Electronic Structure and Reactivity of Low-Valent Aluminium Compounds

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Low-valent main group compounds hold promise as potential mimics of transition metal catalysts, offering potential advantages in terms of sustainability, cost-effectiveness, and environmental impact. To date, a large number of low-valent compounds have been successfully stabilised, including multiple-bonded and anionic species, many of which have challenged our understanding of bonding.[1] Their unique electronic properties facilitate activation of strong bonds, and within this sphere, the activation of E–H bonds (E = H, B, C, N etc.) by low-valent aluminium(I) carbene analogues has become a focal point of current research effort.[2] For example, H_2 bond cleavage is not only a critical reaction relevant to an enormous range of catalytic processes, but also a fundamental transformation that is used as to benchmark the reactivity profiles of novel systems in small molecule activation. Details of the underlying reaction mechanism often remain contentious and poorly understood. As such, the elucidation of novel pathways for the activation of H_2 is of widespread importance to scientists with interests as diverse as catalysis, organic/inorganic synthesis, and even energy storage.

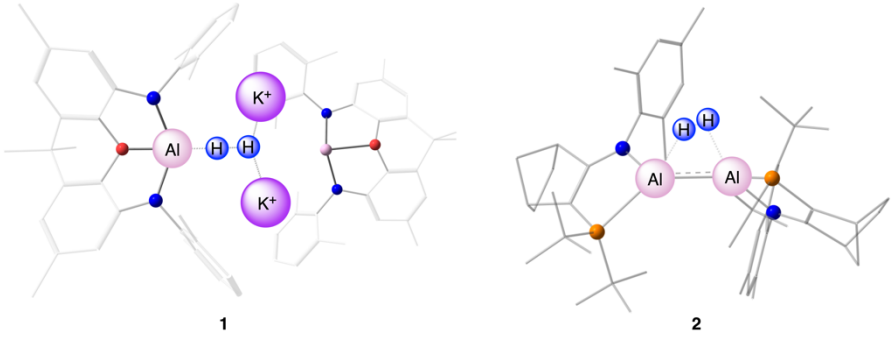

Figure 1. Activation of hydrogen by low-valent Al(I) complexes **1** and **2**.

Combining quantum chemical and experimental studies, we have probed the mechanism for H_2 activation by two different Al(I) complexes, i.e. the K^+-stabilised contacted dimer pair [K{Al(NON)}]$_2$ (**1**, Figure 1)[3] and amidophophine-stabilised dialumene (**2**).[4,5] We propose two new mechanistic pathways for these systems that directly contradict currently accepted classical models of single centre reactivity for carbene-like Al(I) species, with wider significance for the catalytic application of Al(I) complexes in E-H bond activation.[6,7]

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