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Notes

Reactivity of Decamethylzirconocene Trihydride Anion with Protic Reagents

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*Summary: The reactions of [(C$_5$Me$_5$)$_2$ZrH$_3$Li]$_3$ (**1**) with 2,6-diisopropylphenol, aniline, and o-methoxyaniline gave Cp*$_2$ZrH(OC$_6$H$_3$(2,6-i-Pr$_2$)) (**2**), Cp$_2$*Zr(NHPh)$_2$ (**3**), and Cp$_2$*Zr(NH(C$_6$H$_4$OMe))$_2$ (**4**), respectively. In contrast, reaction of **1** with thiophenol afforded [(Cp*$_2$ZrH$_3$)(LiTHF)]$_2$(LiSPh) (**5**). The implications of these results are considered. Crystallographic data for **3**−**5** are reported.*

Interest in early transition metal hydride chemistry has led to the characterization of a variety of monomeric and dimeric early metal polyhydrides.[1−8] Only two recent reports have described anionic early metal hydrides. While Andersen et al. have recently reported the synthesis and reactivity of the Ti(III) hydride Cp*$_2$Ti(μ-H)$_2$Li(tmed),[9] we have been investigating the chemistry of anionic Zr(IV) trihydride complex [(C$_5$Me$_5$)$_2$ZrH$_3$Li]$_3$, **1**.[10] The species **1**, which is trimeric in the solid state, has been shown to act as a catalyst precursor for the dehydro-coupling of primary phosphines to P$_5$R$_5$ and higher oligomers.[11,12] In addition, we have studied the stoichiometric activity of **1** with secondary phosphine chalcogenides.[13] These earlier studies confirm that **1** reacts with P−H bonds. It is noteworthy that both this catalytic and stoichiometric reactivity of **1** is in marked contrast to that of the neutral Zr(IV) hydride complexes. In this article, we probe the reactivity of **1** with other protic reagents. Thus reactions of **1** with aryl species of the form ArEH (E = O, NH, S) are investigated and the implications of this chemistry considered.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O$_2$-free N$_2$ employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified, employing a Grubb's type column systems manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Avance-300 and 500 operating at 300 and 500 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to SiMe$_4$. ^{31}P NMR spectra were recorded on a Bruker Avance-300 and are referenced to 85% H$_3$PO$_4$. Guelph Chemical Laboratories (Guelph, Ontario) performed combustion analyses. The compound [(C$_5$Me$_5$)$_2$ZrH$_3$Li]$_3$ (**1**) was prepared via literature methods.[10] All other reagents were purchased from the Aldrich Chemical Co.

Synthesis of Cp*$_2$ZrH(OC$_6$H$_3$(2,6-*i*-Pr$_2$)), 2. To a stirred solution of **1** (25 mg, 0.07 mmol) in THF (5 mL) was added 2,6-diisopropylphenol (0.07 mmol, 12.4 μL). Effervescence occurred immediately on addition of the phenol. The solution was stirred for 24 h, the solvent removed, and the residue recrystallized from benzene (3 mL), affording colorless crystals (0.055 mmol, yield 78%). ^{1}H NMR (C$_6$D$_6$) δ: 1.29 (d, 6H, $|J_{H-H}|$ = 6.6 Hz CH(C*H*$_3$)$_2$), 1.41 (d, 6H, $|J_{H-H}|$ = 6.6 Hz, CH(C*H*$_3$)$_2$) 1.82 (s, 30H, *Me*$_5$*Cp*), 3.27 (p, 1H, $|J_{H-H}|$ = 6.6 Hz, C*H*(CH$_3$)$_2$), 3.70 (p, 1H, $|J_{H-H}|$ = 6.6 Hz, C*H*(CH$_3$)$_2$), 4.39 (s, 1H, Zr*H*) 6.97 (t, 1H, $|J_{H-H}|$ = 7.5 Hz, *p*-Ph), 7.14 (d, 2H, $|J_{H-H}|$ = 7.5 Hz, *m*-Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ: 11.50, 24.65, 24.97, 25.31, 26.23, 119.26, 120.25, 123.87, 124.30. Anal. Calcd for C$_{32}$H$_{59}$OZr: C, 69.75; H, 10.79. Found: C, 69.54; H, 10.56.

