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Terminal chalcogenido complexes of zirconium: syntheses and reactivity of $Cp^*_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te) [1]

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Abstract

The terminal zirconium chalcogenido complexes $Cp^*_2Zr(E)(NC_5H_5)$ ($Cp^* = \eta^5$-C_5Me_5; E = O, S, Se, Te) are conveniently synthesized by the reactions of $Cp^*_2Zr(CO)_2$ with either N_2O or the elemental chalcogen (S, Se, Te) in the presence of pyridine. The [Zr=E] functionalities in these complexes are highly reactive and undergo a variety of 1,2-addition and cycloaddition reactions, resulting in a diverse array of products. For example, reactions of the zirconium oxo complex $Cp^*_2Zr(O)(NC_5H_5)$ yield $Cp^*_2Zr(OH)_2$, $Cp^*_2Zr(\eta^2$-$O_2CMe)(\eta^1$-OCOMe), $Cp^*_2Zr(OPh)_2$, $Cp^*_2Zr(OH)(NH_2)$, $Cp^*_2Zr(OH)(NHPh)$, $Cp^*_2Zr(OH)[\eta^2$-$N(Ph)NH_2]$, $Cp^*_2Zr(H)(OSiH_2Ph)$, $[Cp^*_2Zr(H)](\mu$-O)$[Cp^*_2Zr(OH)]$, $Cp^*_2Zr(OH)[\eta^1$-$OC(R)=CH_2]$ (R = Me, Ph, Bu^t), $Cp^*_2Zr(OH)I$, $Cp^*_2Zr(OMe)I$, $Cp^*_2Zr(OSiMe_3)Cl$, $Cp^*_2Zr[\eta^2$-OCH(R)OCH(R)O] (R = H, Pr^i, Bu^t), and $Cp^*_2Zr[\eta^2$-OC(Ph)NC(Ph)N].

Keywords: Zirconium; Oxo; Selenido; Sulfido; Tellurido; Chalcogen

1. Introduction

Over recent years, the subject of metal–ligand multiple bonding has attracted considerable attention [1]. The majority of these studies have relied on the use of various sterically-demanding ancillary ligands to provide coordination environments capable of sustaining terminal metal–ligand multiple bonds. For instance, in 1972, Green et al. used the cyclopentadienyl ligand ($Cp = \eta^5$-C_5H_5) to prepare Cp_2MoO and Cp_2WO [2], classic examples of metal oxo complexes supported only by organic ligands. [2] Today, organometallic oxo complexes are numerous; [3] nevertheless, it must be emphasized that the ability to sustain a multiple bond varies considerably as a function of the transition metal. For example, metal–ligand multiple bonding is common for the Group 5–8 transition metals, but rare for the Group 4 metals (Ti, Zr, Hf) and unknown for the Group 3 metals (Sc, Y, La). In particular, prior to our work, molecular terminal oxo complexes of the Group 4 metals were known for titanium alone, with only bridging μ-oxo complexes, e.g. $[(\eta^5$-$C_5H_5)_2Zr(\mu$-$O)]_3$ [8], having been isolated previously for zirconium and hafnium. [4] Furthermore, the now classic text *Metal–Ligand Multiple Bonds* [1], published in 1988, is devoid of structurally-characterized examples of complexes with multiple bonds to either zirconium or hafnium; [5] the situation soon changed, however, with the isolation of the terminal imido complexes $Cp_2Zr(NBu^t)(THF)$ [15] and $(Bu^t_3SiNH)_2Zr(NSiBu^t_3)(THF)$ [16], as reported by Bergman and Wolczanski, respectively. [6] Other recent developments in the chemistry of multiply bonded zirconium complexes include the syntheses of: *(i)* the

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[1] Dedicated to Malcolm L.H. Green, a true inspiration, on the occasion of his 60th birthday. Happy birthday Malcolm!

[2] The pentamethylcyclopentadienyl derivative Cp^*_2WO has also been reported; see Ref. [3–5].

[3] For example, see [6] and Herrmann's papers entitled *Multiple Bonds Between Main Group Elements and Transition Metals*: for part 154 see [7].

[4] A related hypervalent zirconocene oxo complex $[Cp_2Zr(\mu$-$O)]_3(\mu_3$-O) has been reported [9]. However, it is now recognized that the complex should be formulated as the bridging hydroxide complex $\{[Cp_2Zr(\mu$-$OH)]_3(\mu_3$-$O)\}\{CF_3SO_3\}$ [10].

[5] In contrast, however, multiple-bonding to titanium is well-precedented. For example, the terminal [Ti=O] moiety has been stabilized by porphyrin, dibenzotetraaza[14]annulene, phthalocyanine, triazacyclononane and pentamethylcyclopentadienyl ligation [11–14].

[6] Since these initial reports, other terminal imido complexes of both zirconium and hafnium have appeared in the literature; for example see Ref. [17,18].

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terminal phosphinidene complex $Cp_2Zr[PC_6H_2Bu^t_3](PMe_3)$ [19]; *(ii)* the terminal alkylidene complex $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2PPr^i_2)_2]Zr{=}CHPh(Cl)$ [20] [7]; and *(iii)* the terminal chalcogenido complexes $Cp^*_2Zr(S)(NC_5H_4R)$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = H, Bu^t) [24–26] and $(dmpe)_2M(TeR)_2(Te)$ (M = Zr, Hf; R = $Si(SiMe_3)_3$) [27]. In this paper, we describe the syntheses and reactivity of the complete series of terminal chalcogenido complexes of zirconium $Cp^*_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te), [8] which are counterparts to Green's molybdenum and tungsten oxo and sulfido complexes. [9]

2. Results and discussion

2.1. Syntheses of the terminal chalcogenido complexes $Cp^*_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te)

Many of the recent attempts to synthesize terminal chalcogenido complexes of zirconium have focused on zirconocene derivatives. With the exception of the sulfido complex $Cp^*_2Zr(S)(NC_5H_5)$ [24–26], however, other derivatives have previously been generated as only transient species. For instance, one of the earliest discussions of the existence of $[(\eta^5\text{-}C_5R_5)_2Zr{=}E]$ species considered that $Cp^*_2Zr(OH)_2$ and $Cp^*_2Zr(OH)Cl$ could be potential precursors to a terminal zirconium oxo complex [30]. However, apart from the presence of the $[Cp^*_2ZrO]^+$ fragment in the mass spectrum of $Cp^*_2Zr(OH)_2$, studies on these precursors have not furnished any additional evidence for the terminal oxo complex $[Cp^*_2Zr{=}O]$. Bergman, however, has reported mechanistic studies which provide excellent evidence that the zirconium oxo species $[Cp^*_2Zr{=}O]$ may in fact be generated as a reactive intermediate by both *(i)* elimination of benzene from $Cp^*_2Zr(OH)(Ph)$ and *(ii)* deprotonation of $Cp^*_2Zr(OH)(OSO_2CF_3)$ [24–26]. Unfortunately, attempts to trap the reactive intermediate $[Cp^*_2Zr{=}O]$ to give an isolated complex in which the Zr=O multiple bond remained intact were not successful. For example, although $[Cp^*_2Zr{=}O]$ could be trapped by nitriles and diphenylacetylene to yield the oxametallacycles $Cp^*_2Zr[\eta^2\text{-}OC(R){=}NC(R){=}N]$ (R = Ph, Bu^t) and $Cp^*_2Zr[\eta^2\text{-}OC(Ph){=}C(Ph)]$ respectively, attempts to preserve the zirconium–oxo multiple bond by trapping with dative ligands such as pyridines, pyridine *N*-oxide, and phosphine oxides were unsuccessful [24]. [10] More recently, Bergman provided evidence for the generation of the less-substituted $[Cp_2Zr{=}O]$ intermediate by a [4 + 2] retrocycloaddition of the azaoxametallacycle $Cp_2Zr[\eta^2\text{-}N(Ar)C(Me){=}C(Ph)CH(Ar')O]$ [31].

With respect to terminal sulfido derivatives, Tainturier et al. suggested that the redistribution of $[Cp^{Bu^t}_2Zr](\mu\text{-}S)_2[ZrCp_2]$ into $[Cp^{Bu^t}_2Zr(\mu\text{-}S)]_2$ and $[Cp_2Zr(\mu\text{-}S)]_2$ provided evidence for dissociation into the monomeric terminal sulfido species $[Cp^{Bu^t}_2Zr{=}S]$ and $[Cp_2Zr{=}S]$ ($Cp^{Bu^t} = \eta^5\text{-}C_5H_4Bu^t$) as reactive intermediates [32]. The first substantial evidence for the existence of zirconium complexes with terminal chalcogenido ligands, however, was provided by Bergman who, as indicated above, synthesized $Cp^*_2Zr(S)(NC_5H_4R)$ (R = H, Bu^t) by the dehydrohalogenation of $Cp^*_2Zr(SH)I$ with $KN(SiMe_3)_2$ in the presence of pyridine [24–26].

Inspired by Bergman's synthesis of $Cp^*_2Zr(S)(NC_5H_5)$, we rationalized that the corresponding terminal oxo complex $Cp^*_2Zr(O)(NC_5H_5)$ should be isolable if the reactive intermediate $[Cp^*_2Zr{=}O]$ could be generated under sufficiently mild conditions. In this regard, Bottomley et al. [33] had previously described the use of N_2O as an efficient oxo-transfer reagent [11] to Cp^*_2Ti, but the oxo-bridged complex $Cp^*Ti(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2TiCp^*$ was obtained rather than a terminal oxo complex. Significantly, and of considerable relevance to a potential synthesis of $Cp^*_2Zr(O)(NC_5H_5)$, Andersen demonstrated that, in the presence of pyridines, the reaction of N_2O with Cp^*_2Ti (and also $Cp^*_2Ti(\eta^2\text{-}C_2H_4)$) may be diverted to yield the terminal oxo complexes $Cp^*_2Ti(O)(NC_5H_4R)$ (R = H, Ph) [11].

Andersen's isolation of the titanium oxo complex $Cp^*_2Ti(O)(NC_5H_5)$ suggested that zirconium derivatives could, in principle, be synthesized by an analogous method. Unfortunately, however, the zirconium analogues of Cp^*_2Ti and $Cp^*_2Ti(\eta^2\text{-}C_2H_4)$ are unknown. Furthermore, although the diphenylacetylene adduct of zirconocene $Cp^*_2Zr(\eta^2\text{-}C_2Ph_2)$ is known and is reactive towards N_2O, Hillhouse demonstrated that the product of this reaction is the oxametallacycle $Cp^*_2Zr[\eta^2\text{-}OC(Ph){=}C(Ph)]$, rather than a terminal oxo complex [36]. As a result, we found it necessary to explore the potential use of other precursors, such as the divalent dicarbonyl $Cp^*_2Zr(CO)_2$ [37,38], which we had previ-

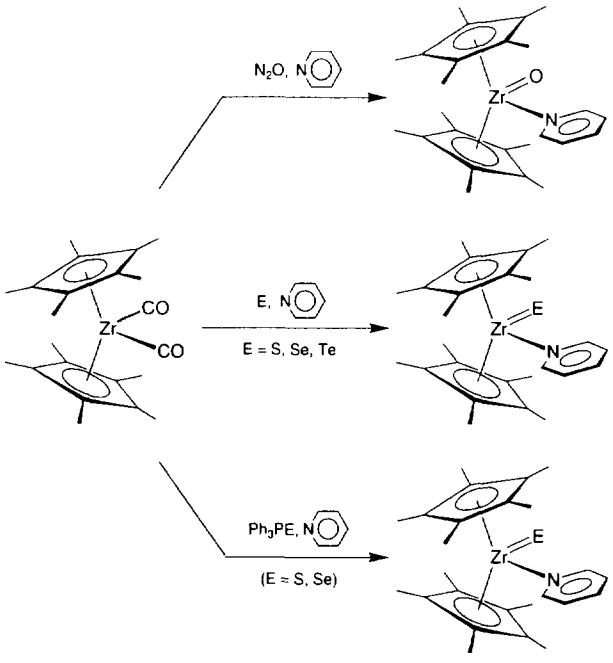
[7] Unstable terminal alkylidene complexes [21,22] and Fischer carbene derivatives [23] of zirconocene had been reported prior to Fryzuk's isolation of the benzylidene complex.

[8] Although there may be some controversy as to whether or not oxygen is included as a chalcogen, the term chalcogen has been approved by IUPAC as the collective name for the Group 16 elements: O, S, Se, Te, Po; see Ref. [28].

[9] Some of this work has been communicated, see Ref. [29].

[10] ^1H NMR spectroscopy did, however, provide evidence for a triphenylphosphine oxide adduct, $Cp^*_2Zr(O)(OPPh_3)$, but this complex could not be isolated in pure form; see Ref. [21] of Ref. [24].

[11] Holm and Donahue have described a thermodynamic scale for oxygen atom transfer reagents [34]; also, for a theoretical investigation concerning how N_2O bonds to transition metal centers, see Ref. [35].



Scheme 1.

ously demonstrated to be a useful reagent for the synthesis of the terminal sulfido derivative $Cp_2^* Zr(S)(NC_5H_5)$ via reaction with sulfur in the presence of pyridine [39]. Significantly, we discovered that $Cp_2^* Zr(O)(NC_5H_5)$ is readily synthesized by the reaction of $Cp_2^* Zr(CO)_2$ with N_2O and pyridine at 80 °C (Scheme 1). Likewise, the tetramethylethylcyclopentadienyl analogue $Cp_2^{Et*} Zr(O)(NC_5H_5)$ ($Cp^{Et*} = \eta^5$-C_5Me_4Et) may be synthesized by the corresponding reaction with $Cp_2^{Et*} Zr(CO)_2$ [40].

$Cp_2^* Zr(O)(NC_5H_5)$ and $Cp_2^{Et*} Zr(O)(NC_5H_5)$ are the first well-characterized terminal zirconium oxo complexes, with the structure of the latter having been determined by X-ray diffraction. [12] Subsequent to the initial report of $Cp_2^* Zr(O)(NC_5H_5)$ [29] and $Cp_2^{Et*} Zr(O)(NC_5H_5)$ [40], several other zirconyl derivatives have been described, with Floriani reporting the synthesis and structural characterization of the anionic porphyrinogen oxo complexes $[\{\eta^5$-η^1-η^5-η^1-$Et_8C_4(C_4H_2N)_3(C_5H_3N)\}Zr{=}O\}_2(\mu$-$K)_2]$, $[\{\eta^5$-η^1-η^5-η^1-$Et_8C_4(C_4H_2N)_3(3$-$EtC_5H_2N)\}Zr{=}O\}_2(\mu$-$K)_2]$, and $[\{\eta^1$-η^1-η^5-η^1-$Et_7C_4(C_4H_2N)_3(CH_2CH_2C_5H_2N)\}$-$Zr{=}O\}_2(\mu$-$Li)_2]$ [42,43,48]. [13] The oxo ligands of these complexes, however, interact with the counter-cations, thereby giving rise to dinuclear structures that are linked by four-membered $[M_2O_2]$ rings (M = K, Li).

The terminal oxo ligand in $Cp_2^* Zr(O)(NC_5H_5)$ is characterized by an IR absorption at 780 cm^{-1} attributable to ν(Zr=O), which has been assigned by comparison with the IR spectra of the other chalcogenido derivatives, $Cp_2^* Zr(E)(NC_5H_5)$ (E = S, Se, Te), described below. [14] For reference, ν(M=O) stretching frequencies for other zirconium oxo and related derivatives are listed in Table 1.

By comparison with other transition metal complexes with terminal oxo ligands, the ν(M=O) stretching frequencies for these complexes are particularly low. Indeed, the first metallocene oxo complexes, Cp_2MO (M = Mo, W), were described as 'deviant' in this respect [49]. Bercaw categorized metal–oxo complexes with stretching frequencies in the range of ca. 930–1000 cm^{-1} as 'class *a*' (i.e. those in which the metal–oxo bond order is close to three), and those below ca. 930 cm^{-1} as 'class *b*' (i.e. those in which the metal–oxo bond order is close to two) [3,4]. The low value of ν(Zr=O) for $Cp_2^* Zr(O)(NC_5H_5)$ (and also for the other metallocene derivatives) is in accord with the notion that the Zr=O interaction possesses little triple bond $\bar{Z}r{\equiv}\overset{+}{O}$ character. Such a description would be expected on the basis of both *(i)* the 18-electron nature of the zirconium center, and *(ii)* the commonly used MO description for bent metallocene derivatives [50]. Nevertheless, it should be noted that triple bond contributions of the type $\bar{Z}r{\equiv}\overset{+}{O}$ could occur at the expense of the Zr–Cp* interactions. Indeed, MO calculations on molybdenocene oxo derivatives indicate that there is an interaction between a b_2 (d_{yz}) orbital on molybdenum and the oxygen p_y orbital [51]. [15] However, since the b_2 orbital on molybdenum is also involved in bonding to the cyclopentadienyl ligands, the result is the generation of three molecular orbitals: one strongly bonding, one almost non-bonding, and one antibonding, with the first two being occupied. In fact, the 'non-bonding' b_2 orbital is slightly Mo–O antibonding, so that its occupation results in the overall Mo–O bond order being reduced considerably from three. The triple bond formalism $\bar{M}o{\equiv}\overset{+}{O}$ for such complexes is not, therefore, particularly appropriate, as illustrated by the lengths of

[12] Some other claims of terminal oxo complexes of zirconium have been published. However, none of these compounds have been structurally characterized so that the presence of a terminal oxo ligand is questionable; see Ref. [41].

[13] A neutral hafnium oxo complex, $\{\eta^5$-η^1-η^1-η^1-$Et_8C_4(C_4H_2N)_2(C_5H_3N)(3$-$EtC_5H_2N)\}Hf{=}O$, has also been synthesized, but has not been structurally characterized. See Ref. [43].

[14] ν(Zr=E) for the heavier chalcogenido derivatives are believed to be less than 400 cm^{-1} but have not been identified with certainty. Cundari [44] calculated ν(Zr=E) values for the series of hypothetical derivatives Cp_2ZrE: O, 945 cm^{-1}; S, 484 cm^{-1}; Se, 328 cm^{-1}; Te, 248 cm^{-1}.

[15] For discussions on multiple bonding in related imido derivatives see Refs. [47,52].

Table 1
ν(M=O) stretching frequencies for zirconium oxo and related derivatives

Compound	ν(M=O)/cm^{-1}	Reference
$Cp^*_2Zr(O)(NC_5H_5)$	780	this work
$Cp^*_2Zr(O)(NC_5H_4Bu^t)$	784	this work
$Cp^{Et*}_2Zr(O)(NC_5H_5)$	773	[40]
$Cp^*_2Hf(O)(NC_5H_5)$	773	[45,46]
$Cp^{Et*}_2Hf(O)(NC_5H_5)$	770	[45,46]
$Cp^*_2Ti(O)(NC_5H_5)$	852	[11]
Cp^*_2VO	855	[11]
$Cp^*_2Ta(O)H$	850	[47]
Cp_2MoO	793–868	[2]
Cp_2WO	799–879	[2]
Cp^*_2WO	860	[3,4]
$[\{\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8C_4(C_4H_2N)_3(C_5H_3N)Zr{=}O\}_2(\mu\text{-}K)_2]$	780	[42]
$[\eta^1\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_7C_4(C_4H_2N)_3(CH_2CH_2C_5H_2N)Zr{=}O\}_2(\mu\text{-}Li)_2]$	776	[48]
$[\{\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^5\text{-}Et_8C_4(C_4H_2N)_3(3\text{-}CH_2{=}CHC_5H_2N)Zr{=}O\}_2(\mu\text{-}Na)_2]$	785	[43]
$[cis\text{-}Et_8C_4(C_4H_2N)_2(C_5H_3N)(m\text{-}MeC_5H_2N)Hf{=}O]$	826	[43]

the Mo=O bonds: specifically, the Mo=O bond lengths of 1.721(2) Å for $(\eta^5\text{-}C_5H_4Me)_2MoO$ [53] and 1.706(4) Å for $(\eta^5\text{-}C_5H_4Bu^t)_2MoO$ [54] are slightly longer than the mean bond length of 1.678 [40] Å observed for other Mo(IV) oxo complexes which exhibit a considerable degree of triple bond $\overline{Mo}\equiv\overset{+}{O}$ character [55]. Moreover, as noted above, the ν(Mo=O) stretching frequencies in these molybdenocene complexes are significantly lower in energy than those for other molybdenum oxo complexes.

