ORGANOMETALLICS
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Dinuclear Cationic Zirconium Hydrides Stabilized by the *N,N*-Dibenzylcyclam Ancillary Ligand

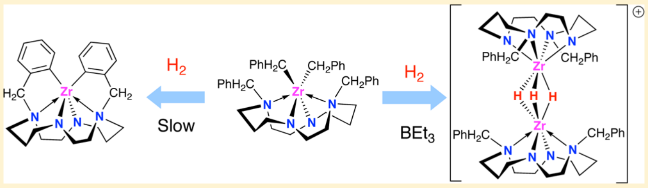
Rui F. Munhá,[†,‡] Joachim Ballmann,[‡] Luis F. Veiros,[†] Brian O. Patrick,[‡] Michael D. Fryzuk,*[,‡] and Ana M. Martins*[,†]

[†]Centro de Química Estrutural, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais No. 1, 1049-001 Lisboa, Portugal

[‡]Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1

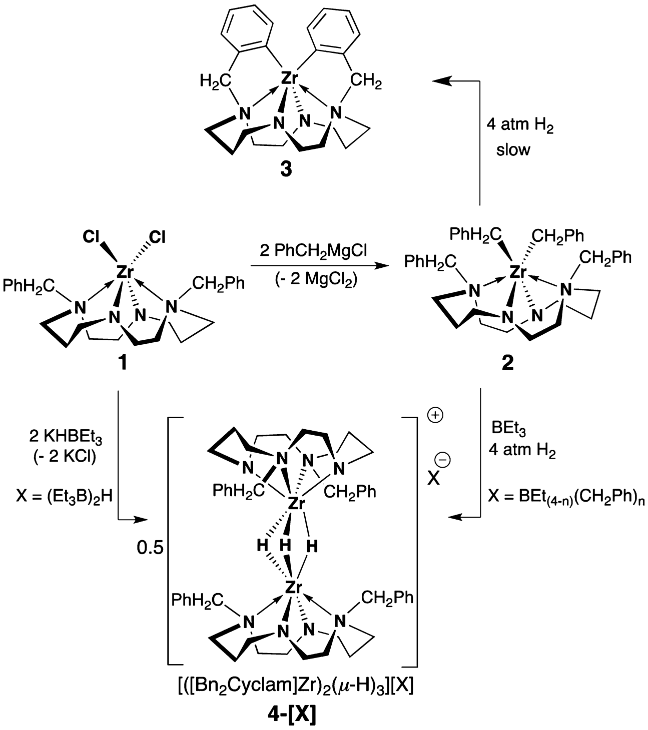
Ⓢ *Supporting Information*

ABSTRACT: The reaction of $[Bn_2Cyclam]ZrCl_2$ (Bn = benzyl) with 2 equiv of $KHBEt_3$ generates the ionic dinuclear zirconium derivative $[([Bn_2Cyclam]Zr)_2(\mu\text{-}H)_3][(Et_3B)_2H]$. An analogous trihydride is obtained when $[Bn_2Cyclam]Zr(CH_2Ph)_2$ reacts with BEt_3 in the presence of dihydrogen, whereas in the absence of BEt_3, the bis(ortho-metalated) derivative $[(C_6H_4CH_2)_2Cyclam]Zr$ is obtained. DFT calculations support the stability of a cationic dinuclear trihydride complex in comparison to the neutral dinuclear tetrahydride.



Not only are zirconium hydride complexes important reagents in organic synthesis[1−10] but they have also been used in the reduction of small molecules such as CO_2 and CO;[11−20] in addition, certain zirconium hydride species have been found useful in the preparation of dinitrogen complexes via dihydrogen elimination.[21,22] For the vast majority of structurally characterized zirconium hydride complexes, cyclopentadienyl-type ligands are typically found to stabilize these derivatives; in fact, the bis(cyclopentadienyl) motif dominates this chemistry.[14,23−36] For some time we have been interested in alternative ligand environments[37−42] in an attempt to expand early-transition-metal chemistry and, in particular, to explore the use of group 4 and 5 hydride complexes that can serve as entry points into N_2 activation.[43] For this reason, we investigated the formation of zirconium hydride derivatives stabilized by the *N,N*-dibenzylcyclam ($Bn_2Cyclam$) ancillary ligand,[44] in an effort to build on the alkyl and amido chemistry already reported for complexes of this type.[45−47] Herein we report the synthesis and characterization of a unique dinuclear zirconium hydride species that is unexpectedly cationic.

