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SUPPLEMENTARY INFORMATION

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The role of the metal-bound N–H functionality in Noyori-type molecular catalysts

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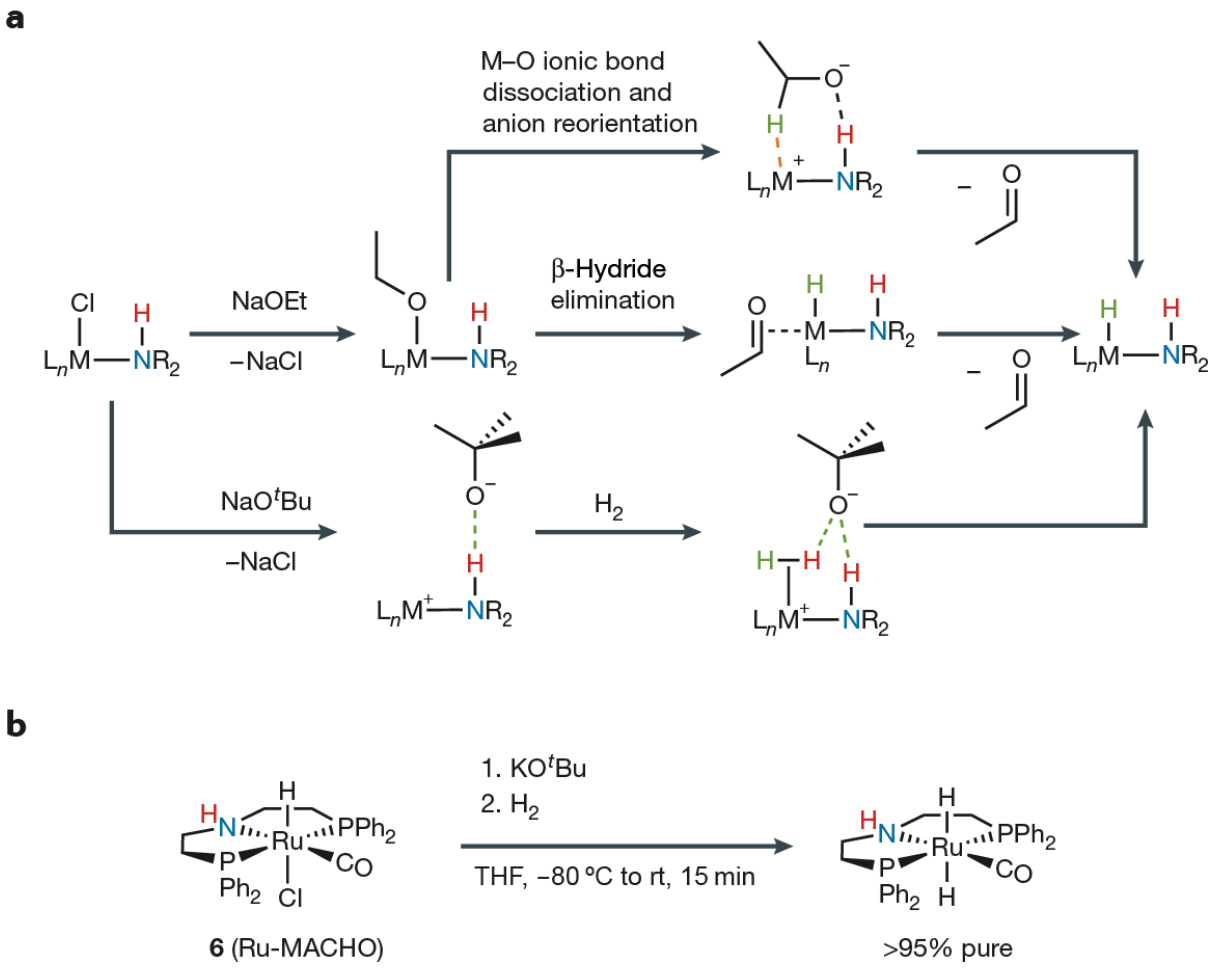

Figure S1 | **Reversible hydrogenation of esters mediated by M/N–H catalysts. a** | A prototypical chlorido precatalyst can be converted to a catalytically active hydrido complexes through one of three main mechanisms involving a stoichiometric amount of inorganic base (NaOEt or KO^{t}Bu). In principle **b** | The chlorohydrido Ru-MACHO precatalyst **6** can be converted to a dihydrido derivative that is active for ester hydrogenation[1].

