of the copper site induced by the Ir–enolate interaction could allow the 4s orbital to mix to some extent with the molecular orbital containing the unpaired spin density. Since spin density in the 4s orbital produces a hyperfine coupling of opposite sign to that arising from core polarization, the 4s spin density can be estimated. Depending on whether the sign of A_{iso} is positive or negative (i.e., whether the magnitude of the interaction from the 4s spin density is greater than or less than that for core polarization), the 4s spin density is calculated as either 5.5% or 2% by comparing our values of +110 or +330 MHz with literature values.[38]

Acknowledgment. This research was supported by a generous grant from Dow Chemical Co. We thank Professor R. L. Belford for helpful discussions. NMR spectra were measured at the University of Illinois NSF Regional NMR Facility (NSF CHE 79-16100).

Registry No. *cis*-$PtCl_2(HacacP)_2$, 81141-53-9; $PtCl_2(COD)$, 12080-32-9; *cis*-$PdCl_2(HacacP)_2$, 81141-54-0; $PdCl_2(COD)$, 12107-56-1; *trans*-$IrCl(CO)(HacacP)_2$, 81157-62-2; $IrCl(CO)_2$(*p*-toluidine), 14243-22-2; *trans*-$RhCl(CO)(HacacP)_2$, 91312-15-1; $Rh_2Cl_2(CO)_4$, 14523-22-9; $PtCl_2\{Cu(acacP)_2\}\cdot 2CH_2Cl_2\cdot H_2O$, 91383-66-3; $PtCl_2\{Ti(acacP)_2Cl_2\}$, 91312-16-2; $PdCl_2\{Cu(acacP)\}$, 81141-52-8; $IrCl(CO)\{Cu(acacP)^2\}$, 91312-17-3; $IrCl(CO)\{Cu(acacP)_2\}SO_2$, 91327-60-5; $IrCl(CO)\{Zn(acacP)_2\}$, 91312-18-4; $Zn(acacP)_2$, 91312-19-5; $IrCl(CO)\{Zn(acacP)_2\}SO_2$, 91327-61-6; $IrCl(CO)(HacacP)_2SO_2$, 91327-62-7.

Reactions of Water and Ammonia with Bis(pentamethylcyclopentadienyl) Complexes of Zirconium and Hafnium

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Abstract: The propensity for the group 4B metal center to form extremely strong bonds with oxygen and nitrogen donors is often invoked as an important driving force in the reductions of carbon monoxide and dinitrogen with organometallic derivatives of these metals, e.g., $Cp^*{}_2ML_x$ ($Cp^* = \eta^5\text{-}C_5Me_5$; M = Ti, Zr, Hf). In order to assess some of the fundamental bonding properties of hydroxide, oxo, and amide ligands with bis(pentamethylcyclopentadienyl) derivatives of zirconium and hafnium, the reactivities of water and ammonia with several $Cp^*{}_2ML_x$ (M = Zr, Hf) complexes have been examined. Water reacts in a clean, stepwise manner with $Cp^*{}_2MH_2$ (M = Zr, Hf) to afford $Cp^*{}_2M(H)(OH)$, $(Cp^*{}_2MH)_2O$, $Cp^*{}_2M(OH)_2$, and finally $Cp^*{}_2M(OH)_2\cdot H_2O$. $Cp^*{}_2M(H)(Cl)$ yields $Cp^*{}_2M(OH)(Cl)$. $Cp^*{}_2MH_2$ reacts with $Cp^*{}_2M(OH)(X)$ (X = Cl, OH, H) to afford $Cp^*{}_2(X)M\text{–}O\text{–}M(H)Cp^*{}_2$. In all cases, conversion of a M–H bond to an M–O bond is accompanied by H_2 evolution. Similarly, ammonia reacts rapidly with $Cp^*{}_2MH_2$ to yield $Cp^*{}_2M(H)(NH_2)$ and H_2. Excess ammonia or $Cp^*{}_2MH_2$ do not react further, although exchange with free $^{15}NH_3$ is observed. $Cp^*{}_2Hf(H)(NH_2)$ reacts with H_2O to afford $Cp^*{}_2Hf(H)(OH)$ and NH_3, but not $Cp^*{}_2Hf(OH)(NH_2)$. Free water undergoes rapid proton exchange and slower oxygen exchange with the hydroxo derivatives. $(Cp^*{}_2ZrN_2)_2N_2$ reacts rapidly and cleanly with an equivalent of water to produce N_2 (3 equiv) and $(Cp^*{}_2ZrH)_2O$. Evidence in support of a stepwise oxidative addition of both O–H bonds via the intermediacy of $Cp^*{}_2Zr(H)(OH)$ is presented. ^1H and ^{17}O NMR spectra of these new compounds are also tabulated.

Introduction

The chemistry of the group 4B metals (Ti, Zr, Hf) in their higher oxidation states is dominated by the propensity of these metals to form extremely strong bonds with "hard" ligands such as O, N, F and Cl donors.[1] We have been interested in defining some of the fundamental bonding properties of such hard ligands with the zirconium and hafnium bis(pentamethylcyclopentadienyl) fragments, because these strong metal–ligand interactions are often invoked as important driving forces in reductions of carbon monoxide and dinitrogen with derivatives of $(\eta^5\text{-}C_5Me_5)_2M$ (M = Ti, Zr, Hf) (eq 1, 2).[2,3] Furthermore, it has been long recognized that essentially all $(\eta^5\text{-}C_5Me_5)_2ML_x$ compounds react vigorously with moisture to give soluble species, so that a systematic investigation of the water decomposition of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$, $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(\mu\text{-}N_2)$, and related compounds seemed warranted. Finally, the observed stability of the hydrido amide complexes $(\eta^5\text{-}C_5Me_5)_2HfH(NHR)$ (R = Ph, tol) caused us to question whether the isoelectronic hydrido hydroxide complex $(\eta^5\text{-}C_5Me_5)_2HfH(OH)$ might be formed in reactions of water with $(\eta^5\text{-}C_5Me_5)_2HfH_2$.[4] Very few hydroxo hydride complexes are known, but they are considered to be important intermediates in "water splitting" reactions.[5,6]

$$(\eta^5\text{-}C_5Me_5)_2ZrH_2 + CO + H_2 \rightarrow (\eta^5\text{-}C_5Me_5)_2ZrH(OMe) \quad (1)$$

$$[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(\mu\text{-}N_2) + 4HCl \rightarrow 2(\eta^5\text{-}C_5Me_5)_2ZrCl_2 + N_2H_4 + 2N_2 \quad (2)$$

There exists a large body of literature describing the interactions of water with cyclopentadienyl ($Cp \equiv \eta^5\text{-}C_5H_5$) complexes of Ti, Zr, and Hf,[7] with the earliest such study dating back to the first

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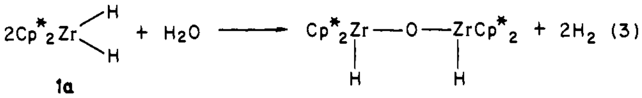
reports of the bis(cyclopentadienyl) complexes Cp_2MX_2 (M = Ti, Zr; X = halide) by Wilkinson.[8] A common characteristic of these reactions with water (or some other oxygen atom source) is the facile formation of robust μ-oxo complexes containing two $(Cp_2MCl)_2(\mu\text{-O})$, M = Ti[9] or Zr,[10] three $(Cp_2TiCl)_2(\mu\text{-O})_2(CpTiCl)$[11] and $(CpZr)_3(\mu\text{-O})_3$,[12] four $(CpTi)_4(\mu\text{-O})_4$,[13] six $(CpTi)_6(\mu_3\text{-O})_8$,[14] or more[7a] metal centers. Very few terminal titanyl, zirconyl, or hafnyl complexes are known.[15] Although water is the most common source of these μ-oxo ligands, other substrates such as N_2O,[16] CO_2,[12] and CO[14,17] have been observed to serve as oxo sources in various group 4B systems.

