

Alkane Dehydrogenation: α,β -Double C-H Bond Activation of Ethane and Higher Alkanes by a Transient Titanium Alkylidyne

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Alkanes pose an important challenge to chemists because of their great abundance and remarkable stability, borne out of the strong C–H and C–C bonds, large HOMO-LUMO gap and pK_a , and their extraordinarily low binding affinities towards transition metals. Of particular interest is ethane, the second largest component of natural gas, because of its potential for being converted into more valuable C_2 compounds such as ethene. The transient titanium alkylidyne $(PNP)Ti\equiv C^tBu$ ($PNP^- = N[2-P^iPr_2-4\text{-methylphenyl}]_2^-$) has been previously shown to activate C–H bonds of unactivated aromatic and aliphatic substrates at room temperature by a 1,2-addition across the $Ti\equiv C$ linkage to form the corresponding $(PNP)Ti=CH^tBu(R)$ complex. This reactivity has now been extended to ethane which undergoes ambient-temperature CH-activation and then subsequent β -hydrogen abstraction by the adjacent alkylidene ligand to furnish an ethylene-adduct of titanium in high yield. Oxidation with N_2O or N_3R releases ethylene and gives quantitative conversion to the corresponding titanium oxo or imido, respectively. Details of this transformation, including structural elucidation by 1D and 2D NMR spectroscopy and single crystal X-ray diffraction are presented. Extension of this reactivity to linear alkanes as well as reactions of the titanium-ethylene adduct as a Ti^{II} synthon are also presented and discussed.