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Hydride-Bridged Heterobimetallic Complexes of Zirconium and Aluminum

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Summary: *Treatment of [Cp_2ZrCl_2] with $LiAlH_4$ and then [H_3GaL] or of preformed [Cp_2ZrH_2] with [H_3AlL] affords the heterobimetallic complexes [$Cp_2ZrH(\mu\text{-}H)_2\text{-}AlH_2(L)$] (L = quinuclidine (**1**), NMe_3 (**2**)). Density functional calculations gives an energy of association of “Cp_2ZrH_2” and “H_3AlNH_3” of -28.9 kcal mol^{-1}; cf. -28.8 kcal mol^{-1} for two Cp_2ZrH_2 units.*

Transition-metal aluminohydrides are important intermediates in catalytic processes and organic synthesis.[1] However, only a few structures of bimetallic complexes of this type with a purely hydridic environment have been reported, reflecting their low stability, and to date none have been established for zirconium.[1,2] The synthetically important zirconocene hydrides [$Cp_2ZrCl(H)$]$_x$ and [Cp_2ZrH_2]$_x$ (Cp = η-C_5H_5) are believed to be polymeric in the solid state and dimeric in solution.[3−5] Alkyl substitution on the cyclopentadienyl ring yields dimeric species in the solid state possessing $Zr(\mu\text{-}H)_2Zr$ units, established for [Cp'_2ZrH_2]$_2$ (Cp′ = η-C_5H_4R; R = Me,[6] Bu^t,[7] $SiMe_3$[8]), or even monomeric species in the case of [$Cp^*_2ZrH_2$] (Cp* = η-C_5Me_5), where associative hydride bridging is circumvented by the bulky cyclopentadienyl rings.[9] Continuing our interest in heterobimetallic main-group/transition-metal hydride complexes,[10] we report herein the preparation, structural characterization, and theoretical treatment of [$Cp_2Zr(H)(\mu\text{-}H)_2AlH_2(NR_3)$]. These represent the first structurally authenticated zirconocene aluminohydrides and confirm the presence of the $Zr(\mu\text{-}H)_2M$ moiety in such complexes.

Two synthetic routes have been established. First, reaction of [Cp_2ZrCl_2] with excess $LiAlH_4$ in THF followed by [H_3GaL] affords colorless [$Cp_2Zr(H)(\mu\text{-}H)_2AlH_2(L)$] (L = quinuclidine, **1**; L = NMe_3, **2**) in *ca.* 50% yield from light purple solutions, along with a metal powder derived from the second hydride source (Scheme 1).[11] The source of the color of the solutions is not yet clear; however, it may be due to the presence of a reduced (Zr^{3+}) species as a minor product. Presumably the gallane acts not only as the source of the amine but also as a hydride source, reducing the second chloride to a hydride. The reaction is much slower if [H_3AlNR_3] is used instead of the corresponding gallane in the second step. The product surprisingly shows little or no solubility in common organic solvents, with the exception of THF. Also noteworthy is that reducing the solution to dryness *in vacuo*, while initially resulting in an off-white powder of the product, eventually results in large-scale decomposition to a gray powder. If the above reaction is carried out with addition of just amine in the second step, the same product is not obtained. The previously reported[4] nonstabilized polymeric complex [$Cp_2Zr(H)AlH_4$] was prepared from the reaction of $Cp_2Zr(H)Cl$ with $LiAlH_4$, supporting the above hypothesis.

Complexes **1** and **2** can be considered as adducts of [Cp_2ZrH_2] and [H_3AlNR_3] and therefore were envisaged to be accessible from the direct reaction of these two parts. Indeed, reaction of zirconocene dihydride[4] with [H_3AlNR_3] in THF at room temperature (Scheme 1) yields the same product as the first route. The only observable difference is a slightly more intense purple colour of the solution, even though the isolated crystal-

