COMMUNICATION

H_2 activation by zirconaziridinium ions: σ-bond metathesis *versus* frustrated Lewis pairs reactivity†‡

Peter H. M. Budzelaar,*[,a] David L. Hughes,[b] Manfred Bochmann,[b] Alceo Macchioni[c] and Luca Rocchigiani*[,b]

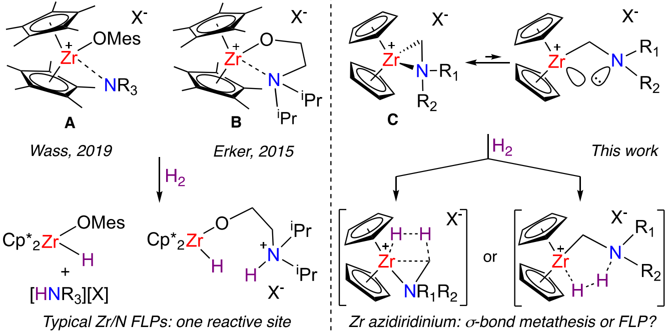
Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Zirconaziridinium ions $[Cp_2Zr(\eta^2\text{-}CH_2NR_2]^+$ can potentially activate H_2 by two routes: σ-bond metathesis, or FLP reactivity. We show here that Zr-C hydrogenolysis by σ-bond metathesis precedes and enables subsequent heterolytic H_2 cleavage by FLP pathways. DFT calculations show the involvement of transition states with approximately linear N···H···H and bent Zr···H···H arrangements without any direct Zr-amine interaction.

Heterolytic H_2 activation is a key step of many catalytic reactions.[1] It relies on the cooperation between a highly electrophilic fragment and a Lewis base, either intra- or intermolecularly, for inducing H-H splitting into proton and hydride ions. Deprotonation of acidic H_2 complexes of transition metal fragments is a notable example.[1] This concept has drawn a skyrocketing attention with the discovery of Frustrated Lewis pairs (FLPs),[2] where unquenched reactivity between highly electrophilic Lewis acids and sterically encumbered Lewis bases can be used as a tool for enabling hydrogen activation in non-metallic systems and metal-free hydrogenation catalysis.

The introduction of FLP concepts in the molecular design of systems that can activate H_2 heterolytically is attractive also in transition metal chemistry,[3] as it might open reaction pathways that are not available to metal fragments lacking in the pertinent d-orbital features. One successful case is that of d^0 zirconocenium(IV) cations, which have emerged as suitable FLP components, mainly in combination with phosphines.[4] Zr(IV)/amine systems have appeared more recently,[5] and H_2 cleavage has been achieved both with intermolecular $[Cp^*_2Zr(OMes)]^+/NR_3$ pairs **A**,[5a] and intramolecular ones, such as the $[Cp^*_2ZrOCH_2CH_2N^iPr_2]^+$ cation **B**[5b] ($Cp^*=\eta^5\text{–}C_5Me_5$, $Mes=2,4,6\text{-}Me_3\text{-}C_6H_2$, Scheme 1). In these complexes, the apparent lack of interaction between Zr and the N donor is key for triggering FLP reactivity. The efficiency of the latter is also ensured by the presence of the robust oxide ligand, which prevents hydrogenolysis side reactions.



Scheme 1 H_2 activation by Zr/N FLPs versus Zr aziridinium salts; $X^-=B(C_6F_5)_4^-$

A few years ago, we became interested in zirconaziridinium salts $[Cp_2Zr(\eta^2\text{-}CH_2NR_2][X]$ (**C**, Scheme 1) as model systems for the investigation of ion-pairing effects in olefin polymerization catalysis.[6] These complexes are fluxional and undergo nitrogen pyramidal inversion and back-skip,[7] owing to the reduced interaction between the Lewis sites arising from ring strain. The capability of the Zr–N bond to reversibly break and re-form made us wonder whether **C** might act as a transient FLP upon ring-opening.

