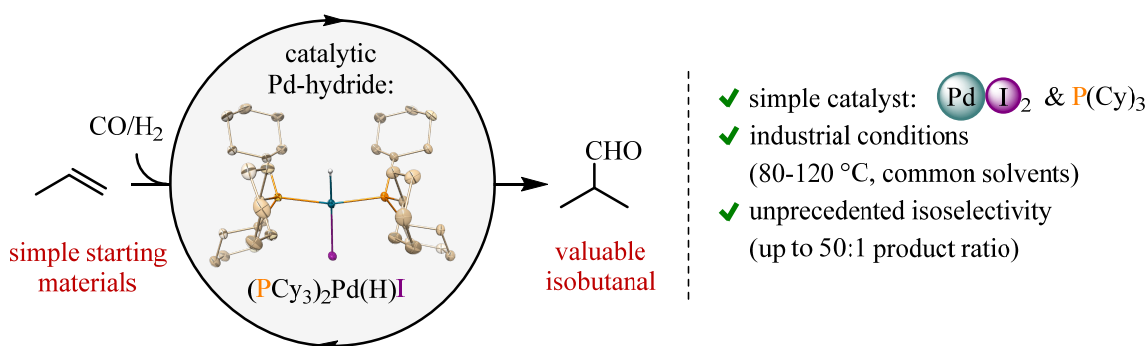


ISO-SELECTIVE HYDROFORMYLATION OF PROPYLENE BY IODIDE-ASSISTED PALLADIUM-CATALYSIS

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Hydroformylation of propylene is one of the most significant reactions in the chemical industry, producing each year >7 million tons of a mixture of valuable *n*-butanal and isobutanal with a 100% atom economy from simple starting materials. The commonly employed Rh- and Co-based catalysts form preferentially *n*-butanal over the iso-product. Because of the increasing demand for products derived from iso-aldehydes, there have been sizeable research efforts toward developing isoselective methods. However, limited progress has been achieved, with no industrial process established thus far.^[1]



Given atypical selectivity patterns, Pd-based hydroformylation catalysts represent an attractive alternative to common Rh- and Co-based catalysts.^[2,3] Here I will present our studies establishing the first example of a highly isoselective hydroformylation of short-chain aliphatic alkenes, such as propylene, occurring in the presence of an iodide-dependent Pd-based catalyst.^[4] Attractively, the process involves only palladium(II) iodide, a simple alkyl monophosphine, such as tricyclohexylphosphine, and a green solvent, such as anisole. Furthermore, the isoselectivity is preserved under industrially relevant conditions (> 80 °C), with up to >50:1 iso/*n* ratios. The experimental and computational mechanistic studies that gave insights into the origin of the catalytic activity and the unusual isoselectivity will be discussed.

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[3] Zhang, Y., Torker, S., Sigrist, M., Bregović, N. & Dydio, P. Binuclear Pd(I)–Pd(I) Catalysis Assisted by Iodide Ligands for Selective Hydroformylation of Alkenes and Alkynes. *J. Am. Chem. Soc.* **142**, 18251–18265 (2020).

[4] Sigrist, M., Zhang, Y., Antheaume, C. & Dydio, P. Isoselective Hydroformylation of Propylene by Iodide-Assisted Palladium Catalysis. *Angew. Chemie Int. Ed.* **61**, (2022).