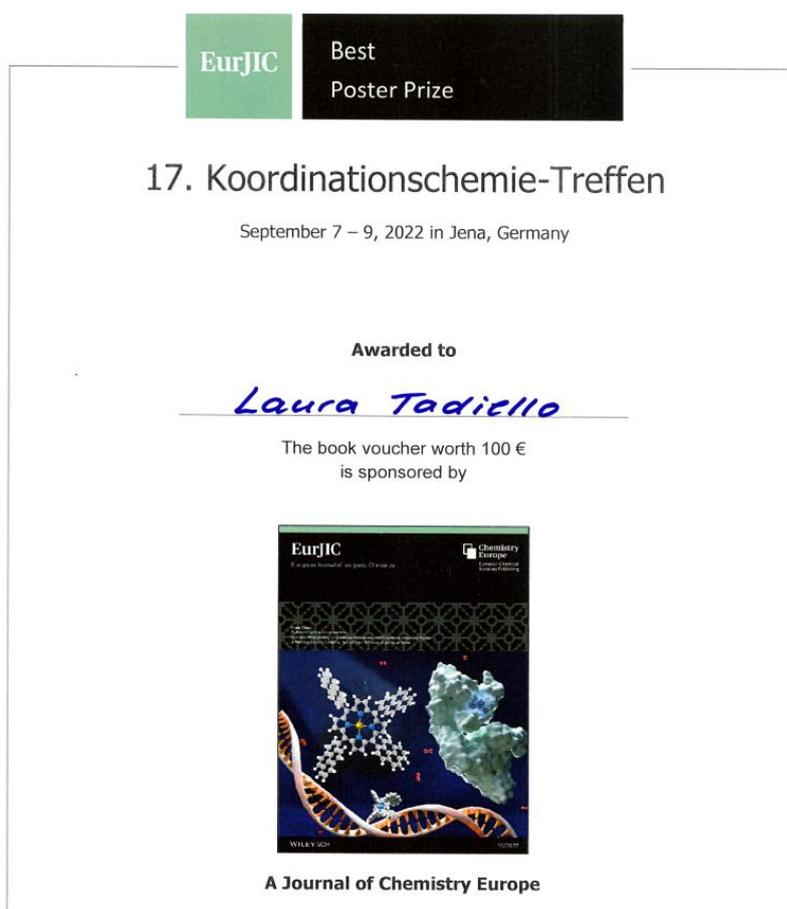


## Posterpreis für Laura Tadiello

Laura Tadiello aus der Themengruppe " Mechanismen der Homogenen Katalyse" hat auf dem 17. Koordinationschemie-Treffen in Jena einen Posterpreis erhalten.



Herzlichen Glückwunsch!

Das Poster finden Sie auf der folgenden Seite

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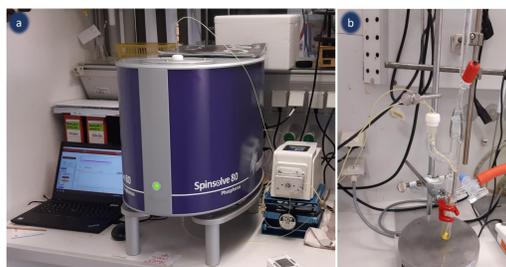
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## Introduction

Flow NMR spectroscopy is an increasingly attractive technique which allows to monitor product formation as well as detecting catalyst activation and deactivation processes.<sup>1</sup> Low-cost benchtop spectrometers are also increasingly being employed,<sup>2</sup> although they are not suitable for organometallic complexes that are sensitive to air and moisture. Herein, we first present the practical aspects of the development of our customised flow setup and afterwards demonstrate its feasibility with highly oxygen-sensitive species. The investigation is carried out in real time under realistic preparative conditions, allowing the formation of the desired organometallic species without degradation. Non-invasive low-field flow (LFF)  $^{31}\text{P}$  NMR reaction monitoring allows to detect the evolution of new species under realistic reaction conditions with efficient stirring, no delays and without any eventual issues introduced by subsequent manipulation of the NMR sample. Tools such as subsequent additions as well as solvent suppression have been exploited to shed light on  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra.

