PhD Thesis

Catalytic activity of new water-soluble Pd-salan complexes

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Introduction and objectives

Environmental awareness appears in both chemical research and industry. The basic principles of "green chemistry" include the use of non-toxic solvents, inexpensive materials and catalysts, mild reaction conditions and the development of atom-efficient reactions.

Usage of water as solvent is a conspicuous way to execute "greener" reactions. One reason is that the price of water is significantly lower compared to the commonly used solvents. Besides it is non-toxic and non-flammable what makes water attractive when compared to the common organic solvents. In addition, it is suitable for construction of biphasic systems in which a water-soluble catalyst can be recovered by phase separation once the reaction ended.

In aqueous organometallic catalysis the most widely used catalysts are metal complexes of tertiary phosphines and N-heterocyclic carbenes, although N- and/or O-donor ligands may also play a crucial role. Less attention has been devoted to the study of complexes with multidentate N,O-donor ligands the group of which includes the various salenes (double Schiff base ligand of ethylene diamine and salicylaldehyde), too. Use of Schiff base ligands and their complexes in aqueous catalysis is hindered by their propensity to hydrolysis. Hydrogenation of the salen C=N bonds results in amines (salans) with much higher stability in aqueous solutions.

Palladium-based catalysts are extremely versatile. There are numerous reactions catalyzed by palladium applied in industrial scale too. Although palladium is an expensive metal, its price is much lower than that of Rh, Pt, Ir or Os.

During my doctoral research my goals were to prepare new, water-soluble salan type ligands and their Pd-complexes and to study the catalytic

activity of these Pd-compounds in hydrogenation and redox isomerization of allylic alcohols and in Sonogashira coupling reactions.

Catalytic redox isomerization of allylic alcohols is a 100 % atom economical reaction, allowing the synthesis of aldehydes and ketones without the need for separate oxidation and reduction steps. Redox isomerization can be part of the hydrogenation of allylic alcohols, when the reaction is carried out in hydrogen atmosphere. Therefore the selectivity of the catalyst can be examined too.

The Sonogashira reaction is one of the most important cross-coupling reactions in organic chemistry. It is a powerful method to create $C(sp^2)$–C(sp) bonds.

In aqueous-phase organometallic catalysis products are usually isolated by extraction with organic solvents. This is a fast and effective method in case of small scale reactions for determining reaction parameters (reaction kinetics, activity and selectivity of the catalyst, etc.). However, in order to eliminate pollution of the environment, it is of paramount importance to devise methods for product isolation without a need to use toxic organic solvents. For this purpose I aimed to develop a “greener” procedure of Sonogashira coupling reactions.

Applied experimental techniques

The ligands and their Pd-complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, ESI-TOF mass spectrometry and elemental analysis. The single-crystal X-ray structures of two ligands were also determined. The hydrogenation and Sonogashira reactions were carried out in heavy-walled glass tube reactors and reaction vessels designed for these purposes. Reaction mixtures were analyzed by gas chromatography and ^{1}H NMR spectroscopy. The purity of isolated products in Sonogashira coupling was also checked by gas chromatography and ^{1}H NMR spectroscopy.

The ^{1}H and ^{13}C NMR spectra of samples were recorded on a Bruker Avance 360 MHz spectrometer at room temperature. ESI mass spectra were recorded on a Bruker micrOTOFQ ESI-TOF mass spectrometer by Dr. Lajos Nagy. Elemental analysis was carried out on an Elementar varioMicro cube instrument (CHNS) by Dr. Attila Kiss. Single-crystal X-ray diffraction data collection was carried out on a Bruker-Nonius MACH3 diffractometer equipped with a point detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by Dr. Attila Bényei. The structures were solved by SIR-92 program and refined by full-matrix least-squares method on F^2, using the SHELXL-97 package in collaboration with Dr. Antal Udvardy. The gas chromatographic measurements were carried out on an Agilent 7890A gas chromatograph, equipped with FID and autosampler. The separation was performed with temperature programming using HP-5 30 m × 0.32 mm × 0.25 μm column.

