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Preliminary Communication

Multiple bonds between hafnium and the chalcogens: syntheses and structures of the terminal chalcogenido complexes $(\eta^5\text{-}\mathrm{C_5Me_4R})_2\mathrm{Hf(E)(NC_5H_5)}$ $(\mathrm{E = O, S, Se, Te})$ *

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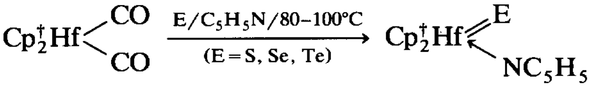
Abstract

The series of terminal hafnium chalcogenido complexes $(\eta^5\text{-}\mathrm{C_5Me_4R})_2\mathrm{Hf(E)(NC_5H_5)}$ (E = S, Se, Te; R = Me, Et) has been synthesized by the reactions of $(\eta^5\text{-}\mathrm{C_5Me_4R})_2\mathrm{Hf(CO)_2}$ with the chalcogens E in the presence of $\mathrm{NC_5H_5}$. The oxo derivatives $(\eta^5\text{-}\mathrm{C_5Me_4R})_2\mathrm{Hf(O)(NC_5H_5)}$ are prepared by the reaction of the tellurido complexes $(\eta^5\text{-}\mathrm{C_5Me_4R})_2\mathrm{Hf(Te)(NC_5H_5)}$ with $\mathrm{N_2O}$. The structures of the complete series of chalcogenido complexes $(\eta^5\text{-}\mathrm{C_5Me_4Et})_2\mathrm{Hf(E)(NC_5H_5)}$ (E = O, S, Se, Te) have been determined by X-ray diffraction.

Key words: Hafnium; Chalcogens; Multiple bonding

Terminal metal-ligand multiple bonding is a common feature of the chemistry of many of the transition elements with oxo, nitrido, imido, alkylidene and alkylidyne ligands [1]. However, in contrast to the Groups 5, 6, 7 and 8 transition elements, the occurrence of metal–ligand multiple bonding for the Group 4 transition metals is substantially less well documented. In particular, complexes that exhibit metal–ligand multiple bonding of the heavier congeners Zr and Hf are not common. For example, whereas titanium complexes that exhibit terminal metal–ligand multiple bonding have been known since at least 1968 [2], the first such zirconium complexes, namely the imido derivatives $\mathrm{Cp_2Zr(NBu^t)(THF)}$ [3] and $\mathrm{(Bu^t_3SiNH)_2Zr(NSiBu^t_3)(THF)}$ [4], were reported as late as 1988, by Bergman and Wolczanski, respectively [5]. Bergman has subsequently isolated the first terminal sulfido complexes of zirconium, specifically $\mathrm{Cp^*_2Zr(S)(NC_5H_5)}$ and $\mathrm{Cp^*_2Zr(S)(NC_5H_4Bu^t)}$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$) [6], while Arnold has reported the first tellurido complexes, namely $\mathrm{(dmpe)_2M(TeR)_2(Te)}$ [M = Zr; Hf; R = $\mathrm{Si(SiMe_3)_3}$] [7,8]. More recently, we have isolated the first terminal oxo complexes of zirconium $\mathrm{Cp^{\dagger}_2Zr(O)(NC_5H_5)}$ [9] ($\mathrm{Cp^{\dagger}} = \mathrm{Cp^*}$ or $\mathrm{Cp^{Et*}}$; and $\mathrm{Cp^{Et*}} = \eta^5\text{-}\mathrm{C_5Me_4Et}$), which are analogues of the titanium oxo complexes $\mathrm{Cp^*_2Ti(O)(NC_5H_5)}$ and $\mathrm{Cp^*_2Ti(O)(NC_5H_4Ph)}$ synthesized by Andersen [2i,10]. Furthermore, we have extended this methodology so that the series of terminal zirconium-chalcogenido complexes $\mathrm{Cp^{\dagger}_2Zr(E)(NC_5H_5)}$ (E = O, S, Se, Te) is now known [11,12]. Here we describe the syntheses and structures of the first complete series of terminal chalcogenido complexes of hafnium [13 *].

