

Influence of copper(I) halides on the reactivity of aliphatic carbodiimides

Valentina Ferraro ^{1,*}, Marco Bortoluzzi ¹

¹ Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155, 30170 Mestre (VE), Italy. E-mail:valentina.ferraro@unive.it

Carbodiimides are widely exploited in organic synthesis, and the reactivity of these compounds can be enhanced by the addition of copper(I) halides to the reaction medium. The mild reaction conditions provide an alternative and selective synthetic approach with respect to the utilization of Brønsted acids.

The influence of copper(I) halides CuX (X = Cl, Br, I) on the electronic structure of diisopropylcarbodiimide and dicyclohexylcarbodiimide was investigated by means of DFT methods. The coordination of the considered carbodiimides occurs by one of the nitrogen atoms, with the formation of linear complexes having formula [CuX(carbodiimide)]. Besides varying the carbon-nitrogen bond lengths and orders, the interaction with Cu(I) reduces the electron density on the carbodiimides and alters the energies of the [NCN]-centred unoccupied orbitals, enhancing the reactivity towards nucleophiles. The computed Fukui functions suggest negligible interaction of Cu(I) with incoming nucleophiles, and the reactivity of carbodiimides is altered by coordination mainly because of the increased electrophilicity of the [NCN] fragments. CuX essentially behave as Lewis acids, and the nature of X influences the Cu-N bond strength, the carbodiimide→CuX donation and the energies of frontier unoccupied orbitals. CuCl is actually the most employed catalyst in combination with carbodiimides, but some of the results here provided suggest that the reactivity could be yet more enhanced by its replacement with CuI.