List of abbreviations

BuHSS	hydrogenated sulfosalen ligand with 1,4-butanediyl amine bridge
CyHSS	hydrogenated sulfosalen ligand with 1,2-cyclohexadiyl amine bridge
DMF	dimethylformamide
dPhHSS	hydrogenated sulfosalen ligand with 1,2-diphenyl-1,2-ethanediyl amine bridge
ESI-MS	electrospray ionization-mass spectrometry
FID	flame ionization detector
HSS	hydrogenated sulfosalen ligand
NMR	nuclear magnetic resonance
[Pd(BuHSS)]	Pd-complex of BuHSS
[Pd(PhHSS)]	Pd-complex of PhHSS
[Pd(CyHSS)]	Pd-complex of CyHSS
[Pd(dPhHSS)]	Pd-complex of dPhHSS
[Pd(HSS)]	Pd-complex of HSS
PhHSS	hydrogenated sulfosalen ligand with 1,2-benzenediyl amine bridge
SDS	sodium dodecyl sulfate
TEA	triethylamine
THF	tetrahydrofuran
TOF	turn over frequency, defined as (mol of product) × ((mol of catalyst) × h)$^{-1}$.

New scientific results

1. Five sulfonated salan type ligands were synthesized with a simple modified procedure which results in a high overall yield (Fig. 1).

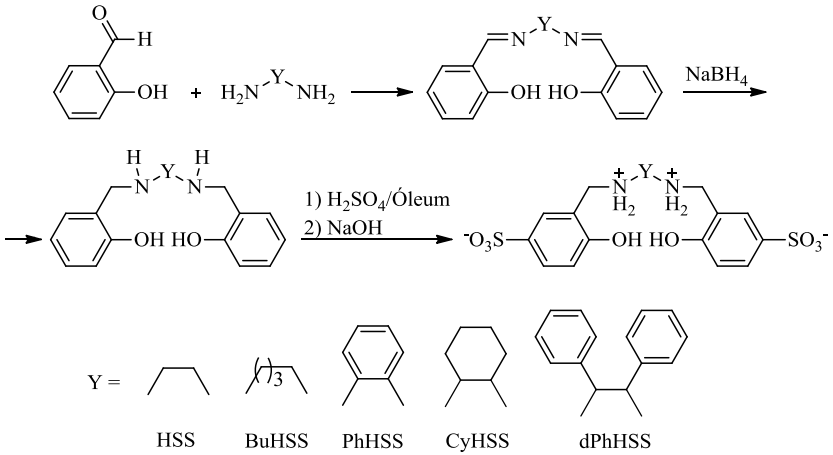


Fig. 1: Synthesis of sulphosalan ligands

Among the synthesized sulfonated salan type ligands four are new compounds (BuHSS, PhHSS, CyHSS, dPhHSS). Briefly, salicylaldehyde was reacted with the appropriate diamine, the product diimines were reduced by $NaBH_4$ and the resulting amines were sulfonated in the mixture of cc.H_2SO_4 and fuming sulfuric acid (oleum). After dilution of the sulfonation mixture and adjusting the pH to 5, the zwitterionic forms of the free acid ligands were obtained. These are sparingly soluble in water, in contrast to the Na-salts which are well soluble.

Altogether the modified procedure is simpler and the overall yield of HSS (29 % based on commercially available salen) is higher than that of the literature method for this ligand (7 %), despite the low yield of the sulfonation step.

The ligands were characterized by ^{1}H and ^{13}C NMR spectroscopy, ESI-TOF mass spectrometry and elemental analysis. The single-crystal X-ray structure of HSS and BuHSS ligands were also determined.

2. New water-soluble Pd(II)-salan type complexes were synthesized and characterized.

The Pd(II) complexes of sulfosalan type ligands (Fig. 2) were prepared by stirring equimolar amounts of $(NH_4)_2[PdCl_4]$ and HSS in aqueous solution at pH 7.5 for 10 h at 60 °C followed by precipitation with ethanol. These compounds are soluble in water and in DMSO but insoluble in apolar organic solvents. The Pd-salans are stable in the air and their aqueous solution can be stored for months.

