Dynamic Interligand Hydrogen Transfer in Some η^5-Cyclopentadienylzirconium and -hafnium Tetrahydroborates

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Abstract: The compounds $(\eta^5\text{-}C_5H_5)_2Zr(BH_4)_2$, $(\eta^5\text{-}C_5H_5)_2Hf(BH_4)_2$, and $(\eta^5\text{-}C_5H_5)_2Zr(H)BH_4$ exhibit exchange of C_5H_5 and BH_4 hydrogens which is rapid on the proton NMR time scale at elevated temperatures. The process is found to be predominantly unimolecular, with free energies of activation ($\Delta G^\ddagger$) for the above compounds of 21.3 ± 0.4, 19.4 ± 0.4, and 19.6 ± 0.4 kcal/mol (395°K), respectively. For $(C_5H_5)_2Zr(H)BH_4$, the hydrido hydrogen also appears to become involved in the exchange process at higher temperatures, with $\Delta G^\ddagger = 20.9 \pm 0.5$ kcal/mol (395°K). The interchange process also occurs for $(C_5H_5)_2Zr(BD_4)_2$ in the solid state, but more slowly. The possible mechanisms of this prototropic rearrangement are discussed, and the likely importance of $\eta^1\text{-}C_5H_4M$ carbene-ylid complexes along the reaction coordinate is underscored.

It is becoming apparent that the activation and transfer of cyclopentadienyl ring hydrogen atoms may represent an important reaction pattern for $(\eta^5\text{-}C_5H_5)M$ compounds, M = transition metal or actinide. In several cases it has been shown that this hydrogen can be transferred intramolecularly and stereospecifically to another ligand in the complex.[3] Similar intra- or intermolecular processes also represent plausible components of pathways for the formation of a number of $M(\eta^5{:}\eta^1\text{-}C_5H_4)_2M$ and $M(\eta^5{:}\eta^5\text{-}C_{10}H_8)M$ species from $(\eta^5\text{-}C_5H_5)M$ complexes.[4-8] In this paper we report several cases where intramolecular reversible hydrogen transfer between an $\eta^5\text{-}C_5H_5$ group and another ligand (BH_4) on the same metal atom is actually rapid on the NMR time scale. We have alluded to such processes previously,[9] and present here a full exposition of our investigations on bis(η^5-cyclopentadienyl)tetrahydroborates of four-valent zirconium and hafnium. It is seen that such hydrogen transfer processes are far more facile and widespread than previously thought. In addition, our results add another dimension to the scope of metal tetrahydroborate molecular dynamics.

Experimental Section

The known compounds $(\eta^5\text{-}C_5H_5)_2Zr(BH_4)_2$,[9a,10] $(\eta^5\text{-}C_5H_5)_2Zr(H)BH_4$,[9a,11] and $(\eta^5\text{-}C_5H_5)_2Hf(BH_4)_2$[9a,12] were prepared according to literature methods and were doubly sublimed. The starting materials $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ and $(\eta^5\text{-}C_5H_5)_2HfCl_2$ were purchased from Research Organic/Inorganic Chemical Corporation and were used without further purification. $LiBH_4$ and $LiBD_4$ were purchased from Alfa-Ventron Inorganic Chemicals and used without further purification. All sample manipulations and preparations were carried out in an atmosphere of prepurified nitrogen or in vacuo. All tetrahydroborates were stored under nitrogen at −35° in the dark in order to avoid decomposition. Solvents were distilled from sodium–potassium alloy-benzophenone immediately prior to use.

Molecular Weight Studies. The solution molecular weight of $(C_5H_5)_2Zr(H)BH_4$, which had not been reported, was determined cryoscopically in benzene using the apparatus described previously[13] (calcd, 237 for a monomer; found, 258).

Spectroscopic Measurements. Nujol mulls for infrared spectra were prepared in a nitrogen-filled glove box and were examined between sodium chloride or potassium bromide plates. In all cases, possible decomposition was monitored by observing changes in the spectra effected over a period of several scans. Infrared spectra were recorded on Beckman IR-5 and IR-9 and Perkin-Elmer Model 267 spectrophotometers and were calibrated with polystyrene film.