The literature describing analogous reactions using anhydrous ammonia is much smaller than that for water, "Bis(titanocene)", $(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)_3Ti_2$, is reported to react with NH_3 to give a compound of stoichiometry $Cp_4Ti_2N_2H_3$ which has been formulated as "$[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-NH})]_2(\mu\text{-H})$" on the basis of a preliminary X-ray crystal structure determination and gas evolution measurement,[18] Ammonia and $(Cp_2TiCl)_2$ are reported to yield $Cp_2TiCl(NH_3)$.[19] In these regards, we have investigated the reactivities of water and ammonia with several $(\eta^5\text{-}C_5Me_5)_2ML_x$ (M = Zr, Hf) complexes, and the results of these studies are reported herein.

Results and Discussion

Reactions of Zirconium and Hafnium Hydrides with Water and Ammonia. Water reacts vigorously with toluene solutions of $Cp^*_2ZrH_2$ (**1a**) ($Cp^* \equiv \eta^5\text{-}C_5Me_5$)[20] in a 1:2 stoichiometric fashion to yield molecular hydrogen and an oxo-bridged hydrido complex $(Cp^*_2ZrH)_2O$ (**2a**), as shown in eq 3. Dimeric **2a** can be isolated as colorless crystals from a cold toluene–petroleum ether mixture and has been characterized by a molecular weight measurement, elemental analysis, and ^1H NMR, ^{17}O NMR, and infrared spectroscopic methods. While analogous complexes are known for unsubstituted (C_5H_5) and monosubstituted (C_5H_4Me) cy-



$$2Cp^*_2Zr\langle{}^{H}_{H} + H_2O \longrightarrow \underset{\displaystyle H}{Cp^*_2Zr}{-}O{-}\underset{\displaystyle H}{ZrCp^*_2} + 2H_2 \quad (3)$$

1a **2a**

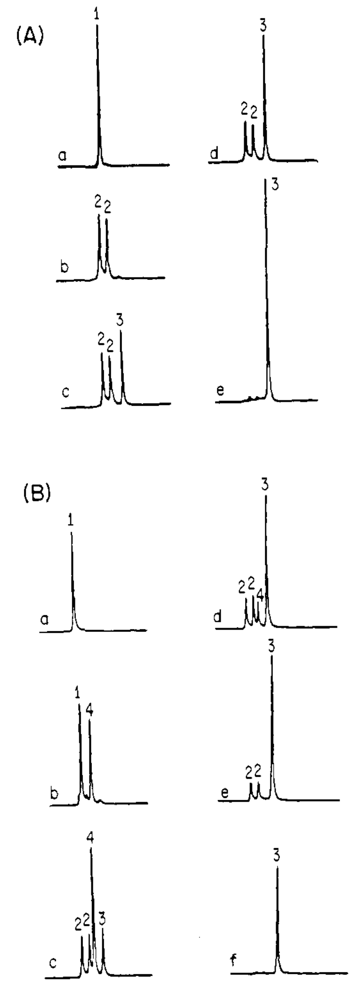


Figure 1. ^1H NMR spectra in the Cp* region showing the titration of $Cp^*_2MH_2$ (M = Zr, Hf) with water. (A) $Cp^*_2ZrH_2$ with a, 0.0 equiv of H_2O; b, 0.5 equiv of H_2O; c, 1.0 equiv of H_2O; d, 1.5 equiv of H_2O; e, 2.0 equiv of H_2O. (B) $Cp^*_2HfH_2$ with a, 0.0 equiv of H_2O; b, 0.6 equiv of H_2O; c, 1.0 equiv of H_2O; d, 1.3 equiv of H_2O; e, 1.7 equiv of H_2O; f, 2.0 equiv of H_2O. The numbers above the resonances correspond to those in the text.

Table I. Proton NMR Data

compd	$\delta(^1H)$ (multi, rel int, assignt)[b]
$(Cp^*_2ZrH)_2O$ (**2a**) mol wt 709 (741 calcd)[a]	1.92 (s, 30 H, C_5Me_5), 2.00 (s, 30 H, C_5Me_5); 5.50 (s, 2 H, ZrH)
$(Cp^*_2HfH)_2O$ (**2b**)	2.00 (s, 30 H, C_5Me_5), 2.08 (s, 30 H, C_5Me_5), 9.79 (s, 2 H, HfH)
$Cp^*_2Zr(OH)_2$ (**3a**)	1.83 (s, 30 H, C_5Me_5), 3.47 (s, 2 H, OH)
$Cp^*_2Hf(OH)_2$ (**3b**) mol wt 466 (483 calcd)[a]	1.85 (s, 30 H, C_5Me_5), 2.98 (s, 2 H, OH)
$Cp^*_2HfH(OH)$ (**4**)	1.95 (s, 30 H, C_5Me_5); 4.60 (s, 1 H, OH), 10.17 (s, 1 H, HfH)
$Cp^*_2ZrCl(OH)$ (**6a**)	1.83 (s, 30 H, C_5Me_5), 5.09 (s, 1 H, OH)
$Cp^*_2HfCl(OH)$ (**6b**)	1.87 (s, 30 H, C_5Me_5), 4.38 (s, 1 H, OH)
$(Cp^*_2ZrH)O$-$[Cp^*_2Zr(OH)]$ (**7**)	1.84 (s; 15 H, C_5Me_5), 1.94 (s, 15 H, C_5Me_5), 2.00 (s, 15 H, C_5Me_5), 2.06 (s, 15 H, C_5Me_5), 3.41 (s, 1 H, OH), 5.59 (s, 1 H, ZrH)
$(Cp^*_2ZrCl)O$-(Cp^*_2ZrH) (**8**)	1.86 (s, 15 H, C_5Me_5); 1.94 (s, 15 H, C_5Me_5); 1.99 (s, 15 H, C_5Me_2); 2.08 (s, 15 H, C_5Me_5); 5.72 (s, 1 H, ZrH)
$Cp^*_2ZrH(NH_2)$ (**9a**) mol wt 374 (379 calcd)[a]	1.95 (s, 30 H, C_5Me_5), 4.42 (br s, 2 H, NH_2), 4.83 (s, 1 H, ZrH)
$Cp^*_2HfH(NH_2)$ (**9b**)	1.94 (s, 30 H, C_5Me_5), 3.99 (br s, 2 H, NH_2),[c] 9.30 (s, 1 H, HfH)

[a] Molecular weights were determined by the Signer method in benzene solution by using azobenzene as the standard. Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 82–21. [b] Recorded in C_6D_6 solution, chemical shifts reported in δ from internal $SiMe_4$. [c] $^1J_{^{15}NH} = 66.8$ Hz.

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[17] This has recently been observed in both zirconium (Andersen, R. A., private communication) and hafnium (Teuben, J. H., private communication) organometallic systems.

[18] No hydrogen atoms were located in the X-ray experiment and only the geometry of the $C_{20}Ti_2N_2$ skeleton has been established. The number of hydrogen atoms bonded to the nitrogen and titanium atoms is a matter of speculation. Armor, J. N. *Inorg. Chem.* **1978**, *17*, 203–13.

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[20] Abbreviations used throughout: Bu = $n\text{-}C_4H_9$; Cp = $\eta^5\text{-}C_5H_5$; Cp* = $\eta^5\text{-}C_5(CH_3)_5$; Et = C_2H_5; Me = CH_3; Ph = C_6H_5; tol = $p\text{-}CH_3C_6H_4$.

