tionship between one of the hydrides and the PPh_3 ligand.[10] By analogy, the structure adopted by **3a,c** is IV.

Complete characterization of **3a,c** is hampered by the instability of these compounds. Decomposition of **2a,c** frequently produces some **1a,c** in addition to **3a,c**, but addition of excess Ag^+ does not produce **3a,c** in higher yield. In one experiment decomposition of **2a** produced **1a** and **3a** in 30 and 42% yields, respectively, based upon the initial quantity of **1a**. Treatment of **3** with triethylamine or methanol does not give neutral products analogous to **5a** and **5b**. In fact, ruthenium analogues to **5a** and **5b** appear to be unstable. The new cations **3a,c** therefore cannot be prepared by the route used for **4a,b**.

The chemistry of the cation radicals **2a–e** is currently under investigation. In addition to $O-CH_3$ bond cleavage, the reactivity for ligand substitution, hydride transfer to unsaturated hydrocarbons, and reductive elimination of C–H or H–H bonds may differ significantly from the reactivity of the diamagnetic precursors, thus providing an excellent opportunity to explore the enhanced reactivity of odd-electron cluster species.

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[10] **4a**: ^1H NMR ($CDCl_3$) −12.33 (d, 2 H_A), −14.49 (t, 1 H_B) ppm, J_{AB} = 1.4 Hz; ^{13}C NMR ($CDCl_3$) 161.8 (s, 2 C), 164.4 (s, 1 C), 166.8 (s, 1 C), 170.1 (s, 1 C), 170.2 (s, 1 C), 170.5 (s, 2 C), 172.0 (s, 2 C) ppm. **4b**: ^1H NMR ($CDCl_3$) −11.89 (d, 1 H, J_{PH} = 7.3 Hz), −12.03 (d, 1 H, J_{PH} = 30.5 Hz), −13.78 (d, 1 H, J_{PH} = 9.3 Hz) ppm; ^{13}C NMR ($CDCl_3$) 165.4 (s, 1 C), 165.7 (d, 1 C, J_{PC} = 8.6 Hz), 166.1 (s, 1 C), 168.0 (d, 1 C, J_{PC} = 9.6 Hz), 170.6 (s, 1 C), 170.7 (s, 1 C), 171.2 (s, 1 C), 173.6 (s, 1 C), 175.0 (d, 1 C, J_{PC} = 8.6 Hz) ppm; ^{31}P NMR ($CDCl_3$) 9.53 ppm.

Rapid and Efficient Procedures for the Synthesis of Monocyclopentadienyl Complexes of Hafnium and Zirconium

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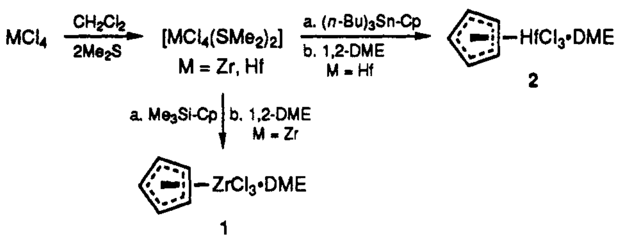
Summary: Bis(dimethyl sulfide) complexes of zirconium(IV) chloride and hafnium(IV) chloride have been found to undergo facile substitution reactions with 1-(trimethylsilyl)cyclopenta-2,4-diene and 1-(tri-*n*-butylstannyl)cyclopenta-2,4-diene, respectively, to afford the corresponding (η^5-cyclopentadienyl)trichlorozirconium and -hafnium complexes in good to excellent yield.