In view of the successful use of $Cp^*_2Zr(CO)_2$ for the syntheses of the oxo and sulfido complexes $Cp^*_2Zr(O)(NC_5H_5)$ and $Cp^*_2Zr(S)(NC_5H_5)$ [39], we also explored the possibility of synthesizing the selenido and tellurido analogues by similar methods. Accordingly, $Cp^*_2Zr(Se)(NC_5H_5)$ and $Cp^*_2Zr(Te)(NC_5H_5)$ may be synthesized by the reactions of $Cp^*_2Zr(CO)_2$ with one equivalent of the elemental chalcogen in the presence of pyridine (Scheme 1), thereby establishing a general method of synthesis for the entire series of terminal chalcogenido complexes $Cp^*_2Zr(E)(NC_5H_5)$ (E = O, S, Se, Te). The tetramethylethylcyclopentadienyl counterparts $(\eta^5\text{-}C_5Me_4Et)_2Zr(E)(NC_5H_5)$ (E = S, Se, Te) have likewise been prepared and structurally-characterized by X-ray diffraction. [16]

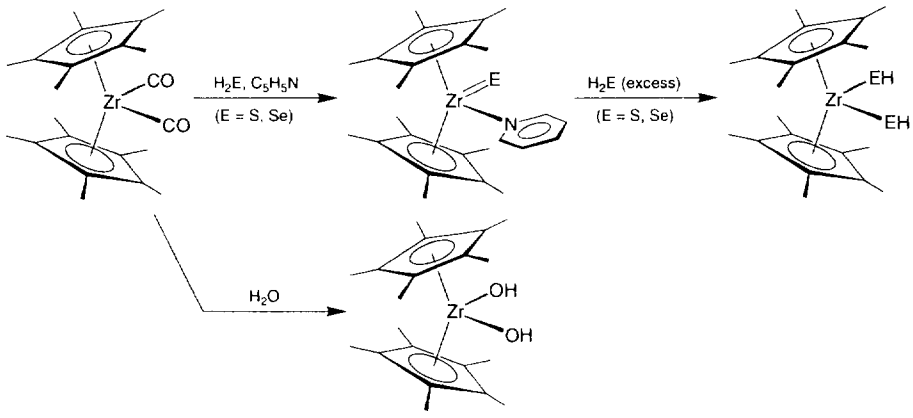
The importance of a dative ligand in stabilizing the terminal chalcogenido moiety $[Cp^*_2Zr{=}E]$ is evident because such complexes have not been isolated in their absence. For example, the reaction of $Cp^*_2Zr(CO)_2$ with N_2O in the absence of pyridine is not clean, giving a mixture of which the major component is tentatively identified [17] as $Cp^*_2Zr_2(\eta^5{:}\eta^1{:}\mu\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2$; [18] Similarly, in the absence of pyridine, $Cp^*_2Zr(CO)_2$ reacts with excess sulfur, selenium, and tellurium to give $Cp^*_2Zr(\eta^2\text{-}E_3)$ (E = S, Se, Te) [57], rather than terminal chalcogenido derivatives. A notable exception, however, is the selenido–carbonyl derivative $Cp^*_2Zr(Se)(CO)$, obtained by the reaction of $Cp^*_2Zr(CO)_2$ with one equivalent of selenium [58]. Pyridine, therefore, plays an important role in stabilizing all the terminal chalcogenido moieties in the above complexes (and also the titanium [11] and hafnium [45] counterparts). Presumably, the ability of pyridine to stabilize such complexes is a consequence of it being not only a good σ-donor but also a flat molecule which experiences minimal steric interactions with the Cp^* ligands. In this regard, 4-substituted pyridines (e.g. 4-$Bu^tC_5H_4N$) may also be used to prepare stable terminal chalcogenido complexes, e.g. $Cp^*_2Zr(O)(NC_5H_4\text{-}4\text{-}R)$, but 2-substituted derivatives (e.g. 2,6-dimethylpyridine, 2-vinylpyridine, and quinoline), which would exhibit increased steric interactions with both the Cp^* and chalcogenido ligands, have not yet yielded stable $Cp^*_2Zr(O)(NC_5H_4\text{-}2\text{-}R)$ derivatives. [19]

[16] For the hafnium analogues, see Ref. [45]; for some other examples of series of isostructural terminal chalcogenido derivatives of the transition metals, see Ref. [56].

[17] The identification of $Cp^*_2Zr_2(\eta^5{:}\eta^1{:}\mu\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2$ is provided by several observations: *(i)* when the reaction is monitored by ^{1}H NMR spectroscopy, two new Cp^* resonances of equal intensity appear at δ 2.16 and 1.87 ppm (C_6D_6), most likely corresponding to the two non-bridging η^5-Cp^* ligands in $Cp^*_2Zr_2(\eta^5{:}\eta^1{:}\mu\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2$; *(ii)* Cp^*H, the expected side-product in the formation of $Cp^*_2Zr_2(\eta^5{:}\eta^1{:}\mu\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2$, is observed by ^{1}H NMR spectroscopy; *(iii)* C and H elemental analysis is consistent with $Cp^*_2Zr_2(\eta^5{:}\eta^1{:}\mu\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2$. Anal. Found: C, 58.0; H, 7.7. Calc.: C, 58.2; H, 7.2%.

[18] Bottomley et al. have synthesized the titanium analogue $Cp^*_2Ti_2(\eta^5{:}\eta^1{:}\mu\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2$ by the reaction of Cp^*_2Ti with N_2O, see Ref. [33].

[19] Moreover, attempts to trap $[Cp^*_2Zr{=}O]$ with furan and tetrahydrofuran have been unsuccessful.



Scheme 2.

2.2. Other chalcogen transfer reagents for the syntheses of $Cp_2^* Zr(E)(NC_5H_5)$

In addition to N_2O and the elemental chalcogens, we have explored the use of other chalcogen transfer reagents for the syntheses of $Cp_2^* Zr(E)(NC_5H_5)$ (E = O, S, Se, Te). [20] These studies have established that triphenylphosphine sulfide and triphenylphosphine selenide are capable of transferring their chalcogen atoms to zirconium. Thus, $Cp_2^* Zr(CO)_2$ reacts with Ph_3PS and Ph_3PSe in the presence of pyridine to give $Cp_2^* Zr(S)(NC_5H_5)$ and $Cp_2^* Zr(Se)(NC_5H_5)$ respectively (Scheme 1). [21] In contrast, Ph_3PO was found to be ineffective for the synthesis of $Cp_2^* Zr(O)(NC_5H_5)$. [22]

Interestingly, H_2S and H_2Se are also capable of generating $Cp_2^* Zr(S)(NC_5H_5)$ [39] and $Cp_2^* Zr(Se)(NC_5H_5)$ upon reaction with *excess* $Cp_2^* Zr(CO)_2$ in the presence of pyridine (Scheme 2). [23,24] However, in the presence of excess H_2S and H_2Se, the hydrochalcogenido derivatives $Cp_2^* Zr(SH)_2$ and $Cp_2^* Zr(SeH)_2$ [61] are obtained in preference. Likewise, the dihydroxide $Cp_2^* Zr(OH)_2$ is obtained from the reaction of $Cp_2^* Zr(CO)_2$ with excess H_2O at ca. 80 °C, [25] with no evidence for the formation of a terminal oxo complex in the presence of pyridine and excess $Cp_2^* Zr(CO)_2$ (Scheme 2).

2.3. Influence of cyclopentadienyl substituents on the stability of terminal zirconium–chalcogenido complexes

The successful isolation of the series of terminal chalcogenido complexes $Cp_2^* Zr(E)(NC_5H_5)$ and $Cp_2^{Et*} Zr(E)(NC_5H_5)$ (E = O, S, Se, Te) is in large part due to the steric demands of the highly substituted cyclopentadienyl ligands which enforce the formation of monomeric derivatives. For example, the reaction of $Cp_2Zr(CO)_2$ with N_2O in the presence of pyridine at 80 °C gives the previously reported zirconocene oxo trimer $[Cp_2Zr(\mu\text{-}O)]_3$, [26] with no evidence for the formation of $Cp_2Zr(O)(NC_5H_5)$ (Scheme 3). Likewise, for the heavier chalcogens, only bridging chalcogenido complexes have been obtained for zirconocene derivatives with cyclopentadienyl ligands (Cp^R) that are less sterically demanding than bulky Cp^*. In contrast to the zirconium oxo trimer $[Cp_2Zr(\mu\text{-}O)]_3$, the heavier chalcogens typically form *dimeric* derivatives $[(Cp^R)_2Zr(\mu\text{-}E)]_2$, as illustrated by the sulfido, selenido, and tellurido complexes $[Cp_2Zr(\mu\text{-}S)]_2$ [60,63,64], $[Cp_2^{Bu^t}Zr(\mu\text{-}S)]_2$ [32,65–68], $[Cp_2^{Bu^t}Zr(\mu\text{-}Se)]_2$, [32,65–69] and $[Cp_2^{Bu^t}Zr(\mu\text{-}Te)]_2$ [65,70,71]. [27]

[20] For a review of the reactions of organometallic compounds with various chalcogen-containing reagents, see Ref. [59].

[21] The reaction between $Cp_2^* Zr(CO)_2$ and ethylene sulfide in the presence of pyridine at 85 °C gives a mixture of products of which $Cp_2^* Zr(S)(NC_5H_5)$ is a component.

[22] Thus, $Cp_2^* Zr(CO)_2$ does not react with Ph_3PO in the presence of pyridine at 135 °C to give $Cp_2^* Zr(O)(NC_5H_5)$. Furthermore, since $Cp_2^* Zr(O)(NC_5H_5)$ does not react with PPh_3 over a period of 1 day at 50 °C (but decomposes at 135 °C) it is evident that there must be a significant kinetic barrier for oxo transfer in this system.

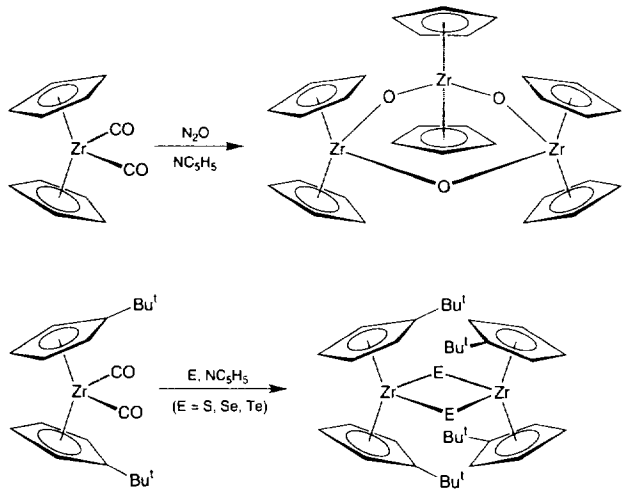
[23] Bottomley et al. have investigated the reactions of $Cp_2^* Zr(CO)_2$ with stoichiometric quantities of H_2S and H_2Se in the absence of pyridine and reported the products to be $[Cp_2^* Zr(\mu\text{-}E)]_2$ (E = S, Se) [60]. However, subsequent work has demonstrated that, for the case of H_2S, the isolated product is actually $[Cp_2^* Zr(SH)]_2(\mu\text{-}S)$, see Ref. [39].

[24] Although H_2S and H_2Se are not commonly used reagents for the syntheses of terminal chalcogenido complexes, they have, however, been used to prepare the terminal chalcogenido complexes of molybdenum and tungsten, $M(PMe_3)_4(E)_2$ (M = Mo, W; E = S, Se), see Ref. [56].

[25] It should be noted that previous reports describe $Cp_2^* Zr(CO)_2$ to be inert to H_2O [60,62]. However, we find the formation of the dihydroxide $Cp_2^* Zr(OH)_2$ to be quite reproducible.

[26] $[Cp_2Zr(\mu\text{-}O)]_3$ was first reported by Floriani [8] as the product obtained from the reaction of $Cp_2Zr(CO)_2$ with CO_2.

[27] In addition to the discussion concerning $[Cp_2^* Zr(\mu\text{-}S)]_2$ (see footnote 23), other syntheses of $[Cp_2^* Zr(\mu\text{-}S)]_2$ have been reported: *(i)* the reaction of $Cp_2^* Zr(CH{=}CH_2)_2$ with sulfur [72]; *(ii)* the reaction of $Cp_2^* ZrCl_2$ with 'Li_2S' [73]. In neither of these examples, however, has the structure of $[Cp_2^* Zr(\mu\text{-}S)]_2$ been confirmed by X-ray diffraction.



Scheme 3.

Consequently, attempts to synthesize the terminal chalcogenido complexes $Cp_2^{Bu'}Zr(E)(NC_5H_5)$ via the reactions of $Cp_2^{Bu'}Zr(CO)_2$ with elemental sulfur, selenium and tellurium in the presence of pyridine were unsuccessful, with the bridged complexes $[Cp_2^{Bu'}Zr(\mu\text{-}S)]_2$, $[Cp_2^{Bu'}Zr(\mu\text{-}Se)]_2$ and $[Cp_2^{Bu'}Zr(\mu\text{-}Te)]_2$ being obtained in preference (Scheme 3). The formation of the tellurido-bridged complex $[Cp_2^{Bu'}Zr(\mu\text{-}Te)]_2$ by the aforementioned reaction is precedented by Arnold's report that $[Cp_2^{Bu'}Zr(\mu\text{-}Te)]_2$ is obtained by the t-butylpyridine-induced elimination of $Te(SiPh_3)_2$ from $Cp_2^{Bu'}Zr(TeSiPh_3)_2$ [74]. Significantly, even though a terminal tellurido complex was not observed spectroscopically during the course of the latter transformation, Arnold's kinetic studies suggest that $Cp_2^{Bu'}Zr(Te)(NC_5H_4Bu')$ is, in fact, an intermediate.

2.4. Reactivity of $Cp_2^*Zr(E)(NC_5H_5)$ (E = O, S, Se, Te)

2.4.1. Reactivity of the [Zr = E] functionality

The reactivity of the [Zr=E] moieties of $Cp_2^*Zr(E)(NC_5H_5)$ (E = O, S, Se, Te) is dominated by the electrophilic character of the d^0 zirconium centers coupled with highly basic, nucleophilic, chalcogenido ligands, i.e. $[Zr^{\delta+}=E^{\delta-}]$. [28] In particular, for the zirconium oxo derivative, X-ray diffraction studies have suggested that the interaction may be aptly represented as $[Zr^+-O^-]$ [40], a result that is also supported by Cundari's computational studies [44]. Such dipolar character facilitates extensive reactivity of the [Zr=E] multiple bonds, especially with polar ($X^{\delta+}-Y^{\delta-}$) substrates, which may be broadly classified as 1,2-addition and cycloaddition reactions.

[28] For a discussion of the electrophilic vs. nucleophilic character of complexes with multiply bonded alkylidene, imido and oxo ligands, see Refs. [51,75].

2.4.1.1. 1,2-Addition reactions. The terminal chalcogenido complexes $Cp_2^*Zr(E)(NC_5H_5)$ are subject to reactions with both polar ($X^{\delta+}-Y^{\delta-}$) and non-polar substrates to give products of the type $Cp_2^*Zr(EX)(Y)$ that may be considered to be derived from a formal 1,2-addition [29] across the [Zr=E] double bond. Examples of X–Y bonds which partake in such 1,2-addition reactions include H–X (X = Cl; NH_2, NHPh, $N(Ph)NH_2$; OH, SH, SeH; $CH_2C(O)R$; SiH_2Ph; H), Me_3Si–Cl, and CH_3–I. Such reactivity is illustrated below, with particular emphasis given to the chemistry of the zirconium oxo derivative $Cp_2^*Zr(O)(NC_5H_5)$.

(i) Addition of H–Cl. The [Zr=E] moieties in $Cp_2^*Zr(E)(NC_5H_5)$ react instantaneously with a variety of reagents bearing acidic functional groups. Thus, $Cp_2^*Zr(O)(NC_5H_5)$ reacts with $HCl_{(g)}$ to yield a mixture of the previously reported compounds $Cp_2^*Zr(OH)Cl$ [30] and $Cp_2^*ZrCl_2$ [62], with excess $HCl_{(g)}$ yielding only the latter complex (Scheme 4). Likewise, the heavier chalcogenido derivatives $Cp_2^*Zr(E)(NC_5H_5)$ (E = S, Se, Te) also react with $HCl_{(g)}$ to give $Cp_2^*ZrCl_2$.

(ii) Addition of H–E bonds (E = O, S, Se). The terminal chalcogenido complexes $Cp_2^*Zr(E)(NC_5H_5)$ are extremely sensitive to moisture, and react instantly with one equivalent of water to give the hydroxy derivatives $Cp_2^*Zr(OH)(EH)$ (E = O [62], S, [31] Se [32]) which have been structurally characterized by X-ray diffraction (Scheme 4). [33] However, with the exception of the oxo complex, the reactions are not entirely clean, since small quantities of $Cp_2^*Zr(OH)_2$ and $Cp_2^*Zr(EH)_2$ are also formed, presumably as a consequence of ligand redistribution. Furthermore, removal of the liberated H_2E and addition of excess water results in the formation of the dihydroxide $Cp_2^*Zr(OH)_2$ as the final product.

In addition to water, hydrogen sulfide and hydrogen selenide also undergo 1,2-addition across the [Zr=E] functionality (Scheme 5). Thus, $Cp_2^*Zr(S)(NC_5H_5)$ re-

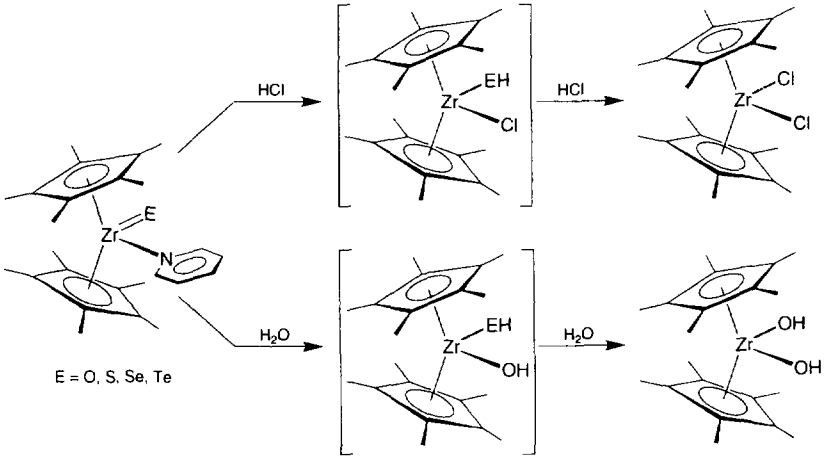
[29] The term '1,2-addition' is only intended to describe the relationship of the product to the terminal chalcogenido complex. It is not indended to provide a mechanistic description of the reaction.

[30] $Cp_2^*Zr(OH)Cl$ was first prepared by the reaction of Cp_2^*ZrHCl with water [62] and has been structurally-characterized by X-ray diffraction [30].

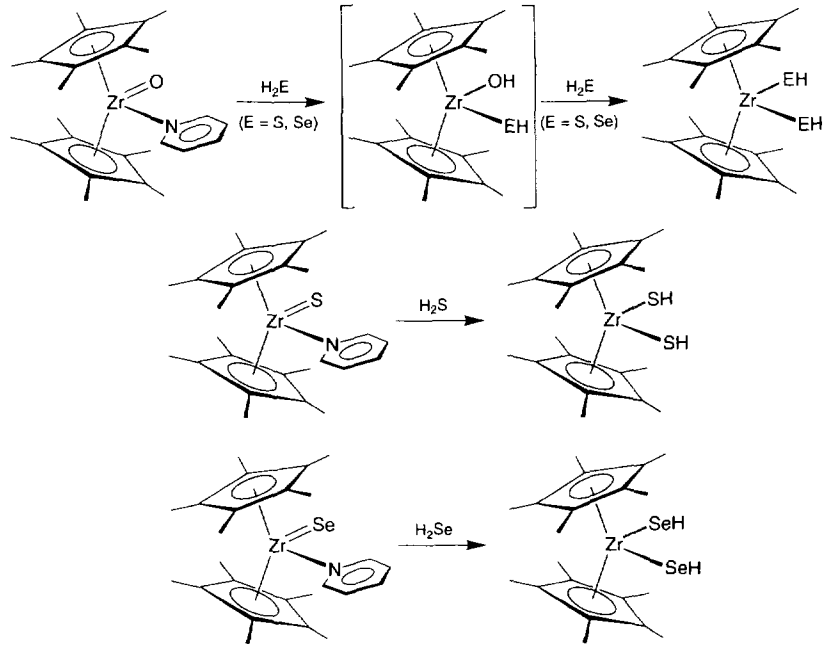
[31] $Cp_2^*Zr(OH)(SH)$ has also been obtained as a mixture with $Cp_2^*Zr(OH)_2$ by the reaction of $Cp_2^*Zr(SH)_2$ with water; see Ref. [73].

