J. Am. Chem. Soc. **1994**, *116*, 606–615

Terminal Oxo, Sulfido, Selenido, and Tellurido Complexes of Zirconium, $(\eta^5\text{-}C_5Me_4R)_2Zr(E)(NC_5H_5)$: Comparison of Terminal Zr—E Single and Zr═E Double Bond Lengths

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Received June 21, 1993. Revised Manuscript Received November 3, 1993[⊛]

Abstract: The series of terminal zirconium chalcogenido complexes $(\eta^5\text{-}C_5Me_4R)_2Zr(E)(NC_5H_5)$(E = O, S, Se, Te; R = Me, Et) has been synthesized by the reactions of $(\eta^5\text{-}C_5Me_4R)_2Zr(CO)_2$ with either N_2O or the elemental chalcogen (E = S, Se, Te) in the presence of NC_5H_5. The tellurido complex $(\eta^5\text{-}C_5Me_5)_2Zr(Te)(NC_5H_5)$ reacts instantaneously with N_2O to give the oxo derivative $(\eta^5\text{-}C_5Me_5)_2Zr(O)(NC_5H_5)$. The hydrochalcogenido derivatives $(\eta^5\text{-}C_5Me_5)_2Zr(EH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$ have been obtained by the reactions of $(\eta^5\text{-}C_5Me_5)_2Zr(E)(NC_5H_5)$ with $PhC(O)CH_3$, thus demonstrating the basicity of the chalcogenido ligands in these complexes. The structures of the chalcogenido $(\eta^5\text{-}C_5Me_4Et)_2Zr(E)(NC_5H_5)$(E = O, S, Se, Te) and hydrochalcogenido $(\eta^5\text{-}C_5Me_5)_2Zr(EH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$ (E = O, S, Se) complexes have been determined by X-ray diffraction, thereby allowing a comparison of Zr—E single and Zr═E double bond lengths to be made for a series of structurally-related compounds. A consideration of the difference in lengths of the M—E single and M═E double bonds, with respect to the difference in single and double bond covalent radii of the chalcogens, leads to the conclusion that the double bond covalent radius of zirconium in the $[(\eta^5\text{-}C_5R_5)_2Zr]$ system is *ca.* 0.07 Å shorter than its single bond covalent radius. For the heavier chalcogens (S, Se, and Te), the Zr—E single and Zr═E double bond lengths may be predicted reasonably well on the basis of the sum of the covalent radii of Zr and E. In contrast, both the Zr–O single and double bond lengths are anomalously short, a result that is consistent with Coulombic stabilization by an ionic contribution, *i.e.* $Zr^{\delta+}\text{–}O^{\delta-}$. Thus, the zirconium–oxo interaction in $Cp^{Et*}{}_2Zr(O)(NC_5H_5)$ is proposed to be represented by the resonance structures Zr═O ↔ Zr^+—O^-. In contrast, for the heavier chalcogens, the resonance form Zr^+—E^- is considered to play a less significant role in describing the bonding within the zirconium–chalcogenido moiety.

Introduction

Complexes containing metal–ligand multiple bonds have recently received much attention.[1] Interest in these complexes derives from their intrinsic reactivity and also the roles that such species may play in a number of important transformations (*e.g.* metal-mediated oxidations). However, although terminal M═X (*e.g.* X = O, NR, CR_2) and M≡X (*e.g.* X = N, CR) multiple bonds are common, their occurrence diminishes rapidly as the X substituent descends the Periodic Table.[2] Such an observation is presumably a reflection of both (i) the decreased $d\pi\text{–}p\pi$ overlap and (ii) the increased tendency of the larger atoms to bridge two or more metal centers. Therefore, one of our interests has focused on the syntheses of transition metal complexes with terminal M═X multiple bonds to the heavier group VI elements.[3] As part of these studies, we have recently described the synthesis of *trans*-$W(PMe_3)_4(Te)_2$, the first transition metal complex with a terminal tellurido ligand.[4,5]

In this paper we report the first complete series of terminal chalcogenido complexes of zirconium, namely $Cp^{\dagger}{}_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te; $Cp^{\dagger}$ = Cp^* or Cp^{Et*}; Cp^* = $\eta^5\text{-}C_5Me_5$; and Cp^{Et*} = $\eta^5\text{-}C_5Me_4Et$).[6] The structures of the complexes $Cp^{Et*}{}_2Zr(E)(NC_5H_5)$ have been determined by X-ray diffraction, with the aim of providing insight into the nature of the bonding within the zirconium–chalcogenido moiety. These studies provide evidence that the zirconium–chalcogenido interaction is substantially more ionic for the oxo derivative than for its heavier congeners, so that the resonance structure Zr^+—O^- provides an important contribution. Furthermore, a comparison between Zr—E single and Zr═E double bond lengths in $[(\eta^5\text{-}C_5R_5)_2Zr]$ derivatives suggests that the double bond covalent radius of zirconium in $[(\eta^5\text{-}C_5R_5)_2Zr]$ derivatives is *ca.* 0.07 Å shorter than its single bond radius.

Results and Discussion

(i) Syntheses of Terminal Chalcogenido Zirconium Complexes $Cp^{\dagger}{}_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te). We have recently reported the syntheses of the first terminal zirconium oxo complexes $Cp^{\dagger}{}_2Zr(O)(NC_5H_5)$ by oxygen atom transfer[7] from N_2O to $Cp^{\dagger}{}_2Zr(CO)_2$ in the presence of pyridine.[8–10] These oxo derivatives are analogues of the first terminal chalcogenido complexes of zirconium to be isolated, namely the sulfido derivatives $Cp^*{}_2Zr(S)(NC_5H_4R)$ (R = H, Bu^t), that were reported by Bergman

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[⊛] Abstract published in *Advance ACS Abstracts*, December 15, 1993.

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(5) More recent examples of terminal tellurido complexes include $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$,[5a] $(dmpe)_2M(TeR)_2(Te)$ (M = Zr, Hf; R = $Si(SiMe_3)_3$),[5b] $Cp^*Nb(PMe_3)(NAr)(Te)$ (Ar = 2,6-$C_6H_3Pr^i{}_2$),[5c] and $[\{(Me_3Si)NCH_2CH_2\}_3N]TaTe$.[5d] (a) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 9822–9823. (b) Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240–6242. (c) Siemeling, U.; Gibson, V. C. *J Chem. Soc., Chem. Commun.* **1992**, 1670–1671. (d) Christou, V.; Arnold, J. *Angew. Chem.* **1993**, *105*, 1551–1553; *Angew. Chem.. Int. Ed. Engl.* **1993**, *32*, 1450–1452.

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(7) For recent reviews on oxygen atom transfer reactions see: (a) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571–589. (b) Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125–1136.

(8) Howard, W. A.; Waters, M.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4917–4918.

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(10) For another recent example of a terminal zirconium oxo complex see: Jacoby, D.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1993**, *115*, 7025–7026.

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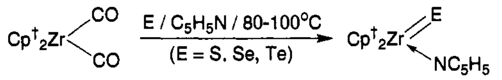
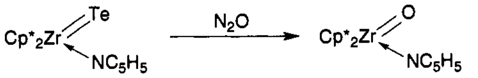
in 1990.[11,12] Significantly, Bergman demonstrated that the [$Cp^*_2Zr{=}S$] moiety could be generated by dehydrohalogenation of $Cp^*_2Zr(SH)I$ and subsequently trapped by pyridine to give $Cp^*_2Zr(S)(NC_5H_4R)$ (R = H, Bu^t). More recently, we have reported that $Cp^*_2Zr(S)(NC_5H_5)$ may also be synthesized by an alternative method that involves the direct reaction of $Cp^*_2Zr(CO)_2$ with sulfur in the presence of pyridine.[13] Modification of this approach has now allowed the syntheses of the related terminal selenido and tellurido derivatives $Cp^\dagger_2Zr(E)(NC_5H_5)$ (eq 1). Hence, the



(1)

complete series of terminal chalcogenido complexes $Cp^\dagger_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te) is now available for study. As such, we are provided with a rare opportunity to investigate the chemistry of the metal–chalcogenido moiety as a function of the chalcogen in a structurally related series of compounds. The emphasis of this paper is principally concerned with structural aspects of the chalcogenido complexes $Cp^{Et*}_2Zr(E)(NC_5H_5)$, while complete details of the reactivity and spectroscopic properties of the $Cp^*_2Zr(E)(NC_5H_5)$ complexes will be described in a future publication.[14] Nevertheless, at this point we wish to mention two aspects of the chemistry of these complexes that are particularly noteworthy. Firstly, each of the complexes $Cp^*_2Zr(E)(NC_5H_5)$ (E = S, Se, Te) reacts rapidly with N_2O at room temperature to give, *inter alia*, the oxo derivative $Cp^*_2Zr(O)(NC_5H_5)$. However, only the reaction of the tellurido derivative is clean (eq 2).[15] Secondly, each of the chalcogenido complexes reacts with



(2)

the methyl ketone $PhC(O)CH_3$ to give the hydrochalcogenido enolate derivatives $Cp^*_2Zr(EH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$ (eq 3).[16] As noted previously for the oxo derivative,[8] this reaction reveals the basicity of the chalcogenido ligands in these complexes.

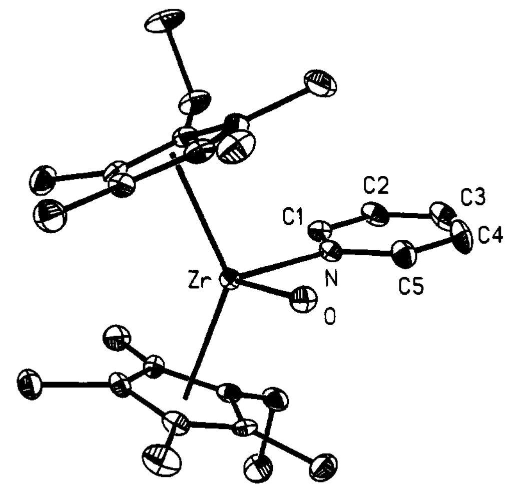


Figure 1. Molecular structure of $Cp^{Et*}_2Zr(O)(NC_5H_5)$.

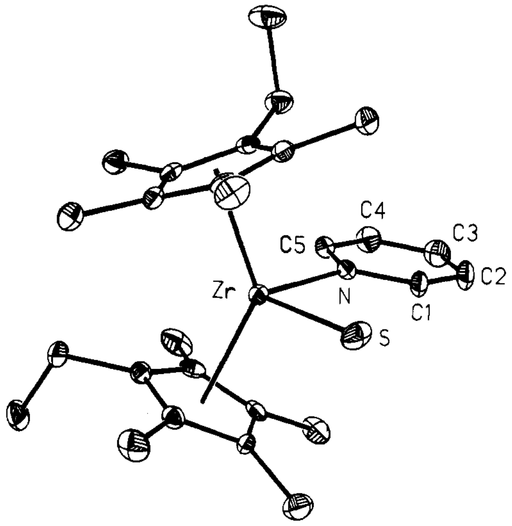
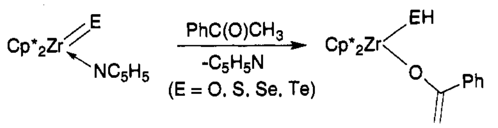


Figure 2. Molecular structure of $Cp^{Et*}_2Zr(S)(NC_5H_5)$.



(3)

(ii) Molecular Structures of the Terminal Chalcogenido Complexes $Cp^{Et*}_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te). Returning to the emphasis of this paper, the molecular structures of the chalcogenido complexes $Cp^{Et*}_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te) have been determined by single-crystal X-ray diffraction, as shown in Figures 1–4. The η^5-tetramethylethylcyclopentadienyl derivatives, rather than the η^5-pentamethylcyclopentadienyl derivatives, were chosen for this study due to the better quality of the crystals obtained for the $Cp^{Et*}_2Zr(E)(NC_5H_5)$ complexes. Selected bond lengths and angles are presented in Tables 1–4. The structure of $Cp^{Et*}_2Zr(S)(NC_5H_5)$ is, as expected, similar to that of $Cp^*_2Zr(S)(NC_5H_4Bu^t)$, which was structurally characterized by Bergman.[11b] Specifically, the Zr=S bond length in $Cp^{Et*}_2Zr(S)(NC_5H_5)$ [2.334(2) Å] compares favorably with that in $Cp^*_2Zr(S)(NC_5H_4Bu^t)$ [2.316(1) Å].

Of particular significance, the complexes $Cp^{Et*}_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te) represent the first complete series of terminal chalcogenido complexes of the transition metals to be structurally characterized. The terminal Zr=E bond lengths for the series of chalcogenido complexes are summarized in Table 5.