In contrast to **A** and **B**, cations **C** provide a mechanistic dichotomy: apart from their potential as FLPs, it could also be envisaged that they cleave H_2 by σ-bond metathesis of the Zr-C bond.[8] These two pathways would compete with each other and potentially affect the outcome of the reaction. For instance, Erker reported that vinyl or phenyl-bridged Zr/P FLPs readily cleave H_2 heterolytically, but a following irreversible protonation of the transient hydrido phosphonium products led ultimately to inactive hydrido phosphine cations, where the bridge is cleaved.[4c,9]

---

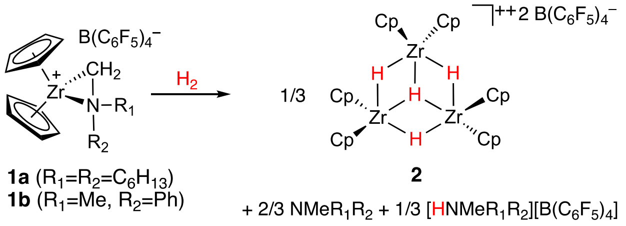
[a] *Department of Chemistry, University of Naples Federico II, Via Cintia, I-80126, Naples, Italy. Email: p.budzelaar@unina.it*
[b] *School of Chemistry, University of East Anglia, Norwich Research Park, NR4 7TJ, Norwich, UK. Email:L.Rocchigiani@uea.ac.uk*
[c] *Department of Chemistry, Biology and Biotechnology and CIRCC, University of Perugia, Via Elce di Sotto, 8, 06123, Perugia, Italy*

†Electronic Supplementary Information (ESI) available: details on experimental procedures, DFT calculations, X-Ray diffraction and xyz files of optimized structures. See DOI: 10.1039/x0xx00000x

‡ Dedicated to the memory of Professor Hans Herbert Brintzinger.

Herein we show that this behaviour is completely reversed in zirconaziridinium ion pairs: σ-bond metathesis of the carbon spacer in **C** is fast and preferred over heterolytic H_2 activation. However, this does not quench the reactivity of the system. Instead, it offers an unprecedented entry for heterolytic splitting of H_2, which takes place by exploiting acid-base cooperation as in typical FLPs, demonstrating that steric frustration is not always a requirement for promoting small molecule activation in this family of compounds.

Alkyl and aryl substituted Zr-aziridinium pairs **1a-b** react readily with H_2 in C_6D_5Cl (1 atm, 25 °C) to give a mixture of species, which evolves into a single, poorly soluble Zr-containing complex **2** over the course of 5 minutes (**1a**) or 24 hours (**1b**). On the basis of its NMR features, the product was formulated as a dicationic hydride complex featuring a $Zr_3(\mu^2–H)_3(\mu^3–H)$ core (Scheme 2). **2** is characterized by two low-frequency shifted signals typical of bridging Zr hydrides, resonating at δ_H=–3.87 (doublet, longitudinal relaxation time T_1=458 ms) and δ_H=–5.76 ppm (quartet, T_1=270 ms) and showing a relative 3:1 intensity and J_{HH}=12 Hz. ^1H NOESY NMR spectroscopy indicated that they interacted solely with cyclopentadienyl substituents (δ_H=6.00 ppm), meaning that there is no residual interaction with the amine. The structure of **2** was confirmed by X-Ray diffraction methods (Figure 1).



Scheme 2 Hydrogenolysis of zirconaziridinium salts to give **2** (C_6D_5Cl, 25 °C).

