

Preliminary communication

Monoindenyl halides of zirconium and hafnium. The preparation of $[(\eta^5\text{-C}_9\text{H}_7)\text{ZrCl}_3]_n$ and $[(\eta^5\text{-C}_9\text{H}_7)\text{HfCl}_2(\mu\text{-Cl})]_2$ and the crystal structure of $[(\eta^5\text{-C}_9\text{H}_7)\text{HfCl}_2(\mu\text{-Cl})]_2$

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Abstract

The monoindenyl species $[(\eta^5\text{-C}_9\text{H}_7)\text{ZrCl}_3]_n$ and $[(\eta^5\text{-C}_9\text{H}_7)\text{HfCl}_2(\mu\text{-Cl})]_2$ have been prepared. The structurally characterized hafnium dimer represents the first structurally characterized Cp (or substituted Cp) hafnium trichloride complex.

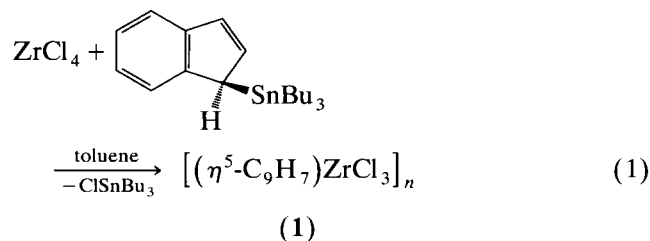
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Monocyclopentadienyl complexes of the early transition metals have been studied extensively over the past 30 years [1]. Specifically, the chemistry of CpMCl_3 ($\text{M} = \text{Ti}, \text{Zr},$ and Hf) complexes and their derivatives is of interest because the monocyclopentadienyl complexes display different reactivity towards an assortment of reagents than do the related Cp_2MCl_2 complexes [2]. While monocyclopentadienyl complexes of titanium(IV) have been investigated well, the chemistry of CpZrCl_3 , CpHfCl_3 , and related monocyclopentadienyl compounds, has been explored less [3]. Preparation of CpZrCl_3 can be accomplished by the photochlorination of Cp_2ZrCl_2 [3]; $\text{CpHfCl}_3(\text{thf})_2$ is obtained by treating HfCl_4 with MgCp_2 in refluxing decalin followed by crystallization from THF [4]. Although CpZrCl_3 has been structurally characterized, to date there are no reported structures for base-free cyclopentadienyl or substituted cyclopentadienyl hafnium trichlorides [5].

We wish to report the synthesis, characterization, and reactivity of the Group 4 indenyl metal trichlorides $[(\text{C}_9\text{H}_7)\text{ZrCl}_3]_n$ and $[(\text{C}_9\text{H}_7)\text{HfCl}_2(\mu\text{-Cl})]_2$; the crystal structure of $[(\text{C}_9\text{H}_7)\text{HfCl}_2(\mu\text{-Cl})]_2$ has also been determined [6]. The only previously known indenyl (C_9H_7) metal halides are the bis-indenyl dichlorides of Group 4

[7], and the recently reported indenyl complexes $(\eta^5\text{-C}_9\text{H}_7)\text{TiCl}_3$ [6] and $(\eta^5\text{-C}_9\text{H}_7)_2\text{NbCl}_2$ [8]. To take advantage of soluble byproducts, 1-trimethylsilylindene and 1-tributylstannyliindene were used as indenyl transfer agents [9]; the use of silicon- and tin-substituted cyclopentadienyl reagents for the transfer of a single cyclopentadienyl ligand to transition metals is well-known [10].

The addition of 1-tri-n-butylstannyliindene, 1-(Bu_3Sn) C_9H_7 , to a room temperature suspension of ZrCl_4 in toluene produces $(\eta^5\text{-C}_9\text{H}_7)\text{ZrCl}_3$ (**1**) in 78% yield as a bright yellow precipitate; the reaction of ZrCl_4 with 1-(Me_3Si) C_9H_7 gives a mixture of products. After being thoroughly washed with pentane, **1** gives satisfactory analyses for C, H, and Cl. (Eq. (1)) [11].

