

CO₂-DERIVED CARBONATES AND POLYCARBONATES TO METHANOL AND DIOLS VIA METAL LIGAND COOPERATIVE CATALYSIS

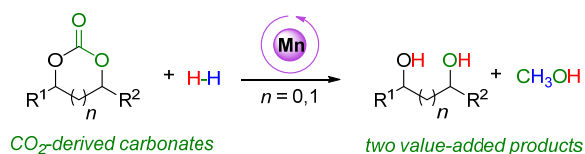
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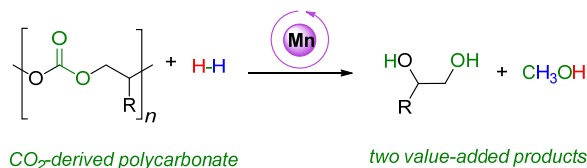
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To satisfy energy demands of an increasing world population, fossil fuels including coal, petroleum and natural gas are being burnt in countless amount. Together they contribute into the environment more than 30 billion tonnes of CO₂.^[1] The catalytic hydrogenation of an abundant, safe and renewable CO₂ to methanol is very attractive and required due to "methanol economy"^[2]. Among CO₂ hydrogenation products, methanol is most attractive because it is already one of the most important building blocks used today on a large scale to produce a variety of chemicals and products. The first example of base-metal catalysed hydrogenation of the CO₂-derived-carbonates to alcohols is presented.^[3] The well-defined Mn(I)-PNN complex operates at low catalyst loading (as low as 0.5 mol %) and under mild conditions. The method provides a practical route to convert CO₂ to methanol with the co-production of the value-added vicinal diols. Range of five- and six-membered cyclic organic carbonates as well as polycarbonates were successfully applied in the transformation producing methanol and diols in high yields. Experimental and computational studies indicate a metal ligand cooperative catalysis mechanism.^[4]

a) indirect reduction of CO₂ to alcohols



b) recycling of polycarbonates to valuable products



Scheme 1. Unprecedented base-metal catalysed hydrogenation of organic carbonates.

[1] IPCC, 2007: Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III of the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Geneva, Switzerland, 2008.

[2] Olah, G. A. *Angew. Chem. Int. Ed.* **2005**, *44*, 2636–2639

[3] Zubar, V.; Lebedev, Y.; Azofra, L.M.; Cavallo, L.; El-Sepelgy, O. Rueping, M. *Angew. Chem. Int. Ed.* **2018**, *57*, 13439–13443; *Angew. Chem.* **2018**, *130*, 13627–13631.

[4] For independent parallel studies, see: a) Kumar, A.; Janes, T.; Espinosa-Jalapa, N. A.; Milstein, D. *Angew. Chem. Int. Ed.* **2018**, *57*, 12076–12080; *Angew. Chem.* **2018**, *130*, 12252–12256. b) Kaithal, A.; Hölscher, M.; Leitner, W. *Angew. Chem. Int. Ed.* **2018**, *57*, 13449–13453; *Angew. Chem.* **2018**, *130*, 13637–13641.