

# SYNTHESIS AND REACTIVITY OF WELL-DEFINED IMIDO TITANIUM ALKYL CATIONS: TI-R BOND INSERTION VS TI=NR CYCLOADDITION WITH UNSATURATED SUBSTRATES

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Mountford et al recently described the combinatorial synthesis and evaluation of two families of highly active imido-supported Ziegler-type ethylene polymerisation catalysts.<sup>1</sup> These catalysts are isolobal analogues of Group 4 metallocenes Cp<sub>2</sub>MCl<sub>2</sub> and are the most active of their type reported to date.<sup>2</sup> The catalytically active species in these systems are 14 valence electron alkyl cations such as [Ti(N<sup>t</sup>Bu)(TACN)Me]<sup>+</sup> (Figure 1: **1**<sup>+</sup>, TACN = trimethyltriazacyclononane).<sup>3</sup> The chemistry of imido-supported alkyl cations is virtually unexplored, and is particularly interesting since these highly electron-deficient compounds can in principle react at either the Ti-alkyl (*via* insertion) or Ti=NR (*via* cycloaddition) bonds.<sup>4</sup> In this presentation we describe a DFT mechanistic study of the reaction between the highly reactive imido titanium cation **1**<sup>+</sup> and a range of unsaturated substrates including carbodiimides, isocyanates and terminal and internal alkynes (Figure 1). The electronic preferences underlying their different reaction pathways (i.e. Ti-Me bond insertion vs Ti=NR bond cycloaddition) will be discussed theoretically. C-H bond activation and related products will be presented in the reaction of **1**<sup>+</sup> with PhCCH. The differences of reactivity between complexes **1**<sup>+</sup> and [Ti(N<sup>t</sup>Bu)(TACN)Cl]<sup>+</sup> will be also analyzed from a computational perspective. DFT optimized geometries and calculated NMR and infrared results are used to characterize reaction products and to explore Ti...H-C agostic interactions in some insertion complexes.

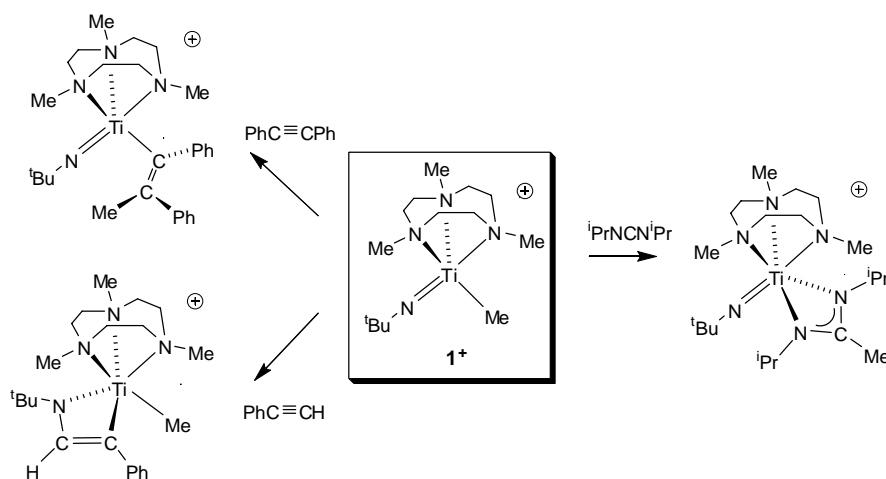


Figure 1. Selected reactions (Ti=N<sup>t</sup>Bu cycloaddition and Ti-Me insertion) of the 14 valence electron methyl cations [Ti(N<sup>t</sup>Bu)(TACN)Me]<sup>+</sup> (**1**<sup>+</sup>)

[1] Mountford, P. et al. *Chem. Commun.* **2004**, 434 and *Chem. Commun.* **2006**, 436.

[2] Bolton, P. D.; Mountford, P. *Adv. Synth. Catal.* **2005**, 347, 355.

[3] Bolton, P. D.; Clot, E.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2005**, 3313.

[4] Hazari, N.; Mountford, P. *Acc. Chem. Res.* **2005**, 38, 839.