

**Short thesis for the degree of doctor of philosophy (PhD)**

**Mechanochemical transformations of 1,3,5-triaza-7-phosphatricyclo[3.3.1.1<sup>3,7</sup>.0]decane and its complexes with Ag(I) and Ru(II) ions**

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## List of abbreviations

acetylene dicarboxylic acid: but-2-indic acid

acrylic acid: prop-2-enoic acid

acrylic acid methyl ester: methyl acrylate, methyl prop-2-enoate

C<sub>10</sub>H<sub>14</sub>: *p*-Cymene, 1-isopropyl-4-methylbenzene

citraconic acid: (2*Z*)-2-methylbut-2-enedioic acid

ESI-MS: electrospray ionization mass spectrometry

glutaconic acid: pent-2-enedioic acid

itaconic acid: 2-propene-1,2-dicarboxylic acid

maleic acid: (*Z*)-2-butenedioic acid; fumaric acid: (*E*)-2-butenedioic acid

NMR: Nuclear Magnetic Resonance spectroscopy

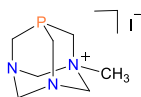
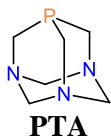
P-(2-carboxyethyl)-PTA: 7-(2-carboxyethyl)-1,3,5-triaza-7-(phosphoniatricyclo)[3.3.1.1<sup>3,7</sup>]-decane

ppm: parts per million, the measure of chemical shift

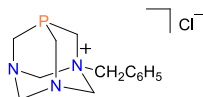
PTA: 1,3,5-triaza-7-phosphatricyclo[3.3.1.1<sup>3,7</sup>]decane

rpm: revolutions per minute (rad min<sup>-1</sup>)

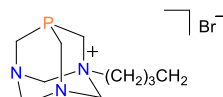
## The compounds included in the thesis



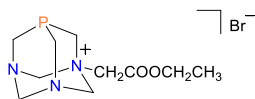
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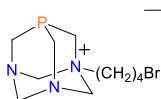
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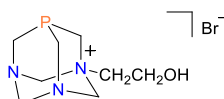
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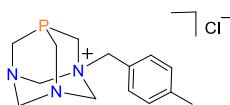
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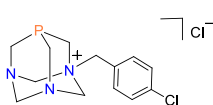
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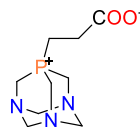
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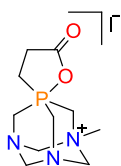
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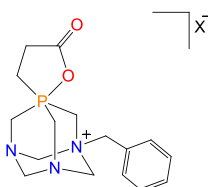
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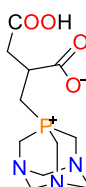
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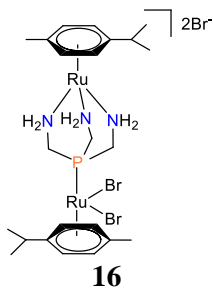
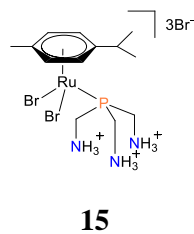
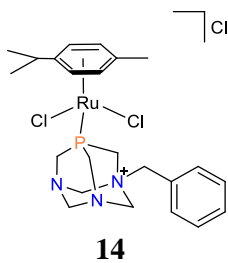
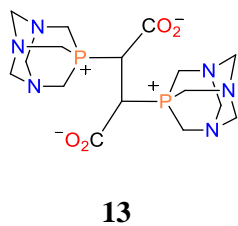
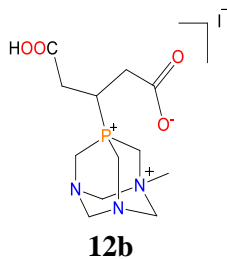
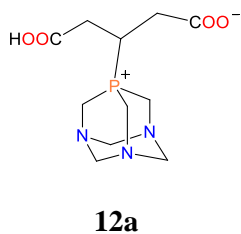
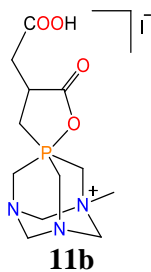
**10a**



**10 b) X=Br;  
c) X= Cl;  
d) X= BPh<sub>4</sub>**



**11a**



## I. Introduction and objective

In order to responsibly protect our environment, we need to develop processes that will allow us to produce important raw materials for it, while adhering to the principles of "green chemistry". Most industrial processes are carried out in expensive, toxic and flammable organic solvents. What could be greener than not using solvents at all to carry out reactions? With the help of ball mills, we have the opportunity to produce products that are not formed under classical treatment conditions, thus providing us with a new opportunity to develop new families of compounds.

My doctoral thesis focuses on transformation of a tricyclic water-soluble phosphine, the phosphorus-containing analogue of urotropine, 1,3,5-triaza-7-phosphatricyclo[3.3.1.1<sup>3,7</sup>]decane (PTA). Nowadays, there is a great demand for the development of new antimicrobial agents, as many microorganisms have become resistant to drugs available in the market.

Researchers try to produce and test new drugs with better pharmacokinetic properties in the clinic. Such potentially bioactive substances could be derivatives of PTA containing silver(I) ions.