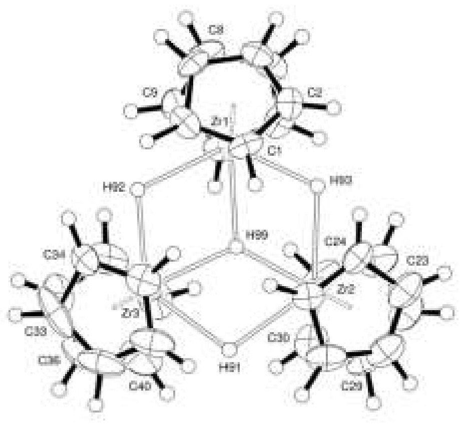
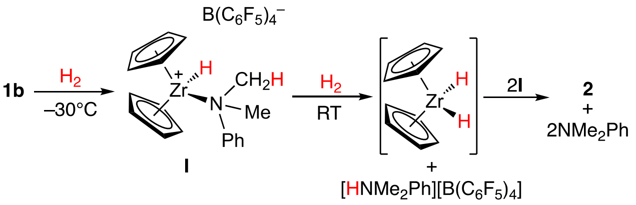


Figure 1 Molecular structure of the cation of **2**, indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. (anions and solvent molecules omitted for clarity).

The main structural feature is the planar arrangement of the metal-hydride core, whose atoms were all observed in the electron density map and freely refined. The molecular structure of **2** shows the μ^3 hydride sitting inside the hexagon described by alternating zirconium-μ^2 hydrido units. Zr–H bond distances fall in the range 2.24–2.06 Å and 2.18–1.89 Å for the μ^2 and μ^3 moieties, respectively. Two independent $B(C_6F_5)_4^–$ anions were identified in the unit cell, in line with the proposed dicationic character of **2**. To the best of our knowledge, **2** is the first example of homoleptic dicationic $[Zr_3H_4]$ core in zirconium hydride chemistry.[10-12]

In the case of **1b,** the ^1H NMR spectrum obtained after complete conversion showed that 1 equiv. of anilinium salt (δ_H(NH)=6.82 ppm) and 2 equiv. of aniline are generated per Zr cluster. Their signals are averaged, reasonably due to fast proton shuttling.[13] This was also observed upon mixing genuine samples of NMe_2Ph and $[HNMe_2Ph][B(C_6F_5)_4]$ in C_6D_5Cl. Analogously, in the reaction of **1a** with H_2 the presence of $[HNMe(C_6H_{13})_2][B(C_6F_5)_4]$ (δ_H(NH)=7.48 ppm) was observed. The formation of ammonium salts implies that heterolytic splitting of H_2 has occurred.

To obtain more insight into the reaction mechanism, hydrogenolysis of **1b** was performed at –30 °C. The first ^1H NMR spectrum recorded soon after the addition of H_2 showed the presence of **1b** and a new intermediate **I**, which formed quantitatively over the course of few hours. No traces of either **2** or aniline/anilinium were observed at this point. The NMR features of **I** are compatible with a zirconocene monohydrido amine complex (Scheme 3). The terminal hydride was identified as a singlet at δ_H=4.72 ppm, while the presence of a singlet at δ_H=2.18, with a relative intensity of 6 protons, accounted for the presence of two equivalent methyl groups (see ESI for additional details).



Scheme 3 Hydrogenolysis of **1b** at –30° C (C_6D_5Cl) and proposed route to **2**.

Upon warming the sample to RT, **I** was slowly converted into **2** over a period of 24 hours. This suggests that trinuclear **2** is the product of heterolytic H_2 splitting by the monohydride **I**. This would afford the anilinium salt and Cp_2ZrH_2, which is trapped by residual **I** cations generating **2** and liberating N,N-dimethyl aniline (Scheme 3).

2 was also found to be the product of the reaction between Cp_2ZrH_2 and $[HNMe_2Ph][B(C_6F_5)_4]$. This indicates that the formation of **2** is favoured over amine coordination after the initial hydride protonation. The reaction goes to completion much faster than in the hydrogenolysis case (10 minutes), likely owing to the presence of a local excess of Cp_2ZrH_2 upon reaction with the ammonium salt.