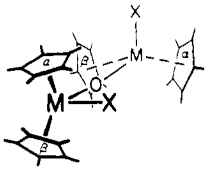
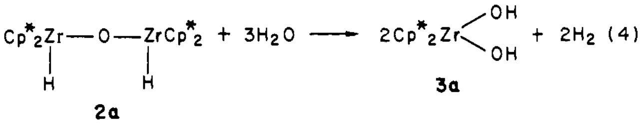


Figure 2. Perspective view of $(Cp^*{}_2MX)_2O$ showing the origin of ring inequivalency for the Cp* ligands. The Cp* groups labeled α are "eclipsed" by the ligand X on the adjacent metal center.

clopentadienyl systems (cf. $[(\eta^5\text{-}C_5H_5)_2ZrCl]_2O$[10] and $[(\eta^2\text{-}C_5H_4Me)_2ZrCl]_2O$[21]), the formation of **2a**, a molecule containing two $[(\eta^5\text{-}C_5Me_5)_2ZrH]$ fragments linked by a single atom oxo bridge, is somewhat surprising owing to the steric bulk of the pentamethylcyclopentadienyl rings. Molecular models of **2a** indeed show considerable steric congestion, and the dimeric structure is readily ruptured upon treatment of **2a** with water (eq 4) to yield



$$Cp^*{}_2Zr(H){-}O{-}Zr(H)Cp^*{}_2 + 3H_2O \longrightarrow 2Cp^*{}_2Zr(OH)_2 + 2H_2 \quad (4)$$

2a **3a**

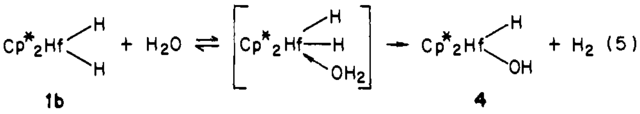
the bis(hydroxo) derivative $Cp^*{}_2Zr(OH)_2$ (**3a**) with concomitant evolution of 2 equiv of dihydrogen. No intermediates are observed by ^1H NMR spectroscopy, even at low temperature (−50 °C), for this **2a** → **3a** conversion. The results of a titration of **1a** with 2 equiv of water are shown in Figure 1A.

The ^1H NMR spectrum (see Table I) of **2a** shows two resonances in the methyl region, indicating the presence in solution of two types of C_5Me_5 groups. The parent ring systems (C_5H_5) exhibit *equivalent* cyclopentadienyl rings in solution; however, the solid-state (X-ray) structures of these unsubstituted and monosubstituted ring derivatives do show two chemically distinct types of rings. For example, $(Cp_2ZrCl)_2O$ possesses an approximately linear Zr–O–Zr′ bridge (169°) and the Cl–Zr–O, Cl′–Zr′–O dihedral angle of 74° results in a pseudoeclipsed conformation with respect to each Cl atom and one C_5H_5 ring on the adjacent metal (see Figure 2).[10] Electronically, this ligand arrangement allows for maximum π overalp between the two orthogonal filled p orbitals of the oxo ligand and the appropriate empty metal π-accepting orbitals.[22] The equivalency (single resonance) of the C_5H_5 rings in solution suggests the electronic barrier to rotation about the M–O–M bridge is small and due, perhaps, to resonance contributions of the type $M{=}O{-}M \leftrightarrow M{-}\dot{O}{=}M$, as well as $M{=}O{=}M$.[23] For the C_5Me_5 system, steric factors appear to dominate, resulting in a much higher barrier to rotation.

Two bands are observed in the infrared spectrum of **2a** (Nujol mull) corresponding to the Zr–O–Zr′ stretching modes, appearing at 658 (vs) and 593 cm^{-1} (s). These bands shift upon oxygen-18 isotopic substitution in **2a**-^{18}O to 640 (vs) and 582 cm^{-1} (s), respectively.[24]

The bis(hydroxo) complex **3a** can be isolated from cold petroleum ether as large, colorless prisms and can be further purified by vacuum sublimation (130 °C, 10^{-4} torr). Alternatively, **3a** can be conveniently prepared on a large scale by treatment of a THF solution of $Cp^*{}_2ZrCl_2$ with 2 equiv of *n*-BuLi followed by hydrolysis and subsequent sublimation of the residue. **3a** reacts slowly with atmospheric moisture to form a yellow monohydrate (**3a**·H_2O), which loses water to regenerate **3a** upon sublimation.

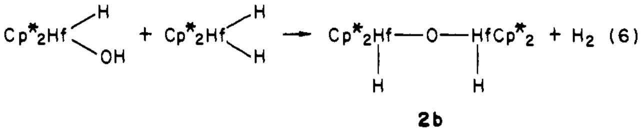
Water and $Cp^*{}_2HfH_2$ (**1b**) react in a 1:1 stoichiometry in benzene or ether with evolution of hydrogen to give $Cp^*{}_2HfH(OH)$ (**4**) (see Figure 1B) as depicted in eq 5. This hydroxo hydride



$$Cp^*{}_2HfH_2 + H_2O \rightleftharpoons [Cp^*{}_2Hf(H)_2(OH_2)] \rightarrow Cp^*{}_2Hf(H)(OH) + H_2 \quad (5)$$

1b **4**

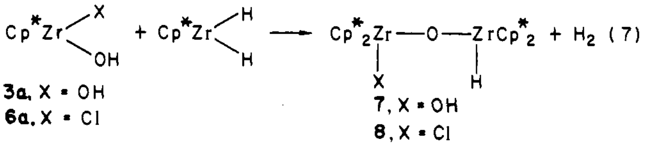
complex can be isolated in good yield (~60%) from cold petroleum ether as colorless crystals and exists as a monomer in benzene solutions. The initial step in the formation of **4** is probably association of a Lewis base (H_2O) to a strong Lewis acid (**1b**), followed by rapid H_2 elimination.[25] **4** undergoes a slow reaction with $Cp^*{}_2HfH_2$ (15 min, 25 °C) to yield the oxo-bridged hydrido complex $(Cp^*{}_2HfH)_2O$ (**2b**) and dihydrogen (eq 6). Thus, in



$$Cp^*{}_2Hf(H)(OH) + Cp^*{}_2HfH_2 \rightarrow Cp^*{}_2Hf(H){-}O{-}Hf(H)Cp^*{}_2 + H_2 \quad (6)$$

2b

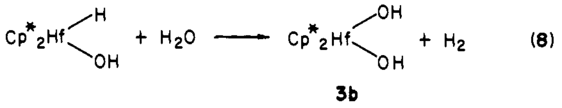
reactions of **1a** with H_2O, the zirconium analogue of **4** is strongly implicated as a reactive intermediate in the formation of **2a**. Consistent with this notion is the observation that this dimerization reaction seems to be general for other stable zirconium hydroxo complexes, as shown in eq 7, to give μ-oxo species with concomitant



$$Cp^*{}_2Zr(X)(OH) + Cp^*{}_2ZrH_2 \longrightarrow Cp^*{}_2Zr(X){-}O{-}Zr(H)Cp^*{}_2 + H_2 \quad (7)$$

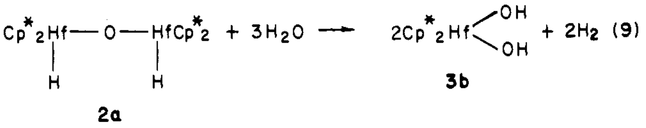
3a, X = OH
6a, X = Cl
7, X = OH
8, X = Cl

H_2 evolution. The ^1H NMR spectra of **7** and **8** show separate resonances for all four (C_5Me_5) rings, as expected for a static structure as illustrated in Figure 2. Water reacts further with **4** or **2b** with evolution of H_2 to yield the bis(hydroxo) complex $Cp^*{}_2Hf(OH)_2$ (**3b**) (eq 8, 9). No intermediates are spectroscopically observed in either reaction. Similarly, water and the monohydrido complexes $Cp^*{}_2MHCl$ (**5a**, M = Zr; **5b**, M = Hf) react to yield $Cp^*{}_2M(OH)Cl$ (**6a**, M = Zr; **6b**, M = Hf) (eq 10).



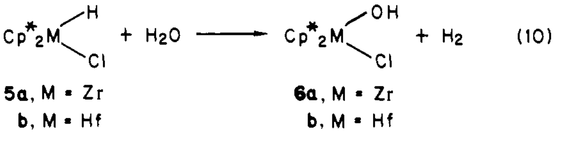
$$Cp^*{}_2Hf(H)(OH) + H_2O \longrightarrow Cp^*{}_2Hf(OH)_2 + H_2 \quad (8)$$

3b



$$Cp^*{}_2Hf(H){-}O{-}Hf(H)Cp^*{}_2 + 3H_2O \longrightarrow 2Cp^*{}_2Hf(OH)_2 + 2H_2 \quad (9)$$

2a **3b**



$$Cp^*{}_2M(H)Cl + H_2O \longrightarrow Cp^*{}_2M(OH)Cl + H_2 \quad (10)$$

5a, M = Zr
b, M = Hf
6a, M = Zr
b, M = Hf

Ammonia reacts with benzene solutions of **1a** and **1b** to yield the amido complexes $Cp^*{}_2MH(NH_2)$ (**9a**, M = Zr; **9b**, M = Hf) as colorless, monomeric crystalline materials (eq 11). It is noteworthy that while the zirconium hydroxo hydride complex

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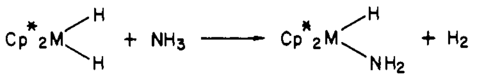
[21] Interestingly, the introduction of a *single* methyl group onto each Cp ring in this complex results in a substantial perturbation of the Zr_2Cl_2O core and an opening of the Cl–Zr–O, Cl′–Zr′–O dihedral angle by about 10° compared to the unsubstituted molecule. Petersen, J. L. *J. Organomet. Chem.* **1979**, *166*, 179–92.