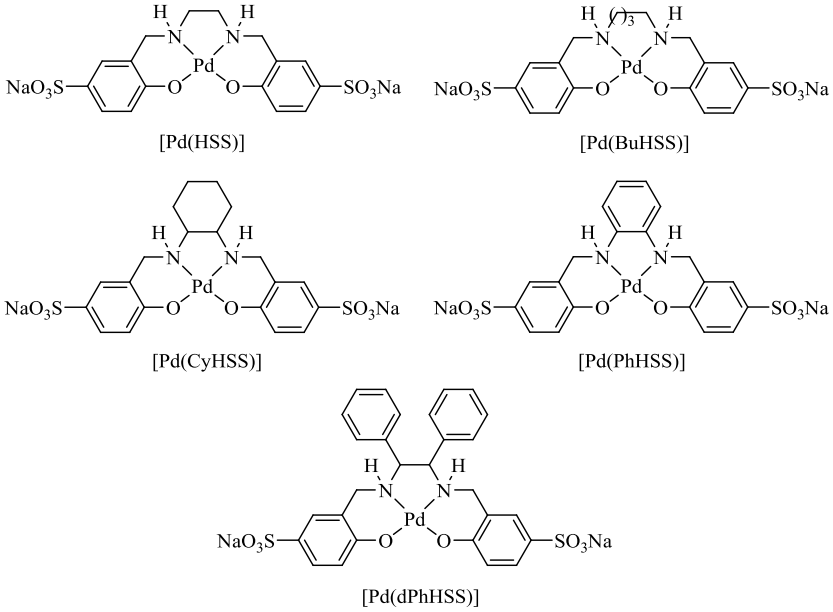


Fig. 2: Pd-salan type catalysts

Due to the slow complex formation even at 60 °C, direct pH-potentiometric studies could not be carried out to determine the stability of the complexes at various pHs. Above pH 6 no reaction was observed with H_2 under pressures up to 9 bar (no metal formation was seen) and no Pd−hydride species could be detected by ^{1}H NMR spectroscopy. However, in more acidic solutions reaction with hydrogen resulted in the formation of a black precipitate and consequently all our investigations were done at pH ≥ 6.

3. Pd(II)-salan type complexes were found highly active catalysts in hydrogenation and redox isomerization of allylic alcohols.

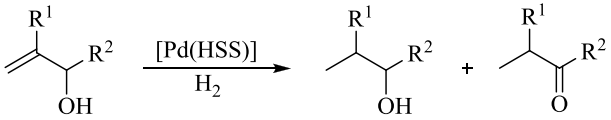
The [Pd(HSS)] complex was found to be stable above pH 6 and under 9 bar of hydrogen pressure at 80 °C. This catalyst was used both as prepared in situ and as an isolated solid. In both forms it catalyzed the hydrogenation and redox isomerization of allylic alcohols (Table 1).

First reactions were done with the *in situ* prepared catalyst using seven substrates from the series of allylic alcohols. According to the results, the reactions became faster with increasing chain length of the alk-1-en-3-ol substrates (Table 1, entries 1-7). Therefore, most of the further measurements were made with oct-1-en-3-ol.

The isolated solid [Pd(HSS)] showed substantially higher catalytic activity than the in situ catalyst (Table 1, entry 7 vs 10). Since the only difference between the two kinds of reaction mixtures was the presence of a stoichiometric amount of NH_4Cl in solutions of the *in situ* catalyst, I checked the effect of chloride on the rate of the reaction of oct-1-en-3-ol. As can be seen from Table 1 (entries 8 and 9), addition of NaCl decreased the catalytic activity of the isolated complex to about the level of the in situ prepared

catalyst. This effect was not investigated in detail; however, it shows that coordinating ligands, such as chloride, may easily occupy free coordination site(s) on Pd and inhibit the catalytic process.