Therefore, the aim of my doctoral work is, on the one hand, to produce 1,3,5-triaza-7-phosphatricyclo[3.3.1.1<sup>3,7</sup>]decane (PTA) in a less environmentally damaging way, in accordance with the basic

principles of chemistry, by alternative energy transfer (mechanochemical activation):

- a) *N*-alkyl derivatives with alkyl halides,
- b) *P*-alkylated derivatives with activated unsaturated carboxylic acids,
- c) half-sandwich Ru(II) complexes.

Thus, I produce by mechanochemical activation known PTA derivatives, which were previously produced in solution, thereby drawing attention to the use of an easily accessible ball mill in laboratory conditions.

Further aim of my thesis is to characterize, in solution and solid phase, the Ag(I)-containing coordination polymers with potentially bioactive effects formed by the interaction of PTA derivatives prepared by mechanochemical means, or PTA itself, with silver salts containing various anions.

## II. Experimental methods

For mechanochemical synthesis, I used a RETSCH PM 100 high-efficiency planetary ball mill. In some cases, I used "homemade" ball mill, meaning 2-3 pieces of Teflon-coated magnetic stir bars in 5 mL well-sealed glass jar.

In most cases,  $^{31}\text{P}$  NMR measurements were used to monitor the formation and check the purity of the compound prepared in classical solvents and solvent-free mediums.

The structure of new and known compounds was identified by  $^{31}\text{P}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectroscopy on a BRUKER DRX 360 spectrometer, which was supported by elemental analysis, mass spectrometry, infrared spectroscopy, and single-crystal X-ray crystallography measurements.

The IR spectra were recorded on a Perkin Elmer Instruments Spectrum One FT-IR ATR device.

The ESI-MS experiments were carried out by Dr. Cynthia Nóra Nagy, Assistant Professor, using a CE-qTOF/MS instrument at the Department of Inorganic and Analytical Chemistry, University of Debrecen.

Elemental analysis measurements were performed by Dr. Attila Szikszai-Kiss, Associate Professor, at the Department of Organic Chemistry, University of Debrecen, using an Elementar Vario Micro (CHNS) instrument.

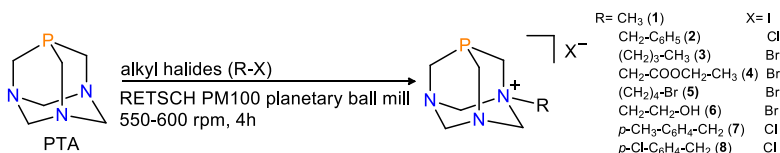
The X-ray crystallographic data of the new compounds were collected using a) a Bruker D8 VENTURE instrument with a photon-counting detector b) a Bruker-Nonius MACH3 four-circle point detector diffractometer by Dr. Attila Bényei Associate Professor (University of Debrecen) c) a SuperNova CCD diffractometer by Dr. Éva Kováts Senior Research Fellow (The HUN-REN Wigner Research Centre for Physics).

### III. New scientific results

#### 1. Preparation of *N*-alkylated PTA derivatives under mechanochemical conditions in a planetary ball mill

I developed an environmentally friendly, highly efficient, green synthesis method for the production of known *N*-alkyl derivatives of PTA in a planetary ball mill.

PTA was ground with various alkyl halides (*Figure 1*) in a RETSCH PM 100 planetary ball mill.



**Figure 1.** Reaction of PTA with various alkyl halides in a planetary ball mill

The <sup>31</sup>P NMR chemical shifts of mechanochemically prepared *N*-alkylated PTA derivatives were the same as prepared in solution.

The yields of *N*-alkylation reactions carried out by mechanochemical activation are summarized in Table 1. For comparison, I also present the yields of known reactions performed in solvent.

In general, I could to produce the appropriate cationic PTA derivatives in an outstanding yield in the planetary ball mill, and the products did not require further purification.

**Table 1.** *N*-alkylation of PTA under different reaction conditions

	<b>Yield in organic solvent</b> * (%)	<b>Green yield</b> (%) <sup>b</sup>
<b>1</b>	66	95
<b>2</b>	43	95
<b>3</b>	80	98
<b>4</b>	78	91
<b>5</b>	43 <sup>a</sup>	97
<b>6</b>	66 <sup>a</sup>	91
<b>7</b>	79 <sup>a</sup>	93
<b>8</b>	73 <sup>a</sup>	90

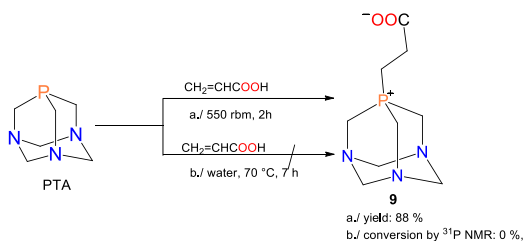
*Conditions:* planetary ball mill, 550-600 rpm, 12 ml stainless steel grinding jar, 6 grinding balls ( $\varnothing = 5$  mm), 4 h, 0.64 mmol PTA (100 mg),  $n_{RX} : n_{PTA} = {}^a 2.3-2.5; {}^b 1.6-1.9$ , \* literature yields

PTA with 1,4-dibromobutane formed only the monosubstituted *N*-alkylated product (**6**) in both hot acetone and planetary ball mill.

