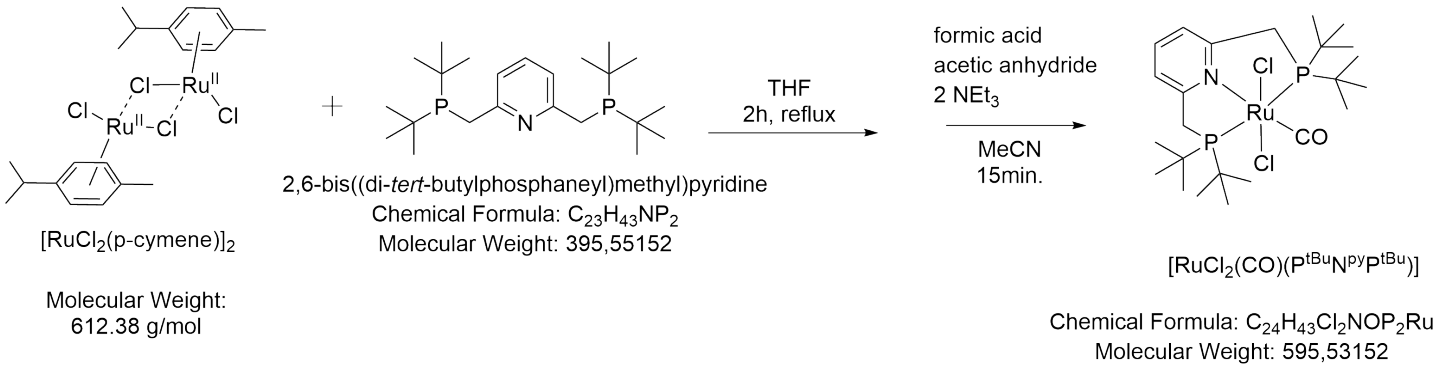
AEI-053: Synthesis of [RuCl2(CO)(PNP)] with 2,6-Bis(P,P-di(tertbutyl)phosphinomethyl)pyridine

Date: 2022-12-15
Tags: Dichloro PNP [RuCl2(CO)(PNP)] AEI P(tBu)N(py)P(tBu)
Status: Done
Created by: Alexander Eith

Reaction scheme/sample structure

similar to [Experiment] AEI-050: Synthesis of [RuCl2(CO)(PNP)] with 2,6-Bis(P,P-di(tertbutyl)phosphinomethyl)pyridine



$[RuCl_2(p\text{-cymene})]_2$

Molecular Weight: 612.38 g/mol

2,6-bis((di-*tert*-butylphosphaneyl)methyl)pyridine
Chemical Formula: $C_{23}H_{43}NP_2$
Molecular Weight: 395,55152

$[RuCl_2(CO)(P^{tBu}N^{py}P^{tBu})]$

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

Reagents

Name	Amount [mmol]	Equivalents	$Mass_{theo,pure}$ [mg]	Purity [%]	$Mass_{theo}$ [mg]	$Mass_{exp}$ [mg]	Molar mass [g/mol]	$Volume_{theo}$ [ml]	$Volume_{exp}$ [ml]	Density [g/mL]
[RuCl2(p-cymene)]2	0.125	0.5	76.5	/	/	76.5	612.38	/	/	/
PNP, 2,6-Bis(P,P-di(tertbutyl)phosphinomethyl)pyridine ([Experiment] AEI-047: Synthesis of 2,6-Bis(P,P-di(tertbutyl)phosphinomethyl)pyridine)	0.25	1	98.89	96.5	102.5	102.63	395.55152	/	/	/
THF	/	/	/	/	/	/	/	15	/	/
n-heptane	/	/	/	/	/	/	/	10 + 3	/	/
formic acid	8.3	27	384.65	/	/	/	46.03	0.315	0.32	1.22
acetic anhydride	8.3	27	853.16	/	/	/	102.09	0.790	0.79	1.08
triethylamine	16.6	54	1679	/	/	/	101.19	2.30	2.3	0.73
toluene	/	/	/	/	/	/	/	15	/	/

Procedure/observations

All steps (unless stated otherwise) were carried out under argon using either standard Schlenk technique or in an argon filled glovebox (MBRAUN). [Protocol] Schlenk Technique

