

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

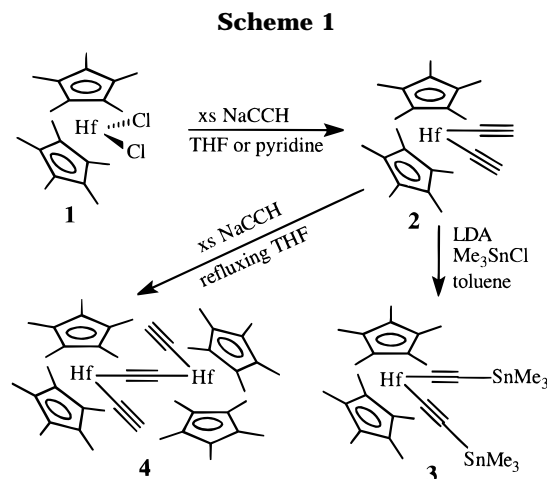
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Received July 16, 1996[®]

Summary: Reaction of Hf^*Cl_2 (**1**; Hf^* = decamethylhafnocene), with excess sodium acetylide at room temperature results in the synthesis of $\text{Hf}^*(\text{CCH})_2$ (**2**). The identical reaction in refluxing THF results in the dimeric product $[(\mu_2\text{-C}_2)(\text{Hf}^*\text{CCH})_2]$ (**4**). Subsequent reaction of **2** with lithium diisopropylamide (LDA) in the presence of trimethyltin chloride resulted in the trimetallic $\text{Hf}^*(\text{CCSnMe}_3)_2$ (**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 properties³ 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 $\text{H}(\text{CCHf}^*\text{CC-CC})\text{Hf}^*\text{CCH}$ 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.

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

[®] Abstract published in *Advance ACS Abstracts*, October 1, 1996.

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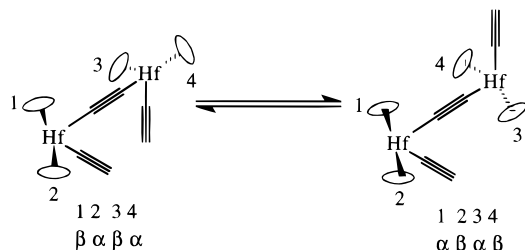
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(7) **Synthesis of $\text{Hf}^*(\text{CC-C}_6\text{H}_4\text{CH}_3)_2$:** *p*-Tolylacetylene (138.5 mg, 1.20 mmol) and *n*-butyllithium (0.75 mL, 1.6 M in hexanes, 1.20 mmol) were placed into THF (25 mL) via syringe, and the mixture was stirred for 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, CH tolyl), 6.91 (d, 4H, CH tolyl), 2.14 (s, 30H, C_5Me_3), 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 $\text{Hf}-\text{C}_2-\text{Hf}$ 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 $\text{Hf}(1)-\text{C}(23)-\text{C}(24)$ (171°) and $\text{C}(23)-\text{C}(24)-\text{Hf}(2)$ linkages (172°) between the two hafnium atoms and the acetylene spacer. The $\text{C}(23)-\text{C}(24)$ bond length is 1.24 Å.

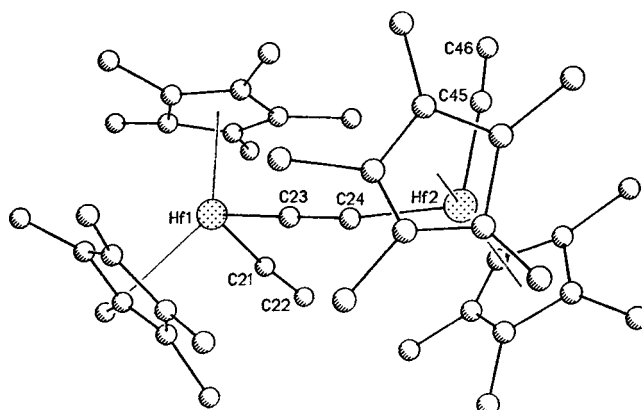


Figure 1. PLUTO drawing of **4**. Selected bond distances (Å) and angles (deg): $\text{Hf}(1)-\text{C}(21) = 2.17(2)$, $\text{Hf}(1)-\text{C}(23) = 2.25(2)$, $\text{C}(21)-\text{C}(22) = 1.25(3)$, $\text{C}(23)-\text{C}(24) = 1.24(3)$, $\text{Hf}(1)-(\text{Cp}^* \text{ centroids}) = 2.228$ and 2.241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

There is a nearly right angle between the two acetylene groups bonded to a hafnium atom: $\angle \text{C}(21)-\text{Hf}(1)-\text{C}(23) = 94.9^\circ$.¹¹

Compounds **2** and **4** are the first examples of an early-transition-metal metallocene with a terminal σ -bond ($-\text{CCH}$) 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}

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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 $\text{Hf}^*(\text{CCH})_2$, $\text{Hf}^*(\text{CCSnMe}_3)_2$, and $[(\mu_2-\text{C}_2)(\text{Hf}^*\text{CCH})_2]$ (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: $P1$ (No. 2), $a = 9.927(6)$ Å, $b = 14.133(5)$ Å, $c = 15.488(9)$ Å, $\alpha = 71.75(4)^\circ$, $\beta = 88.04(5)^\circ$, $\gamma = 88.63(4)^\circ$, $V = 2062(2)$ Å³, $Z = 2$. 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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