Three possible covalent resonance forms may be considered to describe the metal–chalcogenido interaction, as shown in Scheme 1. Of these three resonance forms, the zirconium–chalcogenido

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(12) For some recent related examples of multiple bonding in complexes of Ti, Zr, and Hf see: (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705–3723. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729–8731. (c) Walsh, P. J.; Carney, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6343–6345. (d) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731–8733. (e) Cummins, C. C.; Van Duyne, G. D.; Schaller, C. P.; Wolczanski, P. T. *Organometallics* **1991**, *10*, 164–170. (f) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664–665. (g) Profilet, R. D.; Zambrano, C. H.; Fanwick, P. E.; Nash, J. J.; Rothwell, I. P. *Inorg. Chem.* **1990**, *29*, 4362–4364. (h) Arney, D. J.; Bruck, M. A.; Huber, S. R.; Wigley, D. E. *Inorg. Chem.* **1992**, *31*, 3749–3755. (i) Bai, Y.; Roesky, H. W.; Noltemeyer, M.; Witt, M. *Chem. Ber.* **1992**, *125*, 825–831. (j) Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336–5337. (k) Hou, Z.; Breen, T. L.; Stephan, D. W. *Organometallics* **1993**, *12*, 3158–3167.

(13) Howard, W. A.; Parkin, G. *Organometallics* **1993**, *12*, 2363–2366.

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(15) For example, the reaction between $Cp^*_2Zr(Se)(NC_5H_5)$ and N_2O immediately gives a mixture of $Cp^*_2Zr(O)(NC_5H_5)$ and $Cp^*_2ZrSe_3$. Howard, W. A.; Parkin, G.; Rheingold, A. L., Unpublished results.

(16) Some other examples of [M]–TeH and [M]–SeH complexes include $[(CO)_4M(EH)]_2$ (M = Mn, E = Se, Te; M = Re, E = Se),[16a] $[(CO)_5M(EH)]^-$ and $[(CO)_5M(EH)M(CO)_5]^-$ (M = Cr, W; E = Se, Te),[16b] $[\{CpCr(CO)_3\}_2(\mu\text{-}TeH)]^+$,[16c] $(dppe)Ni(SeH)_2$,[16d] $Cp^*Re(CO)_2(H)(TeH)$,[16e] $Cp^*_2Ti(SeH)_2$,[16f] $Cp_2TiCl(SeH)$,[16g] $Cp_2Ti(SeH)_2$,[16g] and $RhIr(H)(\mu\text{-}SeH)(CO)_2(dppm)_2$.[16h] (a) Küllmer, V.; Vahrenkamp, H. *Chem. Ber.* **1977**, *110*, 228–236. (b) Hausmann, H.; Höfler, M.; Kruck, T.; Zimmermann, H. W. *Chem. Ber.* **1981**, *114*, 975–981. (c) Herrmann, W. A.; Rohrmann, J.; Ziegler, M. L.; Zahn, T. *J. Organomet. Chem.* **1984**, *273*, 221–232. (d) Schmidt, M.; Hoffmann, G. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 598–599. (e) Herrmann, W. A.; Hecht, C.; Herdtweck, E.; Kneuper, H.-J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 132–134. (f) Bottomley, F.; Chin, T.-T.; Egharevba, G. O.; Kane, L. M.; Pataki, D. A.; White, P. S. *Organometallics* **1988**, *7*, 1214–1221. (g) Bottomley, F.; Day, R. W. *Organometallics* **1991**, *10*, 2560–2563. (h) McDonald, R.; Cowie, M. *Inorg. Chem.* **1993**, *32*, 1671–1680.

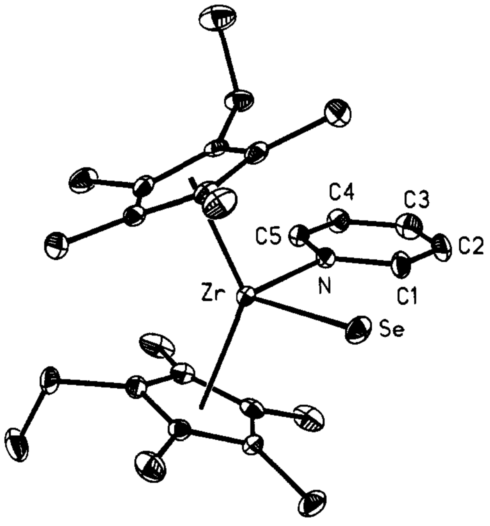


Figure 3. Molecular structure of $Cp^{Et*}{}_2Zr(Se)(NC_5H_5)$.

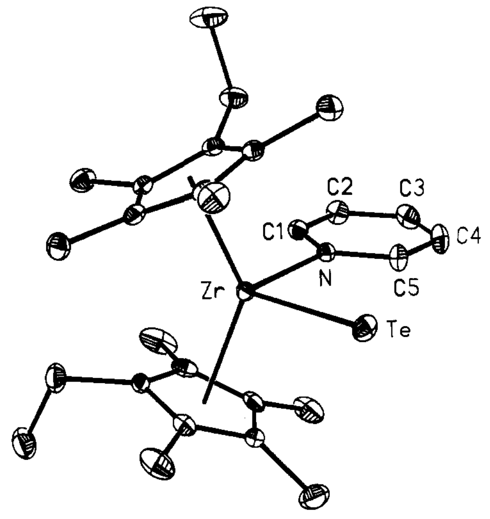


Figure 4. Molecular structure of $Cp^{Et*}{}_2Zr(Te)(NC_5H_5)$.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Cp^{Et*}{}_2Zr(O)(NC_5H_5)$

Zr–O	1.804(4)	Zr–N	2.363(5)
Zr–C(11)	2.640(7)	Zr–C(12)	2.572(6)
Zr–C(13)	2.566(7)	Zr–C(14)	2.626(7)
Zr–C(15)	2.671(6)	Zr–C(31)	2.656(7)
Zr–C(32)	2.665(7)	Zr–C(33)	2.589(5)
Zr–C(34)	2.595(8)	Zr–C(35)	2.606(6)
N–C(1)	1.343(9)	N–C(5)	1.343(9)
C(1)–C(2)	1.373(10)	C(2)–C(3)	1.345(12)
C(3)–C(4)	1.362(16)	C(4)–C(5)	1.370(10)
O–Zr–N	90.9(2)	Zr–N–C(1)	126.2(4)
Zr–N–C(5)	116.5(4)	C(1)–N–C(5)	117.3(6)
N–C(1)–C(2)	122.4(7)	C(1)–C(2)–C(3)	119.5(8)
C(2)–C(3)–C(4)	119.2(7)	C(3)–C(4)–C(5)	119.5(9)
N–C(5)–C(4)	122.0(8)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Cp^{Et*}{}_2Zr(S)(NC_5H_5)$

Zr–S	2.334(2)	Zr–N	2.356(5)
Zr–C(11)	2.624(6)	Zr–C(12)	2.616(6)
Zr–C(13)	2.574(6)	Zr–C(14)	2.571(6)
Zr–C(15)	2.591(6)	Zr–C(21)	2.612(6)
Zr–C(22)	2.567(6)	Zr–C(23)	2.611(6)
Zr–C(24)	2.605(6)	Zr–C(25)	2.619(6)
N–C(1)	1.337(8)	N–C(5)	1.338(8)
C(1)–C(2)	1.381(10)	C(2)–C(3)	1.361(13)
C(3)–C(4)	1.357(11)	C(4)–C(5)	1.375(10)
S–Zr–N	93.7(1)	Zr–N–C(1)	121.3(4)
Zr–N–C(5)	122.2(4)	C(1)–N–C(5)	116.3(5)
N–C(1)–C(2)	122.8(7)	C(1)–C(2)–C(3)	119.1(7)
C(2)–C(3)–C(4)	119.6(7)	C(3)–C(4)–C(5)	118.0(7)
N–C(5)–C(4)	124.2(6)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Cp^{Et*}{}_2Zr(Se)(NC_5H_5)$

Zr–Se	2.480(1)	Zr–N	2.353(6)
Zr–C(11)	2.625(7)	Zr–C(12)	2.600(7)
Zr–C(13)	2.572(7)	Zr–C(14)	2.585(7)
Zr–C(15)	2.581(7)	Zr–C(21)	2.590(7)
Zr–C(22)	2.552(7)	Zr–C(23)	2.608(8)
Zr–C(24)	2.611(7)	Zr–C(25)	2.605(7)
N–C(1)	1.365(10)	N–C(5)	1.328(10)
C(1)–C(2)	1.393(11)	C(2)–C(3)	1.351(13)
C(3)–C(4)	1.369(12)	C(4)–C(5)	1.385(11)
Se–Zr–N	94.4(1)	Zr–N–C(1)	121.2(5)
Zr–N–C(5)	122.1(5)	C(1)–N–C(5)	116.5(6)
N–C(1)–C(2)	121.1(7)	C(1)–C(2)–C(3)	120.4(8)
C(2)–C(3)–C(4)	119.3(8)	C(3)–C(4)–C(5)	117.9(8)
N–C(5)–C(4)	124.6(7)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Cp^{Et*}{}_2Zr(Te)(NC_5H_5)$

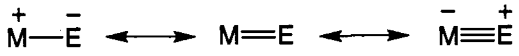
Zr–Te	2.729(1)	Zr–N	2.370(4)
Zr–C(11)	2.616(6)	Zr–C(12)	2.591(6)
Zr–C(13)	2.563(5)	Zr–C(14)	2.590(6)
Zr–C(15)	2.596(6)	Zr–C(21)	2.574(5)
Zr–C(22)	2.554(6)	Zr–C(23)	2.620(6)
Zr–C(24)	2.619(5)	Zr–C(25)	2.583(6)
N–C(1)	1.347(7)	N–C(5)	1.338(7)
C(1)–C(2)	1.381(8)	C(2)–C(3)	1.389(9)
C(3)–C(4)	1.356(9)	C(4)–C(5)	1.399(8)
Te–Zr–N	94.3(1)	Zr–N–C(1)	119.4(4)
Zr–N–C(5)	122.7(4)	C(1)–N–C(5)	117.7(5)
N–C(1)–C(2)	122.7(5)	C(1)–C(2)–C(3)	119.2(6)
C(2)–C(3)–C(4)	118.4(6)	C(3)–C(4)–C(5)	120.0(6)
N–C(5)–C(4)	122.1(6)		

Table 5. Summary of Coordination Changes in $Cp^{Et*}{}_2Zr(E)(NC_5H_5)$

	d(Zr=E)/ Å	d(Zr—N)/ Å	E—Zr—N/ deg	d(Zr—C_{av})/ Å	Δ(E—O)/ Å[a]
O	1.804(4)	2.363(5)	90.9(2)	2.62[6]	0
S	2.334(2)	2.356(5)	93.7(1)	2.60[3]	0.53
Se	2.480(1)	2.353(6)	94.4(1)	2.59[7]	0.67
Te	2.729(1)	2.370(4)	94.3(1)	2.59[4]	0.93

[a] Δ(E—O) is the difference in double bond lengths between d(Zr=E) and d(Zr=O).

Scheme 1



$$\overset{+}{M}-\overset{-}{E} \longleftrightarrow M=E \longleftrightarrow \overset{-}{M}\equiv\overset{+}{E}$$

interactions in $Cp^{\dagger}{}_2Zr(E)(NC_5H_5)$ would be aptly represented as Zr=E covalent double bonds on the basis of both (i) the 18-electron nature of the zirconium center and (ii) the proposed MO description for bent metallocene derivatives.[17] Nevertheless, it is important not to neglect the role of single bond contributions of the type Zr^+—E^-, especially in view of the reactivity exhibited by these complexes.[18] Likewise, the role of triple bond contributions of the type $Zr^- \equiv E^+$, which would occur at the expense of the Zr—$Cp^{\dagger}$ interactions, should also be considered.[19-21]

The largest increment in Zr=E double bond length (0.53 Å) is that between the oxo and sulfido derivatives, a difference that is substantially larger than would be predicted (0.39 Å) on the basis of the double bond radii (r_{db}) for O and S (see Table 6).[22]

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(17) (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742. (b) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149–167.

(18) For example, the ability of the zirconium–oxo complex $Cp^*{}_2Zr(O)(NC_5H_5)$ to dehydrohalogenate alkyl halides and enolize methyl ketones demonstrates the basicity of the oxo ligand. See ref 8.