The hydrogenolysis pathways outlined above have been modelled by DFT calculations (PCM/M062X/cc-pVTZ//TPSSh/Def2SVP, see ESI for details), starting from **1b**. In analogy with the experimental results, the reaction cascade was found to start with an easy direct hydrogenolysis of the Zr-C bond affording intermediate **I**, with a barrier of only 13.7 kcal/mol, corresponding to a fast reaction (Figure 2, left).[14]

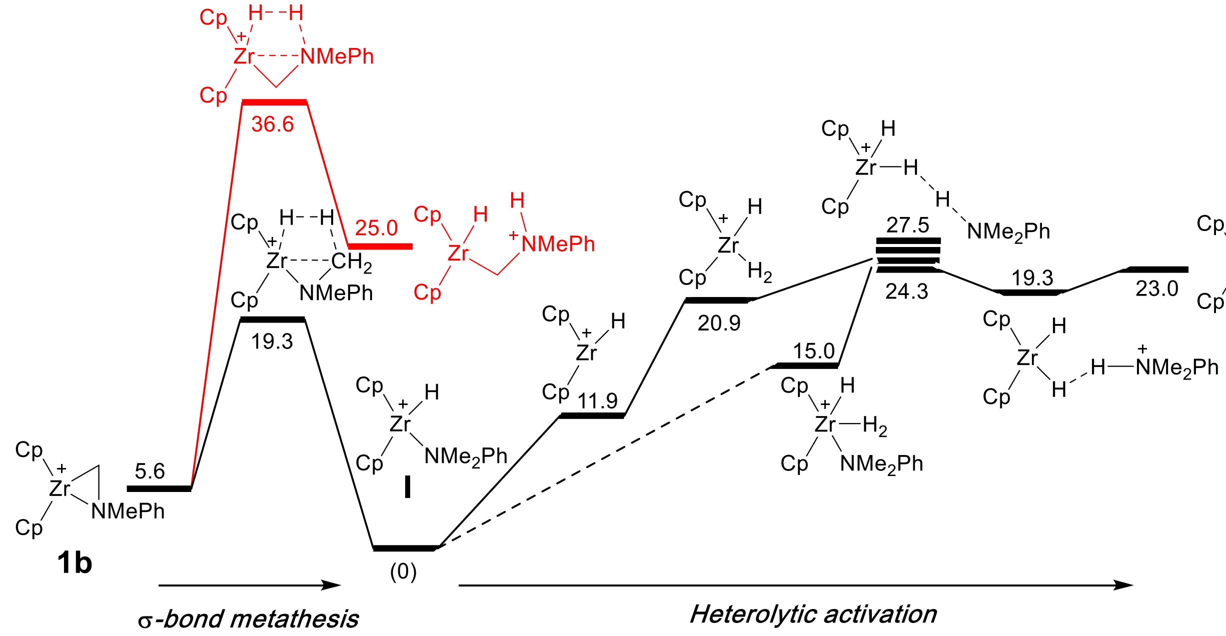


Figure 2 Free energy profile (kcal/mol) for the reaction of **1b** with H_2; the dashed line indicates a connection involving an additional transition state (not shown).

Hydrogenolysis of the Zr-N bond to give hydrido-ammonium is far more difficult: the calculated barrier of over 30 kcal/mol shows that this path is not competitive and confirms that **1b** is prevented from behaving as a FLP.

Heterolytic hydrogen activation is subsequently promoted by **I** as shown in the right side of Figure 2. There are in fact several transition states (we located at least 5) that are rather similar and have similar energies (within the band of 24-28 kcal/mol above **I**). They differ in the orientation of the amine moiety relative to the zirconocene fragment. Two of the lowest-energy ones are shown in Figure 3.