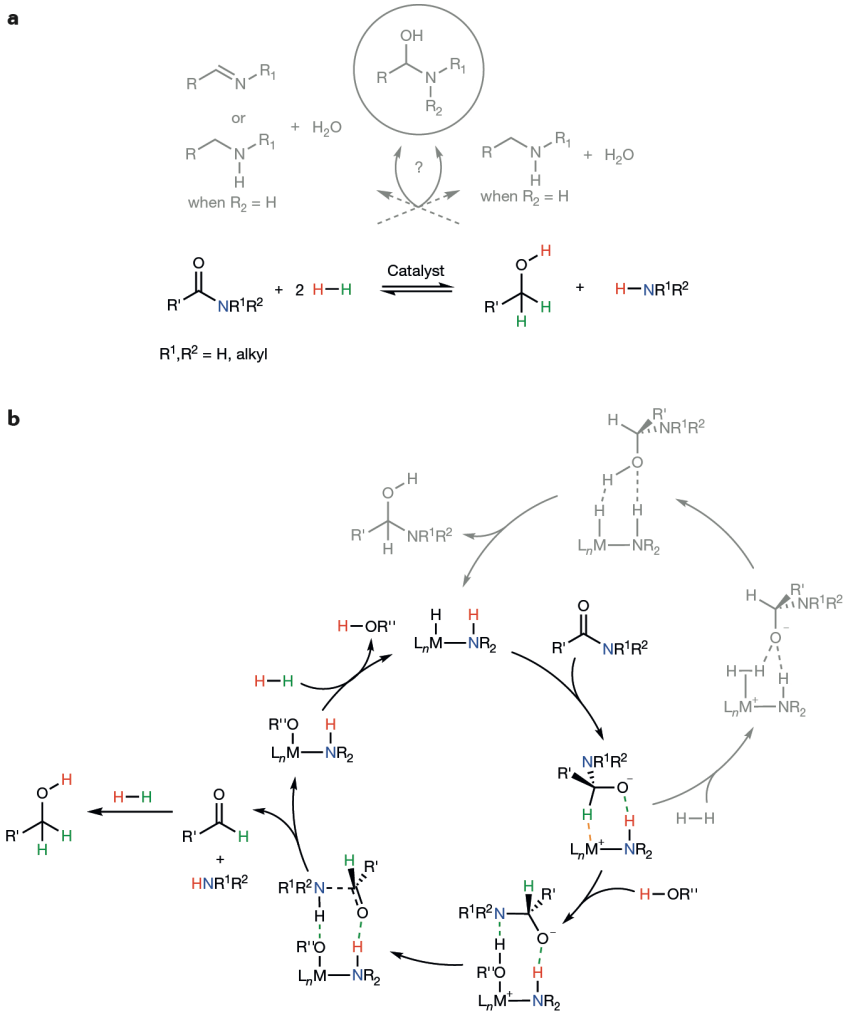

Figure S2 | **Reversible hydrogenation of carboxamides mediated by Noyori- type M/N–H catalysts. a** | Carboxamides typically undergo deaminative hydrogenation to afford primary alcohols and amines but can also undergo deoxygenative hydrogenation to afford an amine and water in some cases. Speculatively, hemiaminals can also be formed under kinetic control (cf. fluoroester hydrogenation)[1,2], providing that they are relatively stable and isolable[3–6]. The reverse reaction, catalytic dehydrogenative coupling of primary alcohols with amines, can in addition and/or preferentially afford imines, or even amines. **b** | A simplified catalytic cycle for carboxamide ($R'C(O)NR^1R^2$) hydrogenation into hemiaminals is postulated in this Perspective. Alternative products include primary alcohols ($R'CH_2OH$) and amines HNR^1R^2, as seem in recent studies[7].

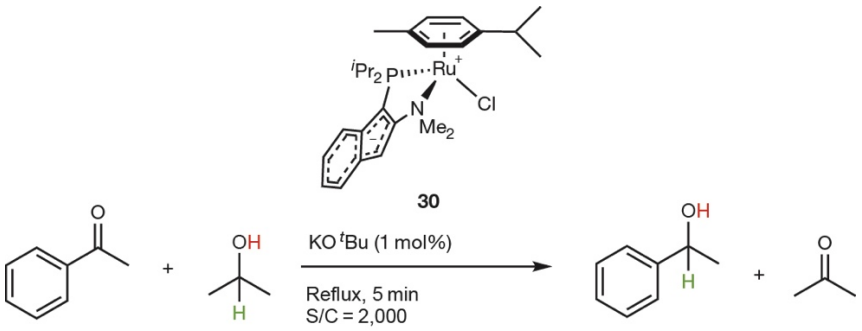

Figure S3 | **Transfer hydrogenation of acetophenone with a complex lacking an NH functionality.** The TOF reaches 50 s^{-1} after 20 s (Refs[8,9]).

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