The advantages of the mechanochemical synthesis method are proven by **6** compounds produced in white microcrystalline form, while under solvent conditions the compound can only be isolated as an oil.

## 2. Preparation of P-(2-carboxyethyl)-PTA (9) under conventional and solvent-free conditions

It was proved that the known P-(2-carboxyethyl)-PTA (9) can be prepared by the reaction of PTA and acrylic acid in ball mill, while the phosphonium salt is not formed under conventional solvent conditions (Figure 2).



**Figure 2.** Preparation of P-(2-carboxyethyl)-PTA (9) via different reaction routes

The production of P-(2-carboxyethyl)-PTA (9) in a ball mill also supports the efficiency of mechanochemical synthesis method.

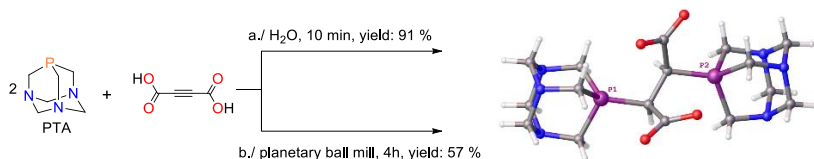
### 3. Preparation of the adduct (**13**) formed by the reaction of PTA and acetylene dicarboxylic acid and its Ag(I)-containing coordination polymer

**3.1.** I was the first who prepared a zwitterionic double phosphobetaine (**13**) by the reaction of acetylene dicarboxylic acid and two equivalents of phosphine

a./ in aqueous medium,

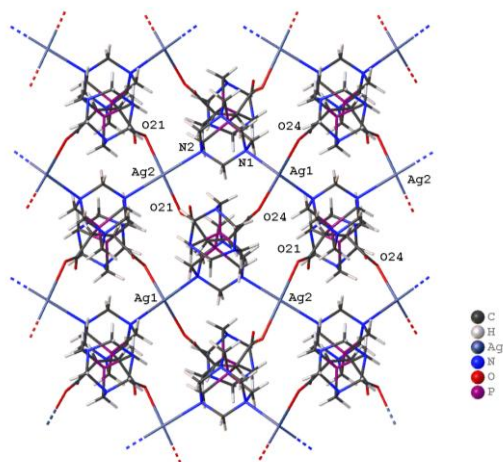
b./ by dry milling the reactants (*Figure 3*).

The structure of phosphonium salt **13** was determined by multinuclear NMR and ESI-MS spectroscopy, and its purity was confirmed by elemental analysis. The solid-state structure of the zwitterionic compound was also supported by SCXRD (*Figure 3*).



**Figure 3.** Preparation and solid-phase molecular structure of zwitterionic double phosphobetaine (**13**) (Water molecules are omitted for clarity.)

**3.2.** A two-dimensional self-assembled coordinated polymer was crystallized by the interaction of an aqueous solution of (**13**) and an aqueous solution of Ag-triflate. The structure of the photosensitive coordination polymer shows in Figure 4. Despite our best efforts, we were able to determine the structure of the polymer with large structural errors.



**Figure 4.** Two-dimensional coordination polymer formed by the reaction of zwitterionic phosphobetaine (**13**) and  $\text{CF}_3\text{SO}_3$

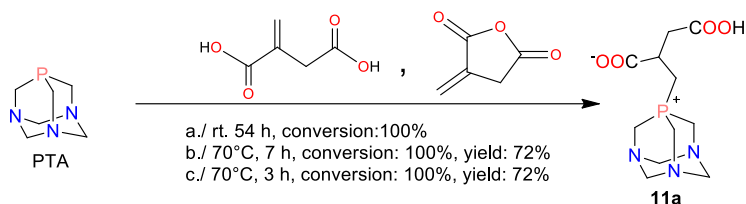
The new zwitterionic double phosphobetaine containing two PTA units which can be used as supramolecular synthon for preparation of  $\text{Ag}^+$ -based coordination polymers in aqueous systems, due to its large number of nitrogen and oxygen donor atoms.

#### **4. Reaction of PTA with olefin carboxylic acids in water and solvent-free media**

Researchers of Department of Physical Chemistry previously reported the formation of air-stable water-soluble phosphobetaines in the reactions of PTA and activated olefin dicarboxylic acids in aqueous media.

#### 4.1. Reaction of itaconic acid with PTA in aqueous medium

New phosphonium salt was isolated first time from the interaction of PTA with itaconic acid (a five-carbon olefin dicarboxylic acid with the double bond in the exo position) and cyclic itaconic acid anhydride in aqueous medium (*Figure 5*). It was demonstrated that at room temperature, PTA reacts with itaconic acid in water and the reaction is complete within 54 hours (**a**), 100% conversion was observed with itactic acid in 7 hours (**b**) and with cyclic itaconic acid anhydride in 3 hours at 70°C (**c**).