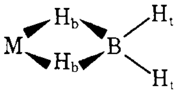
Samples for nuclear magnetic resonance spectra were loaded into septum-capped sample tubes in a nitrogen-filled glove box and dry, degassed solvents added via syringe. In certain cases, sample tubes were fitted with ground-glass joints and connected to a vacuum line after loading. Solvents were freeze–thaw degassed and dried before distilling into the sample tube, which was then sealed under vacuum.

Proton magnetic resonance spectra were recorded on Varian T60 and Perkin-Elmer R20-B (60 MHz) and Bruker HFX-90 (90 MHz) spectrometers. Heteronuclear noise-modulated boron-11 decoupling at 90 MHz was performed on the HFX-90 equipped with a Schomandl ND30M frequency synthesizer, a Bruker B-SV2 broadband power amplifier, and an appropriate ^{11}B matching preamplifier network. At each temperature, power, bandwidth, and frequency were adjusted for maximum decoupling. Variable temperature studies were accomplished on the HFX-90 with the calibrated Bruker-B-ST 100/700 temperature control unit. Spectra were calibrated with a Hewlett-Packard Model 5216A frequency counter. At 60 MHz, heteronuclear decoupling was performed on the R20-B spectrometer using a Schomandl ND30M frequency synthesizer, a Perkin-Elmer Model R-209PA rf power amplifier, and a Calrad Model 65-287 rf power meter, employed to maximize output. Variable temperature studies were conducted with the Perkin-Elmer Model R-202VT temperature controller; spectra were calibrated with a Model TR-3824X frequency counter. To minimize thermal decomposition while recording spectra at higher temperatures, the NMR spectrometer was equilibrated at each new temperature minus the sample tube. The sample tube was then introduced and field homogeneity and, if required, decoupling was optimized as rapidly as possible while the sample was warming up (2-3 min). The relevant areas of the spectrum were next recorded twice, field homogeneity was checked on internal benzene, and the sample tube was removed and quickly cooled in ice water.

Samples for electron paramagnetic resonance spectra were prepared in Schlenk apparatus and were syringed into quartz capillary sample tubes fitted with Teflon high vacuum stopcocks. Spectra were recorded on a Varian E-4 X-band electron paramagnetic resonance spectrometer operating at a frequency of 9 GHz and were calibrated with DPPH. The temperature was varied through the use of a Bruker B-ST 100/700 temperature control unit.

Results

Structure and Synthesis. All of the cyclopentadienyl compounds involved in this investigation, $(\eta^5\text{-}C_5H_5)_2Zr(BH_4)_2$, $(\eta^5\text{-}C_5H_5)_2Hf(BH_4)_2$, $(\eta^5\text{-}C_5H_5)_2Zr(BD_4)_2$, and $(\eta^5\text{-}C_5H_5)Zr(H)(BH_4)$ possessed two π-bonded cyclopentadienyl rings, as verified by vibrational (infrared[14] and Raman[15]) spectroscopy. In addition, the tetrahydroborate ligation has been assigned[9a] a bidentate (A) geometry in all cases. These compounds were synthesized by the literature procedures.[10-12]



A

(C$_5$H$_5$)$_2$Zr(BH$_4$)$_2$ and (C$_5$H$_5$)$_2$Hf(BH$_4$)$_2$. Interligand Proton Exchange. Figure 1 presents high temperature ^{1}H NMR spectra of $(C_5H_5)_2Hf(BH_4)_2$ as a solution in toluene-d_8. The low field singlet resonance is ascribed to the C_5H_5 protons, while the broad high field multiplet is due to the BH_4 protons, coupled to ^{11}B ($I = \frac{3}{2}$, 81.2% abundant) and ^{10}B ($I = 3$, 18.8% abundant). As the temperature is raised, the C_5H_5 singlet begins to broaden. With the aid of ^{11}B decoupling, it is also evident that the BH_4 singlet is broadening. Without ^{11}B irradiation, the BH_4 multiplet sharpens slightly (a boron quadrupolar relaxation effect due to decreasing molecular rotational correlation time)[16] and then, at highest temperatures, also begins to collapse. $(C_5H_5)_2Zr(BH_4)_2$ exhibits analogous dynamic behavior, though the onset is 20-30° higher in temperature. Reference to internal benzene or to the solvent $-CH_2H$ multiplet indicates the broadening does not arise from deterioration of resolution. Rather, it arises from a heretofore unobserved interligand hydrogen transfer—*dynamic interchange of C_5H_5 and BH_4 protons.* We offer the following additional support for this process. The C_5H_5 line shape is invariant to ^{11}B irradiation, eliminating boron quadrupolar effects[16] as causes of the spectral collapse.[17] Also, it seems unlikely that $J_{B-H(C_5H_5)}$ is of sufficient magnitude to cause a quadrupole-induced broadening in the C_5H_5 resonance which is comparable to that observed for the BH_4 protons.[16] That the broadening of the C_5H_5 and ^{11}B decoupled BH_4 resonances is nearly the same is consistent with an exchange process between two nearly equally populated (10/8) sites.[22] The broadening is reversible on lowering the temperature. Thermal decomposition, which is evidenced by discoloration and the appearance of new resonances in the η^5-C_5H_5 region, has thwarted observation of the spectral coalescence point at higher temperature.