Table 6. Single and Double Bond Covalent Radii for the Chalcogens[a]

	r_{sb}/Å[b]	r_{db}/Å[c]	$[r_{sb} - r_{db}]$/ Å	$[r_{db}(E) - r_{db}(O)]$/ Å
O	0.66	0.55	0.11	0
S	1.04	0.94	0.10	0.39
Se	1.17	1.07	0.10	0.52
Te	1.37	1.27	0.10	0.72

[a] Data taken from Pauling L. *The Nature of The Chemical Bond* 3rd ed.; Cornell University Press: Ithaca, 1960; p 224, with the exception of r_{db}(O) which was taken from Jolly, W. L. *Modern Inorganic Chemistry*; McGraw-Hill Book Co.: New York, 1984; p 53. [b] r_{sb} = single bond covalent radius. [c] r_{db} = double bond covalent radius.

For comparison, a similar trend is also observed for the tertiary phosphine complexes R_3PE,[23,24] in which the difference of *ca.* 0.47 Å between $d(P^+–O^-)$ and $d(P^+–S^-)$ is also greater than would be predicted on the basis of the covalent radii of O and S.[25] However, in contrast to the exceptionally large increase in bond lengths between the oxo and sulfido complexes, the increaments in bond length between the sulfido, selenido, and tellurido derivatives of $Cp^{Et*}{}_2Zr(E)(NC_5H_5)$ (and also R_3PE) are close to those predicted on the basis of r_{db}(E). The variations in $d(Zr{=}E)$ and $d(P^+—E^-)$ as a function of the chalcogen are shown in Figure 5. Furthermore, the incremental changes relative to oxygen of (i) $d(Zr{=}E)$, (ii) $d(P^+—E^-)$, and (iii) r_{db} (E), as summarized in Figure 6, clearly illustrate the anomalous nature of the increase in bond length between the oxo and sulfido derivatives for both $Cp^{Et*}{}_2Zr(E)(NC_5H_5)$ and R_3PE, a point to which we will return (*vide infra*).

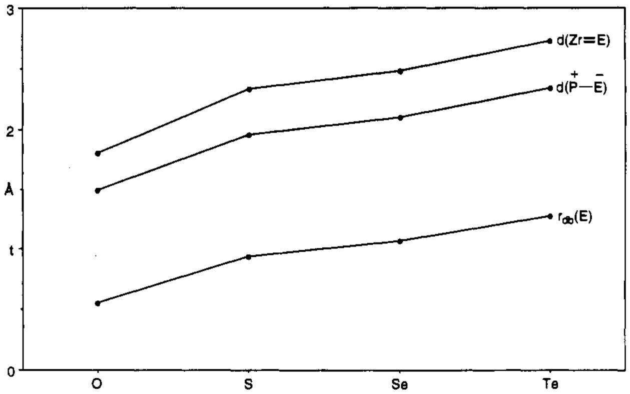

Figure 5. Variations in $d(Zr{=}E)$ and $d(P^+—E^-)$ as a function of the chalcogen.

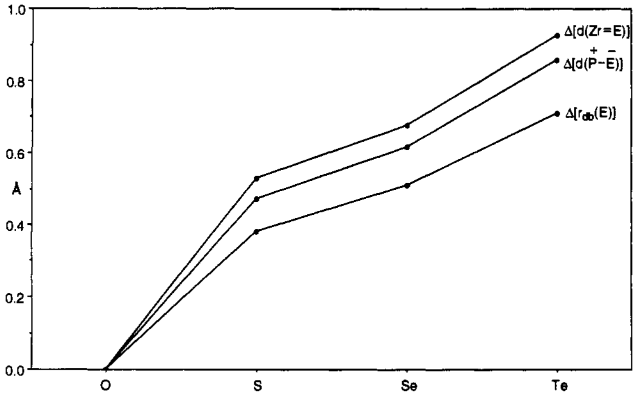

Figure 6. Incremental changes relative to oxygen of (i) $d(Zr{=}E)$, (ii) $d(P^+—E^-)$, and (iii) $r_{db}(E)$. $\Delta[d(Zr{=}E)] = d(Zr{=}E) - d(Zr{=}O)$; $\Delta[d(P^+—E^-)] = d(P^+—E^-) - d(P^+—O^-)$; $\Delta[r_{db}(E)] = r_{db}(E) - r_{db}(O)$.

(iii) **Comparison of Zr═E Double and Zr—E Single Bond Lengths.** In addition to establishing a series of Zr═E double bond lengths, we have also sought to provide a comparison between terminal Zr═E double and Zr—E single bond lengths in a structurally-related system. For this purpose, we have determined the structures of the hydrochalcogenido derivatives $Cp^*{}_2Zr(EH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$ (E = O, S, Se) described above. A notable feature of these complexes (shown in Figures 7–9) is the near linearity of the enolate ligand at oxygen. Selected bond lengths and angles for $Cp^*{}_2Zr(EH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$ (E = O, S, Se) are presented in Tables 7–9. The hydrotellurido derivative $Cp^*{}_2Zr(TeH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$, however, has not yet been structurally determined by X-ray diffraction.[26] Therefore, for the purposes of this study, we have estimated a value of 2.874[14] Å for a Zr–Te single bond length in the $[Cp^\dagger{}_2Zr]$ system, on the basis of the Zr–Te bond lengths in the related complexes $Cp^*{}_2ZrTe_3$,[27] $[(\eta^5\text{-}C_5H_4Bu^t)_2Zr(\mu\text{-}Te)]_2$,[28] and $[(\eta^5\text{-}C_5H_4Bu^t)_2Zr]_2(\mu\text{-}Te)(\mu\text{-}O)$.[29] Similarly, average values of Zr–E single bond

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(19) However, evidence which suggests that the resonance form $M^-{\equiv}E^+$ does not play a major role in the description of the metal–chalcogenido moiety of metallocene derivatives is provided by the molybdenum oxo complex $(\eta^5\text{-}C_5H_4Me)_2MoO$.[19a] Specifically, the Mo═O bond length of 1.721(2) Å in $(\eta^5\text{-}C_5H_4Me)_2MoO$ is slightly longer than the mean bond length of 1.678[40] Å observed for other Mo(IV) oxo complexes which exhibit a degree of triple bond $Mo^-{\equiv}O^+$ character.[19b] Moreover, the low value of ν(Mo═O) in the complex Cp_2MoO (793–868 cm^{-1})[19c] is also in accord with the notion that the molybdenum–oxo interaction is best described as a double bond with little triple bond character (*i.e.* a class *b* oxo complex).[19d,e] (a) Silavwe, N. D.; Chiang, M. Y.; Tyler, D. R. *Inorg. Chem.* **1985**, *24*, 4219–4221. (b) Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899–3903. (c) Green, M. L. H.; Lynch, A. H.; Swanwick, M. G. *J. Chem. Soc. Dalton Trans.* **1972**, 1445–1447. (d) Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391–393. (e) Parkin, G.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 2053–2082.

(20) For discussions on multiple bonding in related imido derivatives see ref 12a and: (a) Parkin, G.; van Asselt, A.; Leahy, D. J.; Whinnery, L.; Hua, N. G.; Quan, R. W.; Henling, L. M.; Schaefer, W. P.; Santarsiero, B. D.; Bercaw, J. E. *Inorg. Chem.* **1992**, *31*, 82–85. (b) Antonelli, D. M.; Schaefer, W. P.; Parkin, G.; Bercaw, J. E. *J. Organomet. Chem.* in press. (c) Jørgensen, K. A. *Inorg. Chem.* **1993**, *32*, 1521–1522. (d) Anhaus, J. T.; Kee, T. P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642–1643. (e) Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H.; Davis, W. M. *Inorg. Chem.* **1991**, *30*, 3595–3604. (f) Glueck, D. S.; Green, J. C.; Michelman, R. I.; Wright, I. N. *Organometallics* **1992**, *11*, 4221–4225.

(21) In addition to the covalent resonance structures of Scheme 1, consideration should also be given to the possibility that the bonding within the zirconium–chalcogenido moiety is best described as predominately ionic, *i.e.* $Zr^{2+}E^{2-}$. However, such a viewpoint would appear to be inappropriate for these complexes since the bond lengths predicted [$d(Zr{=}O)$ = 2.19 Å, $d(Zr{=}S)$ = 2.68 Å, $d(Zr{=}Se)$ = 2.82 Å, and $d(Zr{=}Te)$ = 3.05 Å] from the sums of ionic radii reported by Shannon [$r(Zr^{4+}$,8-coord.) = 0.84 Å, $r(O^{2-})$ = 1.35 Å, $r(S^{2-})$ = 1.84 Å, $r(Se^{2-})$ = 1.98 Å, and $r(Te^{2-})$ = 2.21 Å] are ***all*** substantially longer, by *ca.* 0.3–0.4 Å, than the actual bond lengths. See: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

(22) Pauling, L. *The Nature of The Chemical Bond, 3rd ed.*; Cornell University Press: Ithaca, 1960.

(23) It should be noted that the bonding in R_3PE complexes is best described as a combination of the single bond $P^+—E^-$ and triple bond $P^-{\equiv}E^+$ resonance forms, with a bond order that is accordingly intermediate. The double bond representation P═E is not an appropriate description for the bonding since the π-interactions (*e* symmetry) must occur in a pairwise manner in these complexes. (a) Lucken, E. A. C.; Whitehead, M. A. *J. Chem. Soc.* **1961**, 2459–2463. (b) Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 1922–1930. (c) Schmidt, M. W.; Gordon, M. S. *Can. J. Chem.* **1985**, *63*, 1609–1615. (d) Streitwieser, A., Jr.; Rajca, A.; McDowell, R. S.; Glaser, R. *J. Am. Chem. Soc.* **1987**, *109*, 4184–4188. (e) Molina, P.; Alajarín, M.; Leonardo, C. L.; Claramunt, R. M.; Foces-Foces, M. C.; Cano, F. H.; Catalán, J.; Paz, J. L. G.; Elguero, J. *J. Am. Chem. Soc.* **1989**, *111*, 355–363.

(24) A survey of the Cambridge Crystallographic Database for R_3PE complexes gives the mean bond lengths d(P–O) = 1.487 Å, d(P–S) = 1.960 Å, d(P–Se) = 2.105 Å, d(P–Te) = 2.368 Å.

(25) A similar trend is also observed for carbon–halogen bonds, in which the difference in C–F and C–Cl bond lengths (0.4 Å) is greater than the difference in covalent radii (0.2 Å) of F and Cl.[25a] However, it should be noted that a new value for the covalent radius of F (0.54 Å) has recently been proposed,[25b] and based upon this value the predicted difference in C–F and C–Cl bond lengths is close to the observed difference. (a) Trotter, J. In *The Chemistry of the Carbon–Halogen Bond*; Patai, S., Ed.; Wiley: New York, 1973; Part 1, pp 49–62. (b) Gillespie, R. J.; Robinson, E. A. *Inorg. Chem.* **1992**, *31*, 1960–1963.

(26) $Cp^*{}_2Zr(TeH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$ exhibits limited stability in solution, so far preventing the formation of X-ray quality crystals.

(27) Howard, W. A.; Parkin, G.; Rheingold, A. L. Unpublished results.

(28) Erker, G.; Mühlenbernd, T.; Nolte, R.; Petersen, J. L.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1986**, *314*, C21–C24.

(29) Erker, G.; Nolte, R.; Tainturier, G.; Rheingold, A. *Organometallics* **1989**, *8*, 454–460.

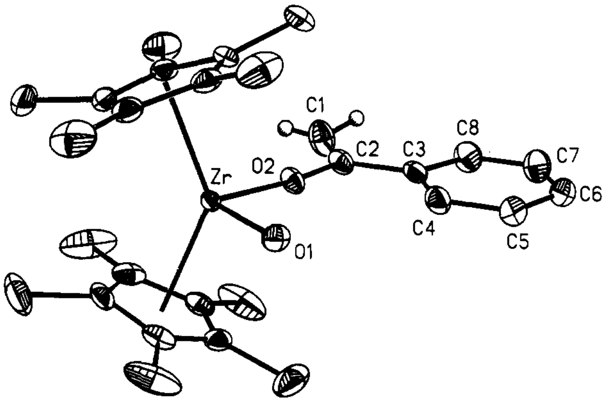

Figure 7. Molecular structure of $Cp^*_2Zr(OH)\{\eta^1\text{-}OC(Ph)=CH_2\}$.

