UNIVERSITY OF BUCHAREST
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DOCTORAL THESIS

ASYMMETRIC HYDROGENATION OF DOUBLE BOND C=N ON CSILP- AND CSILC-TYPE CATALYSTS

- Abstract -

PhD Student:

Podolean Iunia

PhD Supervisor:

Prof. Dr. Vasile I. Pârvulescu

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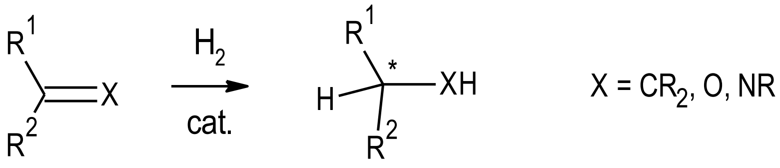
CHAPTER I: ASYMMETRIC CATALYSIS IN NON-CONVENTIONAL REACTION MEDIA

Introduction

The first chapter is an introductive overview. A critical review of literature data was realized in this chapter, with regard to the main aspects discussed in this thesis: the principles of green chemistry and asymmetric catalysis [1, 2]; asymmetric hydrogenation reaction and especially the asymmetric hydrogenation of C=N double bond [3]. This analysis considered the possible mechanisms for AH and ATH, effect of the ligand and transitional metal nature, homogeneous catalysts immobilization using different methods, with or without ionic liquid. The concept of SILP (Supported Ionic Liquid Phase), types and synthesis methods were also discussed [4, 5].

Asymmetric catalysis represents the "high-tech" of the modern chemistry which attracted a major academic and industrial interest in the last years. A synthesis of the literature data regarding the principles of asymmetric catalysis and real examples of it practical application is presented in this subchapter.

Compounds with chiral center, adjacent to the nitrogen are widespread in nature and play an important role in chemistry and pharmaceuticals. Asymmetric hydrogenation of C=N bond is an attractive way for synthesis of compounds such as amino acids, alkaloids, hormones, nitro sugars etc. The H_2 activation process by the transition metal complexes is well studies in the literature. In contrast, activation of imines and respectively the step of H-atom transfer to C = N bond has not been fully elucidated



Scheme 1.21: Asymmetric hydrogenation of double bond C=X

Factors differentiating hydrogenation of imines from other double bonds C = X (X = C, O) are therefore analyzed. Also there are comparatively analyzed, based on bibliographic data, reaction conditions and results for the hydrogenation reaction of prochiral imines with iridium-, ruthenium-, rhodium- and other metal-based catalysts.

Heterogenization of homogeneous catalyst is attractive in terms of it recycle and reuse. The immobilization methods of homogeneous complexes on the inorganic supports are discussed in this part, as well as their advantages and disadvantages and the types of inorganic supports.

In the subchapter describing the SILP (*Supported Ionic Liquid Phase*) concept is performed an overview of synthesis methods and their advantages.

WORKING HYPOTHESIS

The aim of this thesis was to investigate new methods and materials for immobilization of homogeneous catalysts and their application in asymmetric hydrogenation reactions, based on the state of the art. To achieve this goal the following objectives have been stated:

1. Synthesis of catalysts based on Ru, Ir and Rh, modified with BINAP-, DPEN-, DuPHOS-type ligands. Testing of catalysts for the asymmetric hydrogenation of imines in biphasic media using asymmetric hydrogenation (AH) and asymmetric transfer hydrogenation (ATH) mechanisms.
2. Study of the behavior of the ionic liquids in biphasic reactions or as solvents, and factors influencing the enantiomeric excess of the reaction product, separation of reaction product and leaching of the homogeneous complex. The role of solvent in homogeneous and biphasic reaction has also been studied in this chapter.
3. Synthesis of the heterogenized catalysts, where homogeneous complexes are anchored to the mesoporous or nanostructured materials in ionic liquid phase, via covalent bonding or absorption.
4. Characterization of the obtained complexes using techniques such as: XRD, RMN, elemental analysis, BET, DRIFT, TG-DTA etc.
5. Performing the catalytic tests for enantioselective hydrogenation with the obtained systems.

The original part of this thesis is represented by heterogenized systems based on ionic liquids and mesoporous materials, and especially the use of carbon nanotubes and carbon monoliths as support for SILP-type catalysts. A new element is also represented by the method that anchors the both - ionic liquids and homogeneous complexes on the surface of MCM-41 and carbon nanostructured materials. Application of resulting catalysts in the asymmetric hydrogenation of imines is also of particular interest because of its complexity and attractiveness.

Therefore the objectives set in this study sought to make contributions as:

- Establishing the effect of the ionic liquid used as a solvent and the interactions that occur between ionic liquid-solvent-metal complex-substrate-product of the reaction, in the enantioselective reaction.

- Development of new heterogeneous CSILP- (Supported Chiral Ionic Liquid Phase) and CSILC- (Chiral Catalysts Supported Ionic Liquid) type complexes based on ordered mesoporous silica and carbon materials.
- Assessment of the relationship between the enantiomeric excess of the reaction on the one hand and the heterogenization method and involved support on the other hand.