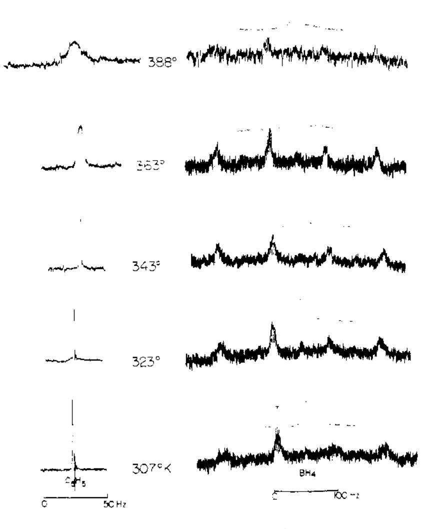


Figure 1. Variable temperature 60-MHz ^{1}H NMR spectra of $(\eta^5$-$C_5H_5)_2Hf(BH_4)_2$ as a solution in toluene-d_8. The inset resonances are with decoupling of ^{11}B. The peak marked T is due to traces of $C_6D_5CD_2H$. For numerical data, see Table I.

Table I. Nuclear Magnetic Resonance Data for Zirconium and Hafnium Tetrahydroborates[a]

Compound	
$(\eta^5$-$C_5H_5)_2Zr(BH_4)_2$	4.29 (10 H, s), 9.22 (8 H, br, quar, J = 85 Hz)
$(\eta^5$-$C_5H_5)_2Zr(BD_4)_2$	4.43 (10 H, s)
$(\eta^5$-$C_5H_5)_2Zr(H)BH_4$	4.30 (10 H, s), 5.47 (1 H, s), 10.2 (4 H, br, quar, J = 91 Hz)
$(\eta^5$-$C_5H_5)_2Hf(BH_4)_2$	4.36 (10 H, s), 8.44 (8 H, br, quar, J = 86 Hz)

[a] Shifts expressed in τ values, TMS = 10: s = singlet, quar = quartet, br = broad. Spectra recorded in benzene-d_6 or toluene-d_8.