[32] $Cp_2^*Zr(Te)(NC_5H_5)$ also reacts with H_2O, giving $Cp_2^*Zr(OH)_2$ and a silvery-gray film (probably elemental Te) as the final products. $Cp_2^*Zr(OH)(TeH)$ may be an intermediate in this reaction, but this compound must be unstable. ^1H NMR data for $Cp_2^*Zr(OH)(TeH)$ (δ ppm, C_6D_6): 1.83 (s, 30H, $2\eta^5\text{-}C_5(CH_3)_5$) 4.46 (s, 1H, OH) −7.75 (s, 1H, TeH, $^1J_{Te-H}$ = 70 Hz).

[33] For the structure of $Cp_2^*Zr(OH)_2$ see Ref. [30]; the structures of $Cp_2^*Zr(OH)(SH)$ and $Cp_2^*Zr(OH)(SeH)$ will be described in a subsequent report.



Scheme 4.



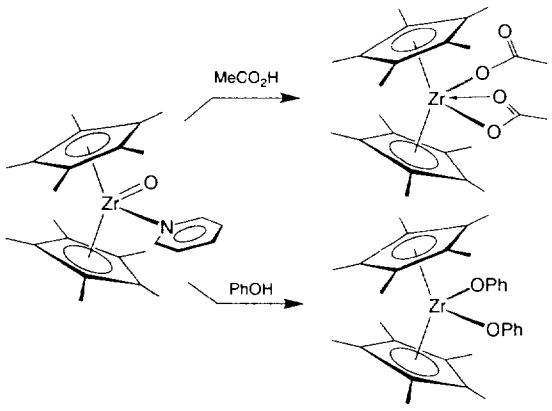
Scheme 5.

acts with H_2S at room temperature to give $Cp_2^* Zr(SH)_2$ [39,73], while $Cp_2^* Zr(SeH)_2$ is obtained from the corresponding reaction of $Cp_2^* Zr(Se)(NC_5H_5)$ with H_2Se. [34] Likewise, the reactions of $Cp_2^* Zr(O)(NC_5H_5)$ with excess H_2S and H_2Se give $Cp_2^* Zr(SH)_2$ and $Cp_2^* Zr(SeH)_2$ respectively, via the hydroxy derivatives $Cp_2^* Zr(OH)(SH)$ and $Cp_2^* Zr(OH)(SeH)$, as illustrated in Scheme 5.

The rapid and irreversible reaction of H_2O with the [Zr=O] group of$Cp_2^* Zr(O)(NC_5H_5)$ to give the dihydroxide $Cp_2^* Zr(OH)_2$ provides an interesting contrast to the chemistry of the related tungsten system. Thus, whereas $Cp_2^* Zr(OH)_2$ is stable with respect to the elimination of water, the tungsten analogue $[Cp_2^* W(OH)_2]$ is unstable. Specifically, $[Cp_2^* W(OH)_2]$ was proposed as the intermediate responsible for exchange of oxygen atoms between $Cp_2^* W{=}O$ and $H_2^{18}O$, and has not been otherwise detected [3,4]. It is likely that the origin of the enhanced stability of $Cp_2^* Zr(OH)_2$ compared with that of $[Cp_2^* W(OH)_2]$ is the 16-electron configuration of the zirconium center in $Cp_2^* Zr(OH)_2$, which promotes oxygen-to-zirconium lone pair donation and strengthens the Zr–OH interaction. [35]

[34] The molecular structure of $Cp_2^* Zr(SeH)_2$ has been determined by X-ray diffraction [76].

[35] In contrast, both $Cp_2^* W{=}O$ and $[Cp_2^* Zr{=}O]$ would be expected to have similar M=O bond orders, despite the fact that the metal centers are 18-electron and 16-electron respectively, since the metallocene fragment is not capable of supporting a triply bonded ligand without compromising the metal–Cp^* interactions.



Scheme 6.

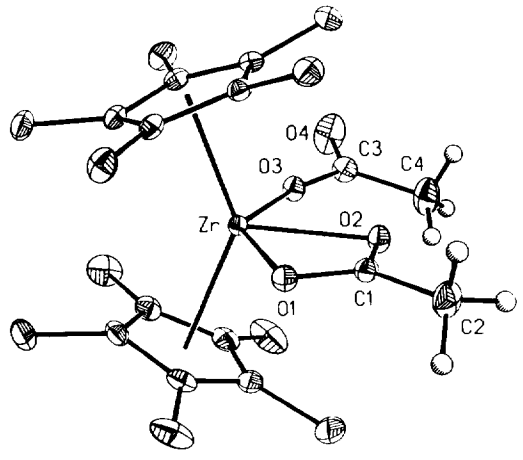


Fig. 1. Molecular structure of $Cp_2^* Zr(\eta^2\text{-}O_2CMe)(\eta^1\text{-}OCOMe)$.

Table 2
Selected bond lengths (Å) and angles (deg) for $Cp_2^* Zr(\eta^2\text{-}OCOMe)(\eta^1\text{-}OCOMe)$

Zr–O(1)	2.297(2)	Zr–O(2)	2.271(2)
Zr–O(3)	2.067(2)	O(1)–C(1)	1.263(3)
O(2)–C(1)	1.264(3)	C(1)–C(2)	1.501(4)
O(3)–C(3)	1.295(3)	C(3)–O(4)	1.205(4)
C(3)–C(4)	1.488(5)	Zr–C(11)	2.556(3)
Zr–C(12)	2.558(3)	Zr–C(13)	2.565(3)
Zr–C(14)	2.554(3)	Zr–C(15)	2.562(3)
Zr–C(31)	2.571(3)	Zr–C(32)	2.553(3)
Zr–C(33)	2.587(3)	Zr–C(34)	2.595(3)
Zr–C(35)	2.557(3)		
Zr–O(1)–C(1)	92.3(2)	Zr–O(2)–C(1)	93.4(2)
Zr–O(3)–C(3)	161.8(2)	O(1)–C(1)–O(2)	117.8(2)
O(1)–Zr–O(2)	56.5(1)	O(1)–Zr–O(3)	135.8(1)
O(2)–Zr–O(3)	79.3(1)	O(1)–C(1)–C(2)	120.7(3)
O(2)–C(1)–C(2)	121.5(3)	O(3)–C(3)–O(4)	124.0(3)
O(3)–C(3)–C(4)	116.3(3)	O(4)–C(3)–C(4)	119.7(3)

The zirconium oxo moiety of $Cp_2^* Zr(O)(NC_5H_5)$ is also reactive towards organic substrates with OH functional groups, such as carboxylic acids and alcohols. For instance, $Cp_2^* Zr(O)(NC_5H_5)$ reacts instantaneously with acetic acid to produce $Cp_2^* Zr(\eta^2\text{-}O_2CMe)(\eta^1\text{-}OCOMe)$, as illustrated in Scheme 6. [36] The molecular structure of $Cp_2^* Zr(\eta^2\text{-}O_2CMe)(\eta^1\text{-}OCOMe)$ has been determined by X-ray diffraction (Fig. 1), demonstrating that one of the acetate ligands is coordinated in a unidentate fashion, while the other is bidentate. Selected bond lengths and angles for $Cp_2^* Zr(\eta^2\text{-}O_2CMe)(\eta^1\text{-}OCOMe)$ are listed in Table 2, from which it is evident that the two [Zr–O] bond lengths of the bidentate acetate ligand (2.297(2) Å and 2.271(2) Å) are significantly longer than that of the unidentate acetate ligand (2.067(2) Å). [37]

$Cp_2^* Zr(O)(NC_5H_5)$ also reacts immediately with phenol (Scheme 6) and methanol. The reaction with phenol gives $Cp_2^* Zr(OPh)_2$ [80] via an intermediate that is tentatively identified as $Cp_2^* Zr(OPh)(OH)$ [80]. Similarly, the reaction of $Cp_2^* Zr(O)(NC_5H_5)$ with methanol yields a mixture of products which are tentatively identified as $Cp_2^* Zr(OMe)(OH)$, $Cp_2^* Zr(OMe)_2$, and $Cp_2^* Zr(OH)_2$. [38,39]

(iii) Addition of N–H bonds. [N–H] bonds are also reactive towards the [Zr=O] functionality. For example, $Cp_2^* Zr(O)(NC_5H_5)$ reacts immediately with excess ammonia at room temperature to give the hydroxy–amide complex $Cp_2^* Zr(OH)(NH_2)$ (Scheme 7). [40] Likewise, $Cp_2^* Zr(O)(NC_5H_5)$ undergoes 1,2-addition of the [N–H] bonds of $PhNH_2$ and $PhNHNH_2$ to give $Cp_2^* Zr(OH)(NHPh)$ and $Cp_2^* Zr(OH)[\eta^2\text{-}N(Ph)NH_2]$ respectively. The molecular structure of $Cp_2^* Zr(OH)(NHPh)$ has been determined by X-ray

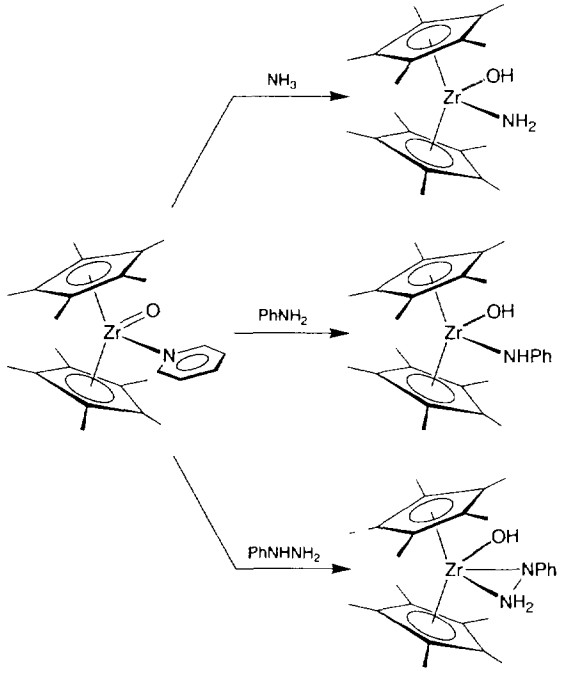
[36] For reference, bridging zirconocene oxo complexes are also reactive towards carboxylic acids. For example, $[Cp_2ZrBr]_2(\mu\text{-}O)$ reacts with Cl_3CCOOH to give a mixture of Cp_2ZrBr_2 and $Cp_2Zr(OCOCCl_3)_2$ [77], while the chloride analogue $[Cp_2ZrCl]_2(\mu\text{-}O)$ reacts with RCOOH (R = H, Me, ^{t}Bu, Ph) to give $Cp_2Zr(\eta^2\text{-}OCOR)Cl$ [78].

[37] For some other structurally-characterized zirconocene carboxylate derivatives, see Ref. [79].

[38] It is most likely that $Cp_2^* Zr(OMe)(OH)$ is the initial product, from which $Cp_2^* Zr(OH)_2$ and $Cp_2^* Zr(OMe)_2$ are obtained as a result of ligand exchange. However, the possibility that adventitious water is responsible for the formation of $Cp_2^* Zr(OH)_2$ cannot be excluded.

[39] Although $Cp_2^* Zr(OMe)(OH)$ and $Cp_2^* Zr(OMe)_2$ were not isolated from the mixture of products, support for their formulation is provided by ^{1}H NMR spectroscopy. Furthermore, the product that is proposed to be $Cp_2^* Zr(OMe)_2$ is also obtained by the reaction of $Cp_2^* Zr(CH_3)_2$ with methanol. ^{1}H NMR data for $Cp_2^* Zr(OMe)(OH)$ (δ ppm, C_6D_6): 1.87, (s, 30H, 2 $\eta^5\text{-}C_5(CH_3)_5$] 3.66, (s, 1H, OH) 3.92, (s, 3H, OCH_3). ^{1}H NMR data for $Cp_2^* Zr(OMe)_2$ (δ ppm, C_6D_6): 1.92, (s, 30H, 2 $\eta^5\text{-}C_5(CH_3)_5$) 4.00, (s, 6H, 2 OCH_3).

[40] Interestingly, Hillhouse and Bercaw [62] reported that the attempts to synthesize the unknown hafnium analogue $Cp_2^* Hf(OH)(NH_2)$ by treating $Cp_2^* Hf(H)(NH_2)$ with one equivalent of H_2O resulted in the formation of $Cp_2^* Hf(H)(OH)$ instead.



Scheme 7.

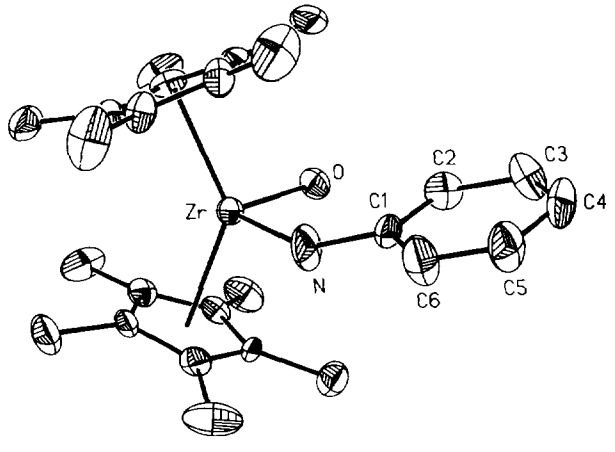


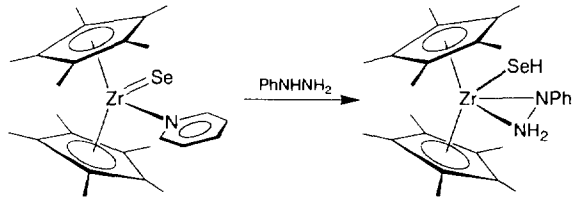
Fig. 2. Molecular structure of $Cp_2^*Zr(OH)(NHPh)$.

Table 3
Selected bond lengths (Å) and angles (deg) for $Cp_2^*Zr(OH)(NHPh)$

Zr–O	2.061(7)	Zr–N	2.117(9)
N–C(1)	1.390(15)	Zr–C(11)	2.567(14)
Zr–C(12)	2.567(13)	Zr–C(13)	2.585(13)
Zr–C(14)	2.552(13)	Zr–C(15)	2.559(11)
Zr–C(31)	2.602(10)	Zr–C(32)	2.527(12)
Zr–C(33)	2.533(12)	Zr–C(34)	2.536(11)
Zr–C(35)	2.586(11)		
O–Zr–N	98.4(4)	Zr–N–C(1)	139.3(8)
N–C(1)–C(2)	121.2(11)	N–C(1)–C(6)	122.1(11)

diffraction (Fig. 2) and selected metrical data are listed in Table 3. [41] The reaction with $PhNHNH_3$ is noteworthy since it gives $Cp_2^*Zr(OH)[\eta^2\text{-}N(Ph)NH_2]$ rather than its isomeric derivative $Cp_2^*Zr(OH)[\eta^2\text{-}NHNH(Ph)]$. [42,43,44]

The selenido ligand of $Cp_2^*Zr(Se)(NC_5H_5)$ is also capable of deprotonating phenylhydrazine to give $Cp_2^*Zr(SeH)(\eta^2\text{-}NPhNH_2)$ (Eq. (1)). ^1H NMR spectroscopic data which support the formulation of $Cp_2^*Zr(SeH)(\eta^2\text{-}NPhNH_2)$ include resonances attributable to a [SeH] ligand at δ −2.30 ppm ($^1J_{Se-H}$ = 34 Hz) and to a $[NH_2]$ group at δ 1.87 ppm.



(1)

(iv) Addition of Si–H, H–H, and C–H bonds. The high reactivity of the zirconium oxo complex $Cp_2^*Zr(O)(NC_5H_5)$ is underscored by its facile reactions with relatively non-polar H–X bonds. For example, the Si–H bond of phenylsilane reacts immediately with $Cp_2^*Zr(O)(NC_5H_5)$ at room temperature to give the siloxy-hydride derivative, $Cp_2^*Zr(H)(OSiH_2Ph)$ (Scheme 8), characterized by resonances at δ 6.29 and 5.71 ppm attributable to the [Zr–H] and [Si–H] moieties respectively.

A further illustration of the high reactivity of the [Zr=O] functionality is provided by the facile reaction of $Cp_2^*Zr(O)(NC_5H_5)$ with H_2 at 80 °C to give the dinuclear hydroxy–hydride complex $[Cp_2^*Zr(H)](\mu\text{-}O)[Cp_2^*Zr(OH)]$, as illustrated in Scheme 8. [45,46] A

[41] For some other structurally-characterized [Zr–NHPh] complexes, see Ref. [81].

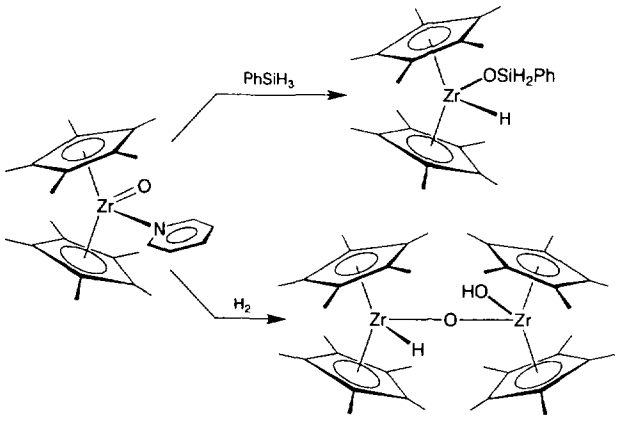
[42] Evidence which supports the structure in preference to the isomeric $Cp_2^*Zr(OH)[\eta^2\text{-}NHNH(Ph)]$ structure includes: *(i)* the observation of a 1:2 ratio of integrals in the ^1H NMR spectrum for the [Zr–OH] and [Zr–NH_2] moieties; *(ii)* an X-ray diffraction study which indicates an almost planar geometry at the phenyl-substituted nitrogen atom. However, the structure is not reported here owing to the presence of disorder between the OH and NH_2 groups.

[43] Structurally-characterized complexes with $[\eta^2\text{-}N(Ph)NH_2]$ and related ligands are not common, but some examples include $[Cp_2W(\eta^2\text{-}NPhNH_2)][BF_4]$ [82,83], $[Tp]TiCl_2(\eta^2\text{-}NPhNH_2)$ [84,85], $[Tp]TiCl_2(\eta^2\text{-}NMeNMe_2)$ [84], $CpTiCl_2(\eta^2\text{-}NPhNH_2)$ [86], $CpTiCl_2(\eta^2\text{-}NHNMe_2)$ [86], and $Cp_2Zr[\eta^1\text{-}OC(Ph)=CH_2][\eta^2\text{-}N(Ph)NH(Ph)]$ [87].

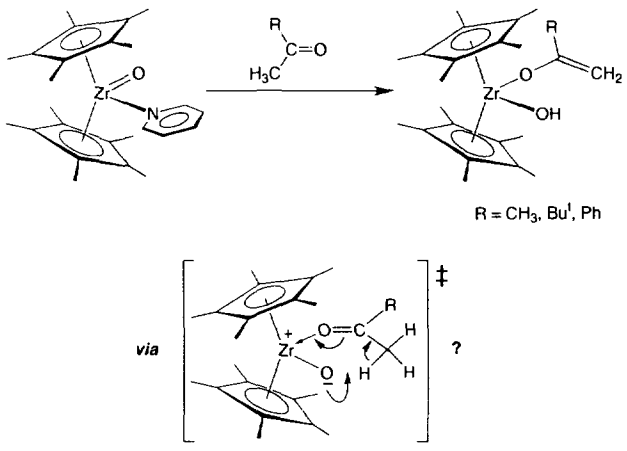
[44] For a crystallographically characterized permethylzirconocene-hydroxo-hydrazonido complex, $Cp_2^*Zr(OH)[\eta^2\text{-}N(Me)N=CTol_2]$, see [88].

[45] $[Cp_2^*Zr(H)](\mu\text{-}O)[Cp_2^*Zr(OH)]$ is also obtained by the reaction of $Cp_2^*ZrH_2$ with $Cp_2^*Zr(OH)_2$; see Ref. [62].

[46] In contrast, no reaction was observed between $Cp_2^*Zr(S)(NC_5H_5)$ and dihydrogen at 80 °C for 8 days.



Scheme 8.



Scheme 9.