Table 1: Hydrogenation and redox isomerization of allylic alcohols[a]



	Catalyst	R^1	R^2	Yield (%)[b]/TOF (h^{-1})			
				Hydrogenation		Redox isomerization	
1	*in situ*	H	H	19[c]	38	2[c]	4
2	*in situ*	CH_3	H	7[c]	14	3[c]	6
3	*in situ*	H	CH_3	26[c]	52	6[c]	12
4	*in situ*	H	C_2H_5	54[c]	108	17[c]	34
5	*in situ*	H	C_3H_7	70	140	16	32
6	*in situ*	H	C_4H_9	70	140	17	34
7	*in situ*	H	C_5H_{11}	71	142	19	38
8	isolated + NaCl (1:1)	H	C_5H_{11}	83	166	13	26
9	isolated + NaCl (1:10)	H	C_5H_{11}	78	156	14	28
10	isolated[d]	H	C_5H_{11}	74	296	26	104
11	*in situ*[e]	H	C_5H_{11}	36	144	10	40
12	isolated[f]	H	C_5H_{11}	65	1300	20	400
13	isolated[g]	H	C_5H_{11}	79	1580	20	400

[a]Conditions (except where noted): $0.25 \cdot 10^{-3}$ mol substrate, $1.25 \cdot 10^{-6}$ mol catalyst, 3 mL 0.2 M phosphate buffer pH = 6.05, 5 bar H_2, 1 hour, 80 °C. [b]Yield determined by GC. [c]Yield determined by ^{1}H NMR spectroscopy. [d]30 min. [e]$0.625 \cdot 10^{-6}$ mol catalyst. [f]$1.25 \cdot 10^{-7}$ mol catalyst. [g]$1.25 \cdot 10^{-7}$ mol catalyst, 9 bar H_2.

4. The reaction conditions were optimized for the hydrogenation and redox isomerization of oct-1-en-3-ol.

In aqueous systems, the pH of the catalyst solution may have a dramatic influence on the activity and selectivity of the catalyst. With [Pd(HSS)] as catalyst, the overall conversion of oct-1-en-3-ol was only slightly effected by changes in the pH; however, there was a significant increase in the selectivity toward hydrogenation.

The reaction was feasible at low temperatures, nevertheless the reaction rate increasing exponentially with the increase of the temperature.

An increase of the hydrogen pressure resulted in an increased rate of overall conversion of oct-1-en-3-ol; however, this was mostly manifested in the production of the saturated alcohol. The TOF under 9 bar H_2 pressure is 1980 h^{-1}.

The product distribution was studied by varying the amount of catalyst and the [PdBuHSS] proved to be active at high substrate loadings. The time course of the hydrogenation and redox isomerization was examined under optimized conditions: 2000/1 = [substrate]/[catalyst] ratio, at 80 °C and 1 bar H_2 pressure the conversion is 93 % in 3 hours reaction time.

Recycling experiments showed that the activity of the catalyst dropped significantly after the first reaction, followed by smaller changes in the consecutive runs. After the fifth run the catalyst still retained 40 % of its original activity.

The catalytic activity of Pd-salan complexes was compared (Table 2). The [Pd(PhHSS)] catalyst showed the highest activity and the [Pd(CyHSS)], [Pd(dPhHSS)] and [Pd(BuHSS)] showed comparable activities. In each reaction the saturated alcohol is the main product.

Table 2: Hydrogenation and redox isomerization of oct-1-en-3-ol with Pd(II)-salan type complexes[a]

	Catalyst	Conversion (%)		Overall TOF (h^{-1})
		Hydrogenation	Redox isomerization	
1	[Pd(HSS)]	42	26	680
2	[Pd(BuHSS)]	64	23	870
3	[Pd(CyHSS)]	74	21	950
4	[Pd(PhHSS)]	69	30	990
5	[Pd(dPhHSS)]	70	23	930

[a]Conditions: $0.25 \cdot 10^{-3}$ mol substrate, $2.5 \cdot 10^{-7}$ mol catalyst, 3 mL 0.2 M phosphate buffer pH = 6.05, 1 bar H_2, 1 hour, 80 °C.