The intramolecularity of the exchange process (or at least of the rate-determining step) is supported by the fact that line shapes are essentially invariant to a threefold dilution of the sample. Further support for the proposition of intramolecular, interligand prototropism is provided by the observation that the process even occurs in the solid state. The infrared spectrum of solid $(C_5H_5)_2Zr(BD_4)_2$, prepared in the normal manner[9a,10] but not sublimed, is shown in Figure 2A. The bands at 1842 and 1770 cm^{-1} are assigned to the symmetrically and antisymmetrically coupled B-D$_t$ stretching vibrations.[9a,23] On heating the solid under nitrogen for several hours at 120° (Figure 2B) new bands appear. The singlet band at 2427 cm^{-1} is logically assigned[9a] to a B-H$_t$ stretch of a BD$_t$H$_t$ group. In comparison, $(C_5H_5)_2Zr(BH_4)_2$ exhibits bands at 2430 and 2380 cm^{-1} (in solution),[9a] the presence of a BH_2 group and attendant kinematic coupling producing a doublet. By the same reasoning, the band at 2020 cm^{-1} is assigned to a B-H$_b$ stretch of a BD$_b$H$_b$ moiety; the corresponding band in $(C_5H_5)_2Zr(BH_4)_2$ occurs at 2140 cm^{-1}. The new band at 1800 cm^{-1} is assigned to ν_{B-D_t} of a BD$_t$H$_t$ group, while the new band at 1850 cm^{-1} may be a ν_{B-D_t} of a D$_b$H$_b$BD$_t$H$_b$ functionality. Deuterium substitution in the cyclopentadienyl ring will foster a C-D stretching vibration; this is assigned on the basis of intensity (ν_{C-H} is relatively weak)[14] and position, to the band at 2291 cm^{-1}. This assignment yields a ν_{C-H}/ν_{C-D} of 1.36, which can be compared to a value of ca. 1.33 for perdeuterioferrocene,[24] 1.35 for a similar exchange product of $(\eta^5$-$C_5H_5)_2VBD_4$,[9b] and 1.30-1.35 for perdeuteriobenzene.[23a] The ^{1}H NMR spectrum of this product reveals diminution of the C_5H_5 resonance and appearance of a BH resonance. Thus, the hydrogen interchange process also occurs in the solid state. Though, a priori, this observation does not exclude intermolecular processes, they seem less likely considering the size and mobility of the reacting species. Intramolecular bond-breaking tautomeric rearrangements of organometallics in the solid state are sometimes quite rapid.[25]

(C$_5$H$_5$)$_2$Zr(H)BH$_4$. Molecular Dynamics. High temperature ^{11}B-decoupled ^{1}H NMR spectra of $(\eta^5$-$C_5H_5)_2Zr(H)BH_4$ are presented in Figure 3. Assignments are the same as in the bis(tetrahydroborates), except that the resonance at τ 5.47 is due to the single metal hydride proton.[9a,11] On cessation of ^{11}B irradiation, the BH_4 resonance reverts to the usual broad quartet, the hydride resonance broadens by ca. 1 Hz, and the C_5H_5 resonance is unchanged. On raising the temperature, the cyclopentadienyl and borohydride resonances begin to broaden. For initial line broadening accompanying chemical exchange between unequally populated sites, theory[22] predicts that the BH_4 resonance should broaden by a factor of 2.5 ($^{10}/_4$) more than the C_5H_5 resonance. We find this to be approximately the case.[26] Though the metal hydride resonance remains sharp during the onset of rapid C_5H_5-BH_4 proton exchange (Figure 3), at the highest temperatures achieved, it also begins to broaden, indicating a second proton permutation pro-

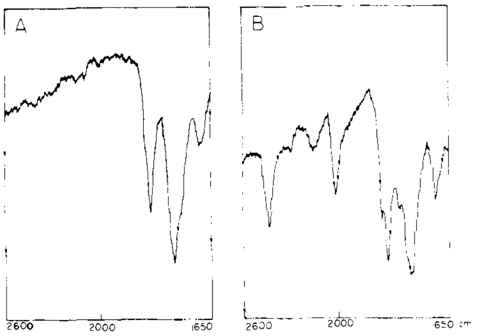


Figure 2. Solid state (Nujol mull) infrared spectra of (η^5-$C_5H_5)_2Zr(BD_4)_2$ immediately after isolation (A) and after heating for 12 hr at 120° in the solid state (B).

