

The Anionic Zirconocene Trihydride: $[\text{Cp}^*_2\text{ZrH}_3]^-$

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Abstract: Synthetic pathways to several salts of the anion $[\text{Cp}^*_2\text{ZrH}_3]^-$ have been developed. Reaction of $\text{Cp}^*_2\text{ZrH}_2$ (**3**) prepared from $[\text{Cp}^*_2\text{Zr}(\text{N}_2)]_2(\mu\text{-N}_2)$ (**2**), with KH in THF, afforded $[\text{Cp}^*_2\text{ZrH}_3]\text{K}$ (**1**) in a 74% yield. In a similar manner, addition of LiH gave $[\text{Cp}^*_2\text{ZrH}_3]\text{Li}$ (**4**). While this synthetic pathway provides reproducible routes to **1** and **4**, purification of **2** is problematic. Another preparation involving the reaction of $\text{Cp}^*_2\text{ZrCl}_2$ with 3 equiv of *n*-BuLi under H_2 affords **4**·**0.5**(LiCl·THF). Alternatively, reaction of $\text{Cp}^*_2\text{ZrCl}_2$ with LiAlH_4 afforded the species $\text{Cp}^*_2\text{ZrH}(\mu^2\text{-H}_2\text{AlH}_2)$ (**5**) in virtually quantitative yield. Subsequent reaction of **5** with *n*-BuLi afforded the direct and high-yield conversion to **4**. Deuteration and NMR studies infer attack of BuLi occurs at the Al center exclusively prompting transfer of a hydride to Zr and liberation of the Zr trihydride anion. Variable-temperature ^1H NMR spectra and H/D scrambling experiments for **4** and **4-d**₃ are consistent with the hydride exchange process mediated by ion pairing while T_1 studies infer a classical trihydride formulation is appropriate. Crystallographic studies of **4**·**0.5**(LiCl·THF), **5**, and **4** also affirm cation–anion pairing in **4** and **4**·**0.5**(LiCl·THF) and hydride bridging between Al and Zr in **5**.

Introduction

While the hydrogen atom is the simplest possible ligand available for a transition metal, it is the ever expanding vistas of transition metal hydride chemistry that prompts continuing interest.¹ In the realm of group IV metal hydride complexes, the chemistry of the oligomeric species $(\text{Cp}_2\text{ZrHCl})_n$ has been the subject of on-going study² since its discovery in 1970.³ Other Ti, Zr, and Hf metallocene hydride complexes have been prepared and characterized. While sterically less demanding ancillary ligands result in dimeric or polymeric complexes of the form $[\text{Cp}_2\text{MH}_2]_n$,^{4–7} species such as Cp^*_2MH_2 are monomeric.^{8–10} In a similar vein, monocyclopentadienyl complex hydrides such as $[\text{Cp}^*\text{ZrH}_2(\text{BH}_4)]_2$,¹¹ $\text{Cp}^*_2\text{Zr}_2\text{H}_3\text{Cl}_3(\text{PMe}_3)$,¹² and $[\text{Cp}^*\text{HfH}_2\text{Cl}]_4$ ¹³ form dimers and tetramers, respectively. Monomeric and dimeric Zr and Hf polyhydride species such as $\text{M}_2\text{H}_3(\text{BH}_4)_5(\text{PMe}_3)_2$, $\text{MH}(\text{BH}_4)_3(\text{dmpe})$, and $\text{MH}_2(\text{BH}_4)_2(\text{dmpe})_2$ have also been described¹⁴ as well as complexes of the form