Scheme 1



We have previously reported the preparation of the zirconium(IV) *N,N*-dibenzylcyclam dichloride complex **1** (Scheme 1) and its further reactivity with a variety of alkyl Grignard or lithium reagents that allows access to the corresponding dialkyl derivatives $[Bn_2Cyclam]ZrR_2$ (R = Me, Bu, CH_2Ph).[46] Unfortunately, attempts to hydrogenate these dialkyl species directly to putative dihydride species of the general formula $([Bn_2Cyclam]ZrH_2)_x$ failed even under 4 atm pressure of H_2. This is in contrast with the many known zirconocene dialkyl complexes and related derivatives (Cp'_2ZrR_2) that have been reported to react with H_2 under a variety of conditions via a σ-bond metathesis type process to generate hydrides.[26,31,48−51] In the case of the aforementioned cyclam-ligated zirconium dialkyl derivative species, there is no apparent reaction with H_2, only the observation of the bis(ortho-metalated) derivative $[(C_6H_4CH_2)_2Cyclam]Zr$ (**3**)[46] (Scheme 1) via a competing slow alkane elimination; the rate of

Received: June 7, 2012
Published: July 6, 2012

formation of **3** is independent of the H_2 pressure, which strongly precludes the formation of hydride intermediates. Interestingly, the rate of formation of **3** via thermolysis depends on the nature of the alkyl group and is slowest for R = CH_2Ph.

Hydride complexes could be accessed, however, by a metathesis reaction of the dichloro species **1** with potassium triethylborohydride ($KBEt_3H$). Thus, the reaction of 2 equiv of $KBEt_3H$ with **1** results in the clean formation of the new dinuclear hydrido species **4-[$(Et_3B)_2H$]** in 95% yield (Scheme 1). The ^1H NMR spectrum of **4-[$(Et_3B)_2H$]** is quite complicated and is suggestive of low symmetry.[45,46] This in itself was strong evidence that the species formed was not a dihydride derivative, e.g. $([Bn_2Cyclam]ZrH_2)_x$, as such species would be expected to have C_2 symmetry if mononuclear, on the basis of previous studies.[45,46] Of particular note are the hydride signals that appear as two nearly coincident singlets at approximately 6 ppm in d_8-THF;[15,52] interestingly, these two singlets are in a 2:1 ratio and integrate to three H's per two $[Bn_2Cyclam]Zr$ units, which suggests a dinuclear structure with a core corresponding to $Zr_2(\mu\text{-}H)_3$. The ionic nature of the complex was also suggested by the presence of a set of signals assigned to $[(Et_3B)_2H]^-$; this included a characteristic resonance assigned to the bridging B−H of $[Et_3B{-}\mathit{H}{-}BEt_3]^-$ at −2.31 ppm and a ^{11}B NMR spectrum displaying a broad peak at approximately 12 ppm.[53] As observed in other systems,[53] a compound of the formula **4-[$(Et_3B)_2H$]** is in equilibrium with **4-[Et_3BH]** and free BEt_3. In fact, yellow X-ray-quality crystals of **4-[Et_3BH]** could be grown from THF that provided information on the structure of this latter derivative.

The ORTEP diagram of **4-[Et_3B-H]** is shown in Figure 1 and shows that this species consists of a dinuclear trihydride cation and a triethylborohydride anion. The coordination geometry of each seven-coordinate zirconium center is a distorted capped trigonal prism, with three symmetrically bridging hydrides (1.5 independent atoms) with Zr−H bond lengths of 1.95(4) and 1.99(3) Å. The latter are comparable to those in other zirconium hydride complexes[30,54] as are the Zr−N_{amine} bond lengths at 2.384(3) and 2.390(3) Å and the Zr−N_{amido} distances at 2.059(3) and 2.062(2) Å, all within the previously observed values for zirconium complexes incorporating this ligand set.[44−46] The two macrocyclic ligands are twisted with respect to each other, with the amine units of one zirconium center facing the amido donors of the other metal center (Figure 1). While cationic zirconium hydride complexes are known, structurally characterized examples are relatively rare.[55−59]