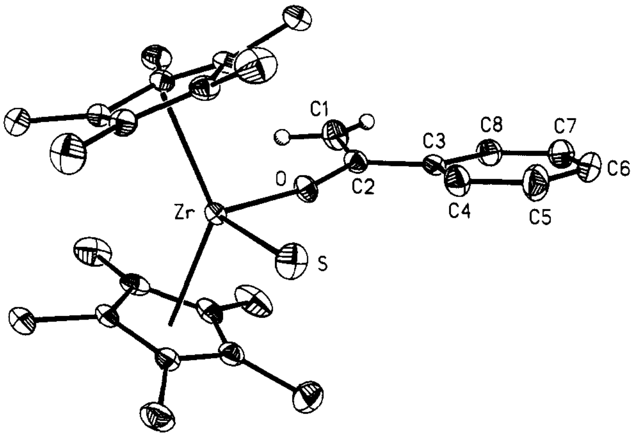

Figure 8. Molecular structure of $Cp^*_2Zr(SH)\{\eta^1\text{-}OC(Ph)=CH_2\}$.

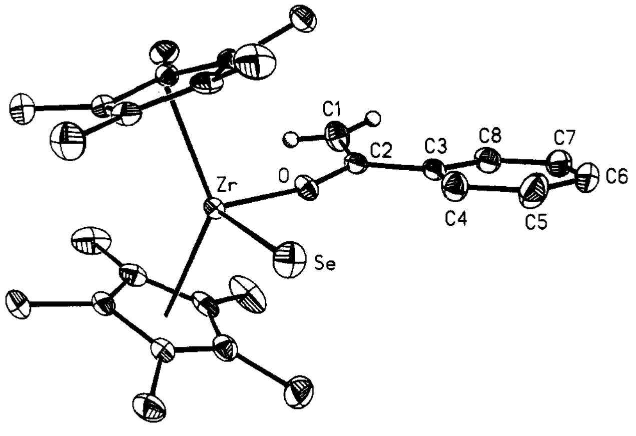

Figure 9. Molecular structure of $CP^*_2Zr(SeH)\{\eta^1\text{-}OC(Ph)=CH_2\}$.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*_2Zr(OH)\{OC(Ph)=CH_2\}$

Zr–O(1)	2.010(2)	Zr–O(2)	1.993(2)
Zr–C(11)	2.557(4)	Zr–C(12)	2.547(4)
Zr–C(13)	2.577(3)	Zr–C(14)	2.555(4)
Zr–C(15)	2.563(3)	Zr–C(31)	2.571(3)
Zr–C(32)	2.557(4)	Zr–C(33)	2.567(4)
Zr–C(34)	2.576(3)	Zr–C(35)	2.549(3)
O(2)–C(2)	1.348(5)	C(1)–C(2)	1.319(6)
C(2)–C(3)	1.477(5)	C(3)–C(4)	1.385(5)
C(3)–C(8)	1.396(6)	C(4)–C(5)	1.389(6)
C(5)–C(6)	1.368(8)	C(6)–C(7)	1.351(10)
C(7)–C(8)	1.377(7)		
O(1)–Zr–O(2)	98.1(1)	Zr–O(2)–C(2)	174.6(2)
O(2)–C(2)–C(1)	121.6(4)	O(2)–C(2)–C(3)	114.8(3)
C(1)–C(2)–C(3)	123.6(4)	C(2)–C(3)–C(4)	121.3(3)
C(2)–C(3)–C(8)	122.1(3)	C(4)–C(3)–C(8)	116.6(3)
C(3)–C(4)–C(5)	121.6(4)	C(4)–C(5)–C(6)	120.1(5)
C(5)–C(6)–C(7)	119.3(4)	C(6)–C(7)–C(8)	121.4(5)
C(3)–C(8)–C(7)	121.0(5)		

Table 8. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*_2Zr(SH)\{OC(Ph)=CH_2\}$

Zr–S	2.535(2)	Zr–O	1.987(3)
Zr–C(11)	2.560(6)	Zr–C(12)	2.585(5)
Zr–C(13)	2.582(5)	Zr–C(14)	2.537(5)
Zr–C(15)	2.552(6)	Zr–C(31)	2.528(5)
Zr–C(32)	2.565(5)	Zr–C(33)	2.580(5)
Zr–C(34)	2.584(6)	Zr–C(35)	2.574(5)
O–C(2)	1.354(6)	C(1)–C(2)	1.319(8)
C(2)–C(3)	1.483(7)	C(3)–C(4)	1.374(8)
C(3)–C(8)	1.404(8)	C(4)–C(5)	1.373(9)
C(5)–C(6)	1.391(10)	C(6)–C(7)	1.363(10)
C(7)–C(8)	1.351(9)		
S–Zr–O	98.4(1)	Zr–O–C(2)	168.8(3)
O–C(2)–C(1)	122.1(5)	O–C(2)–C(3)	114.0(4)
C(1)–C(2)–C(3)	123.9(5)	C(2)–C(3)–C(4)	121.1(5)
C(2)–C(3)–C(8)	121.8(5)	C(4)–C(3)–C(8)	117.1(5)
C(3)–C(4)–C(5)	121.5(6)	C(4)–C(5)–C(6)	120.1(6)
C(5)–C(6)–C(7)	118.6(6)	C(6)–C(7)–C(8)	121.3(6)
C(3)–C(8)–C(7)	121.3(6)		

Table 9. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*_2Zr(SeH)\{OC(Ph)=CH_2\}$

Zr–Se	2.669(1)	Zr–O	2.012(5)
Zr–C(11)	2.578(8)	Zr–C(12)	2.598(7)
Zr–C(13)	2.587(7)	Zr–C(14)	2.534(6)
Zr–C(15)	2.555(7)	Zr–C(31)	2.537(7)
Zr–C(32)	2.552(7)	Zr–C(33)	2.606(7)
Zr–C(34)	2.579(7)	Zr–C(35)	2.582(7)
O–C(2)	1.323(8)	C(1)–C(2)	1.322(11)
C(2)–C(3)	1.497(10)	C(3)–C(4)	1.390(11)
C(3)–C(8)	1.389(11)	C(4)–C(5)	1.390(13)
C(5)–C(6)	1.382(14)	C(6)–C(7)	1.364(15)
C(7)–C(8)	1.361(13)		
Se–Zr–O	98.3(1)	Zr–O–C(2)	168.5(4)
O–C(2)–C(1)	122.4(7)	O–C(2)–C(3)	114.5(6)
C(1)–C(2)–C(3)	123.0(7)	C(2)–C(3)–C(4)	119.8(7)
C(2)–C(3)–C(8)	121.6(7)	C(4)–C(3)–C(8)	118.6(7)
C(3)–C(4)–C(5)	119.1(8)	C(4)–C(5)–C(6)	121.8(9)
C(5)–C(6)–C(7)	117.7(9)	C(6)–C(7)–C(8)	122.1(9)
C(3)–C(8)–C(7)	120.7(8)		

lengths for a series of related $(\eta^5\text{-}C_5R_5)_2Zr(EX)Y$ (E = O, S, Se) derivatives have been obtained and the data are summarized in Table 10.[30]

Examination of Table 10 and Figure 10 reveals that, as expected, each Zr═E double bond is substantially shorter than the corresponding Zr—E single bond, the difference ranging from 0.19 Å for oxygen to 0.15 Å for tellurium. However, it is particularly noteworthy that the relative decrease in the length of the double bond, compared to that of the single bond, is greatest for the oxo derivative (9.6% decrease)[31] and least for the tellurido derivative (5.0% decrease). Such an observation is presumably a reflection of the general abilities of oxygen and tellurium to partake in multiple bonding.[2] For example, the stability of R_3PO contrasts with the marked instability of R_3PTe, which dissociates readily into PR_3 and Te.[32,33]

The difference in Zr—E single and Zr═E double bond lengths may be anticipated to be a reflection of the different single and double bond covalent radii of both the chalcogen and zirconium.[34] The data presented in Figure 10 clearly indicate that the differences in Zr—E and Zr═E bond lengths are consistently greater, by an average of ca. 0.07 Å,[35] than the difference in

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(30) The structural database for the Zr–E single bond lengths is provided in the supplementary material.

(31) For reference, the decrease in bond length between typical C—O single (1.41 Å) and C═O double (1.20 Å) bonds is *ca.* 14.9%. See: March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; p 19.

(32) (a) Zingaro, R. A.; Steeves, B. H.; Irgolic, K. *J. Organomet. Chem.* **1965**, *4*, 320–323. (b) Steigerwald, M. L.; Sprinkle, C. R. *Organometallics* **1988**, *7*, 245–246.

Table 10. Comparison of Zr=E Double and Zr—E Single Bond Lengths

	d(Zr=E)/Å[a]	d(Zr—E)/Å[b]	[d(Zr—E) − d(Zr=E)]/Å	% dec[c]
O	1.804(4)	1.996[32]	0.192	9.6
S	2.334(2)	2.520[11]	0.186	7.4
Se	2.480(1)	2.658[10]	0.178	6.7
Te	2.729(1)	2.874[14]	0.145	5.0

[a] d(Zr=E) for the complexes $\mathrm{Cp^{Et*}_2Zr(E)(NC_5H_5)}$. [b] d(Zr—E) is the average value for a series of complexes $\mathrm{Cp^*_2Zr(EX)Y}$. See supplementary material for the database. The number in parentheses indicates the standard deviation. [c] Percent decrease is defined as 100[d(Zr—E) − d(Zr=E)]/d(Zr—E).

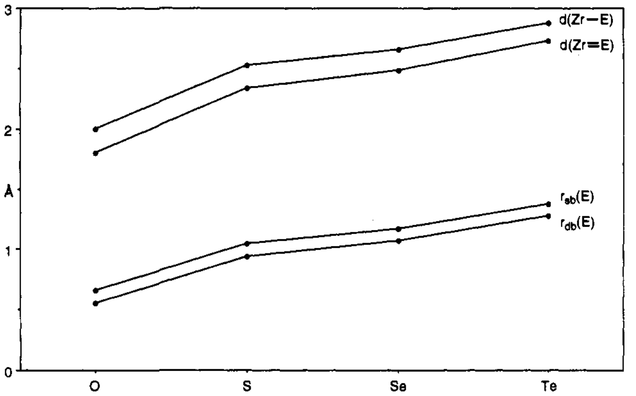

Figure 10. Comparison of Zr—E single and Zr=E double bond lengths.

single and double bond radii for each of the chalcogens. Therefore, the double bond covalent radius of zirconium in these complexes is estimated to be ca. 0.07 Å shorter than its single bond radius.

At this point it is worth emphasizing the importance of considering structurally-related molecules when comparing Zr—E single and Zr=E double bond lengths. For example, although the Zr=Te double bond length in $\mathrm{Cp^{Et*}_2Zr(Te)(NC_5H_5)}$ [2.729(1) Å] compares favorably with that recently reported by Arnold for the first terminal tellurido complex of zirconium, namely $\mathrm{(dmpe)_2Zr(Te)[TeSi(SiMe_3)_3]_2}$ [d(Zr=Te) = 2.650(1) Å],[5b,36] it should be noted that the Zr=Te double bond length in $\mathrm{Cp^{Et*}_2Zr(Te)(NC_5H_5)}$ is also almost identical to those of the formal single bonds [2.724(1)-2.751(1) Å] in $\mathrm{Zr[TeSi(SiMe_3)_3]_4}$.[5b] Clearly, the Zr—TeR bonds in $\mathrm{Zr[TeSi(SiMe_3)_3]_4}$ are foreshortened due to substantial π-donation from Te to the highly Lewis acidic zirconium center, and so are not representative of Zr—Te single bonds.[37] It is, therefore, evident that a *dative*[38] π-bond ($\mathrm{Zr^-{=}Te^+{-}R}$) may be sufficiently strong to shorten a formal Zr—Te single bond [2.724(1)-2.751(1) Å] in $\mathrm{Zr[TeSi(SiMe_3)_3]_4}$ to a value comparable to that for a normal covalent Zr=Te double bond [2.729(1) Å].

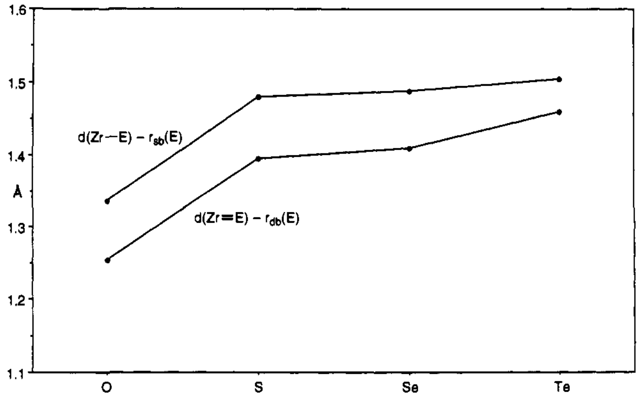

Figure 11. Effective single and double bond covalent radii of Zr in $[(\eta^5\text{-}\mathrm{C_5R_5})_2\mathrm{Zr}]$ complexes.