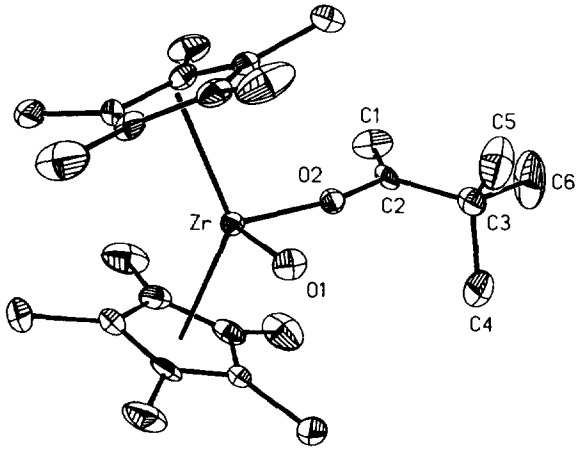


Fig. 3. Molecular structure of $Cp_2^*Zr(OH)[\eta^1\text{-}OC(Bu^t)=CH_2]$.

Table 4
Selected bond lengths (Å) and angles (deg) for $Cp_2^*Zr(OH)[\eta^1\text{-}OC(Bu^t)=CH_2]$

Zr–O(1)	2.001(6)	Zr–O(2)	2.006(5)
Zr–C(11)	2.573(9)	Zr–C(12)	2.603(9)
Zr–C(13)	2.565(9)	Zr–C(14)	2.561(12)
Zr–C(15)	2.583(10)	Zr–C(31)	2.562(10)
Zr–C(32)	2.546(10)	Zr–C(33)	2.603(7)
Zr–C(34)	2.570(7)	Zr–C(35)	2.570(9)
O(2)–C(2)	1.367(9)	C(1)–C(2)	1.333(14)
C(2)–C(3)	1.573(13)	C(3)–C(4)	1.496(14)
C(3)–C(5)	1.511(15)	C(3)–C(6)	1.491(13)
O(1)–Zr–O(2)	98.7(2)	Zr–O(2)–C(2)	169.9(6)
O(2)–C(2)–C(1)	126.4(8)	O(2)–C(2)–C(3)	108.9(7)
C(1)–C(2)–C(3)	124.6(7)	C(2)–C(3)–C(4)	111.9(7)
C(2)–C(3)–C(5)	111.7(8)	C(2)–C(3)–C(6)	112.2(8)
C(4)–C(3)–C(5)	103.0(9)	C(4)–C(3)–C(6)	108.9(9)
C(5)–C(3)–C(6)	108.6(8)		

plausible pathway for the formation of $[Cp_2^*Zr(H)](\mu\text{-}O)[Cp_2^*Zr(OH)]$ involves initial addition of H_2 to give the hydroxy–hydride intermediate $[Cp_2^*Zr(OH)H]$ followed by trapping with either itself or $Cp_2^*Zr(O)(NC_5H_5)$. [47]

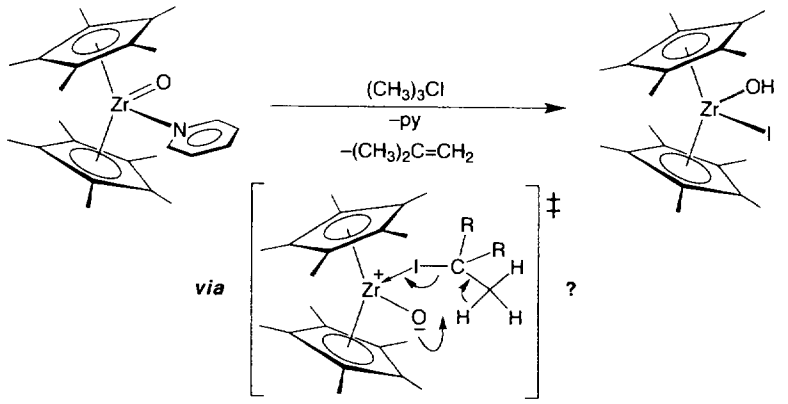
The multiply bonded zirconium–chalcogenido moieties in $Cp_2^*Zr(E)(NC_5H_5)$ are also capable of undergoing 1,2-addition of activated C–H bonds. For example, $Cp_2^*Zr(E)(NC_5H_5)$ react with methyl ketones to give O-bound enolate derivatives. [48] Thus, Me_2CO and $Bu^tC(O)Me$ react with $Cp_2^*Zr(O)(NC_5H_5)$ to give $Cp_2^*Zr(OH)[\eta^1\text{-}OC(Me)=CH_2]$ and $Cp_2^*Zr(OH)[\eta^1\text{-}OC(Bu^t)=CH_2]$ respectively, with the structure of the latter derivative having been determined by X-ray diffraction (Fig. 3). [49] Selected bond lengths and angles are listed in Table 4. Likewise, all of the chalcogenido complexes $Cp_2^*Zr(E)(NC_5H_5)$ (E = O, S, Se, Te) react with PhC(O)Me to give the enolate complexes, $Cp_2^*Zr(EH)[\eta^1\text{-}OC(Ph)=CH_2]$ [40]. The acetone–enolate derivative $Cp_2^*Zr(SeH)[\eta^1\text{-}OC(Me)=CH_2]$ has also been isolated. Although mechanistic studies have not yet been carried out, a potential mechanism for the C–H bond activation reaction could involve initial coordination of the ketone to the zirconium center, followed by deprotonation via a six-membered ring (Scheme 9).

The reaction of $Cp_2^*Zr(O)(NC_5H_5)$ with Bu^tI also involves cleavage of a C–H bond. Thus,

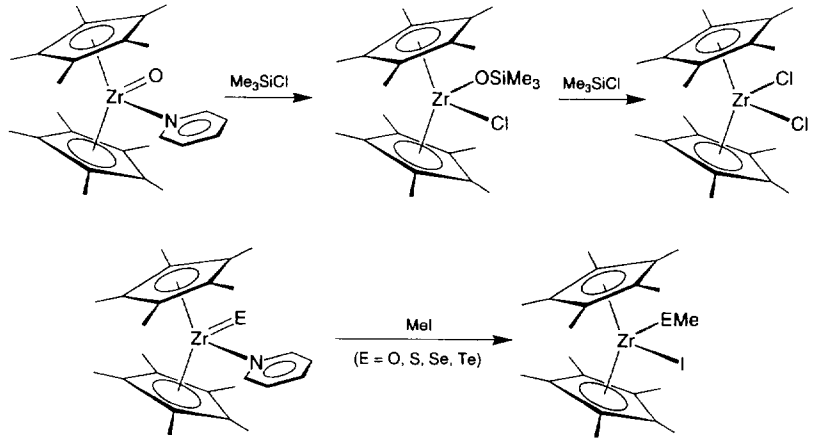
[47] The hafnium analogue $Cp_2^*Hf(OH)H$ has been isolated, see Ref. [62].

[48] In addition to methyl ketones, other ketones also react with $Cp_2^*Zr(O)(NC_5H_5)$. However, to date, only methyl ketones have produced clean results. For instance, $Cp_2^*Zr(O)(NC_5H_5)$ reacts with diethyl ketone to yield a mixture of products, which are probably the geometric isomers, *cis*- and *trans*-$[Cp_2^*Zr(OH)[\eta^1\text{-}OC(Et)=CHMe]$.

[49] Zirconocene enolate complexes, e.g. $Cp_2Zr[\eta^1\text{-}OC(Ph)=CH_2][\eta^1\text{-}C(SiMe_3)=CHPh]$ [89] and $Cp_2Zr[\eta^1\text{-}OC(Ph)=CH_2][\eta^2\text{-}N(Ph)NH(Ph)]$ [87] are well-precedented; for example see Refs. [90].



Scheme 10.



Scheme 11.

$Cp_2^*Zr(O)(NC_5H_5)$ reacts cleanly with Bu^tI at room temperature to give the hydroxy–iodide derivative $Cp_2^*Zr(OH)I$, accompanied by elimination of isobutene (Scheme 10). [50] A potential mechanism for the dehydrohalogenation involves a six-membered transition state (similar to that proposed for the aforementioned enolization reactions) via prior coordination of Bu^tI to the zirconium center. [51]

The dehydrohalogenation of Bu^tI provides an interesting contrast to the corresponding reaction with MeI, which, as described in more detail below, gives an alkoxy–iodide product $Cp_2^*Zr(OMe)I$. Furthermore, Pr^iI also undergoes dehydrohalogenation with $Cp_2^*Zr(O)(NC_5H_5)$ to give $Cp_2^*Zr(OH)I$ and propene, while the corresponding reaction of $Cp_2^*Zr(O)(NC_5H_5)$ with EtI produces a mixture. On the basis of ^1H NMR spectroscopy, the mixture is proposed to comprise $Cp_2^*Zr(OH)I$ and $Cp_2^*Zr(OEt)I$ as a consequence of both dehydrohalogenation and alkylation pathways. [52,53] Evidently, the course of the reaction, i.e. 1,2-addition vs. dehydrohalogenation, depends strongly upon the nature of the alkyl iodide, with the ease of the dehydrohalogenation reaction relative to addition across the Zr=O bond increasing along the series $CH_3I < CH_3CH_2I < (CH_3)_2CHI < (CH_3)_3CI$.

(v) Addition of carbon–halogen and silicon–halogen bonds. 1,2-Addition reactions of the Zr=E double bonds

[50] The sulfido derivative $Cp_2^*Zr(S)(NC_5H_5)$ also dehydrohalogenates Bu^tI to give inter alia $Cp_2^*Zr(SH)I$ and $Me_2C=CH_2$.

[51] An alternative possibility involves the initial formation of the t-butoxy intermediate $Cp_2^*Zr(OBu^t)I$, followed by subsequent elimination of isobutylene. Precedent for such a possibility is provided by the observations that: *(i)* t-butoxy permethylzirconocene complexes, e.g. $Cp_2^*Zr(OBu^t)H$ [80], are known; *(ii)* t-butoxide derivatives of other transition metals may undergo elimination of isobutylene, e.g. the conversion of $[W_2(OBu^t)_7]^-$ to $[W_2(OBu^t)_6(\mu\text{-}O)(\mu\text{-}H)]^-$ [91,92].

[52] $Cp_2^*Zr(OEt)(I)$ was not isolated or further characterized. ^1H NMR data for $Cp_2^*Zr(OEt)(I)$ (δ ppm, C_6D_6): 1.92 (s, 30H, 2 $\eta^5\text{-}C_5(CH_3)_5$) 1.17 (t, 3H, OCH_2CH_3, $^3J_{H-H} = 7$Hz) 4.12 (q, 2H, OCH_2CH_3, $^3J_{H-H} = 7$Hz).

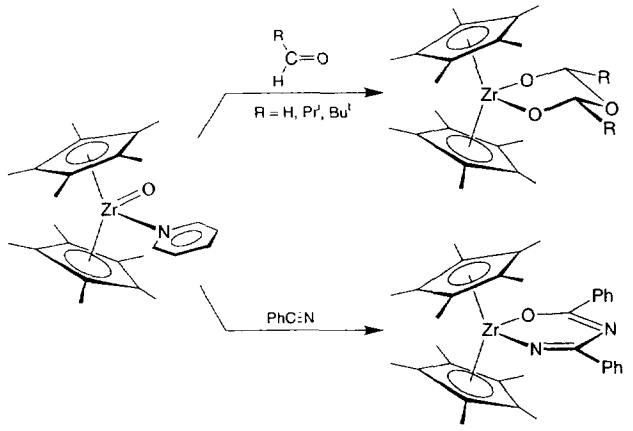
[53] Preliminary mechanistic studies using CD_3CH_2I and CH_3CD_2I demonstrate that the hydrogen of the hydroxide group is derived from the β-CH_3 group. The ratio of $Cp_2^*Zr(OEt)I$ to $Cp_2^*Zr(OH)I$ (or $Cp_2^*Zr(OD)I$) in the product mixture is greater for the reaction with CD_3CH_2I than with CH_3CD_2I, thereby demonstrating that zirconium hydroxide formation (and elimination of C_2H_4) is subject to a kinetic deuterium isotope effect.

are not limited to reagents of the type H–X; aprotic reagents such as CH_3I and Me_3SiCl also undergo these reactions. Thus, $Cp^*_2Zr(O)(NC_5H_5)$ reacts immediately with Me_3SiCl to give the siloxy-chloride derivative $Cp^*_2Zr(OSiMe_3)Cl$ (Scheme 11). [54,55] The latter complex may also be generated by the reaction of $Cp^*_2ZrCl_2$ with one equivalent of $KOSiMe_3$ in toluene at 90 °C. Significantly, $Cp^*_2Zr(OSiMe_3)Cl$ reacts with excess Me_3SiCl at room temperature to give the dichloride $Cp^*_2ZrCl_2$ and $(Me_3Si)_2O$. Therefore, Me_3SiCl is capable of completely abstracting the oxo ligand from the zirconium center in $Cp^*_2Zr(O)(NC_5H_5)$. In this regard, the reaction of $Cp^*_2Zr(O)(NC_5H_5)$ with Me_3SiCl differs from the reaction with $PhSiH_3$, since the latter reagent does not abstract the oxo ligand from the zirconium center.

The reaction of $Cp^*_2Zr(O)(NC_5H_5)$ with Me_3SiCl is analogous to that of the tungsten oxo complex $Cp^*_2W{=}O$ with Me_3SiCl, which gives sequentially $Cp^*_2W(OSiMe_3)Cl$ and $Cp^*_2WCl_2$ [3,4]. Likewise, Geoffroy reported the corresponding transformations for the tungstenocene derivative $Cp_2W{=}O$ [95].

As stated above, MeI undergoes 1,2-addition across the [Zr=O] multiple bond in $Cp^*_2Zr(O)(NC_5H_5)$ to give the methoxy iodide derivative $Cp^*_2Zr(OMe)I$ (Scheme 11). [56] Moreover, the heavier chalcogenido complexes $Cp^*_2Zr(E)(NC_5H_5)$ (E = S, Se, Te) also react with methyl iodide to yield the methylchalcogenolate complexes $Cp^*_2Zr(EMe)I$ at room temperature (Scheme 11). [57,58] The formation of the methoxy–iodide complex $Cp^*_2Zr(OMe)I$ contrasts with the reactivity of the related tungstenocene–oxo complex, Cp^*_2WO. Interestingly, rather than producing $Cp^*_2W(OMe)I$, the reaction between Cp^*_2WO and MeI involves alkylation of the tungsten center and the formation of an oxo–alkyl derivative, $[Cp^*_2W(O)Me][I]$ [3,4]. The contrast in reactivities is clearly a consequence of the d^0 vs. d^2 nature of the metal centers, with the d^0 Zr center of $Cp^*_2Zr(O)(NC_5H_5)$ being incapable of reacting in the nucleophilic sense observed for the d^2 tungsten center in Cp^*_2WO.

2.4.1.2. Cycloaddition reactions. Whereas methyl ketones are deprotonated by $Cp^*_2Zr(E)(NC_5H_5)$, aldehydes selectively undergo cycloaddition reactions to produce six-membered oxametallacycles. For example, $Cp^*_2Zr(O)(NC_5H_5)$ reacts with paraformaldehyde, isobutyraldehyde, and pivalaldehyde to produce the oxametallacycles $Cp^*_2Zr[\eta^2\text{-}OCH(R)OCH(R)O]$ (R = H, Pr^i, Bu^t), as shown in Scheme 12. [59] The formation of the six-membered derivatives $Cp^*_2Zr[\eta^2\text{-}OCH(R)OCH(R)O]$ presumably involves initial [2 + 2] cycloaddition to give a four-membered metallacycle $Cp^*_2Zr[\eta^2\text{-}OCH(R)O]$, followed by insertion of RCHO. [60] There is substantial precedence for such [2 + 2] cycloaddition reactions of early metal–oxo complexes: for example, $Cp^*_2Ti(O)(NC_5H_5)$ reacts with allene and acetylenes to give $Cp^*_2Ti[\eta^2\text{-}OC(=CH_2)CH_2]$ [101] and $Cp^*_2Ti[\eta^2\text{-}OC(R)C(R)]$ [102] respectively, while $[\eta^4\text{-}Me_4taa]Ti{=}O$ undergoes cycloaddition reactions with activated ketones and other substrates [12,13]. Likewise, $[Cp^*_2Zr{=}O]$ and $[Cp^*_2Zr{=}S]$ generated in situ have been shown to react with alkynes (e.g. Ph_2C_2) to give the four-membered ring derivatives $Cp^*_2Zr[\eta^2\text{-}OC(R)C(R)]$ and $Cp^*_2Zr[\eta^2\text{-}SC(R)C(R)]$ respectively [27]. [61]



Scheme 12.

The molecular structure of $Cp^*_2Zr[\eta^2\text{-}OCH(Bu^t)OCH(Bu^t)O]$ has been determined by X-ray diffraction (Fig. 4) and selected bond lengths and angles are listed in Table 5. The diffraction study demonstrates that the six-membered ring in $Cp^*_2Zr[\eta^2\text{-}OCH(Bu^t)OCH(Bu^t)O]$ exhibits an approximate chair conformation, with the bulky t-butyl groups occupying the more spacious equatorial rather than axial positions. The Cp^* ligands occupy both axial and equatorial positions and are consequently inequivalent as judged

[54] The zirconocene analogues $Cp_2Zr(OSiMe_3)Cl$ [93] and $Cp_2Zr(OSiPh_3)Cl$ [94] have been reported, with the structure of the latter complex being determined by X-ray diffraction.

[55] Similarly, $Cp^*_2Ti(O)(NC_5H_5)$ reacts with Me_3SiN_3 to give $Cp^*_2Ti(OSiMe_3)(N_3)$; see footnote 32 of Ref. [17].

[56] $Cp^*_2Zr(OMe)I$ has been described previously in the literature, although full characterization data were not reported; see Ref. [23].

[57] A related series of bis(methyl) chalcogenolate complexes, $Cp_2Zr(EMe)_2$ (E = O [96], S [32], Se [97,98], Te [32]), have been reported.

[58] For some reviews that include a discussion of zirconocene–chalcogenolate complexes, see Ref. [99].

[59] The same products, and unreacted starting material, are also obtained if only one equivalent of the aldehyde is used.

[60] In this regard, MeCHO has been reported to insert into the four-membered metallacycle $Cp_2Ti[\eta^2\text{-}C(Me){=}C(Me)CH_2]$ to give the thermally unstable, six-membered metallacycle $[Cp_2Ti[\eta^2\text{-}OCH(Me)C(Me){=}C(Me)(CH_2)]$; see Ref. [100].

[61] For [2 + 2] cycloaddition reactions of $Cp_2W{=}O$, see Ref. [95].

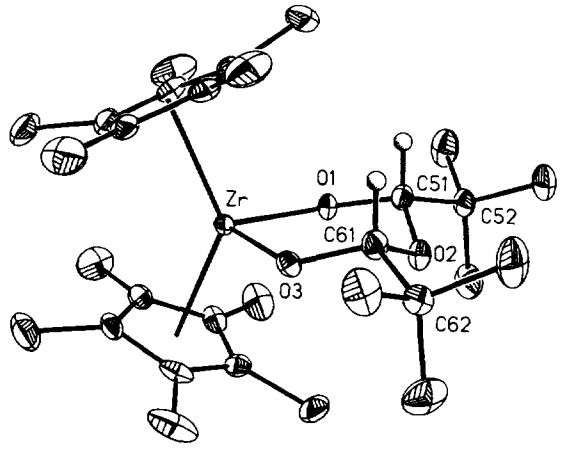


Fig. 4. Molecular structure of $Cp_2^* Zr[\eta^2$-OCH(Bu^t)OCH(Bu^t)O].