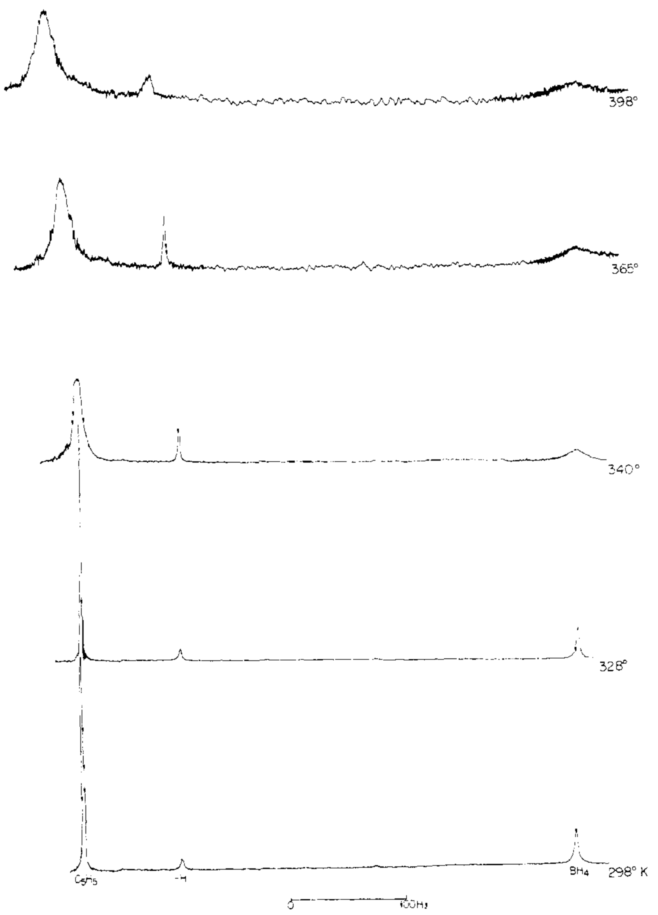


Figure 3. Variable temperature 90-MHz ^1H NMR spectra of (η^5-$C_5H_5)_2Zr(H)BH_4$ in toluene-d_8 with broad-band decoupling of ^{11}B. For numerical data, see Table I.

cess.[27] All of the line shapes at high temperatures are within experimental error, independent of concentration over a fourfold range, supporting the unimolecularity of the process. No exchange of protons with added ferrocene or $(C_5H_5)_2Zr(BH_4)_2$ was observed. Efforts to reach higher temperatures with $(C_5H_5)_2Zr(H)BH_4$ solutions resulted in extensive and rapid sample decomposition, evidenced by a red-violet coloration and the appearance of a new C_5H_5 resonance (vide infra). Attempts to unambiguously confirm the exchange process involving the metal hydride by spin saturation transfer experiments[28,29] were unsuccessful. It is unlikely that the BH_4 proton T_1 would be inordinately short as a consequence of either dipolar or scalar interactions,[16] but the presence of traces of paramagnetic decomposition products (vide infra) might reduce all T_1's to the point that saturation was competitively quenched.

The spectral behavior described above is largely, but not totally, reversed on lowering the temperature. A small residual line broadening (1-4 Hz) of the C_5H_5 and BH_4 resonances remains on returning the sample to ambient temperature. A similar effect is observed in samples heated in an oil bath until a pink coloration is observed. This slight residual peak broadening is eliminated by lowering the temperature 5-10° or by dilution. Thus, though the hydrogen exchange process observed is predominantly unimolecular, as deduced from the experiments described in the preceding paragraph, it appears that heating does generate a new complex which induces a small intermolecular component to the broadening process.

Though the exact nature of the $(C_5H_5)_2Zr(H)BH_4$ thermolysis product(s) was not explored in great detail, several additional experiments were conducted. Initial heating (e.g., 15 min at 110°) of $(C_5H_5)_2Zr(H)BH_4$ toluene-d_8 solutions in an NMR tube produced the above-mentioned pink coloration and slight broadening of the η^5-C_5H_5 resonance at room temperature. Bubbling small amounts of hydrogen gas through the solution discharged both of these effects. Prolonged heating (24 hr at 110°) produced a dark red solution and dark violet precipitate. The ^1H NMR spectrum exhibited a new η^5-C_5H_5 resonance at τ 4.08; the $(C_5H_5)_2Zr(H)BH_4$ cyclopentadienyl resonance was not significantly broader than after the initial heating. Upon raising the temperature, the C_5H_5 protons of the diamagnetic thermolysis product do not become involved in the exchange process. Heating a toluene solution of $(C_5H_5)_2Zr(H)BH_4$ in an EPR spectrometer revealed only traces of EPR-active species. A weak, broadened (line width ≈ 40 G) signal is observed at $g = 1.967$. Only scant EPR data are available for $(C_5H_5)_2Zr^{III}$ complexes;[30] the compound believed to be $(C_5H_5)_2Zr[P(CH_3)_2]_2^-$ has $g = 1.989$.[30] When a larger sample of $(C_5H_5)_2Zr(H)BH_4$ is thermolyzed in toluene, a dark blue-violet solid can be isolated by evaporation of the solvent. After washing with pentane and vacuum drying, it exhibits bands in the infrared (Nujol mull, cm^{-1}) at: 2395 (m, br), 2290 (w, br), 2100 (w, br), 2040 (vw), 1900 (w, br), 1301 (w), 1259 (s), 1090 (m, br), 1010 (s), 799 (s), 720 (m). It is clear that this compound is an η^5-C_5H_5 complex with bridge and terminal B-H bonds. Notably absent is a terminal Zr-H stretch, found in the starting material at 1620 cm^{-1}. The band at 1259 cm^{-1} may be a Zr-H-Zr bridge stretch.[31]

