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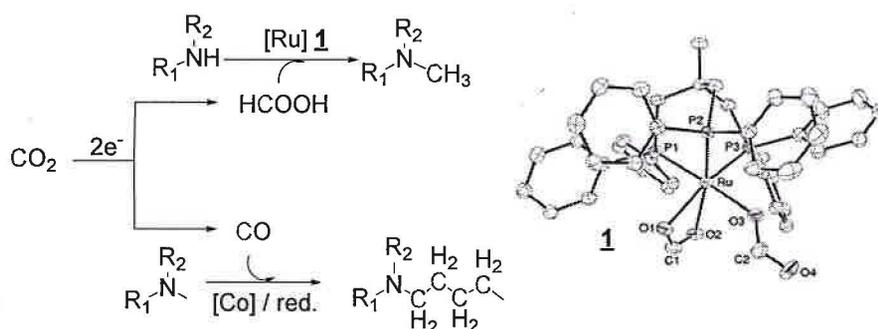
Indirect synthesis of methyl and alkylamines from CO₂S. Savourey,¹ T. Nasr-Allah,¹ G. Lefèvre,¹ J.C. Berthet,¹ T. Cantat *¹

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In the past few years CO₂ has been investigated as a C1 building block for the synthesis of a variety of chemicals and especially methylamines.¹ However due to the inertness of CO₂, the methylation of amines require either the use of activated hydrides (silanes/boranes) whose by-products are not recyclable, or the use of large excess of H₂ yielding poor faradaic efficiencies. On the other hand, great improvements have been made for the 2-electron reduction of CO₂ to CO or HCOO⁻ offering convenient platforms for the indirect synthesis of chemicals from CO₂.² However to the best of our knowledge, neither HCOO⁻ nor CO has been reported for the synthesis of methyl or alkylamines.

We therefore report the first ruthenium catalyzed synthesis of methylamines using HCOOH as the unique source of carbon and hydrogen.³ Thanks to a theoretical and experimental approach,⁴ we were able to achieve quantitative yield for the methylation of amines. If the use of HCOOH is limited to the synthesis of methylamines, we also developed the synthesis of alkylamines via the homologation of amines, using CO as a building block.⁵ Amines bearing an alkyl chain of up to 5 carbons were synthesized from the corresponding methylamines in one pot thanks to a cobalt catalyst.



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