A computational study of the reactions of a β-diketiminatoaluminium(I) complex with the hydrogen atom and the electron†

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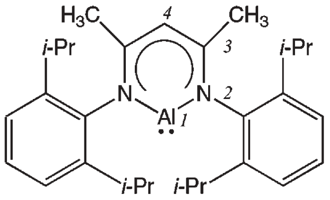
A computational study has been performed to examine the reactions of a model β-diketiminatoaluminium (I) complex with the hydrogen atom and with the electron. It was found that the hydrogen atom adds to the metal centre exothermically ($\Delta H_{rxn} = -202$ kJ mol^{-1}), and the spin density in the resulting radical resides entirely on the β-diketiminato ligand. The spin density of the corresponding radical anion is very similar to the H-adduct.

Recently there have been some exciting advances in the preparation of group 13 carbene analogues. Highlights include the gallium anion **[(DAB)Ga]**$^-$ (DAB = 1,4-diazabutadiene)[1] and, more recently, neutral gallium[2] and aluminium carbene analogues (**1**) have been reported.[3] These latter compounds are stabilised by the β-diketiminato ligand,[1,4] and the availability of a lone pair of electrons on the metal site has been illustrated by formation of donor–acceptor complexes.[5–7]



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Radicals of the Group 13 elements have attracted attention due to their unusual structural, spectral, and reactive properties.[8,9] A recent report described the syntheses of several aluminium containing cyclopropene analogues, and their formation was suggested to involve a novel tricoordinate aluminium radical **[1-I]**$^\bullet$.[10] Although not detected spectroscopically, evidence for the existence of **[1-I]**$^\bullet$ was provided using elegant trapping experiments.

Our interest in the reactivity of nucleophilic carbenes, specifically the imidazol-2-ylidenes[11] has led us to study the reactivity of carbenes with simple reagents, including radicals. Recently we performed an extensive computational study on the addition chemistry of imidazol-2-ylidenes and hydrogen atoms. Furthermore, we experimentally confirmed our computational studies using muonium (Mu), which can be viewed as a "light isotope" of hydrogen. The results of this study[12] indicate that the hydrogen atom adds exothermically to the carbeneic site of imidazol-2-ylidenes with almost no barrier to reaction, to produce a pyramidal carbon centred radical. Recently there has been an EPR and computational study of the addition of several free radicals to N-heterocyclic silylenes.[13] The relationship between imidazol-2-ylidenes and compounds such as **1** has led us to examine the chemistry of low valent aluminium compounds with hydrogen atoms and we note that Reiher and Sundermann have studied the reaction of a model aluminium carbene analogue with nucleophilic and electrophilic reagents as a way of understanding the chemistry of the parent compound.[14] Studying the reaction of these species with a radical is a way to probe the structure of the parent compound using experimentally measurable quantities (hyperfine coupling constants). The reactions of formally aluminium(I) compounds with hydrogen atoms are of fundamental importance due to the importance of aluminium hydrides in synthetic organic chemistry and materials chemistry. Here we report the results of a computational study of the reactions between **2**, a somewhat simplified model compound of **1**, and the hydrogen atom and the electron.

Aluminocarbene **2** has four possible sites where atomic hydrogen atom could add. As shown in Fig. 1, four reactions of **2** with the hydrogen atom were examined.‡ These studies show that reaction at all four likely sites proceeds exothermically, with the most stable isomer resulting from the addition of the hydrogen atom to the aluminium atom, thus supporting the postulated existence of **[1-I]**$^\bullet$ as an intermediate in the syntheses mentioned earlier. Addition of a hydrogen atom to the aluminium centre is exothermic by *ca.* 200 kJ mol^{-1} , whereas addition to the ligand sites occurs less exothermically. Addition of a hydrogen atom to imidazol-2-ylidenes is also exothermic by 180 kJ mol^{-1}, thus providing an example of the parallel reactivity between the group 13 carbene analogue **1** and the related imidazol-2-ylidenes.

The calculated ring parameters for **2** are close to those experimentally determined by X-ray crystallography for **1**.[3] Significant structural changes occur upon addition of the hydrogen

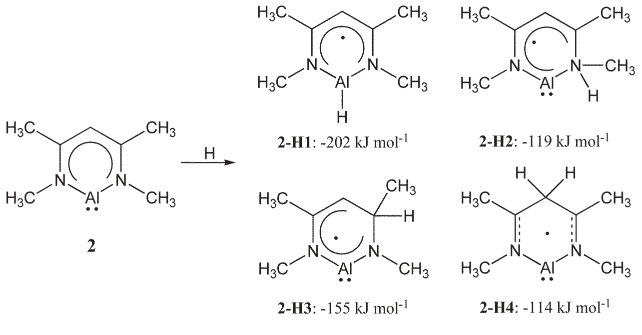

Fig. 1 Possible sites of hydrogen atom addition to **2** and calculated heats of formation (UB3LYP/6-31G++(d,p)).

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† Electronic supplementary information (ESI) available: calculated atomic coordinates. See http://www.rsc.org/suppdata/cc/b4/b414665d/

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Table 1 Computed bond lengths (Å) and bond angles (°) of **2**, **[2-H1]**$^{\bullet}$ and **[2]**$^{\bullet -}$ calculated at the UB3LYP/6-31++G(d,p) level of theory, compared with X-ray data for **1** (ref. 3).