$\text{Hf}_2\text{H}_3(\text{BH}_4)_3(\text{npp})_2$ and $\text{Hf}_2\text{H}_4(\text{BH}_4)_2(\text{npp})_2$.¹⁵ More recently, Choukroun et al. have described the electrochemical reduction of the dimeric species $[(\text{C}_5\text{H}_4\text{EMe}_3)_2\text{ZrH}_2]$ (E = C, Si) to generate monomeric Zr(III) hydride anions.⁵ The propensity of these early metal hydrides to dimerize or oligomerize results from the Lewis acidity of the electron deficient metal center. Although this can be superseded by steric demands, early metal based hydridic anions analogous to the main group hydrides are unknown. In this paper, we describe synthetic routes as well as the spectral and structural properties of salts of the first such early metal based hydride anion, $[\text{Cp}^*_2\text{ZrH}_3]^-$. This group IV, 18 electron species, although isoelectronic with the known group V compounds Cp_2MH_3 (M = Ta, Nb),¹⁶ exhibits strongly hydridic character in contrast to the acidic nature of the group V analogs. Preliminary reports of the reactivity have illustrated the utility of this anion in the catalytic oligomerization of phosphines.¹⁷

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2 -free N_2 employing either Schlenk line techniques or a Vacuum Atmospheres or Innovative Technologies inert atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N_2 and degassed by the freeze–thaw method at least three times prior to use. All organic reagents were purified by conventional methods. ^1H , ^2H , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on Bruker Avance 300- and 500-MHz spectrometers. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to SiMe_4 . Combustion analyses were performed by Galbraith Laboratories Inc. Knoxville, TN, or Schwarzkopf Laboratories, Woodside, NY. $[\text{Cp}^*_2\text{Zr}(\text{N}_2)]_2(\mu\text{-N}_2)$ (**2**)¹⁸ and $\text{Cp}^*_2\text{ZrH}_2$ (**3**)⁹ were prepared via literature methods. All other reagents were purchased from the Aldrich Chemical Co.

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Table 1. Crystallographic Parameters

formula	$\text{C}_{30}\text{H}_{35}\text{AlZr}$	$\text{C}_{44}\text{H}_{74}\text{Li}_3\text{OCIZr}_2$	$\text{C}_{60}\text{H}_{99}\text{Li}_3\text{Zr}_3$
formula weight	513.81	857.78	1114.93
cryst color	colorless	colorless	colorless
crystal size	$0.45 \times 0.14 \times 0.24$	$0.35 \times 0.16 \times 0.25$	$0.25 \times 0.15 \times 0.15$
<i>a</i> (Å)	8.726(2)	14.8745(2)	21.8731(3)
<i>b</i> (Å)	21.100(7)	14.8793(4)	14.4422(3)
<i>c</i> (Å)	11.748(4)	15.6523(4)	19.8738(3)
α (deg)		111.885(1)	
β (deg)	100.74(3)	112.346(1)	107.399(1)
γ (deg)		95.271(1)	
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$C2/c$
vol (Å ³)	2125(1)	2860.9(1)	5990.8(2)
D_{calcd} (g cm ⁻³)	1.61	1.00	1.24
<i>Z</i>	4	2	4
abs coeff, μ (cm ⁻¹)	5.77	4.34	5.50
scan speed (deg/min)	8.0 ($\theta/2\theta$), (1–3 scans)	na	na
scan range (deg)	$K\alpha_1 -1.0$, $K\alpha_2 +1.0$	na	na
bkgd/scan ratio	0.5	na	na
no. of data collected	3865	12286	13799
2θ range (deg)	4.5–50.0	4.5–50.0	4.5–56.4
data $F_o^2 > 3\sigma(F_o^2)$	2365	7296	5713
no. of variables	199	450	350
trans. factors	0.241–1.000	0.5488–0.6630	0.2830–0.3684
<i>R</i> (%) ^a	6.4	7.2	4.8
<i>R</i> _w (%) ^a	5.8	7.3	4.5
largest Δ/σ	0.02	0.02	0.01
goodness of fit	2.26	3.23	2.93

^a All data collected at 24 °C with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = \sum[|(F_o| - |F_c|)|^2/\sum|F_o|^2]^{0.5}$.