(iv) Nature of the Zr—E Single and Zr=E Double Bond Interactions. In view of the fact that the difference in Zr=O and Zr=S bond lengths (0.53 Å) is greater than would have been predicted (0.39 Å) on the basis of r_{db}(E), another issue to be considered is concerned with the relative degrees of covalence of the Zr—E and Zr=E interactions. If the Zr—E and Zr=E bond lengths are described well by the sum of two covalent radii, subtraction of the respective single and double bond radii of the chalcogens should provide a consistent set of single and double bond radii of zirconium in these complexes. Indeed, as shown in Figure 11, the single bond covalent radius of zirconium (*ca.* 1.49 Å), as determined by reference to the covalent radii of S, Se, and Te, compares favorably with that proposed by Pauling (1.45 Å).[22] It is also noteworthy that a similar treatment for other $(\eta^5\text{-}\mathrm{C_5R_5})_2\mathrm{Zr(X)Y}$ complexes gives covalent radii of zirconium in a similar range, *ca.* 1.47-1.58 Å.[39] However, this approximation breaks down upon consideration of the Zr—O single bond, for which a covalent radius of 1.34 Å for Zr would be predicted. Thus, the Zr—O single bond lengths in these complexes are approximately 0.11 Å shorter than would have been predicted on the basis of the sum of the covalent radii, whereas the Zr—E single bond lengths for the heavier chalcogens (S, Se, Te) are close (and, in fact, slightly longer) to the sum of the respective covalent radii. Examination of Figure 11 indicates that a similar conclusion would be obtained upon consideration of Zr=E double bond lengths.

Evidently, both Zr—O single and Zr=O double bonds in these complexes are anomalously short. It it likely that this shortening reflects an ionic contribution $\mathrm{Zr^{\delta+}{-}E^{\delta-}}$ which becomes more significant for the more electronegative chalcogen. Indeed, the empirical Schomaker–Stevenson equation would predict a shortening of *ca.* 0.2 Å for a Zr—O bond due to a polar contribution.[40] Thus, in addition to the resonance form Zr=O, it appears that the resonance form $\mathrm{Zr^+{-}O^-}$ also provides an important contribution for the description of the zirconium–oxo interaction in

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[33] Similarly, (i) whereas CO is a stable molecule, CS polymerizes above −160 °C,[33a,b] and (ii) whereas carbonyl derivatives of the transition metals are common, tellurocarbonyl complexes are rare.[33c,d] (a) Broadhurst, P. V. *Polyhedron* **1985**, *4*, 1801–1846. (b) Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 635. (c) Clark, G. R.; Marsden, K.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1988**, *338*, 393–410. (d) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 1206–1207.

[34] Evidence that the covalent radius of zirconium is constant across the series of chalcogenido complexes is provided by the observation that there are only small perturbations in both the Zr-pyridine and $\mathrm{Zr{-}Cp^{Et*}}$ interactions. Thus, the Zr-N and Zr-C bond lengths exhibit the narrow ranges of 2.35–2.37 and 2.59–2.62 Å, respectively, for the series of complexes $\mathrm{Cp^{Et*}_2Zr(E)(NC_5H_5)}$ (E = O, S, Se, Te).

[35] The differences range from 0.045 Å for Te to 0.086 Å for S.

[36] Furthermore, the observation that the Zr=Te bond length in 18-electron $\mathrm{Cp^{Et*}_2Zr(Te)(NC_5H_5)}$ is marginally longer than that in formally 16-electron $\mathrm{(dmpe)_2Zr(Te)[TeSi(SiMe_3)_3]_2}$ also supports the proposal that the interaction in $\mathrm{Cp^{Et*}_2Zr(Te)(NC_5H_5)}$ is best represented as a Zr=Te double bond, with little contribution from the canonical form $\mathrm{Zr^-{\equiv}Te^+}$.

[37] Such an argument closely resembles that described by Caulton to explain the observation that the Ti-Cl bond length in $\mathrm{TiCl_4}$ [2.170(2) Å][37a] is almost 0.2 Å shorter than that in either $(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{TiCl_2}$ [2.364(3) Å][37b] or $(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{TiCl(OEt)}$ [2.405(1) Å].[37c] (a) Morino, Y.; Uehara, H. *J. Chem. Phys.* **1966**, *45*, 4543–4550. (b) Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622–1629. (c) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009–3014.

[38] Haaland, A. *Angew. Chem., Int. Engl.* **1989**, *28*, 992–1007.

[39] For example, extraction of the mean Zr-X bond lengths for a series of ziconocene halide derivatives from the Cambridge Crystallographic Database gives the following estimates for the covalent radius of Zr: Zr–Cl = 2.490[67] Å, r(Cl) = 0.99, and r(Zr) = 1.50 Å; Zr–Br = 2.608[10] Å, r(Br) = 1.14, and r(Zr) = 1.47 Å; Zr–I = 2.914[19] Å, r(I) = 1.33 Å, and r(Zr) = 1.58 Å. Furthermore, the Zr–C bond lengths in $\mathrm{Cp_2ZrMe_2}$ [2.273(5) and 2.280(5) Å] correspond to a covalent radius of r(Zr) = 1.51 Å. See: Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750–755.

[40] It should be noted that the Schomaker–Stevenson equation, $d(\mathrm{A{-}B}) = r(\mathrm{A}) + r(\mathrm{B}) - c|\chi(\mathrm{A}) - \chi(\mathrm{B})|$,[40a] has been both modified by Pauling (reference 22) and criticized.[40b,c] (a) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37–40. (b) Wells, A. F. *J. Chem. Soc.* **1949**, 55–67. (c) Wells, A. F.; *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: London, 1984; pp 287–291.

Table 11. Comparison of Experimental and Calculated Zr=E Bond Lengths

	(Zr=E)/Å	
	expt[a]	calcd[b]
O	1.804(4)	1.76
S	2.334(2)	2.28
Se	2.480(1)	2.42
Te	2.729(1)	2.68

[a] For $\mathrm{Cp^{Et*}{}_2Zr(E)(NC_5H_5)}$. [b] For $[\mathrm{Cp_2ZrE}]$. Cundari, T. R., personal communication.

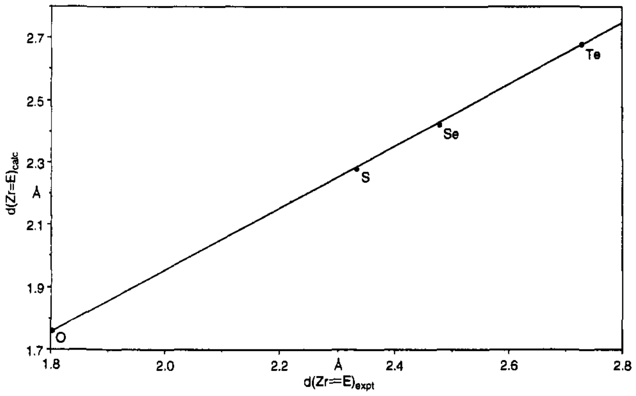

Figure 12. Comparison of calculated and experimental Zr=E double bond lengths.

$\mathrm{Cp^{Et*}{}_2Zr(O)(NC_5H_5)}$. In contrast, for the heavier chalcogens, the lower electronegativity of E, coupled with the longer Zr–E bond length, would result in a lower Coulombic stabilization for the $\mathrm{Zr^+}$–$\mathrm{E^-}$ resonance form.[41] As such, the ionic contribution $\mathrm{Zr^+}$–$\mathrm{E^-}$ would be expected to play a less significant role in describing the zirconium–chalcogenido moiety for the heavier chalcogens.

In support of the above suggestions, Cundari has recently performed effective core potential (ECP) calculations on the hypothetical pyridine-free complexes $[\mathrm{Cp_2Zr{=}E}]$.[42] The data presented in Table 11 show that there is good agreement between ECP results and the experimental data, as found in previous studies of transition metal–ligand multiple bonding.[42] The calculated Zr=E bond lengths are only *ca.* 0.05 Å (2–3%) shorter than those determined experimentally, a difference that may reflect the fact that the computation was actually performed on a pyridine-free complex, and not the pyridine adduct $\mathrm{Cp^{Et*}{}_2Zr(O)(NC_5H_5)}$. Nevertheless, there is excellent agreement between the computational and experiment in terms of the predicted increase in Zr=E bond length as a function of the chalcogen (Figure 12). Thus, the calculated increase in Zr=E bond length between oxo and sulfido derivatives (0.52 Å) is effectively identical to that measured experimentally for $\mathrm{Cp^{Et*}{}_2Zr(E)(NC_5H_5)}$ (0.53 Å). Furthermore, the computational study also supports the notion that the Zr=E interaction is substantially more ionic for oxygen than for the other chalcogens.[42] Analysis of localized orbitals for $[\mathrm{Cp_2Zr{=}E}]$ shows that the orbitals in the Zr=E bonding region are more polarized toward the chalcogenido ligand for oxygen than for the heavier chalcogens, suggesting a greater contribution from the ionic structure $\mathrm{Zr^+}$—$\mathrm{E^-}$ for E = O, and a greater contribution from the covalent structure Zr=E for E = S, Se, and Te.

How general is the above discussion of multiple bonding in transition metal–chalcogenido complexes? The complexes that have been studied in this paper are all rather rare examples of terminal chalcogenido complexes in which the configuration of the metal centers is 18-electron in the absence of lone-pair donation from the chalcogen. As such, the importance of the $\mathrm{M^-{\equiv}E^+}$ resonance structure is diminished for these complexes. In contrast, for complexes with formally ≤16-electron metal centers, a more significant role would be expected for the resonance structure $\mathrm{M^-{\equiv}E^+}$, with a formal charge distribution that would serve to counter that of the resonance structure $\mathrm{M^+}$—$\mathrm{E^-}$. Since the resonance structure $\mathrm{M^+}$—$\mathrm{E^-}$ is most important for the more electronegative oxo derivative, it would seem likely that the influence of the resonance structure $\mathrm{M^-{\equiv}E^+}$ would be manifested most in differences between metal–oxo and metal–sulfido bond lengths. It is, therefore, noteworthy that for the electronically unsaturated tungsten complexes $\mathrm{W(E)X_4}$ (E = O, S, Se; X = F, Cl, Br),[43] the average increase in W=O and W=S bond lengths (*ca.* 0.42 Å) is less than that for the oxo and sulfido zirconium complexes $\mathrm{Cp^{Et*}{}_2Zr(E)(NC_5H_5)}$ (0.53 Å). However, we cannot at present identify that such a structural difference is indeed only a consequence of the ≤16-electron *versus* 18-electron nature of the metal centers in these complexes.

Accordingly, further structural and reactivity studies of isostructural terminal chalcogenido derivatives are warranted, in order to provide a more comprehensive understanding of both the electronic structure and reactivity of metal–chalcogen multiple bonds.

Conclusion

In summary, the two series of chalcogenido and hydrochalcogenido complexes $\mathrm{Cp^{\dagger}{}_2Zr(E)(NC_5H_5)}$ and $\mathrm{Cp^*{}_2Zr(EH)}\{\eta^1\text{-}\mathrm{OC(Ph){=}CH_2}\}$ (E = O, S, Se, Te) have been prepared. X-ray structure determinations on the complexes $\mathrm{Cp^{Et*}{}_2Zr(E)(NC_5H_5)}$ have provided the first comparison of M—E single and M=E double bond lengths for the complete series of chalcogens, demonstrating that the relative difference between M—E single and M=E double bonds decreases in the order O > S > Se > Te, a sequence that correlates with the general tendency of the chalcogen to engage in multiple bonding. A consideration of the difference in M—E single and M=E double bonds, with respect to the difference in single and double bond covalent radii of the chalcogens, leads to the conclusion that the double bond covalent radius of zirconium in the $[(\eta^5\text{-}\mathrm{C_5R_5})_2\mathrm{Zr}]$ system is *ca.* 0.07 Å shorter than its single bond covalent radius. For the heavier chalcogens (S, Se, and Te), the Zr—E single and Zr=E double bond lengths are predicted reasonably well on the basis of the sum of the covalent radii of Zr and E. In contrast, both the Zr—O single and double bond lengths are anomalously short, a result that is consistent with a considerable ionic contribution. As such, the resonance form $\mathrm{Zr^+}$—$\mathrm{O^-}$ is suggested to provide an important contribution for the description of the zirconium–oxo interaction in $\mathrm{Cp^{Et*}{}_2Zr(O)(NC_5H_5)}$, *i.e.* Zr=O ↔ $\mathrm{Zr^+}$—$\mathrm{O^-}$, whereas for the less electronegative heavier chalcogens (S, Se, and Te), the resonance form $\mathrm{Zr^+}$—$\mathrm{E^-}$ is considered to play a less significant role in describing the bonding within the zirconium—chalcogenido moiety.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, or Schlenk techniques.[44] Solvents were purified and degassed by standard procedures. ^{1}H and ^{13}C NMR spectra were measured on Varian VXR 200, 300, and 400 spectrometers.

