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Preliminary communication

Monoindenyl halides of zirconium and hafnium. The preparation of $[(\eta^5\text{-}C_9H_7)ZrCl_3]_n$ and $[(\eta^5\text{-}C_9H_7)HfCl_2(\mu\text{-}Cl)]_2$ and the crystal structure of $[(\eta^5\text{-}C_9H_7)HfCl_2(\mu\text{-}Cl)]_2$

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Abstract

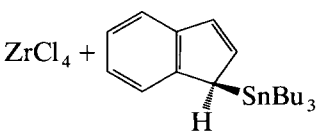
The monoindenyl species $[(\eta^5\text{-}C_9H_7)ZrCl_3]_n$ and $[(\eta^5\text{-}C_9H_7)HfCl_2(\mu\text{-}Cl)]_2$ have been prepared. The structurally characterized hafnium dimer represents the first structurally characterized Cp (or substituted Cp) hafnium trichloride complex.

Keywords: Zirconium; Hafnium; Indenyl derivatives; Halides

Monocyclopentadienyl complexes of the early transition metals have been studied extensively over the past 30 years [1]. Specifically, the chemistry of $CpMCl_3$ (M = Ti, 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]; $CpHfCl_3(thf)_2$ 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 $[(C_9H_7)ZrCl_3]_n$ and $[(C_9H_7)HfCl_2(\mu\text{-}Cl)]_2$; the crystal structure of $[(C_9H_7)HfCl_2(\mu\text{-}Cl)]_2$ has also been determined [6]. The only previously known indenyl (C_9H_7) metal halides are the bis-indenyl dichorides of Group 4 [7], and the recently reported indenyl complexes $(\eta^5\text{-}C_9H_7)TiCl_3$ [6] and $(\eta^5\text{-}C_9H_7)_2NbCl_2$ [8]. To take advantage of soluble byproducts, 1-trimethylsilylindene and 1-tributylstannylindene 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-butylstannylindene, $1\text{-}(Bu_3Sn)C_9H_7$, to a room temperature suspension of $ZrCl_4$ in toluene produces $(\eta^5\text{-}C_9H_7)ZrCl_3$(**1**) in 78% yield as a bright yellow precipitate; the reaction of $ZrCl_4$ with $1\text{-}(Me_3Si)C_9H_7$ gives a mixture of products. After being thoroughly washed with pentane, **1** gives satisfactory analyses for C, H, and Cl. (Eq. (1)) [11].



$$\xrightarrow[-ClSnBu_3]{\text{toluene}} \left[(\eta^5\text{-}C_9H_7)ZrCl_3\right]_n \qquad (1)$$

(**1**)

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 AB_2 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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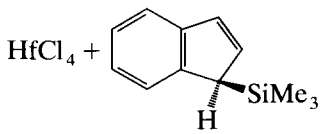
is most likely to be an η^5-species in solution. We have not yet been able to grow X-ray quality crystals of **1** but, given its low solubility, it is likely polymeric; the cyclopentadienyl analogue, $CpZrCl_3$, has an extended chloride-bridged polymeric structure [5].

If $HfCl_4$ and one equivalent of 1-trimethylsilylindene are refluxed overnight in toluene, bright yellow crystals of $[(\eta^5\text{-}C_9H_7)HfCl_2(\mu\text{-}Cl)]_2$ (**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].



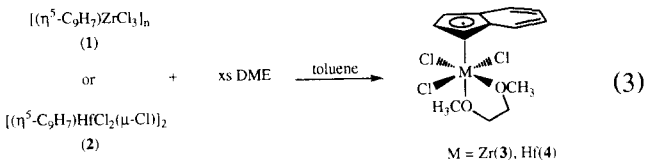
$$\xrightarrow[-ClSiMe_3]{\text{toluene, reflux}} [(\eta^5\text{-}C_9H_7)HfCl_2(\mu\text{-}Cl)]_2 \quad (2)$$

(2)

The ^1H NMR spectrum of **2** contains AA'BB' and AB_2 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, $[(\eta^5\text{-}C_9H_7)HfCl_2(\mu\text{-}Cl)]_2$, 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 $(C_5Me_5)HfCl_2\{Si(SiMe_3)_3\}$ and $(C_5Me_5)HfCl_2\{Ge(SiMe_3)_3\}$ [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 monoindenylhafnium 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 $CpHfCl_3$(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 $(\eta^5\text{-}C_9H_7)MCl_3$(DME) (**3**, M = Zr; **4** M = Hf) are isolated (Eq. (3)).