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[11] The following preparations are examples and can be interchanged for either product. **1**, [$Cp_2Zr(H)(\mu\text{-}H)_2AlH_2(quinuclidine)$]: To a stirred THF solution of [Cp_2ZrCl_2] (0.73 g, 2.5 mmol) was added $LiAlH_4$ (0.19 g, 5 mmol) at 0 °C, and the mixture was warmed to room temperature and stirred for 6 h. To the almost colorless solution was added $H_3Ga(quinuclidine)$ (0.46 g, 2.5 mmol), and the mixture was stirred for 48 h, which resulted in a metallic precipitate and a pale purple solution. Filtration, concentration, and cooling to −25 °C resulted in the isolation of a white crystalline product (0.48 g, 53%). Anal. Calcd for $C_{17}H_{28}NAlZr$: C, 56.00; H, 7.74, N, 3.84. Found: C, 56.30; H, 7.71; N, 3.99. Mp: >100 °C dec. IR (Nujol mull): ν_{Al-H} 1736 cm^{-1}, ν_{Zr-H} 1544 cm^{-1}. **2,** [$Cp_2Zr(H)(\mu\text{-}H)_2AlH_2(NMe_3)$]: To a stirred THF suspension of Cp_2ZrH_2 (0.73 g, 2.5 mmol) was added [H_3AlNMe_3] (0.22 g, 2.5 mmol) at 0 °C, and the mixture was warmed to room temperature and stirred overnight, which produced a purple solution. Filtration, concentration, and cooling to −25 °C resulted in the isolation of a white crystalline product (0.44 g, 56%). Anal. Calcd for $C_{13}H_{24}$-NAlZr: C, 49.96; H, 7.74; N, 4.48. Found: C, 49.6; H, 7.66; N, 4.6. Mp: >100 °C dec. IR (Nujol mull): ν_{Al-H} 1768 cm^{-1}, ν_{Zr-H} 1556 cm^{-1}.

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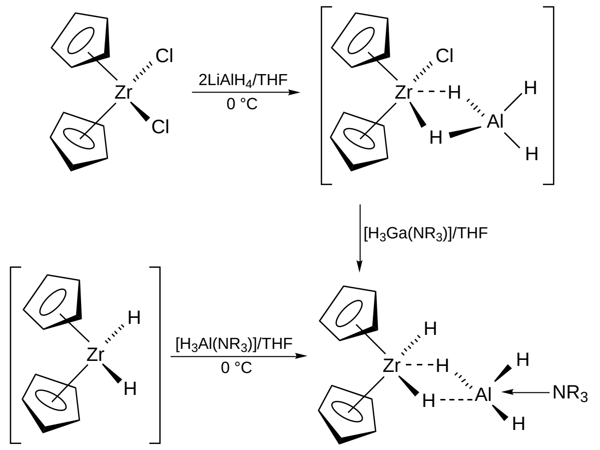
Scheme 1



NR_3 = quinuclidine (**1**), NMe_3 (**2**)

line product is still colorless. This reaction is relevant to the work of Schwartz *et al.*,[12] where the reaction of zirconocene dihydride with a dialkylaluminum hydride resulted in a thermally unstable material, assigned as the triply bridged $[Cp_2Zr(\mu\text{-}H)_3Al^iBu_2]$ species on the basis of ^1H NMR data. In light of the present results it is more likely to be the doubly bridged species $[Cp_2Zr(H)(\mu\text{-}H)_2Al^iBu_2]$ that is undergoing rapid hydride environment exchange. Interestingly, when Schwartz et al. added NEt_3 to the complex, Cp_2ZrH_2 precipitated from the solution, rather than an amine-stabilized product, indicating that there is an equilibrium present in solution. It is possible that an equilibrium and/or rapid hydride exchange exists in solution for complexes **1** and **2**, as ^1H NMR spectroscopy in d_8-THF showed only peaks attributable to the amine and cyclopentadienyl ligands.

Compounds **1** and **2** are white air- and moisture-sensitive crystalline solids, which decompose without melting at temperatures >100 °C to give a black, highly moisture sensitive powder. Infrared analysis reveals that the Al−H and the Zr−H stretches are influenced by the ligand. For complex **1** strong bands are seen at 1736 and 1544 cm^{-1}, respectively, while for complex **2** they occur at 1768 and 1556 cm^{-1}. The difference in the Al−H stretching frequencies is consistent with that found in the parent alane derivatives $[H_3AlNR_3]$ in which that of trimethylamine appears at higher wavenumber than that of the quinuclidine (1770 cm^{-1}; *cf.* 1720 cm^{-1}). It is not clear if the Zr−H−Al stretches are observed as part of Al−H absorption peaks, which are fairly broad, or occur at lower wavenumbers and are hidden.