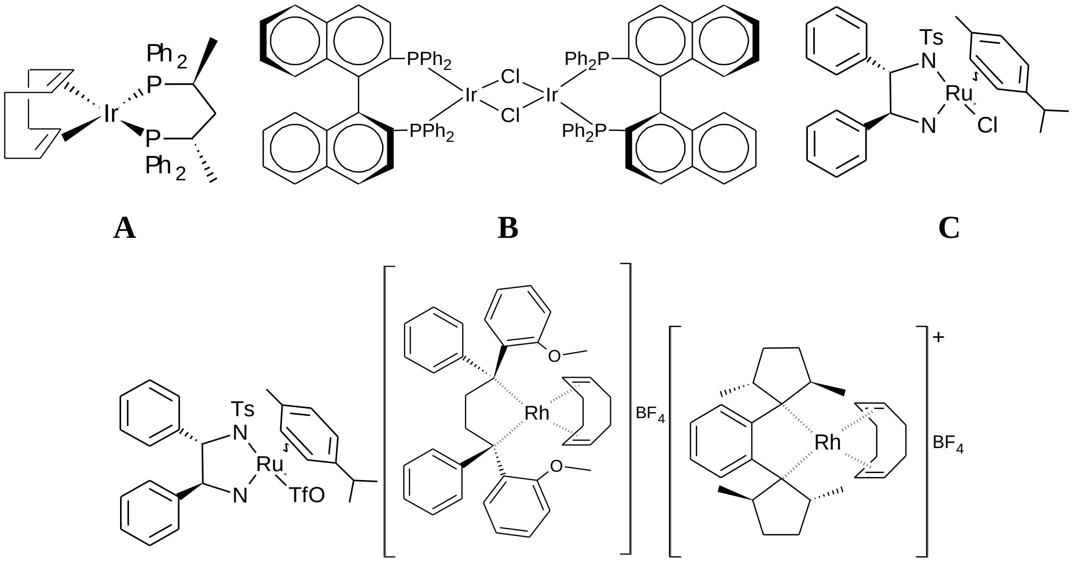
CHAPTER II: THE SOLVENT EFFECT IN HYDROGENATION REACTION OF DOUBLE BOND C=N

In this chapter was studied the solvent role for homogeneous hydrogenation of imines and dimethylitaconate in the biphasic media where one of the phases was represented by an ionic liquid. The aim of this study was a more detailed investigation of the influence of solvent and chemical nature of ionic liquids for double bond hydrogenation, especially C = N.

Experimental part.

All syntheses and manipulations were performed under an inert atmosphere to prevent the oxidation of air sensitive homogeneous catalysts. The experiments were carried out by using standard Schlenk techniques in a glove-box (850-NB Nitrogen dry-box de la Plas-Labs).

Prepared and purchased organometallic chiral Ru, Rh and Ir complexes and investigated Ionic liquids are presented in table 2.5, scheme 2.7 and scheme 2.8.



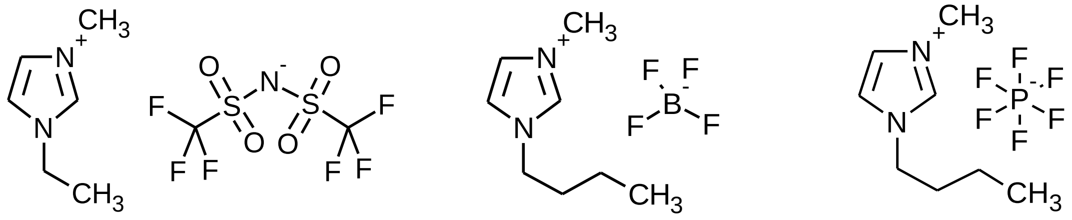
A **B** **C**

D **E** **F**

Scheme 2.7. Structure of chiral organometallic complexes based on Ru, Rh and Ir.

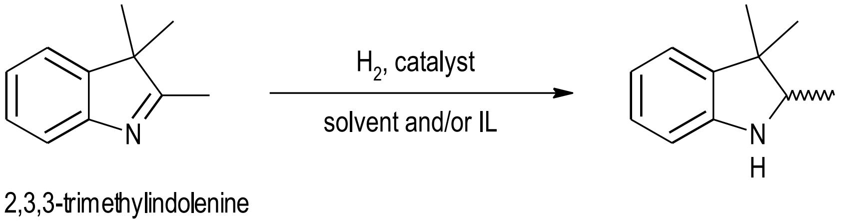
Table 2.5: Investigated chiral organometallic complexes based on Ru, Rh și Ir

Abbreviation	Complex	Chiral ligand
A	IrCl(COD)]$_2$ /(S, S)-BDPP	(2*S*,4*S*)-2,4-Bis(diphenylphosphino)pentane
B	[IrCl(S)-BINAP]$_2$	(*S*)-(−)-(1,1′-Binaphthalene-2,2′-diyl)bis(diphenylphosphine)
C	RuCl(*p*-cymene)[(*S*,*S*)-Ts-DPEN]	(1*S*,2S)-(+)-1,2-Diphenylethylenediamine
D	RuOTf(*p*-cymene)[(S,S)-Ts-DPEN]	(1*S*,2*S*)-(+)-1,2-Diphenylethylenediamine
E	[Rh(COD)(S,S)-DIPAMP][BF$_4$]	(1S,2S)-(+)-Bis[(2-methoxyphenyl) phenylphosphino]ethane
F	[Rh(COD)(R,R)-Me-DuPHOS][BF$_4$]	(-)-1,2-Bis((2R,5R)-2,5-dimethylphospholano)benzene

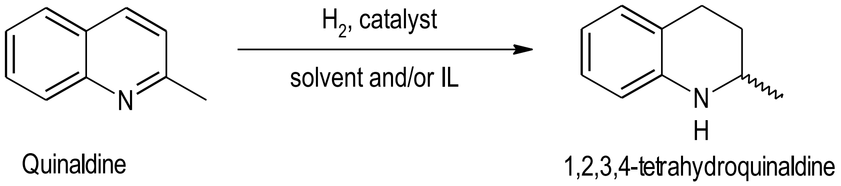

[EMIM][NTf$_2$] [BMIM][BF$_4$] [BMIM][PF$_6$]

Scheme 2.8. Structures of investigated ionic liquids

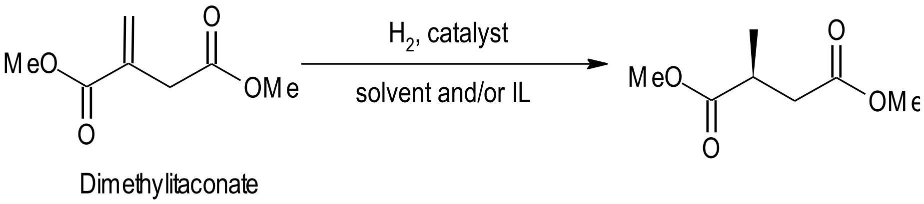
2 cyclic imines: quinaldine (Q: scheme 2.10) and trimethylindolenine (TMI: scheme 2.9) and dimethylitaconate (DMI: scheme 2.11) were used for catalytic tests.



Scheme 2.9: Enantioselective hydrogenation of thrimethylindolenine



Scheme2.10: Enantioselective hydrogenation of quinaldine



Scheme 2.11: Enantioselective hydrogenation of dimethylitaconate.

All reactions took place with 100% selectivity to amine product. The reaction products were analyzed using High Performance Liquid Chromatography HPLC, with Agilent Technologies chromatograph equipped with Daicel Chiralpack OD-H chiral column, 25 cm x 4,6 mm, 5µm particle size, mobile phase: mixture of n-hexan/i-PrOH = 90/10, flow = 0.6 mL min^{-1}, detector DAD UV-Vis: wavelength = 254 nm.

