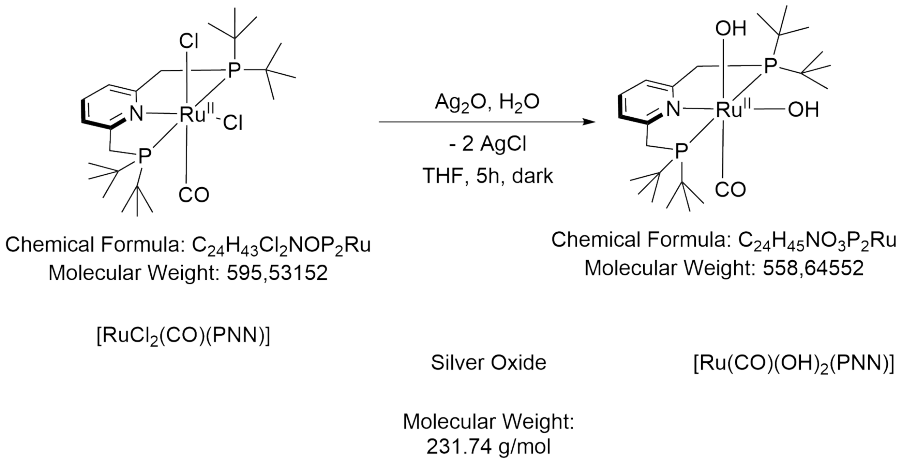
AE-382: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h

Date: 2024-11-13
Tags: Dihydroxo | Ag2O | PNP | P(tBu)N(py)P(tBu) | [Ru(CO)(OH)2(PNP)] | NMR | ESI-MS | AE | MS | reference analytics | 1H | 31P | Elemental Analysis
Category: Two-photon
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 Experiment - AE-238: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h Experiment - AE-252: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h AE-310: 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-261: Synthesis of [RuCl2(CO)(PNP)] with 2,6-Bis((tert-butyl)phosphinomethyl)pyridine via [RuCl2(CO)(p-cymene)] (AE-261-1)	0.827	1.00	-	492.57	595.53	/	/	/
Ag_2O	20667-12-3	5.078	6.14	1176.88	1176.70	231.74	/	/	/
H2O	Experiment - KRA-104: Degassing of Milli-Q water	193.54	234	3487	/	18.02	3.49	3.6	0.998
THF	Experiment - KRA-080: Degassing of THF	/	/	/	/	/	25	25	/
n-Heptane	Experiment - AE-121: Degassing of n-Heptane	/	/	/	/	/	/	20	/

Work-up Reagents

Name	CAS Number /	Inventory number	$Mass_{exp}$ [g]	Volume [ml]	Concentration [M]
THF	Experiment - KRA-080: Degassing of THF	/	/	25 +20	/
n-heptane	Experiment - AE-121: Degassing of n-Heptane	/	/	59 + 55	/
MeCN	AE-152: Degassing of MeCN	/	/	6	/

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, by either wrapping the flasks containing either or both in Aluminium foil or by tuning off the light in the lab and fumehood

Date	Time	Step	Observations
14.11	9:10	A 50mL- Schlenk flask was prepared, by heating under vacuum	
	9:30	[$RuCl_2$(CO)(PNP)] and Ag2O was weighted in air into the reaction schlenk flask and the flask was set under argon.	
		The light in the fumehood was turned out	
	10:10	THF (25 mL) was added to the reaction schlenk flask.	
	10:15	Water (3.6 mL) was added to the reaction schlenk flask	
	10:15 - 15:15	The reaction mixture was stirred for 5 h at 700 rpm. During this the flask was wrapped with aluminium foil	Start of reaction.jpg after reaction.jpg
	15:15 - 15:20	The reaction mixture was allowed to settle	