The solid-state structures of **1** and **2**[13] are shown in Figure 1. The two complexes are isostructural with respect to the metal center environments, and in both cases all hydride ligands were located and refined. The structures confirm that the zirconium retains the oxidation state +4, with the complex effectively being an adduct between Cp_2ZrH_2 and H_3AlNR_3. Geometry about the aluminum centers is approximately trigonal bipyramidal in both cases, with the amine and a bridging hydride (Hb) in the apical positions. The second bridging hydride (Ha) bisects the Hb-Zr−Hc angle. The terminal hydride (Hc) to Zr distance and the distances of Zr-bridging hydrides are all comparable to those reported for the dimer $[(\eta^5\text{-}C_5H_2Me)_2ZrH(\mu\text{-}$

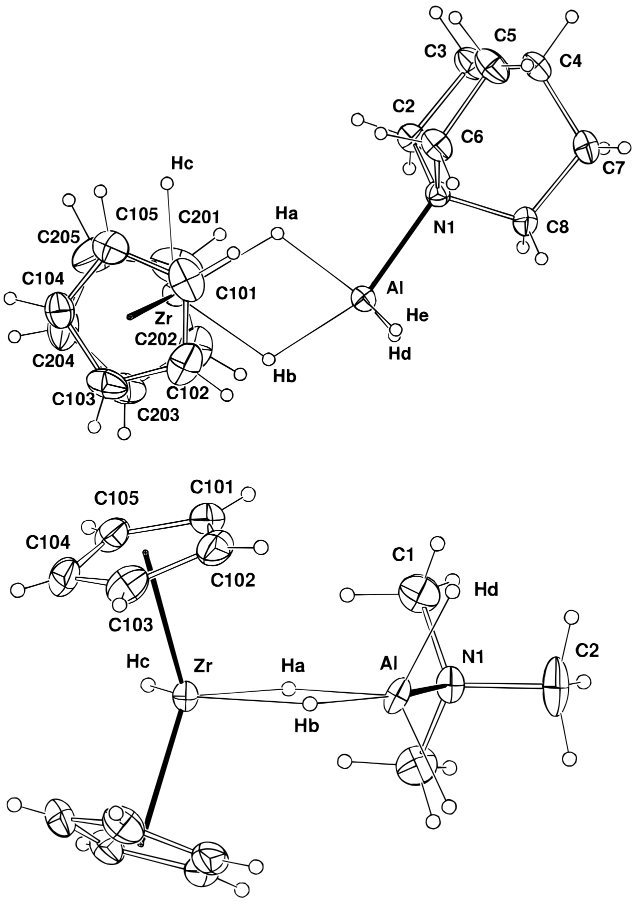


Figure 1. Projections of (a, top) **1**, $[Cp_2Zr(H)(\mu\text{-}H)_2AlH_2(\text{quinuclidine})]$ and (b, bottom) **2**, $[Cp_2Zr(H)(\mu\text{-}H_2)_2\text{-}AlH_2(NMe_3)]$. Selected distances (Å) and angles (deg): **1**, Zr⋯Al = 3.0005(7), Zr−C = 2.470(2)−2.498(3), Zr−centroid, = 2.193, 2.199, Zr−Ha−c 1.91(2), 1.83(2), 1.79(3), Al−N(1) = 2.066(2), Al−Ha,b,d,e = 1.72(3), 1.79(2), 1.58(3), 1.47(3), centroid(1)−Zr−centroid(2) = 137.8, centroid(1)−Zr−Ha−c = 109.4, 100.7, 98.9, centroid(2)−Zr−Ha−c = 112.8, 98.6, 97.5, Ha−Zr−Hb,c = 66(1), 63(1), Hb−Zr−Hc = 129(1), Zr−Ha,b−Al = 111(1), 112(1), N(1)−Al−Ha,b,d,e = 87.8(7), 158.1(7), 94.2(9), 96.6(9), Ha−Al−Hb,d,e = 71(1), 122(1), 117(1), Hb−Al−Hd,e = 93(1), 97(1), Hd−Al−He = 121(2); **2**, Zr⋯Al = 2.994(3), Zr−C = 2.493(5)−2.503(5), Zr−centroid, = 2.189, Zr−Ha−c = 2.02(5), 1.99(5), 1.84(6), Al−N(1) = 2.071(5), Al−Ha,b,d = 1.77(5), 1.94(5), 1.76(3), centroid−Zr−centroid = 138.3, centroid−Zr−Ha−c = 110.8, 97.0, 98.2; Ha−Zr−Hb,c = 75(2), 62(3), Hb−Zr−Hc = 136(3), Zr−Ha,b−Al = 104(2), 99(2), N(1)−Al−Ha,b,d = 80(2), 162(2), 96(1), Ha−Al−Hb,d = 82(2), 121(1), Hb−Al−Hd = 93(1), Hd−Al−Hd′ = 119(2).