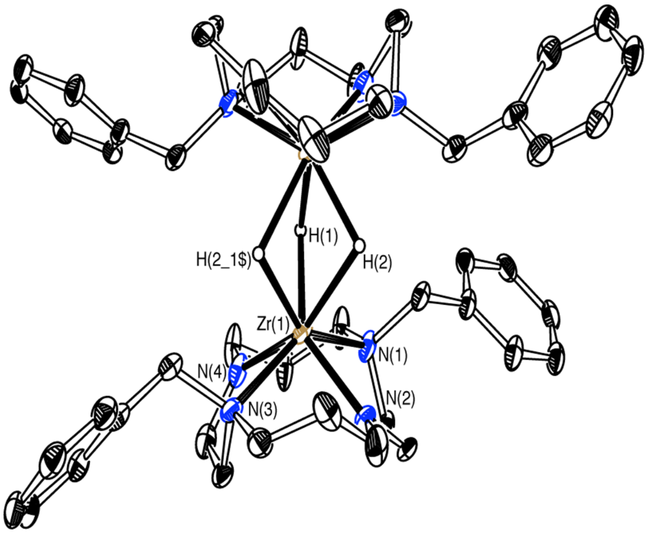


Figure 1. ORTEP (50% thermal ellipsoids) of $[([Bn_2Cyclam]Zr)_2(\mu\text{-}H)_3][Et_3BH]$ (**4-[Et_3BH]**). Half of the molecule is generated by the symmetry operation $-x, y, -z + {}^1/_2$. Not shown are the hydrogen atoms, except for the zirconium hydrido ligands, the disordered triethylborohydride anion, and cocrystallized THF, for the sake of clarity. Selected bond lengths (Å) and angles (deg): [N4Plane]- - -Zr(1) = 0.968(1), Zr(1)- - -Zr(1_$1) = 3.1567(5), Zr(1)−H(11) = 1.99(3), Zr(1)−H(21) = 1.95(4), Zr(1)−N(1) = 2.384(3), Zr(1)−N(2) = 2.059(3), Zr(1)−N(3) = 2.390(3), Zr(1)−N(4) = 2.062(2); N(1)−Zr(1)−N(3) = 140.12(10), N(2)−Zr(1)−N(4) = 113.97(11), H(1)−Zr(1)−H(21) = 67.3(14).

The formation of this cationic dizirconium trihydride was surprising, as metathesis of the dichloride **1** with 2 equiv of $KBEt_3H$ would normally be expected to generate the neutral dihydride $[Bn_2Cyclam]ZrH_2$, on the basis of simple stoichiometry.[60] In an effort to understand how a cationic dinuclear trihydride is formed, a computational analysis[61] was performed on the observed dinuclear trihydride cation and likely neutral intermediates in the presence of BEt_3. Calculations show that the reaction of BEt_3 with the putative neutral dihydride $[Bn_2Cyclam]ZrH_2$ to generate the monohydride $([Bn_2Cyclam]ZrH)(HBEt_3)$ is uphill energy-wise by +26.9 kcal/mol. The dimerization of $[Bn_2Cyclam]ZrH_2$ to give the dizirconium tetrahydride $([Bn_2Cyclam]Zr)_2(\mu\text{-}H)_4$ is favorable by −21.4 kcal/mol, indicating that the dinuclear species is more stable than the mononuclear dihydride. Interestingly, the calculations also show that BEt_3 is a strong enough Lewis acid to abstract a hydride ligand from dinuclear $([Bn_2Cyclam]Zr)_2(\mu\text{-}H)_4$ to give $[([Bn_2Cyclam]Zr)_2(\mu\text{-}H)_3][BEt_3H]$, albeit by a stabilization of only $\Delta E = -0.9$ kcal/mol. Overall these calculations show that the formation of the dinuclear trihydride derivative is a favorable process.

As already mentioned (Scheme 1), the direct reaction of the dibenzyl complex **2** with H_2 did not lead to hydride derivatives; rather, intramolecular cyclometalation to generate **3** was observed. On the assumption that cationic alkyl complexes should be more reactive to H_2 addition,[62−64] we reexamined the reaction of **2** with dihydrogen in the presence of Lewis acids. Treatment of $[Bn_2Cyclam]Zr(CH_2Ph)_2$ with 1 equiv of BEt_3 under H_2 gave $[([Bn_2Cyclam]Zr)_2(\mu\text{-}H)_3][BEt_{4-n}(CH_2Ph)_n]$ (**4-[$BEt(R)_3$]**: R = Et, CH_2Ph) as the major product (Scheme 1). The NMR spectrum of **4** unequivocally shows that a cationic trihydride identical with **4-[$(Et_3B)_2H$]** was isolated, although the stoichiometry of the anion is ambiguous. The ^1H NMR spectra of **4-[$(Et_3B)_2H$]** (bottom, *black*) and **4-[$BEt(R)_3$]** (R = Et, CH_2Ph) (*blue*) are depicted in Figure 2. The spectral overlay makes it easy to identify the resonances corresponding to the $B\mathit{CH_2Ph}$ and $B\mathit{Et}$ moieties. However, integration of the signals in comparison to the macrocyclic $N\mathit{CH_2}$ resonances does not allow a clear identification of the stoichiometry of the anion; it is suggested that a mixture of anions of the general formula $[BEt_{4-n}(CH_2Ph)_n]^-$ (n = 1−3) is present on the basis of the analysis of the aromatic region of the spectrum (insert area, *blue*), where different sets of signals assigned to the ortho, meta, and para protons of $BCH_2\mathit{Ph}$ are observed.