[22] A qualitative description of bonding in $(Cp_2ML)_2O$ dimers is detailed in ref 21. Also see: Lauher, J. W.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–42.

[23] For these bent metallocene complexes a fourth possible resonance form, $M{\equiv}O{:}{\rightarrow}M$, can be excluded by molecular orbital arguments.[22]

[24] These compare with intense Zr–O–Zr′ stretching modes at 777 and 748 cm^{-1} for $(Cp_2ZrCl)_2O$. Brainina, E. M.; Freidlina, R. Kh.; Nesmevanov, A. N. *Dokl. Akad. Nauk SSSR* (*Engl. Transl.*) **1964**, 1113–15.

[25] It has been demonstrated that other small Lewis bases interact with **1** in just this manner.[2b] However, direct protonation of the Hf–H bond by water to give H_2 and a $[Cp^*{}_2HfH][OH]$ intermediate followed by rapid hydroxide association to hafnium cannot be excluded. Reaction of D_2O with C_6D_6 solutions of **1b** yields $Cp^*{}_2HfH(OD)_2$ thus providing experimental evidence that the mechanism of hydrogen elimination in eq 5 is best described as a protonolysis of the hydride instead of base (H_2O) induced reductive elimination of H_2 followed by (or concomitant with) oxidative addition of an O–H bond of water.

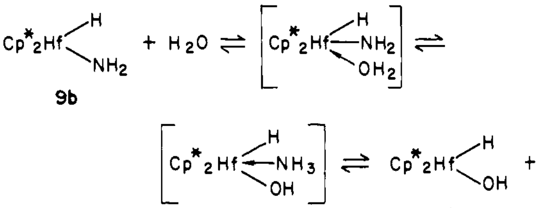


(11)

1a, M = Zr **9a**, M = Zr
b, M = Hf **b**, M = Hf

$[Cp^*_2ZrH(OH)]$ is never observed in water reactions, the analogous amido species **9a** is quite stable. Additionally, neither **9a** nor **9b** show a propensity at ambient temperature toward dimerization in reactions analogous to those shown in eq 6 and 7. Steric factors might well be responsible for this: molecular models show significant intramolecular ring–ring contacts for $(Cp^*_2MH)_2O$ when the M–O–M angle deviates markedly from linearity. Thus, sp hybridization about a bridging oxo ligand results in a linear bridge and decreased steric congestion; however, an sp-hybridized nitrogen is unreasonable for a M–NH–M species, precluding an analogous linear structure.[26]

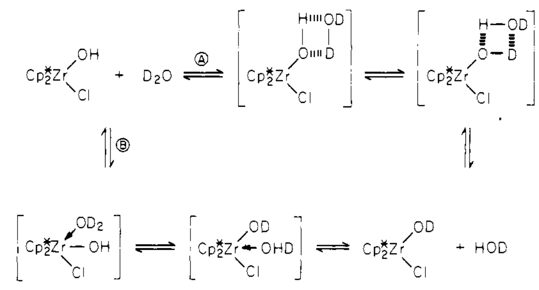
Exchange Reactions. In contrast to reactions in which H_2O converts hydride complexes into hydroxides with H_2 evolution (eq 4, 5, 8, 9, and 10), $Cp^*_2HfH(NH_2)$ reacts rapidly with water (1 equiv) to yield $Cp^*_2HfH(OH)$ and ammonia (but not $Cp^*_2Hf(OH)(NH_2)$). As depicted in eq 12, this transformation probably



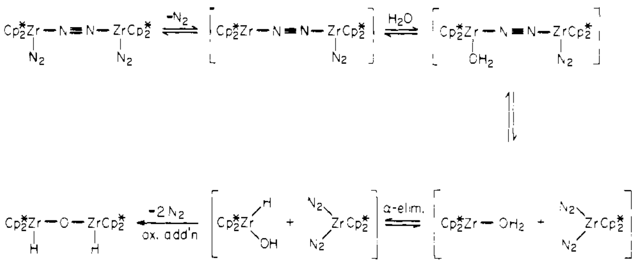
9b **4** (12)

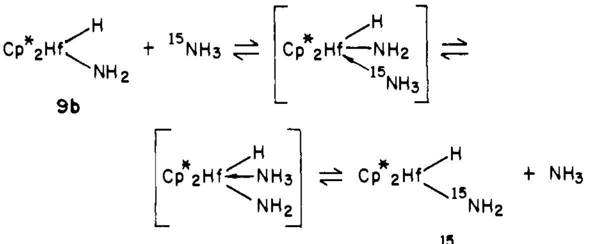
proceeds by way of a water coordination complex that undergoes a proton exchange followed by ligand (NH_3) dissociation to give the observed products. Intramolecular hydrogen bonding could be prominent for such intermediates and would be expected to facilitate such a proton transfer.[27] In light of this, elucidation of the nature of the interaction of the water molecule with zirconium in **3a·H₂O** could prove informative. The interaction of **9b** with $^{15}NH_3$ at ambient temperature results in a similar but slower exchange reaction to give an equilibrium (~1:1) mixture of **9b** and **9b-**^{15}N (eq 13). This reaction is conveniently monitored by ^1H NMR spectroscopy (**9b-**^{15}N, $^1J_{^{15}NH}$ = 66.8 Hz) and by analysis of the resulting gas mixture by mass spectrometry.

Scheme I



Scheme II





9b (13) **9b-**^{15}N

Addition of water to benzene solutions of the hydroxo derivatives **3** or **6** results in broadening of their otherwise sharp hydroxyl proton resonances (90 MHz, ^1H NMR), suggesting a rapid proton exchange on the NMR time scale; an added excess of D_2O results in the disappearance of the hydroxyl resonances. Not only do the hydroxyl protons exchange with those of added water, but also the hydroxyl oxygens exchange with the water oxygen atoms, as well. The rate of incorporation of ^{17}O from labeled $^{17}OH_2$ (50% enrichment) into the hydroxyl ligands can be monitored by ^{17}O NMR spectroscopy and is dramatically slower than the rate of deuterium incorporation under similar conditions. Thus, although no rigorous quantitative evaluations of the rates of thes exchanges have been attempted, with 2 equiv of added water the proton exchange reactions occur almost instantly at ambient temperature while the oxygen exchange takes several hours ($t_{1/2} \approx 2$ h for formation of an equilibrium concentration of $Cp^*_2Zr(^{17}OH)Cl$). Further discussion of the ^{17}O NMR data is given below. These results imply that the major pathways responsible for these two types of exchanges are different. While the mechanism analogous to that depicted in eq 12 accounts for both oxygen and proton exchange, a more facile process for proton exchange must exist, perhaps involving intermediates in which the water molecule undergoing exchange is not in the first coordination sphere of the metal. As illustrated in Scheme I, both routes A and B result in proton exchange, but only B results in oxygen atom exchange.