Synthesis of Cp$_2$*Zr(NHPh)$_2$, 3, and Cp$_2$*Zr(NH(C$_6$H$_4$OMe))$_2$, 4. These compounds were prepared in a similar manner, and thus only one representative preparation is detailed. To a solution of **1** (150 mg, 0.40 mmol) in THF (5 mL) was added aniline (70μL, 80 mmol) with stirring. Gas evolution occurred with a simultaneous color change from colorless to bright yellow. After stirring for 24 h, the solvent was evaporated. The bright yellow residue was dissolved in benzene, filtered, and allowed to stand. Slow evaporation of the solvent afforded bright yellow blocks (207 mg, 94% yield). **3**: ^{1}H NMR (C$_6$D$_6$) δ: 1.79 (30H, s, *Me*$_5$*Cp*), 5.49 (2H, s, N*H*), 6.70 (2H, t, 7 Hz, *p*-Ph), 6.81 (4H, d, $|J_{H-H}|$ = 7 Hz, *o*-Ph), 7.05 (4H, t, $|J_{H-H}|$ = 7 Hz, *m*-Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ: 6.37, 112.13, 114.33, 114.83, 122.70, 123.65, 124.94, 149.07. Anal. Calcd for C$_{32}$H$_{42}$N$_2$Zr: C, 70.40; H, 7.75. Found: C, 70.19; H, 7.42. **4**: ^{1}H NMR (C$_6$D$_6$) δ 1.93 (30H, s, *Me*$_5$*Cp*), 3.02 (6H, s,

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Table 1. Crystallographic Parameters

	3	**4**	**5**
formula	$C_{32}H_{42}N_2Zr$	$C_{34}H_{46}N_2O_2Zr$	$C_{54}H_{87}Li_3O_2SZr_2$
MW	545.92	605.95	1003.56
a (Å)	10.6594(4)	22.31180(10)	10.52610(5)
b (Å)	12.1266(5)	24.07750(10)	13.44040(5)
c (Å)	22.6549(9)	16.0629(2)	19.7311(1)
α (deg)			89.5942(8)
β (deg)	93.432(1)	133.9880(10)	81.5529(4)
γ (deg)			84.0388(3)
cryst syst	momoclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$
vol (Å^3)	2923.2(2)	6208.57(9)	2746.134(12)
D_{calcd} (g cm^{-1})	1.24	1.30	1.21
Z	4	4	2
abs coeff, μ, cm^{-1}	3.97	3.86	4.53
no. of data collected	17 109	15 401	13 881
data $F_o^2 > 3\sigma(F_o^2)$	4649	4197	9147
no. of variables	316	353	580
R (%)	4.7	5.3	4.9
R_w (%)	6.0	14.7[b]	13.2[b]
goodness of fit	2.22	1.17	1.03

[a] All data collected at 24 °C with Mo Kα radiation ($\lambda = 0.71069$ Å), $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^2)^2]]^{0.5}$. [b] Weighted *R* based on all data.

CH$_3$), 3.32 (2H, s, *NH*), 6.59(2H, d, $|J_{H-H}| = 7$ Hz, Ph), 6.69 (2H, m, Ph), 6.83 (4H, m, Ph); $^{13}C\{^1H\}$ NMR (C6D6) δ 11.99, 55.71, 111.35, 120.10, 121.23, 122.01, 126.14, 136.47, 147.23.

