Synthesis of an Alkyne-Bridged Decamethylhafnocene Dimer and Related Alkyne-Substituted Monomers

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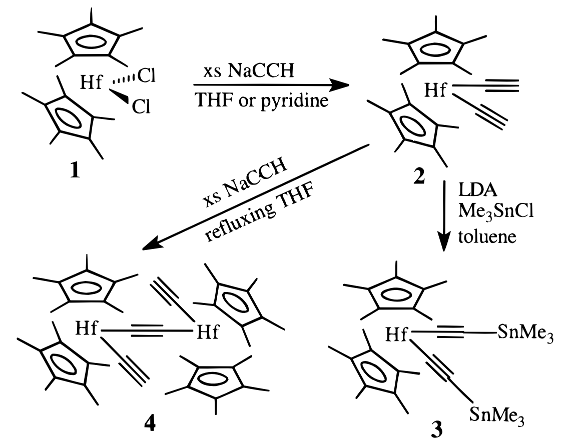
Summary: Reaction of Hf^*Cl_2 *(**1**;* Hf^* *= decamethylhafnocene), with excess sodium acetylide at room temperature results in the synthesis of* $Hf^*(CCH)_2$ *(**2**). The identical reaction in refluxing THF results in the dimeric product* $[(\mu_2\text{-}C_2)(Hf^*CCH)_2]$ *(**4**). Subsequent reaction of **2** with lithium diisopropylamide (LDA) in the presence of trimethyltin chloride resulted in the trimetallic* $Hf^*(CCSnMe_3)_2$ *(**3**).*

In recent years, much attention has been given to metal-containing polymers as sources of novel materials in terms of their electronic,[1] optical,[2] and magnetic properties[3] or as precursors to ceramics by thermal decomposition.[4] Initially, we desired to synthesize a group 4 α,ω-metallocene alkynyl polymer via transmetalation of the group 4 metallocene dichloride with a dilithiated alkyne, such as dilithioacetylene. The resulting polymer would consist entirely of the group 4 metal, carbon, and hydrogen, which would be desirable as a polymeric metal carbide ceramic precursor.[4b] Additionally, it was hoped that a group 4 metallocene polymer with alkynyl and/or aromatic bridging ligands would exhibit enhanced NLO properties. EHMO calculations of $H(CCHf^*CC{-}CC)Hf^*CCH$ indicated that its LUMO exhibits extensive conjugation along the oligomer backbone with good overlap between the alkynyl spacer π orbitals and the hafnium d orbitals. The LUMO may be accessed by an optically pumped excitation, by a chemical reduction of the oligomer, or by substitution of the hafnium (d^0) with a group 5 (d^1) metal to give an "inherently doped" oligomer. Thus, the main chain conjugation was expected to show interesting electronic properties.

Scheme 1



The reactions of Hf^*Cl_2 (**1**) with lithium acetylides were investigated as models for polymerization reactions.[5,6] The alkyl-substituted Cp is expected to impart better hydrolytic stability and solubility to the monomers and polymers once synthesized. It was found, however, that reactions of **1** with *stoichiometric* amounts of lithium *p*-tolylacetylide resulted in the incomplete substitution of chloride ligands with the acetylide groups. Thus, synthesis of high-molecular-weight alkynyl−hafnocene polymers under similar conditions is not feasible.

It was possible to obtain acceptable yields of the disubstituted products by using a 3-fold excess of lithium *p*-tolylacetylide.[7] While not useful in itself for making high-MW polymers, this reaction does give access to new polymer precursors. Synthesis of **2**, as shown in Scheme 1, was realized in >50% yield from the reaction of **1** with excess sodium acetylide in THF or pyridine at room temperature for 1 day. Pyridine was used to decrease the possibility of oxygen abstraction by the oxophilic Hf from THF. Compound **2** is a

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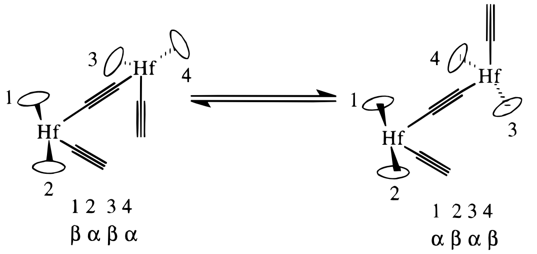
(7) **Synthesis of** $\mathbf{Hf^*(CC\text{-}C_6H_4CH_3)_2}$: *p*-Tolylacetylene (138.5 mg, 1.20 mmol) and *n*-butyllithium (0.75 mL, 1.6 M in hexanes, 1.20 mmol) were placed into THF (25 mL) via syringe, and the mixture was stirred for 1 h. The light yellow solution was transferred via cannula to a solution of Hf^*Cl_2 (100 mg, 0.19 mmol) in THF (5 mL). The reaction mixture was heated to reflux and stirred for 2 h before the THF was removed and the residue extracted with hexanes. The resulting bronze solution was filtered and concentrated, giving orange crystals (101 mg, 0.15 mmol, 78% yield). ^1H NMR (300 MHz, 25 °C, C_6D_6): δ 7.50 (d, 4H, C*H* tolyl), 6.91 (d, 4H, C*H* tolyl), 2.14 (s, 30H, C_5Me_5), 2.01 (s, 6H, *Me* tolyl).

Scheme 2



yellow, moderately air-stable solid that is readily soluble in ordinary organic solvents.