A comment on the thermodynamics of these exchange reactions involving N and O donor atoms is in order. Group 4B (Ti, Zr, Hf) elements form extremely strong bonds with hard class A ligands such as Cl, OH, NH_2, and O. For example, the average homolytic metal–ligand bond dissociation energy for $Zr(O\text{-}i\text{-}Pr)_4$ is 123,9 kcal/mol, for $Zr(NMe_2)_4$ is 83.7 kcal/mol, and for $ZrCl_4$

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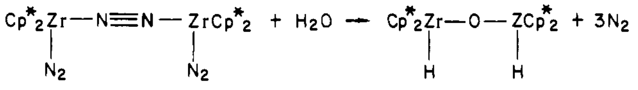
(26) Imido bridges (which are necessarily bent) are accessible in the sterically less demanding Cp_2M systems (cf. $(Cp_2TiCl)_2(\mu\text{-}NR)$: (a) Coutts, R. S. P.; Surtees, J. R. *Aust. J. Chem.* **1966**, *19*, 387–92. (b) Coutts, R. S. P.; Wailes, P. C. *Ibid.* **1971**, *24*, 1075–8. It is generally assumed that good π donor ligands (like F^-, OR^-, or NR_2^-) form strong π bonds with early transition metals when such interactions are possible (i.e., if there exists an energetically accessible, unoccupied metal-based acceptor orbital of π symmetry, oriented for effective overlap with an appropriate filled ligand donor orbital).[26c] We[4] and others[26d] have observed, however, that while electronic considerations favor good π bonding between M and the (otherwise) nonbonding electron pair of nitrogen in $Cp^*_2MX(NRR')$ complexes (M = Zr, Hf, Th, U; R, R' = H, alkyl, aryl), steric requirements often apparently prevent the amide from adopting the rotational conformation necessary for $N_{p\pi}$–$M_{d\pi}$ bonding. For example, $Cp^*_2HfH(NMe_2)$ exhibits inequivalent amido methyl resonances in its low-temperature ^1H NMR spectrum (−80 °C, 500 MHz, C_7D_8 solution) with a substantial activation barrier (13.5 ± 1 kcal/mol) for equilibration of the amide's methyl groups. These results indicate that the preferred conformation has an orthogonal orientation of the nitrogen donor and low-lying, empty acceptor orbital in the equatorial plane of the $[Cp^*_2Hf]$ moiety ($1a_1$). Models show that the electronically preferred $Hf{=}NR_2$ conformation (with C–N–C ⊥ H–Hf–N) is sterically disfavored due to bodacious amide–C_5Me_5 ring contacts. In contrast, models for the parent NH_2 system (**9b**) suggest no prohibitive steric interactions between the NH_2 group and the C_5Me_5 ring atoms. Accordingly, the low-temperature ^1H NMR spectra (500 MHz, −90 °C) of both **9b** and **9b-**^{15}N exhibit equivalent amide proton resonances consistent with the $Hf{=}NH_2$ conformation. (c) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389–98. (d) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206.

(27) Hydrogen bonding could also be a key factor in the kinetic preference for hydrolysis at $M{-}NR_2$ (instead of at M–H) to give **4**. Interestingly, experimental data recently reported (Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–32) appear to indicate that **4** + NH_3 is thermodynamically preferred (by ~10 kcal·mol⁻¹) over $Cp^*_2Hf(OH)(NH_2)$ + H_2 in eq 12. Moreover, treatment of **9b** with D_2O affords a mixture of $Cp^*_2Hf(OD)(H)$, $Cp^*_2Hf(OH)(H)$, and NH_nD_{3-n} but *no* defectable $Cp^*_2Hf(OD)(D)$ or $Cp^*_2Hf(OH)(D)$. Thus reactions of eq 5 and 12 proceed by Lewis base coordination → proton transfer → Lewis base dissociation rather than via reductive elimination of H_2 or NH_3 followed by oxidative addition of D_2O.

117,2 kcal/mol.[28] For the reaction $M-NH_2 + H_2O \rightleftharpoons M-OH + NH_3$, production of the metal hydroxo species and ammonia should be thermodynamically favored (as is indeed observed), by roughly 23 kcal/mol.[29] An associative intermediate, such as that depicted in eq 13, could provide a low activation alternative to an energetically unreasonable first step involving $M-NH_2$ bond dissociation (homolytic or heterolytic). Associative mechanisms probably likewise provide low-energy pathways for the degenerate exchanges ($M-NH_2 + {}^*NH_3 \rightleftharpoons M-{}^*NH_2 + NH_3$ and $M-OH + {}^*OH_2 \rightleftharpoons M-{}^*OH + OH_2$) that are essentially thermoneutral processes even though the M-OR bond strength is nearly 125 kcal/mol and the $M-NR_2$ bond strength is almost 85 kcal/mol.

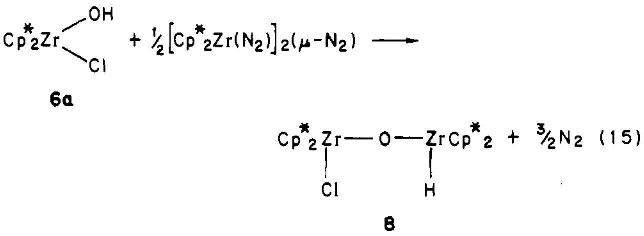
Oxidative Addition Reactions. The divalent zirconium complex $[Cp^*_2Zr(N_2)]_2(\mu-N_2)$ (**10**) reacts rapidly and cleanly with 1 equiv of H_2O to produce **2a** with vigorous evolution of dinitrogen (eq 14). This reaction, formally an oxidative addition of both O-H bonds of a water molecule, results in a formal 4-electron reduction of H_2O and represents unprecedented formation of a group 4B metal hydride from water! Although the reaction proceeds with no spectroscopically detectable intermediates, a mechanism involving stepwise oxidative additions seems more reasonable than a single concerted process (see Scheme II). It has been previously shown that the terminal N_2 ligands in **10** are labile,[30] thus N_2 dissociation followed by H_2O coordination to give a water complex is a likely initial sequence (cf. the stepwise replacement of N_2 in **10** by the Lewis base CO).[31] A simple α-elimination would then afford a zirconiumn(IV) hydroxo hydride species and leave a zirconium (II) center that could subsequently oxidatively add the hydroxyl O-H bond. The reaction shown in eq 15 provides plausibility for this final oxidative addition step: $Cp^*_2Zr(OH)Cl$ reacts with **10** in a 2:1 stoichiometry to give the oxo-bridged dimer $(Cp^*_2ZrH)O(Cp^*_2ZrCl)$ (**8**). Furthermore, ammonia and **10** react to give $Cp^*_2ZrH(NH_2)$ and uncharacterized decomposition products; the amido hydride complex **9a** is produced in 40-50% yield (isolated by vacuum sublimation at 110 °C) as determined by ^1H NMR spectroscopy, even when an excess of ammonia is used.[32]



$$Cp^*_2Zr(N_2)-N\equiv N-ZrCp^*_2(N_2) + H_2O \rightarrow Cp^*_2Zr(H)-O-ZrCp^*_2(H) + 3N_2 \qquad (14)$$

10 **2a**

(14)



$$Cp^*_2Zr(OH)(Cl) + \tfrac{1}{2}[Cp^*_2Zr(N_2)]_2(\mu-N_2) \longrightarrow Cp^*_2Zr(Cl)-O-ZrCp^*_2(H) + \tfrac{3}{2}N_2 \qquad (15)$$

6a **8**

Table II. ^{17}O NMR Data for Oxo and Hydroxo Complexes

compd[a]	$\delta(\mu\text{-O})$[b]	$\delta(OH)$[b]	$^1J_{OH}$, Hz
$(Cp^*_2ZrH)_2O$ (**2a**)	581		
$(Cp^*_2HfH)_2O$ (**2b**)	503		
$Cp^*_2Zr(OH)_2$ (**3a**)		175	78
$Cp^*_2Hf(OH)_2$ (**3b**)		144	78
$Cp^*_2HfH(OH)$ (**4**)		206	88
$Cp^*_2ZrCl(OH)$ (**6a**)		231	78
$Cp^*_2HfCl(OH)$ (**6b**)		193	78
$(Cp^*_2ZrH)O[Cp^*_2Zr(OH)]$ (**7**)	532	183	78
$(Cp^*_2ZrCl)O(Cp^*_2ZrH)$ (**8**)	576		

[a] Compounds enriched to ~50% ^{17}O. [b] Spectra measured at 12.5 MHz in C_6D_6 solution and chemical shifts reported in ppm relative to neat $H_2O = \delta(O)$ (capillary insert). See ref 36.