Synthesis of $[\text{Cp}^*_2\text{ZrH}_3]\text{K}$ (1). A solution of **3** (131 mg, 0.36 mmol) in THF (3 mL) was stirred at room temperature. KH (52 mg, 1.3 mmol) was added, and the mixture was stirred for 4 days, then filtered through Celite. The solvent was evaporated, and the residue was washed with benzene to give **1** as an off-white powder (108 mg, 74%). ¹H NMR (THF-*d*₈, 25 °C): 1.95 (s, 30H), 1.46 (t, 1H, $|J_{\text{H-H}}| = 18$ Hz), 1.11 (d, 2H, $|J_{\text{H-H}}| = 18$ Hz). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): 109.7, 13.1. Anal. Calcd for $\text{C}_{28}\text{H}_{49}\text{KO}_2\text{Zr}$ (1·2THF): C, 61.37; H, 9.01. Found: C, 61.18; H, 8.97.

Synthesis of $[\text{Cp}^*_2\text{ZrH}_3]\text{Li}$ (4). (i) A suspension of **3** (59 mg, 0.16 mmol) and LiH (13 mg, 1.6 mmol) in THF (5 mL) was stirred at room temperature for 5 days. The solution was filtered through Celite, and the solvent was evaporated. The residue was washed with hexanes and benzene to give **4** as an off-white powder (29 mg, 48%). (ii) A solution of $\text{Cp}^*_2\text{ZrH}_2\text{AlH}_3$ (**5**, 294 mg, 0.747 mmol) in ether (10 mL) was stirred at room temperature. *n*-BuLi (2.4 M in hexanes, 0.65 mL, 1.56 mmol) was added, and the solution was stirred overnight. The white precipitate was collected and washed with ether to yield **4** (194 mg, 70%). X-ray quality crystals were obtained from a THF solution on standing for several days. Data are given below.

Synthesis of $[\text{Cp}^*_2\text{ZrH}_3]\text{Li} \cdot 0.5(\text{LiCl} \cdot \text{THF})$ (4·0.5(LiCl·THF)**).** A solution of $\text{Cp}^*_2\text{ZrCl}_2$ (80 mg, 0.185 mmol) in toluene (10 mL) was stirred under H₂ at –78 °C. *n*-BuLi (2.4 M in hexane, 0.25 mL, 0.60 mmol) was added, and solution was stirred for 1 h, then allowed to warm to room temperature overnight. The solvent was evaporated, and the residue was extracted with THF and filtered through Celite. On standing for several days, large colorless crystals of **4·0.5(LiCl·THF)** deposited from the solution (42 mg, 65% yield). ¹H NMR (THF-*d*₈, 25 °C): 1.95 (s, 30H), 0.86 (d, 2H, $|J_{\text{H-H}}| = 17$ Hz), 0.39 (t, 1H, $|J_{\text{H-H}}| = 17$ Hz). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): 110.09, 12.82. Anal. Calcd for $\text{C}_{22}\text{H}_{37}\text{Li}_{1.5}\text{O}_{0.5}\text{Zr}$: C, 45.81; H, 6.47. Found: C, 45.75; H, 6.40.

Synthesis of $[\text{Cp}^*_2\text{ZrD}_3]\text{Li}$ (4-d**₃).** **4-d**₃ was prepared from **5-d**₃ by method (iii) as described above. ¹H NMR (THF-*d*₈, 25 °C): 1.95 (s, 30H). ²H NMR (THF, 25 °C): 1.97 (s, 3D). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): 111.19, 12.81.

Synthesis of $\text{Cp}^*_2\text{ZrH}(\mu^2\text{-H}_2\text{AlH}_2)$ (5**).** A solution of $\text{Cp}^*_2\text{ZrCl}_2$ (442, 1.02 mmol) in THF (6 mL) was stirred at room temperature. A suspension of LiAlH₄ (85 mg, 2.2 mmol) in THF (2 mL) was added,

and the mixture was stirred for 1.5 h, then filtered through Celite. The solvent was evaporated, and the residue was extracted with hexanes. Filtration and evaporation of the solvent gave **5** as a white powder (393 mg, 98%). Recrystallization from a saturated toluene solution gave colorless crystals suitable for crystallography. ¹H NMR (C₆D₆, 25 °C): 4.88 (br s, 2H), 4.25 (br s, 1H), 1.96 (s, 30H), –1.53 (br s, 1H), –2.14 (br s, 1H). ¹H NMR (C₇D₈, –23 °C): 4.79 (s, 2H), 3.88 (s, 1H), 2.01 (s, 30H), –1.44 (s, 1H), –1.93 (s, 1H). ¹³C{¹H} NMR (C₆D₆, 25 °C): 114.84, 12.38. Anal. Calcd for $\text{C}_{20}\text{H}_{35}\text{ZrAl}$: C, 61.02; H, 8.96. Found: C, 60.80; H, 8.85.

