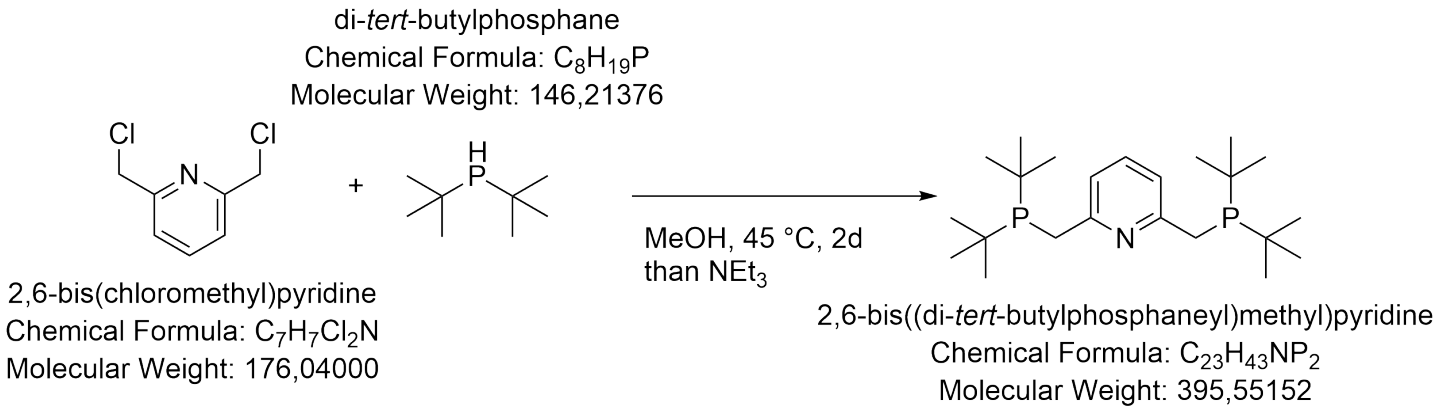
AE-253: Synthesis of 2,6-Bis(P,P-di(tertbutyl)phosphinomethyl)pyridine

Date: 2024-04-04
Tags: PNP P(tBu)N(py)P(tBu) NMR AE Ligand Synthesis Future 1H 31P
Status: Done
Created by: Alexander Eith

Reaction scheme/sample structure



Literature/reference experiments

Literature	https://doi.org/10.1021/om800425p https://doi.org/10.1021/om010719v
Reproduction	/
Related experiments	Experiment - AE-219: Synthesis of 2,6-Bis(P,P-di(tertbutyl)phosphinomethyl)pyridine Experiment - AEI-047: Synthesis of 2,6-Bis(P,P-di(tertbutyl)phosphinomethyl)pyridine

Reagents

Name	CAS-Number/Experiment-Number	Amount [mmol]	Equivalents	$Mass_{theo}$ [g]	$Mass_{exp}$ [g]	Molar mass [g/mol]	$Volume_{theo}$ [mL]	$Volume_{exp}$ [mL]	Density [g/mL]
2,6-bis(chloromethyl)pyridine	3099-28-3	15.91	1	2.800	2.80	176.04	/	/	/
MeOH	Experiment - JSC-KS-20: Degassing of MeOH	/	/	/	/	/	/	12	/
di-(tertbutyl)phosphine (50 % in toluene, assumed as wt%)	819-19-2	34.20	2.15	10.00 (5.0 g di-(tertbutyl)phosphine)	10.001	146.21	/	/	/
triethylamine	121-44-8	35.79	2.25	3.622	/	101.2	4.961	5.0	0.73
toluene	Experiment - AEI-016: Degassing of Toluene	/	/	/	/	/	/	20 + 25	/
Diethylether	Experiment - AEI-068: Degassing of Diethylether	/	/	/	/	/	/	40 + 25	/

Procedure/observations

All steps (unless stated otherwise) were carried out under argon using standard Schlenk technique.

Date	Time	Step	Observations
05.04		Two schlenk flasks (25 and 50 mL) were flask set under Argon.	
	13:40	In the glovebox tBu2PH (10.001 g) was weighed in the 25 mL flask	clear liquid.
	14:40	2,6-bis(chloromethyl)pyridine was weigehd in air to the 50 mL flask and the atmosphere was changed to argon	2,6-bis(chloromethyl)pyridine white, crystaline solid
	14:55	MeOH (12 mL) were added to the tBu2Ph flask	after addition of MeOH.jpg
	15:00	The tBu2PH solution was added to the pyridine flask	
	15:00 - 15:10	The reaction mixture was stirred at room temperature.	After a short time everything dissolved. start of reaction.jpg
	15:10 -	The reaction mixture was heated to 45 °C	after-reaction-at-45-°C.jpg
08.04	8:55 - 13:35	The heating was turned of and the reaction mixture was cooled down to rt	
	13:35	NEt3 (5.0 mL) was added in approx. 20 s	
	13:40 - 13:45	The obtained mixture was dried under reduced pressure	When strating the drying most of the mixture solidified and through boiling was moved upwards in the Schlenk tube, so that the drying was stopped after approx. 1 mL. solidified reaction mixture during removing of solvent.jpg remainder: clean colling trap good, to avoid the smell of phosphines in the lab
	14:05	Toluene (20 mL) was added	
		The solid was dissolved by stirring for approx. 5 min.	Still solid remained but it was moved to the bottom of the flask bad qualtiy after addition of toluene.jpg
	14:10 - 14:20	Approx. 10 mL of the reaction mixture was removed under reduced pressure.	after reducing volume for approx 10 mL.jpg
	14:25 - 14:40	The mixture was filtered according to [Protocol] Cannula Filtration/Transfer	
	14:40 - 15:05	The residue was washed with toluene (2 * 10 mL, 1 * 5 mL)	residue after toluene washing.jpg, in toluene after washing.jpg