The terminal zirconium chalcogenido complexes $\mathrm{Cp^{\dagger}_2Zr(E)(NC_5H_5)}$ are readily prepared by a general method that involves the reaction of $\mathrm{Cp^{\dagger}_2Zr(CO)_2}$ with either $\mathrm{N_2O}$ or the elemental chalcogen (E = S, Se, Te) in the presence of pyridine [11,12]. This method is readily adapted for the sulfido, selenido, and tellurido derivatives of hafnium $\mathrm{Cp^{\dagger}_2Hf(E)(NC_5H_5)}$ in *ca.* 70 to 95% yield (eqn. (1)) [14*,15*].



$$\mathrm{Cp^{\dagger}_2Hf(CO)_2} \xrightarrow[\mathrm{(E=S,\ Se,\ Te)}]{\mathrm{E/C_5H_5N/80\text{–}100^{\circ}C}} \mathrm{Cp^{\dagger}_2Hf(E)(NC_5H_5)} \qquad (1)$$

Unfortunately, this approach is not successful for syntheses of the hafnium oxo complexes $\mathrm{Cp^{\dagger}_2Hf(O)(NC_5H_5)}$. Thus, whereas the reactions between $\mathrm{Cp^{\dagger}_2Zr(CO)_2}$ and $\mathrm{N_2O}$ in the presence of $\mathrm{NC_5H_5}$ give the zirconium oxo complexes $\mathrm{Cp^{\dagger}_2Zr(O)(NC_5H_5)}$, the corresponding reactions of the hafnium analogues $\mathrm{Cp\dagger_2Hf(CO)_2}$ result in significant decomposition at the temperatures required to effect reaction. Nevertheless, the hafnium oxo complexes may be synthesized by the reactions of the tellurido derivatives $\mathrm{Cp^{\dagger}_2Hf(Te)(NC_5H_5)}$ with $\mathrm{N_2O}$ at room temperature (eqn. (2)), thereby completing the series of hafnium chalcogenido complexes [15].

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* Dedicated to Professor Helmut Werner on the occasion of his 60th Birthday. Happy Birthday, Helmut!

* Reference number with asterisk indicates a note in the list of references.

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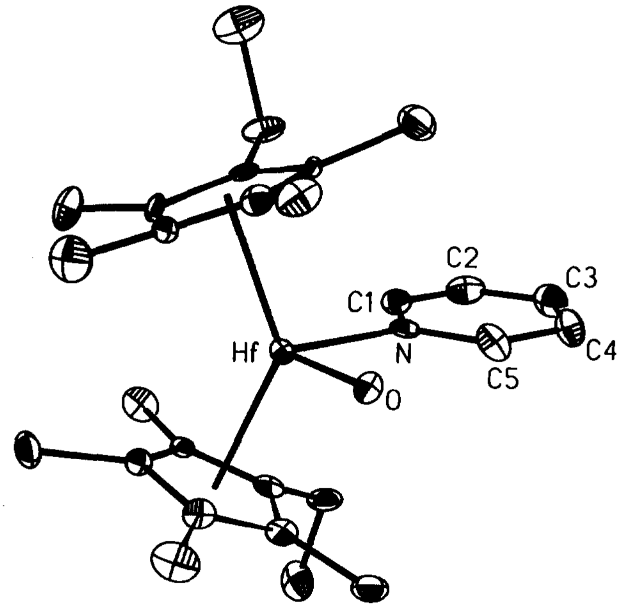


Fig. 1. Molecular structure of Cp$_2^{\text{Et*}}$Hf(O)(NC$_5$H$_5$) (20% thermal ellipsoids).

