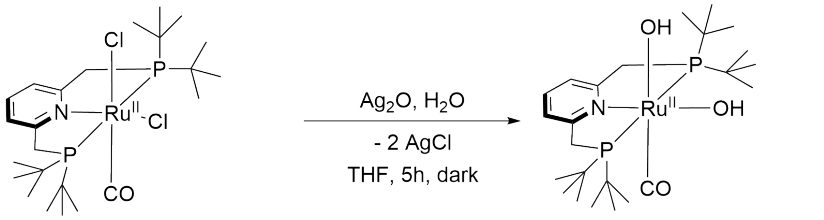
# AE-252: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h

**Date:** 2024-04-04
**Tags:** Dihydroxo Ag2O PNP P(tBu)N(py)P(tBu) [Ru(CO)(OH)2(PNP)] NMR AE Future reference analytics 1H 31P stability test
**Status:** Done
**Created by:** Alexander Eith

## Reaction scheme/sample structure




Chemical Formula: $C_{24}H_{43}Cl_2NOP_2Ru$
Molecular Weight: 595,53152

[$RuCl_2(CO)(PNN)$]

Silver Oxide

Molecular Weight: 231.74 g/mol

Chemical Formula: $C_{24}H_{45}NO_3P_2Ru$
Molecular Weight: 558,64552

[$Ru(CO)(OH)_2(PNN)$]

## Literature/reference experiments

| | |
|---|---|
| **Literature** | https://doi.org/10.1039/D1EE01053K |
| **Reproduction** | / |
| **Related experiments** | Experiment - AE-KRA-204: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h<br>Experiment - AE-238: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h |

## Reagents

| Name | CAS-Number/Expermient-Number | Amount [mmol] | Equivalents | $Mass_{theo}$ [mg] | $Mass_{exp}$ [mg] | Molar mass [g/mol] | $Volume_{theo}$ [ml] | $Volume_{exp}$ [ml] | Density [g/mL] |
|---|---|---|---|---|---|---|---|---|---|
| [RuCl2(CO)(PNP{tBu})] | Experiment - AE-232: Synthesis of [RuCl2(CO)(PNP)] with 2,6-Bis((tert-butyl)phosphinomethyl)pyridine via [RuCl2(CO)(p-cymene)] -2 | 0.232 | 1.00 | 138.24 | 138.24 | 595.53 | / | / | / |
| $Ag_2O$ | 20667-12-3 | 1.425 | 6.14 | 330.29 | 329.81 | 231.74 | / | / | / |
| H2O | Experiment - KRA-104: Degassing of Milli-Q water | 54.32 | 234 | 978.8 | / | 18.02 | 0.981 | 0.98 | 0.998 |
| THF | Experiment - KRA-080: Degassing of THF | / | / | / | / | / | 6.9 | 7 + 11 | / |
| n-Heptane | Experiment - AE-121: Degassing of n-Heptane | / | / | / | / | / | / | 13 | / |

## Procedure/observations

All steps, unless mentioned otherwise, were carried out under argon using standard Schlenk technique or in an argon

filled glovebox. (see Protocol Protocol - Schlenk Technique)

Due to the instability of $Ag_2O$ and Dihydroxo to the light, the procedure was done mostly in the dark. The precise measures, which were taken, are listed in "**Steps**".