	15:20 - 15:50	The mixture was filtered through a pore 4 frit according to Protocol - Filtration with frit technique into a 100 mL-Schlenk	
	15:50 - 16:05	The reaction flask was washed with MeCN (2 * 3 mL)	1st washing: yellowish liquid phase 2nd washing: nearly clear liquid phase
	16:05 - 17:05	The solvents of the filtrate were removed under reduced pressure. • When approx. 5 mL were left the water bath was removed and the mxiture was allowed to freeze (at approx. 16:20) • At 16:45 the water bath was added again to slowly melt the remaining solvent	This procedure avoids bubbling up of the mixture
		The solid was stored in the dark at - 20 °C	Dark borwnish solid Solid after night.jpg
15.11	10:20 - 10:30	To the solid THF (25 mL) was added und the obtained mixture was stirred and shaken strongly for approx. 7 min	after adding THF.jpg
	10:30 - 10:37	n-heptane (50 mL) was added to the mixture	after adding n-hept.jpg
	11:17 - 12:00	The mixture was filtered through a pore 3 frit according to Protocol - Filtration with frit technique into a 100 mL-Schlenk	
	12:03 - 12:10	The solid was washed with n-heptane (3 * 3 mL)	
	12:13 -13:17	The solid was dried under reduced pressure	
	13:30 - 13:40	The solid was transfferred into a 2 mL vial in a 10 mL Schlenk flask	Some material was lossed, since it sticked stongly to any surface
		During this an aliqoute (approx. 5 mL) was transfferred into another 10 mL Schlenk flask	
	13:45 - 14:35	Both flasks were dried under reduced pressure	
		Both flask were set under argon	
	14:50	From the aliquote n NMR sample was prepared in DMSO-d6 according to Protocol - Preparation of NMR Sample	**AE-382-1** **AE-382-1.jpg**
		The remaining solid was stored in the dark under argon at -20 °C	**AE-382-1** Product.jpg

04.12		Further workup, since in 1H NMR some more sideproducts are observed (with all remaining **AE-382-1**)	
		A 100 mL flask was prepared	
		The vial containing **AE-382-1** was added to the flask is Ar counterflow	
	16:05	To the 100 mL flask THF (20 mL) was added	in THF.jpg dark suspension
		It was tried to remove th vial without sucess	
	16:07 - 16:12	The flask was shaken to get all solids out of the vial	
	16:12 - 16:23	The flask was stirred	brownish suspension
	16:23 - 16:30	To the flask n-heptane (52 mL) was added	after n-hept.jpg orange solution, brownish.gray solid
	16:30 - 16:32	The suspension was stirred	
		The flask was stored in the dark in Equipment - Freezer Lab E004 CEEC II under Ar	
05.12		The obtained suspension was warmed to rt	before filt.jpgorange solution, brownish.gray solid
	10:40 - 14:30	The suspension was filtered through a pore 4 filter frit	Very slow filtration, filtration was stopped after approx. 40 mL of solvent
	14:30 - 14:50	The obtained filter residue was washed with n-Heptane (1 * 1.5 mL)	washing of filterate on 1st frit.jpg
	14:50 - 14:58	The obtained solid (**AE-382-2**) was dried under reduced pressure	
	14:53	The filteration setup was changed to a pore 3 frit. Therefore the new frit was connected with a "Vakuumvorstoß", closed and set under inert conditons. Afterwards the cannula, still conected to the flask containing the suspesion, was attached in Ar counterflow. Then the reciving flask was added under Ar counterflow and the filtration was continued	
	14:56 - 15:13	The remaining suspension was filtered through a pore 3 filter frit	
	15:15 - 15:20	The obtained residue (**AE-382-3**) was washed with n-heptane (3 * 1 mL)	