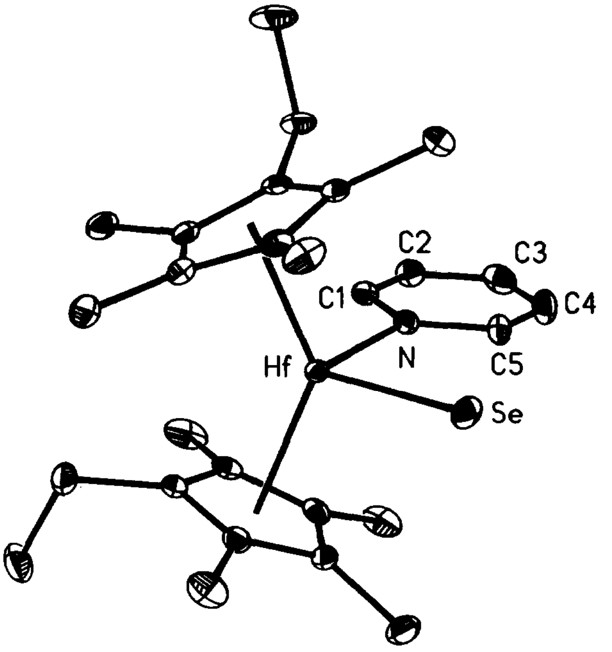
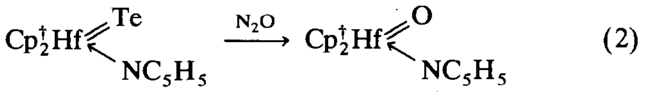


Fig. 3. Molecular structure of Cp$_2^{\text{Et*}}$Hf(Se)(NC$_5$H$_5$) (20% thermal ellipsoids).



$$\text{Cp}^{\dagger}_{2}\text{Hf}{\overset{\text{Te}}{\underset{\text{NC}_5\text{H}_5}{\lessgtr}}} \xrightarrow{\text{N}_2\text{O}} \text{Cp}^{\dagger}_{2}\text{Hf}{\overset{\text{O}}{\underset{\text{NC}_5\text{H}_5}{\lessgtr}}} \qquad (2)$$

The structures of the chalcogenido complexes Cp$_2^{\text{Et*}}$Hf(E)(NC$_5$H$_5$) (E = O, S, Se, Te) have been determined by X-ray diffraction, and ORTEP drawings are presented in Figs. 1–4 [16*]. The complexes Cp$_2^{\text{Et*}}$Hf(E)(NC$_5$H$_5$) (E = O, S, Se, Te) represent the first complete series of terminal chalcogenido complexes of hafnium to be structurally characterized. The Hf=E double bond lengths are summarized in Table 1, which also includes, for comparison, the bond lengths of the zirconium analogues [11]. Examination of Table 1 indicates that the Hf=E bond lengths are very similar

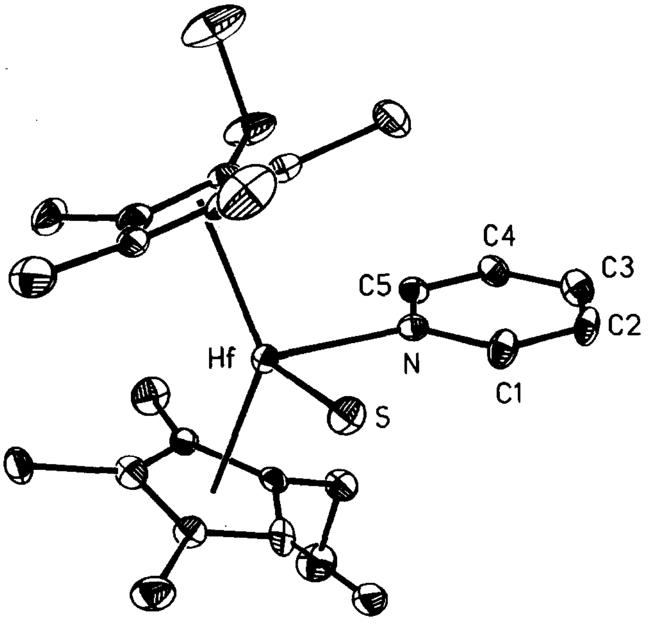


Fig. 2. Molecular structure of Cp$_2^{\text{Et*}}$Hf(S)(NC$_5$H$_5$) (20% thermal ellipsoids).

