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DOI: 10.1039/c6cc05445e www.rsc.org/chemcomm Two-coordinate terminal zinc hydride complexes: synthesis, structure and preliminary reactivity studies<sup>†</sup>

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The first examples of essentially two-coordinate, monomeric zinc hydride complexes, LZnH (L =  $-N(Ar)(SiR_3)$ ) (Ar =  $C_6H_2\{C(H)Ph_2\}_2R'-$ 2,6,4; R = Me, R' =  $Pr^i$  (L'); R =  $Pr^i$ , R' = Me (L\*); R =  $Pr^i$ , R' =  $Pr^i$  (L<sup>+</sup>)) have been prepared and shown by crystallographic studies to have near linear N–Zn–H fragments. The results of computational studies imply that any Ph...Zn interactions in the compounds are weak at best. Preliminary reactivity studies reveal the compounds to be effective for the stoichiometric hydrozincation and catalytic hydrosilylation of carbonyl compounds.

A key area of study in the field of main group/post transition metal organometallic chemistry is the realisation of catalytic regimes which achieve synthetic transformations normally the preserve of expensive and toxic heavy transition metal systems.<sup>1</sup> Within this realm, terminal zinc hydride complexes are emerging as both novel synthetic targets, and as efficient catalysts for a variety of processes. These processes include the hydrosilylation or hydrogenation of unsaturated substrates (e.g. CO2, ketones, aldehydes, imines and nitriles), and the alcoholysis of silanes.<sup>2</sup> Several mechanistic pathways have been proposed for these transformations, which involve, for example, the Zn-H moiety participating in substrate insertion/ $\sigma$ -bond metathesis chemistry, or the Lewis acid activation of substrate or silane.<sup>2e</sup> All of these pathways are reliant on the electrophilicity of the zinc centre of the catalyst, which suggests that lower coordinate terminal zinc hydride complexes maybe more catalytically active than currently available three- and higher coordinate systems, e.g. 1-4 (Fig. 1).<sup>2</sup>

Clearly, in order to access monomeric, two-coordinate zinc hydride complexes of the type, LZnH, sterically bulky monodentate anionic ligands (L) would be required. However, such systems have

 $Mes^{N} \xrightarrow{N}_{A} N_{Mes} N_{H} \xrightarrow{N}_{H} Mes^{N} \xrightarrow{N}_{H} Mes^{N} \xrightarrow{N}_{H} Mes^{N} \xrightarrow{N}_{H} Mes^{N} \xrightarrow{N}_{H} Mes^{N} \xrightarrow{N}_{H} \xrightarrow{N}_{H} Mes^{N} \xrightarrow{N}_{H} \xrightarrow{N$ 

Fig. 1 Examples of catalytically active terminal zinc hydride complexes (Dip = 2,6-diisopropylphenyl, Mes = mesityl, Py = 2-pyridyl).

not been observed to date, even when extremely bulky ligands at zinc are employed. A case in point here are Power's terphenyl substituted zinc hydrides, e.g.  $\{Ar'Zn(\mu-H)\}_2$   $(Ar' = C_6H_3(C_6H_3Pr_2^i)^2$ 2,6)<sub>2</sub>-2,6), which exist as three-coordinate hydride bridged dimers in the solid state.<sup>3</sup> It occurred to us that we might be able to circumvent dimerisation of related LZnH units by incorporation of "super bulky" amide ligands, e.g. -N(Ar)(SiR<sub>3</sub>) (Ar =  $C_6H_2\{C(H)Ph_2\}_2R'-2,6,4; R = Me, R' = Pr^i(L'); R = Pr^i, R' = Me$ (L\*);  $R = Pr^{i}$ ,  $R' = Pr^{i}$  (L<sup>†</sup>)) developed in our group.<sup>4</sup> In this respect, we have shown these amides to be more sterically imposing than substituted terphenyl ligands, and have successfully utilised them for the kinetic stabilisation of an array of unprecedented low-coordinate s-, p- and d-block metal-metal bonded systems,<sup>5</sup> and p-block metal hydride complexes.<sup>6</sup> Most relevant to this study are the recently reported zinc(I) dimers and mixed valence tri-zinc systems, LZn–ZnL and LZn–Zn–ZnL (L = bulky amide), which were shown to be devoid of bridging hydride ligands.<sup>5b</sup> Here we report the first examples of essentially twocoordinate, monomeric zinc hydride complexes, and describe preliminary investigations into their use for the stoichiometric and catalytic transformation of carbonyl compounds.

