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# Titanium (IV) complex as catalyst to synthesize urea, thio-urea and guanidine

Well-defined organometallic complexes have played a pivotal role in homogeneous catalysis and in the development of environmentally benign processes. A number of transition and lanthanide metal complexes have already proven to be excellent catalysts in the formation of C-N bond via hydoamination reaction. Guanidine are commonly employed for several purposes. They can serve as building blocks in various pharmaceutical and natural products. They act as organic bases and catalyse various organic transformations.

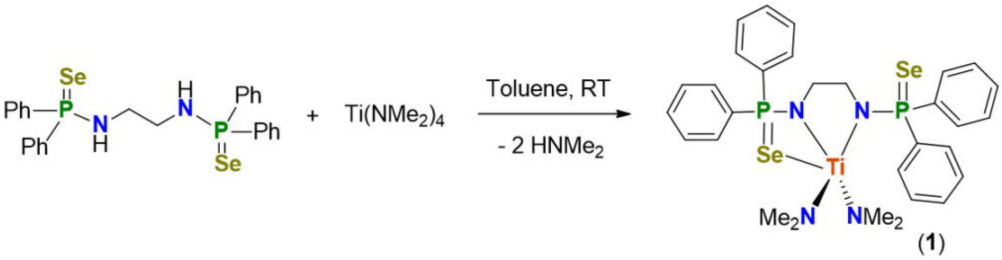


Fig. 1. Synthesis of titanium (IV) complex 1.

They are also used as ancillary ligands in the preparation of a variety of metal complexes including those of main, transition and lanthanides metals. Urea and thio-urea functional groups also perform significant roles in organic, medicinal, supramolecular, and material chemistry. Earlier, main group metal complexes, such as $LiN(SiMe_3)_2$, alkyl aluminium, $[Al(NMe_2)_3]_2$ and magnesium metal complexes and variety of transition metal complexes such as Zn and V imido complexes have been utilized for the synthesis of guanidine and urea. In addition, commercially available alkyl metal complexes $ZnEt_2$, $MgBu_2$, n-BuLi, $AlR_3$, and $Zn(OTf)_2$ have also been explored to be the efficient catalysts for this reaction. Titanium being the more abundant, in-expensive and relatively low toxic metal, can be potentially useful for this purpose. Further, its bio-affinity makes it suitable for innumerable applications in chemical synthesis.

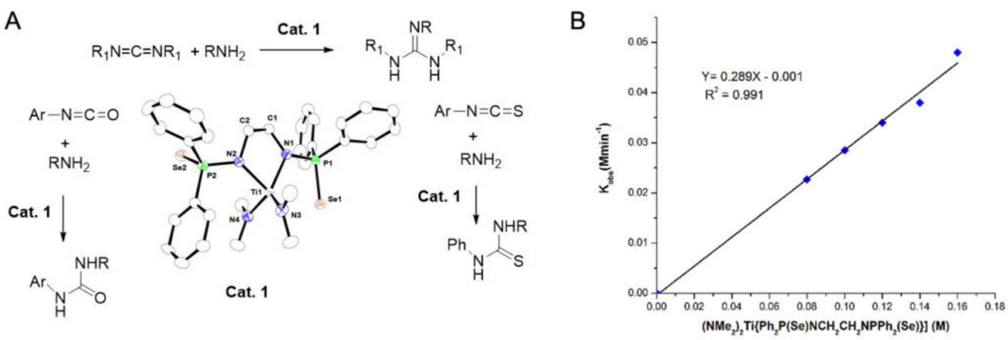


Fig. 2. A. Hydroamination of a number of amines with carbodiimides, isocyanates, and isothiocyanates using catalyst 1.
B. Plot of Kobs vs. [Catalyst 1)] for the reaction of constant concentration of 4-chlorophenylisocyanate and amine.

This triggered us to synthesize a tetra-dentate dianionic bis(phosphinoselenoic amide) ligand supported titanium(IV) complex [{Ph2P(Se)NCH2CH2NPPh2(Se)}M(NMe2)2] (**1**) and the solid state structure of this complex was confirmed through single crystal x-ray analysis (Fig. 1). We have employed the titanium complex **1** as a competent pre-catalyst for the hydroamination of a number of primary/secondary amines with carbodiimides, isocyanates, and isothiocyanates to give guanidine, urea and thio-urea respectively (Fig. 2A). Titanium complex **1** displayed high efficiency of conversion with an excellent tolerance toward several heteroatoms such as oxygen, sulphur and nitrogen, in addition to a number of functional groups like NO2, F, Cl and I, thus manifesting its versatility as a pre-catalyst for this reaction. The kinetic studies suggested that the amine addition reactions with isocyanates showed first order kinetics with respect to titanium catalyst **1**, amines and isocyanates (Fig. 2B). The most plausible mechanism of the hydroamination reaction was established by isolating 1,1 dimethylphenyl urea as side product. In conclusion, a bis(phosphinoselenoic amide) supported titanium(IV) complex acted as a competent pre-catalyst for the hydroamination of primary/secondary amines to carbodiimides, isocyanates, and isothiocyanates.

***Jayeeta Bhattacharjee, Tarun K Panda***
*Department of Chemistry, Indian Institute of Technology Hyderabad (IITH), Kandi, Telangana, India*

## Publication

Hydroamination of carbodiimides, isocyanates, and isothiocyanates by a bis(phosphinoselenoic amide) supported titanium(iv) complex.
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