5. The Pd(II)-salan type complexes are active catalysts in copper-free Sonogashira coupling in water.

The [Pd(BuHSS)] complex was studied as catalyst for Sonogashira coupling of phenylacetylene and iodobenzene in the presence of air.

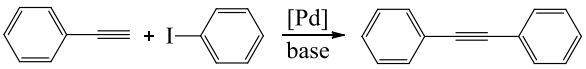
The effect of various inorganic and organic bases on the yield of Sonogashira coupling was examined. The highest conversion was achieved with triethylamine, with an optimum TEA to substrate (iodobenzene) ratio of 4. With the increase of the [substrate]/[catalyst] ratio the turnover frequency changed according to a maximum curve and the highest TOF observed was 1620 h^{-1} determined at a [substrate]/[catalyst] = 3000 (80 °C, 30 min. reaction time). Strong inhibition by copper(I) was observed. The reaction proceeded – albeit slowly – at low temperatures (e.g. at 40 °C) too, what is an important condition in reactions of heat sensitive compounds. With an [substrate]/[catalyst] = 3000 the maximum TOF, 2190 h^{-1} was observed at 120 °C. The addition of phase transfer catalyst (SDS) to the reaction mixture did not increase the conversion significantly (highest conversion with SDS

76 %, without 66 %). With the aim of increasing the solubility of the organic components in water, the reaction was also run in the presence of tetrahydrofuran (THF) as co-solvent. Small amounts of THF did not change the conversion, however, at water/THF = 2/1 significant decrease of the yield was observed. Under optimized conditions ([substrate]/[catalyst] = 3000, 80 °C, in water) the reaction proceeded fast until about 70 % conversion followed by a lower, but steady progress until completion in 4 h (97 % conversion).

Recycling of the [Pd(BuHSS)]-containing aqueous phase in biphasic Sonogashira coupling was also studied. Although the yields decreased steadily, the catalyst was still active in the 4th cycle with a TOF = 330 h^{-1}.

[Pd(HSS)], [Pd(PhHSS)], [Pd(dPhHSS)], [Pd(BuHSS)] and [Pd(CyHSS)] showed comparable activities, with [Pd(CyHSS)] being the most effective catalyst (Table 4).

Table 4: Sonogashira coupling of iodobenzene and phenylacetylene with Pd(II)-tetrahydrosalen complexes[a]

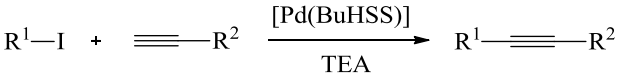


	Catalyst	Conversion (%)	TOF (h^{-1})
1	[Pd(HSS)]	46	1380
2	[Pd(BuHSS)]	51	1530
3	[Pd(CyHSS)]	55	1650
4	[Pd(PhHSS)]	33	990
5	[Pd(dPhHSS)]	54	1620

[a]Conditions: $1.67 \cdot 10^{-7}$ mol catalyst, $5 \cdot 10^{-4}$ mol iodobenzene, $7.5 \cdot 10^{-4}$ mol phenylacetylene (1.5 eqv.), $2 \cdot 10^{-3}$ mol TEA, 3 mL water, 60 min, 80 °C, air.

