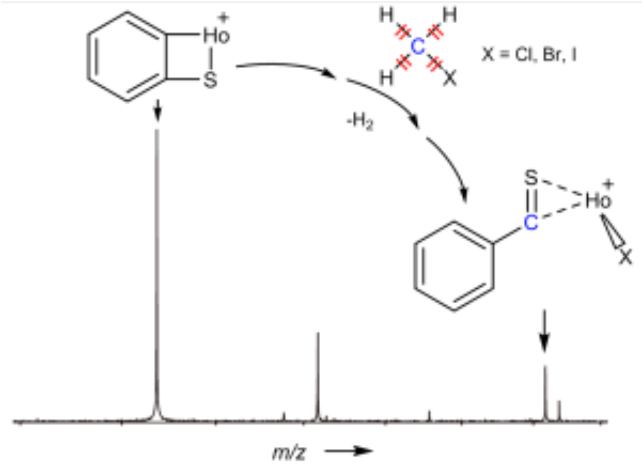
A novel, unexpected example of C1 chemistry!

C1 chemistry refers to the conversion of simple molecules containing one carbon atom only, such as the greenhouse gases methane and carbon dioxide or poisonous carbon monoxide, into higher-value products. One classical example in chemical industry, proposed by Fischer and Tropsch already in 1928, is to build liquid hydrocarbons $C_nH_{(2n+2)}$ composed of carbon atoms from gaseous CO. The perhaps most famous example in biology is provided by the photosynthesis in plants. Here, with the help of sunlight carbon dioxide and water are transformed in a miraculous way into valuable organic matter – no life without photosynthesis! Man-made or biological catalysts are required to achieve these seemingly simple processes, and a challenging object of investigation for chemists is to develop efficient catalysts for the conversion of C1 chemicals at environmentally benign conditions.



Studies of the reaction mechanisms by which the C1 compounds are incorporated into higher building blocks help to improve the rational catalyst design for C1 chemistry, rather than relying entirely on trial-and-error based procedures. Our approach is to monitor catalytic reactions at a truly molecular level in the idealized gas phase, where the processes are not obscured by ill-defined side effects. Here we present such a gas-phase transformation, in which the carbon atom of methyl halides (CH_3X, X = Cl, Br, I) gets embedded into a larger molecule. In CH_3X, the carbon atom is surrounded by one halogen and three hydrogen atoms. In organic synthesis, these substrates are often used as methylating reagent from which the intact CH_3 group is transferred to different types of substrates; here - as in many other examples of organic reactions using methyl halides - only the C–X bond gets cleaved. In contrast, we came across an unprecedented example in which all four atoms are detached from the central carbon of CH_3X, as shown in the Figure; clearly, a sort of a molecular strip tease has taken place!

Mechanistic details on the reaction path were revealed by sophisticated experiments combined with computational studies. Based on these findings we were able to show that the carbon atom of CH_3X ends up as $[C_6H_5C(S)HoX]^+$, thus demonstrating that all four ligands are indeed detached

from the central carbon of CH_3X. This work provides an alternative approach for the transformation of C1 chemicals. Who knows what is it good for?!

Publication

Stripping" the Carbon Atom of Methyl Halide by a Cationic Holmium Complex: A Gas-Phase Study.
Zhou S, Schlangen M, Li J, Wu XN, Schwarz H
Chemistry. 2015 Oct 5;21(41)