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(41) These arguments bear some relation to the discussion of the bonding in the PO moiety in $\mathrm{R_3PO}$. See ref 23d.

(42) Cundari, T. R. (Chemistry, Memphis State University), personal communication. Methods used in the calculation of multiply bonded chalcogenides are as described in Cundari, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 7879–7888 and references therein. The good agreement between the ECP results and the experimental data bodes well for the prediction of transition metal–chalcogen multiple bond lengths in other systems. T.R.C. acknowledges the San Diego Supercomputer Center, the Cornell National Supercomputer Facility, and the Joint Institute for Computational Science for these calculations.

(43) Average bond lengths: *d*(W=O) = 1.678[12] Å, *d*(W=S) = 2.100[14] Å, *d*(W=Se) = 2.216[13] Å. See: Page, E. M.; Rice, D. A.; Hagen, K.; Hedberg, L.; Hedberg, K. *Inorg. Chem.* **1991**, *30*, 4758–4761.

(44) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. *A.C.S. Symp. Ser.* **1987**, *357*, 6–23. (b) Burger, B. J.; Bercaw, J. E. *A.C.S. Symp. Ser.* **1987**, *357*, 79–97.

All *J* values are given in hertz. IR spectra were recorded as KBr pellets on a Perkin-Elmer 1600 FTIR spectrophotometer and the data are reported in reciprocal centimeters. Mass spectra were obtained on a Nermag R10-10 mass spectrometer using chemical ionization ($\mathrm{NH_3}$ or $\mathrm{CH_4}$) techniques. Elemental analyses were measured using a Perkin-Elmer 2400 CHN elemental analyzer. $\mathrm{Cp^{*}{}_2Zr(S)(NC_5H_5)}$ was prepared as reported previously.[13] $\mathrm{Cp^{Et*}{}_2ZrCl_2}$ was prepared by a method analogous to that used for $\mathrm{Cp^{*}{}_2ZrCl_2}$.[45] $\mathrm{Cp^{*}{}_2Zr(E)(NC_5H_5)}$ (E = O, Se, Te) were prepared by methods analogous to those described below for $\mathrm{Cp^{Et*}{}_2Zr(E)(NC_5H_5)}$, and will be reported fully in a future publication.[14]

Synthesis of $\mathrm{Cp^{Et*}{}_2Zr(CO)_2}$. A mixture of $\mathrm{Cp^{Et*}{}_2ZrCl_2}$ (2.00 g, 4.34 mmol) and Mg powder (0.55 g, 22.6 mmol) in THF (30 mL) at –78 °C was treated with $\mathrm{HgCl_2}$ (*ca.* 10 mg) and CO (1 atm.). The mixture was stirred as it was allowed to warm to room temperature. After *ca.* 5 h the reaction mixture became dark (almost black). The solvent was removed under reduced pressure after 1 day, and the product was extracted into pentane until the extracts were almost colorless. The combined extracts were passed through a column (*ca.* 7 cm) of deactivated (5%) alumina, concentrated, and cooled to –78 °C, depositing $\mathrm{Cp^{Et*}{}_2Zr(CO)_2}$ as black needles. The $\mathrm{Cp^{Et*}{}_2Zr(CO)_2}$ was isolated by filtration and dried *in vacuo* (1.70 g, 87%). Anal. Calcd for $\mathrm{Cp^{Et*}{}_2Zr(CO)_2}$: C, 64.7%; H, 7.7%. Found: C, 64.9%; H, 7.8%. MS: *m/z* 444 (M). IR data: 2962 (vs), 1928 (vs) [ν(CO)], 1826 (vs) [ν(CO)], 1456 (s), 1379 (m), 1085 (m), 1027 (m), 964 (w), 715 (w). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.72 & 1.78 [12H each, s, $2\{\eta^5\text{-}\mathrm{C_5(C\mathit{H}_3)_4CH_2CH_3}\}$], 2.17 [4H, q, $^3J_{\mathrm{H}}$ = 7, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4C\mathit{H}_2CH_3}\}$], 0.91 [6H, t, $^3J_{\mathrm{H-H}}$ = 7, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C\mathit{H}_3}\}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): δ 10.8 & 11.0 [4C each, q, $^1J_{\mathrm{C-H}}$ = 126, $2\{\eta^5\text{-}\mathrm{C_5(\mathit{C}H_3)_4CH_2CH_3}\}$], 105.5, [4C, s, $2\{\eta^5\text{-}\mathrm{\mathit{C}_5(CH_3)_4CH_2CH_3}\}$], 106.6 [4C, s, $2\{\eta^5\text{-}\mathrm{\mathit{C}_5(CH_3)_4CH_2CH_3}\}$], 112.3 [2C, s, $2\{\eta^5\text{-}\mathrm{\mathit{C}_5(CH_3)_4CH_2CH_3}\}$], 19.8 [2C, t, $^1J_{\mathrm{C-H}}$ = 127, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4\mathit{C}H_2CH_3}\}$], 16.1 [2C, q, $^1J_{\mathrm{C-H}}$ = 125, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2\mathit{C}H_3}\}$], 273.1 [2C, s, $\mathrm{Zr(\mathit{C}O)_2}$].

Synthesis of $\mathrm{Cp^{Et*}{}_2Zr(O)(NC_5H_5)}$. A mixture of $\mathrm{Cp^{Et*}{}_2Zr(CO)_2}$ (1.01 g, 2.3 mmol) and excess pyridine (*ca.* 2 mL) in toluene (*ca.* 10 mL) was treated with $\mathrm{N_2O}$ and stirred at 85 °C for *ca.* 12 h. The volatile components were removed under reduced pressure and the product was washed with pentane giving $\mathrm{Cp^{Et*}{}_2Zr(O)(NC_5H_5)}$ as a pink solid, which was dried *in vacuo* (0.36 g, 33%). Anal. Calcd for $(\eta^5\text{-}\mathrm{C_5Me_4Et})_2\mathrm{Zr(O)(NC_5H_5)}$: C, 66.9%; H, 8.1%; N, 2.9%. Found: C, 66.1%; H, 8.1%; N, 2.6%. MS: *m/z* 484 ($\mathrm{M^+}$ + 1). IR data: 3055 (m), 2883 (vs), 1598 (m), 1448 (vs), 1372 (s), 1210 (m), 1164 (w), 1048 (s), 951 (w), 830 (w), 773 (vs) [ν(Zr═O)], 711 (s), 633 (m), 527 (w). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.92, 1.93, 1.97 & 2.01 [6H each, s, $2\{\eta^5\text{-}\mathrm{C_5(C\mathit{H}_3)_4CH_2CH_3}\}$], 2.26 [4H, q, $^3J_{\mathrm{H-H}}$ = 7, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4C\mathit{H}_2CH_3}\}$], 1.04 [6H, t, $^3J_{\mathrm{H-H}}$ = 7, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C\mathit{H}_3}\}$], 6.46 [2H, m, $\mathrm{NC_5\mathit{H}_5}$], 6.76 [1H, m, $\mathrm{NC_5\mathit{H}_5}$], 7.55 [1H, m, $\mathrm{NC_5\mathit{H}_5}$], 9.22 [1H, m, $\mathrm{NC_5\mathit{H}_5}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): δ 11.4 [4C, q, $^1J_{\mathrm{C-H}}$ = 126, $2\{\eta^5\text{-}\mathrm{C_5(\mathit{C}H_3)_4CH_2CH_3}\}$], 11.5 [4C, q, $^1J_{\mathrm{C-H}}$ = 126, $2\{\eta^5\text{-}\mathrm{C_5(\mathit{C}H_3)_4CH_2CH_3}\}$], 115.3, 115.9, 116.4, 116.5, 121.6 [2C each, s, $2\{\eta^5\text{-}\mathrm{\mathit{C}_5(CH_3)_4CH_2CH_3}\}$], 20.0 [2C, t, $^1J_{\mathrm{C-H}}$ = 126, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4\mathit{C}H_2CH_3}\}$], 15.4 [2C, q, $^1J_{\mathrm{C-H}}$ = 126, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2\mathit{C}H_3}\}$], 122.9 [1C, d, $^1J_{\mathrm{C-H}}$ = 166, $\mathrm{N\mathit{C}_5H_5}$], 124.8 [1C, d, $^1J_{\mathrm{C-H}}$ = 166, $\mathrm{N\mathit{C}_5H_5}$], 137. 7 [1C, d, $^1J_{\mathrm{C-H}}$ = 162, $\mathrm{N\mathit{C}_5H_5}$], 148.8 [1C, d, $^1J_{\mathrm{C-H}}$ = 180, $\mathrm{N\mathit{C}_5H_5}$], 158.1 [1C, d, $^1J_{\mathrm{C-H}}$ = 185, $\mathrm{N\mathit{C}_5H_5}$].

Synthesis of $\mathrm{Cp^{Et*}{}_2Zr(S)(NC_5H_5)}$. A mixture of $\mathrm{Cp^{Et*}{}_2Zr(CO)_2}$ (0.51 g, 1.1 mmol), $\mathrm{S_8}$ (0.024 g, 0.09 mmol), and excess pyridine (*ca.* 1.6 mL) in toluene (*ca.* 5 mL) was stirred at 85 °C for *ca.* 12 h. The volatile components were removed under reduced pressure and the product was washed with pentane giving $\mathrm{Cp^{Et*}{}_2Zr(S)(NC_5H_5)}$ as a bright orange solid, which was dried *in vacuo* (0.13 g, 35% based on sulfur). Anal. Calcd for $\mathrm{Cp^{Et*}{}_2Zr(S)(NC_5H_5)}$: C, 64.7%; H, 7.9%; N, 2.8%. Found: C, 64.7%; H, 7.7%; N, 3.7%. IR data: 3054 (m), 2963 (vs), 1599 (m), 1439 (vs), 1372 (s), 1210 (s), 1150 (w), 1064 (m), 965 (w), 761 (m), 709 (m), 413 (s). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.89, 1.96, 2.02 & 2.06 [6H each, s $2\{\eta^5\text{-}\mathrm{C_5(C\mathit{H}_3)_4CH_2CH_3}\}$], 2.33 [4H, q, $^3J_{\mathrm{H-H}}$ = 7, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4C\mathit{H}_2CH_3}\}$], 1.02 [6H, t, $^3J_{\mathrm{H-H}}$ = 7, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C\mathit{H}_3}\}$], 6.20, 6.30, 6.62, 7.23 & 9.45 [1H each, m, $\mathrm{NC_5\mathit{H}_5}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): δ 12.57 (2C), 12.63 (2C), 12.7 (4C) [q, $^1J_{\mathrm{C-H}}$ = 126, $2\{\eta^5\text{-}\mathrm{C_5(\mathit{C}H_3)_4CH_2CH_3}\}$], 117.8 (2C), 118.2 (2C) 118.81 (2C), 118.84 (2C), 124.2 (2C) [s, $2\{\eta^5\text{-}\mathrm{\mathit{C}_5(CH_3)_4CH_2CH_3}\}$], 21.1 [2C, t, $^1J_{\mathrm{C-H}}$ = 127, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4\mathit{C}H_2CH_3}\}$], 15.0 [2C, q, $^1J_{\mathrm{C-H}}$ = 126, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2\mathit{C}H_3}\}$], 122.2 [1C, d, $^1J_{\mathrm{C-H}}$ = 166, $\mathrm{N\mathit{C}_5H_5}$], 124.1 [1C, d, $^1J_{\mathrm{C-H}}$ = 168, $\mathrm{N\mathit{C}_5H_5}$], 137.4 [1C, d, $^1J_{\mathrm{C-H}}$ = 165, $\mathrm{N\mathit{C}_5H_5}$], 148.5 [1C, d, $^1J_{\mathrm{C-H}}$ = 180, $\mathrm{N\mathit{C}_5H_5}$], 162.0, [1C, d, $^1J_{\mathrm{C-H}}$ = 190, $\mathrm{N\mathit{C}_5H_5}$].