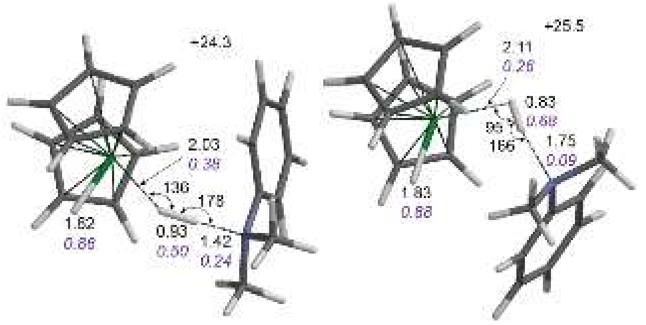


Figure 3. Two of the lowest-energy H_2 cleavage transition state. Distances in Å, angles in °, Wiberg bond indexes in purple and italics.

They all feature a near-linear N···H···H arrangement, a bent Zr···H···H geometry, and no direct Zr-amine interaction.[15] Below the level of these TSs, complex **I** can dissociate the amine or capture an H_2 molecule (between the hydride and amine positions); these are rapid pre-equilibria and hence kinetically irrelevant (Curtin-Hammett principle). Based on the above, this system differs from standard FLP systems as there is sufficient space for the amine to coordinate to the metal, and the adduct can even capture H_2. However, at the top of the cleavage barrier no Zr-amine interaction remains. The effective H_2 cleavage barrier is relatively high because, regardless of which specific TS is taken, complete Zr-amine dissociation is required.

Formation of the dihydride is highly endergonic so one would not expect it to be observable. However, reaction of the dihydride with $Cp_2ZrH(NMe_2Ph)^+$ to first form binuclear and then trinuclear species is exergonic (-1.1 kcal/mol overall), so the dihydride could be trapped by still-present $Cp_2ZrH(NMe_2Ph)^+$, eventually driving cluster formation to completion. Unfortunately, exploring actual reaction paths involving binuclear and trinuclear species was not feasible and so we only calculated the final product $Cp_6Zr_3H_4^{2+}$ and a few plausible binuclear species (see ESI).

The same reaction pathway has been investigated by replacing the aniline with NMe_3 in order to model the reaction with **1a**. The differences are rather modest. Hydrogenolysis of the zirconaziridine is calculated to be easier by ~2 kcal/mol, dissociation of amine from **I** is ~4 kcal/mol more difficult, and the H_2 cleavage barrier is ~3 kcal/mol higher, all due to the higher basicity of NMe_3 compared to $PhNMe_2$ (see ESI for details). These results suggest that formation of **2** should be slower with NMe_3 than with $PhNMe_2$ due to the stronger coordination of the former amine (16.9 vs 11.9 kcal/mol). This seems to disagree with the observed faster reaction obtained with **1a** vs **1b**. However, preliminary calculations show that $NMeEt_2$ - a better model for $NMe(C_6H_{13})_2$ than NMe_3 - binds to Zr by only 10.5 kcal/mol, i.e. more weakly than NMe_3 or even $PhNMe_2$, and this should translate directly into a lower H_2 cleavage barrier for **1a**.

The role of the Lewis basicity was also probed by calculating the energy profile for the hydrogenolysis of the phosphine complex $Cp_2ZrH(PMe_3)^+$. We find that, as in the NMe_3 case, heterolytic H_2 cleavage is considerably endergonic and formation of detectable amounts of Cp_2ZrH_2 is not to be expected. In addition, the calculated barrier for H-H cleavage is 31.5 kcal/mol, i.e. about 4 kcal/mol higher than for the NMe_3 case, suggesting that no H_2 activation would take place. This fits with early observations by Jordan on the hydrogenolysis of $Cp_2ZrMe(PMe_3)$ and $Cp_2ZrMe(PMe_3)_2$, for which only σ-bond metathesis of the Zr-Me group was observed .[16]

The picture emerging from DFT calculations indicates that H_2 splitting in this class of compounds is notably affected by the delicate balance between steric and electronic factors, and that it is made energetically feasible in this case only by the trapping of Cp_2ZrH_2 into the trimetallic **2**. To further validate this hypothesis, we computationally explored H_2 activation by $Cp_2Zr(OPh)(NMe_3)^+$, where the phenoxy substituent prevents the formation of any multinuclear species. In this case hydrogen activation by the aryloxide compound proceeds very similar to **I** with a somewhat higher H_2 cleavage barrier (28.2 vs 24.3 kcal/mol). However, the lack of trimerisation leaves the final product uphill and no H_2 activation by this system should be expected.