It has been shown that the solvent is of great importance for both - enantiomeric excess of the reaction product and the substrate conversion. Hydrogenation reaction of imines with Ir and Ru complexes was carried with good results in the presence of polar solvents. It has been shown that in some cases the presence of MeOH is essential for catalytic cycle involving prochiral imines. It was also demonstrated that use of Noyori-type Ru complexes require a slightly acidic reaction medium. Acidity can result even from homogeneous complex, and no additives are required as for Ir-based complexes.

Comparative results for two used ionic liquids EMIM[NTf$_2$] and BMIM[BF$_4$], showed that using BMIM[BF$_4$] led to higher enantiomeric excess (*e.e.*).

Giernoth and Krumm reported trimethylindoleine hydrogenation in ionic liquids [C10mpy][BTA] and [C10mim][BF$_4$] which took place with 82-86% *e.e.* at 40 atm of H$_2$ 50°C [6], in presence of TBAI and trifluoroacetic acid. These conversions are comparable to those obtained in this study using IL EMIM[NTf$_2$] and BMIM[BF$_4$]. Conversion and *e.e.* values decreased with about 30%, following the recycle of systems IL - solubilized complex,

Similar results were obtained for quinaldine hydrogenation. The use of triflic acid-modified Ru complex led to higher conversion of the substrate and reaction product *e.e.* than those obtained using RuCl(*p*-cymene)[(S,S)-Ts-DPEN]. Increase of the substrate / complex ratio at 500 resulted in a significant decrease of conversion value. The optimal ratio was set at S / C = 100.

Reaction occurred with good *e.e.*, but with low substrate conversions in biphasic reaction media. Nature of anion also proved important. Thus, replacement of BF$_4$ ion with PF$_6$ resulted in an increase of *e.e.* value to about 85%.

The reaction product recovery from IL medium is an important issue for catalysis performed in IL. Only 35% of the product and / or unhydrogenated substrate were recovered with hexane.

Product extraction with toluene was 2 times more efficient. But use of toluene has generated no change in substrate conversion or *e.e.*

Rh complexes were not selective for prochiral imines hydrogenation. For comparison Rh complexes were tested for C=C double bond hydrogenation of dimethyitaconate (DMI). It was observed that both temperature and pressure particularly influenced the result of the enantioselective reaction. The enantiomeric excess of the reaction product and substrate conversion for reaction performed in IL in one of phase were higher compared with homogeneous reaction under the same conditions. The Rh complex **F** was also tested in hydrogenation reaction under hydrogen flow. Under these conditions *e.e.* value was maintained at the same level after the recycle of system ionic liquid-solubilized complex.

To better understand the influence of solvent for extraction and diffusion phenomena, the partition coefficient of the substrate and reaction product between ionic liquid BMIM [PF6] and used immiscible solvents was determined (table 2.9.)

Toluene and *t*-BuOH extract better the reaction product. It was demonstrated by higher recovery rate of the reaction product (table 2.7 Nr. cr. 9-13).

Table 2.9: Partition coefficient values for quinaldine and 2,3,3 trimethylindolenine between BMIM [PF_6] and molecular solvents.

compound	**Hexane**	**Toluene**	***t*-BuOH**
Quinaldine	0,8	1,2	2,65
1,2,3,4- tetrahydroquinaldine	1,3	5,8	6,7

The catalytic tests were repeated for quinaldine in the presence of complex D in BMIM[PF_6] with *t*-BuOH.

Enantiomeric excess obtained in these conditions was higher than in homogeneous reaction. About 3% decrease of enantiomeric excess and conversion values resulted after each recycle for three successive cycles of the solubilized complex

CHAPTER III: MESOPOROUS ORGANIZED MATERIALS

The aim of this chapter was the synthesis of heterogenized catalysts based on mesoporous organized materials. The classification of mesoporous organized materials, methods for synthesis and the most attractive properties in terms of catalysis were discussed in bibliographic part. Functionalization methods of these materials were also analyzed.

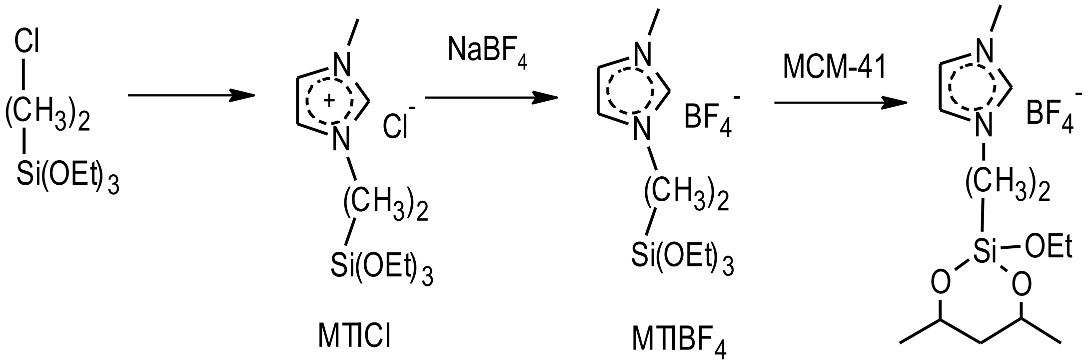
Experimental part

The following methods were used to achieve the heterogenization of organometallic complexes on mesoporous organized materials: physisorption, covalent bonding and respectively multiple physisorption specific for SILP-type catalysts. Resulting materials were analyzed using specific techniques: diffuse reflectance infrared Fourier transform spectroscopy, X-ray diffraction, nitrogen adsorption-desorption, thermogravimetric analysis, elemental analysis. The pure supports were used as reference for all characterizations. Subsequently, the resulted catalysts were tested in asymmetric hydrogenation reaction of imines. Results of catalytic tests were evaluated following correlation of catalyst type with synthesis method and effectiveness and recyclability for studied reactions.

CSILP- (Chiral Supported Ionic Liquid Phase) type catalysts were obtained by classical physisorption.