	15:30 - 17:05	AE-382-2 and -3 were dried under reduced pressure	
		Both were stored on the frit in the dark under Ar in Equipment - Freezer Lab E004 CEEC II	
09.12	10:40	**AE-382-3**: The solid was transffered into a 1.5 mL screw cap vial in a10 mL Schlenk flask. during this approx. 5 mg were added to another 10 mL Schlenk flask to prepare an NMR sample.	
		Both flasks were set under argon and stored in Equipment - Freezer Lab E004 CEEC II in the dark under Ar	
12.12	11:05	To the flask containing the NMR sample DMSO-d6 (0.75 mL) was added	-3 in DMSO-d6.jpg brownish solution
	11:05 - 11:10	The obtained solution was stirred	
	11:10	An NMR sample was prepard according to Protocol - Preparation of NMR Sample	AE-382-3.jpgbrownish solution
15.01	10:05	**AE-382-2**: The solid was transffered into a 1.5 mL screw cap vial in a10 mL Schlenk flask. during this approx. 4 mg were added to another 10 mL Schlenk flask to prepare an NMR sample.	
		Both flasks were set under argon and **AE-382-2** was stored in Equipment - Freezer Lab E004 CEEC II in the dark under Ar	
	10:25	To the flask containing the NMR sample MeCN-d3 (0.65 mL) was added	
		An NMR sample was prepard according to Protocol - Preparation of NMR Sample	AE-382-2.jpg
13.03		A 10 mL and a 5 mL Schlenk flask were prepared, each containing a 1.5 mL screw cap vial without lid	
	13:45	An sample for an elemental analysis was prepared by weighing in 3.75 mg of **AE-382-2** into the vial of the 10 mL Schlnek flask and setting it under argon afterwards.	**AE-382-EA** (AE382a on sheet, since max. 6 letters)
	13:50	An sample for MS was prepared. Therefore 1.62 mg of **AE-382-2** was transferred into the vial of the 5 mL Schlenk flask in air. Afterwards the flask was set under argon.	**AE-382-MS**

	14:00	The sample was submitted to Nicole Fritz. Further work done by Nicole: Rough description of sample handling: The flask was opened to air and a small amount (approx. 0.1 mg) was taken out and diluted in acetonitril (ACN) 3 times. After taking out the small amount the flask was closed again. Afterwards the sample was injected into the MS device. Before and after the measurment a calibration measurement was performed. (**AE-382-MS ACN_1**) After approx. 10 min a sample of the same solution was measured (**AE-382-MS ACN_1_10min**) A new sample was prepared the same way as the first sample (**AE-382-MS ACN_2**) A new sample was prepared analog to the first sample, but the small amount taken out was first dissolved in water (approx. 0.5 mL) and than diluted with ACN (**AE-382-MS H2O_ACN**)	
31.03	/	The elemental analysis of **AE-382-EA** was measured by Sandra Köhn	

Analysis

Date	Time	Sample name	Analysis method	Used device	Solvent	Raw Data	Processed Data	Used for plotting	Comparative Data	Interpretation
18.11	13:21	AE-382-1	NMR 1H, 31P{1H}quant	IAAC 400 MHz I	DMSO-d6	AE-382-1.zip	AE-382-1_10.nmrium	/	AE-310: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h	As expected. Only minor impurities
12.12	/	AE-382-3	NMR 1H, 31P{1H}quant	IAAC 400 MHz I	DMSO-d6	AE-382-3.zip	2024-12-13_12-58-51.zip_AE-382-3_10.nmrium	/	/	As expected. Only minor impurities
15.01	17:31	AE-382-2	NMR 1H, 31P{1H}quant	IAAC 400 MHz I	MeCN-d3	AE-382-2.zip	AE-382-2_10.nmrium	/	/	As expected. Only minor impurities
13.03	14:10	AE-382-MS ACN_1	ESI-MS	ESI-TOF-Bruker	MeCN	AE-382-MS-ACN_1.xy	AE-382-2-MS-ACN_1.txt AE-382-MS-ACN_1.png	ESI-MS.py	C24H43NO3P2RuCO.csv calculated via https://www.envipat.eawag.ch/index.php	Very weak singal which could be M+H, but significant signals at higher mass, full interpreation pending Main signal could be from carbonate forming and removing both OH groups through addition of CO2
13.03	14:20	AE-382-MS ACN_1_10min	ESI-MS	ESI-TOF-Bruker	MeCN	AE-382-MS-ACN_1_10min.xy	AE-382-2-MS-ACN_1_10min.txt AE-382-MS-ACN_1_10min.png	ESI-MS.py	C24H43NO3P2RuCO.csv calculated via https://www.envipat.eawag.ch/index.php	Significantly different pattern -> most likely decompostion
13.03	14:30	AE-382-MS ACN_2	ESI-MS	ESI-TOF-Bruker	MeCN	AE-382-MS-ACN_2.xy	AE-382-2-MS-H2O_ACN.txt AE-382-MS-ACN_2.png	ESI-MS.py	C24H43NO3P2RuCO.csv calculated via https://www.envipat.eawag.ch/index.php	Very weak singal which could be M+H, but significant signals at higher mass, full interpreation pending Weaker signal than ACN_1. signal at 627 less pronaunced. Main signal at 586 u (delta to expected: 28 u
13.03	14:35	AE-382-MS H2O_ACN	ESI-MS	ESI-TOF-Bruker	MeCN + H2O	AE-382-MS-H2O_ACN.xy	AE-382-2-MS-ACN_2.txt AE-382-MS-H2O_ACN.png	ESI-MS.py	C24H43NO3P2RuCO.csv calculated via https://www.envipat.eawag.ch/index.php	Very weak singal which could be M+H, but significant signals at higher mass, full interpreation pending Some new, high mass peaks
31.03	/	AE-382-EA	elemental analysis	?	/	AE-382-EA.jpg	C: 49.78 % H: 6.94 % N: 2.45 %	/	C: 51.6 % H: 8.12 % N: 2.51 %	C and H contant to low by 1.8 pp for C and 1.2 pp for H. N content fits roughly

