



Selective hydration of nitriles to amides with Rh(I)(NHC) complex catalyst

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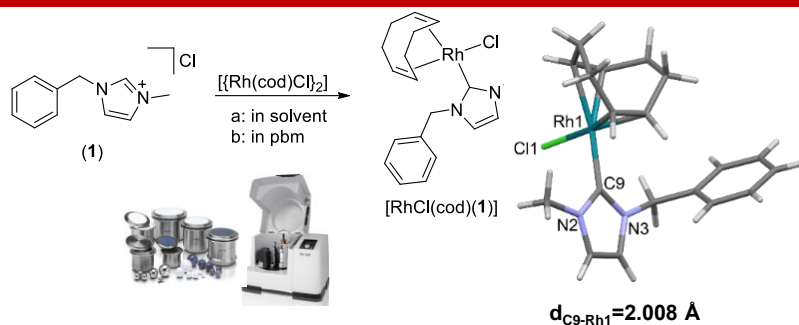
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Introduction

Hydration of nitriles to amides is a 100% atom-economic reaction. Selective hydration of nitriles to amides is a significant chemical reaction in organic synthesis because amides play a key role in the synthesis of many organic compounds. Traditionally, amides were prepared by acid- or base-catalysed reactions; however, this often leads to over-hydrolysis. Therefore, catalytic systems have been developed to prevent hydration at the amide stage; for example, enzyme- or transition metal catalysed reactions have become increasingly popular.

Synthesis of Rh(I)NHC complex catalyst

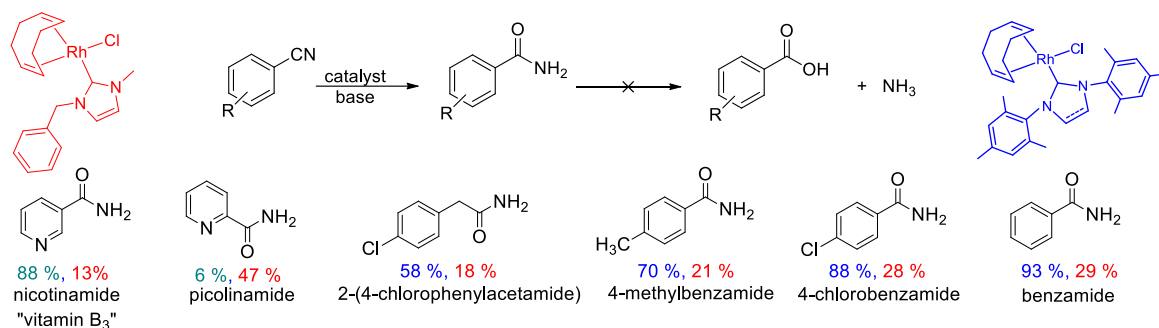


$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ/ppm : **181.9 ppm** (d, $^1J_{\text{Rh-C}} = 50.2 \text{ Hz}$)

Yield: a) solvent (toluene): **77%** b) planetary ball mill: **75%**

^{13}C NMR spectra were recorded on Bruker Avance 360 MHz spectrometer and were referenced to residual solvent peaks. Single crystal X-ray diffraction (SCXRD) measurement was performed using Bruker D8 Venture diffractometer.

Results of catalytic hydration reactions of various aromatic nitriles



Reaction conditions:

1 mmol nitrile, **1 mol%** or **5 mol%** $[\text{RhCl}(\text{cod})(\text{IMes})]$, 0.01 mmol NaOH, 1.5 mL 2-propanol, 1.5 mL H_2O , **1 h**, **reflux [1]**; 0.5 mmol nitrile, **2 mol%** $[\text{RhCl}(\text{cod})(1)]$, 0.01 mmol NaOH, 1.0 mL 2-propanol, 1.0 mL H_2O , **1 h**, **reflux**

Gas chromatographic measurements were done with the use of an Agilent Technologies 7890 A instrument (HP-5 0.25 $\mu\text{m} \times 30 \text{ m} \times 0.32 \text{ mm}$ or OPTIMA-1 (30 $\text{m} \times 0.32 \text{ mm} \times 1.25 \mu\text{m}$), FID 300 °C; carrier gas: nitrogen 1.9 mL/min).

Conclusion

We have realised one-step syntheses of the $[\text{RhCl}(\text{cod})(\text{NHC})]$ complex without generating free carbene ligands or silver-NHC complexes. Furthermore, an efficient mechanochemical synthesis method was developed, with shorter reaction times and reduced reliance on organic solvents compared to the classical solution synthesis of the same compounds. An efficient catalytic system for the selective hydration of nitriles to the corresponding amides in a water/2-propanol solvent, with tolerance of air and several functional groups, is also described.

Acknowledgement

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Reference

[1] Czégéni C. E., De S., Udvardy A., Derzsi N. J., Papp G., Papp G., Joó F., *Catalysts*. **2020**, *10*, 125.