6. The scope of the Pd-sulfosalan complex-catalyzed Sonogashira coupling reaction was determined (Table 5).

Table 5: Sonogashira coupling of aryl iodides and terminal alkynes[a]



	Aryl halide	Terminal alkyne	Conversion (%)
1	iodobenzene	phenylacetylene	51
2	iodobenzene	4-ethynylanisole	60
3	iodobenzene	propargyl alcohol	60[b]
4	iodobenzene	4-ethynylpyridine	15[b]
5	iodobenzene	4-ethynyltoluene	25
6	iodobenzene	1-bromo-4-ethynylbenzene	59
7	4-iodoanisole	phenylacetylene	35
8	4-iodoaniline	phenylacetylene	34
9	1-iodo-4-nitrobenzene	phenylacetylene	87
10	1-bromo-4-iodobenzene	phenylacetylene	93
11	2,4-difluoro-iodobenzene	phenylacetylene	37
12	pentafluoro-iodobenzene	phenylacetylene	42[b]
13	2-iodopyridine	phenylacetylene	36[b]
14	bromobenzene	phenylacetylene	64[c]
15	4-bromoanisole	phenylacetylene	46[c]
16	1,2-dibromobenzene	phenylacetylene	86[c]
17	1,3-dibromobenzene	phenylacetylene	89[c]
18	1,4-dibromobenzene	phenylacetylene	85[c]
19	1-chloro-4-bromobenzene	phenylacetylene	66[c]
20	1-bromonaphthalene	phenylacetylene	16[c]
21	chlorobenzene	phenylacetylene	22[d]
22	1,2-dichlorobenzene	phenylacetylene	69[d]

[a]Conditions: $1.67 \cdot 10^{-7}$ mol [Pd(BuHSS)], $5 \cdot 10^{-4}$ mol aryl halide, $7.5 \cdot 10^{-4}$ mol terminal alkyne, $2 \cdot 10^{-3}$ mol Et_3N, 3 mL water, 80 °C, 1 h. [b]6 h. [c]$1 \cdot 10^{-6}$ mol [Pd(BuHSS)], 20 h. [d]$5 \cdot 10^{-6}$ mol [Pd(BuHSS)], 20 h.

In general, aryl halides with electron withdrawing substituents showed higher reactivity, while aryl halides with electron donating

substituents showed diminished reactivity, due to the strengthening and weakening of the carbon-halogen bond. Additionally the reaction rate was significantly decreased when one of the reaction partners contained a heteroatom. Also, the conversion was higher in the case of coupling phenylacetylene with an aryl halide containing a heteroatom.

The coupling of various bromo- and chloroarenes with phenylacetylene can be performed with [Pd(BuHSS)] using higher catalyst loadings (0.5–1.0 mol%). Dibromobenzenes were particularly reactive with conversions in the 85–89 % range (20 h reaction time).

To achieve substantial conversion of chloroarenes, the amount of catalyst had to be raised to 1 mol%; under such conditions chlorobenzene was coupled with phenylacetylene with 22 % conversion, while 1,2-dichlorobenzene reacted with 69 % conversion.

7. A "greener" procedure of Sonogashira coupling was developed.

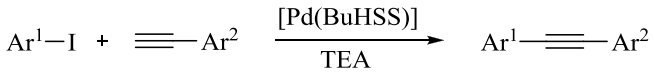
In general, the Sonogashira reactions were performed with excess of the alkyne in the presence of TEA. In coupling of phenylacetylene with iodobenzene the yield obtained in 1 h decreased from 58 % to 35 % when the [alkyne]/[aryl halide] ratio was decreased from 2/1 to 1/1. Encouraged by the finding that no side products were formed, in the rest of the studies I used longer reaction times (unoptimized) to achieve 100 % conversions. Under such conditions the water-insoluble products precipitated from the aqueous reaction mixture.