Table 5
Selected bond lengths (Å) and angles (deg) for $Cp_2^* Zr[\eta^2$-OCH(Bu^t)OCH(Bu^t)O]

Zr–O(1)	2.011(4)	Zr–O(3)	2.007(3)
Zr–C(11)	2.602(6)	Zr–C(12)	2.615(6)
Zr–C(13)	2.570(6)	Zr–C(14)	2.544(6)
Zr–C(15)	2.557(6)	Zr–C(31)	2.557(6)
Zr–C(32)	2.608(7)	Zr–C(33)	2.572(6)
Zr–C(34)	2.601(7)	Zr–C(35)	2.592(6)
O(1)–C(51)	1.413(6)	O(3)–C(61)	1.402(7)
C(51)–O(2)	1.403(7)	C(61)–O(2)	1.387(8)
C(51)–C(52)	1.537(9)	C(61)–C(62)	1.545(8)
C(52)–C(53)	1.493(9)	C(62)–C(63)	1.510(10)
C(52)–C(54)	1.499(10)	C(62)–C(64)	1.518(9)
C(52)–C(55)	1.538(8)	C(62)–C(65)	1.514(10)
O(1)–Zr–O(3)	87.1(1)	Zr–O(1)–C(51)	126.4(3)
Zr–O(3)–C(61)	125.2(3)	O(1)–C(51)–O(2)	111.4(4)
O(3)–C(61)–O(2)	113.3(5)	C(51)–O(2)–C(61)	114.8(4)
O(1)–C(51)–C(52)	112.6(5)	O(3)–C(61)–C(62)	112.4(5)
O(2)–C(51)–C(52)	109.3(5)	O(2)–C(61)–C(62)	109.8(5)
C(51)–C(52)–C(53)	108.4(5)	C(61)–C(62)–C(63)	110.7(5)
C(51)–C(52)–C(54)	111.5(5)	C(61)–C(62)–C(64)	108.2(5)
C(51)–C(52)–C(55)	107.7(5)	C(61)–C(62)–C(65)	109.2(5)
C(53)–C(52)–C(54)	111.1(6)	C(63)–C(62)–C(64)	109.7(6)
C(53)–C(52)–C(55)	109.2(5)	C(63)–C(62)–C(65)	109.4(6)

by ^{1}H NMR spectroscopy. In contrast, the ^{1}H NMR spectrum of the unsubstituted derivative $Cp_2^* Zr[\eta^2$-$OCH_2OCH_2O]$ exhibits a single set of resonances for both the Cp^* ligands and $[CH_2]$ groups at room temperature, which is presumably indicative of rapid inversion of chair conformations.

The formation of the cycloaddition product $Cp_2^* Zr[\eta^2$-OCH(Pr^i)OCH(Pr^i)O] upon reaction of $Cp_2^* Zr(O)(NC_5H_5)$ with Pr^{i}CHO is notable since, unlike Bu^{t}CHO or $[CH_2O]$, Pr^{i}CHO has an α hydrogen available for deprotonation. Thus, by analogy with the reactions of the methyl ketones described above, enolization of Pr^{i}CHO to give the hypothetical product, $Cp_2^* Zr(OH)(\eta^1$-OCH=CMe$_2$), could have occurred. However, only cycloaddition is actually observed for Pr^{i}CHO.

In addition to cycloaddition reactions with aldehydes, $Cp_2^* Zr(O)(NC_5H_5)$ also rapidly undergoes a cycloaddition reaction with PhCN to give the six-membered metallacycle $Cp_2^* Zr[\eta^2$-OC(Ph)NC(Ph)=N] (Scheme 12), a complex that was first synthesized by Bergman as a result of trapping in situ generated $[Cp_2^* Zr{=}O]$ with PhCN [24–26].

2.4.2. Pyridine exchange

The synthetic studies described above emphasize that the pyridine ligand is critical to the stability of the terminal chalcogenido zirconocene derivatives. Indeed, the pyridine ligands of all the $Cp_2^* Zr(E)(NC_5H_5)$ derivatives are characterized by five inequivalent resonances in their ^{1}H NMR spectra, so that pyridine dissociation (and also rotation about the Zr–N bond) must be slow on the NMR time scale. [62] Nevertheless, ligand exchange is quite facile on the chemical time scale (Scheme 13). For example, $Cp_2^* Zr(O)(NC_5H_5)$ reacts readily with excess 4-t-butylpyridine to give $Cp_2^* Zr(O)(NC_5H_4Bu^t)$. [63] As would be expected, the exchange reaction is reversible and $Cp_2^* Zr(O)(NC_5H_4Bu^t)$ reacts with excess pyridine to regenerate $Cp_2^* Zr(O)(NC_5H_5)$. [64] Similar exchange reactions are also observed for the sulfido, selenido and tellurido derivatives $Cp_2^* Zr(E)(NC_5H_5)$, but it is yet to be determined whether these exchange reactions involve an associative or dissociative mechanism.

Exchange of coordinated pyridine by CO is also possible. For example, exposure of a benzene solution of $Cp_2^* Zr(Se)(NC_5H_5)$ to CO (1 atm) results in pyridine release and the formation of the non-classical carbonyl $Cp_2^* Zr(Se)(CO)$ [58]. However, under these conditions the reaction proceeds to only ca. 10% conversion (as judged by ^{1}H NMR spectroscopy). [65,66] The pyridine ligand of the tellurido derivative $Cp_2^* Zr(Te)(NC_5H_5)$ is also displaced by CO at room temperature (Scheme 13),

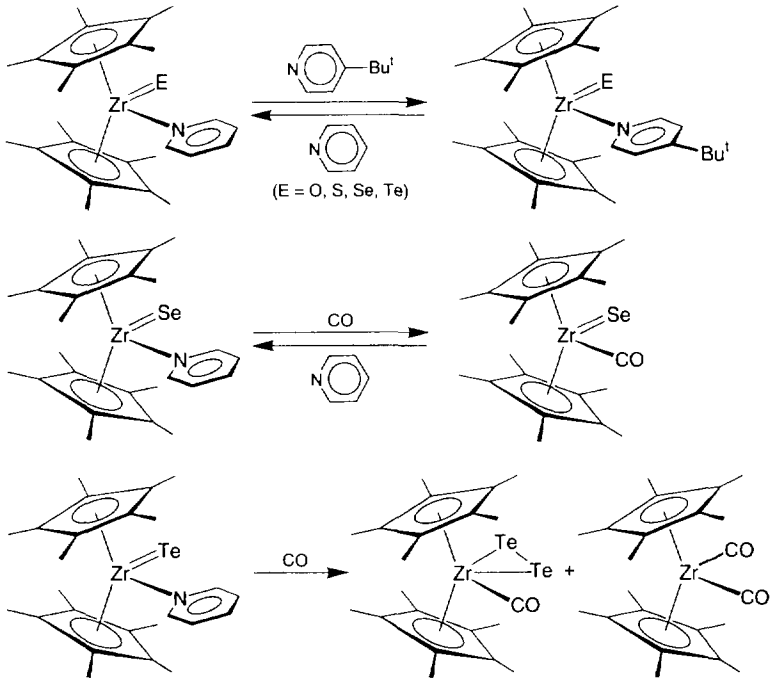
[62] Such inequivalence was first noted by Bergman for the sulfido derivative, see Ref. [24].

[63] $Cp_2^* Zr(O)(NC_5H_4Bu^t)$ may also be synthesized by the reaction of $Cp_2^* Zr(CO)_2$ with N_2O in the presence of Bu^{t}C$_5$H$_4$N.

[64] However, in contrast to the facile exchange with substituted pyridines, $Cp_2^* Zr(O)(NC_5H_5)$ does not exchange the pyridine ligand with THF.

[65] Addition of pyridine to $Cp_2^* Zr(Se)(CO)$ results in the rapid formation of $Cp_2^* Zr(Se)(NC_5H_5)$; see Ref. [58].

[66] $Cp_2^* Zr(CO)_2$ is also observed by ^{1}H NMR in the reaction of $Cp_2^* Zr(Se)(NC_5H_5)$ with excess CO. Whether or not $Cp_2^* Zr(\eta^2$-$Se_2)(CO)$ is formed is uncertain because the chemical shifts of $Cp_2^* Zr(CO)_2$ and $Cp_2^* Zr(\eta^2$-$Se_2)(CO)$ are similar.

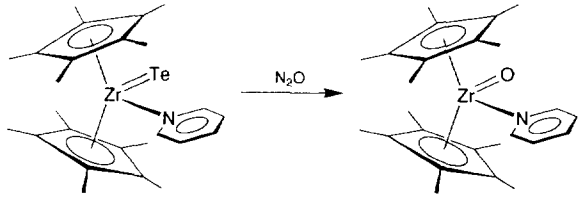


Scheme 13.

but the proposed tellurido-carbonyl $Cp_2^* Zr(Te)(CO)$ [67] has only been spectroscopically observed as an intermediate in the reaction, which ultimately yields a mixture of $Cp_2^* Zr(CO)_2$ and $Cp_2^* Zr(\eta^2\text{-}Te_2)(CO)$ [57]. In contrast to $Cp_2^* Zr(Se)(NC_5H_5)$ and $Cp_2^* Zr(Te)(NC_5H_5)$, however, the oxo and sulfido complexes $Cp_2^* Zr(O)(NC_5H_5)$ and $Cp_2^* Zr(S)(NC_5H_5)$ are stable in the presence of CO at room temperature.

2.4.3. Chalcogenido ligand exchange

The possibility of interconverting the chalcogenido complexes $Cp_2^* Zr(E)(NC_5H_5)$ (E = O, S, Se, Te) by chalcogen exchange was also explored. Significantly, the terminal tellurido complex $Cp_2^* Zr(Te)(NC_5H_5)$ reacts instantaneously with N_2O at room temperature to give the oxo derivative (Eq. (2)). [68] The sulfido and selenido complexes $Cp_2^* Zr(S)(NC_5H_5)$ and $Cp_2^* Zr(Se)(NC_5H_5)$ also react with N_2O at room temperature to yield $Cp_2^* Zr(O)(NC_5H_5)$. The latter reactions are not clean, however, and result in the formation of a mixture of $Cp_2^* Zr(O)(NC_5H_5)$ and $Cp_2^* Zr(\eta^2\text{-}E_3)$ (E = S [63], Se [57]). Likewise, the reactions of $Cp_2^* Zr(O)(NC_5H_5)$ with elemental sulfur, selenium, and tellurium do not provide a useful method for synthesizing the terminal chalcogenido complexes $Cp_2^* Zr(E)(NC_5H_5)$; for example, $Cp_2^* Zr(O)(NC_5H_5)$ reacts with S and Se to give, inter alia, the trichalcogenido complexes $Cp_2^* Zr(\eta^2\text{-}S_3)$ and $Cp_2^* Zr(\eta^2\text{-}Se_3)$, while no reaction is observed with Te under comparable conditions.



(2)

3. Summary

In summary, the series of terminal chalcogenido complexes of zirconium $Cp_2^* Zr(E)(NC_5H_5)$ (E = O, S, Se, Te) are conveniently synthesized by the reactions of $Cp_2^* Zr(CO)_2$ with either N_2O or the elemental chalcogen (S, Se, Te) in the presence of pyridine. The [Zr=E] functionalities in these complexes are highly reactive towards a large variety of substrates, with reactivity patterns that are indicative of an electrophilic d^0 zirconium center coupled to a highly nucleophilic chalcogenido ligand, i.e. $[Zr^{\delta+}=E^{\delta-}]$. Thus, the [Zr=E] functionalities are observed to undergo *(i)* formal 1,2-addition reactions with polar substrates ($X^{\delta+}$–$Y^{\delta-}$) to

[67] NMR spectroscopic data for $Cp_2^* Zr(Te)(CO)$ in C_6D_6: ^1H, δ 1.85 ppm; ^{13}C, δ 244.5 ppm.

[68] The reaction between $Cp_2^* Zr(Te)(NC_5H_5)$ and N_2O is accompanied by deposition of a dark, silvery mirror, which is believed to be elemental tellurium, although no definitive test was carried out to identify it.

give complexes of the type $Cp_2^*Zr(EX)Y$, and *(ii)* cycloaddition reactions with aldehydes and PhCN. Specific illustrations which serve to emphasize the high reactivity associated with the [Zr=O] moiety of $Cp_2^*Zr(O)(NC_5H_5)$ include its rather facile reaction towards H_2 and activated C–H bonds (e.g. enolization of ketones and dehydrohalogenation of alkyl iodides). The zirconium oxo complex $Cp_2^*Zr(O)(NC_5H_5)$ also exhibits some interesting contrasts with its permethyltungstenocene counterpart, Cp_2^*WO. For example, whereas the tungsten complex Cp_2^*WO is thermodynamically stable with respect to addition of water, the zirconium complex $Cp_2^*Zr(O)(NC_5H_5)$ reacts instantaneously and irreversibly to give $Cp_2^*Zr(OH)_2$. Finally, while both oxo complexes undergo a common reaction with Me_3SiCl to give sequentially $Cp_2^*M(OSiMe_3)Cl$ and $Cp_2^*MCl_2$, the corresponding reactions with methyl iodide result in alkylation of the oxo ligand in $Cp_2^*Zr(O)(NC_5H_5)$ to give $Cp_2^*Zr(OMe)I$, but alkylation of the tungsten center in Cp_2^*WO to give $[Cp_2^*W(O)Me][I]$. Such contrast in reactivities is clearly associated with the d^0 vs. d^2 nature of the respective metal centers, with the d^0 Zr center incapable of reacting in a nucleophilic fashion.

4. Experimental section

4.1. General considerations

All manipulations were performed using a combination of glovebox, high-vacuum, or Schlenk techniques. Solvents were purified and degassed by standard procedures. ^1H NMR spectra were measured on Varian VXR 200, 300, and 400 spectrometers in C_6D_6. ^{13}C and ^{77}Se NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 75.429 MHz and 57.22 MHz respectively. ^1H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity ($\delta = 7.15$ for C_6D_5H) or the ^{13}C resonances ($\delta = 128.0$ for C_6D_6), respectively. ^{77}Se chemical shifts are reported in ppm relative to neat Me_2Se ($\delta = 0$) and were referenced using a solution of Ph_2Se_2 in C_6D_6 ($\delta = 460$) as external standard [103]. Coupling constants are reported in hertz. NMR data are listed in Table 6. IR spectra were recorded as KBr pellets on a Perkin–Elmer 1600 FTIR spectrophotometer and the data are reported in wavenumbers. Elemental analyses were determined using a Perkin–Elmer 2400 CHN analyzer. Mass spectra were obtained on a Nermag R10-10 mass spectrometer using chemical ionization (NH_3 or CH_4) techniques. $Cp_2^*Zr(CO)_2$ [37], $Cp_2Zr(CO)_2$ [37], $Cp_2^{Bu'}ZrCl_2$ [104], and $Cp_2^*Zr(S)(NC_5H_5)$ [39] were synthesized as previously reported.

4.2. Synthesis of $Cp_2^{Bu'}Zr(CO)_2$

A mixture of $Cp_2^{Bu'}ZrCl_2$ (2.51 g, 6.21 mmol) and Mg powder (0.85 g, 34.8 mmol) (50 mesh) in THF (15 ml) at −78 °C was treated with Hg (ca. 0.01 ml) and CO (1 atm). The mixture was stirred as it was allowed to warm to room temperature. After ca. 2 h, the reaction mixture became black. The solvent was removed under reduced pressure after 2 days, and the product was extracted into pentane until the extracts were almost colorless. The combined extracts were passed through a column (ca. 7 cm) containing deactivated alumina (5%, neutral), concentrated, and cooled to −78 °C, depositing $Cp_2^{Bu'}Zr(CO)_2$ as a dark green microcrystalline solid. The product was isolated by filtration and dried in vacuo (0.39 g, 16%). Anal. Found: C, 61.9; H, 7.4. $C_{20}H_{26}O_2Zr$. Calc.: C, 61.7; H, 6.7%. IR data: 2956 (s), 2901 (m), 2865 (m), 1955 (vs) (ν_{CO}), 1858 (vs) (ν_{CO}), 1479 (m), 1458 (m), 1361 (m), 1274 (m), 1039 (m), 1020 (w), 845 (m), 801 (m), 773 (s). ^1H NMR data (C_6D_6): 4.96 (t, $^3J_{H-H} = 3$, 4H of $2\{\eta^5\text{-}C_5H_4C(CH_3)_3\}$), 5.01 (t, $^3J_{H-H} = 3$, 4H of $2\{\eta^5\text{-}C_5H_4C(CH_3)_3\}$), 1.04 (s, 18H of $2\{\eta^5\text{-}C_5H_4C(CH_3)_3\}$). Selected $^{13}C\{^1H\}$ NMR data (C_6D_6): 32.4 ($\eta^5\text{-}C_5H_4C(CH_3)_3$), 266.2 (CO).

4.3. Synthesis of $Cp_2^*Zr(O)(NC_5H_5)$

A mixture of $Cp_2^*Zr(CO)_2$ (0.33 g, 0.79 mmol) and excess pyridine (ca. 2 ml) in toluene (5 ml) was treated with N_2O (1 atm) and stirred at 85 °C for ca. 12 h. The volatile components were removed under reduced pressure and the solid residue was washed with pentane (3 × 5 ml). The product was extracted twice from the solid residue with toluene (50 ml and 15 ml), and the extracts were combined. The volatile components of the extract were removed under reduced pressure, giving $Cp_2^*Zr(O)(NC_5H_5)$ as an orange-red crystalline solid (0.21 g, 58%). Anal. Found: C, 65.1; H, 7.5; N, 3.1. $C_{25}H_{35}NOZr$. Calc.: C, 65.7; H, 7.7; N, 3.1%. MS: m/z 456 (M + 1). IR data: 2902 (vs), 1599 (m), 1479 (vs), 1440 (vs), 1375 (s), 1207 (m), 1063 (m), 1024 (m), 780 (vs) ($\nu_{Zr=O}$), 712 (s), 634 (w).

4.4. Synthesis of $Cp_2^*Zr(O)(NC_5H_4Bu')$

A mixture of $Cp_2^*Zr(CO)_2$ (0.50 g, 1.20 mmol) and 4-t-butylpyridine (0.50 g, 3.7 mmol) in toluene (5 ml) was stirred under N_2O (1 atm) at 80 °C overnight. The volatile components were removed under reduced pressure, and the solid residue was washed with pentane (3 × 5 ml). The product, a tan powder, was dried in vacuo (0.43 g, 70%). Anal. Found: C, 67.0; H, 7.8; N, 3.6. $C_{29}H_{43}NOZr$. Calc.: C, 67.9; H, 8.5; N, 2.7%. MS: m/z 512 (M + 1). IR data: 2964 (s), 2905 (s), 2723 (w), 1614 (m), 1479 (m), 1372 (m), 1274 (w), 1232 (w),

Table 6
^{1}H and ^{13}C NMR data [a]

Compound/assignment	δ (ppm)	Coupling (Hz)
$Cp^*_2Zr(O)(NC_5H_5)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.92	s
NC_5H_5		
2H	6.42	m
1H	6.73	m
1H	7.54	m
1H	9.24	m
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.5	q, $^{1}J_{C-H}=125$
$2(\eta^5\text{-}C_5(CH_3)_5)$	116.1	s
NC_5H_5		
1C	122.8	d, $^{1}J_{C-H}=165$
1C	125.0	d, $^{1}J_{C-H}=168$
1C	137.7	d, $^{1}J_{C-H}=163$
1C	148.6	d, $^{1}J_{C-H}=179$
1C	157.9	d, $^{1}J_{C-H}=190$
$Cp^*_2Zr(O)(NC_5H_4Bu^t)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.97	s
$NC_5H_4(C(CH_3)_3)$	0.86	s
$NC_5H_4(C(CH_3)_3)$		
2H	6.68	m
1H	7.58	m
1H	9.22	m
$Cp^*_2Zr(Se)(NC_5H_5)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.93	s
NC_5H_5		
1H	6.12	m
1H	6.22	m
1H	6.57	m
1H	7.12	m
1H	9.42	m
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	13.2	q, $^{1}J_{C-H}=126$
$2(\eta^5\text{-}C_5(CH_3)_5)$	119.2	s
NC_5H_5		
1C	121.7	d, $^{1}J_{C-H}=172$
1C	123.4	d, $^{1}J_{C-H}=172$
1C	137.3	d, $^{1}J_{C-H}=164$
1C	147.4	d, $^{1}J_{C-H}=178$
1C	162.5	d, $^{1}J_{C-H}=191$
$Cp^*_2Zr(Se)(NC_5H_4Bu^t)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.98	s
$NC_5H_4(C(CH_3)_3)$	0.81	s
$NC_5H_4(C(CH_3)_3)$		
1H	6.27	m
1H	6.55	m
1H	7.17	m
1H	9.35	m
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	13.2	q, $^{1}J_{C-H}=126$
$2(\eta^5\text{-}C_5(CH_3)_5)$	119.1	s
$NC_5H_4(C(CH_3)_3)$	29.8	q, $^{1}J_{C-H}=126$
$NC_5H_4(C(CH_3)_3)$	34.7	s
$NC_5H_4(C(CH_3)_3)$		
1C	119.3	d, $^{1}J_{C-H}=163$
1C	120.7	d, $^{1}J_{C-H}=164$
1C	147.4	d, $^{1}J_{C-H}=177$
1C	162.4	s

Table 6 (continued)