Monocyclopentadienyl complexes of hafnium and zirconium possess reactivity profiles that differ considerably from those of their bis-η^5-C_5H_5 counterparts. It is, therefore, not surprising that these complexes have assumed an increasingly important role in synthetic[2] and mechanistic[3] endeavors. Despite the intensifying interest in these compounds, practical routes for their preparation in pure form remain very few in number. At the present time, the most widely utilized procedure for the synthesis of $CpZrCl_3$ involves the free-radical chlorination of zirconocene dichloride.[4] This method is somewhat exacting and can on occasion give varying amounts of $ZrCl_4$ as a consequence of over-chlorination.[5] The preparation of $CpHfCl_3$ via the chlorination of Cp_2HfCl_2 has not been reported. However, the expense of Cp_2HfCl_2 would likely categorize such an approach as an act of desperation. The published synthesis of the hafnium derivative is nevertheless laborious. It involves the treatment of a 10% excess of $HfCl_4$ with 0.5 equiv of Cp_2Mg and subsequent purification by multiple recrystallizations to furnish the bis(tetrahydrofuran) complex $CpHfCl_3{\cdot}2THF$ free of $HfCl_4$ and Cp_2HfCl_2 in a maximum of 25% yield.[6] In this paper, we report a direct, one-step procedure that is suitable for the preparation of $CpZrCl_3$ and $CpHfCl_3$ as the corresponding 1,2-DME complexes in high yield.

Scheme I



Results and Discussion. As part of our continuing interest in the synthetic applications of the early transition elements, we required large quantities of *pure* $CpZrCl_3$ complexes. In 1980, Clark and co-workers reported that $CpTiCl_3$ could be synthesized in high yield via the reaction of $TiCl_4$ with 1-(trimethylsilyl)cyclopenta-2,4-diene (TMSCp).[7] It was therefore, at first, quite surprising that $CpZrCl_3$ and $CpHfCl_3$ had not been prepared by analogous procedures. In an effort to explore this possibility, several attempts were made to effect the direct cyclopentadienylation of commercial $ZrCl_4$ in CH_2Cl_2 with TMSCp. Unfortunately, under these *heterogeneous* reaction conditions, partial polymerization of the TMSCp was found to occur with concomitant formation of Cp_2ZrCl_2 as well as intractable side products. Attempts to utilize soluble complexes of the type $ZrCl_4{\cdot}2OR_2$ formed by the treatment of $ZrCl_4$ with various ethers (e.g., Et_2O, $(i\text{-}Pr)_2O$, and $PhOCH_3$ (2 equiv/equiv of Zr)) in the above process gave no appreciable reaction.

In sharp contrast to these discouraging results, simple exposure of TMSCp (1 equiv) to the homogeneous complex prepared in situ by the treatment of $ZrCl_4$ *with* $(CH_3)_2S$ *(2 equiv,* CH_2Cl_2*, 0 °C) led to the formation of* $CpZrCl_3{\cdot}2SMe_2$ *in excellent yield after several minutes.*

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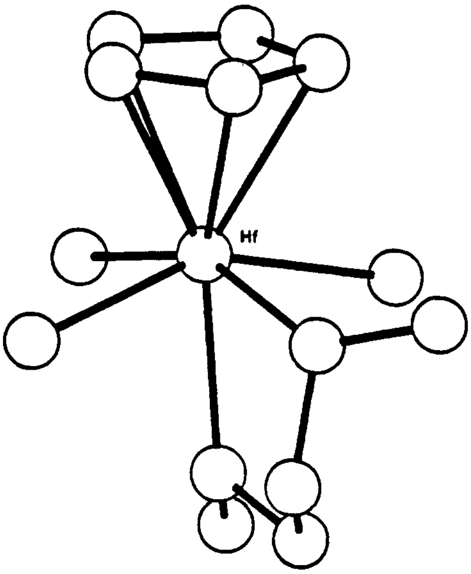

Figure 1. Crystal structure for $CpHfCl_3{\cdot}DME$ (2).

The relative lability of the $(CH_3)_2S$ ligands in this complex precluded its isolation in analytically pure form. However, simple addition of 1,2-DME (5 equiv) prior to purification allowed the isolation of the known complex $CpZrCl_3{\cdot}DME$ (1)[8] in 69–74% isolated yield.[9]

In addition, (η^5-cyclopentadienyl)trichlorohafnium complexes could be readily prepared via a related experimental procedure. In this instance it was found necessary to employ 1-(tri-*n*-butylstannyl)cyclopenta-2,4-diene[10] as the cyclopentadienyl anion equivalent. Accordingly, treatment of a CH_2Cl_2 solution of $HfCl_4{\cdot}2SMe_2$ (formed in situ from $HfCl_4$ and 2 equiv of Me_2S) with 1 equiv of $(n\text{-}Bu)_3SnCp$ (25 °C, 2 h) followed by the addition of 1,2-DME (5 equiv) furnished the new complex $CpHfCl_3{\cdot}DME$ (2) in 55–64% isolated yield. It is also of interest in a preparative context that less than 1% of the dicyclopentadienyl complexes Cp_2ZrCl_2 and Cp_2HfCl_2 was obtained from either of the above procedures (Scheme I).