| Date | Time | Step | Observations |
|---|---|---|---|
| 04.04 | 13:00 | A 25mL-brown glas Schlenk flask was prepared, by heating under vacuum | |
| | 13:15 | $[RuCl_2(CO)(PNP)]$ (138.24 mg) was weighted in air into the reaction schlenk flask and the flask was set under argon. | |
| | | The substance was stored under argon ar rt | |
| 05.04 | 8:20 | Ag2O (329.81 mg) was weighted under air into the reaction schlenk flask and the flask was set under argon. | |
| | | The light in the fumehood was turned out | |
| | 8:45 - 8:46 | THF (7.0 mL) and water (0.98 mL) were added to the reaction schlenk flask. | |
| | 8:46 - 13:54 | The reaction mixture was stirred for 5 h at 750 rpm. After approx. 3 h the flask was covered in aluminium foil and the light in the fumehood was turned on | |
| | | The light was turned off and the aluminium foil was removed | |
| | 13:54 - 13:58 | The reaction mixture was allowed to settle | after-reaction.jpg |
| | 13:58 | The reaction mixture was filtrated through a PTFE-syringe-filter (0.20 µm) into a separate 25 mL-Schlenk flask, equipped with a stirring bar. | after-1st-filt.jpg |
| | 14:08 - 14:23 | The solvents of the first flask was removed under reduced pressure. | wet-raw-product.jpg |
| | - 14:48 | The obtained solid was dried under reduced pressure | |
| | 15:25 | To the solid THF (11 mL) was added und the obtained mixture was stirred and shaken strongly for approx. 5 min | Some solids remained in-THF.jpg |
| | 15:36 | n-heptane (10 mL) was added to the mixture | More solids formed, after addition of hept.jpg, after addition of hept settled.jpg |

| | | | |
|---|---|---|---|
| | 16:00 - 16:55 | The mixture was filtered through a pore 5 frit according to Protocol - Filtration with frit technique into a 100 mL-Schlenk | Slow filtration, first filt was coloureless likely due to strong vacuum, whcih leads to evaportation of THF. After approx. 1.5 mL start of typical purple colour. after-approx-1-mL-during-filt.jpg after-approx-2-mL-of-filt.jpg |
| | 16:55 - 17:05 | The solid was washed with n-heptane (3 * 1 mL) | after-filt.jpg |
| | 17:06 - 17:08 | The solid was dried under reduced pressure | prod-A.jpg |
| 09.04 | 11:23 - 15:35 | The solid was dried under reduced pressure | |
| | 15:50 | The solid was transffered into a vial in a 10 mL Schlenk flask | AE-252-1, final prod.jpg |
| | 16:00 | A sample (3.2 mg) was transferred into another 10 mL Schlenk flask | |
| | 16:16 | To the sample Milli-Q water (1 mL) was added | |
| | | The mixture was stirred for apporx. 2 min | NMR sample in water.jpg |
| | 16:18 | A NMR sample was preapred according to Protocol - Preparation of NMR Sample, during the trasnfer the mixture was filtered through a PA syringe filter (pore diamter = 0.22 µm) | AE-252-1, NMR sample after filt.jpg |
| | | The remaining solid of AE-252-1 was stored on the frit at -20 °C in the dark under argon | |
| 22.04 | | The same NMR tube, which was used for AE-252-1 was submitted again as **AE-252-2** | NMR-2.jpg |
| 17.05 | | Two 10 mL-Schlenk flasks were prepared | |
| | 12:50 | To each flask **AE-252-1** (approx. 4 mg) was added and the flask were set under argon again | |
| | 13:10 | To one flask THF-d8 (0.7 mL) was added (**AE-252-3**) and the obtained suspension was stirred | in THF.jpg |
| | | To the other flask toluene-d8 (0.7 mL) was added (**AE-252-4**) and the obtained suspension was stirred | in tol.jpg |
| | 13:25 | Both, **AE-252-3 and -4**, were transffered in separate Yound type NMR tubes according to Protocol - Preparation of NMR Sample | NMR in tol.jpg NMR in THF.jpg |
| | | From both, **AE-252-3 and -4** NMR spectra were masured | |
| 08.07 | 15:00 | The sample **AE-280-2** was used to prepare an NMR in DMF-d7 accoring to Protocol - Preparation of NMR Sample | |

