General Introduction

In recent years, the transition metal reagents are widely used in organic synthesis. Among the transition metal reagents that are used in their various oxidation states in organic synthesis, the titanium reagents are by far the most versatile. The applications of titanium reagents range from their use in achieving better selectivity of known organic transformations to the exploration of novel reactions.

Several titanium reagents have become indispensable in organic transformations. The use of TiCl₄ as Lewis acid is well-established chemistry of wide scope. The Ziegler-Natta catalysis using TiCl₄-AlEt₃, is an important polymerization process (eq 1).

Molecular nitrogen can be fixed under mild conditions using TiCl₄/RMgX or RLi, Cp₂TiCl₂/RMgX or RLi or LiAlH₄. Later, KOBu-t and sodium naphthalenide along with TiCu was used for the reduction of N₂ to NH₃. The titanium-nitrogen complex [TiNMg₂Cl₂·THF], prepared using TiCu-Mg under N₂, converts acid chlorides to primary amides (eq 2). More recently, it has been reported that TiCu, in alliance with Li/TMScI, mediates the nitrogen-fixation reactions (eq 3).
The low valent titanium species, generated by the reduction of TiCl$_4$ using metals and metal hydrides, have found numerous applications in deoxygenative reductive coupling of carbonyl compounds (e.g. McMurry reaction, eq 4).\textsuperscript{7}

The Cp$_2$TiCl$_2$ is a reagent of choice for many catalytic and stoichiometric reactions.\textsuperscript{8} In combination with (CH$_3$)$_3$Al (Tebbe reagent), it has been used for olefination of carbonyl compounds (eq 5).

The TiCl$_4$/CH$_2$Br$_2$/Zn reagent system is used in Wittig type olefination of carbonyl compounds (eq 6).\textsuperscript{9}

The Me$_2$TiCl$_2$ reagent (Reetz reagent) has been employed in gem-dimethylation of carbonyl compounds (eq 7).\textsuperscript{10}
Numerous reports indicate that the transmetalation of RLi or RMgX reagents with titanium reagents leads to better chemo-, regio-, and stereoselectivities.\textsuperscript{11} In recent years, there have been sustained efforts on the preparation and use of 1,2-diorganometallic reagents (eq 8).\textsuperscript{12, 13}

The Kulinkovich reaction involving organotitanium species is a useful reaction for the preparation of cyclopropyl derivatives (eq 9).\textsuperscript{14}

The Kulinkovich recipe Ti(OPr-i)\textsubscript{2}/i-PrMgX has been widely used in many synthetic transformations.\textsuperscript{15}

In continuation of our efforts on the preparation and use of ‘Cp\textsubscript{2}Ti\textsuperscript{12} and 1,2-diorganometallics prepared using TiCl\textsubscript{4}/Mg/BrCH\textsubscript{2}CH\textsubscript{2}Br,\textsuperscript{13} we have undertaken the present study, which deals with the development of reactive organotitanium
intermediates formed in the reaction of various organic substrates using the TiCl₄/R₃N reagent system.

References