The crystal structure of $CpHfCl_3{\cdot}DME$ (2) is that of a distorted octahedron, in close analogy with the known zirconium complex 1 (Figure 1).[8,11]

The foregoing examples constitute the first one-step processes for direct conversion of group IV metal halides into the corresponding monocyclopentadienyl complexes in high yield. It is anticipated that the expanded availability of $CpZrCl_3$ and $CpHfCl_3$ derivatives made possible by these procedures will greatly facilitate the exploitation of these complexes in synthetic and mechanistic investigations.

Experimental Section. Reactions were performed in oven-dried glassware under nitrogen. Dimethoxyethane (DME) was distilled from sodium benzophenone ketyl, dichloromethane from calcium hydride, and dimethyl sulfide from lithium aluminum hydride. ^1H and ^{13}C NMR spectra were obtained at 300 and 75.4 MHz, respectively. TMSCp and $(n\text{-}Bu)_3SnCp$ were prepared by the published methods.[7,10]

(η^5-Cyclopentadienyl)trichlorozirconium Dimethoxyethane Complex (1). To a stirred suspension of zirconium tetrachloride (23.30 g, 100 mmol) in 200 mL of dichloromethane was added dimethyl sulfide (12.40 g, 14.7 mL, 200 mmol) at 0 °C. The resulting clear solution was then treated dropwise with TMSCp (13.83 g, 100 mmol) whereupon a solid immediately began to form. The ice bath was removed, and the reaction mixture was stirred 2 h at room temperature. DME (50 mL) was then added, and the reaction mixture was subsequently concentrated to a volume of ca. 30 mL. The suspension was transferred to a fritted funnel, washed with 2 × 30 mL of DME, and dried under vacuum to afford 25.64 g of $CpZrCl_3{\cdot}DME$ (1; 72%) as a white crystalline powder. ^1H NMR ($CDCl_3$): δ 6.66 (s, 5 H, C_5H_5), 4.10 (broad s, 4 H, OCH_2), 3.88 (broad s, 6 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 119.6, 72.9, 64.7. Exact mass: calcd for $C_5H_5ZrCl_3$, 259.8505, found, 259.8504.

(η^5-Cyclopentadienyl)trichlorohafnium Dimethoxyethane Complex (2). To a stirred suspension of hafnium tetrachloride (1.600 g, 5 mmol) in 10 mL of dichloromethane was added dimethyl sulfide (0.621 g, 0.74 mL, 10 mmol) at 25 °C. The resulting mixture was then treated with $(n\text{-}Bu)_3SnCp$ (1.776 g, 5 mmol), and the reaction mixture was stirred for 2 h at 25 °C. DME (5 mL) was then added, and the reaction mixture was processed as before to provide 1.393 g of $CpHfCl_3{\cdot}DME$ (2; 63%) as a white crystalline powder. This product was found to contain ca. 3% of $CpZrCl_3(DME)$ arising from the $ZrCl_4$ impurity present in commercial $HfCl_4$. ^1H NMR ($CDCl_3$): δ 6.51 (s, 5 H, C_5H_5), 4.10 (broad s, 4 H, OCH_2), 3.90 (broad s, 6 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 117.2, 73.0, 64.5. Exact mass: calcd for $C_5H_5HfCl_3$, 349.8925; found, 349.8922.

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[9] It is worthy of note that direct exposure of C_5H_6 to CH_3ZrCl_3[12] or $ZrCl_4{\cdot}2SMe_2$ in the presence of LiH did not produce appreciable quantities of $CpZrCl_3$ complexes.

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