^{17}O NMR Spectroscopy. Several research groups have recently demonstrated the utility of ^{17}O NMR spectroscopy in elucidating structures for transition-metal oxo complexes.[33] ^{17}O NMR has similarly proved to be a valuable method of characterizing the oxo and hydroxo complexes reported here. Chemical shift and $^1J_{OH}$ coupling data for several of these compounds (see Table II) show the presence of two types of oxygen-containing ligands: (1) oxo groups that exhibit resonances around 500 ppm (relative to water) and no proton coupling and (2) hydroxo groups that exhibit resonances between 140 and 250 ppm with $^1J_{^{17}OH} \approx 80$ Hz (verified by decoupling experiments). Line widths for the OH resonances are typically about 50-60 Hz, while the μ-oxo resonances are somewhat sharper, typically 20-30 Hz. Although no detailed quantitative interpretation of these chemical shifts seems warranted, it is noteworthy that the low-field chemical shift values for the μ-oxo ligands are consistent with those for bridging oxo ligands in other systems containing W, Mo, Nb, Ta, V, and Ti.[33],[34]

^{17}O NMR spectroscopy also provided a convenient means for observing the dynamic water-exchange process (see above) for the hydroxo complexes. While long accumulation times (~15 min per spectrum for adequate signal-to-noise) prevented rigorous kinetic analysis of the exchange phenomena, a qualitative picture of the time scale of the exchange process was obtained.

Conclusions

Water has been shown to react vigorously but selectively with bis(pentamethylcyclopentadienyl)zirconium and hafnium hydrido complexes to give new hydrido, hydroxo, and μ-oxo complexes containing the Cp^*_2M fragments (M = Zr, Hf). The chemistry of the Zr and Hf systems studied seem to parallel one another, although as usual the reactions involving Hf are slower than those with Zr. For example, the reactive intermediate $Cp^*_2MH(OH)$ can be isolated from the reaction of $Cp^*_2MH_2$ with H_2O if M = Hf, but for M = Zr this hydroxo hydride complex is never observed, quickly reacting with another equivalent of $Cp^*_2ZrH_2$ to afford $(Cp^*_2ZrH)_2O$. Although similar μ-oxo complexes are well-known for the parent cyclopentadienyl systems (Cp_2M), we find it somewhat surprising that a single atom bridge between two bulky Cp^*_2M fragments is stable.

Similar reactivity is observed between ammonia and $Cp^*_2MH_2$. In contrast to the water reactions, however, $Cp^*_2MH(NH_2)$ is stable for M = Zr as well as M = Hf. Indeed, the amido species show no proclivity toward dimerization to form μ-imido complexes, presumably owing to the increased steric congestion expected about an sp^2 (bent) imido bridge compared to an sp (linear) oxo bridge.[26]

When water or ammonia is allowed to react with the Zr(II) complex $[Cp^*_2Zr(N_2)]_2(\mu-N_2)$, formal oxidative addition of O-H or N-H bonds occurs. In the case of water, *both* O-H bonds are oxidatively added to yield the dihydrido dimer $(Cp^*_2ZrH)_2O$, formally a four-electron reduction of a water molecule. Other

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(28) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71-110.

(29) Using the average homolytic bond dissociation energies from ref 26 along with literature values for $H_2O \rightarrow OH\cdot + H\cdot$ (116 kcal/mol), $NH_3 \rightarrow NH_2\cdot + H\cdot$ (100 kcal/mol), and $HCl \rightarrow Cl\cdot + H\cdot$ (102 kcal/mol) (Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976), the following approximate ΔH terms can be derived: $M-NH_2 + H_2O \rightleftharpoons M-OH + NH_3$ (M = Zr, -22 kcal/mol; M = Hf, -23 kcal/mol); $M-OH + HCl \rightleftharpoons M-Cl + H_2O$ (M = Zr, -7 kcal/mol; M = Hf, -5 kcal/mol).

(30) Manriquez, J. M.; McAlister, D. R.; Rosenberg, E.; Shiller, A. M.; Williamson, K. L.; Chan, S. I.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3078-83.

(31) Marsella, J. A.; Curtis, C. J.; Bercaw, J. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 7244-46. Supporting the notion that N_2 dissociation followed by coordination of water is a likely sequence is the observation that H_2O does not react (3 days, 80 °C) with $Cp^*_2Zr(CO)_2$, a molecule that requires photolytic conditions for CO displacement.

(32) Manriquez, J. M.; Bercaw, *J. E. J. Am. Chem. Soc.* **1974**, *96*, 6229-30. Importantly, **9a** does not react with **10** (C_6D_6, 25 °C), consistent with the observation that **9a** does not react with **1a**.

(33) (a) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93-103. (b) Miller, K. F.; Wentworth, R. A. D. *Ibid.* **1979**, *18*, 984-88.

(34) (a) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1978**, *100*, 4891-93. (b) Besecker, C. J.; Klemperer, W. G. *Ibid.* **1980**, *102*, 7598-600. (c) Day, V. W.; Fredrich, M. F.; Thompson, M. R.; Klemperer, W. G.; Liu, R.-S. Shum, W. *Ibid.* **1981**, *103*, 3597-99.

M(OH) bonds will similarly oxidatively add to the dinitrogen complex to give μ-oxo hydrides (M–OH + M′ → M–O–M′–H). The reactions of $Cp^*_2MH_2$ or $[Cp^*_2M(N_2)]_2(\mu\text{-}N_2)$ (M = Zr, Hf) with other transition-metal hydroxo and amido complexes might prove to be a general synthetic route to hterobimetallic μ-oxo (or possibly even μ-imido) species containing the Cp^*_2MH fragment.

Experimental Section

General Considerations. Compounds were handled in an inert-atmosphere glovebox and reactions effected by using high-vacuum techniques. Gas evolution measurements were performed by using standard Toepler techniques and the identities of the gases determined by mass spectrometry (Du Pont 21-492 instrument) or by selective burning of the gases over CuO with use of a Toepler pump for circulation. Rigorously dry, oxygen-free solvents were vacuum transferred from green "titanocene"[35] and used throughout. Infrared spectra were recorded in Nujol mulls by using a Beckman 4240 spectrophotometer and were calibrated with a polystyrene film. Proton and oxygen-17 NMR spectra were recorded in C_6D_6 or C_7D_8 solution with an internal $SiMe_4$ reference and external water reference, respectively, by using a JEOL-FX90Q spectrometer.[36] Open-faced, screw-capped 5-mm NMR tubes equipped with gas-tight septa (Wilmad, Inc.) were used with a microliter syringe in the titration studies of $Cp^*_2ZrH_2$ and $Cp^*_2HfH_2$ with H_2O. Elemental analyses were performed by Dornius and Kolbe Microanalytisches Laboratorium (West Germany) and Alfred Bernhardt (West Germany).

Deionized, distilled water was used without further purification; $^{17}OH_2$ (50% ^{17}O) and $^{18}OH_2$ (98% ^{18}O) were purchased from Monsanto Research Corp. (Mound Facility) and used directly without further purification. $^{15}NH_3$ was prepared from $^{15}NH_4Cl$ (99% ^{15}N, Stohler Isotope Chemicals) and NaOH and trap-to-trap distilled prior to usage. Ammonia direct from a gas cylinder was freeze–pump–thawed prior to usage to remove residual noncondensable gases. $[Cp^*_2ZrN_2]_2N_2$[30] and $Cp^*_2ZrH_2$[2b] were prepared according to literature methods. Cp^*_2ZrHCl was prepared by metathesis of equimolar amounts of $Cp^*_2ZrH_2$ and $Cp^*_2ZrCl_2$ in C_6H_6 under an H_2 atmosphere. $Cp^*_2HfH_2$ was prepared from $Cp^*_2HfCl_2$, *n*-BuLi, and H_2 and was recrystallized from petroleum ether.[37] Cp^*_2HfHCl was prepared from $Cp^*_2HfH_2$ and CH_3Cl in benzene.[37]

Preparation of $(Cp^*_2ZrH)_2O$ (2a). Method A. To a cooled (−78 °C), stirred solution of $Cp^*_2ZrH_2$ (0.20 g, 0.55 mmol) in 5 mL of toluene was added 0.5 equiv (8.6 μL) of H_2O. The solution was slowly warmed to ambient temperature and, after gas evolution had ceased (0.98 equivalent H_2/Zr) was recooled to −78 °C causing a colorless, microcrystalline material to precipitate. The volume of toluene was reduced under vacuum to ca. 2 mL, and then 5 mL of petroleum ether was added and the mixture was filtered while cold to yield 0.17 g (84%). Anal. Calcd for $C_{40}H_{62}OZr_2$: C, 64.80; H, 8.43; Zr, 24.61. Found: C, 64.53, H, 7.81, Zr, 25.13. **2a**-^{18}*O* and **2a**-^{17}*O* were analogously prepared from the appropriately labeled water. **Method B.** Using a procedure similar to method A,a 0.25-g sample of $(Cp^*_2ZrN_2)_2N_2$ in 10 mL of toluene was treated with 1 equiv of H_2O (5.6 μL), yielding 1.42 equiv of N_2/Zr and **2a** in 78% isolated yield (0.18 g).