**Figure 5.** Aqueous synthesis of **11a** phosphonium salt  
(conversion: based on their  $^{31}\text{P}$  NMR spectra)

Based on literature data and my experiments, I established the following reactivity order of olefin dicarboxylic acids with PTA: maleic acid >> itaconic acid > trans-glutaconic acid > citraconic acid >> fumaric acid > mesaconic acid.

## 4.2. Reaction of PTA with olefin dicarboxylic acids under solvent-free conditions in a planetary ball mill

It was proved that grinding PTA and olefin dicarboxylic acids (maleic acid, glutaconic acid and itaconic acid) in a planetary ball mill yielded the same phosphonium salts as the aqueous synthesis.

The reaction of phosphine and olefin dicarboxylic acids in a solid-state medium resulted in 100% conversion within 4 hours (*Table 2*). The mechanochemical preparation was more efficient than the aqueous synthesis with maleic acid and itaconic acid, while the opposite result was obtained with glutaconic acid.

**Table 2.** The P-alkylation of PTA under different conditions

Unsaturated carboxylic acid	Aqueous synthesis		Mechanochemical synthesis	
	Conversion *, % (Reaction time, hour)	Yield (%)	Conversion *, % (Grinding time, hour)	Yield (%)
glutaconic acid (12a)	100 (3)	87c	100 (4)	74
itaconic acid (11a)	100 (7)	72c	100 (4)	77
maleic acid	100 (3)	74a	100(4)	91
citraconic acid	40 (48)	40b	5 (8)	did not determine

*Conditions:* Aqueous synthesis: 1 mmol PTA, 1 mmol unsaturated carboxylic acid 2.5 mL water,

<sup>a</sup>1 °C 3 h, <sup>b</sup>70 °C, 48 h, <sup>c</sup>70 °C, 3 h. Mechanochemical synthesis with RETSCH PM 100 planetary ball mill: 550 rpm, stainless steel 12 mL grinding jar, 6–8 pcs (Ø = 8 mm) bearing balls, 4 h grinding time, 1 mmol PTA, 1 mmol carboxylic acid. \*Based on their <sup>31</sup>P NMR spectra.

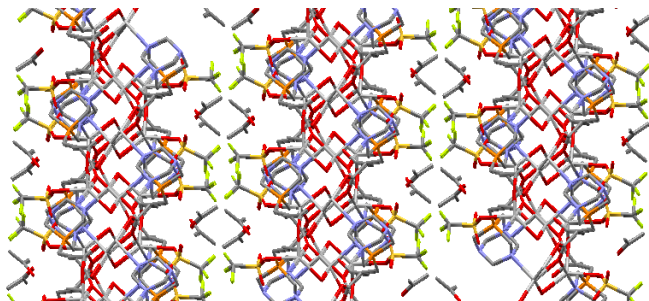
I determined the solid-state structure of the phosphonium salt **11a** by SCXRD, in which strong hydrogen bonds are formed due to the

protonated and deprotonated carboxylate groups and a water molecule present, forming the layered structure.

### 4.3. Reaction of **11a** and AgCF<sub>3</sub>SO<sub>3</sub> in aqueous medium

A new, photosensitive, two-dimensional coordination polymer, [Ag<sub>4</sub>(**11a**)<sub>2</sub>(2H<sub>2</sub>O)(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(aceton)<sub>2</sub>]<sub>n</sub>, was successfully crystallized.

I dissolved **11a** and AgCF<sub>3</sub>SO<sub>3</sub> in water, then I layered the acetone on top. After two weeks, in the absence of light, several products were formed: e.g. a photosensitive silver-containing powder that did not show any tendency to crystallize, or metallic silver, as well as a few photosensitive crystals, the structure of which was revealed by single-crystal X-ray diffraction. The polymer [Ag<sub>4</sub>(**11a**)<sub>2</sub>(2H<sub>2</sub>O)(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(aceton)<sub>2</sub>]<sub>n</sub> has a layered structure (*Figure 6*), in which Ag...Ag interactions are also present.



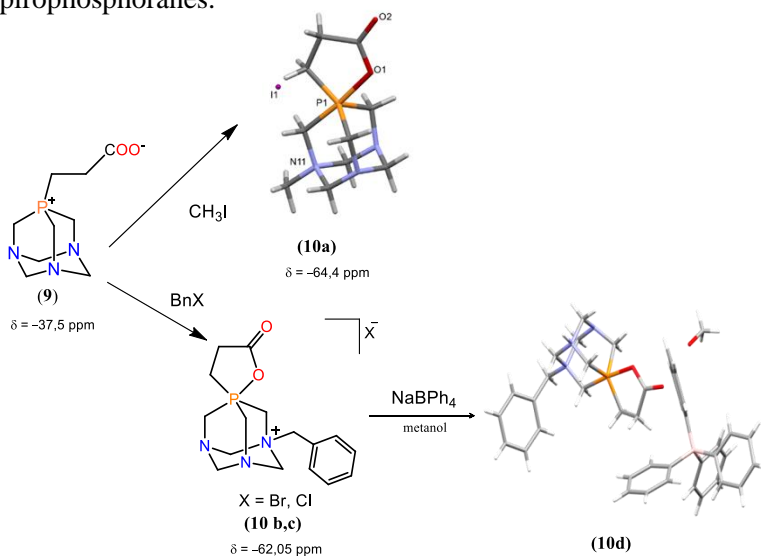
**Figure 6.** Polymer layers in a two-dimensional coordination polymer