	15:10 - 15:45	The solution was dried under reduced pressure	
	16:00	Et2O (40 mL) was added to the solid and the mixture was stirred	in Et2O before filt.jpg
	16:07 - 16:18	The mixture was filtered according to [Protocol] Cannula Filtration/Transfer	
	16:18 - 16:30	The residue was washed with Et2O (2 * 10 mL, 1 * 5 mL)	fresidue after Et2O washing.jpg, filtrate in Et2O.jpg
	16:35 - 16:43	The solvents were removed under reduced pressure	prod before drying.jpg
	16:43 - 16:46	The white solid was dried under reduced pressure	
		The solid was stored under argon at rt	
09.04	10:20 - 11:15	The white solid was dried under reduced pressure	
		The solid was stored under argon at rt	
10.04	09:40	The sample was moved in a glovebox (K004, box JSC) and stored there in a snap on cap vial at rt	AE-253-1, some material was lost during the transfer (approx. 0.1 to 0.2 g)
	10:40	A NMR sample was prepared in DCM-d2 in the glovebox using a Young-type NMR-tube	AE-253-1

Analysis

Date	Time	Sample name	Analysis method	Analytik device	Solvent	Raw Data	Processed Data	Comparative Data	Interpretation
10.04	13:21	AE-253-1	NMR 1H, 31P{1H}quant	IAAC 400 MHz I	CD2Cl2	AE-253-1.zip	AE-253-1_12.nmrium	Experiment - AE-219: Synthesis of 2,6-Bis(P,P-di(tertbutyl)phosphinomethyl)pyridine -1	Main species is desired product. One significant impurity is observed (Maybe mono substituted species??)

Product characterization

	mass [mg]	purity [%]	$mass_{pure}$ [mg]	amount [mmol]	Yield [%]	Desciption
AE-253-1	4427	90 accoding to AE-254-NMR-puritiy.xlsx	3984	10.07	63	white fluffy poweder, approx. 20 mL

Future recommendations

Old procedure	Problem	Suggested new procedure
Removing of solvent after addition of NEt3	reaction mixture solidifies and solvents cant be removed	First add toluene, should be more than the volume of MeOH, than remove the undisired reaction components, which can be removed (MeOH, NEt3, HPtBu2). A large amount of toluene can be used, since in the next step the reaction mixture is washed with toluene
Adding of 20 mL toluene for the filtration	to small amount, first washing apparetnly still gave a concnetrated solution	Use for this scale approx. 40 mL toluene for the solution of the product
Using a 50 mL flask	to small volume to add enough toluene	Use a larger flask and keep in mind, that toluene is added to the reaction mixture after the reaction

Linked experiments

- AEI-016: Degassing of Toluene
- AEI-047: Synthesis of 2,6-Bis(P,P-di(tertbutyl)phosphinomethyl)pyridine
- JSC-KS-20: Degassing of MeOH
- AEI-068: Degassing of Diethylether
- AE-219: Synthesis of 2,6-Bis(P,P-di(tertbutyl)phosphinomethyl)pyridine

Linked resources

Protocol - Preparation of NMR Sample

Protocol - Cannula Filtration/Transfer

Protocol - Schlenk Technique

Attached files

20240410_113207.jpg
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20240410_105147.jpg
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AE-254-NMR-puritiy.xlsx
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AE-253-1_12.nmrium
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AE-253-1.zip
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after-reaction-at-45-°C.jpg
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in-toluene-after-washing.jpg
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residue-after-toluene-washing.jpg
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filtrate-in-Et2O.jpg
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fresidue-after-Et2O-washing.jpg
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prod-before-drying.jpg
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solidified-reaction-mixture-during-removing-of-solvent.jpg
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bad-qualtiy-after-addition-of-toluene.jpg
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after-reducing-volume-for-approx-10-mL.jpg
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in-Et2O-before-filt.jpg
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start-of-reaction.jpg
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after-addition-of-MeOH.jpg
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Comment

On 2024-04-16 11:47:13 Jacob Schneidewind wrote:
Notes:
* specifying which glovebox was used - creating equipment entry in database for glovebox (location, manufacturer, type)
* procedure table: moving 08.04 date one row down, deleting "8:55" part
* procedure table: specifying that product was stored in JSC container in glove box
* procedure table: green highlighting for NMR analysis

Unique eLabID: 20240404-816f06aa33b650a3d2bd0e34a124d2291cb28aee
Link: https://elab.water-splitting.org/experiments.php?mode=view&id=929