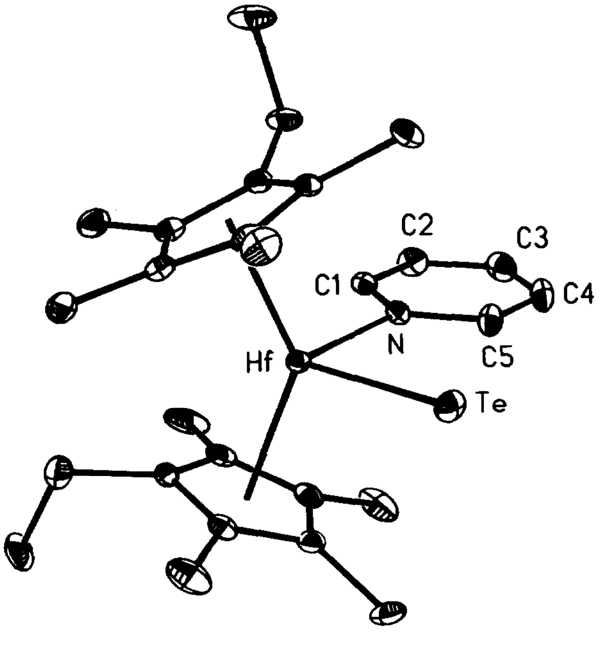


Fig. 4. Molecular structure of Cp$_2^{\text{Et*}}$Hf(Te)(NC$_5$H$_5$) (20% thermal ellipsoids).

TABLE 1. Comparison of Zr=E and Hf=E bond lengths in $Cp_2^{Et*}M(E)(NC_5H_5)$ (M = Zr, Hf)

	d(Zr=E)/Å	d(Hf=E)/Å	Calcd. (Hf=E)/Å [a]
O	1.804(4)	1.826(9)	1.76
S	2.334(2)	2.311(3)	2.28
Se	2.480(1)	2.467(1)	2.41
Te	2.729(1)	2.716(1)	2.67

[a] For $[Cp_2HfE]$. T.R. Cundari, personal communication.

to the corresponding Zr=E bond lengths, as would be anticipated on the basis of the Lanthanide Contraction. Indeed, the Hf=E (E = S, Se, Te) bond lengths appear to be slightly shorter than the corresponding Zr=E bond lengths [17 *]. However, in view of the limited data base available for such complexes, we hesitate to attach too much significance to the observation that the Hf=O bond length is slightly longer than that for Zr=O. This is especially so for the present situation, due to the fact that the hafnium oxo complex was prepared from the tellurido derivative, and that isostructural impurities may play a significant role in artificially modifying apparent bond lengths as determined by X-ray diffraction [18].

The Hf=E bond lengths in $Cp_2^{Et*}Hf(E)(NC_5H_5)$ may also be compared with the results of effective core potential calculations by Cundari on the hypothetical pyridine-free complexes $[Cp_2Hf{=}E]$, which are summarized in Table 1 [19*].

In summary, the first series of terminal chalcogenido complexes of hafnium $Cp_2^{\ddagger}Hf(E)(NC_5H_5)$ (E = O, S, Se, Te) has been prepared, and X-ray structure determinations on the complexes $Cp_2^{Et*}Hf(E)(NC_5H_5)$ have provided a comparison between Hf=E and Zr=E multiple bond lengths.

Acknowledgments

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13 We are considering here only the non-radioactive chalcogens, thereby excluding polonium from the discussion.

14 For example, the synthesis of $Cp_2^*Hf(Se)(NC_5H_5)$ is as follows: A mixture of $Cp_2^*Hf(CO)_2$ (230 mg, 0.45 mmol), Se (33 mg, 0.42 mmol), and an excess of C_5H_5N (*ca.* 1 mL) in toluene (4 ml) was stirred at 80°C for 12 h. The mixture was cooled to room temperature, depositing red-orange needles that were separated, washed with pentane, and dried *in vacuo*. Yield of $Cp_2^*Hf(Se)(NC_5H_5)$: 190 mg (73% based on Se).

15 ^1H NMR data for $Cp_2^*Hf(O)(NC_5H_5)(C_6D_6)$: δ 1.93 [30 H, s,

$2\{\eta^5\text{-}C_5(CH_3)_5\}]$, 6.40 [2H, m, NC_5H_5], 6.68 [1H, m, NC_5H_5], 7.45 [1H, m, NC_5H_5], 9.42 [1H, m, NC_5H_5].

^1H NMR data for $Cp^*_2Hf(S)(NC_5H_5)(C_6D_6)$: δ 1.95 [30 H, s, $2\{\eta^5\text{-}C_5(CH_3)_5\}]$, 6.22 [1H, m, NC_5H_5], 6.32 [1H, m, NC_5H_5], 6.62 [1H, m, NC_5H_5], 7.24 [1H, m, NC_5H_5], 9.71 [1H, m, NC_5H_5].

