MECHANISTIC STUDY OF THE MECHANOChemICAL ACETATE-ASSISTED C–H ACTIVATION WITH [Cp*RhCl₂]₂

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The use of mechanochemistry to carry out solventless metal-catalyzed C–H functionalizations through the formation of metallacycles is gaining ground in chemical synthesis. [1] However, until now, little is known about the mechanistic steps leading to the C–H activation under mechanochemical conditions. In this work, we studied the mechanochemical formation of rhodacycles by ball milling N-substrates and [Cp*RhCl₂]₂ in the presence of NaOAc. Ex-situ analysis of the mechanochemical reactions revealed the formation of unusual crystalline intermediates between the substrates and the rhodium dimer prior to the C–H activation step (Scheme; top). This sequence of events differs from the generally accepted steps in solution in which cleavage of [Cp*RhCl₂]₂ is initiated by acetate ions (Scheme; bottom). [2]

The results of this investigation clarify some of the fundamental aspects of mechanochemical cyclorhodations and are expected to help in the design of better catalysts and processes for mechanochemical metal-catalyzed C–H functionalizations.

REFERENCES