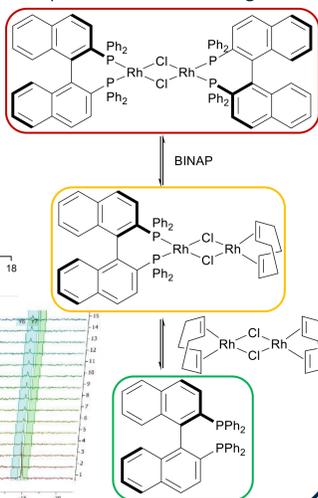
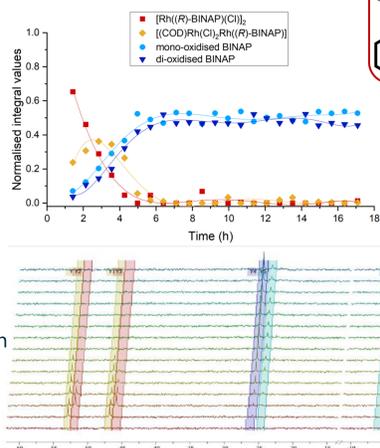
## Results

### Synthesis of $[\text{Rh}((R)\text{-BINAP})(\mu\text{-Cl})_2]$ – Stepwise additions

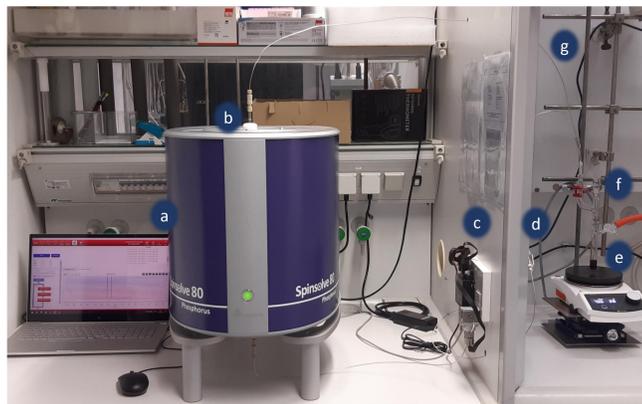


Commercially available setup:  
a) outside of the fume hood: benchtop NMR spectrometer with flow NMR cell and peristaltic pump;  
b) inside the fume hood: Schlenk flask with rubber septum and PTFE tubing.

Subsequent additions proved to be feasible. Free BINAP is recorded in the first spectrum; then  $[(\text{COD})\text{Rh}(\text{Cl})_2\text{Rh}((R)\text{-BINAP})]$  and finally  $[\text{Rh}((R)\text{-BINAP})(\mu\text{-Cl})_2]$ . Afterwards, undesired oxidation is occurring with the commercially available setup.



### Customised setup

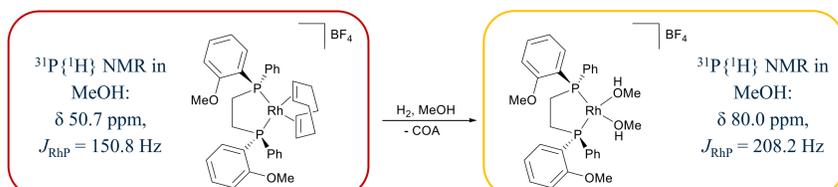


Anaerobic conditions were reached with our customised setup: a) benchtop NMR spectrometer; b) flow NMR cell; c) micro annular gear pump; d) inline filter; e) Schlenk flask; f) glass adapter; g) SS capillaries.