Compound/assignment	δ (ppm)	Coupling (Hz)
1C	162.6	d, $^{1}J_{C-H}=188$
$Cp^*_2Zr(Te)(NC_5H_5)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.92	s
NC_5H_5		
1H	6.06	m
1H	6.18	m
1H	6.56	m
1H	6.94	m
1H	9.30	m
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	14.7	q, $^{1}J_{C-H}=126$
$2(\eta^5\text{-}C_5(CH_3)_5)$	120.1	s
NC_5H_5		
1C	121.0	d
1C	122.2	d
1C	137.6	d
1C	145.4	d
1C	162.6	d
$Cp^*_2Zr(OH)(SH)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.81	s
OH	4.36	s
SH	0.83	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.5	q, $^{1}J_{C-H}=126$
$2(\eta^5\text{-}C_5(CH_3)_5)$	119.2	s
$Cp^*_2Zr(OH)(SeH)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.82	s
OH	4.56	s
SeH	−1.72	s, $^{1}J_{Se-H}=28$
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.8	q, $^{1}J_{C-H}=127$
$2(\eta^5\text{-}C_5(CH_3)_5)$	119.2	s
^{77}Se NMR		
SeH	27	d, $^{1}J_{Se-H}=28$
$Cp^*_2Zr(SeH)_2$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.85	s
$2SeH$	−0.74	s, $^{1}J_{Se-H}=30$
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	12.8	q, $^{1}J_{C-H}=127$
$2(\eta^5\text{-}C_5(CH_3)_5)$	120.1	s
^{77}Se NMR		
$2SeH$	267	d, $^{1}J_{Se-H}=30$
$Cp^*_2Zr(\eta^2\text{-}OCOMe)(\eta^1\text{-}OCOMe)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.80	s
$2(OCO(CH_3))$	2.01	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.0	q, $^{1}J_{C-H}=127$
$2(\eta^5\text{-}C_5(CH_3)_5)$	121.3	s
$2(OCO(CH_3))$	24.5	q, $^{1}J_{C-H}=128$
$2(OCO(CH_3))$	178.8	s
$Cp^*_2Zr(OH)(NHPh)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.75	s
OH	4.94	s
$NH(C_6H_5)$	3.60	broad s
$NH(C_6H_5)$		
3H	6.75	m
2H	7.27	t, $^{3}J_{H-H}=8$

Table 6 (continued)

Compound/assignment	δ (ppm)	Coupling (Hz)
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.2	q, $^1J_{C-H}$ = 126
$2(\eta^5\text{-}C_5(CH_3)_5)$	119.3	s
C_6H_5		
1C	114.7	d, $^1J_{C-H}$ = 159
2C	118.2	d, $^1J_{C-H}$ = 151
2C	128.9	d, $^1J_{C-H}$ = 158
1C	155.8	s
$Cp_2^*Zr(OH)(NH_2)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.83	s
OH	2.70	s
NH_2	3.02	broad s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.0	q, $^1J_{C-H}$ = 126
$2(\eta^5\text{-}C_5(CH_3)_5)$	117.0	s
$Cp_2^*Zr(OH)(\eta^2\text{-}NPhNH_2)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.73	s
OH	3.20	s
$\eta^2\text{-}NH_2NPh$	2.20	s
$\eta^2\text{-}NH_2N(C_6H_5)$		
1H	6.51	m
2H	6.75	m
2H	7.26	m
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.1	q, $^1J_{C-H}$ = 126
$2(\eta^5\text{-}C_5(CH_3)_5)$	117.2	s
$\eta^2\text{-}NH_2N(C_6H_5)$		
2C	115.5	d, $^1J_{C-H}$ = 160
2C	129.3	d, $^1J_{C-H}$ = 144
1C	155.1	s
1C	not located	
$Cp_2^*Zr(SeH)(\eta^2\text{-}NPhNH_2)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.69	s
SeH	−2.30	s, $^1J_{Se-H}$ = 34
$\eta^2\text{-}NH_2NPh$	1.87	s
$\eta^2\text{-}NH_2N(C_6H_5$		
2H	6.74	m
3H	7.23	m
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.9	q, $^1J_{C-H}$ = 127
$2(\eta^5\text{-}C_5(CH_3)_5)$	117.4	s
$\eta^2\text{-}NH_2N(C_6H_5)$		
1C	116.7	d, $^1J_{C-H}$ = 160
2C	129.0	d, $^1J_{C-H}$ = 157
1C	154.4	s
2C	not located	
$Cp_2^*Zr(H)(OSiH_2Ph)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.91	s
$Zr\text{-}H$	6.29	s
$OSiH_2(C_6H_5)$	5.71	s
$OSiH_2(C_6H_5)$		
1H	7.22	m
2H	7.27	m
2H	7.80	m
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.9	q, $^1J_{C-H}$ = 126
$2(\eta^5\text{-}C_5(CH_3)_5)$	118.3	s
$OSiH_2(C_6H_5)$		
2C	128.1	d, $^1J_{C-H}$ = 159
1C	129.7	d $^1J_{C-H}$ = 159
2C	134.2	d, $^1J_{C-H}$ = 158
1C	138.0	s
$Cp_2^*Zr(OSiMe_3)(Cl)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.85	s
$OSi(CH_3)_3$	0.30	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	12.0	q, $^1J_{C-H}$ = 127
$2(\eta^5\text{-}C_5(CH_3)_5)$	121.6	s
$OSi(CH_3)_3$	4.8	q, $^1J_{C-H}$ = 118
$Cp_2^*Zr(OMe)(I)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.90	s
OCH_3	3.85	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	12.7	q, $^1J_{C-H}$ = 127
$2(\eta^5\text{-}C_5(CH_3)_5)$	121.3	s
OCH_3	60.7	q, $^1J_{C-H}$ = 140
$Cp_2^*Zr(SMe)(I)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.95	s
OCH_3	2.57	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	13.4	q, $^1J_{C-H}$ = 126
$2(\eta^5\text{-}C_5(CH_3)_5)$	122.5	s
SCH_3	22.9	q, $^1J_{C-H}$ = 138
$Cp_2^*Zr(SeMe)(I)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.95	s
$SeCH_3$	2.57	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	13.5	q, $^1J_{C-H}$ = 127
$2(\eta^5\text{-}C_5(CH_3)_5)$	122.5	s
$SeCH_3$	10.7	q, $^1J_{C-H}$ = 141
$Cp_2^*Zr(TeMe)(I)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.97	s
$TeCH_3$	2.51	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	14.0	q, $^1J_{C-H}$ = 126
$2(\eta^5\text{-}C_5(CH_3)_5)$	122.5	s
$TeCH_3$	−18.9	q, $^1J_{C-H}$ = 141
$Cp_2^*Zr(OH)(I)$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.86	s
OH	5.55	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	12.6	q, $^1J_{C-H}$ = 127
$2(\eta^5\text{-}C_5(CH_3)_5)$	121.0	s
$Cp_2^*Zr(OH)[\eta^1\text{-}OC(Me)=CH_2]$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.86	s
OH	4.27	s
$\eta^1\text{-}OC(CH_3)=CH_2$	4.05	s
	4.09	s
$\eta^1\text{-}OC(CH_3)=CH_2$	1.86	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	10.9	q, $^1J_{C-H}$ = 126
$2(\eta^5\text{-}C_5(CH_3)_5)$	119.8	s
$\eta^1\text{-}OC(CH_3)=CH_2$	85.6	t, $^1J_{C-H}$ = 155
$\eta^1\text{-}OC(CH_3)=CH_2$	not observed [b]	
$\eta^1\text{-}OC(CH_3)=CH_2$	23.8	q, $^1J_{C-H}$ = 119

Table 6 (continued)

Compound/assignment	δ (ppm)	Coupling (Hz)
$Cp_2^*Zr(OH)[\eta^1\text{-}OC(Bu^t)=CH_2]$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.89	s
OH	4.16	s
$\eta^1\text{-}OC[C(CH_3)_3]=CH_2$	3.80	broad s
	3.93	broad s
$\eta^1\text{-}OC[C(CH_3)_3]=CH_2$	1.27	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.4	q, $^1J_{C-H}=126$
$2(\eta^5\text{-}C_5(CH_3)_5)$	119.9	s
$\eta^1\text{-}OC[C(CH_3)_3]=CH_2$	84.1	t, $^1J_{C-H}=154$
$\eta^1\text{-}OC[C(CH_3)_3]=CH_2$	172.8	s
$\eta^1\text{-}OC[C(CH_3)_3]=CH_2$	30.2	q, $^1J_{C-H}=126$
$\eta^1\text{-}OC[C(CH_3)_3]=CH_2$	38.2	s
$Cp_2^*Zr(SeH)[\eta^1\text{-}OC(Me)=CH_2]$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	1.87	s
SeH	−1.31	s, $^1J_{Se-H}=32$
$\eta^1\text{-}OC(CH_3)=CH_2$	3.99	s
	4.04	s
$\eta^1\text{-}OC(CH_3)=CH_2$	1.81	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.9	q, $^1J_{C-H}=127$
$2(\eta^5\text{-}C_5(CH_3)_5)$	120.5	s
$\eta^1\text{-}OC(CH_3)=CH_2$	86.9	t, $^1J_{C-H}=156$
$\eta^1\text{-}OC(CH_3)=CH_2$	162.5	s
$\eta^1\text{-}OC(CH_3)=CH_2$	22.8	q, $^1J_{C-H}=116$
$Cp_2^*Zr[\eta^2\text{-}OCH(Bu^t)OCH(Bu^t)O]$		
^{1}H NMR		
$1(\eta^5\text{-}C_5(CH_3)_5)$	1.80	s
$1(\eta^5\text{-}C_5(CH_3)_5)$	1.95	s
$2Bu^t$	1.20	s
$2OCHBu^t$	4.52	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.4	q, $^1J_{C-H}=126$
	11.8	q, $^1J_{C-H}=126$
$2(\eta^5\text{-}C_5(CH_3)_5)$	120.0	s
	121.0	s
$C(CH_3)_3$	26.6	q, $^1J_{C-H}=126$
$C(CH_3)_3$	37.1	s
$2CHBu^t$	108.2	d, $^1J_{C-H}=157$
$Cp^*2Zr[\eta^2\text{-}OCH_2OCH_2O]$		
^{1}H NMR		
$2(\eta^5\text{-}C_5(CH_3)_5$	1.88	s
$2CH_2$	5.34	s
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5$	11.2	q, $^1J_{C-H}=126$
$2(\eta^5\text{-}C_5(CH_3)_5$	120.9	s
$2CH_2$	93.9	t, $^1J_{C-H}=162$
		t, $^3J_{C-H}=6$
$Cp_2^*Zr[\eta^2\text{-}OCH(Pr^i)OCH(Pr^i)O]$		
^{1}H NMR		
$1(\eta^5\text{-}C_5(CH_3)_5$	1.81	s
$1(\eta^5\text{-}C_5(CH_3)_5$	1.91	s
$2CH(CH_3)_2$	1.15	d, $^3J_{H-H}=8$
	1.19	d, $^3J_{H-H}=8$
$2CH(CH_3)_2$	not located [c]	
$2CHPr^i$	4.44	d, $^3J_{H-H}=8$
^{13}C NMR		
$2(\eta^5\text{-}C_5(CH_3)_5)$	11.1	q, $^1J_{C-H}=126$
	11.6	q, $^1J_{C-H}=126$
$2(\eta^5\text{-}C_5(CH_3)_5)$	119.9	s
	120.7	s
$2CH(CH_3)_2$	19.3	q, $^1J_{C-H}=124$
$2CH(CH_3)_2$	36.9	d, $^1J_{C-H}=126$
$2CHPr^i$	107.0	d, $^1J_{C-H}=153$

[a] In C_6D_6. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet.
[b] Insufficient signal to noise ratio.
[c] Resonance obscured by (η^5-C_5Me_5) resonances.

1072 (w), 1021 (m), 844 (w), 784 (s) ($\nu_{Zr=O}$), 726 (w), 665 (w), 579 (w).

4.5. Synthesis of $Cp_2^*Zr(Se)(NC_5H_5)$

A mixture of $Cp_2^*Zr(CO)_2$ (1.05 g, 2.51 mmol), selenium powder (0.19 g, 2.41 mmol of 'Se'), and excess pyridine (ca. 5 ml) in toluene (10 ml) was stirred at 85 °C overnight. The volatile components of the reaction mixture were removed under reduced pressure, leaving a greenish brown solid residue which was washed with pentane (3 × 5 ml). The product was dried and isolated as a green-brown crystalline solid (1.01 g, 81% based on selenium). Anal. Found: C, 57.8; H, 6.8; N, 3.0. $C_{25}H_{35}NSeZr$. Calc.: C, 57.8; H, 6.8; N, 2.7%. IR data: 3050 (w), 2970 (m), 2943 (s), 2889 (vs), 1601 (m), 1480 (m), 1439 (vs), 1372 (s), 1211 (m), 1066 (m), 1022 (s), 961 (w), 805 (w), 756 (m), 706 (s), 634 (w), 597 (w).

4.6. Synthesis of $Cp_2^*Zr(Se)(NC_5H_4Bu^t)$

A mixture of $Cp_2^*Zr(CO)_2$ (0.23 g, 0.55 mmol), selenium powder (0.04 g, 0.51 mmol of 'Se'), and excess 4-t-butylpyridine (ca. 2 ml) in toluene (5 ml) was stirred at ca. 80 °C for 12 h. The volatile components of the reaction mixture were removed under reduced pressure, leaving a residue which was washed several times with pentane (10 ml portions) and dried in vacuo giving a green-brown crystalline solid (0.22 g, 75% based on selenium). Anal. Found: C, 60.5; H, 7.8; N, 3.0. $C_{29}H_{43}NSeZr$. Calc.: C, 60.5; H, 7.5; N, 2.4%.

4.7. Synthesis of $Cp_2^*Zr(Te)(NC_5H_5)$

A mixture of $Cp_2^*Zr(CO)_2$ (0.38 g, 0.90 mmol), tellurium powder (0.11 g, 0.87 mmol of 'Te'), and excess pyridine (ca. 1 ml) in toluene (5 ml) was stirred at 80 °C. After 1 h, the CO containing atmosphere in the ampoule was removed and replaced with argon. The mixture was subsequently stirred overnight, after which the volatile components were removed under reduced pressure. The dull red residue obtained was washed with pentane (4 × 5 ml) and dried in vacuo giving a brick red microcrystalline solid (0.33 g, 67% based on tellurium). Anal.

Found: C, 52.0; H, 6.0; N, 2.7. $C_{25}H_{35}NTeZr$. Calc.: C, 52.8; H, 6.2; N, 2.5%. IR data: 3050 (w), 2889 (vs), 1600 (m), 1481 (s), 1438 (vs), 1373 (s), 1210 (s), 1066 (m), 1022 (s), 755 (m), 704 (s), 634 (w).

4.8. Reaction of $Cp_2^* Zr(CO)_2$ with Ph_3PE (E = S, Se) and pyridine

The reaction of $Cp_2^* Zr(CO)_2$ (ca. 10 mg) in C_6D_6 (1 ml) with Ph_3PE (E = S, 14 mg; E = Se, 13 mg) in pyridine (ca. 15 μl) was monitored by ^1H NMR spectroscopy, which demonstrated the formation of $Cp_2^* Zr(E)(NC_5H_5)$ to be complete within 2 days at 90 °C for $Cp_2^* Zr(S)(NC_5H_5)$ and within 3.5 days at 50 °C for $Cp_2^* Zr(Se)(NC_5H_5)$.

4.9. Reaction of $Cp_2^* Zr(CO)_2$ with H_2Se and pyridine

A mixture of $Cp_2^* Zr(CO)_2$ (ca. 20 mg) and excess pyridine in C_6D_6 (1 ml) was treated with H_2Se (less than one equivalent). ^1H NMR spectroscopy demonstrated the formation of $Cp_2^* Zr(Se)(NC_5H_5)$ to be complete within 3 days at 85 °C.

4.10. Reaction of $Cp_2^* Zr(CO)_2$ with H_2O

A solution of $Cp_2^* Zr(CO)_2$ (ca. 10 mg) in C_6D_6 (1 ml) was treated with H_2O (ca. 20 μl) and heated at ca. 80 °C. The reaction was monitored by ^1H NMR spectroscopy, which demonstrated the formation of $Cp_2^* Zr(OH)_2$ to be complete within 5 days. Likewise, $Cp_2^* Zr(OH)_2$ was also formed when the reaction between $Cp_2^* Zr(CO)_2$ and H_2O was carried out in the presence of pyridine.

4.11. Reaction of $Cp_2 Zr(CO)_2$ with N_2O and pyridine

A mixture of $Cp_2Zr(CO)_2$ (ca. 10 mg, 0.04 mmol) and pyridine (excess) in C_6D_6 (1 ml) was heated under N_2O (1 atm) for ca. 12 h at 80 °C giving $[Cp_2Zr(\mu\text{-}O)]_3$, as identified by comparison with the ^1H NMR data of an authentic sample [8].

4.12. Reactions of $Cp_2^{Bu^t} Zr(CO)_2$ with E (S, Se, Te) and pyridine

The reactions between $Cp_2^{Bu^t} Zr(CO)_2$ and E (S, Se, Te) in the presence of pyridine were monitored by ^1H NMR spectroscopy and the products identified as $[Cp_2^{Bu^t} Zr(\mu\text{-}E)]_2$ by comparison with the ^1H NMR data reported in the literature (E = S [67], Se [67], Te [71]). For example, a mixture of $Cp_2^{Bu^t} Zr(CO)_2$ (3 mg, 0.08 mmol), Se (6 mg, 0.008 mmol) and pyridine (excess) in C_6D_6 (1 ml) was heated at 80 °C for ca. 12 h to give $[Cp_2^{Bu^t} Zr(\mu\text{-}Se)]_2$, as identified by ^1H NMR spectroscopy.

4.13. Reaction of $Cp_2^* Zr(E)(NC_5H_5)$ with HCl

A solution of $Cp_2^* Zr(O)(NC_5H_5)$ (ca. 10 mg) in C_6D_6 (1 ml) was treated with $HCl_{(g)}$. ^1H NMR spectroscopy demonstrated the formation of a mixture of $Cp_2^* Zr(OH)Cl$ and $Cp_2^* ZrCl_2$ to be complete within 10 min at room temperature. In the presence of excess $HCl_{(g)}$ complete conversion to $Cp_2^* ZrCl_2$ was observed. Likewise, the reaction of $Cp_2^* Zr(E)(NC_5H_5)$ (E = S, Se, Te) with excess $HCl_{(g)}$ was demonstrated to give $Cp_2^* ZrCl_2$ by ^1H NMR spectroscopy.

4.14. Reaction of $Cp_2^* Zr(O)(NC_5H_5)$ with H_2O

A solution of $Cp_2^* Zr(O)(NC_5H_5)$ (ca. 10 mg) in C_6D_6 (1 ml) was treated with H_2O. ^1H NMR spectroscopy demonstrated the formation of $Cp_2^* Zr(OH)_2$ to be complete within 5 min at room temperature.

4.15. Reaction of $Cp_2^* Zr(S)(NC_5H_5)$ with H_2O: synthesis of $Cp_2^* Zr(OH)(SH)$

(a) A stirred suspension of $Cp_2^* Zr(S)(NC_5H_5)$ (0.20 g, 0.42 mmol) in benzene (5 ml) was treated with H_2O (7.6 μl, 0.42 mmol) and stirred for 20 min at room temperature. Over this period the mixture became yellow and clear. The volatile components were removed by lyophilization to give $Cp_2^* Zr(OH)(SH)$ as a yellow solid (0.14 g, 81%). *Note*: the product is contaminated with small amounts of $Cp_2^* Zr(OH)_2$ and $Cp_2^* Zr(SH)_2$ (ca. 10% of each as judged by ^1H NMR spectroscopy). Anal. Found: C, 58.8; H, 7.6. $C_{20}H_{32}OSZr$: Calc.: C, 58.3; H, 7.8%. IR data: 3673 (m), 3567 (s, br), 2905 (vs), 2723 (w), 1490 (s), 1439 (vs), 1379 (vs), 1261 (w), 1164 (w), 1063 (w), 1024 (s), 806 (w), 555 (vs).

(b) A solution of $Cp_2^* Zr(S)(NC_5H_5)$ (ca. 10 mg) in C_6D_6 (1 ml) was treated with excess H_2O (ca. 15 μl) and observed by ^1H NMR spectroscopy to give an approximately 1:1 mixture of $Cp_2^* Zr(OH)(SH)$ and $Cp_2^* Zr(OH)_2$ within 30 min at room temperature. The volatile components were removed, excess H_2O was added and the mixture heated at 110 °C to convert the mixture to $Cp_2^* Zr(OH)_2$.