Initial attempts to prepare zinc hydride complexes involved treatment of amido zinc alkyls with silanes or boranes, though this route ultimately proved unsuccessful.<sup>7</sup> Subsequently, three

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previously reported amido zinc bromide compounds were reacted with an excess of NaH, which led to good isolated yields of the monomeric, terminal zinc hydride complexes, 5-7, upon work-up (Scheme 1).<sup>8,9</sup> Given this result, and considering that there is only one structurally authenticated example of a terminal cadmium hydride complex,<sup>3</sup> and no reports of terminal mercury hydrides, the heavier group 12 iodide compounds, L'CdI and L\*HgI, were treated with excess NaH. However, these reactions led to deposition of the metal involved and formation of the secondary amines, L'H or L\*H at ambient temperature. The same products resulted from the reactions of L'CdI and L\*HgI with K[HBEt<sub>3</sub>] at -30 °C, but small amounts of the known metal(1) dimers, L'CdCdL' and L\*HgHgL\*, were also isolated.<sup>5b</sup> These dimers probably result from intermediate metal hydrides, L'CdH and L\*HgH, which are unstable to loss of H2 under the reaction conditions employed (cf. higher thermal stability of zinc hydride complexes). It is of note that the formation of group 12 metal(I) dimers *via* metal(II) hydride complexes has precedent in the literature.<sup>3</sup>

The zinc hydride complexes 5–7 are all colourless crystalline solids that are stable to temperatures in excess of 180 °C in the solid state. The simplicity of their NMR spectra suggest they possess time averaged  $C_s$  symmetry in solution at 20 °C, with the mirror plane including the SiCNZnH moiety. Interestingly, their <sup>1</sup>H NMR spectra all exhibit similar zinc hydride resonance chemical shifts ( $\delta = 1.85$ –1.87 ppm) that, to the best of our knowledge, are at higher field than those for any previously reported terminal zinc hydride complex (*e.g.* 1  $\delta = 4.39$  ppm;<sup>2i</sup> 2  $\delta = 5.60$  ppm<sup>2h</sup>). Compounds 5–7 display Zn–H stretching bands in their infrared spectra that lie at similar frequencies ( $\nu = 1892$ –1901 cm<sup>-1</sup>), and which are at markedly higher wavenumbers than found for all other terminal zinc hydrides, (*e.g.* 2  $\nu = 1729$  cm<sup>-1</sup>,<sup>2h</sup> 3  $\nu = 1734$  cm<sup>-12f</sup>). This is as would be expected for two-coordinate species.

X-ray crystal structures of 5 and 7 were obtained, and these showed the complexes to be essentially isostructural (see Fig. 2 for the molecular structure of 5).<sup>10</sup> The hydride ligands of the compounds were located from difference maps and refined isotropically. The Zn–H distance in 7 (1.50(5) Å) lies within the



Fig. 2 Molecular structure of **5** (25% thermal ellipsoids; hydrogen atoms, except H(1), omitted).

range observed for reported terminal zinc hydride complexes,<sup>11</sup> and is close to the sum of the covalent radii for Zn and H (1.53 Å).<sup>12</sup> Although the Zn–H distance for 5 was restrained, the N-Zn-H angles for both complexes were freely refined. This revealed them to be close to linear (5  $171(2)^{\circ}$ , 7  $167(2)^{\circ}$ ; cf.  $126.2(1)^{\circ}$  for three-coordinate  $ZnH{N(SiMe_3)_2}(IPr)$ , IPr = $C{N(C_6H_3Pr_2^i-2,6)}_2^{2c}$ , which provides further evidence for the essentially two-coordinate nature of the compounds (cf. linear H-Zn-H<sup>13</sup>). Moreover, there are no C<sub>Ph</sub>···Zn separations in either compound that are <2.95 Å (N.B.  $\sum$  covalent radii for C and Zn = 1.95  $Å^{12}$ ), though the large steric bulk of the amide ligand is the likely cause of the slight deviations from linearity for the N-Zn-H fragments. In contrast, the presumably more Lewis acidic Zn centres in the precursor complexes, L\*ZnBr and  $L^{\dagger}ZnBr$ , lead to weak  $C_{Ph} \cdots Zn$  interactions (closest *ca.* 2.85 Å) and narrower angles at the metal centre (*ca.*  $159^{\circ}$ ).<sup>5b</sup> Importantly, the structural characterisation of monomeric 5 and 7 confirms the absence of any bridging hydride ligands in our previously reported zinc(1) dimers, *e.g.* L\*ZnZnL\*.<sup>5b</sup>