Though full characterization of the $(C_5H_5)_2Zr(H)BH_4$ thermolysis product(s) will be deferred to a later contribution, it is evident that hydrogen is lost on thermolysis and that the resulting species are cyclopentadienyl zirconium hydroborates, possibly in the formal $+3$[30,32] or $+2$[33] oxidation states. Though paramagnetic entities were detected by EPR, the NMR shows the major product to be diamagnetic. A plausible explanation for the spectral line broadening is that the thermolysis product is hydrogen deficient (H or H_2) and rapidly interconverts with $(C_5H_5)_2Zr(H)BH_4$ by H or H_2 transfer. In the former case, traces of a catalyst such as $(C_5H_5)_2ZrBH_4$[34] would induce, by virtue of the paramagnetism, measurable broadening in the exchange-perturbed ^1H NMR spectrum, even though actual ring-ligand hydrogen exchange was not occurring. The contribution of this concentration-dependent effect to line widths is minor at temperatures where intramolecular exchange is rapid.

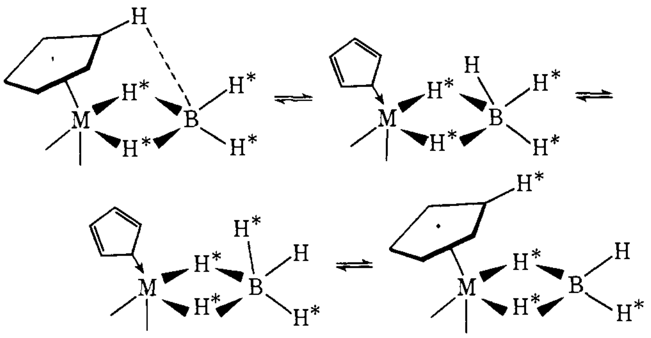
Energetic Considerations. It is possible to derive free energies of activation for ring-BH_4 hydrogen interchange from the solutions to the modified Bloch equations for initial line broadening.[22,35] At 395°K, $\Delta G^\ddagger = 21.3 \pm 0.4$ kcal/

mol ($(C_5H_5)_2Zr(BH_4)_2$) 19.4 ± 0.4 kcal/mol ($(C_5H_5)_2Hf(BH_4)_2$), and 19.6 ± 0.4 kcal/mol ($(C_5H_5)_2Zr(H)BH_4$). For exchange involving the metal hydride of the latter compound, $\Delta G^{\ddagger} = 20.9 \pm 0.5$ kcal/mol at 395°K.

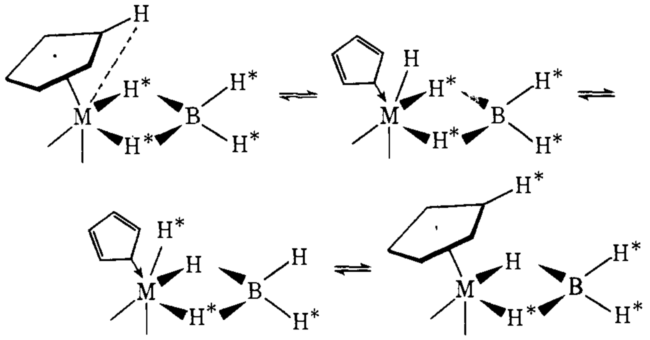
Discussion

Although a number of examples now exist where hydrogen atoms are transferred from a cyclopentadienyl ring to another ligand in a metal complex (e.g., $(C_5H_5)_3UR$ and $(C_5H_5)_3ThR$ compounds thermolyze by intramolecular, stereospecific elimination of RH where the H is derived from a cyclopentadienyl ring[3a-c]) this work represents the first case reported where such a process is so facile as to be rapid on the NMR time scale. The present results demonstrate that rapid, predominantly intramolecular exchange of hydrogen atoms between η^5-C_5H_5 and BH_4 ligands takes place in $(C_5H_5)_2Zr(BH_4)_2$, $(C_5H_5)_2Hf(BH_4)_2$, and $(C_5H_5)_2Zr(H)BH_4$ at elevated temperatures. This not only occurs in solution but also in the solid state.