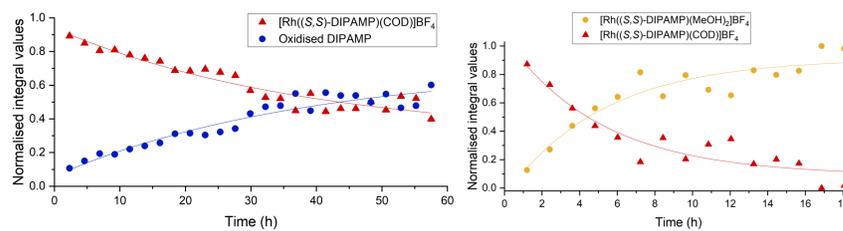
Equipment evolution:  
a) peristaltic pump BT100-2J;  
b) deformed tubing after extensive use of solvents; c) hermetic inert pump mzs-6355-cy-f; d) high performance pump mzs-2905;  
e) magnetic hermetic pump mzs-2965-hs-f; f) inline filter F-MI2-T; g) inlet filter F-MI0; h) inline filter F-MI0-s-f8.



### Hydrogenation of $[\text{Rh}((S,S)\text{-DIPAMP})(\text{COD})]\text{BF}_4$ – Inertness



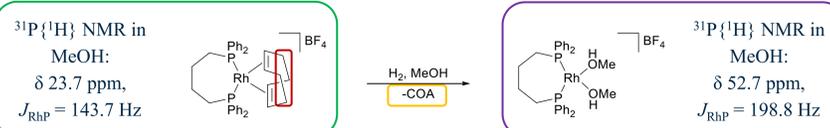
Only with the customised air-tight setup, the formation of highly oxygen-sensitive solvent complex  $[\text{Rh}((S,S)\text{-DIPAMP})(\text{MeOH})_2]\text{BF}_4$  could be monitored (right). Otherwise, only the undesired oxidation of the DIPAMP ligand was detected (left).



via commercially available setup

via our customised setup

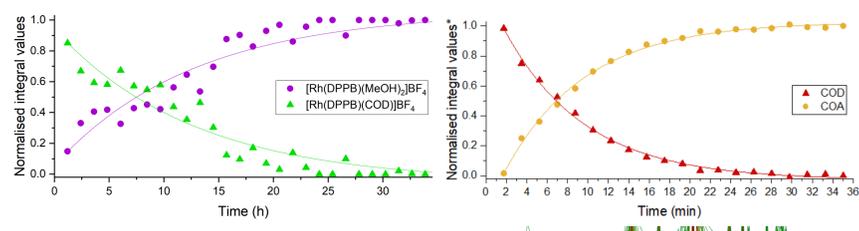
### Hydrogenation of $[\text{Rh}(\text{DPPB})(\text{COD})]\text{BF}_4$ – Mass transfer



$^1\text{H}$  NMR of  $\text{COD}(\text{CH}_2)$  in MeOH:  $\delta$  2.4 ppm

$^1\text{H}$  NMR of  $\text{COA}$  in MeOH:  $\delta$  1.6 ppm

*In situ* experiment performed in static mode in a J Young tube (left) has been compared with on-line reaction monitoring (right). The synthesis of  $[\text{Rh}(\text{DPPB})(\text{MeOH})_2]\text{BF}_4$  required approximately one day in static mode because of the limited mass transfer while 30 min were sufficient in flow mode ( $^1\text{H}$  monitoring with solvent suppression).



LF static  $^{31}\text{P}\{^1\text{H}\}$  NMR monitoring

LFF  $^1\text{H}$  NMR monitoring with presaturation

## Conclusions

We have demonstrated that reactions of highly sensitive organometallic systems such as neutral and cationic Rh(I) diphosphine complexes can be followed by non-invasive LFF  $^{31}\text{P}$  NMR reaction monitoring. All components of the setup (e.g., air-tight pump, capillaries, junctions) must be chosen with particular care to allow perfectly inert conditions. Once this has been assured, the system allows reliable real-time reaction monitoring, requiring low maintenance over time. Future studies will focus on the evaluation of polarization transfer to increase the sensitivity of the phosphorus containing species and the inclusion of other spectroscopic as well as analytical tools (e.g., UV-Vis spectroscopy or volumetric analysis) in the system.

[1] Hall, A. M. R.; Dong, P.; Codina, A.; Lowe, J. P.; Hintermair, U. *ACS Catal.* **2019**, *9*, 2079-2090. [2] van Beek, T. A. *Phytochemical Analysis*, **2021**, *32*, 24-37.