In order to probe the electronic structure of 5-7, dispersion corrected DFT calculations (wB97XD, see ESI† for computational details) were carried out on 5 in the gas phase (i.e. 5'). The geometry of the compound optimised to be very similar to that seen in the crystal structure of 5, while an natural population analysis (NPA) revealed considerable charge separation over the NZnH fragment (N -1.42, Zn 1.05, H -0.43). While the HOMO and LUMO of the compound are largely ligand based, the HOMO-11 and HOMO-64 show character corresponding to the Zn-H bond, and a N  $\rightarrow$  Zn  $\pi$ -bonding interaction, of the compound, respectively (Fig. 3). Furthermore, the LUMO+15, predominantly comprises an empty p-orbital at the Zn-centre. No filled MO could be found that exhibited significant C<sub>Ph</sub>···Zn bonding character, which is consistent with our description of the compound as being essentially two-coordinate. It is also interesting to note that the calculated hydride chemical shift  $(\delta = 1.03 \text{ ppm})$  and Zn–H stretching frequency ( $\nu = 1980 \text{ cm}^{-1}$ ) for 5' are not dissimilar to the experimental values for 5–7, which adds weight to the validity of the assignment of the unprecedentedly high field and high wavenumber values for the latter.

So as to investigate the reactivity of the two-coordinate zinc hydride complexes towards unsaturated substrates, compound 5



Fig. 3 (a) HOMO-11, (b) HOMO-64 and (c) LUMO+15 of  ${\bf 5}^{\prime}.$ 

was initially reacted with stoichiometric amounts of benzaldehyde or trifluoroacetophenone in a J. Young's NMR tube. These reactions were complete within seconds under ambient conditions, and NMR analyses of the resultant mixtures showed near quantitative conversions to L'Zn(OCH<sub>2</sub>Ph) and L'Zn{OCH(Ph)(CF<sub>3</sub>)}, respectively. It is of note that a single crystal of {L'Zn(O = CHPh)( $\mu$ -OCH<sub>2</sub>Ph)}<sub>2</sub> was isolated from the former reaction and found to be a benzaldehyde coordinated, alkoxide bridged dimer, as determined by an X-ray crystallographic analysis (see ESI†). This compound presumably formed due to the presence of a slight excess of benzaldehyde in the reaction.

With a view to test our proposal that 5–7 should be more catalytically competent than their higher coordinate counterparts, comparisons of the activity of 7 (5 mol%) and **1** (3 mol%)<sup>2e</sup> towards the hydrosilylation of benzaldehyde and acetophenone, using triethoxysilane, were carried out. While moderate yields of the expected silylether products were obtained (47% and 75% respectively) using 7 as a catalyst, higher yields were previously reported for highly active **1** (*viz.* >98% and 84% respectively).<sup>2e</sup> Moreover, catalytic transformations using **1** were more rapid than those employing 7, presumably because intermediates in the catalytic cycle involving the latter system showed considerable decomposition during the catalytic runs (see ESI† for full details). Similar results were obtained for the hydroboration of the same substrates using HBpin and 7 (5 mol%).

In conclusion, the first examples of essentially two-coordinate zinc hydride complexes have been prepared and shown by crystallographic studies to have near linear N–Zn–H fragments. The results of computational studies imply that any Ph…Zn interactions in the compounds are weak at best, thus confirming the low-coordinate nature of these species. Preliminary reactivity studies revealed the compounds to be very active towards the hydrozincation of aldehydes and ketones. However, when used as catalysts for the hydro-silylation of the same substrate classes, the limited stability of the zinc hydrides under the reaction conditions employed has so far limited their catalytic potential. We are currently developing more robust two-coordinate zinc hydride complexes, and will report on our efforts in this direction in due course.