## 5. Formation of PTA-containing P(V)-spiroposphoranes under mechanochemical conditions

### 5.1. *N*-methylation and *N*-benzylation of P-(2-carboxyethyl)-PTA (**9**) in a ball mill

It was shown that one of the nitrogen atoms of P-(2-carboxyethyl)-PTA (**9**) can be *N*-methylated or *N*-benzylated in a mechanochemical reaction (either in a „*home-made*” or planetary ball mill) (Figure 7).

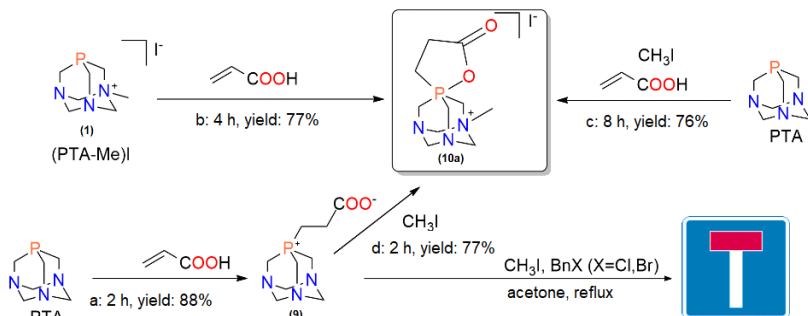
The mechanochemical process led to the formation of P(V)-spiroposphoranes.



**Figure 7.** Formation of P(V)-spiroposphoranes from P-(2-carboxyethyl)-PTA

The solid-phase structure of compounds **10a** and **10d** showed that ring closing reaction occurs in the phosphonium salt during the *N*-alkylation

of nitrogen atom. The atoms of the five-membered ring are in a plane, and in **10a** the methyl group also located into the plane stretched by the ring.



**Figure 8.** Preparation of **10a** via different reaction pathways (**a-d**).

**Conditions:** RETSCH PM 100 ball mill, 550 rpm, stainless steel 12 mL grinding jar, 6–8 ball bearings ( $\text{Ø} = 8$  mm), 1 mmol PTA, 1 mmol acrylic acid, 1 mmol iodomethane. Product identification with  $^{31}\text{P}$  NMR spectroscopy.

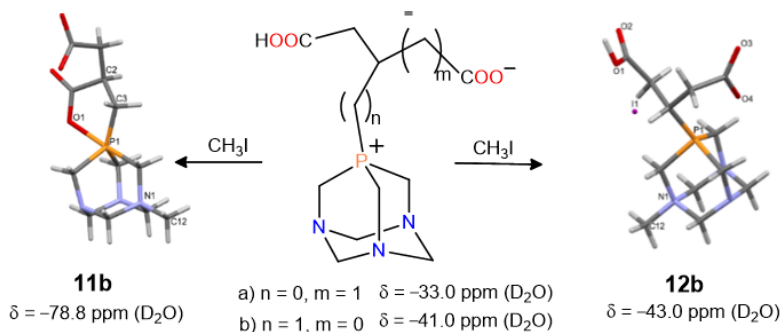
Preparation of compound **10a** via different reaction routes (**a-d**) (*Figure 8*):

- I reacted PTA with acrylic acid in a planetary ball mill (**a**), then I ground it with iodomethane (**d**) (4 h, yield: 77%),
- By grinding  $(\text{PTA-Me})\text{I}$  and acrylic acid (**b**), (4 h, yield: 77%),
- “one jar” reaction, that is by grinding PTA, acrylic acid and iodomethane (**c**) (8 h, yield: 76%),
- I showed that I could not prepare P(V)-spiroposphorane with iodomethane, benzyl chloride or bromide in organic solvents.

I produced the same solid material (Figure 8) in all three reaction routes, which are clearly identical based on their  $^{31}\text{P}$  NMR spectra.

## 5.2. *N*-methylation of PTA-formed adducts (11a,12a) of unsaturated dicarboxylic acids in a “homemade” ball mill

It was showed that both phosphobetaines **11a** and **12a** can be methylated with  $\text{CH}_3\text{I}$  under mechanochemical conditions in a “homemade” ball mill (Figure 9).



