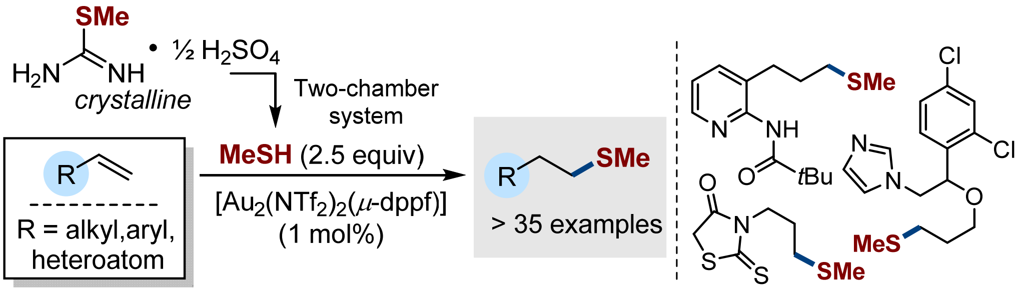
GOLD-PROMOTED *ANTI*-MARKOVNIKOV HYDROTHIOLATION OF OLEFINS USING *EX SITU* GENERATED METHANETHIOL

Steffan K. Kristensen and Troels Skrydstrup

Carbon Dioxide Activation Center (CADIAC), Department of Chemistry and the
Interdisciplinary Nanoscience Center (iNANO), Aarhus University,
Gustav Wieds Vej 14, 8000 Aarhus C (Denmark) - skk@inano.au.dk

We have earlier reported on the use of the two-chamber reactor system, COware®, as a convenient means for performing transition metal-catalyzed transformations with a number of common low molecular weight gases, including CO, H_2, HCN and ethylene generated ex-situ from solid precursors.[1,2]



Here, a protocol for the Au(I)-promoted *anti*-Markovnikov hydrothiolation of olefins exploiting *ex situ* generated methanethiol is reported.[3] By treating the commercially available *S*-methylisothiourea hemisulfate salt with NaOH, a stoichiometric amount of methanethiol could be generated under safe and reliable conditions. Over 30 olefins could be converted under the optimized reaction conditions to the corresponding hydrothiolated adduct in good to excellent yields. Mechanistic studies suggest the intermediacy of methylthiyl radicals generated from digold complexes as shown from the isolation and characterization of several gold(I) complexes generated under the reaction conditions.

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[1] S. D. Friis, A. T. Lindhardt, T. Skrydstrup, *Acc. Chem. Res.* **2016**, *49*, 594.

[2] S. K. Kristensen, E. Z. Eikeland, E. Taarning, A. T. Lindhardt, T. Skrydstrup, *Chem. Sci.* **2017**, *8*, 8094.

[3] S. K. Kristensen, S. L. R. Laursen, E. Taarning, T. Skrydstrup, *Angew. Chem. Int. Ed.* **2018**, *42*, 13887.