Synthesis of $\mathrm{Cp^{Et*}{}_2Zr(Se)(NC_5H_5)}$. A mixture of $\mathrm{Cp^{Et*}{}_2Zr(CO)_2}$ (0.45 g, 1.0 mmol), Se powder (0.072 g, 0.91 mmol), and excess pyridine (*ca.* 1.6 mL) of toluene (*ca.* 5 mL) was stirred at 85 °C for *ca.* 12 h. The volatile components were removed under reduced pressure and the product was washed with pentane giving $\mathrm{Cp^{Et*}{}_2Zr(Se)(NC_5H_5)}$ as a brown-green solid, which was dried *in vacuo* (0.32 g, 65% based on Se). Anal. Calcd for $\mathrm{Cp^{Et*}{}_2Zr(Se)(NC_5H_5)}$: C, 59.2%; H, 7.2%; N, 2.6%. Found: C, 59.0; H, 7.0%; N, 2.7%. IR data: 2897 (vs), 1599 (m), 1440 (vs), 1368 (s), 1207 (s), 1024 (s), 762 (m), 711 (s), 456 (w). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.88, 1.96, 2.02 & 2.06 [6H each, s, $2\{\eta^5\text{-}\mathrm{C_5(C\mathit{H}_3)_4CH_2CH_3}\}$], 2.36 [4H, q, $^3J_{\mathrm{H-H}}$ = 7, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4C\mathit{H}_2CH_3}\}$], 1.02 [6H, t, $^3J_{\mathrm{H-H}}$ = 7, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C\mathit{H}_3}\}$], 6.16, 6.27, 6.61, 7.15 & 9.40 [1H, each, m, $\mathrm{NC_5\mathit{H}_5}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): δ 13.0 (2C), 13.2 (2C), 13.28 (2C), 13.34 (2C) [q, $2\{\eta^5\text{-}\mathrm{C_5(\mathit{C}H_3)_4CH_2CH_3}\}$], 118.3 (2C), 118.7 (2C), 119.2 (2C), 119.3 (2C), 124.9 (2C) [s, $2\{\eta^5\text{-}\mathrm{\mathit{C}_5(CH_3)_4CH_2CH_3}\}$], 21.7 [2C, t, $^1J_{\mathrm{C-H}}$ = 127, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4\mathit{C}H_2CH_3}\}$], 14.8 [2C, q, $^1J_{\mathrm{C-H}}$ = 126, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2\mathit{C}H_3}\}$], 121.7 [1C, d, $\mathrm{N\mathit{C}_5H_5}$], 123.4 [1C, d, $\mathrm{N\mathit{C}_5H_5}$], 137.3 [1C, d, $\mathrm{N\mathit{C}_5H_5}$], 147.5 [1C, d, $\mathrm{N\mathit{C}_5H_5}$], 162.6 [1C, d, $\mathrm{N\mathit{C}\ 5H_5}$].

Synthesis of $\mathrm{Cp^{Et*}{}_2Zr(Te)(NC_5H_5)}$. A mixture of $\mathrm{Cp^{Et*}{}_2Zr(CO)_2}$ (0.50 g, 1.1 mmol), Te powder (0.125 g, 1.0 mmol), and excess pyridine (*ca.* 1.6 mL) in toluene (*ca.* 4 mL) was stirred at *ca.* 85 °C for 2 days. The volatile components were removed under reduced pressure and the product was washed with pentane giving $\mathrm{Cp^{Et*}{}_2Zr(Te)(NC_5H_5)}$ as a brick-red solid, which was dired *in vacuo* (0.34 g, 57% based on Te). Anal. Calcd for $\mathrm{Cp^{Et*}{}_2Zr(Te)(NC_5H_5)}$: C, 54.4%; H, 6.6%; N, 2.4%. Found: C, 54.1%; H. 6.5%; N, 2.5%. IR data: 2895 (vs), 1598 (m), 1438 (vs), 1371 (s), 1207 (s), 1023 (s), 762 (m), 709 (s). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.84, 1.95, 2.03 & 2.07 [6H each, s, $2\{\eta^5\text{-}\mathrm{C_5(C\mathit{H}_3)_4CH_2CH_3}\}$], 2.41 [4H, q, $^3J_{\mathrm{H-H}}$ = 7, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4C\mathit{H}_2CH_3}\}$], 1.03 [6H, t, $^3J_{\mathrm{H-H}}$ = 7, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2C\mathit{H}_3}\}$], 6.07, 6.19, 6.57, 6.96 & 9.27 [1H each, m, $\mathrm{NC_5\mathit{H}_5}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): δ 14.5 (4C), 14.7 (4C) [q, $2\{\eta^5\text{-}\mathrm{C_5(\mathit{C}H_3)_4CH_2CH_3}\}$], 23.4 [2C, t, $^1J_{\mathrm{C-H}}$ = 126, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4\mathit{C}H_2CH_3}\}$], 14.9 [2C, q, $^1J_{\mathrm{C-H}}$ = 126, $2\{\eta^5\text{-}\mathrm{C_5(CH_3)_4CH_2\mathit{C}H_3}\}$], 121.0 [1C, d, $\mathrm{N\mathit{C}_5H_5}$], 122.1 [1C, d, $\mathrm{N\mathit{C}_5H_5}$], 137.6 [1C, d, $\mathrm{N\mathit{C}_5H_5}$], 145.5 [1C, d, $\mathrm{N\mathit{C}_5H_5}$], 162.4 [1C, d, $\mathrm{N\mathit{C}_5H_5}$] (insufficient signal-to-noise ratio to be able to determine accurately the $\mathrm{C_5(CH_3)_4CH_2CH_3}$ resonances).

Synthesis of $\mathrm{Cp^{*}{}_2Zr(OH)\{\eta^1\text{-}OC(Ph){=}CH_2\}}$. A solution of $\mathrm{Cp^{*}{}_2Zr(O)(NC_5H_5)}$ (0.22 g, 0.50 mmol) in toluene (*ca.* 4 mL) was treated with PhC(O)Me (57 μL, 0.49 mmol). The mixture was stirred at room temperature for 3 h, after which period the volatile components were removed under reduced pressure. The residue was washed with pentane (*ca.* 1 mL) giving $\mathrm{Cp^{*}{}_2Zr(OH)\{\eta^1\text{-}OC(Ph){=}CH_2\}}$ as an orange solid which was dried *in vacuo* (0.15 g, 62%). Anal. Calcd for $\mathrm{Cp^{*}{}_2Zr(OH)\{\eta^1\text{-}OC(Ph){=}CH_2\}}$: C, 67.6%; H, 7.7%. Found: C, 67.5%; H, 7.8%. MS: *m/z* 497 ($\mathrm{M^+}$ + 1). IR data: 3672 (s) [ν(O—H)], 3118 (w), 3057 (m), 2905 (vs), 2724 (w), 1616 (s) [ν(C═C)], 1556 (s), 1492 (s), 1442 (s), 1375 (s), 1295 (vs), 1184 (w), 1115 (s), 1080 (m), 1024, (s), 767 (s), 702 (s), 628 (w), 588 (w), 536 (s). ^{1}H NMR ($\mathrm{C_6D_6}$): 1.85 [30H, s, $2\{\eta^5\text{-}\mathrm{C_5(C\mathit{H}_3)_5}\}$], 4.57 [1H, s, $\mathrm{O\mathit{H}}$], 4.40 [1H, s, $\eta^1\text{-}\mathrm{OC(Ph){=}C\mathit{H}_2}$], 4.87 [1H, s, $\eta^1\text{-}\mathrm{OC(Ph){=}C\mathit{H}_2}$], 7.15 [1H, m, $\eta^1\text{-}\mathrm{OC(C_6\mathit{H}_5){=}CH_2}$], 7.28 [2H, m, $\eta^1\text{-}\mathrm{OC(C_6\mathit{H}_5){=}CH_2}$], 7.86 [2H, m, $\eta^1\text{-}\mathrm{OC(C_6\mathit{H}_5){=}CH_2}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): 11.0 [10C, q, $^1J_{\mathrm{C-H}}$ = 126, $2\{\eta^5\text{-}\mathrm{C_5(\mathit{C}H_3)_5}\}$], 120.0 [10C, s, $2\{\eta^5\text{-}\mathrm{\mathit{C}_5(CH_3)_5}\}$], 85.6 [1C, t, $^1J_{\mathrm{C-H}}$ = 157, $\eta^1\text{-}\mathrm{OC(C_6H_5){=}\mathit{C}H_2}$], 162.2 [1C, s, $\eta^1\text{-}\mathrm{O\mathit{C}(C_6H_5){=}CH_2}$], 125.9 [2C, d, $^1J_{\mathrm{C-H}}$ = 158, $\eta^1\text{-}\mathrm{OC(\mathit{C}_6H_5){=}CH_2}$], 127.5 [2C, d, $^1J_{\mathrm{C-H}}$ = 159, $\eta^1\text{-}\mathrm{OC(\mathit{C}_6H_5){=}CH_2}$], 141.3 [1C, s, $\eta^1\text{-}\mathrm{OC(\mathit{C}_6H_5){=}CH_2}$] (insufficient signal-to-noise ratio to be able to determine accurately the $\mathrm{\mathit{C}_6H_5}$ resonances).

Synthesis of $\mathrm{Cp^{*}{}_2Zr(SH)\{\eta^1\text{-}OC(Ph){=}CH_2\}}$. A solution of $\mathrm{Cp^{*}{}_2Zr(S)(NC_5H_5)}$ (0.21 g, 0.44 mmol) in toluene (*ca.* 4 mL) was treated with PhC(O)Me (52 μL, 0.44 mmol). The mixture was stirred at room temperature for 1 day, after which period the volatile components were removed under reduced pressure. The residue was washed with pentane (*ca.* 1 mL) giving $\mathrm{Cp^{*}{}_2Zr(SH)\{\eta^1\text{-}OC(Ph){=}CH_2\}}$ as a pale yellow solid which dried *in vacuo* (0.17 g, 74%). Anal. Calcd for $\mathrm{Cp^{*}{}_2Zr(SH)\{\eta^1\text{-}OC(Ph){=}CH_2\}}$: C, 65.4%; H, 7.5%. Found: C, 64.9%; H, 7.2%. IR data: 3118 (w), 3057 (m), 2979 (s), 2946 (s), 2904 (vs), 2725 (w), 2596 (w) [ν(S—H)], 1614 (s) [ν(C═C)], 1551 (s), 1490 (s), 1442 (s), 1376 (s), 1298 (vs), 1182, (w), 1114 (vs), 1078 (m), 1019 (vs), 769 (s), 703 (m), 676 (w), 588 (w), 560 (m). ^{1}H NMR ($\mathrm{C_6D_6}$): 1.84 [30H, s, $2\{\eta^5\text{-}\mathrm{C_5(C\mathit{H}_3)_5}\}$], 1.50 [1H, s, $\mathrm{S\mathit{H}}$], 4.38 [1H, s, $\eta^1\text{-}\mathrm{OC(Ph){=}C\mathit{H}_2}$], 4.81 [1H, s, $\eta^1\text{-}\mathrm{OC(Ph){=}C\mathit{H}_2}$], 7.11 [1H, m, $\eta^1\text{-}\mathrm{OC(C_6\mathit{H}_5){=}CH_2}$], 7.26 [2H, m, $\eta^1\text{-}\mathrm{OC(C_6\mathit{H}_5){=}CH_2}$], 7.83 [2H, m, $\eta^1\text{-}\mathrm{OC(C_6\mathit{H}_5){=}CH_2}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): 11.7 [10C, q, $^1J_{\mathrm{C-H}}$ = 127, $2\{\eta^5\text{-}\mathrm{C_5(\mathit{C}H_3)_5}\}$], 120.8 [10C, s, $2\{\eta^5\text{-}\mathrm{\mathit{C}_5(CH_3)_5}\}$], 87.0 [1C, t, $^1J_{\mathrm{C-H}}$ = 157, $\eta^1\text{-}\mathrm{OC(C_6H_5){=}\mathit{C}H_2}$], 162.5 [1C, s, $\eta^1\text{-}\mathrm{O\mathit{C}(C_6H_5){=}CH_2}$], 126.2 [2C, d, $^1J_{\mathrm{C-H}}$ = 158, $\eta^1\text{-}\mathrm{OC(\mathit{C}_6H_5){=}CH_2}$], 127.8 [1C, d, $^1J_{\mathrm{C-H}}$ = 160, η^1-OC-

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(45) Manriquez, J. M.; McAlister, D. R.; Rosenburg, E.; Shiller, A. M.; Williamson, K. L.; Chan, S. I.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3078–3083.