Product characterization and results

Sample	Mass [mg]	Purity	$Mass_{pure}$ [mg]	Amount [µmol]	Yield [%]	Description	Storage location
AE-382-1	149.79	> 96 %	/	0.268	32	grayish olive-ochre very fine, sticky solid, Product.jpg	used
AE-382-3	40.87	> 96 %	/	/	/	grayish olive-ochre very fine, sticky solid	freezer drawer A
AE-382-2	23.87	> 96 %	/	/	/	grayish olive-ochre very fine, sticky solid	freezer drawer A

MS fits to +CO -HO.

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-152: Degassing of MeCN

- 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

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

- AE-261: Synthesis of [RuCl2(CO)(PNP)] with 2,6-Bis((tert-butyl)phosphinomethyl)pyridine via [RuCl2(CO)(p-cymene)]

- AE-281: Stability test of [Ru(CO)(OH)2(PNP{tBu})] (AE-252) under air and afterwards irradiation with 365 nm and white

- AE-310: Synthesis of [Ru(CO)(OH)2(PNPtBu)] using Ag2O, 5 h

Linked resources

Equipment - Freezer Lab E004 CEEC II

Protocol - Preparation of NMR Sample

Protocol - Filtration with frit technique

Protocol - Schlenk Technique

Protocol - Preparation of capillary for H2O-NMR

Attached files

AE-382-EA.jpg
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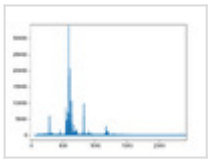

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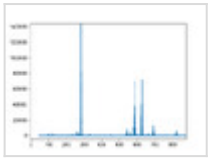

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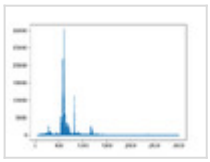

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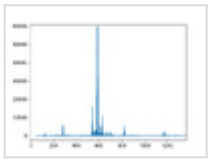

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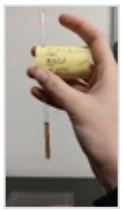

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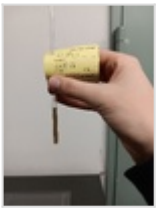

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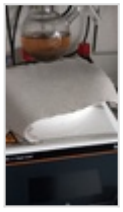

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after-adding-n-hept.jpg
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Start-of-reaction.jpg
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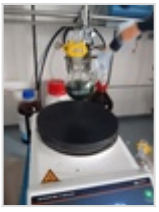

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after-adding-THF.jpg
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Solid-after-night.jpg
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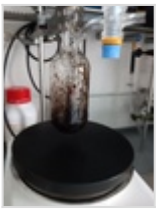

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Comment

On 2024-12-13 13:41:11 Jacob Schneidewind wrote:
Notes:
* adding future recommendation to change MeCN purification step (same as AE-302-1)

Unique eLabID: 20241113-5686e080afe9a3b141d8cfffc3b0f1b849e0097d
Link: https://elab.water-splitting.org/experiments.php?mode=view&id=1502