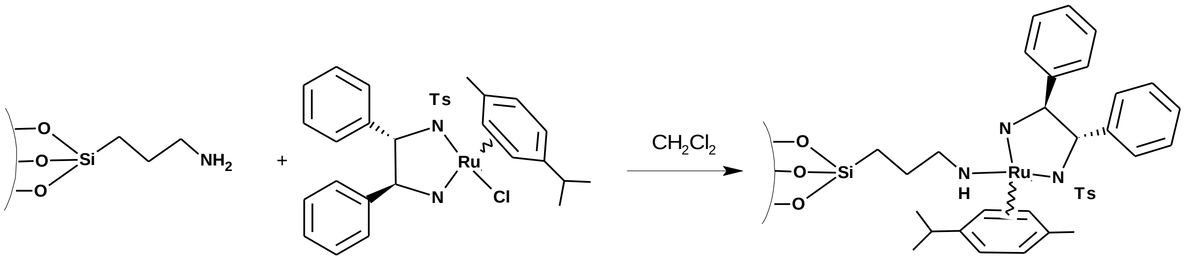
Organometallic chiral complexes were dissolved in ionic liquids and supported on MCM-41. Resulted CSILP catalyst was washed with CH_2Cl_2, to remove the excess of IL and chiral complex, and dried under vacuum.

Method for synthesis of CSILC (Chiral Supported Ionic Liquid Catalysts) is represented in scheme 3.10. [7]



Scheme 3.10: Functionalization of MCM-41 ionic liquid 1-methyl-3-(3-triethoxysilylpropyl)-imidazolium tetrafluoroborate.

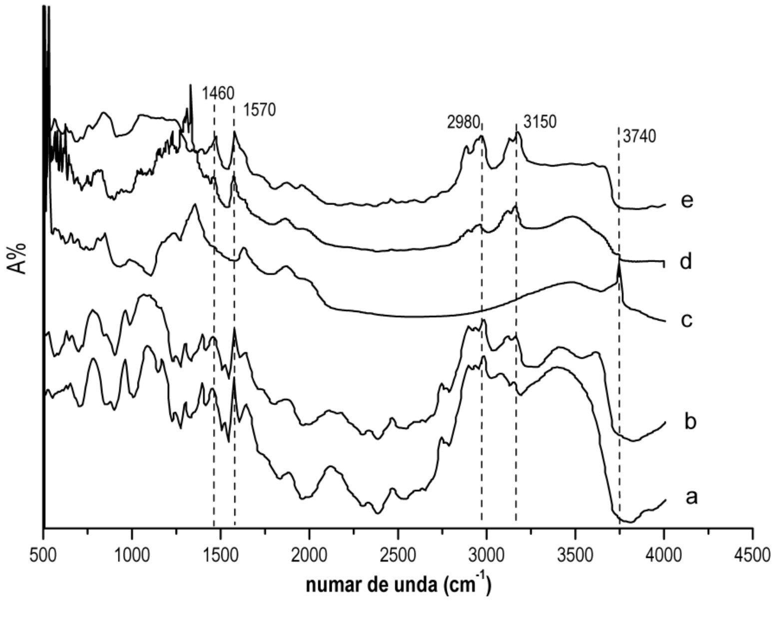
Covalent functionalization of MCM-41 was realized with (3-aminopropyltriethoxysilane linker (scheme 3.6). [8]



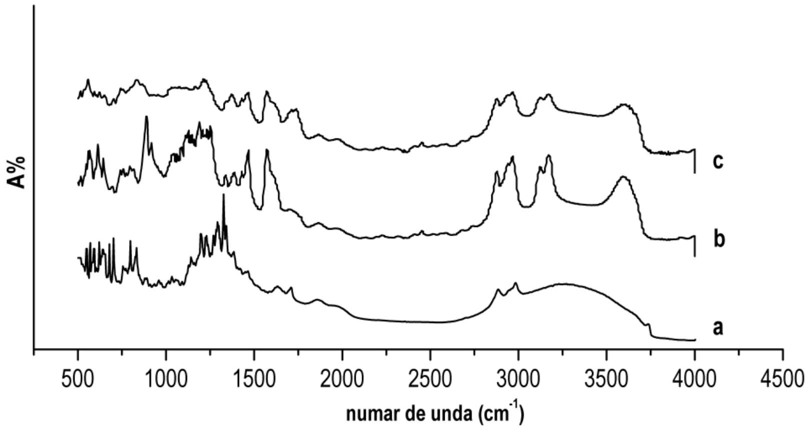
Scheme 3.6: Noyori complex immobilized in MCM-41 pores.

Catalyst characterizations revealed that the structure of mesoporous material MCM-41 remained intact after functionalization steps without any evidence of structural decomposition of the support. Textural properties of the investigated materials indicate the presence of the ionic liquid phase. Nitrogen adsorption-desorption isotherms of type IV are specific for these mesoporous materials. X-ray patterns of modified MCM-41 and neat material support evidence that mesoporous hexagonal symmetrical structure remained intact, regardless the functionalization method.

DRIFT analysis of complex RuCl*(p*-cymene*)[(S,S*)-Ts-DPEN] immobilized by physisorption on MCM-41 (SILC and SILP type catalyst) also confirmed the presence of ionic liquid [BMIM][BF4] and complex RuCl*(p*-cymene*)[(S,S*)-Ts-DPEN] (C) (schemas 3.14 and 3.15).



Scheme 3.14: DRIFT spectra of complex ionic liquid - 1-methyll-3-(3-triethoxysilylpropyl)-imidazolium cloride (MTICl) (a); 1-methyl-3-(3-triethoxysilylpropyl)-imidazolium tetrafluoroborate (b); neat MCM-41 support, (c); MCM-41 functionalized with 1-methyl-3-(3-triethoxysilylpropyl)-imidazolium tetrafluoroborate, (d); CSILC catalyst functionalized with [BMIM][PF$_6$]-**C** (e).



Scheme 3.15: DRIFT spectra for MCM-41 (a), [BMIM][BF$_4$]/MCM-41 (b), and [BMIM][BF$_4$]-**C**/MCM-41, physically adsorbed, (CSILP catalyst) (c).

DRIFT analysis of CSILC catalyst was completed by elemental analysis. The results obtained for pure and functionalized MCM-41 with MTIBF$_4$ are shown in table below.

Table 3.2: Elemental analysis of neat and functionalized MCM-41.