Date	Time	Step	Observations
15.12	9:30	A 10mL and a 50 mL-Schlenk flask were prepared.	
	9:40 - 10:50	A small reflux condenser was prepared, by evacutating it for approx.1 h	

	10:30 - 10:45	PNP was weighed into the 10 mL-flask in a glovebox	white solid
	11:05	[RuCl2(p-cymene)]2 was weighed into the 50 mL flask under air and the flask was subsequently set under argon	red solid
	11:30	To the PNP THF (7.5 mL) and to the [RuCl2(p-cymene)]2 THF (7.5 mL) were added and the mixtures were stirred for 5 min	PNP: turbid solution, Ru: some solid did not dissolve, orange-red solution
	11:35	The PNP mixture was added to the 50 mL flask containing the [RuCl2(p-cymene)]2 mixture	no significant change was observed
	11:35 - 11:55	The mixture was stirred at 500 rpm for approx. 20 min. Thereby the reaction flask was equipped with a small reflux condenser	see: before heating.jpg
	11:55 - 13:55	The mixture was heated to reflux for 2 h, at 400 rpm At 12:15 the mixture started to reflux.	during the heating the colour got darker and more red.
	13:55 - 15:05	The mixture was cooled to rt	clear, dark yellow, orange solution, see: after heating.jpg After some time at rt solids formed, see: solid.jpg
	13:50 - 14:50	The setup for the generation of CO was build up according to [Protocol] Addition of CO by bubbling of CO through the solution	
	15:05	Toluene (15 mL) was added into the flask for the CO generation according to [Protocol] Addition of CO by bubbling of CO through the solution	
	15:10 - 15:15	formic acid and acetic anhydride were added into the flask for the CO generation according to [Protocol] Addition of CO by bubbling of CO through the solution	
	15:23 - 15:41	Triethylamin was added slowly over the next 15 min into the flask for the CO generation according to , both flask were stirred at 500 rpm	Bubbles developed in the clear colorless solution. The reaction mixture became less cloudy and finally formed a solution after the addition of 0.8 mL and approx. 8 min, see clear by CO.jpg
	15:45 - 7:00	The solution was stirred under CO atmosphere at 500 rpm and rt	after CO.jpg
16:12	7:00 - 11:25	The stirring was turned off and the reaction mixture was left standing at rt	orange solution, see: after stirring over night.jpg
	11:25 - 12:55	The volume of the solution was reduced to approx. 5 mL	see: reduced.jpg

	11:55 - 12:15	10 mL n-Heptane were added to the solution and the obtained suspension was stirred for approx. 5 min	see: after precipitation.jpg
	13:45 - 13:55	The cold solution was filtered according to [Protocol] Filtration with frit technique	
	13:55 - 14:05	The obtained solid was washed with n-Heptane (3 * 1 mL)	
	14:10 - 14:55	The solid was dried under reduced pressure	
	14:55	The solid and filtrate were stored under argon at rt	orange-yellow liquid, see filtrate with crystals greenish solid, see filter residue.jpg
19.12	14:20	A NMR-Sample of the solid was prepared according to [Protocol] Preparation of NMR Sample (AEI-050-1)	range brown solution, 13.8 mg
		In the filtrate crystals formed.	See: filtrate with crystals

Analysis

Date	Time	Sample name	Analysis method	Solvent	Raw Data	Processed Data	Interpretation
19.12	15:24	AEI-053-1	1H (-30 - 20 ppm), 31P quant cryo	CD2Cl2	AEI-053-1.zip		Main species can be observed, as in [Experiment] AEI-050: Synthesis of [RuCl2(CO)(PNP)] with 2,6-Bis(P,P-di(tertbutyl)phosphinomethyl)pyridine. But more of the 73 ppm product. In 1H hydrides can be observed as well as very brod peak, suggesting a Ru(III) species.
/	/	SH-03013_A2_a-3	singel crystal XRD	/	SH_03013_A2_a-3.res, SH_03013_A2_a.docx	SH_03013_A2_aresinP1_1.png, SH_03013_A2_aresinP1_2.png, SH_03013_A2_aresinP1_3.png, SH_03013_A2_aresinP1.png	Nice crystal structure, dimer, trans species

Product characterization

		m [mg]	purity	m_{pure} [mg]	n [mmol]	Y [%]