Preparation of $(Cp^*_2HfH)_2O$ (2b). Using a procedure similar to method A for the preparation of **2a** (above), a 0.36-g (0.80-mmol) sample of $Cp^*_2HfH_2$ was treated with 0.5 equiv of H_2O (7.2 μL) and then the solution was heated at 80 °C for 1 h. Workup yielded 0.26 g (71%) of **ib** as a colorless powder. Anal. Calcd for $C_{40}H_{62}OHf_2$: C, 52.46; H, 6.82; Hf, 38.98. Found: C, 52.30; H, 7.01; Hf, 39.32. An NMR titration study shows that upon addition of water, an equimolar mixture of $Cp^*_2HfH_2$ and $Cp^*_2HfH(OH)$ is formed that subsequently dimerizes upon heating with elimination of H_2. **2b**-^{17}*O* was prepared analogously from the labeled (50%) water.

Preparation of $Cp^*_2Zr(OH)_2$ (3a). Method A. A 0.55-g sample (1.51 mmol) of $Cp^*_2ZrH_2$ was dissolved in 10 mL of toluene, and the solution was cooled to −78 °C. To the cooled, stirred solution was added 2 equiv (54.4 μL) of H_2O by using a gas-tight microliter syringe. Immediate, vigorous gas evolution was obvious and continued as the solution was warmed to ambient temperature (1.81 equiv of H_2/Zr). The solvent was removed under vacuum, and 20 mL of petroleum ether was distilled into the reaction flask and the solution cooled to −78 °C and filtered while cold. Concentration of the resulting solution yielded 0.49 g (82%) of large, colorless prisms. **3a** can be sublimed at 130 °C (10^{-4} torr) to give large, colorless needles. A ^1H NMR titration study of **1a** with H_2O shows that the formation of **3a** proceeds via intermediate formation of **2a** followed by hydrolysis to give the product quantitatively. Anal. Calcd for $C_{20}H_{32}O_2Zr$: C, 60.71; H, 8.15; Zr, 23.05. Found: C, 60.60; H, 7.95; Zr, 23.19. **3a**-^{18}*O* and **3a**-^{17}*O* were prepared analogously from the appropriately labeled water. **Method B.** $Cp^*_2ZrCl_2$ (1.00 g, 2.31 mmol) was added to 25 mL of tetrahydrofuran in a sublimation apparatus and cooled to −78 °C. To this mixture was added to 2.2 equiv of *n*-BuLi under a counterflow of argon, and the stirred mixture was warmed to ambient temperature. An excess of water (0.5 mL) was added to the solution, which was stirred for an additional 5 min and then taken to dryness under vacuum. Sublimation of the residue yielded 0.66 g (71%) of **3a**. Recrystallization of the residue (instead of sublimation) from cold petroleum ether resulted in isolation of a yellow crystalline monohydrate $Cp^*_2Zr(OH)_2\cdot H_2O$ (**3a·H₂O**).

Preparation of $Cp^*_2Hf(OH)_2$ (3b). Method A. Using a procedure similar to that for **3a**, method A, 0.31 g (0.69 mmol) of $Cp^*_2HfH_2$ was dissolved in 5 mL of toluene and the solution cooled to −78 °C and stirred vigorously while 2 equiv of H_2O (24.7 μL) was added via syringe. The solution was slowly warmed to ambient temperature, resulting in vigorous gas evolution (1.92 equiv of H_2/Hf). Workup yielded 0.26 g (79%) of colorless crystals. A ^1H NMR titration study of **1b** with H_2O shows that the formation of **3b** proceeds predominately via intermediate formation of $Cp^*_2HfH(OH)$ (with smaller amounts of $(Cp^*_2HfH)_2O$) followed by hydrolysis to give the product. Anal. Calcd for $C_{20}H_{32}O_2Hf$: C, 49.74; H, 6.68; Hf, 36.96. Found: C, 49.74; H, 6.62; Hf, 37.16. **3b**-^{17}*O* was prepared analogously from $^{17}OH_2$. Recrystallization of **3b** in the presence of excess water results in formation of a monohydrate, **3b·H₂O**. Anal. Calcd for $C_{20}H_{34}O_3Hf$: C, 47.95; H, 6.84. Found: C, 48.00; H, 6.50. Sublimation of **3b·H₂O** (140 °C, 10^{-4} torr) results in isolation of water-free **3b**. **Method B.** A 0.21-g (0.23-mmol) sample of $(Cp^*_2HfH)_2O$ was dissolved in 5 mL of toluene, cooled to −78 °C, and 3 equiv (12.4 μL) of H_2O was added via a microliter syringe. Vigorous gas evolution was evident as the solution warmed to ambient temperature (0.90 equiv of H_2/Hf), and workup as in method A yielded 0.14 g (63%) of colorless crystals. As determined spectroscopically by ^1H NMR, this transformation is quantitative.

Preparation of $Cp^*_2HfH(OH)$ (4). $Cp^*_2HfH_2$ (0.25 g, 0.56 mmol) was dissolved in 10 mL of Et_2O, the solution cooled to −78 °C, and 1 equiv of H_2O (10.1 μL) was added rapidly to the vigorously stirred solution. The temperature of the solution was maintained at −78 °C for 15 min, then was slowly warmed to ambient temperature, stirred for an additional 15 min. The solution was recooled to −78 °C and filtered while cold and the solvent removed to yield 0.19 g (73%) of the colorless crystalline material. Anal. Calcd for $C_{20}H_{32}OHf$: C, 51.44; H, 6.91; Hf, 38.22. Found: C, 51.60; H, 6.91; Hf, 38.35. **4**-^{17}*O* was prepared analogously from $^{17}OH_2$.

Preparation of $Cp^*_2Zr(OH)Cl$ (6a). A 0.17-g sample of Cp^*_2ZrHCl was dissolved in 5 mL of toluene and cooled to −78 °C. To the stirred solution was added 1 equiv (7.7 μL) of water via a microliter syringe. The solution was warmed to room temperature, and gas evolution (0.94 equiv H_2/Zr) was vigorous. The toluene was removed under vacuum, and the colorless crystalline material was washed with cold petroleum ether to yield 0.16 g (90%). Anal. Calcd for $C_{20}H_{31}ClOZr$: C, 58.00; H, 7.55; Zr, 22.03. Found: C, 58.07; H, 7.49; Zr, 22.07. **6a**-^{17}*O* was prepared analogously from $^{17}OH_2$. $Cp^*_2Hf(OH)Cl$ (**6b**) was similarly prepared from Cp^*_2HfHCl in 92% yield.

Preparation of $[Cp^*_2Zr(OH)]O(Cp^*_2ZrH)$ (7). $Cp^*_2Zr(OH)_2$ (0.22 g, 0.56 mmol) and $Cp^*_2ZrH_2$ (0.20 g, 0.55 mmol) were dissolved in 5 mL of toluene at −78 °C. Upon warming, gas evolution was evident (0.44 equiv of H_2/Zr). The solution was stirred at room temperature for 5 min, and then the volume of solvent was reduced to ~1 mL under vacuum. Petroleum ether (5 mL) was distilled onto the resulting slurry, and the solution was cooled to −78 °C and filtered while cold to yield 0.26 g (63%) as a colorless white powder. Anal. Calcd for $C_{40}H_{62}O_2Zr_2$: C, 63.44; H, 8.25; Zr, 24.09. Found: C, 63.23; H, 8.44; Zr, 23.95. **7**-^{17}*O* was prepared analogously from **oa**-^{17}*O* and **1a**.

