Synthesis of Clickable *N*-Heterocyclic Carbenes for the Functionalization of Gold

Katharina Pfennigbauer and Brigitte Holzer

Institute of Applied Synthetic Chemistry, TU Vienna, 1040 Vienna, Austria

N-heterocyclic carbenes (*N*HCs) are promising candidates to form thermal and chemical stable self-assembled monolayers (SAMs) which can be employed in various application fields including (bio)sensing and electronics.[1] However, harsh conditions using strong bases and inert atmosphere are typically required for the preparation of the carbene precursors (Figure 1a). Recently, Crudden *et al*. published a synthetic route to *N*HC-based films *via* hydrogen carbonate salts under ambient conditions, in which the counteranion serves as the base to deprotonate the imidazole moiety.[2]

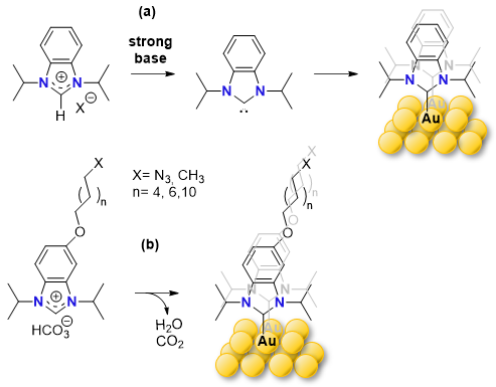

Figure 1 (a) Strategies towards gold surface functionalization using strong base and (b) imidazolium hydrogen carbonates precursors to form self-assembled monolayers.

This work demonstrates a straightforward preparation of (benz-) imidazolium hydrogen carbonates with varied spacer lengths (n=4, n=6, n=10) and different terminal functional groups (Figure 1b, X= azide or alkyl group) as bench stable precursors for the formation of *N*HC films on gold (Figure 1b). By using an exchange resin loaded with HCO_3^- ions, the hydrogen carbonate precursors can be generated from their iodide counterparts.

Selected precursors are immobilized on gold to form SAMs which are tested in surface confined click reactions and the resulting films are analyzed with cyclic voltammetry.

The work highlights the potential of *N*HCs as ligands for gold functionalization and the opportunities for derivatization of the clickable *N*HC-SAMs to enable a wide range of functionalities and applications.

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[1] C. M. Crudden *et al.*, "Ultra stable self-assembled monolayers of N-heterocyclic carbenes on gold," *Nat. Chem.*, 6, 5, 409–414, 2014.

[2] C. M. Crudden *et al.*, "Simple direct formation of self-assembled N-heterocyclic carbene monolayers on gold and their application in biosensing," *Nat. Commun.*, 7, 1–7, 2016.