Linked resources

Protocol - Preparation of NMR Sample

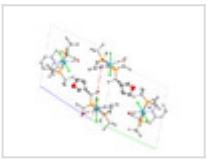
Protocol - Filtration with frit technique

Protocol - Schlenk Technique

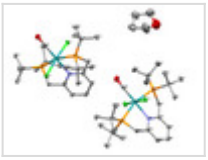
Protocol - Addition of CO by bubbling of CO through the solution using syringe

Attached files

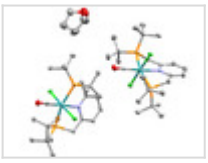
SH_03013_A2_aresinP1.png
sha256: 34b66e6b2c928a8d272cf87baf2dac89047bb4a09bb8c3b6e39cd9a89895c596



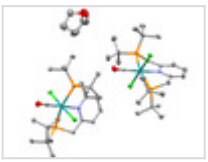
SH_03013_A2_aresinP1_3.png
sha256: 33ddcdd1af236a14f5847000610af74ee8555b414e2d34fbe4e2f1b525932cf2



SH_03013_A2_aresinP1_2.png
sha256: 3e98ff61df19ed394ffe536d83fc9ae3cc039f872b324bb4ecf4c62fe3621153



SH_03013_A2_aresinP1_1.png
sha256: 0870ec9790dc94490833ad9542b19b67c7848146516627890057fdc8120386eb



AEI-053-1_10-2-for-MA.nmrium
sha256: 5a17430b80cb0e4d69b7189db6ee62e1ad1b63b196c648d9b572519b2c5322f6

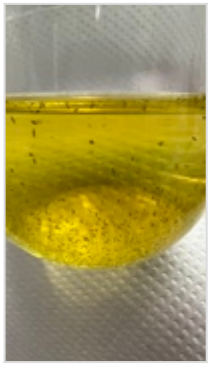
SH_03013_A2_a-3.res
sha256: ee00ca9718093c580311e4886e45b39aa3cc22798a89309af87aece3e4034b11

SH_03013_A2_a.docx
sha256: 1d8077a801fb09d67ecb7a9f6f4567c241aee2089d19b371d2d63940434bc0ca

SH_03013_A2_a-2.res
sha256: 9a7520abae1dedd4817640d94b158c491b373f19010c7f613614908f73ab8e30

AEI-053-1.zip
sha256: 113defac6536cc47b8205e362190e8bb19c503fa7b0ffaca441775e6be347266

filtrate-with-crystals
sha256: 0c1397384c634db8255ff2fa5d569769a087510ec395e72432cc7e81669b1d40



filter-residue.jpg
sha256: b95710b36a5f5ab629b168f2060762c301f119e710b6d5e88a8198f15551c799

after-precipitation.jpg
sha256: 21df48cea5b27b558f7d62934b065af2ebbd2488bcd1a827d87e07037a730595

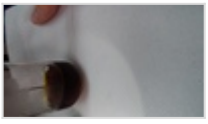
reduced.jpg
sha256: 44bbe6cec3f7db98902087c18ae8aacb02d6c3d3518e5272b8cf9037db6c3048

after-stirring-over-night.jpg
sha256: deb03b0eb16e9de43ebb2ad92ce3143e6d8cfd65a821be8b63f9f68723ac6e86

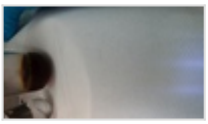
after-CO.jpg

sha256: 8e9f5b6077d752d31270710d2b9f91ed599da85c6a43c9ef4e81f71ea2d57787

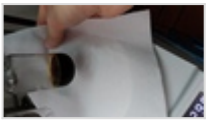
clear-by-CO.jpg
sha256: b9d1fddf27f2671c3c51e4d7543ef7d9d846425ed9a3017432e4d0ecd4153b3e



solid.jpg
sha256: a9c1407b86c33a9c167e360258c2a8d47e830d2e697a43ad95595c61d5a3a14e



after-heating.jpg
sha256: 8faa65c85be99b69196eb4359807a1623746ad7d27bc04750a17c168b646e888



before-heating.jpg
sha256: 6f458ae1a6a945b6fd6bd5bd1c68778f02826a85ca23ff7c8051aae892b2da96

Unique eLabID: 20221215-82804a85eff1107de87b29a0a2642c45e0673de9
Link: https://elab.water-splitting.org/experiments.php?mode=view&id=342