# Analysis

| Date | Time | Sample name | Analysis method | Used device | Solvent | Raw Data | Processed Data | Comparative Data | Interpretation |
|---|---|---|---|---|---|---|---|---|---|
| 10.04 | 10:14 | AE-252-1 | NMR 1H, 31P{1H}quant, 1Hzgespg | IAAC 400 MHz I | H2O | AE-252-1_10.zip | AE-252-1_10.nmrium | Experiment - AE-246: Radiation of [Ru(CO)(OH)2(PNP{tBu})] (AE-238, 97 % pure) 365 nm and white -1 | Desired product. In 31P no impurities are observed. In 1H some small impurities are observed (mainly some residual solvents) |
| 22.04 | 17:56 | AE-252-2 | NMR 1H, 31P{1H}quant, 1Hzgespg | IAAC 400 MHz I | H2O | AE-252-2_10.zip | AE-252-2_10.nmrium | AE-252-1 | No relevant change observed. Slight decrease in intensity. 90 % of the main species is still present. Other 10 % are not observed, but also no solid formation is observed --> maybe formation of [Ru(III)]? but no greenish colour is observed |
| 17.05 | 20:36 | AE-252-3 | NMR 1H, 31P{1H}quant, 1Hzgespg | IAAC 400 MHz I | THF-d8 | AE-252-3-10.zip | AE-252-3_10.nmrium | Experiment - AE-105: Synthesis of [Ru(CO)(OH)2(PNP)] with 2,6-bis(P,P-di(tertbutyl)phosphinomethyl) using Ag2O (AE-105-6)<br>Experiment - AE-KRA-204: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h (AE-204-1) | Significantly lower concentration than in MeCN-d3 and DMSO-d6. But still signals are good observable. Significantly more impurities are observed in 1H and some impurities are observed in 31P. This increase can be likely explained by the low solubility of the desired complex, since most of the material remained undissolved and so leading to a higher proportion of the impurties in the solution.<br>A signal for the residualwater/-OH group is observed, as well as the other expected signals.<br>The Methylene-bridge proton signal is partially overlapped by a solvent peak of the THF |
| 17.05 | 18:46 | AE-252-4 | NMR 1H, 31P{1H}quant, 1Hzgespg | IAAC 400 MHz I | toluene-d8 | AE-252-4-10.zip | AE-252-3_10.nmrium | Experiment - AE-105: Synthesis of [Ru(CO)(OH)2(PNP)] with 2,6-bis(P,P-di(tertbutyl)phosphinomethyl) using Ag2O (AE-105-6)<br>Experiment - AE-KRA-204: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h (AE-204-1)<br>AE-252-3 | Very low intensity.<br>Signals in the 1H can not be atributed due to the low concentratiion.<br>In 31P a weak signal can be observed at 68 ppm. Hight approx. 2 to 3 times the base line noise. |
| 08.07 | 17:00 | AE-252-5 | NMR 1H, 31P{1H}quant | IAAC 400 MHz I | DMF-d7 | AE-252-5.zip | AE-252-5_10.nmrium | / | Good intensity --> good solubility, but slower dissolved than in MeCN<br>Quite large water peak, besides drying over molecular sieve of DMF-d7<br>Other signals can clearly be seen and fit to what was seen in other solvents.<br>Shift in 31 P: 68 ppm<br>Baseline bit wired: in area were signals are (8 to 1 ppm) generally slightly higher than in other area´s. No idea why. |

# Product characterization and results

| Sample | Mass [mg] | Purity | $Mass_{pure}$ [mg] | Amount [µmol] | Yield [%] | Description |
|---|---|---|---|---|---|---|
| AE-252-1 | 40.17 | >97 % | 40.17 | 71.9 | 31 | final prod.jpg |

The product is stable in the dark in water at rt for at least 12 d, with only minor degradation of approx. 10 %
Poorly soluable in THF, very poorly soulable in toluene

No material left

## Future recommendations

| Old procedure | Problem | Suggested new procedure |
|---|---|---|
| Direct after reaction: filtration with PTFE syringe filter | filter gets blocked with larger quantities of Ag2O, high pressure was needed towards the end of the filtration | filtration via a filter paper or a filter frit |