Catalyst	**N [%]**	**C [%]**	**H [%]**	**S [%]**
MCM-41	-	18.2	3.5	-
MTIBF$_4$ / MCM-41 CSILC	2.97	8.63	1.03	-
RuOTf(*p*-cymene)[(S,S)-Ts-DPEN]/MCM-41 CSILC	6.49	22.52	2.89	0.4

The as-synthesized systems were also investigated by combined TG-DTA measurements The main mass loss (4.12%) corresponds to the decomposition of aminopropyl entities. The quantitative analysis of the MCM-41 CSILP-based sample showed that the significant decomposition occurred. 45% of the sample was lost in the 150–400 ◦C temperature range in well defined steps. The shift of the onset decomposition temperature for the CSILP catalyst, compared with that found for the covalently bonded samples, may be attributed to the presence of the thin layer ionic liquid coverage onto the MCM-41surface.

The results for catalytic hydrogenation reactions on MCM-41 supported complexes, wer discussed considering the substrate conversion and *e.e.* of reaction product, chemo-selectivity were unchanged in all cases.

An interesting feature of the asymmetric catalytic synthesis is the nonlinear correlation between the optical purity of the chiral catalyst and that of the reaction product as reported for the first time by Kagan et al.[9]. A strong amplification in the product chirality may come at the expense of a severely suppressed rate of product formation. In other words, there is a relationship between the reaction rate and enantioselectivity and, in general, higher *e.e.*'s were reported at low conversions.

As assumed, homogeneous chiral systems lead to higher conversions compared to heterogeneous systems. The conversion value was depended on used complex. Iridium was more active compared to ruthenium. The effect of the ligand is less pronounced compared with the effect of the metal but are not negligible. For iridium, the combination of (COD)/BDPP (complex A) led to slightly smaller conversions than BINAP (complex B). The % *e.e.*'s were determined by the nature of chiral ligand. The immobilization of homogeneous complexes did result in enhanced *e.e.*'s. Interestingly, the ionic liquid is not a spectator in this process and the replacement of [EMIM][NTf_2] with [BMIM][BF_4] led to an additional decrease of the conversion (from 34.5% to 11.6%) that was accompanied by an additional increase of *e.e.* (from 44.8% to 51.2%).

The decrease of values on the recycle of the biphasic systems solvent / IL was assigned to difficult separation of reaction products and complex deactivation. For CSILP-type catalysts this effect id due to leaching. The leaching was confirmed by the TGA and elemental analysis measurements.

Thus the importance of the support and a solvent is critical to prevent the leaching.

Replacing hexane with *t*-BuOH, a polar solvents, immiscible [BMIM][PF_6], led to *e.e.* value comparable to those obtained for homogeneous reaction. The *e.e* value of the reaction product decreased by approx. 15% after each consecutive recycle and substrate conversion decreased by approximately 60%. When CSILC-type catalyst was used, the results were superior to homogeneous reaction. The conversion decreased considerably on recycle, but *e.e.* remained at 80% after 3 catalytic cycles.

The leaching in *t*-BuOH is much lower and mainly concerns the metal complex. The complex ratio in CSILC-type catalyst remained high, after 3 cycles.

The hydrogenation of dimethylitaconate was performed with Rh based complexes. Catalytic performances of CSILP catalysts were higher for C=C double bond hydrogenation compare to C=N hydrogenation. Using the CSILP catalyst with complex (F) and working under a hydrogen flow led to 99,9% *e.e.*, which exceeded the values obtained under homogeneous reaction conditions (91,0%). Substrate conversion was about 4 times lower when CSILP catalyst was used. The *e.e.* value remained unchanged on catalyst recycles, while the conversion decreased to 7.5%.

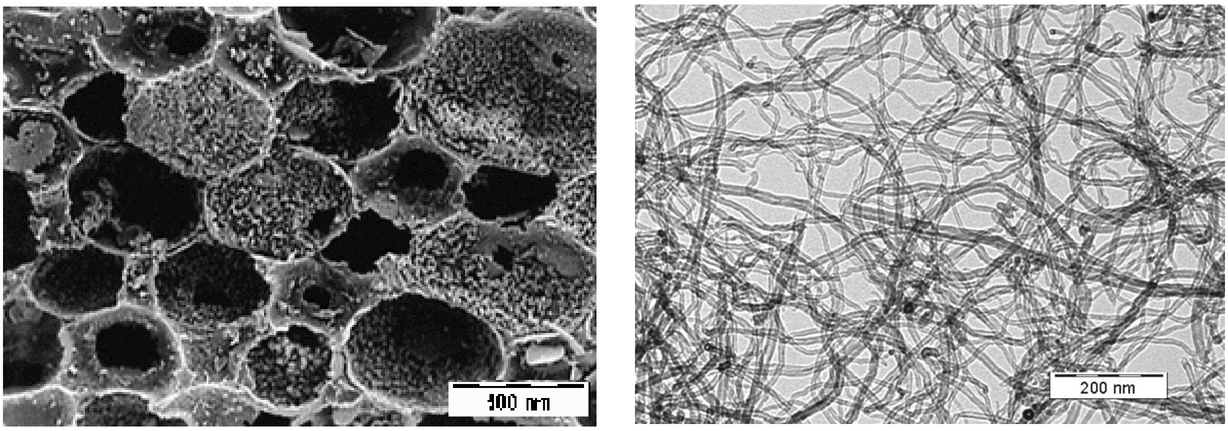
CHAPTER IV: NANOSTRUCTURED MATERIALS

In this chapter were analyzed nanostructured materials like carbon monoliths and nanotubes in terms of their use as support. For this purpose properties of structured carbon materials and their functionalization methods were investigated.

Experimental part

In the experimental part were investigated the immobilization methods of chiral complexes by covalent bondings or by means of absorbed or covalently grafted ionic liquid. In this way CSILP and CSILC catalysts were obtained.