Scheme I



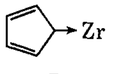
Scheme II



The actual permutation of sites which occurs can be discussed in terms of two mechanistic extremes (Schemes I and II).[36] The transfer process depicted in Scheme I is best interpreted as a protonation reaction of coordinated BH_4^-. This is analogous to the protonation reaction of the uncoordinated BH_4^- anion, which most likely occurs via a five-coordinate BH_5 intermediate.[37,38] The transfer process presented in Scheme II is a variant of an oxidative addition of a ligand C–H bond to a metal center, a reaction for which there is ample precedent,[39] including both cases where the hydrogen is subsequently transferred to another ligand (e.g., an alkyl group)[40] and cases where a cyclopentadienyl ring is the hydrogen donor.[3,41] Scheme II opens the possibility that dynamic interchange of ring or BH_4 hydrogens with the single metal-bound hydrogen would also be expected to occur in $(C_5H_5)_2Zr(H)BH_4$. This is observed to take place, but with a somewhat higher barrier than ring-BH_4 exchange. This could support Scheme I (Scheme II then being a less facile competing process) but it is also possible that the transferred hydrogen and the metal-bound hydrogen occupy unique coordination sites which interconvert only with difficulty. Structurally, either Scheme I or Scheme II is plausible based on the molecular geometry of the closely related compound, $(C_5H_5)_2TiBH_4$.[42] In both cases, tipping of the ring or conversion to a monohapto[43] or trihapto configuration is a reasonable prelude or accompaniment to C–H bond breaking.

Once the C–H bond is ruptured, scrambling of the ring hydrogen with tetrahydroborate hydrogens should be facile. For Scheme I, polytopal pseudorotation processes of the BH_5 ligand would permute terminal hydrogens;[44] at this temperature, rapid bridge-terminal hydrogen interchange is known to be occurring in the ground state structure,[16] so scrambling is complete. For Scheme II, interchange presumably would occur via M–H and M–H–B hydrogen permutation. Analogous bridge-terminal interchange processes are well documented for boron hydrides and metalloboranes,[45] as well as for organozirconium hydrides.[31] Again, the metal-bound hydrogen in $(C_5H_5)_2Zr(H)BH_4$ is required to occupy a relatively inert coordination site, so that interchange with it is more slow.

Regardless of whether the hydrogen is transferred initially to the boron, to the metal, or to a position in between, it is difficult to avoid a resulting complex, which was written in both schemes as B. This is a carbene complex,[46] of which diaryl[47] and dialkyl[48] examples are now known. However, no transition metal cyclopentadienylidene complexes have yet been reported.[49] In view of the highly electrophilic character of this carbene,[50] this is not surprising, and only very electron-rich metals (e.g., thorium(II))[3b,c,4] are expected to stabilize such complexes. This is because resonance hybrid C possesses an antiaromatic four-electron π system, and the aromatic ylid hybrid (E) in which the metal has formally undergone a two-electron oxidation, is expected to be most stable. Indeed, cyclopentadienylidene forms an extremely stable complex of this type with triphenylphosphine.[51] Thus, either Scheme I or II is appropriate in valence bond terms, so long as the hydrogen is transferred formally as H^+ and the cyclopentadienylidene ligand is represented principally as hybrid E;[52] here the metal remains in the +4 oxidation state.



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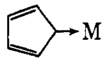

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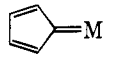

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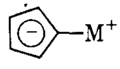

E

A more complete mechanistic description of the hydrogen transfer process related herein awaits additional experimentation. In particular, the kinetic consequences of ligand constraint and isotopic substitution are under investigation. The degree to which such interligand prototropism and carbene-ylid η^1-C_5H_4 intermediates are important in metal η^5-C_5H_5 chemistry will be the subject of further investigations.

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