Synthesis of $\text{Cp}^*_2\text{ZrD}(\mu^2\text{-D}_2\text{AlD}_2)$ (5-d**₅).** (**5-d**₅) was prepared by the same method as above, using LiAlD₄ in the reduction. ¹H NMR (C₆D₆, 25 °C): 2.08 (s, 30H). ²H NMR (C₇H₈, 25 °C): 3.80 (br s, 3D), 0.26 (br s, 1D), –2.56 (br s, 1D).

X-ray Data Collection and Reduction X-ray Quality Crystals of **4·0.5(LiCl·THF), **4**, and **5**.** **4·0.5(LiCl·THF)**, **4**, and **5** were obtained directly from the preparation as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O₂-free environment for each crystal. Diffraction experiments were performed either on a Rigaku AFC5S four-circle diffractometer or a Siemens SMART System CCD diffractometer collecting a hemisphere of data in 1329 frames with 10 s exposure times. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5^\circ < 2\theta < 45\text{--}50.0^\circ$). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed with the SAINT and XPREP processing package. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed by using the TEXSAN solution package operating on a SGI Challenge mainframe computer with remote X-terminals or PC employing X-emulation. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinements.

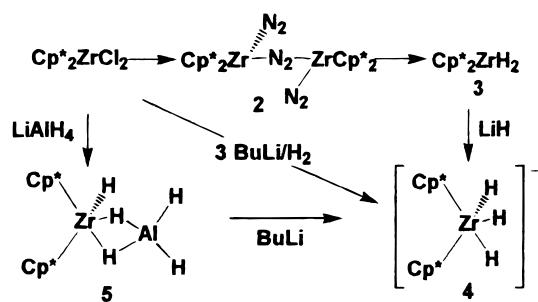
Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.^{19,20} The heavy

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Scheme 1



atom positions were determined by using direct methods employing either the SHELX-86 or Mithril direct methods routines. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F , minimizing the function $\omega(|F_o| - |F_c|)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. In the case of the metal-bound hydrides, the positions of these atoms were determined via a difference Fourier calculation. The positions of these hydrides were refined in the final cycles of refinement although the thermal parameters remained fixed. The final values of R , R_w , and the goodness of fit in the final cycles of the refinements are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

Results and Discussion

Synthesis. We have previously reported that the reaction of Cp*₂ZrCl₂ with excess KH in THF proceeds at room temperature over the course of several hours to give upon filtration addition of hexane and on standing at –30 °C pale yellow crystals of **1**.^{17a} This compound was subsequently formulated as the salt [Cp*₂ZrH₃][K(THF)₂] on the basis of NMR and X-ray crystallographic data. The reactivity of **1** and the ability of **1** to catalyze the P–H bond activation yielding phosphine oligomerization has been communicated.¹⁷ This unprecedented catalytic behavior prompted the present attention to synthetic routes to this unique anion.

Repeated attempts to prepare **1** via the above route were frustrated by capricious yields. The source of the synthetic problems appears to be associated with the purity of commercial KH. In fact, newer samples of KH or KD, which appeared to be cleaner than the original, gave no reaction with Cp*₂ZrCl₂. It was recognized that K metal is frequently a significant impurity in commercial grade KH. Deliberate addition of K in efforts to effect an *in situ* synthetic route involving reduction lead to observation of only minor amounts of **1**. The origin of the fickle nature of this serendipitous synthesis of **1** remains a mystery.