A possible origin of the scrambling of the benzyl and ethyl groups in the anion is described in Scheme 2. Reaction of BEt_3 with dibenzyl **2** would likely generate the benzyl cation

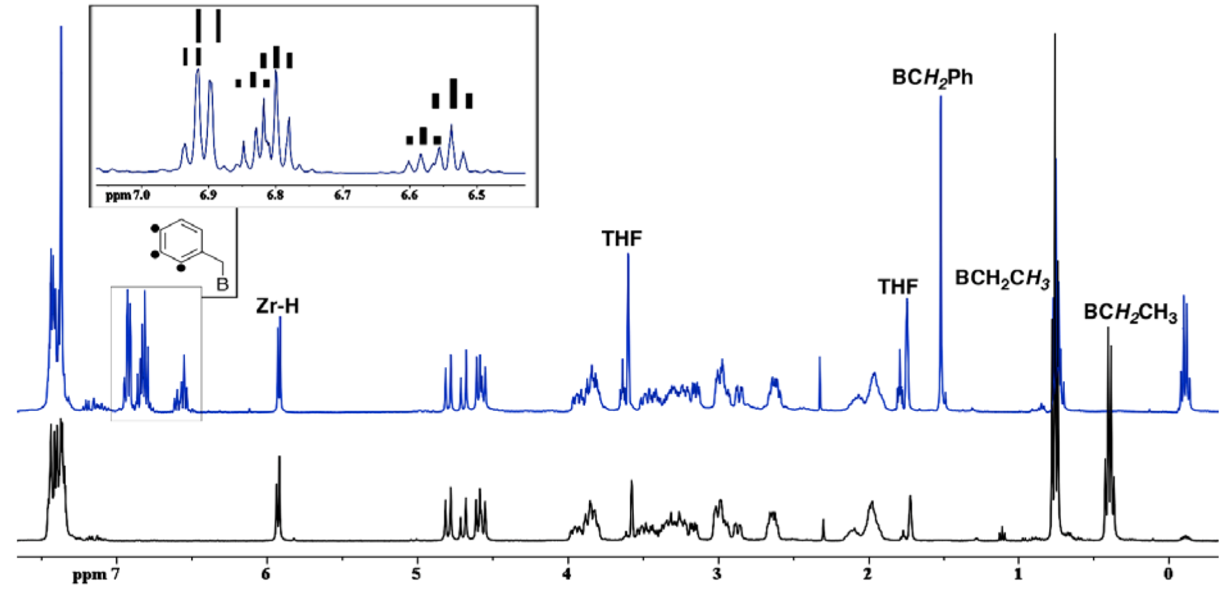
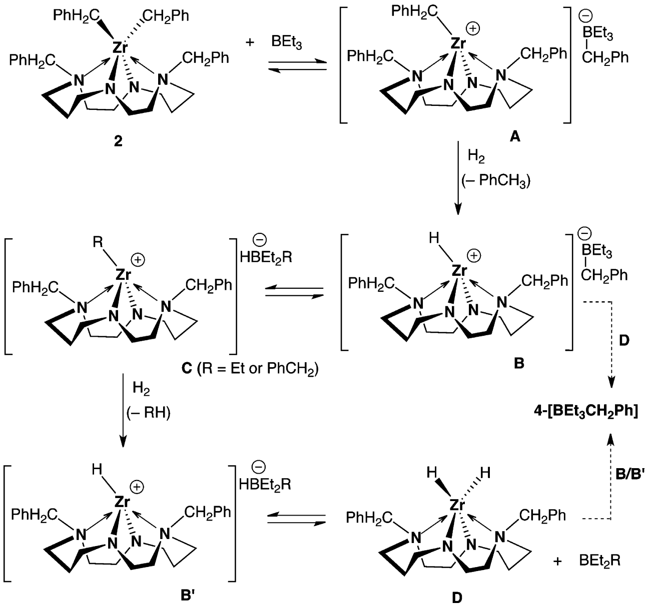


