group and the Cp ligands increases. In particular, we found that Cp_3ZrOH, Cp_3ZrOMe, Cp_3ZrNH_2, and Cp_3ZrNMe_2 should all prefer the **2**-**5**,**1**-**1** structure over the **3**-**5** structure.

Experimental verification of these theoretical predictions has been made difficult by the lack of good structural information on Cp_3MX and related tris(Cp) complexes. Not surprisingly, the structures of such complexes are highly dependent on the steric bulk of the Cp ligand. Erker and coworkers have reported the structures of Cp_3ZrCH_3 and $[Cp_3ZrCO][CH_3B(C_6F_5)_3]$, and both have **3**-**5** structures [8]. Although we have observed that Cp_3ZrCl has a **3**-**5** structure [6], Lukens has reported that $(TMS\text{-}Cp)_3ZrCl$ (TMS-Cp = $C_5H_4SiMe_3$) has a **2**-**5**,**1**-**1** structure from X-ray crystallography [9]; obviously the bulky TMS-Cp ligand could lead to interligand repulsions in the **3**-**5** structure that are not present in smaller Cp ligands. Etievant et al. have reported the preparation of $(MeCp)_3ZrCl$ (MeCp = $C_5H_4CH_3$), and proposed on the basis of NMR data that it also has a **2**-**5**,**1**-**1** structure [10], although a crystal structure was not obtained. Among trivalent complexes, Evans et al. recently reported that $(Me_4Cp)_3Sc$ ($Me_4Cp = C_5Me_4H$) has a **2**-**5**,**1**-**1** structure [11], whereas Cp_3Zr and Cp_3Hf with unsubstituted Cp ligands both exhibit **3**-**5** structures [12].

We believed that some of the challenges in obtaining crystallographically suitable crystals of Cp_3MX complexes could be circumvented by using substituted Cp ligands, although we wanted to use ligands with less steric bulk than TMS-Cp and Me_4Cp. MeCp seemed particularly attractive insofar as it is not significantly larger than the Cp ligand, and ring alkylation has been shown to improve crystallization. In this contribution, we report efforts to synthesize new tris-Cp complexes with both the Cp and the $C_5H_4CH_3$ (MeCp) ligand, and report the structures of two new complexes of the latter ligand, namely $(MeCp)_4Zr$ and $(MeCp)_3HfCl$. The structures of these new complexes, which are **3**-**5**,**1**-**1** and **2**-**5**,**1**-**1** respectively, continue the pattern of structural differences between analogous Zr and Hf tris-Cp complexes with σ-only or weak π-donor X ligands.

2. Experimental

2.1. General experimental procedures

All reactions and manipulations of air and moisture sensitive compounds were performed using standard Schlenk line, high-vacuum line and drybox techniques [13]. Reactions on the Schlenk and high-vacuum lines were performed under an atmosphere of argon, Ar, which was purified by passage through consecutive columns of activated De-Ox catalyst (Johnson and Matthey) and Drierite. All manipulations performed in the glovebox were accomplished using a Braun MB150 inert-atmosphere drybox equipped with a BASF R3-11 catalyst/Linde 13X molecular sieve system. The drybox atmosphere was monitored using titanocene, "Cp_2Ti", as an indicator. All solvents and reagents were purified using standard purification techniques [14]. Prior to use, all glassware was dried in an oven at 200 °C.

Elemental analyses (C and H) were obtained and were within acceptable experimental guidelines. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX-250 or DPX-400 MHz spectrometer controlled with the proprietary X-WINNMR program. NMR spectroscopy of oxygen and moisture sensitive compounds was performed using Wilmad 520-PP NMR tubes sealed by screw caps fitted with silicone septa. Spectra were analyzed using the MESTREC NMR software [15]. Chemical shifts are referenced to tetramethyl silane, TMS, and reported in ppm relative to the residual ^{1}H signal of the NMR solvent used.

All mass spectrometry experiments were performed at the Ohio State University Campus Chemical Instrument Center for Mass Spectrometry and Proteomics Facility. A Bruker Reflex III MALDI-TOF spectrometer was used for data collection. The use of the normal chemical matrices was bypassed as it was shown that the acidic nature of the matrices was detrimental to the moisture and acid-sensitive compounds.

Single-crystal X-ray diffraction data were obtained using a Nonius Kappa CCD Diffractometer equipped with a sealed tube generator with Mo Kα radiation (0.71073 Å). Experiments were run at 200 K using a cooled stream of nitrogen gas from an Oxford Cryosystems Cryostream Cooler.

2.2. Solvents and reagents

Hexanes, purchased from Fischer, were washed with concentrated sulfuric acid and distilled water, predried with magnesium sulfate, $MgSO_4$, and distilled over Na metal into a solvent collection flask containing activated molecular sieves and sealed with a Kontes stopcock. Petroleum ether, purchased from Fischer, was washed with sulfuric acid and distilled water, predried with $MgSO_4$, and freshly distilled over diphosphorus pentoxide, P_2O_5. Toluene, purchased from Mallinckrodt, was distilled over Na metal and distilled into a solvent collection flask containing activated molecular sieves and sealed with a Kontes stopcock. Tetrahydrofuran, THF, purchased from Fischer, was dried over potassium/benzophenone and distilled into a solvent collection flask containing activated molecular sieves and sealed with a Kontes stopcock. Methylene chloride, CH_2Cl_2, purchased from Fischer, was freshly distilled over P_2O_5. Diethyl ether, purchased from Mallinckrodt, was dried over K/benzophenone in a solvent storage flask and vacuum transferred as needed. All solvent collection flasks were stored under an inert atmosphere in the drybox.

NMR solvents were purchased from Cambridge Isotope Laboratories and dried and purified using standard techniques. $CDCl_3$ was dried over P_2O_5, distilled into a solvent collection flask sealed with a Kontes stopcock, degassed by three freeze–pump–thaw (FPT) cycles, and stored in a drybox. The $CDCl_3$ was passed through a column of basic aluminum immediately before use to remove any acidic impurities. Benzene-d_6 and toluene-d_8 were dried over Na metal, distilled into a solvent collection flask, degassed by three FPT cycles, and stored in the drybox.

Cyclopentadiene and methylcyclopentadiene were purchased from Sigma–Aldrich Chemicals as the dimers and cracked by distillation through a Vigreaux column at 170 °C to form the monomer [16]. Na metal was purchased from Sigma–Aldrich Chemicals as