4.16. Reaction of $Cp_2^* Zr(Se)(NC_5H_5)$ with H_2O: synthesis of $Cp_2^* Zr(OH)(SeH)$

A stirred suspension of $Cp_2^* Zr(Se)(NC_5H_5)$ (0.20 g, 0.38 mmol) in benzene (5 ml) was treated with H_2O (7.0 μl, 0.39 mmol) and stirred for 15 min at room temperature. Over this period the mixture became yellow-orange and clear. The volatile components were removed by lyophilization to give $Cp_2^* Zr(OH)(SeH)$ as a yellow solid (0.12 g, 68%). *Note*: the product is contaminated with small amounts of $Cp_2^* Zr(OH)_2$ and $Cp_2^* Zr(SeH)_2$ (ca. 10% of each as judged by ^1H NMR

spectroscopy). Anal. Found: C, 52.9; H, 7.1. $C_{20}H_{32}OSeZr$. Calc.: C, 52.4; H, 7.0%. IR data: 3675 (m), 3534 (s, br), 2903 (vs), 2723 (m), 2330 (m) (ν_{SeH}; 1676 for ν_{SeD}), 1489 (m), 1439 (vs), 1378 (vs), 1261 (w), 1163 (w), 1063 (w), 1023 (s), 805 (w), 534 (s).

4.17. Reaction of $Cp^*_2Zr(O)(NC_5H_5)$ with H_2S

A solution of $Cp^*_2Zr(O)(NC_5H_5)$ in C_6D_6 (1 ml) was treated with H_2S (1 atm). ^1H NMR spectroscopy demonstrated the rapid formation of a mixture of $Cp^*_2Zr(OH)(SH)$ and $Cp^*_2Zr(SH)_2$. Over a period of 4 days, further conversion of $Cp^*_2Zr(OH)(SH)$ to $Cp^*_2Zr(SH)_2$ was observed.

4.18. Reaction of $Cp^*_2Zr(O)(NC_5H_5)$ with H_2Se

A suspension of $Cp^*_2Zr(O)(NC_5H_5)$ (0.20 g, 0.44 mmol) in toluene (5 ml) was stirred under H_2Se (ca. 0.2 atm) at room temperature for 5 min. The volatile components were removed under reduced pressure, giving $Cp^*_2Zr(SeH)_2$ as a yellow-orange solid (0.16 g, 70%).

4.19. Reaction of $Cp^*_2Zr(S)(NC_5H_5)$ with H_2S

A solution of $Cp^*_2Zr(S)(NC_5H_5)$ (ca. 10 mg) in C_6D_6 (1 ml) was treated with H_2S (1 atm). ^1H NMR spectroscopy demonstrated the formation of $Cp^*_2Zr(SH)_2$ to be complete within 5 min at room temperature.

4.20. Reaction of $Cp^*_2Zr(Se)(NC_5H_5)$ with H_2Se: synthesis of $Cp^*_2Zr(SeH)_2$

A suspension of $Cp^*_2Zr(Se)(NC_5H_5)$ (0.33 g, 0.63 mmol) in toluene (5 ml) was stirred under H_2Se (ca. 0.2 atm) at room temperature for 1 h. The volatile components were removed under reduced pressure, giving $Cp^*_2Zr(SeH)_2$ as a yellow-orange solid (0.27 g, 83%). Anal. Found: C, 46.2; H, 6.3. $C_{20}H_{32}Se_2Zr$. Calc.: C, 46.1; H, 6.2%. IR data: 2945 (m), 2888 (vs), 2327 (m) (ν_{SeH}), 1487 (s), 1426 (vs), 1376 (vs), 1024 (vs).

4.21. Synthesis of $Cp^*_2Zr(\eta^2\text{-}O_2CMe)(\eta^1\text{-}OCOMe)$

A mixture of $Cp^*_2Zr(O)(NC_5H_5)$ (100 mg, 0.22 mmol) and excess acetic acid (50 μl, 0.87 mmol) in toluene (ca. 5 ml) was stirred at room temperature for 10 min. The volatile components were removed under reduced pressure at ca. 100 °C, leaving a pale yellow solid. The residue was extracted into pentane (ca. 15 ml), and the volatile components of this solution were removed under reduced pressure, giving $Cp^*_2Zr(\eta^2\text{-}OCOMe)(\eta^1\text{-}OCOMe)$ as a pale yellow-white powder (74 mg, 70%). Anal. Found: C, 59.9; H, 7.7. $C_{24}H_{36}O_4Zr$. Calc.: C, 60.1; H, 7.6%. MS: m/z 478 (M^+). IR data: 2958 (s), 2912 (vs), 1647 (vs), 1541 (vs), 1478 (vs), 1431 (vs), 1364 (vs), 1299 (vs), 1019 (s), 938 (m), 808 (w), 692 (s), 637 (w), 597 (w), 475 (w).

4.22. Reaction of $Cp^*_2Zr(O)(NC_5H_5)$ with PhOH

A solution of $Cp^*_2Zr(O)(NC_5H_5)$ (ca. 20 mg, 0.04 mmol) in C_6D_6 (1 ml) was treated with excess PhOH and monitored by ^1H NMR spectroscopy, which demonstrated the immediate formation of a mixture of compounds identified as $Cp^*_2Zr(OPh)(OH)$ and $Cp^*_2Zr(OPh)_2$ [80]. After 5 h, the latter complex was the principal component.

4.23. Reaction of $Cp^*_2Zr(O)(NC_5H_5)$ with MeOH

A solution of $Cp^*_2Zr(O)(NC_5H_5)$ (20 mg, 0.04 mmol) in C_6D_6 (1 ml) was treated with MeOH (2 μl, 0.05 mmol). ^1H NMR spectroscopy revealed the formation of a mixture of products within 10 min that are tentatively identified as $Cp^*_2Zr(OMe)(OH)$, $Cp^*_2Zr(OMe)_2$, and $Cp^*_2Zr(OH)_2$.

4.24. Synthesis of $Cp^*_2Zr(OH)(NH_2)$

A suspension of $Cp^*_2Zr(O)(NC_5H_5)$ (210 mg, 0.45 mmol) in toluene (5 ml) was stirred under NH_3 (1 atm) for 20 min at room temperature. The volatile components were removed under reduced pressure, giving $Cp^*_2Zr(OH)(NH_2)$ as a fluffy, light pink powder (130 mg, 72%). Anal. Found: C, 60.7; H, 8.8; N, 3.7. $C_{20}H_{33}NOZr$. Calc.: C, 60.9; H, 8.4; N, 3.6%. MS: m/z 394 ($M^+ + 1$). IR data: 3680 (s), 3655 (s), 3510 (m, br), 2908 (vs), 2863 (vs), 2723 (m), 1524 (s), 1494 (s), 1442 (s), 1378 (s), 1025 (m), 806 (w), 555 (vs), 521 (vs).

4.25. Synthesis of $Cp^*_2Zr(OH)(NHPh)$

A mixture of $Cp^*_2Zr(O)(NC_5H_5)$ (200 mg, 0.44 mmol) and aniline (60 μl, 0.66 mmol) in toluene (5 ml) was stirred at 70 °C for 1.5 h. The volatile components were removed under reduced pressure, leaving a brown oily residue which was dissolved in pentane (10 ml). The volatile components of this solution were removed under reduced pressure, giving $Cp^*_2Zr(OH)(NHPh)$ as a dark red-brown crystalline solid (140 mg, 68%). Anal. Found: C, 66.0; H, 7.9; N, 3.5. $C_{26}H_{37}NOZr$. Calc.: C, 66.3; H, 7.9; N, 3.0%. MS: m/z 469 (M^+). IR data: 3663 (w, br) (ν_{O-H}, ν_{N-H}), 3020 (w), 2908 (s), 1591 (s), 1486 (s), 1378 (s), 1356 (w), 1281 (vs), 1173 (w), 1025 (w), 991 (w), 847 (m), 746 (m), 692 (w), 589 (w), 537 (m), 474 (w).

4.26. Synthesis of $Cp_2^*Zr(OH)[\eta^2$-N(Ph)NH$_2$]

A mixture of $Cp_2^*Zr(O)(NC_5H_5)$ (200 mg, 0.44 mmol) and phenylhydrazine (50 μl, 0.51 mmol) in toluene (5 ml) was stirred at room temperature for 10 min. The volatile components were removed under reduced pressure, leaving a brown oily residue which was dissolved in toluene (10 ml). The volatile components of this solution were removed under reduced pressure, giving $Cp_2^*Zr(OH)[\eta^2$-N(Ph)NH$_2$] as a dark pink crystalline solid (160 mg, 75%). Anal. Found: C, 64.0; H, 7.9; N, 5.8. $C_{26}H_{38}N_2OZr$. Calc.: C, 64.3; H, 7.9; N, 5.8%. MS: *m/z* 483 ($M^+ - 1$). IR data: 3678 (w) and 3654 (w) (ν_{O-H} and ν_{N-H}), 2909 (s), 2861 (s), 1592 (s), 1569 (s), 1487 (vs), 1375 (w), 1322 (vs), 1278 (s), 1173 (m), 1088 (w), 1023 (w), 984 (w), 839 (s), 743 (m), 691 (w), 640 (w), 504 (s), 459 (w).

4.27. Synthesis of $Cp_2^*Zr(SeH)[\eta^2$-N(Ph)NH$_2$]

A mixture of $Cp_2^*Zr(Se)(NC_5H_5)$ (200 mg, 0.38 mmol) and phenylhydrazine (40 μl, 0.41 mmol) in toluene (5 ml) was stirred at room temperature for 1 day. The volatile components were removed under reduced pressure, giving $Cp_2^*Zr(SeH)[\eta^2$-N(Ph)NH$_2$] as a light yellow powder (190 mg, 91%). Anal. Found: C, 56.3; H, 6.5; N, 5.7. $C_{26}H_{38}N_2SeZr$. Calc.: C, 56.9; H, 7.0; N, 5.1%. MS: *m/z* 548 (M^+). IR data: 3297 (w), 3240 (w), 3052 (w), 2906 (s), 2364 (w), 2324 (w), 1591 (vs), 1568 (vs), 1489 (vs), 1444 (m), 1378 (m), 1314 (vs), 1276 (vs), 1180 (m), 1023 (m), 986 (m), 838 (s), 744 (m), 693 (w), 661 (m), 596 (w), 404 (m).

4.28. Reaction of $Cp_2^*Zr(O)(NC_5H_5)$ with H_2

A solution of $Cp_2^*Zr(O)(NC_5H_5)$ in C_6D_6 (1 ml) was treated with H_2 (ca. 1 atm). ^{1}H NMR spectroscopy revealed the formation of $[Cp_2^*ZrH](\mu$-O)$[Cp_2^*Zr(OH)]$ [62] to be complete after 1 day at 80 °C.

4.29. Synthesis of $Cp_2^*Zr(H)(OSiH_2Ph)$

A mixture of $Cp_2^*Zr(O)(NC_5H_5)$ (240 mg, 0.53 mmol) and phenylsilane (70 μl, 0.56 mmol) in toluene (5 ml) was stirred at room temperature for 1 h. The volatile components were removed under reduced pressure, leaving an orange solid. The residue was dissolved in pentane (10 ml), and the volatile components of this solution were removed under reduced pressure, giving $Cp_2^*Zr(H)(OSiH_2Ph)$ as an orange crystalline solid (200 mg, 78%). Anal. Found: C, 64.5; H, 8.3. $C_{26}H_{38}OSiZr$. Calc.: C, 64.3; H, 7.9%. MS: *m/z* 483 ($M^+ - 1$). IR data: 2978 (m), 2905 (s), 2095 (vs) (ν_{SiH}), 1570 (m), 1486 (m), 1448 (m), 1428 (s), 1377 (s), 1118 (s), 1066 (w), 1029 (m), 1000 (vs), 992 (vs), 894 (vs), 761 (w), 700 (vs).

4.30. Synthesis of $Cp_2^*Zr(OSiMe_3)(Cl)$

A mixture of $Cp_2^*Zr(O)(NC_5H_5)$ (340 mg, 0.74 mmol) and Me_3SiCl (94 μl, 0.74 mmol) in toluene (5 ml) was stirred at room temperature for 15 min. The volatile components were removed under reduced pressure, leaving $Cp_2^*Zr(OSiMe_3)(Cl)$ as a tan solid (230 mg, 64%). Anal. Found: C, 56.5; H, 7.9. $C_{23}H_{39}ClOSiZr$. Calc.: C, 56.8; H, 8.1%. MS: *m/z* 485 ($M^+ + 1$). IR data: 2906 (s), 1441 (m), 1379 (m), 1246 (s), 927 (vs), 836 (s), 752 (w).

4.31. Reaction of $Cp_2^*Zr(O)(NC_5H_5)$ with excess Me_3SiCl

A solution of $Cp_2^*Zr(O)(NC_5H_5)$ (10 mg, 0.02 mmol) in C_6D_6 (1 ml) was treated with Me_3SiCl (excess). ^{1}H NMR spectroscopy demonstrated the formation of $Cp_2^*ZrCl_2$ to be complete after ca. 12 h at room temperature. The by-product was identified as $(Me_3Si)_2O$ by comparison with the ^{1}H NMR spectrum of an authentic sample.

4.32. Reaction of $Cp_2^*ZrCl_2$ with $KOSiMe_3$

A mixture of $Cp_2^*ZrCl_2$ (10 mg, 0.02 mmol) and $KOSiMe_3$ (4 mg, 0.03 mmol) in C_6D_6 (1 ml) was heated at 85 °C. ^{1}H NMR spectroscopy revealed the formation of $Cp_2^*Zr(OSiMe_3)Cl$ to be complete after ca. 12 h.

4.33. Synthesis of $Cp_2^*Zr(OMe)(I)$

A mixture of $Cp_2^*Zr(O)(NC_5H_5)$ (200 mg, 0.44 mmol) and excess MeI (60 μl, 0.96 mmol) in toluene (5 ml) was stirred at room temperature for 2 h. The volatile components were removed under reduced pressure, giving $Cp_2^*Zr(OMe)(I)$ as a pale yellow crystalline solid (140 mg, 61%). Anal. Found: C, 48.4; H, 6.4. $C_{21}H_{33}IOZr$. Calc.: C, 48.5; H, 6.4%. MS: *m/z* 518 (M^+). IR data: 2980 (m), 2910 (vs), 2809 (s), 1485 (m), 1435 (s), 1378 (s), 1260 (w), 1125 (vs), 1023 (m), 804 (w), 594 (w), 486 (m).

4.34. Synthesis of $Cp_2^*Zr(SMe)(I)$

A solution of $Cp_2^*Zr(S)(NC_5H_5)$ (15 mg, 0.035 mmol) in C_6D_6 (1 ml) was treated with excess MeI (20 μl, 0.32 mmol) for 10 min at room temperature giving $Cp_2^*Zr(SMe)(I)$ in quantitative yield as judged by ^{1}H NMR spectroscopy. The solvent was removed under reduced pressure to give $Cp_2^*Zr(SMe)(I)$ as a pale yellow solid.

4.35. Synthesis of $Cp_2^*Zr(SeMe)(I)$

A mixture of $Cp_2^*Zr(Se)(NC_5H_5)$ (200 mg, 0.39 mmol) and excess MeI (60 μl, 0.96 mmol) in

toluene (5 ml) was stirred at room temperature for 10 min. The volatile components were removed under reduced pressure, giving $Cp^*_2Zr(SeMe)(I)$ as a bright orange crystalline solid (0.20 g, 89%). Anal. Found: C, 43.3; H, 5.9. $C_{21}H_{33}ISeZr$. Calc.: C, 43.3; H, 5.7%. MS: m/z 582 (M^+). IR data: 2982 (s), 2901 (vs), 1483 (s), 1428 (vs), 1376 (vs), 1255 (m), 1125 (vs), 1022 (vs), 899 (w), 805 (w), 595 (w).

4.36. Synthesis of $Cp^*_2Zr(TeMe)(I)$

A mixture of $Cp^*_2Zr(Te)(NC_5H_5)$ (210 mg, 0.37 mmol) and MeI (24 μl, 0.39 mmol) in toluene (5 ml) was stirred at room temperature for 10 min. The volatile components were removed under reduced pressure, giving $Cp^*_2Zr(TeMe)(I)$ as a bright violet crystalline solid (150 mg, 64%). Anal. Found: C, 40.2; H, 5.1. $C_{21}H_{33}ITeZr$. Calc.: C, 40.0; H, 5.3%. MS: m/z 532 (M^+). IR data: 2981 (s), 2898 (vs), 2722 (m), 1484 (s), 1427 (s), 1376 (s), 1203 (m), 1064 (w), 1022 (s), 807 (w), 598 (w), 408 (w).

4.37. Synthesis of $Cp^*_2Zr(OH)(I)$

A mixture of {FUNC {Cp_{2} {*}}}Zr(O)(NC_5H_5) (200 mg, 0.44 mmol) and Bu^tI (55 μl, 0.46 mmol) in toluene (5 ml) was stirred at room temperature for 11 h. The volatile components were removed under reduced pressure, and the remaining solid residue was washed twice with pentane (ca. 2 ml portions) and dried in vacuo. $Cp^*_2Zr(OH)(I)$ was obtained as a pale yellow solid (110 mg, 49%). Anal. Found: C, 47.6; H, 6.0. $C_{20}H_{31}IOZr$. Calc.: C, 47.5; H, 6.2%. MS: m/z 504 (M^+). IR data: 3640 (s) (ν_{OH}), 2904 (vs), 2725 (m), 1489 (s), 1433 (s), 1378 (s), 1260 (w), 1162 (w), 1066 (w), 1023 (s), 807 (w), 595 (m), 538 (s).

4.38. Reaction of $Cp^*_2Zr(O)(NC_5H_5)$ with Pr^iI

A solution of $Cp^*_2Zr(O)(NC_5H_5)$ (10 mg, 0.02 mmol) in C_6D_6 (1 ml) was treated with Pr^iI (2.2 μl, 0.02 mmol). ^1H NMR spectroscopy demonstrated the formation of $Cp^*_2Zr(OH)(I)$ to be complete after ca. 12 h at room temperature. Propene was observed by ^1H NMR spectroscopy to be a side product of this reaction.

4.39. Reaction of $Cp^*_2Zr(O)(NC_5H_5)$ with EtI

A solution of $Cp^*_2Zr(O)(NC_5H_5)$ (10 mg, 0.02 mmol) in C_6D_6 (1 ml) was treated with EtI (1.8 μl, 0.02 mmol). ^1H NMR spectroscopy demonstrated the formation of a mixture of $Cp^*_2Zr(OH)(I)$ (ca. 10%), $Cp^*_2Zr(OEt)(I)$ (ca. 90%), and C_2H_4 to be complete after ca. 4 h at room temperature. Heating the sample at 55 °C overnight did not change the relative quantities of $Cp^*_2Zr(OH)(I)$ and $Cp^*_2Zr(OEt)(I)$.

4.40. Synthesis of $Cp^*_2Zr(OH)[\eta^1\text{-}OC(Me)=CH_2]$

A mixture of $Cp^*_2Zr(O)(NC_5H_5)$ (120 mg, 0.26 mmol) and acetone (25 μl, 0.34 mmol) in toluene (5 ml) was stirred at room temperature for 10 min. The volatile components were removed under reduced pressure, giving $Cp^*_2Zr(OH)(\eta^1\text{-}OCMe=CH_2)$ as a pale light pink crystalline solid (60 mg, 52%). Anal. Found: C, 62.9; H, 8.3. $C_{23}H_{36}O_2Zr$. Calc.: C, 63.4; H, 8.3%.

Table 7
Crystal and intensity collection data

	$Cp^*_2Zr(\eta^2\text{-}O_2CMe)(\eta^1\text{-}OCOMe)$	$Cp^*_2Zr(OH)(NHPh)$	$Cp^*_2Zr(OH)[\eta^1\text{-}OC(Bu^t)=CH_2]$	$Cp^*_2Zr[\eta^2\text{-}OCH(Bu^t)OCH(Bu^t)O]$
Formula	$C_{24}H_{36}O_4Zr$	$C_{26}H_{37}NOZr$	$C_{26}H_{42}O_2Zr$	$C_{30}H_{50}O_3Zr$
Formula weight	479.8	470.8	477.8	549.2
Lattice	monoclinic	monoclinic	monoclinic	monoclinic
Cell constants				
a (Å)	10.145(2)	13.438(4)	10.247(2)	10.576(2)
b (Å)	17.241(4)	12.568(3)	14.209(2)	18.526(4)
c (Å)	13.477(2)	14.856(3)	17.813(3)	15.249(2)
α (deg)	90.0	90.0	90.0	90.0
β (deg)	90.69(1)	104.54(2)	103.01(1)	90.72(1)
γ (deg)	90.0	90.0	90.0	90.0
V (Å^3)	2357(1)	2429(1)	2527(1)	2987(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	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
ρ(calc) (g cm^{-3})	1.35	1.29	1.26	1.22
μ(Mo Kα) (cm^{-1})	4.9	4.7	4.5	3.9
Goodness of fit	1.216	2.019	1.391	1.201
R	0.0295	0.0714	0.0512	0.0440
R_w	0.0437	0.0852	0.0497	0.0520

MS: m/z 434 (M^+). IR data: 3679 (m) (ν_{OH}), 2982 (m), 2911 (s), 1628 (vs) ($\nu_{C=C}$), 1560 (m), 1508 (w), 1491 (w), 1432 (m), 1378 (s), 1362 (s), 1280 (vs), 1043 (s), 987 (w), 871 (w), 781 (m).