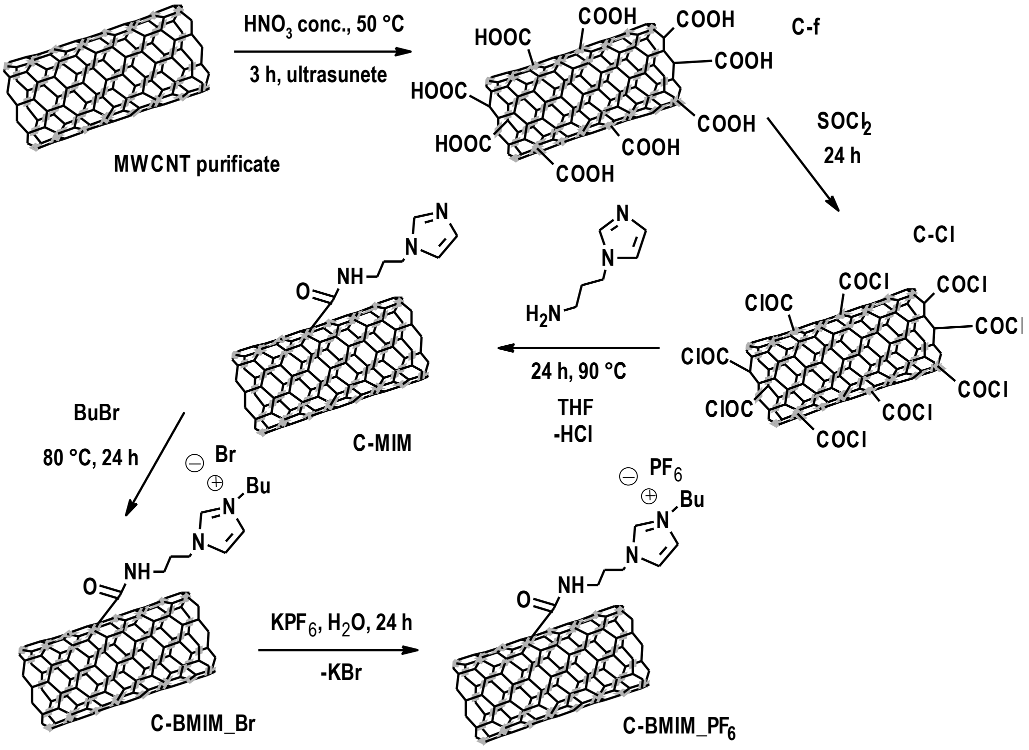
Carbon materials with following characteristics were used as support for chiral complex immobilization: highly porous carbon materials 25HF Ssp = 800 m^2/g, Dp = 2.2 nm and 4F5, Ssp = 600 m^2/g, Dp = 2.4 nm (Ssp = specific surface area, Dp = average pore size) [10]. Purchased MWCNT were prepared by chemical vapor deposition method and presented „armchair” chirality. The multiwalled carbon nanotubes diameter was 5,5 nm, the length 5µm and the number of walls from 3 to 6.



Scheme 4.6: TEM images of the used supports (right MWCNT, left carbon monoliths)

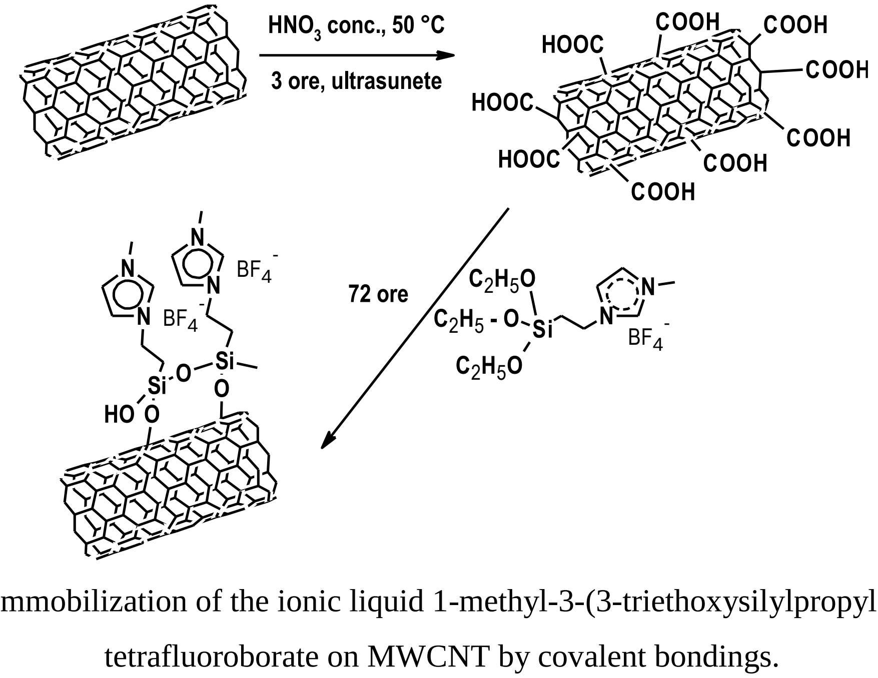
CSILP-type catalysts (Chiral Suported Ionic Liquid Phase) were obtained similar to MCM-41.

To achieve the synthesis of CSILC-type catalyst the ionic liquid was grafted to the carbon nanotube surface by covalent bondings. Subsequently the chiral complex was solubilized in ionic liquid layer. The reported methods were used for carbon nanotubes functionalization [11, 12]. The synthesis is represented in scheme 4.8.



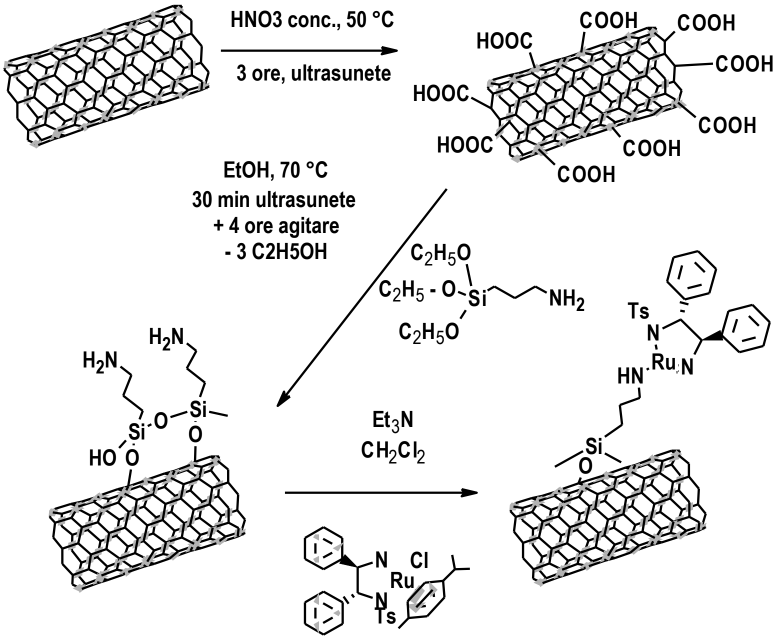
Scheme 4.8: Immobilization of [BMIM][PF_6] on MWCNT thought covalent bondings.

