

Electrophilic activation of water at a carbene-metal interface

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Carbene represents a class of reactive intermediates whose lone pair electrons and vacant orbitals exhibit multifaceted reactivity towards small molecules such as oxygen, hydrogen, and water. Though water activation by carbenes is of synthetic importance, the product is limited to carbenium ions in conventionally employed environments such as solutions or cryogenic matrices [1,2]. For such a nucleophilic activation of water, only the lone pair electrons of the carbene center are involved.

One way to control the carbene reactivity towards water is by tuning the microenvironment of carbene centers, such as introducing metal coordination. However, due to the strong interaction, it was demonstrated that the reactivity of a fluorenylidene carbene is quenched upon adsorption on an Ag(111) surface [3]. Only before binding to the Ag(111) surface, the fluorenylidene carbene is allowed to react with water to form a fluorenyl cation [4].

In this talk, I will present how to tune the reactivity of an aryl carbene, diphenylcarbene, by controlling the vacant orbital of the carbene centers through bonding to copper atoms. Electrophilic activation of water is achieved at the carbene-metal interface. An unprecedented type of reactive intermediate, the hydroxy-diphenylmethanide carbanion, is unambiguously identified by combining low-temperature scanning tunneling microscopy (LT-STM) and infrared reflection absorption spectroscopy (IRRAS).

[1] Costa, P., Fernandez-Oliva, M., Sanchez-Garcia, E., Sander, W. J. Am. Chem. Soc. **136**, 15625-15630 (2014).

[2] Costa, P., Trosien, I., Fernandez-Oliva, M., Sanchez-Garcia, E., Sander, W. Angew. Chem. Int. Ed. **127**, 2694-2698 (2015).

[3] Mieres-Perez, J., Lucht, K., Trosien, I., Sander, W., Sanchez-Garcia, E., Morgenstern, K., J. Am. Chem. Soc. **143**, 4653-4660 (2021).

[4] Cao, Y., Mieres-Perez, J., Lucht, K., Ulrich, I., Paul, S., Sanchez-Garcia, E., Morgenstern, K., Sander, W., J. Am. Chem. Soc. DOI: 10.1021/jacs.2c12274