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Rational Design of Lewis Superacids Leading to an Unprecedented Ti (III) Triflimide Catalysts for the Direct Amination of Alcohols

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PURPOSE OF THE ABSTRACT

The direct amination of alcohols is one of the most attractive reactions to obtained amines. Because alcohols are non-toxic, easily available natural products and because water is the only by-product, this reaction would be the perfect alternative to the current oil-based processes [1].

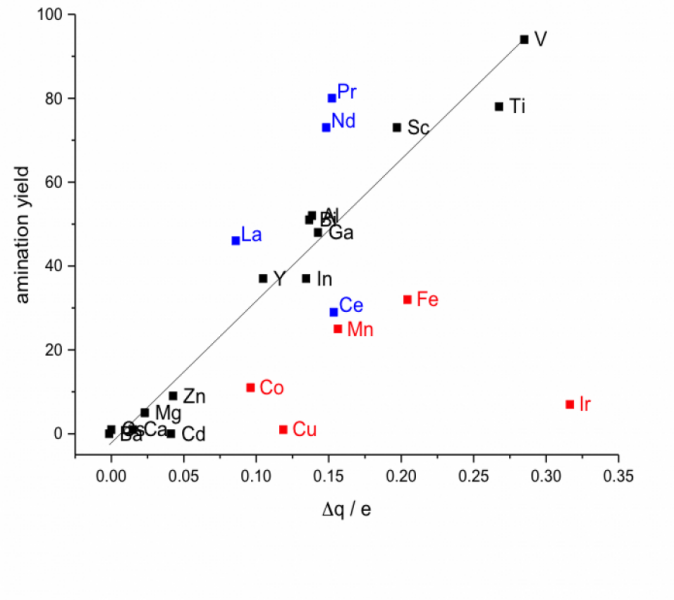
Recently, it was found out that simple Lewis acids such as Al(OTf)3 [2] were able to catalyzed this reaction, avoiding the use of rare noble metal such as Ru or Ir. Unfortunately, the scope of the reaction was limited to electron-poor nitrogen derivatives such as sulfoxamides. In a recent publication, we demonstrated, using electrochemistry, NMR and DFT calculations, that this limitation was due to the deactivation of the catalyst by the amine and that this issue could be overcome using an appropriate solvent [3]. However the scope and yield of the reaction proved quite limited.

Lewis superacids (triflates and triflimides) are widely used in organic synthesis for activating C-O and C-C bonds [4]. Lewis superacids are opening new catalytic ways using low cost and largely available non-noble metal. However, the choice of the metal cation is only rarely satisfactorily justified [5], most of the time the optimization of the catalyst is conducted at defined conditions (temperature, solvent, concentration, ?) within a small range of available metals. Herein, we propose a quantitative and handy scale to describe the catalytic properties of Lewis superacids. The DFT predicted charge variation on OPH3 (Dq) due to its coordination to a Lewis acid was correlated with experimental amination yield (Figure 1) and new promising triflimide salts emerged as potential challengers.

Among them, Ti triflimide seems particularly interesting as it was predicted super-active and uses the abundant Ti. Starting from Ti metal and triflimidic acid a new catalyst was obtained and characterized using TGA, cyclic voltammetry (CV), EPR spectroscopy and elemental analysis. This compound proved to be a mixture of Ti(III) and Ti(IV) triflimide. The unexpected stabilization of Ti(III) was rationalized using CV and DFT calculations. This salt was both efficient in our model amination reaction (Figure 2) and easy to manipulate compared to classical Ti-based Lewis acid such as anhydrous TiCl3 or TiCl4.

These reaction conditions proved efficient for a large variety of substrates including primary and secondary alkyl amines. However, the use of activated benzyl-type alcohol is still needed. The reaction mechanism was studied in detail using EPR spectroscopy combined with DFT calculations.

FIGURES



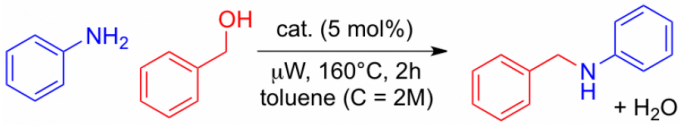


FIGURE 1

Figure 1

Evolution of the amination yield as a function of Dq for a series of metal triflimide salts.

FIGURE 2

Figure 2

Model amination used for screening the catalytic activity of metal triflimide salts.

KEYWORDS

Lewis superacid | Metal triflimides | Titanium | Amination

BIBLIOGRAPHY