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[13] **1** $[Cp_2Zr(H)(\mu\text{-}H)_2AlH_2(\text{quinuclidine})]$: $C_{17}H_{28}AlNZr$, formula weight 364.62, monoclinic, $P2_1/c$, $a = 10.022(2)$ Å, $b = 15.978(2)$ Å, $c = 11.516(1)$ Å, $\beta = 103.26(1)°$, $V = 1794.9(4)$ Å^3, $F(000) = 760$, $\rho_{calc} = 1.349$ g cm^{-3}, μ(Mo Kα) = 6.5 cm^{-1}, A^*(max,min) 1.18, 1.31 (Gaussian), specimen 0.36 × 0.32 × 0.75 mm^3, $Z = 4$, CAD4 diffractometer, Mo Kα radiation, $T = 297$ K, 5219 unique reflections (4289 observed, $I > 2.0\sigma(I)$), $2\theta_{max} = 50°$, $R = 0.030$, $R' = 0.030$, σ weights (statistical weights). Solution by direct methods. **2**, $[Cp_2Zr(H)(\mu\text{-}H_2)AlH_2(NMe_3)]$: $C_{13}H_{24}AlNZr$, formula weight 312.54, orthorhombic, *Pnma*, $a = 13.058(6)$ Å, $b = 13.590(8)$ Å, $c = 8.924(6)$ Å, $V = 1584(2)$ Å^3, $F(000) = 648$, $\rho_{calc} = 1.310$ g cm^{-3}, μ(Mo Kα) = 7.3 cm^{-1}, A^*(max,min) 1.30, 1.39 (Gaussian), 0.60 × 0.32 × 0.45 mm^3, $Z = 4$, CAD4 diffractometer, Mo Kα radiation, $T = 297$ K, 1840 unique reflections (1502 observed, $I > 3.0\sigma(I)$), $2\theta_{max} = 55°$, $R = 0.045$, $R' = 0.052$, σ weights (statistical weights). Solutions by direct methods. Hydrogen atoms were refined in *x*, *y*, *z*, and *U*; other atoms were refined anisotropically.

H)]$_2$.[6] There are no significant differences in the hydride geometries and in the Al−N distances. In the case of **2** the molecules have crystallographic *m* symmetry with the mirror plane passing through Zr, Al, N1, C2 and Ha−c. The Zr···Al separations are similarly long (3.0005(7) and 2.994(3) Å, respectively) and are consistent with no appreciable metal−metal interaction.

Approximate density functional theory[14] has been used to investigate the stabilities of the two systems [$Cp_2Zr(H)(\mu\text{-}H)_2AlH_2(NH_3)$] (= ZrAl) and [$Cp_2Zr(H)(\mu\text{-}H)_2Zr(H)Cp_2$] (= Zr_2). If ZrAl is regarded as an adduct between [Cp_2ZrH_2] and [H_3AlNH_3], two distinct donor-acceptor interactions can be identified. First, a vacant d orbital on the Zr center can accept electron density from the Al−H bond, while a p orbital on Al can accept electron density from the Zr−H bond. This aluminum-based acceptor orbital lies *trans* to the amine and is antibonding with respect to the Al−N bond. As a consequence, Zr−H→Al charge transfer results in elongation of the Al−N bond, consistent with the longer Al−N bond length observed in **1** relative to that in the related monomer [H_3Al(quinuclidine)].[15] In the Zr_2 complex, there are two identical Zr−H→Zr donor−acceptor interactions. The total interaction energies for the two complexes, relative to their component monomers, are very similar (−28.9 kcal mol^{-1} for ZrAl; −28.8 kcal mol^{-1} for Zr_2), supporting the presence of an equilibrium between [Cp_2ZrH_2], [AlH_3NR_3], and [$Cp_2Zr(H)(\mu\text{-}H)_2AlH_2(NR_3)$] in solution. A decomposition of the components of the interaction energy in ZrAl reveals that the contribution of Al−H→Zr charge transfer is more important energetically than Zr−H→Al. Thus, the major role of the [H_3AlNR_3] unit in these complexes is as a hydride donor rather than as a hydride acceptor.

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Supporting Information Available: Tables giving atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for **1** and **2** (11 pages). Ordering information is given on any current masthead page.

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