

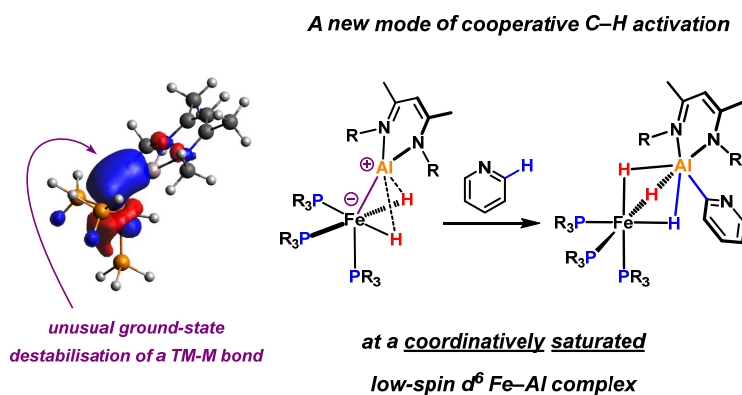
COOPERATIVE C–H BOND ACTIVATION BY A LOW-SPIN d^6 IRON–ALUMINIUM COMPLEX

Nikolaus Gorgas^{a,b}, Andrew J. P. White^b, and Mark R. Crimmin^b

^aInstitute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9, 1060 Vienna, Austria

^bDepartment of Chemistry, Imperial College London, London, W12 0BZ, UK

The reactions of transition metal complexes underpin numerous synthetic processes and catalytic transformations. Typically, this reactivity involves the participation of empty and filled molecular orbitals centred on the transition metal. Kinetically stabilised species, such as octahedral low-spin d^6 transition metal complexes, are not expected to participate directly in these reactions. However, novel approaches that exploit metal ligand-cooperativity offer an opportunity to challenge these preconceptions. Here we show that inclusion of an aluminium-based ligand into the coordination sphere of neutral low-spin d^6 iron complex leads to unexpected reactivity.[1-3] Complexes featuring an unsupported Fe–Al bond are capable of the intermolecular C–H bond activation of pyridines.[1,2] Mechanistic analysis suggests that C–H activation proceeds through a reductive deprotonation in which the two metal centres (Fe and Al) act like a frustrated Lewis-pair. Key to this behaviour is a ground state destabilisation of the d^6 iron complex, brought about by the inclusion of the electropositive aluminium-based ligand. These findings have immediate implications for the design of reagents and catalysts based on 1st row transition metals.



[1] N. Gorgas, A. J. P. White and M. R. Crimmin, *J. Am. Chem. Soc.*, 2022, **144**, 8770–8777.

[2] N. Gorgas, A. J. P. White and M. R. Crimmin, *Chem. Commun.* 2022, **58**, 10849–10852.

[3] B. Stadler, N. Gorgas, A. J. P. White and M. R. Crimmin, *Angew. Chem. Int. Ed.* 2023, **in press**, doi: 10.1002/anie.202219212