Preparation of $(Cp^*_2ZrCl)O(Cp^*_2ZrH)$ (8). Method A. Equimolar amounts of $Cp^*_2ZrH_2$ (0.10 g, 0.27 mmol) and $Cp^*_2Zr(OH)Cl$ (0.11 g, 0.27 mmol) were dissolved in 5 mL of toluene at −78 °C and the solution slowly warmed to room temperature. As the solution warmed, gas evolution was prominent (0.40 equiv of H_2/Zr). Workup as for **7** resulted in isolation of 0.14 g (67%) as a colorless powder. Anal. Calcd for $C_{40}H_{61}ClOZr_2$: C, 61.93; H, 7.93; Zr, 23.52. Found: C, 61.58; H, 7.29; Zr, 23.41. **Method B.** A 0.19-g sample of $Cp^*_2Zr(OH)Cl$ (0.46 mmol) and 0.19 g of $[Cp^*_2Zr(N_2)]_2N_2$ (0.23 mmol) were dissolved in 5 mL of toluene, and the solution was stirred at −78 °C for 5 min and then at room temperature for 20 min during which time the deep purple of the solution dissipated. A Toepler measurement indicated that 0.66 equiv

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of N_2/Zr was produced during the reaction. Workup as for **7** yielded 0.29 g (81%) of colorless crystals. **8**-^{17}*O* was prepared analogously to method B from **6a**-^{17}*O*.

Preparation of $Cp^*_2ZrH(NH_2)$ (9a). Method A. A 0.24-g sample of $Cp^*_2ZrH_2$ (0.66 mmol) was dissolved in 15 mL of petroleum ether and the solution cooled to −78 °C. The solution was stirred, and 1.5 equiv of ammonia was condensed into the reaction vessel. The reaction mixture was warmed to room temperature, and then the solvent was removed under vacuum to yield 0.21 g (84%) of a colorless powder. A Toepler measurement indicated that 0.92 equiv of H_2/Zr was produced during the reaction. Anal. Calcd for $C_{20}H_{33}NZr$: C, 63.43; H, 8.78; N, 3.70. Found: C, 63.40; H, 8.70; N, 3.55. **Method B.** A 0.30-g sample of $[Cp^*_2Zr(N_2)]_2N_2$ was dissolved in 10 mL of toluene and placed in a sublimation apparatus. Two equivalents of NH_3 were condensed into the reaction vessel and the contents stirred at ambient temperature for 1 h during which time the solution changed from deep purple to blood red. The solvent was removed under vacuum and the residue sublimed (110 °C, 10^{-4} torr) to yield 0.13 g (46%) of colorless crystals.

Preparation of $Cp^*_2HfH(NH_2)$ (9b). Using a procedure similar to method A for **9a**, a 0.13-g sample of $Cp^*_2HfH_2$ was dissolved in 10 mL of petroleum ether and the solution stirred at ambient temperature with 2 equiv of NH_3 for 15 min. Removal of solvent under vacuum yielded 0.13 g (97%) of a colorless powder. Anal. Calcd for $C_{20}H_{33}NHf$: C, 51.55; H, 7.14; N, 3.01. Found: C, 51.61; H, 7.13; N, 3.08. ^{9}b-^{15}*N* was prepared analogously from $^{15}NH_3$.

Exchange Experiments. The exchange experiments previously described were effected on NMR tube scales. In a typical experiment, a 25-mg sample of $Cp^*_2Zr(OH)Cl$ was dissolved in 0.5 mL of C_6D_6 and placed, along with a sealed capillary of H_2O (5% ^{17}O) as a reference, in a 5-mm NMR tube with an open-faced cap with a septum. ^{17}O-enriched water was subsequently added through the septum via a microliter syringe, and the reaction was followed by ^{17}O NMR spectroscopy (i.e., the appearance and growth of the resonance corresponding to $Cp^*_2Zr(^{17}OH)Cl$).

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Registry No. 1a, 61396-34-7; **1b**, 81956-87-8; **2a**, 91294-89-2; **2a**-^{18}O, 91294-90-5; **2b**, 91294-91-6; **2b**-^{17}O, 91294-92-7; **3a**, 91294-93-8; **3a**-^{18}O, 91294-94-9; **3a**-^{17}O, 91294-95-0; **3b**, 91294-96-1; **3b**-^{17}O, 91294-97-2; **4**, 91294-98-3; **4**-^{17}O, 91294-99-4; **5a**, 77299-72-0; **5b**, 91295-01-1; **6a**, 91295-02-2; **6a**-^{17}O, 91295-03-3; **6b**, 91295-04-4; **6b**-^{17}O, 91295-05-5; **7**, 91295-06-6; **7**-^{17}O, 91295-07-7; **8**, 91295-08-8; **8**-^{17}O, 91295-09-9; **9a**, 91295-10-2; **9b**, 91295-11-3; **9b**-^{15}N, 91295-12-4; **10**, 54387-50-7; $Cp^*_2ZrCl_2$, 54039-38-2; H_2O, 7732-18-5; ^{18}OHa, 14314-42-2; $^{17}OH_2$, 13768-40-6; NH_3, 7664-41-7; $^{15}NH_3$, 13767-16-3.

Metal Ion Encapsulation: Cobalt Cages Derived from Polyamines, Formaldehyde, and Nitromethane

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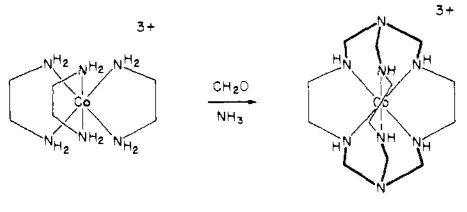
Abstract: The syntheses and characterization of a number of cage complexes derived from the products of the reactions between $Co(en)_3^{3+}$ (en = 1,2-ethanediamine) and $Co(sen)^{3+}$ (sen = 5-(4-amino-2-azabutyl)-5-methyl-3,7-diaza-1,9-nonanediamine) with formaldehyde and nitromethane in basic solution are described. The complexes can all be considered as derivatives of the hexaazamacrobicycle "sarcophagine" or 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane (sar). To confirm the cage structure of the ligands, the crystal structure of the deprotonated complex $[Co(diNOsar\text{-}H)]Cl_2\cdot 4H_2O$ is reported. Crystal data for $[Co^{III}(diNOsar\text{-}H)]Cl_2\cdot 4H_2O$ are the following: space group $P2_12_12_1$, $a = 10.821$ (5) Å, $b = 15.929$ (8) Å, $c = 14.259$ (10) Å, $U = 2457.8$ Å^3, $D_{obsd} = 1.579$ g cm^{-3}, $D_{calcd} = 1.554$ g cm^{-3}, $Z = 4$, 2423 nonzero structure factors ($I > 2.5\sigma I$), and $R = 0{,}048$. Reduction of the nitro-substituted sarcophagine complexes leads to amino-substituted derivatives which in turn may be diazotized to give a variety of new cages, and ultimately reductive elimination of the chloro derivative provides the "parent" complex $Co(sar)^{3+}$. Spectroscopic characterization of these complexes is also given, and the synthetic chemistry is analyzed in detail.

Cyclic, multidentate chelating ligands are the most potent yet often also the most selective of metal-coordinating agents, and in recent publications[1-6] we have described some of our efforts to synthesize macropolycyclic ligands especially suited to the binding of transition metals. The first-developed procedure, **1**,



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which led to the octaazamacrobicycle given the trivial name "sepulchrate",[1-4] seemed open to several obvious changes, one of which was to vary the central atoms of the ligand "caps" (shown as heavy lines in the above diagram). In sepulchrate, these atoms are nitrogen and are derived from ammonia formally acting as a tribasic acid under the preparative conditions. In principle, any other tribasic acid might therefore be expected to provide a substitute for ammonia and there are simple organic examples

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