^1H NMR data for $Cp^*_2Hf(Se)(NC_5H_5)(C_6D_6)$: δ 1.95 [30 H, s, $2\{\eta^5\text{-}C_5(CH_3)_5\}]$, 6.12 [1H, m, NC_5H_5], 6.23 [1H, m, NC_5H_5], 6.53 [1H, m, NC_5H_5], 7.15 (obscured by solvent) [1H, m, NC_5H_5], 9.72 [1H, m, NC_5H_5].

^1H NMR data for $Cp^*_2Hf(Te)(NC_5H_5)(C_6D_6)$: δ 1.94 [30 H, s, $2\{\eta^5\text{-}C_5(CH_3)_5\}]$, 6.07 [1H, m, NC_5H_5], 6.18 [1H, m, NC_5H_5], 6.52 [1H, m, NC_5H_5], 7.15 (obscured by solvent) [1H, m, NC_5H_5], 9.71 [1H, m, NC_5H_5].

16 X-ray data for $Cp^{Et*}_2Hf(E)(NC_5H_5)$: $Cp^{Et*}_2Hf(O)(NC_5H_5)$ is orthorhombic, $Pna2_1$ (No. 33), $a = 18.066(3)$ Å, $b = 9.621(3)$ Å, $c = 14.088(3)$ Å, $V = 2449(1)$ Å^3, $Z = 4$, $R = 0.0392$, $R_w = 0.0374$, GOF = 1.040. $Cp^{Et*}_2Hf(S)(NC_5H_5)$ is orthorhombic, $Pc2_1n$ (No. 33), $a = 9.744(5)$ Å, $b = 14.727(7)$ Å, $c = 17.693(6)$ Å, $V = 2539(2)$ Å^3, $Z = 4$, $R = 0.0269$, $R_w = 0.0368$, GOF = 1.024. $Cp^{Et*}_2Hf(Se)(NC_5H_5)$ is monoclinic, $P2_1/n$ (No. 14), $a = 8.411(1)$ Å, $b = 19.698(3)$ Å, $c = 15.254(2)$ Å, $\beta = 90.13(1)°$, $V = 2527(1)$ Å^3, $Z = 4$, $R = 0.0262$, $R_w = 0.0272$, GOF = 1.146. $Cp^{Et*}_2Hf(Te)(NC_5H_5)$ is monoclinic, $P2_1/n$ (No. 14), $a = 8.617(2)$ Å, $b = 19.679(6)$ Å, $c = 15.250(3)$ Å, $\beta = 90.79(2)°$, $V = 2586(1)$ Å^3, $Z = 4$, $R = 0.0346$, $R_w = 0.0436$, GOF = 1.167. Tables of atom coordinates have been deposited with the Cambridge Crystallographic Data Centre.

17 Other examples in which metal–ligand bonds are slightly shorter for the metals of the third transition series than those of the second transition series include the complexes $M(Me_2PCH_2CH_2PMe_2)_3$ (M = Mo, W; M = Nb, Ta) [17a] [d(Mo–P) = 2.421(3) Å, d(W–P) = 2.414(6) Å; d(Nb–P) = 2.526(3) Å, d(Ta–P) = 2.500(6) Å] and $M(PMe_3)_6$ (M = Mo [17b], W [17c]) [d(Mo–P) = 2.467(2) Å, d(W–P) = 2.455(5) Å]. See: (a) F.G.N. Cloke, P.J. Fyne, V.C. Gibson, M.L.H. Green, M.J. Ledoux, R.N. Perutz, A. Dix, A. Gourdon and K. Prout, *J. Organomet. Chem.*, *277* (1984) 61; (b) M. Brookhart, K. Cox, F.G.N. Cloke, J.C. Green, M.L.H. Green, P.M. Hare, J. Bashkin, A.E. Derome and P.D. Grebenik, *J. Chem. Soc., Dalton Trans.*, (1985) 423; (c) D. Rabinovich, R. Zelman and G. Parkin, *J. Am. Chem. Soc.*, *114* (1992) 4611.

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