Figure 2. 400 MHz ^{1}H NMR spectra in d_8-THF of [([Bn$_2$Cyclam]Zr)$_2$(μ-H)$_3$][(Et$_3$B)$_2$H] (4-[**(Et$_3$B)$_2$H**]) (bottom, *black*), and [([Bn$_2$Cyclam]Zr)$_2$(μ-H)$_3$][BEt$_{4-n}$(CH$_2$Ph)$_n$] (4-[**BEt(R)$_3$**]) (top, *blue*) at 25 °C. The region from 0 to −2 ppm where the signal corresponding to the bridging borohydride of 4-[**(Et$_3$B)$_2$H**] is observed is omitted. The overlay of the two spectra allows clear identification of the benzyl and ethyl boron environments. The insert in the top spectrum (*blue*) shows two sets of signals for the benzyl aryl protons in a 1:2 ratio.

Scheme 2



[[Bn$_2$Cyclam]Zr(CH$_2$Ph)][BEt$_3$(CH$_2$Ph)] (**A**). In the presence of dihydrogen in a THF solution, **A** likely undergoes σ-bond metathesis to generate the hydride cation **B**. Hydride for alkyl exchange from the cation to the anion will result in the formation of **C**, which has a B−*H* moiety in the anion. Further reaction of this new alkyl cation with H$_2$ results in the formation of hydride cation **B′**, which differs from **B** only in the makeup of the anion. Hydride transfer from the anion back to the cation generates the neutral dihydride **D**, which is a key species in the formation of the dinuclear trihydride cation, via a number of different pathways, some of which are indicated in the scheme. The conversion of **B** to **C** can occur by either an ethyl or a benzyl group transfer by a hydride ligand, giving BEt$_3$ or BEt$_2$(CH$_2$Ph), which may explain the ambiguity in the stoichiometry of the anion in **4**. We also examined the reaction of **2** with B(C$_6$F$_5$)$_3$ in the presence of H$_2$. While we have already reported[46] that [[Bn$_2$Cyclam]Zr(CH$_2$Ph)S]$^+$[B(C$_6$F$_5$)$_3$CH$_2$Ph]$^-$ (S = THF) forms in the absence of H$_2$, when dihydrogen is present, there is no evidence of the formation of the dinuclear trihydride. We suggest that the cascade of equilibria in Scheme 2 necessary to produce the cationic trihydride **4**$^+$ is somehow interrupted or prevented by the strongly Lewis acidic B(C$_6$F$_5$)$_3$.

We have demonstrated that a dinuclear zirconium trihydride complex incorporating a dianionic cyclam-based ligand can be prepared via a salt metathesis route using a hydride reagent or from hydrogenolysis of a zirconium dibenzyl derivative in the presence of BEt$_3$. That BEt$_3$ is essential to the latter process is counterintuitive, at least to us, given that it is not as Lewis acidic as B(C$_6$F$_5$)$_3$; nevertheless, we suggest that it can better participate in alkyl group and hydride transfers from boron to zirconium, which allows the final cationic trihydride complex to form. DFT studies show that the cation [([Bn$_2$Cyclam]Zr)$_2$(μ-H)$_3$]$^+$ (**4**$^+$) is slightly more stable than the corresponding dinuclear neutral tetrahydride species ([Bn$_2$Cyclam]Zr)$_2$(μ-H)$_4$. To the best of our knowledge, this represents a rare example of a non-cyclopentadienyl zirconium system where a zirconium hydride is isolated via dihydrogen activation, but only in the presence of BEt$_3$. While the reaction of this dinuclear hydride with N$_2$ does not generate a dinitrogen complex, studies are continuing on the mechanisms that govern the formation of these zirconium hydrides and the reactivity displayed by nitrogen-rich ligated complexes of this type.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving full experimental procedures, representative NMR spectra, details of the preparation of 4-[**BEt$_3$H**], and Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*M.D.F.: e-mail, fryzuk@chem.ubc.ca; fax, +1 604 822-8710; tel, +1 604 822-2471.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

M.D.F. thanks NSERC of Canada for a Discovery Grant. A.A.M. and R.F.M. thank the Fundação para a Ciência e Tecnologia for funding. We thank Nathan Halcovitch for his assistance with the diffraction experiments.

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