Synthesis of [(Cp*$_2$ZrH$_3$)(LiTHF)]$_2$(LiSPh), 5. To a stirred solution of **1** (90 mg, 0.24 mmol) in THF (2 mL) was added thiophenol (0.05 mL, 0.5 mmol). The reaction mixture quickly turned an intense yellow, and gas evolution was evident. After 2 min, the reaction mixture became opaque white. The mixture was allowed to stand for 1 week and the solvent removed. The off-white solid was dissolved in THF (1 mL), and hexane (0.2 mL) was added gently on the surface. Upon standing for 1 week, colorless crystals of **5** were deposited from solution. Yield: 67%. ^1H NMR (THF-d_8) δ: −0.32 (t, 1H, $|J_{H-H}| = 17$ Hz), 0.55 (d, 2H, $|J_{H-H}| = 17$ Hz), 1.88 (s, 15H, *Me*$_5$*Cp*), 1.95 (s, 15H, *Me*$_5$*Cp*), 6.50 (t, 1H, $|J_{H-H}| = 7.2$ Hz, *p*-Ph), 6.69 (t, 2H, $|J_{H-H}| = 7.2$ Hz, *m*-Ph), 7.24 (d, 2H, $|J_{H-H}| = 7.2$ Hz, *o*-Ph). $^{13}C\{^1H\}$ NMR (THF-d_8) δ: 12.50, 12.93, 111.08, 119.24, 127.24, 129.18, 134.63, 136.32. Anal. Calcd for $C_{54}H_{87}O_2Li_3SZr_2$: C, 64.63; H, 8.74. Found: C, 64.39; H, 8.69.

X-ray Data Collection and Reduction. X-ray quality crystals of **3**−**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, O_2-free environment for each crystal. Diffraction experiments were performed on either a Rigaku AFC6 four-circle or a Siemens SMART System CCD diffractometer. In the later case, the data were collected in 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° $< 2\theta <$ 45−50.0°). 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. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using either the SHELXTL or TEXSAN solution packages.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[14] The heavy atom positions were determined using direct methods. 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 $w(|F_o| - |F_c|)^2$ where the weight w 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. The final values of refinement parameters are given in Table 1. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

Results and Discussion

The reactions of [(C$_5$Me$_5$)$_2$ZrH$_3$Li]$_3$ (**1**) with several protic reagents were investigated. Stoichiometric reaction of **1** with 1 equiv of 2,6-diisopropylphenol also proceeds with evolution of gas and affords, upon recrystallization, 78% yield of the product **2**. The ^1H NMR of **2** shows two resonances at 3.27 and 3.70 ppm attributable to the methine protons of inequivalent isopropyl groups. In addition, a resonance at 4.39 ppm is attributable to a Zr hydride. This infers a formulation of **2** as Cp*$_2$ZrH(OC$_6$H$_3$(2,6-*i*-Pr$_2$)). This formulation was confirmed by a preliminary X-ray crystallographic study.[15] The NMR data infer that rotation about the Zr−O bond is restricted. This is not unexpected, as restricted rotation about group IV M−E (E = O, S, N, P) arising from M−E multiple bond character has been described in a number of such systems including the Hf complex Cp*$_2$HfH(NHMe).[16]

A similar reaction of **1** with 2 equiv of aniline proceeds smoothly with the liberation of H_2 and the simultaneous color change from colorless to bright yellow. Recrystallization of the resulting product affords the species **3** in 94% isolated yield. The ^1H NMR data for **3** are consistent with the formulation of this product as Cp$_2$*Zr(NHPh)$_2$, **3**. In a similar manner, reaction of **1** with *o*-methoxyaniline affords Cp$_2$*Zr(NH(C$_6$H$_4$OMe))$_2$, **4**. The formulations of **3** and **4** were confirmed by X-ray crystallography (Figures 1, 2). The structures of these species are similar, with Zr−N distances averaging 2.120(3) and 2.122(3) Å in **3** and **4**, respectively. These bond lengths are typical of those seen for a variety of the Zr amide species.[17] The N−Zr−N angles in these complexes are in the range 98.4(1)−99.2(2)°. The aryl rings of the aniline fragments are oriented in a pseudo-*transoid* disposition with respect to the ZrN$_2$ plane. The planar nature of the N atoms was confirmed with the location and refinement of the nitrogen-bound hydrogen atoms. The observed orientation of the substituents permits some degree of π-bonding between the Zr and N atoms. Such π-donation in similar related metallocene derivatives has been previously described and discussed.