## Linked experiments

- AEI-010: Synthesis of [Ru(CO)(OH)2(PNN)] using Ag2O
- JSC-KS-04: Degassing of n-Heptane
- AEI-024: Synthesis of [Ru(CO)(OH)2(NNN)] with 2,6-bis(N,N-diethylaminomethyl) using Ag2O
- AEI-026: Capillary production
- AEI-048: Synthesis of [Ru(CO)(OH)2(NNN)] with 2,6-bis(N,N-diisopropylaminomethyl) using Ag2O
- AEI-064: Synthesis of [Ru(CO)(OH)2(PNP)] with 2,6-bis(P,P-di(tertbutyl)phosphinomethyl) using Ag2O
- AEI-073: Synthesis of [Ru(CO)(OH)2(PNP)] with 2,6-bis(P,P-di(tertbutyl)phosphinomethyl) using Ag2O
- AE-101: Synthesis of [RuCl2(CO)(PNP)] with 2,6-Bis((tert-butyl)phosphinomethyl)pyridine via [RuCl2(CO)(p-cymene)]
- AE-102: Degassing of THF
- AE-105: Synthesis of [Ru(CO)(OH)2(PNP)] with 2,6-bis(P,P-di(tertbutyl)phosphinomethyl) using Ag2O
- AE-108: Synthesis of [RuCl2(CO)(PNP)] with 2,6-Bis((tert-butyl)phosphinomethyl)pyridine via [RuCl2(CO)(p-cymene)]
- AE-114: Synthesis of [Ru(CO)(OH)2(PNP)] with 2,6-bis(P,P-di(tertbutyl)phosphinomethyl) using Ag2O
- AE-121: Degassing of n-Heptane
- AE-145: Synthesis of [Ru(CO)(OH)2(PNP)] with 2,6-bis(P,P-di(tertbutyl)phosphinomethyl) using Ag2O
- AE-157: Synthesis of [RuCl2(CO)(PNP)] with 2,6-Bis((tert-butyl)phosphinomethyl)pyridine via [RuCl2(CO)(p-cymene)]
- AE-167: Irradiation of PhPDA (365 nm + white LED, gas phase measurement), AE-151, 1.5 mg/mg SDS, 2 mg/mL PhPDA

- AE-198: Synthesis of [Ru(CO)(OH)2(PNP{tBu})] with Ag2O with different reaction times (1, 2, 5, 24 h)

- AE-KRA-204: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h

- AE-208: Degassing of Milli-Q water

- KRA-080: Degassing of THF

- KRA-104: Degassing of Milli-Q water

- AE-230: Synthesis of [RuCl2(CO)(PNP)] with 2,6-Bis((tert-butyl)phosphinomethyl)pyridine via [RuCl2(CO)(p-cymene)]

- AE-232: Synthesis of [RuCl2(CO)(PNP)] with 2,6-Bis((tert-butyl)phosphinomethyl)pyridine via [RuCl2(CO)(p-cymene)]

- AE-238: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h

- AE-246: Radiation of [Ru(CO)(OH)2(PNP{tBu})] (AE-238, 97 % pure) 365 nm and white

## Linked resources

Protocol - Preparation of NMR Sample

Protocol - Filtration with frit technique

Protocol - Schlenk Technique

Protocol - Preparation of capillary for H2O-NMR

## Attached files

AE-252-5_10.nmrium
sha256: 869db83c23f61e22a1483c95583266cd983960baabc6b4d457a748a3a8fa5f14

AE-252-5.zip
sha256: 30e96961f7a4f75e3e676f41ba07e306a630c68a11b726d9260cea229d6358e7

AE-252-3_10.nmrium
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AE-252-4-10.zip
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AE-252-3-10.zip

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NMR-in-THF.jpg
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NMR-in-tol.jpg
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AE-252_Yield_Determination.xlsx
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AE-252-2_10.nmrium
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NMR-2.jpg
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final-prod.jpg
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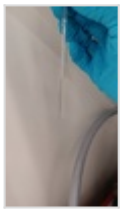

NMR-sample-in-water.jpg
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prod-A.jpg
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after-approx-2-mL-of-filt.jpg
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in-THF.jpg
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wet-raw-product.jpg
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after-1st-filt.jpg
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after-reaction.jpg
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after-filt.jpg
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Link: https://elab.water-splitting.org/experiments.php?mode=view&id=928