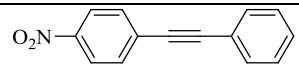
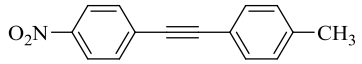
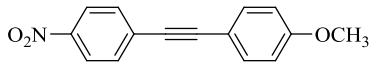
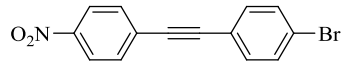
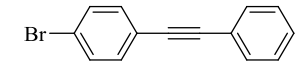
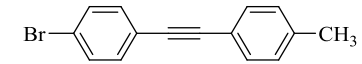
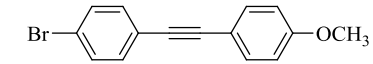
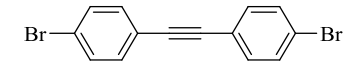
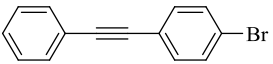
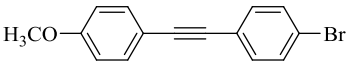
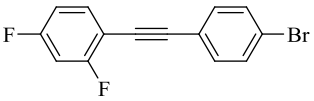
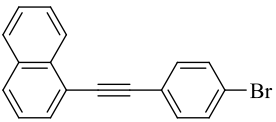
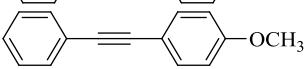
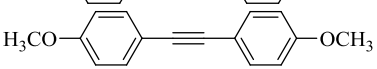
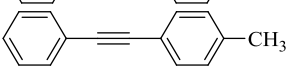
Table 6 shows the isolated yields of diphenylacetylene derivatives obtained in Sonogashira couplings of several aryl iodides and terminal alkynes with [Pd(BuHSS)] catalyst at [substrate]/[catalyst] ratios of 3000/1 or

1000/1, 80 °C and using TEA as base. This simple method which led to full conversion of the starting compounds (applied in 1/1 ratio) and did not require extraction by an organic solvent for product isolation furnished the products in excellent isolated yields.

Replacement of triethylamine by a less harmful base was also deemed necessary for a greener procedure. For this purpose KOH was chosen since of the inorganic bases it had been found to be the most effective. With stoichiometric amounts of aryl halides and terminal alkynes the coupling reaction was not complete even using a higher catalyst loading (1 mol%) and 24 h reaction time. Besides, the products stuck to the magnetic stirring bar so strongly that they could only be removed by dissolution in organic solvents. However, these difficulties could be overcome simply by adding a surfactant, sodium dodecylsulfate (SDS) to the reaction mixture. The reactions became fast enough to achieve 100 % conversions in 24 h, and the products could be easily collected by filtration. It should be added, however, that thorough washings with cold water were needed to remove the surfactant from the products.

Table 6: Sonogashira coupling of aryl iodides and terminal alkynes in water[a]



	Product	Reaction time (h)	Isolated yield (%)
1		4	97
2		12	98
3		12	97
4		6	99
5		8	88
6		12	95
7		12	93
8		12	89
9		6	90
10		12	88
11		12	85[b]
12		12	89[b]
13		12	96[b]
14		12	91[b]
15		12	87[b]

[a]Conditions: 3.34×10^{-7} mol [Pd(BuHSS)], 1×10^{-3} mol aryl iodide, 1×10^{-3} mol terminal alkyne, 4×10^{-3} mol TEA, 3 mL water, 80 °C, air. [b]1.00×10^{-6} mol [Pd(BuHSS)].

List of Publications

Papers related to the dissertation:

[2] Krisztina Voronova, Levente Homolya, Antal Udvardy, Attila C. Bényei, Ferenc Joó: Facile Copper-free Sonogashira Coupling Reactions in Water and in the Presence of Air Catalyzed by Novel Pd-Tetrahydrosalen-Type Complexes. Efficient Greening of the Procedure, *ChemSusChem*, DOI: 10.1002/cssc.201402147.
(IF: 7.475)

[1] Krisztina Voronova, Mihály Purgel, Antal Udvardy, Attila C. Bényei, Ágnes Kathó, Ferenc Joó: Hydrogenation and Redox Isomerization of Allylic Alcohols Catalyzed by a New Water-Soluble Pd-Tetrahydrosalen Complex, *Organometallics*, **2013**, *32*, 4391−4401.
(IF: 4.145)

Posters and lectures related to the dissertation:

[13] Voronova Krisztina, Bunda Szilvia, Joó Ferenc: Vízoldható Pd-tetrahidroszalén katalizátorok alkalmazása Suzuki kapcsolási reakciókban, *XXXVI. Kémiai Előadói Napok*, 2013.10.28–30, Szeged, Hungary (lecture).