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[14] Cromer, D. T.; Mann, J. B. *Acta Crystallogr. Sect. A: Cryst. Phys., Theor. Gen. Crystallogr.* **1968**, *A24*, 390.

[15] Crystallographic data for **2**: $a = 10.278(9)$ Å, $b = 19.199(6)$ Å, $c = 15.927(5)$ Å, $\beta = 103.91(4)°$, $V = 3050(2)$ Å^3, space group: $P2_1/n$ (#14).

[16] Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309−1312.

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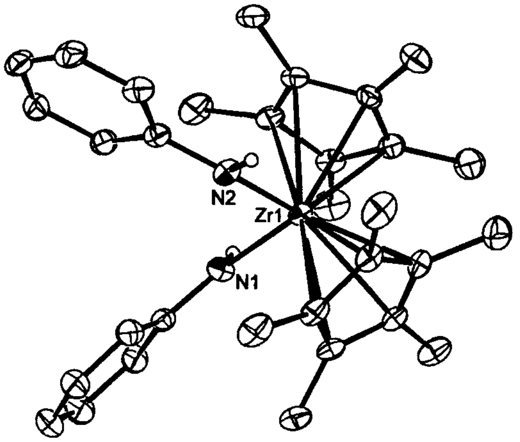


Figure 1. ORTEP drawing of **3**; 30% thermal ellipsoids are shown. Amide hydrogen atoms are shown as open spheres; hydrogen atoms are omitted for clarity. Zr(1)−N(1) 2.117(3) Å; Zr(1)−N(2) 2.124(3) Å; N(1)−Zr(1)−N(2) 98.4(1)°.

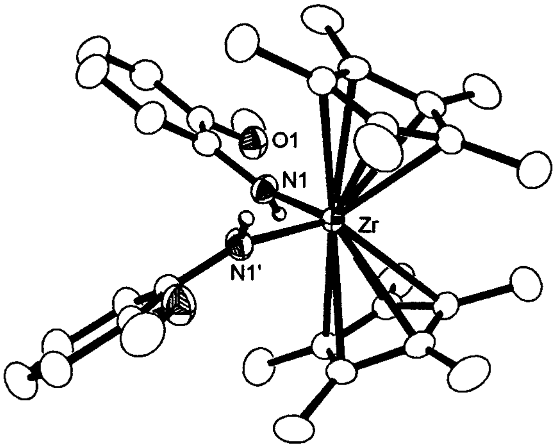


Figure 2. ORTEP drawing **4**; one of the molecules in the asymmetric unit is shown; 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity. Zr(1)−N(1) 2.121(3) Å; Zr(2)−N(2) 2.122(4) Å; N(1)−Zr(1)−N(1)′ 99.2(2)°; N(2)′−Zr(2)−N(2) 98.8(2)°.

In the case of **4**, the methoxy substituents are disposed in an *exo*-fashion, that is, on the “outside” of the ZrN_2 angle, thus minimizing steric congestion.

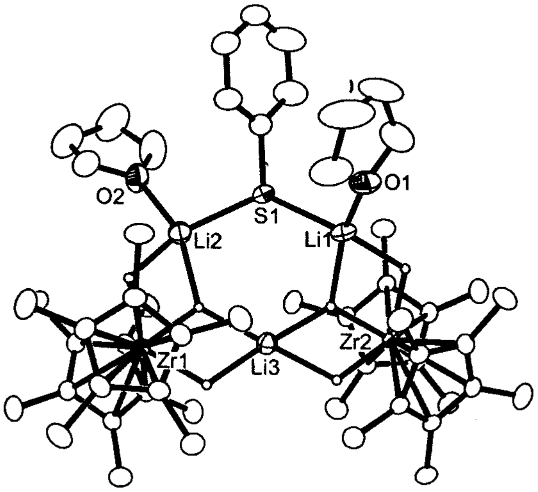
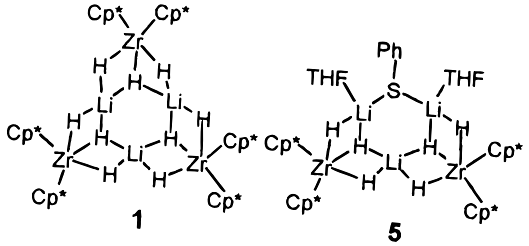