4.41. Synthesis of $Cp^*_2Zr(OH)[\eta^1\text{-}OC(Bu^t)=CH_2]$

A mixture of $Cp^*_2Zr(O)(NC_5H_5)$ (200 mg, 0.44 mmol) and Bu^tCOMe (70 μl, 0.56 mmol) in toluene (5 ml) was stirred at room temperature overnight. The volatile components were removed under reduced pressure, and the solid residue was washed with pentane (ca. 1 ml), and dried in vacuo to give $Cp^*_2Zr(OH)(\eta^1\text{-}OCBu^t=CH_2)$ as a pale pink crystalline solid (120 mg, 57%). Anal. Found: C, 65.4; H, 9.0. $C_{26}H_{42}O_2Zr$. Calc.: C, 65.4; H, 8.9%. MS: m/z 477 ($M^+ + 1$). IR data: 3648 (s) (ν_{OH}), 2958 (s), 2910 (s), 1618 (s) ($\nu_{C=C}$), 1568 (s), 1483 (m), 1441 (m), 1381 (s), 1345 (m), 1290 (s), 1221 (m), 1186 (vs), 1031 (s), 1019 (s), 789 (m), 555 (m), 528 (m).

4.42. Synthesis of $Cp^*_2Zr(SeH)[\eta^1\text{-}OC(Me)=CH_2]$

A mixture of $Cp^*_2Zr(Se)(NC_5H_5)$ (200 mg, 0.39 mmol) and excess acetone (ca. 0.2 ml) in toluene (ca. 5 ml) was stirred at room temperature for 1.5 h. The mixture was briefly warmed (ca. 50 °C) and the volatile components removed under reduced pressure to give $Cp^*_2Zr(SeH)(\eta^1\text{-}OCMe=CH_2)$ as a dull yellow powder (160 mg, 83%). Anal. Found: C, 55.6; H, 7.5. $C_{23}H_{36}OSeZr$. Calc.: C, 55.4; H, 7.3%. IR data: 3104 (w), 2976 (vs), 2946 (vs), 2915 (vs), 2894 (vs), 2725 (w), 2321 (m) (ν_{SeH}), 1631 (vs) ($\nu_{C=C}$), 1568 (s), 1491 (m), 1432 (s), 1367 (vs), 1273 (vs), 1165 (w), 1047 (vs), 991 (m), 875 (m), 788 (s), 521 (m), 505 (m), 480 (m).

4.43. Synthesis of $Cp^*_2Zr[\eta^2\text{-}OCH_2OCH_2O]$

A mixture of $Cp^*_2Zr(O)(NC_5H_5)$ (260 mg, 0.57 mmol) and paraformaldehyde (37 mg, 1.23 mmol) in toluene (5 ml) was stirred at room temperature for 10 min. The volatile components were removed under reduced pressure, giving $Cp^*_2Zr[\eta^2\text{-}OCH_2OCH_2O]$ as a light orange solid (180 mg, 72%). Anal. Found: C, 60.9; H, 8.0. $C_{22}H_{34}O_3Zr$. Calc.: C, 60.4; H, 7.8%. MS: m/z 436 (M^+). IR data: 2903 (s), 2747 (m), 1443 (m), 1378 (m), 1163 (m), 1127 (s), 1095 (vs), 1001 (s), 904 (m), 505 (m), 451 (m).

4.44. Synthesis of $Cp^*_2Zr[\eta^2\text{-}OCH(Pr^i)OCH(Pr^i)O]$

A mixture of $Cp^*_2Zr(O)(NC_5H_5)$ (120 mg, 0.26 mmol) and isobutyraldehyde (50 μl, 0.55 mmol) in toluene (5 ml) was stirred at room temperature for 1 h. The volatile components were removed under reduced pressure, giving $Cp^*_2Zr[\eta^2\text{-}OCH(Pr^i)OCH(Pr^i)O]$ as a pink solid (80 mg, 58%). Anal. Found: C, 64.5; H, 9.5. $C_{28}H_{46}O_3Zr$: Calc.: C, 64.4; H, 8.9%. IR Data: 2947 (s), 2910 (s), 2866 (s), 1653 (w), 1471 (s), 1380 (m), 1354 (m), 1262 (w), 1194 (w), 1080 (vs), 1017 (m), 955 (w), 930 (w), 804 (w), 686 (w), 612 (m).

4.45. Synthesis of $Cp^*_2Zr[\eta^2\text{-}OCH(Bu^t)OCH(Bu^t)O]$

A mixture of $Cp^*_2Zr(O)(NC_5H_5)$ (220 mg, 0.48 mmol) and pivalaldehyde (150 μl, 1.38 mmol) in toluene (5 ml) was stirred at room temperature for 1 h. The volatile components were removed under reduced pressure, giving $Cp^*_2Zr[\eta^2\text{-}OCH(Bu^t)OCH(Bu^t)O]$ as a pink crystalline solid (200 mg, 76%). Anal. Found: C, 65.5; H, 9.0. $C_{30}H_{50}O_3Zr$. Calc.: C, 65.5; H, 9.2%. MS: m/z 548 (M^+). IR data: 2984 (vs), 2939 (vs), 2861 (vs), 2826 (vs), 2724 (s), 2678 (m), 2635 (s), 2142 (w), 2006 (w), 1482 (vs), 1455 (vs), 1384 (vs), 1353 (vs), 1270 (m), 1209 (s), 1168 (m), 1103 (vs), 1030

Table 8
Atomic coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $Cp^*_2Zr(\eta^2\text{-}O_2CMe)(\eta^1\text{-}OCOMe)$

Atom	x	y	z	U [a]
Zr	2123(1)	6441(1)	7247(1)	25(1)
O(1)	3252(2)	6412(1)	5780(1)	35(1)
O(2)	1120(2)	6433(1)	5731(1)	37(1)
C(1)	2198(3)	6410(2)	5271(2)	33(1)
C(2)	2234(4)	6382(2)	4159(2)	56(1)
O(3)	163(2)	6439(1)	7649(1)	36(1)
O(4)	−1800(3)	6644(2)	8287(2)	86(1)
C(3)	−1112(3)	6467(2)	7601(2)	45(1)
C(4)	−1727(4)	6261(3)	6628(3)	69(2)
C(11)	1928(3)	7634(2)	8361(2)	36(1)
C(12)	1579(3)	7885(2)	7388(2)	35(1)
C(13)	2706(3)	7844(2)	6796(2)	34(1)
C(14)	3762(3)	7561(2)	7390(2)	35(1)
C(15)	3281(3)	7443(2)	8358(2)	35(1)
C(21)	1059(4)	7649(2)	9254(2)	53(1)
C(22)	257(3)	8191(2)	7054(3)	50(1)
C(23)	2783(3)	8144(2)	5754(2)	48(1)
C(24)	5162(3)	7466(2)	7058(3)	49(1)
C(25)	4111(3)	7340(2)	9286(2)	49(1)
C(31)	1575(3)	5068(2)	7860(3)	46(1)
C(32)	2432(3)	5396(2)	8571(2)	43(1)
C(33)	3687(3)	5471(2)	8133(2)	41(1)
C(34)	3584(3)	5209(2)	7147(2)	44(1)
C(35)	2273(4)	4977(2)	6967(2)	47(1)
C(41)	197(4)	4794(2)	8060(4)	86(2)
C(42)	2082(5)	5515(3)	9640(3)	72(7)
C(43)	4996(4)	5584(2)	8675(3)	65(1)
C(44)	4725(4)	5102(2)	6468(3)	74(2)
C(45)	1768(5)	4603(2)	6029(3)	79(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(vs), 987 (vs), 928 (vs), 890 (s), 806 (m), 692 (s), 668, (m), 609 (vs), 506 (s).

4.46. Reaction of $Cp_2^* Zr(O)(NC_5H_5)$ with PhCN

A solution of $Cp_2^* Zr(O)(NC_5H_5)$ (10 mg, 0.02 mmol) in C_6D_6 (1 ml) was treated with PhCN (4.5 μl, 0.04 mmol). ^1H NMR spectroscopy demonstrated the formation of $Cp_2^* Zr[\eta^2\text{-}OC(Ph)NC(Ph)N]$ [24–26] to be complete within 15 min at room temperature.

4.47. Pyridine exchange reactions of $Cp_2^* Zr(E)(NC_5H_5)$

(a) A solution of $Cp_2^* Zr(E)(NC_5H_5)$ (E = O, S, Se, Te) (ca. 10 mg) in C_6D_6 (1 ml) was treated with 4-t-butylpyridine (ca. 10 μl). ^1H NMR spectroscopy demonstrated the formation of $Cp_2^* Zr(E)(NC_5H_4Bu^t)$ over a period of ca. 1 h at room temperature. (b) A solution of $Cp_2^* Zr(O)(NC_5H_4Bu^t)$ in C_6D_6 (1 ml) was treated with pyridine. ^1H NMR spectroscopy demonstrated the formation of a mixture of $Cp_2^* Zr(O)(NC_5H_5)$, $Cp_2^* Zr(O)(NC_5H_4Bu^t)$, NC_5H_5, and $NC_5H_4Bu^t$ within 40 min at room temperature.

Table 9
Atomic coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $Cp_2^* Zr(OH)(NHPh)$

Atom	x	y	z	U [a]
Zr	2424(1)	5287(1)	6593(1)	57(1)
O	914(5)	5294(6)	5827(4)	75(3)
N	2566(9)	3641(7)	6900(7)	101(5)
C(1)	2159(10)	2677(9)	6518(8)	62(6)
C(2)	1256(11)	2639(10)	5819(9)	77(6)
C(3)	868(11)	1640(13)	5469(10)	102(7)
C(4)	1342(13)	725(11)	5826(11)	95(8)
C(5)	2203(14)	791(11)	6512(10)	102(8)
C(6)	2578(12)	1727(12)	6852(10)	112(8)
C(11)	3374(9)	4727(10)	5370(9)	84(6)
C(12)	4059(8)	5328(11)	5997(8)	75(5)
C(13)	3720(10)	6382(9)	5949(7)	55(5)
C(14)	2774(10)	6428(10)	5285(8)	66(6)
C(15)	2584(8)	5353(12)	4913(7)	75(6)
C(21)	3534(14)	3575(11)	5130(13)	182(13)
C(22)	5083(10)	4958(12)	6587(12)	143(9)
C(23)	4362(10)	7335(10)	6313(8)	97(7)
C(24)	2140(10)	7406(12)	4967(9)	120(8)
C(25)	1656(12)	5020(14)	4119(8)	152(10)
C(31)	2769(8)	5229(10)	8396(7)	64(5)
C(32)	1718(10)	5320(9)	8017(7)	53(5)
C(33)	1537(9)	6329(9)	7627(7)	60(5)
C(34)	2481(10)	6827(9)	7708(7)	64(5)
C(35)	3248(10)	6146(11)	8187(7)	71(6)
C(41)	3225(12)	4274(13)	8992(8)	132(8)
C(42)	848(10)	4577(10)	8056(9)	95(6)
C(43)	535(11)	6870(11)	7235(9)	113(7)
C(44)	2659(14)	7995(9)	7537(9)	141(10)
C(45)	4359(11)	6380(14)	8619(9)	133(9)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 10
Atomic coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $Cp_2^* Zr(OH)[\eta^1\text{-}OC(Bu^t)=CH_2]$

Atom	x	y	z	U [a]
Zr	1171(1)	5963(1)	7934(1)	36(1)
O(1)	2114(6)	4869(4)	7587(3)	51(3)
O(2)	−608(5)	5826(4)	7192(3)	46(2)
C(1)	−2712(10)	6597(7)	6671(6)	78(5)
C(2)	−1832(8)	5900(7)	6695(4)	60(4)
C(3)	−2079(9)	4999(7)	6169(5)	56(4)
C(4)	−1951(13)	4113(8)	6632(6)	137(8)
C(5)	−1017(10)	4887(8)	5709(5)	123(7)
C(6)	−3418(11)	5014(9)	5624(6)	155(8)
C(11)	1248(9)	7681(6)	7489(5)	46(4)
C(12)	2353(10)	7596(6)	8121(4)	50(4)
C(13)	3251(9)	6959(6)	7918(5)	53(4)
C(14)	2751(11)	6686(6)	7164(6)	57(5)
C(15)	1550(11)	7114(7)	6882(5)	51(5)
C(21)	84(10)	8346(6)	7405(6)	84(6)
C(22)	2591(11)	8281(6)	8799(5)	104(6)
C(23)	4639(10)	6709(7)	8395(7)	126(7)
C(24)	3467(10)	6088(7)	6673(6)	110(7)
C(25)	689(11)	7082(7)	6075(5)	94(6)
C(31)	−330(10)	5445(7)	8831(5)	58(4)
C(32)	373(10)	6232(6)	9172(5)	62(5)
C(33)	1725(9)	5971(7)	9434(4)	56(4)
C(34)	1829(10)	5048(6)	9208(4)	52(4)
C(35)	569(10)	4716(6)	8846(4)	58(4)
C(41)	−1839(9)	5359(8)	8571(5)	107(6)
C(42)	−335(11)	7129(7)	9342(5)	109(7)
C(43)	2776(10)	6511(7)	10005(5)	102(6)
C(44)	3085(10)	4482(6)	9394(5)	92(6)
C(45)	284(11)	3709(6)	8592(5)	92(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

4.48. Reactions of $Cp_2^* Zr(E)(NC_5H_5)$ (E = Se, Te) with CO

A solution of $Cp_2^* Zr(E)(NC_5H_5)$ (ca. 10 mg) in C_6D_6 (1 ml) was treated with CO (1 atm) and the reaction was monitored by ^1H NMR spectroscopy. For the selenido derivative $Cp_2^* Zr(Se)(NC_5H_5)$, ca. 10% conversion to a mixture of $Cp_2^* Zr(Se)(CO)$ and $Cp_2^* Zr(CO)_2$ was observed after 30 min at room temperature, while for the tellurido derivative $Cp_2^* Zr(Te)(NC_5H_5)$, complete conversion to a mixture of $Cp_2^* Zr(\eta^2\text{-}Te_2)(CO)$, $Cp_2^* Zr(CO)_2$, and pyridine was observed after 6 h at room temperature. $Cp_2^* Zr(Te)(CO)$ was observed as an intermediate during the course of the transformation.

4.49. Reaction of $Cp_2^* Zr(Te)(NC_5H_5)$ with N_2O

A solution of $Cp_2^* Zr(Te)(NC_5H_5)$ (13 mg, 0.02 mmol) in C_6D_6 (1 ml) was treated with N_2O (1 atm). ^1H NMR spectroscopy demonstrated the formation of $Cp_2^* Zr(O)(NC_5H_5)$ to be complete within 5 min at room temperature.

Table 11
Atomic coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $Cp_2^* Zr[\eta^2\text{-}OCH(Bu^t)OCH(Bu^t)O]$

Atom	x	y	z	U [a]
Zr	321(1)	7398(1)	8651(1)	31(1)
O(1)	1785(4)	6718(2)	8828(2)	37(1)
O(2)	1310(4)	5867(2)	7753(2)	39(2)
O(3)	−338(3)	6702(2)	7746(2)	37(1)
C(11)	165(7)	8698(3)	8011(5)	57(3)
C(12)	1268(7)	8699(3)	8545(4)	50(3)
C(13)	2140(6)	8228(3)	8182(4)	48(2)
C(14)	1615(6)	7943(3)	7421(4)	49(2)
C(15)	411(6)	8214(3)	7300(4)	53(2)
C(21)	−917(8)	9223(4)	8022(6)	108(4)
C(22)	1569(9)	9227(4)	9268(5)	98(4)
C(23)	3446(7)	8087(4)	8558(6)	87(4)
C(24)	2315(8)	7462(4)	6792(5)	84(3)
C(25)	−461(8)	8078(4)	6533(5)	104(4)
C(31)	−91(6)	7504(4)	10294(4)	52(2)
C(32)	−995(7)	7959(3)	9915(5)	58(3)
C(33)	−1819(6)	7523(4)	9419(4)	57(3)
C(34)	−1472(7)	6801(3)	9549(4)	51(3)
C(35)	−414(7)	6789(3)	10088(4)	50(3)
C(41)	935(8)	7727(5)	10927(5)	101(4)
C(42)	−1234(9)	8734(4)	10170(6)	120(5)
C(43)	−3021(7)	7755(6)	8930(6)	118(5)
C(44)	−2245(7)	6165(4)	9245(5)	90(4)
C(45)	211(8)	6143(4)	10522(5)	85(3)
C(51)	1819(6)	5981(3)	8595(4)	45(2)
C(52)	3161(6)	5664(3)	8643(4)	45(2)
C(53)	3687(7)	5792(4)	9543(5)	81(3)
C(54)	3997(7)	5987(4)	7960(5)	78(3)
C(55)	3056(7)	4847(3)	8482(5)	72(3)
C(61)	15(7)	5974(3)	7680(4)	47(3)
C(62)	−495(6)	5617(3)	6831(4)	47(2)
C(63)	170(8)	5915(4)	6038(4)	95(4)
C(64)	−264(8)	4810(4)	6896(5)	1(4)
C(65)	−1900(7)	5761(4)	6744(5)	82(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

4.50. Reactions of $Cp_2^* Zr(E)(NC_5H_5)$ (E = S, Se) with N_2O

A solution of $Cp_2^* Zr(E)(NC_5H_5)$ in C_6D_6 (1 ml) was treated with N_2O (1 atm). ^1H NMR spectroscopy revealed the formation of mixtures of products at room temperature within 1 h for $Cp_2^* Zr(S)(NC_5H_5)$ and within 5 min for $Cp_2^* Zr(Se)(NC_5H_5)$. $Cp_2^* Zr(O)(NC_5H_5)$ and $Cp_2^* Zr(\eta^2\text{-}E_3)$ were observed in each reaction.

4.51. Reactions of $Cp_2^* Zr(O)(NC_5H_5)$ with S, Se, and Te

A mixture of $Cp_2^* Zr(O)(NC_5H_5)$ (excess) and E (ca. 2–3 mg) in C_6D_6 (1 ml) was monitored by ^1H NMR spectroscopy, which revealed the formation of inter alia $Cp_2^* Zr(\eta^2\text{-}S_3)$ (10 min at room temperature) [69] and $Cp_2^* Zr(\eta^2\text{-}Se_3)$ (8 h at 60 °C). No reaction, however, was observed between $Cp_2^* Zr(O)(NC_5H_5)$ (excess) and Te after 4 days at 90 °C.

[69] $Cp_2^* Zr(S)(NC_5H_5)$, however, was observed after heating the mixture for 1 week at 90 °C.

4.52. X-ray structure determinations

Crystal data, data collection, and refinement parameters for $Cp_2^* Zr(\eta^2\text{-}O_2CMe)(\eta^1\text{-}OCOMe)$, $Cp_2^* Zr(OH)(NHPh)$, $Cp_2^* Zr(OH)[\eta^1\text{-}OC(Bu^t)=CH_2]$, and $Cp_2^* Zr[\eta^2\text{-}OCH(Bu^t)OCH(Bu^t)O]$ are summarized in Table 7, with atomic coordinates listed in Tables 8–11. A representative experimental procedure is given for $Cp_2^* Zr(\eta^2\text{-}O_2CMe)(\eta^1\text{-}OCOMe)$. A single crystal of $Cp_2^* Zr(\eta^2\text{-}O_2CMe)(\eta^1\text{-}OCOMe)$ 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 ($\lambda = 0.71073$ 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 using direct methods and standard difference map techniques using SHELXTL PC™. Systematic absences were consistent uniquely with the space group $P2_1/n$ (No. 14). Hydrogen atoms were included in calculated positions.

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