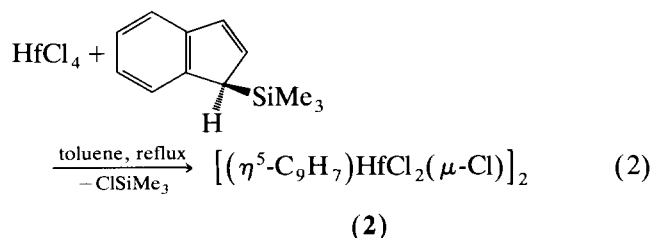


The ^1H NMR spectrum of **1** is interpreted as a typical η^5 -indenyl pattern in which there is an AA'BB' pattern for the six-membered ring protons and an AB₂ pattern for the five-membered ring protons [12]. Although an η^3 -species would exhibit a similar ^1H NMR pattern, **1**

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is most likely to be an η^5 -species in solution. We have not yet been able to grow X-ray quality crystals of **1** but, given its low solubility, it is likely polymeric; the cyclopentadienyl analogue, CpZrCl_3 , has an extended chloride-bridged polymeric structure [5].

If HfCl_4 and one equivalent of 1-trimethylsilylindene are refluxed overnight in toluene, bright yellow crystals of $[(\eta^5\text{-C}_9\text{H}_7)\text{HfCl}_2(\mu\text{-Cl})]_2$ (**2**) are isolated in 80% yield directly from the filtered, hot reaction solution (Eq. (2)); satisfactory analyses for C, H, and Cl are obtained [13].

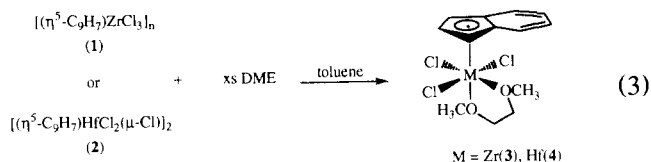


The ^1H NMR spectrum of **2** contains AA'BB' and AB₂ patterns for the six- and five-membered ring protons, respectively, that are similar to those seen for **1** [14].

Single crystals of **2** were obtained by cooling saturated toluene solutions to -20°C [15]. The structural analysis shows that crystals of **2** are composed of chloride-bridged dimers, $[(\eta^5\text{-C}_9\text{H}_7)\text{HfCl}_2(\mu\text{-Cl})]_2$, in the solid state; a perspective view of the molecule is shown in Fig. 1. The dimer possesses a crystallographically-imposed inversion center and the molecule consists of two edge-sharing distorted square pyramids. The two bridgehead carbons in **2** (C(5) and C(10); average Hf–C distance = 2.526(11) Å) form longer M–C bonds than do the three allyl-like carbons (C(11), C(12), and C(13); average Hf–C distance = 2.435(11) Å). This bonding pattern is consistent with the HOMO of the indenyl anion, which has small contributions from the p_z orbitals on the two bridgehead carbons [16], and the differences in the metal–carbon bond distances are normal for an η^5 -indenyl ligand. The average terminal Hf–Cl distance of 2.382(4) Å is only slightly longer than the 2.337(4)–2.354(3) Å range of Hf–Cl distances found in $(\text{C}_5\text{Me}_5)\text{HfCl}_2(\text{Si}(\text{SiMe}_3)_3)$ and $(\text{C}_5\text{Me}_5)\text{HfCl}_2(\text{Ge}(\text{SiMe}_3)_3)$ [17], but is nearly identical to the 2.391(6) and 2.394(6) Å Hf–Cl distances in isopropyl-(cyclopentadienyl-1-fluorenyl)hafnium(IV)dichloride [18]. The bridging Hf–Cl distances of 2.539(11) and 2.513(11) Å represent symmetric chloride bridges, but are longer, as expected, than the terminal chloride distances. In addition to being the first monoindenyl-hafnium species, this dimer represents the first structurally characterized base-free half-sandwich hafnium trichloride complex. The only reported structure of a cyclopentadienyl-hafnium trichloride complex is that of $\text{CpHfCl}_3(\text{DME})$, although no crystallographic details are available [19].

The addition of an excess of 1,2-dimethoxyethane

(DME) to a toluene suspension of **1** or **2** at room temperature gives yellow solutions from which pale yellow needles of $(\eta^5\text{-C}_9\text{H}_7)\text{MCl}_3(\text{DME})$ (**3**, $\text{M} = \text{Zr}$; **4**, $\text{M} = \text{Hf}$) are isolated (Eq. (3)).



The room temperature ^1H NMR spectra of **3** and **4** [20] exhibit typical η^5 patterns for the indenyl ligands and the spectra each contain two broadened singlets for the exchange DME ligands as was found with $\text{CpZrCl}_3(\text{DME})$ [21] and $\text{CpHfCl}_3(\text{DME})$ [19]. The ^1H NMR spectra do not indicate that the indenyl ligand is involved in the exchange of the DME ligands. Although we have not definitively assigned structures to **3** and **4**, the most likely structure is shown in Eq. (3), which is similar to the structures of $\text{CpHfCl}_3(\text{DME})$ [19], and $\text{CpTiCl}_3(\text{dmpe})$ (dmpe = 1,2-bis(dimethylphosphino)-ethane) [22]. The reaction of $(\text{C}_9\text{H}_7)\text{TiCl}_3$ with excess DME results in reduction of the metal center to give a species that contains Ti^{3+} ; the IR spectrum of the sky blue crystals shows no evidence of an indenyl ligand. We have also prepared indenyl-metal halides of niobium and tantalum, which are the subject of another paper [23].