A reliable synthetic pathway to **1** was nonetheless developed by employing a stepwise route involving reduction. The Zr(II) compound [Cp*₂Zr(N₂)₂](μ-N₂) (**2**) was prepared, isolated, and converted to Cp*₂ZrH₂ (**3**) according to the methods of Bercaw et al.¹⁸ Reaction of **3** with KH in THF afforded **1** in a 74% yield. In a similar manner, addition of LiH gave [Cp*₂ZrH₃]⁻ Li (**4**) (Scheme 1). While this synthetic pathway provides

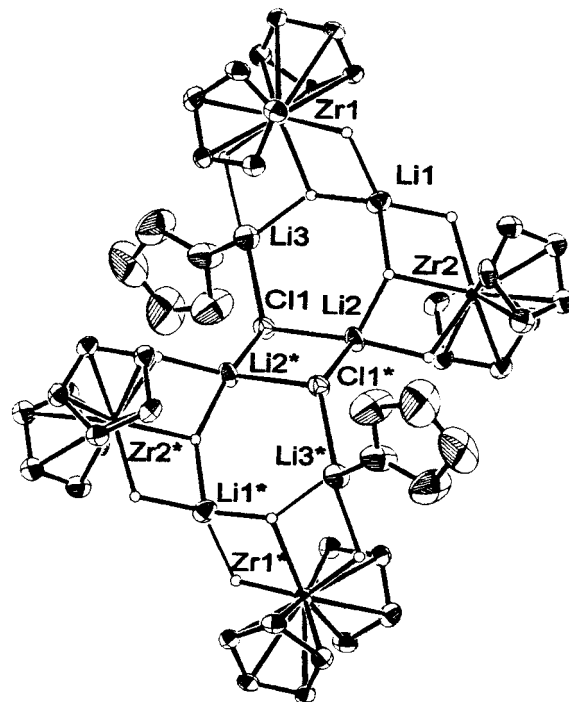


Figure 1. ORTEP drawing of **4**·THF·0.5LiCl; 30% thermal ellipsoids are shown. Hydrogen atoms are shown as open spheres, methyl carbons on the Cp* rings have been omitted for clarity. Zr(1)–Li(1) 3.10(9) Å, Zr(1)–Li(3) 3.20(9) Å, Zr(2)–Li(1) 3.10(9) Å, Zr(2)–Li(2) 3.10(8) Å, Zr–H (av) 2.0(1) Å, Li–Cl 2.4(1) Å, Li–O 1.9(1) Å.

reproducible routes to **1** and **4**, purification of **2** by crystallization is required and this results in low overall yields. Attempts to improve the yield of **3** via addition of H₂ to solutions in which **2** was generated gave product mixtures from which **3** could not be isolated cleanly.

An alternative approach was based on the method of Negishi *et al.*²¹ for the *in situ* generation of Zr(II) species, employing the reaction of Cp*₂ZrCl₂ with *n*-BuLi. Treatment of Cp*₂ZrCl₂ with 2 equiv of *n*-BuLi in THF under an atmosphere of H₂ failed to give **3** cleanly. This is in contrast to the analogous Hf chemistry where Cp*₂HfH₂ is prepared in this manner.²² However, addition of 3 equiv of *n*-BuLi to Cp*₂ZrCl₂ under H₂ afforded insoluble material. ¹H NMR data revealed the presence of the anion [Cp*₂ZrH₃]⁻. Crystallographic data obtained on crystals of this material confirmed the formulation as **4**·0.5(LiCl·THF) (Figure 1, *vide infra*).

