

Chemistry with Methane: Concepts Rather than Recipes

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Four seemingly simple transformations related to the chemistry of methane will be addressed from mechanistic and conceptual points of view, i.e.: 1) metal-mediated dehydrogenation to form metal carbene complexes, 2) the hydrogen-atom abstraction step in the oxidative dimerization of methane, 3) the mechanisms of the $\text{CH}_4 \rightarrow \text{CH}_3\text{OH}$ conversion, and 4) the initial bond scission as well as the rate-limiting step in the selective $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O}$ oxidation. State-of-the-art gas-phase experiments, in conjunction with electronic-structure calculations, permit to identify the elementary reactions at a molecular level and thus to unravel detailed mechanistic aspects. Where appropriate, these results are compared with findings obtained from related, more conventional studies in solution or on surfaces. Three aspects deserve special mentioning: 1) the prominent role of relativistic effects exerted by 5d elements, 2) two-state reactivity as a (new) reaction paradigm, and 3) unparalleled cluster-size and ligand effects on reactivity, all of which matter in the organometallic chemistry with methane at ambient conditions.