## Notes and references

- See for example (a) P. P. Power, Nature, 2010, 463, 171; (b) M. Asay,
  C. Jones and M. Driess, Chem. Rev., 2011, 111, 354; (c) Catalysis Without Precious Metals, ed. R. M. Bullock, Wiley, New York, 2010;
   (d) K. Revunova and G. I. Nikonov, Dalton Trans., 2015, 44, 840.
- Selected recent examples (a) A. Kreider-Mueller, P. J. Quinlivan, M. Rauch, J. S. Owen and G. Parkin, Chem. Commun., 2016, 52, 2358; (b) W. Sattler, S. Ruccolo, M. R. Chaijan, T. N. Allah and G. Parkin, Organometallics, 2015, 34, 4717; (c) A. J. Roberts, W. Clegg, A. R. Kennedy, M. R. Probert, S. D. Robertson and E. Hevia, Dalton Trans., 2015, 44, 8169; (d) P. A. Lummis, M. R. Momeni, M. W. Lui, R. McDonald, M. J. Ferguson, M. Miskolzie, A. Brown and E. Rivard, Angew. Chem., Int. Ed., 2014, 53, 9347; (e) C. Boone, I. Korobkov and G. I. Nikonov, ACS Catal., 2013, 3, 2336; (f) P. Jochmann and D. W. Stephan, Angew. Chem., Int. Ed., 2013, 52, 9831; (g) A. Rit, T. P. Spaniol, L. Maron and J. Okuda, Angew. Chem., Int. Ed., 2013, 52, 4664; (h) W. Sattler and G. Parkin, J. Am. Chem. Soc., 2011, 133, 9708; (i) J. Spielmann, D. Piesik, B. Wittkamp, G. Jansen and S. Harder, Chem. Commun., 2009, 3455.
- 3 Z. Zhu, M. Brynda, R. J. Wright, R. C. Fischer, W. A. Merrill, E. Rivard, R. Wolf, J. C. Fettinger, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2007, **129**, 10847.
- 4 (a) E. W. Y. Wong, D. Dange, L. Fohlmeister, T. J. Hadlington and C. Jones, Aust. J. Chem., 2013, 66, 1144; (b) J. Hicks, T. J. Hadlington, C. Schenk, J. Li and C. Jones, Organometallics, 2013, 32, 323; (c) J. Li, A. Stasch, C. Schenk and C. Jones, Dalton Trans., 2011, 40, 10448.
- 5 See for example (a) A. J. Boutland, D. Dange, A. Stasch, L. Maron and C. Jones, Angew. Chem., Int. Ed., 2016, 55, 9239; (b) J. Hicks, E. J. Underhill, C. E. Kefalidis, L. Maron and C. Jones, Angew. Chem., Int. Ed., 2015, 54, 10000; (c) J. Hicks, C. E. Hoyer, B. Moubaraki, G. L. Manni, E. Carter, D. M. Murphy, K. S. Murray, L. Gagliardi and C. Jones, J. Am. Chem. Soc., 2014, 136, 5283; (d) T. J. Hadlington and C. Jones, Chem. Commun., 2014, 50, 2321; (e) T. J. Hadlington, M. Hermann, J. Li, G. Frenking and C. Jones, Angew. Chem., Int. Ed., 2013, 52, 10389; (f) J. Li, C. Schenk, C. Goedecke, G. Frenking and C. Jones, J. Am. Chem. Soc., 2011, 133, 18622.
- 6 See for example (a) T. J. Hadlington, B. Schwarze, E. I. Izorodina and C. Jones, *Chem. Commun.*, 2015, 51, 6854; (b) T. J. Hadlington, M. Hermann, G. Frenking and C. Jones, *J. Am. Chem. Soc.*, 2014, 136, 3028.
- 7 *N.B.* During the course of this work, the two-coordinate zinc alkyl,  $L''ZnEt (L'' = N(Ar){Si(OBu'_3)}, Ar = C_6H_2{C(H)Ph_2}_2Me-2,6,4)$  was spectroscopically and crystallographically characterised (see ESI† for details).
- 8 *N.B.* Two new amido-zinc bromide complexes, *viz.* L"ZnBr and (BoN)(Me<sub>3</sub>Si)NZnBr(THF) (BoN = B(DipNCH)<sub>2</sub>), were prepared and characterised (see ESI<sup>†</sup>), though their treatment with excess NaH led to intractable product mixtures.
- 9 N.B. During one preparation of L\*ZnH, several crystals of {L\*Zn(μ-OH)}<sub>2</sub> were isolated and structurally characterised (see ESI<sup>†</sup>). The compound presumably arose due to traces of adventitious water in the reaction mixture.
- 10 *N.B.* The crystal structure of **6** was acquired, but the compound was shown to co-crystallise with small amounts (*ca.* 2%) of L\*ZnBr (see ESI<sup>†</sup>). Hence, no discussion on the geometry of the NZnH fragment of **6** is given here.
- 11 As determined from a survey of the Cambridge Crystallographic Database, June, 2016.
- B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan and S. Alvarez, *Dalton Trans.*, 2008, 2832.
- 13 S. Aldridge and A. J. Downs, Chem. Rev., 2001, 101, 3305.