Attempts to uncover alternative synthetic routes to **3** prompted the reaction of Cp*₂ZrCl₂ with a variety of hydride reagents. Reactions with LiBHEt₃ or Red-Al gave uncharacterized products, while the reaction with LiAlH(O-*t*-Bu)₃ afforded only Cp*₂ZrHCl,²³ regardless of the stoichiometry. Precedent for this latter reaction is the analogous reaction involving Cp₂ZrCl₂.³ In contrast, reaction of Cp*₂ZrCl₂ with LiAlH₄ afforded the species Cp*₂ZrH(μ²-H₂AlH₂) (**5**) in virtually quantitative yield. At room temperature, resonances at 4.88 and 4.25 ppm are attributable to the terminal hydrides on Al and Zr, respectively. Resonances at –1.53 and –2.14 ppm are assigned to the two inequivalent hydrides that bridge Zr and Al. The breadth of the signals at room temperature suggests a slow exchange process is operative. However, while these resonances sharpen

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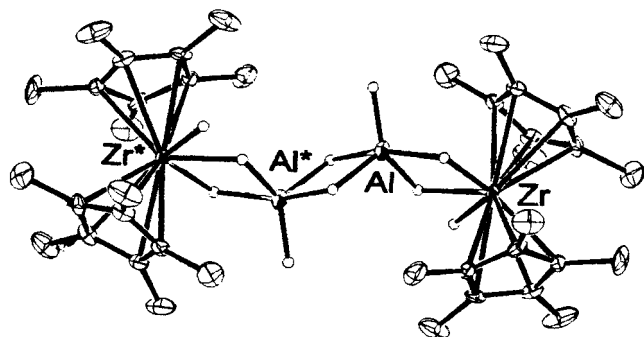


Figure 2. ORTEP drawing of **5**; 30% thermal ellipsoids are shown. Hydrogen atoms are shown as open spheres. Zr–Al 2.938(3) Å, Zr–H_{Al(av)} 1.91(7) Å, Zr–H_{term} 1.82(7) Å, Al–Al* 2.750(6) Å, Al–H_{Zr-(av)} 1.65(7) Å, Al–H_{term} 1.52(6), Al–H_{Al(av)} 1.75(6).

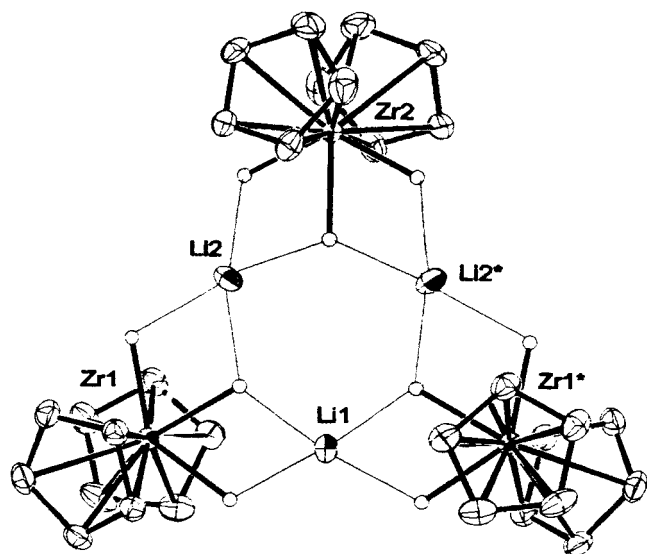


Figure 3. ORTEP drawing of **4**; 30% thermal ellipsoids are shown. Hydrogen atoms are shown as open spheres, methyl carbons on the Cp* rings have been omitted for clarity. Zr(1)–Li(1) 3.212(9) Å, Zr(1)–Li(2) 3.21(1) Å, Zr(2)–Li(2) 3.20(1) Å, Zr–H (av) 1.9(1) Å.

and shift slightly on cooling, warming the sample did not lead to the observation of peak coalescence, rather compound decomposition was evident. The formulation of **5** was confirmed crystallographically. The facile and high-yield synthesis of **5** prompted attempts to remove AlH_3 to obtain **3** knowing that conversion to **4** could subsequently be achieved. Treatment of **5** with a variety of bases including PMe_3 , imidazole, *N*-methylimidazole, and alkoxide failed to achieve the conversion of **5** to **3**. However, reaction of **5** with *n*-BuLi afforded the direct and high-yield conversion to **4** (Scheme 1). This strategy for the production of **4** not only offers a high yield methodology but also precludes the incorporation of LiCl and solvent in the lattice. This latter point was confirmed by crystallographic study of **4** obtained from such a preparation. The solid state structure of **4** (Figure 3) was confirmed as a trimeric aggregate via crystallographic methods.