Table 12. Crystal and Intensity Collection Data for $Cp^{Et*}{}_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te)

	$Cp^{Et*}{}_2Zr(O)(NC_5H_5)$	$Cp^{Et*}{}_2Zr(S)(NC_5H_5)$	$Cp^{Et*}{}_2Zr(Se)(NC_5H_5)$	$Cp^{Et*}{}_2Zr(Te)(NC_5H_5)$
formula	$C_{27}H_{39}NOZr$	$C_{27}H_{39}NSZr$	$C_{27}H_{39}NSeZr$	$C_{27}H_{39}NTeZr$
formula weight	484.8	500.9	547.8	596.4
lattice	orthorhombic	monoclinic	monoclinic	monoclinic
cell constants				
a, Å	9.681(3)	8.414(2)	8.439(1)	8.643(2)
b, Å	14.124(3)	19.760(5)	19.782(4)	19.759(7)
c, Å	18.134(3)	15.305(2)	15.317(3)	15.301(4)
α, deg	90.0	90.0	90.0	90.0
β, deg	90.0	90.91(1)	90.11(1)	90.78(2)
γ, deg	90.0	90.0	90.0	90.0
V, Å^3	2480(1)	2544(1)	2557(1)	2613(1)
Z	4	4	4	4
radiation, (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
space group	*Pc*2$_1$*n* (No. 33)	*P*2$_1$/*n* (No. 14)	*P*2$_1$/*n* (No. 14)	*P*2$_1$/*n* (No. 14)
ρ(calcd), g cm^{-3}	1.30	1.31	1.43	1.52
μ(Mo Kα), cm^{-1}	4.6	5.2	19.7	15.6
goodness of fit	1.152	1.223	1.093	1.489
R	0.0382	0.0412	0.0411	0.0287
$R_w{}^a$	0.0396	0.0454	0.0481	0.0410

^{a} Weighting scheme: $w = [\sigma^2(F) + gF^2]^{-1}$.

Table 13. Crystal and Intensity Collection Data for $Cp^*{}_2Zr(EH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$ (E = O, S, Se)

	$Cp^*{}_2Zr(OH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$	$Cp^*{}_2Zr(SH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$	$Cp^*{}_2Zr(SeH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$
formula	$C_{28}H_{38}O_2Zr$	$C_{28}H_{38}OSZr$	$C_{28}H_{38}OSeZr$
formula weight	497.8	513.9	560.8
lattice	monoclinic	orthorhombic	orthorhombic
cell constants			
a, Å	14.806(2)	9.658(3)	9.684(2)
b, Å	9.725(2)	14.845(5)	14.944(4)
c, Å	18.152(2)	18.090(6)	18.157(3)
α, deg	90.0	90.0	90.0
β, deg	102.35(1)	90.0	90.0
γ, deg	90.0	90.0	90.0
V, Å^3	2553(1)	2594(1)	2628(1)
Z	4	4	4
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
space group	*P*2$_1$/*c* (No. 14)	*P*2$_1$2$_1$2$_1$ (No. 19)	*P*2$_1$2$_1$2$_1$ (No. 19)
ρ(calcd), g cm^{-3}	1.30	1.32	1.41
μ(Mo Kα), cm^{-1}	4.5	5.1	19.2
goodness of fit	1.334	1.124	1.022
R	0.0342	0.0314	0.0353
$R_w{}^a$	0.0484	0.0383	0.0427

^{a} Weighting scheme: $w = [\sigma^2(F) + gF^2]^{-1}$.

$(C_6H_5){=}CH_2]$, 128.0 [2C, d, $^1J_{C-H} = 158$, η^1-$OC(C_6H_5){=}CH_2]$, 140.5 [1C, s, η^1-$OC(C_6H_5){=}CH_2]$.

Synthesis of $Cp^*{}_2Zr(SeH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$. A solution of $Cp^*{}_2Zr(Se)(NC_5H_5)$ (0.26 g, 0.49 mmol) in toluene (*ca.* 4 mL) was treated with PhC(O)Me (60 μL, 0.51 mmol). The mixture was stirred at room temperature for 1 day, after which period the volatile components were removed under reduced pressure. The residue was washed with pentane (*ca.* 1 mL) giving $Cp^*{}_2Zr(SeH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$ as a white solid which was dried *in vacuo* (0.18 g, 61%). Anal. Calcd for $Cp^*{}_2Zr(SeH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$: C, 60.0%; H, 6.8%. Found: C, 60.0%; H, 6.8%. IR data: 3118 (w), 3057 (m), 2979 (s), 2946 (s), 2905 (vs), 2725 (w), 2329 (m) [ν(Se—H)], 1615 (s) [ν(C=C)], 1552 (s), 1490 (s), 1444 (s), 1376 (s), 1307 (vs), 1182 (w), 1113 (vs), 1078 (m), 1018 (vs), 770 (s), 703 (m), 676 (w), 588 (w), 561 (m). ^{1}H NMR (C_6D_6): 1.85 [30H, s, 2$\{\eta^5$-$C_5(CH_3)_5\}]$, −1.05 [1H, s, $^1J_{Se-H} = 33$, Se*H*], 4.40 [1H, s, η^1-$OC(Ph){=}CH_2]$, 4.79 [1H, s, η^1-$OC(Ph){=}CH_2]$, 7.11 [1H, m, η^1-$OC(C_6H_5){=}CH_2]$, 7.26 [2H, m, η^1-$OC(C_6H_5){=}CH_2]$, 7.82 [2H, m, η^1-$OC(C_6H_5){=}CH_2]$. ^{13}C NMR (C_6D_6): 12.0 [10C, q, $^1J_{C-H} = 127$, 2$\{\eta^5$-$C_5(CH_3)_5\}]$, 120.9 [10C, s, 2$\{\eta^5$-$C_5(CH_3)_5\}]$, 87.4 [1C, t, $^1J_{C-H} = 157$, η^1-$OC(C_6H_5){=}CH_2]$, 162.6 [1C, s, η^1-$OC(C_6H_5){=}CH_2]$, 126.5 [2C, d, $^1J_{C-H} = 158$, η^1-$OC(C_6H_5){=}CH_2]$, 127.8 [1C, d, $^1J_{C-H} = 160$, η^1-$OC(C_6H_5){=}CH_2]$, 127.9 [2C, d, $^1J_{C-H} = 159$, η^1-$OC(C_6H_5){=}CH_2]$, 140.2 [1C, s, η^1-$OC(C_6H_5){=}CH_2]$.

Synthesis of $Cp^*{}_2Zr(TeH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$. A solution of $Cp^*{}_2Zr(Te)NC_5H_5)$ (0.26 g, 0.46 mmol) in toluene (*ca.* 4 mL) was treated with PhC(O)Me (54 μL, 0.50 mmol). The mixture was stirred at room temperature for 1 day, after which period the volatile components were removed under reduced pressure. The residue was washed with pentane (*ca.* 1 mL) giving $Cp^*{}_2Zr(TeH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$ as a pink-beige solid which was dried *in vacuo* (0.18 g, 62%).[46] Anal. Calcd for $Cp^*{}_2Zr(TeH)\{\eta^1\text{-}OC(Ph){=}CH_2\}$: C, 55.2%; H, 6.3%. Found: C, 55.2%; H, 6.1%. IR data: 3056 (m), 2979 (s), 2903 (vs), 2724 (w), 2033 (m) [ν(Te—H)], 1683 (w), 1618 (s) [ν(C=C)], 1595 (m), 1563 (s), 1490 (s), 1443 (s), 1376 (s), 1304 (vs), 1180 (w), 1113 (vs), 1077 (m), 1019 (vs), 788 (m), 769 (s), 700 (s), 626 (w), 589 (w), 566 (m), 405 (w). ^{1}H NMR (C_6D_6): 1.87 [30H, s, 2$\{\eta^5$-$C_5(CH_3)_5]$, −7.0 [1H, s, $^1J_{Te-H} = 72$, Te*H*], 4.44 [1H, s, η^1-$OC(Ph){=}CH_2]$, 4.78 [1H, s, η^1-$OC(Ph){=}CH_2]$, 7.10 [1H, m, η^1-$OC(C_6H_5){=}CH_2]$, 7.25 [2H, m, η^1-$OC(C_6H_5){=}CH_2]$, 7.80 [2H, m, η^1-$OC(C_6H_5){=}CH_2]$. ^{13}C NMR (C_6D_6): 12.8 [10C, q, $^1J_{C-H} = 127$, 2$\{\eta^5$-$C_5(CH_3)_5\}]$, 120.9 [10C, s, 2$\{\eta^5$-$C_5(CH_3)_5\}]$, 88.2 [1C, t, $^1J_{C-H} = 158$, η^1-$OC(C_6H_5){=}CH_2]$, 162.8 [1C, s, η^1-$OC(C_6H_5){=}CH_2]$, 126.9 [2C, d, $^1J_{C-H} = 158$, η^1-$OC(C_6H_5){=}CH_2]$, 127.9 [2C, d, $^1J_{C-H} = 158$, η^1-$OC(C_6H_5){=}CH_2]$, 139.5 [1C, s, η^1-$OC(C_6H_5){=}CH_2]$ (insufficient signal-to-noise ratio to be able to determine accurately all the C_6H_5 resonances).

X-ray Structure Determination of $Cp^{Et*}{}_2Zr(O)(NC_5H_5)$. Crystal data, data collection, and refinement parameters for $Cp^{Et*}{}_2Zr(O)(NC_5H_5)$ are summarized in Table 12. A single crystal of $Cp^{Et*}{}_2Zr(O)(NC_5H_5)$ was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite monochromated Mo Kα X-radiation (λ = 0.71073 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was solved

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(46) However, it should be noted that the product is generally contaminated with small amounts of an impurity that is most probably $[Cp^*{}_2Zr\{\eta^1\text{-}OC(Ph){=}CH_2\}]_2(\mu\text{-}Te_2)$.

using Patterson and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[47] Systematic absences were consistent with the space groups $Pc2_1n$ (No. 33) and $Pcmn$ (No. 62), of which the choice $Pc2_1n$ (No. 33) was made, and confirmed by the absence of a mirror plane in the molecule. Hydrogen atoms of the $\mathrm{Cp^{Et*}}$ ligands were included in calculated positions ($d_{\mathrm{C-H}} = 0.96$ Å; $U_{\mathrm{iso}}(\mathrm{H}) = 1.2 \cdot U_{\mathrm{iso}}(\mathrm{C})$). Inversion of configuration indicated the correct choice of enantiomorph. Selected bond lengths and angles for $\mathrm{Cp^{Et*}{}_2Zr(O)(NC_5H_5)}$ are given in Table 1.

X-ray Structure Determination of $\mathrm{Cp^{Et*}{}_2Zr(E)(NC_5H_5)}$ (E = S, Se, Te). Crystal data, data collection, and refinement parameters are summarized in Table 12, and the general procedure is as described for $\mathrm{Cp^{Et*}{}_2Zr(O)(NC_5H_5)}$. Systematic absences were consistent uniquely with the space group $P2_1/n$ (No. 14). Selected bond distances and angles are listed in Tables 2–4.

X-ray Structure Determination of $\mathrm{Cp^*{}_2Zr(OH)\{\eta^1\text{-}OC(Ph){=}CH_2\}}$. Crystal data, data collection, and refinement parameters are summarized in Table 13, and the general procedure is as described for $\mathrm{Cp^{Et*}{}_2Zr(O)(NC_5H_5)}$. Systematic absences were consistent uniquely with the space group $P2_1/c$ (No. 14). Selected bond distances and angles are listed in Table 7.

X-ray Structure Determination of $\mathrm{Cp^*{}_2Zr(EH)\{\eta^1\text{-}OC(Ph){=}CH_2\}}$ (E = S, Se). Crystal data, data collection, and refinement parameters are summarized in Table 13, and the general procedure is as described for $\mathrm{Cp^{Et*}{}_2Zr(O)(NC_5H_5)}$. Systematic absences were consistent uniquely with the space group $P2_12_12_1$ (No. 19). Inversion of configuration indicated the correct choice of enantiomorph. Selected bond distances and angles are listed in Tables 8 and 9.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences (No. DE-FG02-93ER14339), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are very grateful to Professor Dean Roddick and Dr. Patricia Goodson for searches of the Cambridge Crystallographic Database and to Professor Tom Cundari for providing results prior to publication. G.P. is the recipient of an A. P. Sloan Research Fellowship (1991–1993), a Camille and Henry Dreyfus Teacher-Scholar Award (1991–1996), and a Presidential Faculty Fellowship Award (1992–1997).

Supplementary Material Available: Tables of Zr–EX single bond lengths, crystal and intensity collection data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and ORTEP drawings for $\mathrm{Cp^{Et*}{}_2Zr(E)(NC_5H_5)}$ (E = S, Se, Te) and $\mathrm{Cp^*{}_2Zr(EH)\{\eta^1\text{-}OC(Ph){=}CH_2\}}$ (E = O, S, Se) (56 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. Tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for $\mathrm{Cp^{Et*}{}_2Zr(O)(NC_5H_5)}$ are provided in the supplementary material for ref 8.

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(47) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981.