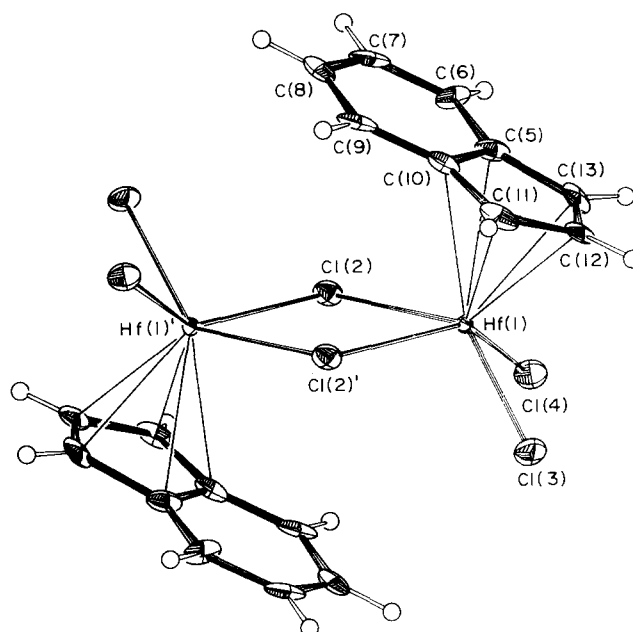


Fig. 1. Molecular structure of $[(\eta^5\text{-C}_9\text{H}_7)\text{HfCl}_2(\mu\text{-Cl})]_2$, **2**. Important bond distances (Å) and angles (deg): Hf–Cl(2) = 2.555(3), 2.568(3), Hf–Cl(3) = 2.374(3), Hf–Cl(4) = 2.389(3), Hf–C(5) = 2.539(11), Hf–C(10) = 2.513(11), Hf–C(11) = 2.427(11), Hf–C(12) = 2.428(10), Hf–C(13) = 2.450(11). Cl(2)–Hf–Cl(2)' = 75.66(9), Cl(2)–Hf–Cl(3) = 84.27(9), Cl(2)'–Hf–Cl(3) = 137.81(9), Cl(2)'–Hf–Cl(4) = 140.39(9), Cl(2)–Hf–Cl(4) = 82.60(9).

Tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles for **2** are available from the Cambridge Crystallographic Data Centre or from R.J.M.

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- [11] Analysis for **1**. C₁₈H₁₄Zr₂Cl₆ calc.(found): C, 34.56(34.62); H, 2.26(2.31); Cl, 34.01(33.85).
- [12] ¹H NMR data for **1**. (CDCl₃, 25°C, 200 MHz): δ 6.10, d (J = 3.1 Hz), 2H; δ 6.42, t (J = 3.1 Hz), 1H; δ 7.22, m, 2H; δ 6.56, m, 2H.
- [13] Analysis for **2**. C₁₈H₁₄Hf₂Cl₆ calc.(found): C, 27.02(27.32); H, 1.76(1.80); Cl, 26.59(26.34).
- [14] ¹H NMR data for **2**. (CDCl₃, 25°C, 200 MHz): δ 6.85, d (J = 3.6 Hz), 2H; δ 7.05, t (J = 3.6 Hz), 1H; δ 7.39, m, 2H; δ 7.79, m, 2H.
- [15] Crystal data for **2** (T = 101 K). Molecular formula = C₁₈H₁₄Hf₂Cl₆; crystal dimensions = 0.20 × 0.40 × 0.37 mm. Crystal system: monoclinic, space group $P2_1/n$, with a = 7.726(2) Å, b = 13.147(3) Å, c = 9.967(3) Å, β = 90.21°. V = 1012.40 Å³, Z = 2, R_F = 0.0328, R_{wF} = 0.0357 for 119 variables and 1202 reflections for which $I > 2.33\sigma(I)$.
Linear absorption coefficient = 109.616 cm⁻¹. An absorption correction was included for hafnium. Hydrogen atoms were placed in fixed idealized positions for the final least-squares cycles. Intensity measurements were carried out using standard techniques similar to those of Churchill: see M.R. Churchill, R.A. Lashewycz and F.J. Rotella, *Inorg. Chem.*, **16** (1977) 265.
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