NMR Studies. Some insight into the mechanism of formation of **4** from **5** was derived from the treatment of **5-d₃** with *n*-BuLi in diethyl ether. This reaction results in the exclusive formation of **4-d₃** as both ^1H and ^2D NMR data showed no evidence of **4** or any mixed hydride–deuteride species. This infers attack of BuLi occurs at the Al center exclusively prompting transfer of a hydride to Zr and liberation of the Zr trihydride anion (Scheme 2). It is the insolubility of **4-d₃** in diethyl ether that effects separation from the Al byproduct.

Scheme 2

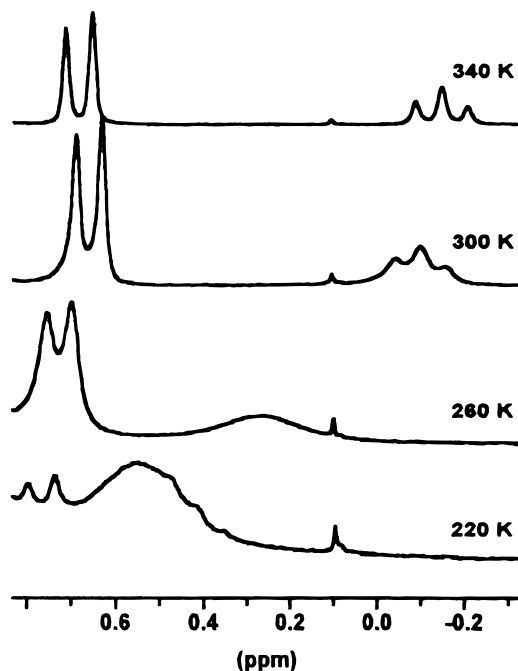
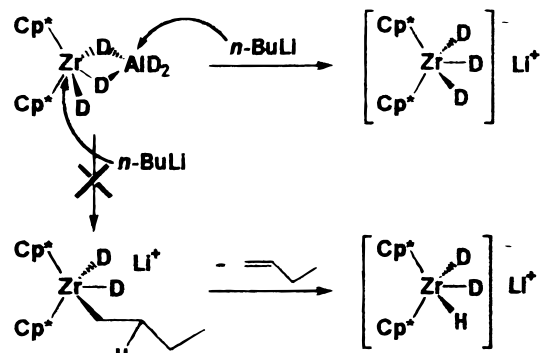


Figure 4. Variable-temperature ^1H NMR spectra of **4**.

Table 2. Chemical Shift and Proton Relaxation Times for Hydrides in **4**^a

temp, °C	$\delta(\text{a})$	$\delta(\text{b})$	$J(\text{a}-\text{b}), \text{Hz}$	$T_1(\text{a}), \text{s}$	$T_1(\text{b}), \text{s}$
333	0.88 (d)	0.34 (t)	17.0	0.94	0.51
313	0.86 (d)	0.36 (t)	17.0	0.65	0.36
277	0.84 (d)	0.44 (t)	17.0	0.43	0.22
253	0.83 (d)	0.49 (br, t)	16.5	0.29	0.14
233	0.82 (d)	0.54 (br, s)	17.5	0.14	0.072

^a (a) denotes the two exo hydrides, (b) the endo hydride.

The ^1H NMR spectra of **1** and **4** include doublet and triplet resonances attributable to the inequivalent hydrides. Differences in the chemical shifts of the hydride resonances for **1** and **4** were attributed to varying degrees of ion pairing in solution. Variable-temperature ^1H NMR spectra for **4** (Figure 4) reveal that upon cooling the hydride resonances broaden and coalesce to a broad resonance at 0.5 ppm. This is attributed to a hydride exchange process that is mediated by ion pairing. This view is supported by the observation of H/D scrambling upon mixing of **4** and **4-d₃**.