(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 $CpZrCl_3$(DME) [21] and $CpHfCl_3$(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 $CpHfCl_3$(DME) [19], and $CpTiCl_3$(dmpe) (dmpe = 1,2-bis(dimethylphosphino)-ethane) [22]. The reaction of $(C_9H_7)TiCl_3$ 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].

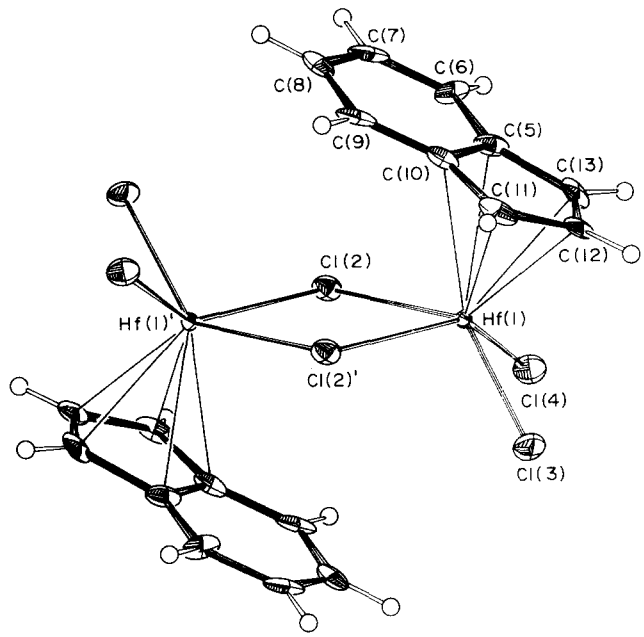


Fig. 1. Molecular structure of $[(\eta^5\text{-}C_9H_7)HfCl_2(\mu\text{-}Cl)]_2$, **2**. Important bond distances (Å) and angles (deg): Hf–Cl(2) = 2.555(3), 2.568(3), Hf–Cl(3) = 2.374(3), Hf–Cl(4) = 2.389(3), Hf–C(5) = 2.539(11), Hf–C(10) = 2.513(11), Hf–C(11) = 2.427(11), Hf–C(12) = 2.428(10), Hf–C(13) = 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**. $C_{18}H_{14}Zr_2Cl_6$ calc.(found): C, 34.56(34.62); H, 2.26(2.31); Cl, 34.01(33.85).

[12] ^{1}H NMR data for **1**. ($CDCl_3$, 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**. $C_{18}H_{14}Hf_2Cl_6$ calc.(found): C, 27.02(27.32); H, 1.76(1.80); Cl, 26.59(26.34).

[14] ^{1}H NMR data for **2**. ($CDCl_3$, 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 = $C_{18}H_{14}Hf_2Cl_6$; 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 Å^3, 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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[20] ^{1}H NMR data for **3**. ($CDCl_3$, 25°C, 200 MHz): δ 3.78, br, s, 6H; δ 3.97, br, s, 4H; δ 6.76, d (J = 3.3 Hz), 2H; δ 6.88, t (J = 3.3 Hz), 1H; δ 7.35, m, 2H; δ 7.70, m, 2H. ^{1}H NMR data for **4**. ($CDCl_3$, 25°C, 200 MHz): δ 3.91, br, s, 6H; δ 4.09, br, s, 4H; δ 6.57, d (J = 3.2 Hz), 2H; δ 6.79, t (J = 3.2 Hz), 1H; δ 7.29, m, 2H; δ 7.68, m, 2H.

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