

Silver-Catalyzed Carbene Functionalization of Methane in Supercritical Carbon Dioxide

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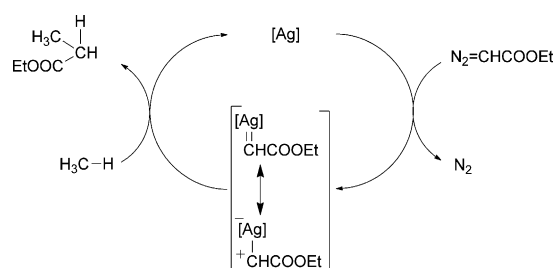
To the surprise of many, carbon–hydrogen insertion can occur in supercritical carbon dioxide between the least reactive hydrocarbon, methane, and the carbene or the carbene-like intermediate formed from ethyl diazoacetate, catalyzed by using a perfluorinated tris(indazolyl)borate (scorpionate) silver complex. Pedro Pérez of the Universidad de Huelva, Michel Etienne of the Université de Toulouse, Gregorio Asensio of the Universidad de Valencia, and their coworkers have reported that in supercritical mixtures of methane and carbon dioxide in combination with ethyl diazoacetate allows dinitrogen extrusion and formation of the methane C–H-insertion product ethyl propanoate.^[1] To accomplish this transformation they had to overcome the nearly universal belief that methane was too unreactive to undergo C–H functionalization with a diazoacetate,^[2] and the practical limitations (catalyst solubility and reactivity, solvent compatibility) that served as barriers to this research.

The first challenge was to find a solvent that was sufficiently inert so that it would not undergo competitive reaction with a metal carbene intermediate. Supercritical carbon dioxide, known for its inertness to these reactions,^[3] was selected. At temperatures and pressures above their critical values (32 °C and 7.4 MPa), carbon dioxide is a fluid capable of solubilizing the molecules involved in the reaction. Methane, which is insoluble in most solvents and has poor solvating ability, is soluble in supercritical carbon dioxide.

The next challenge was the selection of a catalyst that would be soluble in the supercritical fluid. Pérez and coworkers had previously designed highly electrophilic silver catalysts based on perfluorinated tris(indazolyl)borate ligands, and had reported their applications for C–H-insertion reactions with pentane, in which they observed insertion into normally unreactive primary C–H bonds.^[4] Selecting the perfluorinated tris(indazolyl)borate silver complex with the highest selectivity for primary C–H bond insertion, the combination of ethyl diazoacetate and methane in supercritical carbon dioxide at 40 °C and 25 MPa pressure for 14 h produced ethyl propanoate with turnover numbers (TONs) as high as 478 (19% yield). Both diethyl fumarate and diethyl maleate accompany ethyl propanoate and unreacted ethyl diazoacetate. Ethane also underwent insertion under the same conditions of temperature and total pressure to form ethyl butanoate; when the reaction was

run in competition with methane, relative reactivity favored ethane over methane by approximately 7.5:1.

The authors propose a mechanism for the C–H functionalization reaction, in which the silver complex effects dinitrogen extrusion from ethyl diazoacetate to form a ligated silver carbene intermediate, whose association with methane (or hydrocarbons in general) provides generation of ethyl propanoate and release of the active catalyst, and this mechanism is compatible with previous representations of electrophilic metal carbene intermediates (Scheme 1). By obtaining experimentally indistinguishable selectivities for the ethyl diazoacetate-mediated C–H functionalization of pentane in homogeneous pentane (47:44:9 for 3-, 2-, and 1-positions, respectively) and in pentane dissolved in supercritical carbon dioxide (50:39:11 for 3-, 2-, and 1-positions, respectively), the authors demonstrate that carbon dioxide does not measurably alter the course of these reactions.



Scheme 1. Mechanism for the silver carbene mediated C–H insertion.

Since hydrocarbons, especially methane, are major feedstocks for the chemical industry, direct and catalytic transformations of these compounds are of major importance. Oxidative transformations with molecular oxygen or peroxides, among others, are of intense interest.^[5] The catalytic carbene-like C–H functionalization of methane that is presented by G. Asensio, M. Etienne, and P. J. Pérez^[1] is a significant achievement in the long history of attempted approaches to this oxidative transformation, and further research will undoubtedly open additional methodologies. The highly electrophilic perfluorinated tris(indazolyl)borate silver complex, the key ingredient in the success of the reported C–H functionalization of methane, is deserving of the attention that is usually given to copper and rhodium catalysts.

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