In order to determine if the terminal alkyne hydrogen atoms in **2** could be replaced with metals, a reaction of **2** with trimethyltin chloride in the presence of LDA was attempted. The addition of an LDA solution to a solution of **2** and Me_3SnCl in toluene at −78 °C gave compound **3** (Scheme 1) as a moderately air stable, off-white solid in 60% yield. This is the first example of a formation of transient acetylide anion bonded to an early transition metal.[8,9]

When **1** was allowed to react with excess sodium acetylide in refluxing THF, **2** was observed to form initially by ^1H NMR, but its signals slowly disappeared as two new peaks were seen to grow in slightly downfield positions. The mixture was heated to reflux for 3 days, after which time the solvent was removed, and the residue was dissolved in hexane and this solution chromatographed on a silica gel column, affording **4** (Scheme 1) in 50% yield. Compound **4** is a light yellow solid that is stable in air and in solution. Analytical grade, diamond-shaped crystals were grown from hexane by slow evaporation. The FT-IR spectrum exhibits two absorptions at 1938 and 3280 cm^{-1}, associated with alkyne CC and CH stretching modes, respectively.

Compound **4** exhibits fluxional behavior in the ^1H NMR spectrum: the acetylenic protons appear at 3.04 ppm, and two inequivalent Cp* resonances are at 2.09 and 2.14 ppm, respectively, at room temperature. The two Cp* signals coalesce at 105 °C, and cooling the sample to room temperature resulted in the restoration of the original spectrum. These data and molecular modeling suggest that the dimer belongs to the chiral C_2 point group. The two sets of Cp* groups are assigned to α-sites, adjacent to the acetylide group on the neighboring hafnium atom, and β-sites that face away (Scheme 2). The α- and β-sites exchange roles as the ends of the molecule rotate about the $Hf-C_2-Hf$ axis, as this motion interconverts the enantiomers of **4**. The barrier to rotation, 19.5 kcal/mol, was estimated from the coalescence temperature and the separation of the Cp* peaks in the slow exchange limit.[10]

Crystals of **4** suitable for X-ray diffractometry were grown by allowing a concentrated solution of hexane to stand at room temperature for several days. The PLUTO of **4** (Figure 1) features nearly linear Hf(1)−C(23)−C(24) (171°) and C(23)−C(24)−Hf(2) linkages (172°) between the two hafnium atoms and the acetylene spacer. The C(23)−C(24) bond length is 1.24 Å. There is a nearly right angle between the two acetylene groups bonded to a hafnium atom: ∠C(21)−Hf(1)−C(23) = 94.9°.[11]

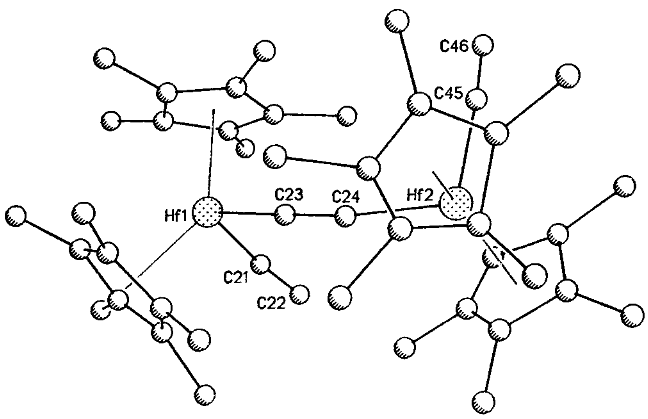


Figure 1. PLUTO drawing of **4**. Selected bond distances (Å) and angles (deg): Hf(1)−C(21) = 2.17(2), Hf(1)−C(23) = 2.25(2), C(21)−C(22) = 1.25(3), C(23)−C(24) = 1.24(3), Hf(1)−(Cp* centroids) = 2.228 and 2.241; C(21)−Hf(1)−C(23) = 94.9(10), C(22)−C(21)−Hf(1) = 173(3), C(24)−C(23)−Hf(1) = 171(2).

Compounds **2** and **4** are the first examples of an early-transition-metal metallocene with a terminal σ-bound (−CCH) acetylide ligand;[12] the synthesis of **3** represents the first evidence for the formation of a terminal acetylide anion bound to an early transition metal.[9] All three compounds are potentially useful organometallic polymer precursors via oxidative coupling of the terminal alkyne groups or by Stille coupling through the alkynyltrimethyltin ligand.[13,14]

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Supporting Information Available: Tables of crystallographic data, atomic positional parameters, thermal parameters, and bond distances and angles and an ORTEP drawing for **4** and text giving details of the preparation of $Hf^*(CCH)_2$, $Hf^*(CCSnMe_3)_2$, and $[(\mu_2\text{-}C_2)(Hf^*CCH)_2]$ (14 pages). Tables of observed and calculated structure factors are available from the authors upon request. Ordering information is given on any current masthead page.

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(11) Crystals suitable for diffractometry were grown by allowing a concentrated solution of hexane to stand at room temperature for several days. Crystallographic data for **4** are as follows: Space group: $P\bar{1}$ (No. 2), $a = 9.927(6)$ Å, $b = 14.133(5)$ Å, $c = 15.488(9)$ Å, $\alpha = 71.75(4)°$, $\beta = 88.04(5)°$, $\gamma = 88.63(4)°$, $V = 2062(2)$ Å^3, $Z = 2$. The Cp* groups on Hf2 are disordered. The disorder was modeled by placing two rigid Cp* groups at variable distances in two slightly different orientations, each at 50% occupancy, and refining with common isotropic thermal parameters for all the Cp* carbon atoms. The Cp* groups are rotated slightly with respect to one another, and their centroids are displaced approximately 0.21 Å from each other. The Hf−ring centroid distances are 2.228 and 2.241 Å for Hf(1) and 2.274, 2.278, 2.290, and 2.317 Å for Hf(2).

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