Another method of obtaining CSILC-type catalysts was those reported for MCM-41 (scheme 4.9).



Scheme 4.9: Immobilization of the ionic liquid 1-methyl-3-(3-triethoxysilylpropyl)-imidazolium tetrafluoroborate on MWCNT by covalent bondings.

RuCl(*p*-cymene)[(S,S)-Ts-DPEN] (C) complex was immobilized on MWCNT by covalent bondings using the method reported for MCM-41 (scheme 4.10) [7].



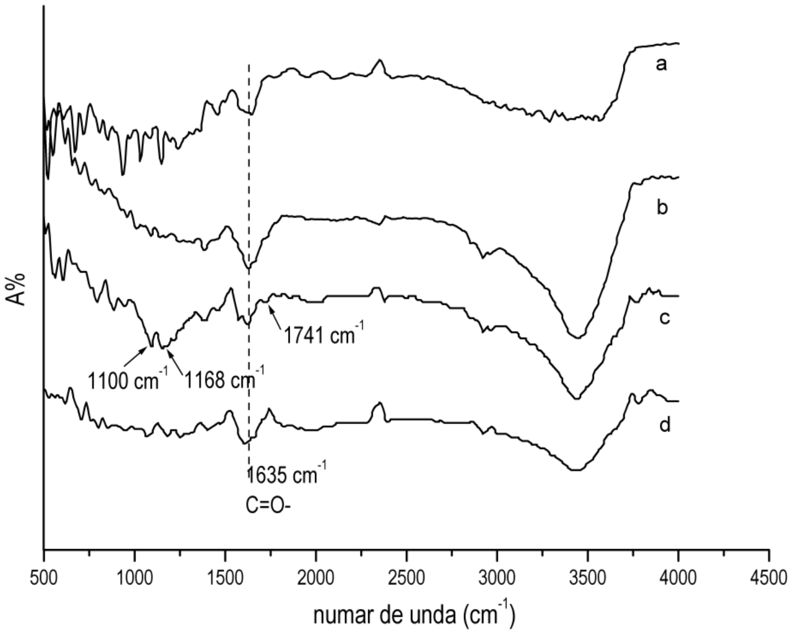
Scheme 4.10: Immobilization of RuCl(*p*-cymene)[(S,S)-Ts-DPEN] complex on MWCNT by covalent bondings.

The XRD pattern of 25HF mesoporous carbon is close to that of graphite and shows two diffraction lines at 2Θ = 23° (d_{002}) and 43.5° (d_{100}). Such XRD pattern corresponds to partially graphitized porous carbon monoliths, in accordance with the literature [13]. As expected, the XRD suggests that the 25HF support has a higher stability than 4F5.

Variation of specific surface area was correlated with the thickness of ionic liquid layer (pure or containing solubilized complex). The presence of ionic liquid led to the specific surface area decrease by about 33%.

The TG-DTA measurements showed a different decomposition behavior of carbon based CSILP catalysts, compared to [BMIM][BF4]-C/MCM-41.

The curve for the [BMIM][BF4]-C/25HF (scheme 4.12) shows that the decomposition of the ionic liquid and of the chiral complex started after 300 ◦C and the weight loss took place in only one step (350–450 ◦C).



Scheme 4.13: DRIFT spectra of neat MWCNT (a); functionalized material C-f (b); C-MIM, (c); C-BMIM-PF_6 (d)

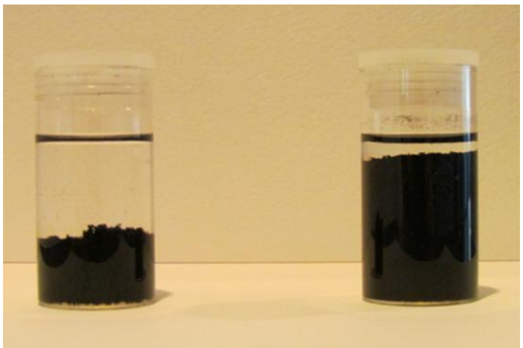
DRIFT spectra of the analyzed CSILC catalysts C-BMIM-PF_6 are represented in scheme 4.13. The elemental analysis data for CSILC catalysts C-BMIM-PF_6 and its fragments showed that the ionic liquid was grafted on CN in accord with used protocol.

The results for elemental analysis of C-MTI-PF_6 are represented in table 4.4.

Table 4.4: Elemental analysis of final C-MTI-PF_6 catalysts and its fragments

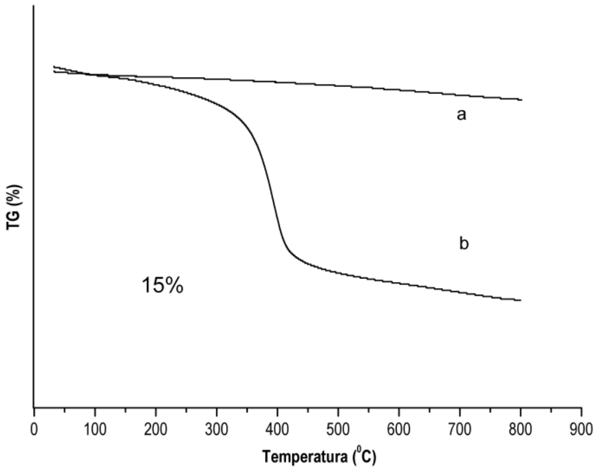
Catalyst	**N [%]**	**C [%]**	**H [%]**	**S [%]**
MWCNT	-	94.20	0.14	-
C-f	0.20	89.33	0.06	-
C-MTI-BF_4	2.517	77.443	1.07	-
RuOTf(*p*-cymene)[(S,S)-Ts-DPEN]/ C-MTI-PF_6	6.181	48.69	3.48	0.57

The simplest test for evidence of CN oxidation is material dispersion in a polar organic solvent. For this test about 10 mg of MWCNT and C-f material were dispersed in 15 mL of acetone in ultrasonic bath. In the scheme 4.15 are presented the images performed after 7 days.



Scheme 4.15: Test for dispersion of pure MWCNT, left, and C-f, right, in acetone, after 7 days. This test showed that the functionalized material do not agglomerate due to the presence of OH groups.