[12] Krisztina Voronova, Levente Homolya, Szilvia Bunda, Antal Udvardy, Attila C. Bényei, Ferenc Joó: New Pd-salan complexes as efficient catalysts for Sonogashira coupling in water, *EuCheMS Conference on Organometallic Chemistry*, 2013.06.30–07.04, St Andrews, Scotland (poster).

[11] Voronova Krisztina, Homolya Levente, Szilvia Bunda, Ferenc Joó: Pd-szalán katalizátorok alkalmazása vizes közegű keresztkapcsolási reakciókban, *47. Komplexkémiai Kollokvium*, 2013.05.29–31, Mátraháza, Hungary (lecture).

[10] Voronova Kristina, Homolya Levente, Joó Ferenc: Foszfin- és rézmentes Sonogashira kapcsolás vízoldható Pd-szalán komplexekkel, *XXXV. Kémiai Előadói Napok*, 2012.10.29–31, Szeged, Hungary (lecture).

[9] Purgel Mihály, Joó Ferenc, Voronova Kristina: A palládium(II)-szulfoszalán – hex-1-én-3-ol rendszer vizsgálata DFT módszerrel, *MTA Reakciókinetikai és Fotokémiai Munkabizottság*, 2012.10.25–26, Gyöngyöstarján, Hungary (lecture).

[8] Purgel Mihály, Joó Ferenc, Voronova Kristina: A palládium(II)-szulfoszalán – hex-1-én-3-ol rendszer vizsgálata DFT módszerrel, *MTA Anyag- és Molekulaszerkezeti Munkabizottság*, 2012.10.12–14, Apáti-puszta, Hungary (lecture).

[7] Ferenc Joó, Csilla Czégéni, Gábor Papp, Henrietta Horváth, Kristina Voronova, Antal Udvardy, Ágnes Kathó: Organometallic catalysis in water: an old wine in new bottle? *XXV. International Conference on Organometallic Chemistry*, 2012.09.02–07, Lisbon, Portugal (lecture).

[6] Voronova Kristina, Joó Ferenc: Synthesis and catalytic activity of a water-soluble Pd-salan complex, *46. Komplexkémiai Kollokvium*, 2012.05.21–23, Mátrafüred, Hungary (lecture).

[5] Voronova Kristina, Joó Ferenc: Redukált szulfoszalén ligandum vízoldható Pd-komplexének előállítása és katalitikus aktivitásának vizsgálata, *XXXIV. Kémiai Előadói Napok*, 2011.11.02–04, Szeged, Hungary (lecture).

[4] Kathó Ágnes, Bertók Ágnes, Udvardy Antal, Szatmári Imre, Papp Gábor, Torma Krisztián, Susmit Basu, Voronova Kristina, Horváth H. Henrietta, Ambróz Almási, Czégéni Csilla Enikő, Ősz Katalin, Horváth Henrietta, Csajbók Éva, Joó Ferenc: Klórozott szénhidrogének reduktív dehalogénezése, *MKE 1. Nemzeti Konferencia*, 2011.05.22–25, Sopron, Hungary (lecture).

[3] Voronova Kristina, Joó Ferenc: Vízoldható Rh- és Ni-szulfoszalén komplexek katalitikus aktivitásának vizsgálata hidrogénezési reakciókban, *45. Komplexkémiai Kollokvium*, 2010.05.26–28, Mátraháza, Hungary (lecture).

[2] Voronova Kristina, Joó Ferenc: Vízoldható komplexek előállítása és katalitikus aktivitásának vizsgálata, *VI. Kárpátaljai Tudományos Diákköri Konferencia*, 2010.05.20, Uzhgorod (Ungvár), Ukraine (lecture).

[1] Voronova Kristina, Joó Ferenc: A szulfonált szalén ligandum ródiummal alkotott komplexének vizsgálata, *Fiatal Kárpátaljai Magyar Kutatók VII. Konferenciája*, 2010.05.15, Beregovo (Beregszász), Ukraine (lecture).