In summary, we have shown that zirconaziridinium ion pairs $[Cp_2Zr(\eta^2\text{-}CH_2NR_2][B(C_6F_5)_4]$ (**1**) react with H_2 undergoing a fast σ-bond metathesis of the Zr-C bond instead of the alternative Frustrated Lewis Pairs pathway. This reaction affords zirconocenium amino hydride complexes (**I**), which behave as FLPs and promote heterolytic H_2 splitting affording ammonium salts and the trimetallic zirconium hydride $[Cp_6Zr_3H_4][B(C_6F_5)_4]_2$ (**2**). The formation of **2** is fundamental in making the overall pathway energetically feasible, despite the fact that it could be seen as just a side reaction.

Our results show that steric frustration is not a prerequisite for heterolytic H_2 activation by $Zr\text{-}NR_3$ Lewis adducts. We demonstrate how H-H bond activation can occur in the continuum between pure FLP and strong Lewis interaction, reminiscent of the case of weakly interacting main group FLPs such as lutidine/$B(C_6F_5)_3$.[17] The delicate balance between steric and electronic factors notably affects the reactivity, to the point that stronger bases such as PR_3 are found computationally to shut down H_2 activation.

The involvement of d orbitals in the FLP reactivity scenario opens up unexpected and varied mechanistic pathways that can be potentially used as a toolbox for the design of novel systems with improved or novel catalytic activity. The implication of these concepts is currently under investigation in our laboratory.

We thank the European Research Council. MB is an ERC Advanced Investigator Award holder (grant no. 338944-GOCAT). LR is also thankful to University of East Anglia for support. AM thanks the University of Perugia and MIUR (AMIS, “Dipartimenti di Eccellenza – 2018-2022” program). We also thank the National Crystallographic Centre at the University of Southampton, U.K. for the measurement of the diffraction intensities.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 (a) K. Gruet, E. Clot, O. Eisenstein, D. H. Lee, B. Patel, A. Macchioni and R. H. Crabtree, *New. J. Chem.*, 2003, **27**, 80; (b) G. J. Kubas, *J. Organomet. Chem.*, 2014, **751**, 33.

2 (a) D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2015, **54**, 6400; (b) D. W. Stephan, *Acc. Chem. Res.*, 2015, **48**, 306; (c) D. W. Stephan, *J. Am. Chem. Soc.* 2015, **137**, 10018; (d) D. W. Stephan, *Science*, 2016, **354**, aaf7229.

3 (a) S. Arndt, M. Rudolph and A. S. K. Hashmi, *Gold Bull.*, 2017, **50**, 267; (b) J. Campos, *J. Am. Chem. Soc.*, 2017, **139**, 2944; (c) S. J. K. Forrest, J. Clifton, N. Fey, P. G. Pringle, H. A. Sparkes and D. F. Wass, *Angew. Chem. Int. Ed.*, 2015, **54**, 2223.