	1	2	[2-H1]$^{\bullet}$	[2]$^{\bullet -}$
Al_1–N_2	1.957(2)	1.989	1.798	1.924
N_2–C_3	1.341(3)	1.338	1.422	1.396
C_3–C_4	1.391(3)	1.406	1.402	1.403
Al_1–H	—	—	1.572	—
N_2–Al_1–N_6	89.86(8)	90.6	109.2	95.7
Al_1–N_2–C_3	128.9(2)	128.1	117.8	125.6
N_2–C_3–C_4	122.8(2)	122.9	121.7	121.8
C_3–C_4–C_5	126.8(2)	127.3	131.7	129.4
H–Al_1–N_2	—	—	125.4	—

atom to form **[2-H1]**$^{\bullet}$, the most significant being the geometry around the aluminium centre which is now trigonal planar (Σ angles = 360°). This is in contrast to hydrogen atom addition to an imidazol-2-ylidene, which exhibits pyramidal geometry upon addition to the carbeneic site. There is also significant shortening (0.191 Å) of the Al_1–N_2 bond upon addition of the hydrogen atom to **2**. This structural modification is consistent with a decrease in the antibonding character of the Al–N bonds upon transformation of the formal lone pair on aluminium to an Al–H bond pair and conversion of an Al(I) site to an Al(III) site. The largest modification of the β-diketiminato ring is observed for the N_2–C_3 distance, which is 1.338 Å in **2** whereas for **[2-H1]**$^{\bullet}$ it is 1.422 Å. Analogous to the reactivity of imidazol-2-ylidenes with hydrogen atoms, there is a significant widening of the N–Al–N angle upon an increase of coordination number at the aluminium site. Clearly the trigonal planar geometry around the aluminium centre, and the structural modifications of the β-diketiminato ring do not suggest an aluminium centred radical, but one in which the electron resides on the ligand (*vide infra*). Taken in concert, the structural parameters for the aluminium centre are consistent with oxidation of the metal to aluminium(III), and reduction of the ligand to a formal charge of −2. Indeed, N_2–C_3 bond lengthening is consistent with this assessment as suggested by an examination of the partial MO diagram for the β-diketiminato ligand,[4] and recent structures of doubly reduced β-diketimates are in accord with our calculations.[15]

In order to confirm our postulate that the β-diketiminato ligand is redox active, we studied the single electron reduction of **2** in order to identify the structural changes that occur upon addition of an electron to **2** *without* modifying the coordination geometry at the aluminium centre. Most noticeable is the modest shortening of the Al–N bond length and minimal widening of the N–Al–N angle, whereas the prominent structural modification is lengthening of the N–C bond to 1.396 Å. This change is again consistent with the reduction of the ligand. The spin density for **[2]**$^{\bullet -}$ has also been determined, and it is, in broad terms, similar to that determined for **[2-H1]**$^{\bullet}$**.** The spin density for both named compounds is ligand centred, reminiscent of previously reported aluminium containing radicals, particularly **Al(dbdab)$_2$**, dbdab = 1,4-di-*tert*-butyl-1,4-diazabutadiene.[16] The unpaired spin density distributions for **[2-H1]**$^{\bullet}$ and **[2]**$^{\bullet -}$ are depicted in Fig. 2 and it is evident that the unpaired spin density in both radicals is located entirely on the β-diketiminato ligand.

The lack of unpaired electron spin density on the hydrogen atom prevents us from experimentally confirming these results using μSR techniques, but the results are nonetheless informative.

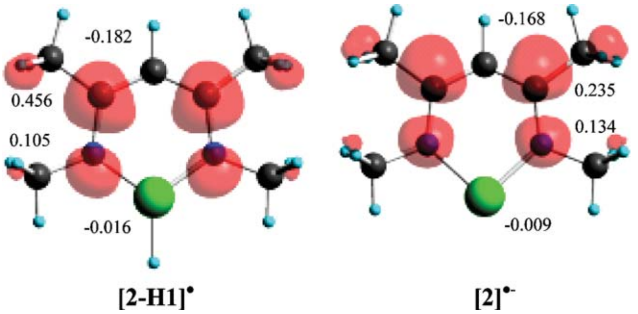

Fig. 2 Optimised geometries (UB3LYP/EPR-III for H,C,N and 6-31++G(d,p) for Al) and spin density plots (UB3LYP/EPR-III) for [2-H1]$^{\bullet}$ and [2]$^{\bullet -}$. The numbers refer to the total unpaired spin density on the atoms in the six-membered ring.

We note the implications of this study with respect to the ligand behaviour of the β-diketiminato ligand in transition metal complexes, and also for the behaviour of this ligand in general. Whereas the imidazol-2-ylidenes act as strong electron pair donors and poor π-electron acceptors, ligands such as **1** can also donate an electron pair; however their π-acceptor properties will be superior to imidazol-2-ylidenes. This transfer will be primarily reflected in the N_2–C_3 bond lengths, with significant lengthening suggesting transfer of electron density. The observation of the β-diketiminato ligand as being redox active portends exciting possibilities for oxidation/reduction addition/elimination chemistry of β-diketiminato complexes, and this is consistent with its recent use in numerous catalytic systems.

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Notes and references

‡ Geometries were calculated using the B3LYP functional[17] with the Gaussian 98 package of programs.[18] The structures were optimised using the 6-31G++(d,p) basis set, and the magnetic properties were calculated using the B3LYP functional with the EPR-III basis set for the C, H and N atoms and the 6-31G++(d,p) basis set for the Al atom.

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