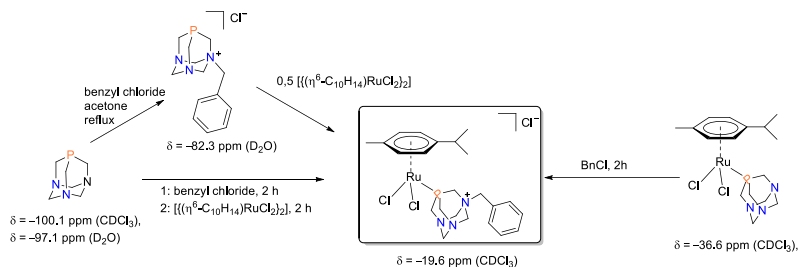
**Figure 9.** Preparation of **11b** and **12b**

From the molecular structures of the compounds, I determined that in the case of **11b**, ring closing reaction also occurred along with *N*-methylation, while in the formation of **12b**, ring closing reaction did not occur. I also concluded this from the  $^{31}\text{P}$  NMR spectrum of **12b**, as I observed the singlet signal at a chemical shift of  $-43 \text{ ppm}$ , which is significantly different from the chemical shifts of the other *N*-alkylated phosphonium salts (**10a**, **10c**, **11b**).

## 6. Half-sandwich Ru(II)-complexes formed with PTA derivatives

### 6.1. Preparation of $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{PTA-Bn})]\text{Cl}$ (**14**) by mechanochemical activation

$[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{PTA-Bn})]\text{Cl}$  (**14**) was prepared via different reaction routes:



**Figure 10.** Preparation of  $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{PTA-Bn})]\text{Cl}$  via different reaction pathways

a./ by grinding  $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{PTA})]$  with benzyl chloride, thus proving that coordinated PTA can also be benzylated by mechanochemical activation (yield: 66%),

b./ “one jar” reaction, i.e. grinding the phosphine and benzyl chloride for 2 hours, then adding  $\{[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]\}_2$  and grinding for another 2 hours (yield: 52%) (Figure 10).

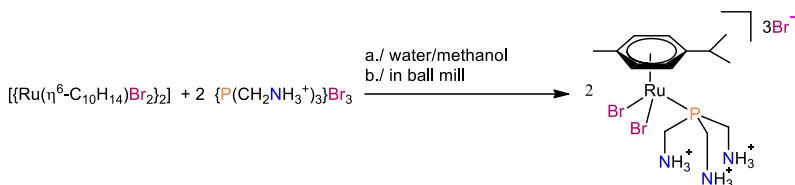
According to  $^{31}\text{P}$  NMR spectra, the  $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2(\text{PTA-Bn})]\text{Cl}$  produced by the mechanochemical and the solvent method was the same.

## 6.2. New half-sandwich Ru(II) complexes containing tris-(aminomethyl)phosphine

$[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuBr}_2\text{P}(\text{CH}_2\text{NH}_3)_3]\text{Br}_3$  in solid form (**15**) was isolated from  $[\{\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})\text{Br}_2\}_2]$  and two equivalents of  $\{\text{P}(\text{CH}_2\text{NH}_3^+)\}_3\text{Br}_3$

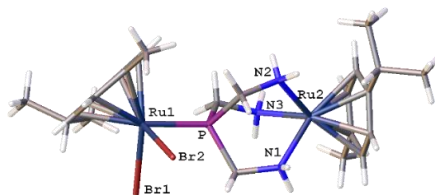
a./ in methanol/water mixture at room temperature, then evaporating the mixture to dryness,

b./ by grinding in a planetary ball mill (*Figure 11*).



**Figure 11.** Preparation of  $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuBr}_2\text{P}(\text{CH}_2\text{NH}_3)_3]\text{Br}_3$  in water/methanol mixture

The mechanochemically prepared  $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuBr}_2\text{P}(\text{CH}_2\text{NH}_3)_3]\text{Br}_3$  in water transformed into the dinuclear complex  $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuBr}_2\{\text{P}(\text{CH}_2\text{NH}_2)_3\}\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})\text{Br}_2]$  (**16**). The structure of the dinuclear complex (*Figure 12*) was confirmed by multinuclear NMR measurements and X-ray diffraction methods.



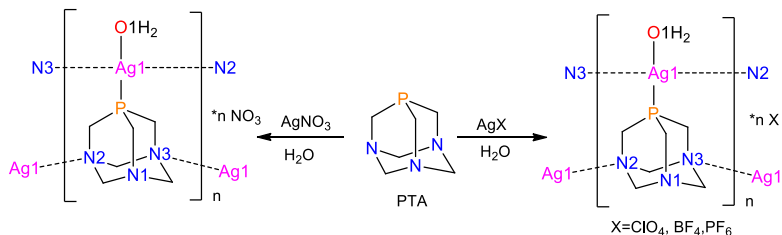
**Figure 12:** Molecular structure of  $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuBr}_2\{\text{P}(\text{CH}_2\text{NH}_2)_3\}\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})]^{2+}$   
(16)

The structures of compounds (15, 16) were confirmed by multinuclear NMR spectroscopy and HR-ESI-MS, too.

## 7. Coordination polymers of PTA and P-(2-carboxyethyl)-PTA (9) formed with Ag(I) salts

### 7.1. Coordination polymers of PTA with Ag salts containing non-coordinating anions

Isostructural crystals were isolated in the reaction of PTA and various AgX salts ( $\text{X} = \text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{ClO}_4^-$ ) in aqueous medium (Figure 13).