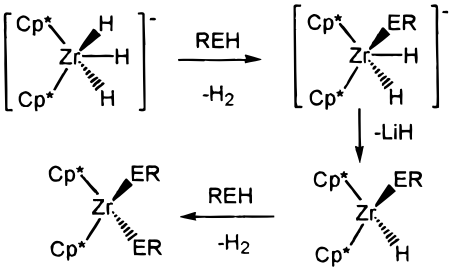
Figure 3. ORTEP drawing of **5**; 30% thermal ellipsoids are shown. Hydride hydrogen atoms are shown as open spheres; the remaining hydrogen atoms are omitted for clarity. S(1)−Li(2) 2.393(9) Å; S(1)−Li(1) 2.405(10) Å; O(1)−Li(1) 1.946(10) Å; O(2)−Li(2) 1.958(10) Å. Li(2)−S(1)−Li(1) 125.2(3)°; O(1)−Li(1)−S(1) 104.2(4)°; O(2)−Li(2)−S(1) 102.8(4)°.

Scheme 1



1 **5**

Scheme 2



In the related reaction of **1** with thiophenol, the reaction quickly became yellow in color. Upon standing, colorless crystals of a new species **5** were obtained. The ^{1}H NMR showed a triplet at −0.32 and a doublet at 0.55 ppm attributable to Zr hydrides. The resonances attributable to the pentamethylcyclopentadienyl ligands and the aryl group of a thiolate implied a ratio of 2:1. The molecular structure of **5** was unambiguously determined by X-ray crystallography (Figure 3). This compound contains two $[Cp^*_2ZrH_3]^-$ and one PhS^- anions and three Li cations. Two Li atoms are bridged by the thiolate and are further bridged by two Zr-bound hydride atoms. A THF molecule completes the coordination spheres of these two Li atoms. A third Li atom is bridged by hydrides between the two Zr centers. The Zr−Li separations range from 3.150(9) to 3.187(8) Å. The Li−S and Li−O bond lengths average 2.399(10) and 1.952(10) Å, respectively while the Li−S−Li angle is 125.2(3)°. This lithium-bridged arrangement in **5** is reminiscent of the trimeric solid-state structure of **1**[13] (Scheme 1).

These reactions of **1** with the protic reagents are thought to proceed through initial protonolysis, affording a transient anionic intermediate of formula $[Cp^*_2ZrH_2(ER)]^-$ (Scheme 2). In the case of phenolate or anilide ligands, steric crowding and π-donation from the donor atom is thought to induce loss of LiH, affording the neutral species $Cp^*_2ZrH(ER)$. Subsequent reaction of such a species with a second equivalent of the protic reagent would yield $Cp^*_2Zr(ER)_2$. This sequence of reactions accounts for the formation of **2**−**4** and is consistent with the related reactions of neutral Zr and Hf dihydrides.[16,18] In a similar manner thiophenol reacts with **1** generating the intermediate $[Cp^*_2ZrH_2(SPh)]^-$. However, in contrast to the systems

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(18) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.

above, the initial anionic intermediate $[Cp^*_2ZrH_2(ER)]^-$ loses LiSPh, providing the thiolate required for the formation of **5**. This is presumably a result of weaker π-donation from S in comparison with the O- and N-based complexes. In the related reactions of **1** with phosphines, the initial intermediate $[Cp^*_2ZrH_2(PHR)]^-$ is also unstable, although in that case, loss of H_2 affords $[Cp^*_2ZrH(PR)]^-$, which undergoes subsequent reaction leading to catalytic dehydrocoupling of P−P bonds.[11,12]

Summary

The reactions of $[(C_5Me_5)_2ZrH_3]Li$ (**1**) with protic reagents described herein demonstrate that the initially formed anionic intermediates $[Cp^*_2ZrH_2(ER)]^-$ are reactive. The course of the subsequent reaction appears to be determined by the strength of the Zr−E interaction.

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Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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