The results of thermogravimetric analysis of pure support and CN functionalized with ionic liquid $MTIBF_4$ are represented in scheme 4.16. Mass loss of functionalized material at temperature around 402^0C indicated that about 15% of ionic liquid $MTIBF_4$ was covalently grafted on the carbon nanotubes surface.



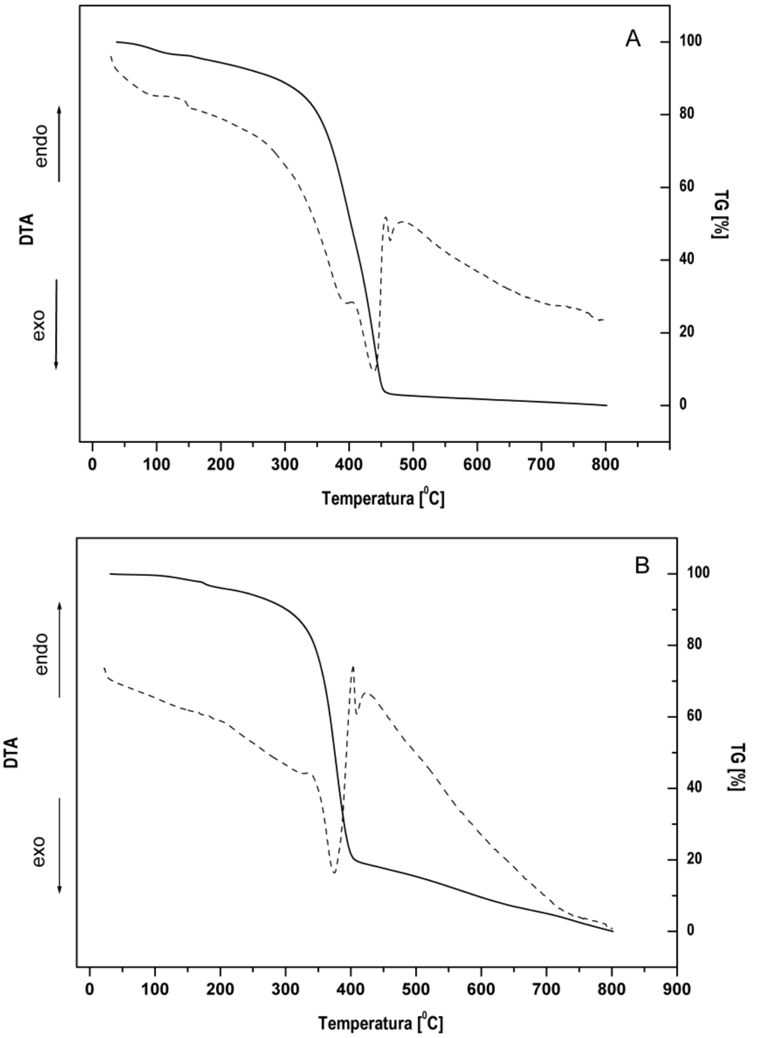
Scheme 4.16: TGA profile for neat MWCNT (a), and functionalized with ionic liquid MTI-BF_4 (b).

Comparative data for MCM-41 showed that not only the nature of the chiral complex or of the ionic liquid but also the nature of the support was found to greatly influence the asymmetric imine hydrogenation. Replacing the mesoporous siliceous MCM-41 support with carbon monoliths led to a significant change in behavior.

CSILC-type catalyst based on MWCNT support C-BMIM-PF_6 was proved to be more stable at recycle.

As expected, the reaction did not took place in nonpolar solvent - hexane. CSILC catalyst C-MTI-PF_6 proved to be more stable than C-BMIM-PF_6. Results for the first reaction were comparable to those obtained for homogeneous reaction. Conversion decreased to approximately 30% while the enantiomeric excess remained constant around 99.9%.

Thermogravimetric and elemental analysis of C-BMIM[PF_6]+RuOTf(*p*-cymene)[(S,S)-Ts-DPEN] catalysts before the reaction and after 3 cycles demonstrated that the ionic liquid remained fixed on MWCNT, but the active catalytic species passed in solution.



Scheme 4.17: TG-DTA pattern for C-BMIM[PF_6]+RuOTf(*p*-cymene)[(S,S)-Ts-DPEN] (a), and twice recycled C-BMIM[PF_6]+RuOTf(*p*-cymene)[(S,S)-Ts-DPEN] (b).

Data obtained using CN based CSILC catalysts compared with those obtained using MCM-41 based CSILP catalysts for quinaldine hydrogenation reaction suggested that CN's have an advantage over MCM-41. Enantiomeric excesses were at the same level, but the conversions obtained with the MCM-41 supports where smaller, and decreased after each recycle. Low conversion can be attributed to the effect of more difficult diffusion in the case of MCM-41 compared to CN where chiral complex is attached to the solid surface.

Comparative tests were performed for catalytic hydrogenation of dimethylitaconate. Dimethylitaconate was hydrogenated with Rh complex solubilized in ionic liquid phase immobilized on NC with an average conversion of 92% and about 96% *e.e.* Catalyst was recycled at least three times without a significant decrease in conversion and *e.e.* values. Diethyl ether as IL-immiscible solvent, contributed to a better catalyst recycle.

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LIST OF PUBLICATION

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1.*"Ionic Liquid Effect on the Reversal of Configuration for the Magnesium(II) and Copper(II) Bis(oxazoline)-Catalysed Enantioselective Diels–Alder Reaction*", Goodrich, P.; Hardacre, C.; Paun, C.; Pârvulescu, V. I.; Podolean, I., *Adv. Synth. Catal.* **2008**, *350*, 2473 – 2476.

2.*"Chiral supported ionic liquid phase (CSILP) catalysts for greener asymmetric hydrogenation processes"*, Podolean, I.; Hardacre, C.; Goodrich, P.; Brun, N.; Backov, R.; Coman, S.M.; Pârvulescu, V.I., *Catal. Today*, **2013**, *200*, 63-73.

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2. *"Support Ionic Liquid Phase (SILP) catalysts for an Enantioselective Diels-Alder Reaction Goodrich"*, P.; Hardacre, C.; Lourenco, M.; de Castro, C.N.; Parvulescu, V.I.; Paun, C.; Podolean, I.; Ribeiro, A., 3rd Congress on Ionic Liquids, May 31-June 4, **2009**, Cairns, Australia, D. MacFarlane and J. Pringle (Eds) p.320 (Poster)

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