4 (a) R. C. Neu, E. Otten, A. Lough and D. W. Stephan, *Chem. Sci.*, 2011, **2**, 170; (b) A. M. Chapman, M. F. Haddow and D. F. Wass, *J. Am. Chem. Soc.*, 2011, **133**, 18463; (b) X. Xu, R. Fröhlich, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Commun.* 2012, **48**, 6109; (c) A. M. Chapman, M. F. Haddow and D. F. Wass, *Eur. J. Inorg. Chem.* 2012, **2012**, 1546; (c) X. Xu, G. Kehr, C. G. Daniliuc and G. Erker, *J. Am. Chem. Soc.*, 2013, **135**, 6465; (d) X. Xu, G. Kehr, C. G. Daniliuc and G. Erker, *J. Am. Chem. Soc.*, 2014, **136**, 12431; (e) A. T. Normand, C. G. Daniliuc, B. Wibbeling, G. Kehr, P. Le Gendre and G. Erker, *J. Am. Chem. Soc.*, 2015, **137**, 10796; (f) O. J. Metters, S. J. K. Forrest, H. A. Sparkes, I. Manners and D. F. Wass, *J. Am. Chem. Soc.*, 2016, **138**, 1994; (g) O. J. Metters, S. R. Flynn, C. K. Dowds, H. A. Sparkes, I. Manners and D. F. Wass, *ACS Catal.*, 2016, **6**, 6601.

5 (a) H. B. Hamilton, A. M. King, H. A. Sparkes, N. E. Pidmore and D. F. Wass, *Inorg. Chem.*, 2019, **58**, 6399; (b) X. Xu, G. Kehr, C. G. Daniliuc and G. Erker, *J. Am. Chem. Soc.*, 2015, **137**, 4550;

6 (a) L. Rocchigiani, C. Zuccaccia, D. Zuccaccia and A. Macchioni, *Chem. Eur. J.* 2008, **14**, 6589; (b) L. Rocchigiani, G. Bellachioma, G. Ciancaleoni, A. Macchioni, D. Zuccaccia and C. Zuccaccia, *Organometallics*, 2011, **30**, 100; (c) L. Rocchigiani, G. Ciancaleoni, C. Zuccaccia and A. Macchioni, *Angew. Chem. Int. Ed.*, 2011, **50**, 11752; (d) L. Rocchigiani, G. Ciancaleoni, C. Zuccaccia and A. Macchioni, *ChemCatChem*, 2013, **5**, 519.

7 (a) L. Rocchigiani, A. Macchioni and C. Zuccaccia, *Organometallics*, 2012, **31**, 4076; (b) K. Plössl, J. R. Norton, J. G. Davidson and E. K. Barefield, *Organometallics*, 1992, **11**, 534.

8 (a) R. F. Jordan and D. F. Taylor, *J. Am. Chem. Soc.*, 1989, **111**, 778; (b) R. Waterman, *Organometallics*, 2013, **32**, 7249.

9 Z. Jian, C. G. Daniliuc, G. Kehr and G. Erker, *Organometallics*, 2017, **36**, 424.

10 Similar anionic M_3H_4 species have been reported with M= Er, Lu or Y, see (a) W. J. Evans, J. H. Meadows, A. L. Wayda, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc.*, 1982, **104**, 2015; (b) W. J. Evans, J. H. Meadows and T. P. Hanusa, *J. Am. Chem. Soc.*, 1984, **106**, 4454.

11 For a mixed-valence $[Zr_3H_5]$ neutral core see: P. J. Chirik, L. M. Henling and J. E. Bercaw, *Organometallics*, 2001, **20**, 534.

12 For a cationic $[Zr_3H_3]$ core structure see: A. G. Carr, D. M. Dawson, M. Thornton-Pett and M. Bochmann, *Organometallics*, 1999, **18**, 2933.

13 Aniline/anilinium exchange is fast also at low temperature and no decoalescence is observed at -50 °C in CD_2Cl_2.

14 H. H. Brintzinger, *J. Organomet. Chem.*, 1978, **171**, 337.

15 T. A. Rokob, A. Bakó, A. Stirling, A. Hamza and I. Pápai, *J. Am. Chem. Soc.,* 2013, **1315**, 4425.

16 R. F. Jordan, C. S. Bajgur, W. E. Dasher and A. L. Rheingold, *Organometallics,* 1987, **6**, 1041.

17 S. J. Geyer and D. W. Stephan, *J. Am. Chem. Soc.,* **2009**, *131*, 3476.