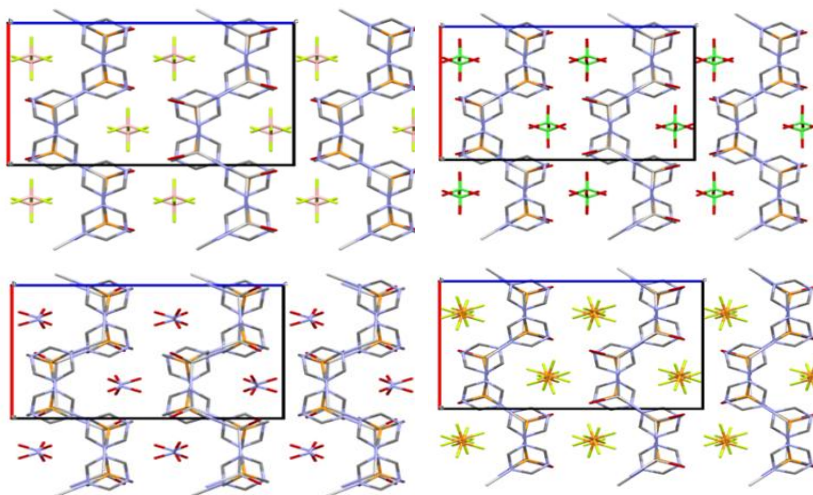


**Figure 13.** Preparation of PTA-based coordination polymers

All of the coordination polymers I have prepared and the known  $[(\text{Ag}(\kappa\text{OH}_2)(\mu_3\text{-PTA-}\kappa^3\text{P:N:N}))_n(\text{NO}_3)_n]$  crystallize in the *Pbca* space

group of the orthorhombic crystal class. The lengths of the unit cells of the compounds are similar. The volume of the unit cells varies in the direction  $\text{BF}_4^- < \text{ClO}_4^- < \text{NO}_3^- < \text{PF}_6^-$  depending on the anion.

The packing arrangements of coordination polymers with the composition  $[(\text{Ag}(\kappa\text{OH}_2)(\mu_3\text{-PTA}-\kappa^3\text{P}:N:N)]_n(\text{X})_n$  ( $\text{X} = \text{BF}_4^-, \text{ClO}_4^-, \text{NO}_3^-, \text{PF}_6^-$ ) are similar (*Figure 14*).



**Figure 14.** Packing diagram of the isostructural coordination polymers  $[(\text{Ag}(\kappa\text{OH}_2)(\mu_3\text{-PTA}-\kappa^3\text{P}:N:N)]_n(\text{X})_n$  ( $\text{X} = \text{BF}_4^-, \text{ClO}_4^-, \text{NO}_3^-, \text{PF}_6^-$ )

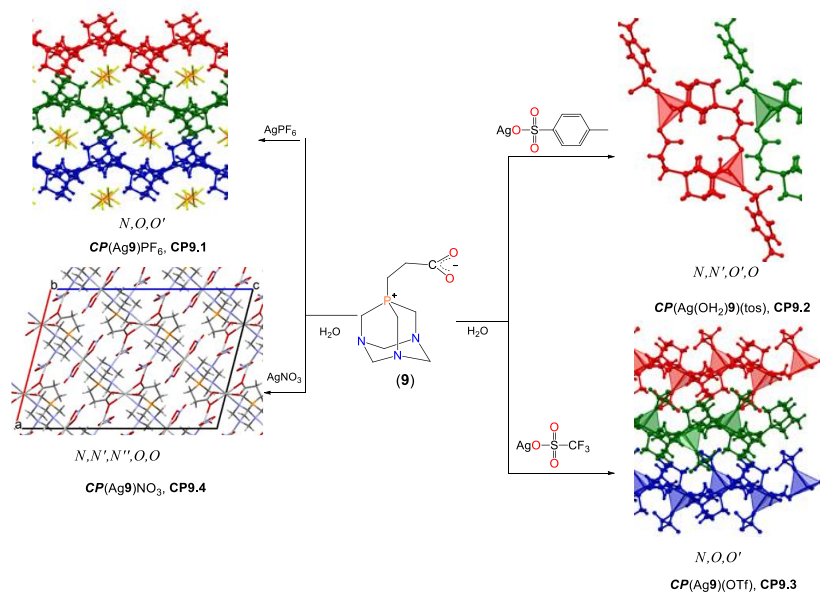
ESI-MS measurements also show that these coordination polymers are unstable in water and dissociate.

The structures of the compounds determined by X-ray diffraction and the composition of the “crystals” are in good agreement with the data determined by elemental analysis. According to the elemental

analysis, one Ag salt and one water molecule are present per phosphine ligand.

## 7.2. Silver(I)-containing polymers of P-(2-carboxyethyl)-PTA (9)

Coordination polymers with various structures were crystallized by the interaction of P-(2-carboxyethyl)-PTA (9) and AgX salts ( $X = \text{PF}_6^-$ ,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ ,  $\text{CF}_3\text{SO}_3^-$ ) in aqueous medium (Figure 15).



**Figure 15:** Reactions of PTA with AgX salts in aqueous medium ( $X = \text{PF}_6^-$ ,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ ,  $\text{CF}_3\text{SO}_3^-$ )

The phosphonium salt P-(2-carboxyethyl)-PTA (9) contains three nitrogen atoms, similar to PTA, but instead of the phosphorus atom there are two oxygen donor atoms. Depending on the properties

of the various donor atoms and the anion, different coordination modes should be expected in its Ag(I)-containing coordination polymers.