The nature of the anion was further probed by T_1 studies. T_1 measurements were performed as a function of temperature (Table 2). At 333 K, the doublet and triplet resonances arising from the hydrides gave T_1 relaxation times of 0.94 and 0.51 s, respectively. These values decreased with temperature to values of 0.14 and 0.072 s at 233 K. While these resonances broadened

and shifted toward each other over this temperature range, the observed coupling constant remained unchanged. These data infer a classical trihydride formulation is appropriate. This is in contrast to the isoelectronic species $(\text{CpSiMe}_3)_2\text{NbH}_3$ for which a dihydrogen–hydride formulation has been implicated by the analogous NMR studies.²³ The inaccessibility of the T_1 (minimum) precluded the computation of the H–H distance²⁴ in solution. However, in the solid state the H–H distance was found to be 2.0(1) Å. This too is consistent with a conventional trihydride formulation.

Structural Studies. Crystallographic study of **4**·0.5(LiCl·THF) (Figure 1) reveals two anionic $[\text{Cp}^*_2\text{ZrH}_3]^-$ units are bridged by one lithium while a second lithium is associated with one of the Zr hydrides and a molecule of THF. In addition, these cation–anion pairs are bridged through one of the hydrides on Zr and a Li atom to an equivalent of LiCl included in the unit cell. The geometry about Zr is as expected, in that the three hydride atoms are located in the plane which bisects the Cp^*_2Zr fragment. The $\text{H}_{\text{exo}}-\text{Zr}-\text{H}_{\text{endo}}$ angles were found to average $66(3)^\circ$ while the $\text{H}_{\text{exo}}-\text{Zr}-\text{H}_{\text{exo}}$ angle is $132(3)^\circ$. The bridging Li–H distances average 1.8(1) Å while the Li–Cl and Li–O distances are also typical at 2.4(1) and 1.9(1) Å, respectively. This geometry is consistent with hydride interaction with the LUMO of the neutral molecule Cp_2MH_2 giving the 18-electron anion, which is isoelectronic with the group V trihydrides Cp_2MH_3 (M = Nb, Ta).²⁵

Crystallographic data for **5** confirmed the AlH_4 fragment forms an approximately symmetric bridge to Zr through two hydrides (Figure 2). These bridging hydrides gave Zr–H distances of 1.89(6) and 1.93(6) Å and Al–H distances of 1.69(6) and 1.62(7) Å while the H–Zr–H and H–Al–H angles were $63(3)^\circ$ and $74(3)^\circ$, respectively. In addition, terminal Zr

and Al hydrides were found at distances of 1.82(7) and 1.52(6) Å, respectively. Finally, the remaining hydride on Al bridges to an adjacent Al atom, giving a pseudo-square-pyramidal geometry about the Al center and an Al–H distance of 1.74(6) Å. The three hydrides bound to Zr lay in the plane bisecting the Cp^*_2Zr fragment with an $\text{H}_{\text{term}}-\text{Zr}-\text{H}_{\text{exo}}$ angle of $108(3)^\circ$.

The crystallographic data for **4**, prepared via the halide free route (i.e. from **5**), reveal the formation of a 2-fold symmetric trimeric aggregate in which lithium atoms are associated with two hydrides from each of two Zr centers (Figure 3). One of the lithium atoms, as well as one Zr atom, sits directly on the crystallographic 2-fold axis. The Zr–H and Li–H distances in **4** average 1.9(1) and 2.0(1) Å.

Summary

Reliable and efficient syntheses of the lithium and potassium salts of the zirconocene based trihydride anion $[\text{Cp}^*_2\text{ZrH}_3]^-$ have been developed. Structural and NMR data for these compounds confirm ion pairing in the solid state and solution, an effect that mediates intermolecular hydride exchange reactions. Further NMR data affirm the formulation of the anion as a classical Zr(IV) trihydride formulation.

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Supporting Information Available: Tables of crystallographic parameters, hydrogen atom parameters and thermal parameters for **1** (45 pages). See any current masthead page for ordering and Internet access instructions.

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