Unexpected Reactivity of a Low Valent Titanocene with Azides.

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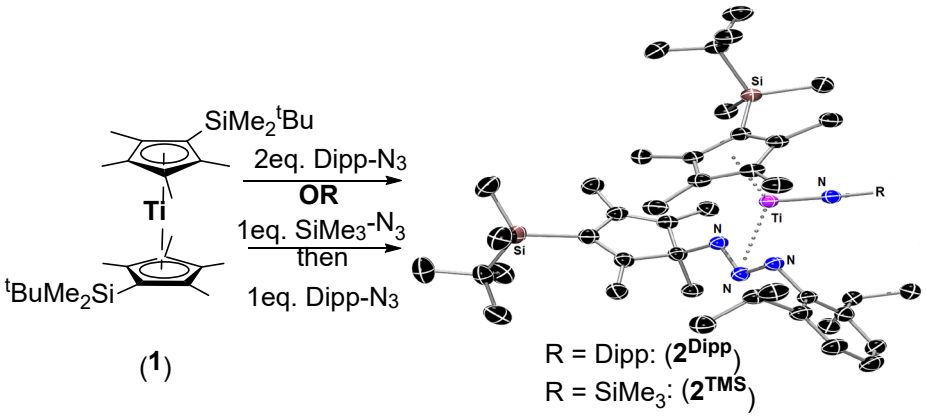
Metallocenes play a pivotal role in the development of organometallic chemistry [1], even after more than 70 years from the disclosure of ferrocene's structure [2]. Titanocenes in particular have been instrumental in understanding fundamental aspects of organometallic chemistry, leading to widespread applications such as olefin oligomerization/polymerization [3]. Of this important class of organometallic complexes, the first ever structurally authenticated Ti(II) complex [Ti(η^5-Cp^s)$_2$] (**1**) (Cp^s = [$C_5Me_4SiMe_2{}^tBu$]$^-$) [4] (Scheme 1) was an important development in the area, but its chemical reactivity has been barely explored. In this talk, we present our research efforts in expanding the chemistry of (**1**). During our investigations, we discovered that reaction of (**1**) with Dipp-N_3 (Dipp = 2,6-diisopropyl-phenyl) results in the formal insertion of one azide to a Ti-C(Cp^s) bond furnishing the Ti(IV) imido complex (**2^{Dipp}**) featuring a new triazenido ligand (Scheme 1). Computations suggest that the formation of (**2^{Dipp}**) proceeds *via* a Ti(IV) terminal imido complex, which has been confirmed experimentally by the synthesis of its congener (**2^{TMS}**) (Scheme 1). Detailed NMR studies show that (**2^{Dipp}**) & (**2^{TMS}**) display fluxional behavior in solution. Finally, the reactivity of (**1**) with other substrates will be presented to showcase its potential to induce reductive transformations.



Scheme 1: Reactivity of (**1**) with organic azides.

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