One-dimensional, chain-like and tubular coordination polymers were crystallized from aqueous solutions of P-(2-carboxyethyl)-PTA (**9**) and AgX (X= PF<sub>6</sub><sup>-</sup>, tos).

A two-dimensional chain polymer was formed in the reaction of AgCF<sub>3</sub>SO<sub>3</sub> and P-(2-carboxyethyl)-PTA (**9**).

The three-dimensional coordination polymer was crystallized from an aqueous solution of P-(2-carboxyethyl)-PTA (**9**) and AgNO<sub>3</sub>. Based on the solid-state molecular structure of the compound, one Ag(I) ion is coordinated to each of the three nitrogen atoms of the PTA unit.

The composition of the light-insensitive coordination polymers was also confirmed by combustion elemental analysis. Diffusion NMR measurements confirmed that these compounds do not retain their polymer structure in water.

## IV. Possible applications of the results

In industry, is known several processes where different *P*-, *N*-alkylated ligands are used, e.g. in transition metal catalysts.

In my thesis, I proved that the use of ball mills can be a modern, efficient method for preparation of these ligands. Mechanochemical reactions can replace large amounts of toxic organic solvents, thus making many organic chemical syntheses less harmful to our environment.

Ball mills can be useful basic tools for carrying out catalytic reactions, where the reaction time and the number of steps required for synthesis can be reduced. In our work, we proved that it is not by chance that solid-phase reactions are considered one of the “ten world-saving chemical processes”.

The new Ag(I)-containing coordination polymers containing PTA units may be potential antimicrobial materials, for which we have already conducted preliminary experiments in collaboration with the colleagues of the Department of Bioengineering, Institute of Biotechnology, University of Debrecen. The Ag(I)-containing compounds could be effectively used for the disinfection of surface and drinking water.



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### List of publications related to the dissertation

#### Foreign language scientific articles in international journals (5)

1. **Szolnoki, C. T.**, Gál, G. T., Kováts, É., Papp, G., Horváth, H., Joó, F., Kathó, Á., Udvardy, A.: A double phosphobetaine formed from 1,3,5-triaza-7-phosphaadamantane (PTA) with acetylenedicarboxylic acid and its Ag(CF<sub>3</sub>SO<sub>3</sub>)-based coordination polymer.  
*Phosphorus Sulfur Silicon Relat. Elem.* 197 (5-6), 561-563, 2021. ISSN: 1042-6507.  
DOI: <http://dx.doi.org/10.1080/10426507.2021.2008928>  
IF: 1.052
2. **Szolnoki, C. T.**, Papp, G., Horváth, H., Joó, F., Kathó, Á., Udvardy, A.: Triprotonated 1,3,5-triaza-7-phosphaadamantane (PTA); fantasy or real intermediate on way from PTA to tetradentate tris(aminomethyl)phosphine?  
*Phosphorus Sulfur Silicon Relat. Elem.* 197 (5-6), 568-570, 2021. ISSN: 1042-6507.  
DOI: <http://dx.doi.org/10.1080/10426507.2021.2014488>  
IF: 1.052
3. Udvardy, A., **Szolnoki, C. T.**, Kováts, É., Nyul, D., Gál, G. T., Papp, G., Joó, F., Kathó, Á.: Water-soluble Ag(I)-based coordination polymers obtained by anion-directed self-assembly of various AgX salts and a phosphobetaine derived from 1,3,5-triaza-7-phosphaadamantane.  
*Inorg. Chim. Acta.* 520, 1-11, 2021. ISSN: 0020-1693.  
DOI: <http://dx.doi.org/10.1016/j.ica.2021.120299>  
IF: 3.118
4. Udvardy, A., **Szolnoki, C. T.**, Borsi-Gombos, R., Papp, G., Kováts, É., Joó, F., Kathó, Á.: Mechanochemical P-derivatization of 1,3,5-Triaza-7-Phosphaadamantane (PTA) and Silver-Based Coordination Polymers Obtained from the Resulting Phosphobetaines.  
*Molecules.* 25 (22), 1-18, 2020. EISSN: 1420-3049.  
DOI: <http://dx.doi.org/10.3390/molecules25225352>  
IF: 4.411





5. Udvardy, A., **Szolnoki, C. T.**, Joó, F., Kathó, Á.: Solvent-free N-alkylation of 1,3,5-triaza-7:  
phospha-adamantane (PTA).

*Phosphorus Sulfur Silicon Relat. Elem.* 194 (4-6), 469-470, 2019. ISSN: 1042-6507.

DOI: <http://dx.doi.org/10.1080/10426507.2018.1539993>

IF: 1.046

**Total IF of journals (all publications): 10,679**

**Total IF of journals (publications related to the dissertation): 10,679**

The Candidate's publication data submitted to the iDEa Tudóstér have been validated by DEENK on the basis of the Journal Citation Report (Impact Factor) database.

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