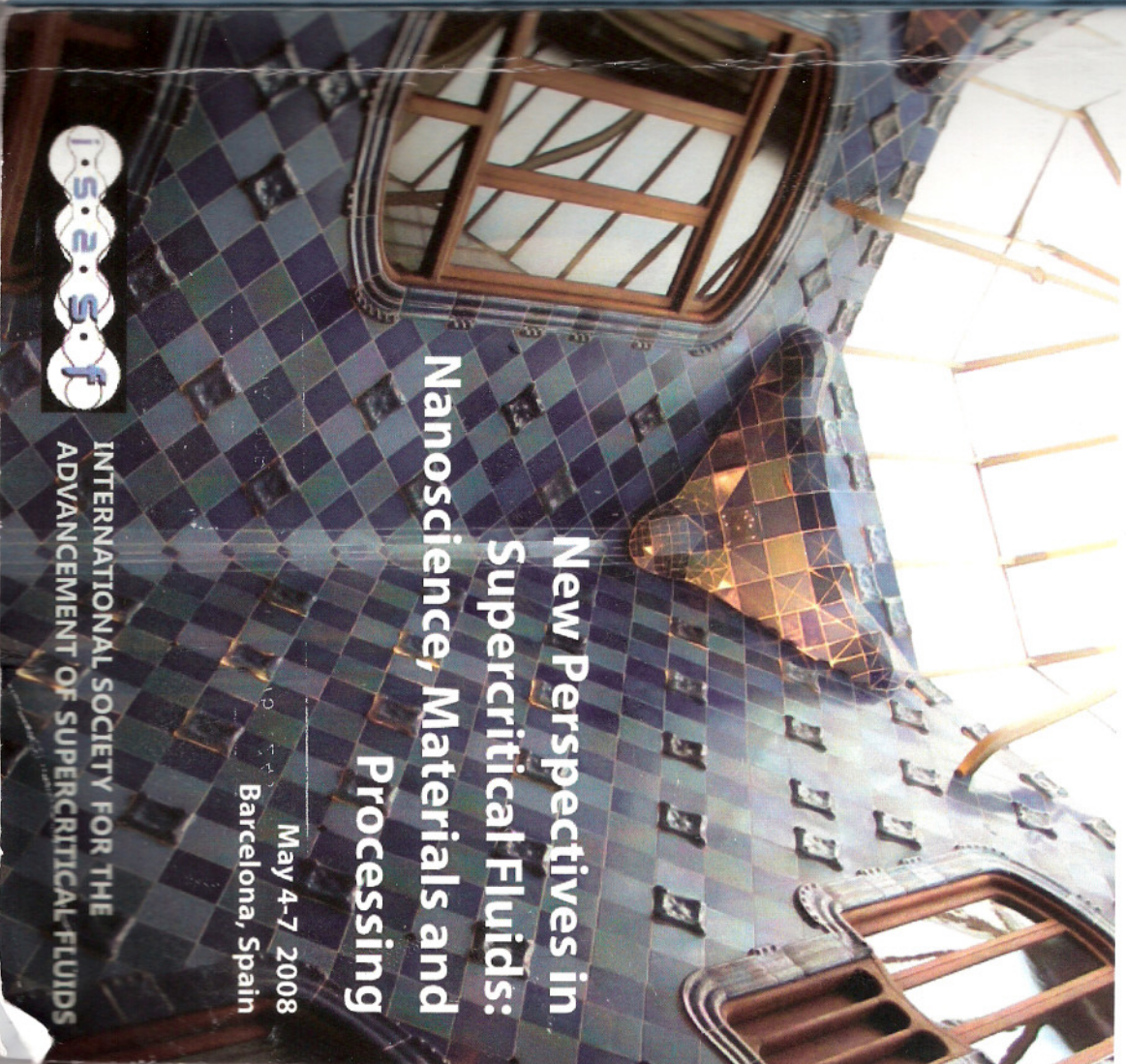


11th European Meeting on Supercritical Fluids



**New Perspectives in
Supercritical Fluids:
Nanoscience, Materials and
Processing**

May 4-7 2008
Barcelona, Spain



INTERNATIONAL SOCIETY FOR THE
ADVANCEMENT OF SUPERCRITICAL FLUIDS

ISBN 2 - 905267 - 58 - 5

#108	MODELING A TRANSPIRING WALL REACTOR FOR SCWO PROCESS APPLYING CFD TOOLS. EVALUATION OF DIFFERENT DESIGNS. Martin A., Bermejo M.-D., Bielsa I. and Cocero M.-J., University of Valladolid (Spain) (PR)	208
#110	SUPERCRITICAL CARBON DIOXIDE COPOLYMERIZATION OF D,L-LACTIDE AND GLYCOLIDE USING ZINC OCTOATE AS CATALYST. Gracia I., Rodriguez J.-F., de Lucas A., Fernandez M.-P. and Mazarro R., University of Castilla-La Mancha, Ciudad Real (Spain) (PR)	209
#111	WASTE POLYSTYRENE RECYCLING BY CIMENE USING SUPERCRITICAL CO₂ FOR SOLVENT RECOVERY. Garcia M.-T., Rodriguez J.-F., de Lucas A., Gracia I. and Duque G., University of Castilla-La Mancha, Ciudad Real (Spain) (PR)	210
#115	REGENERATION OF NO_x CATALYSTS USING SUPERCRITICAL AND SUBCRITICAL WATER. Asencio I., Camarillo R., Lozano and Rincon J., University of Castilla la Mancha, Toledo (Spain) (PR)	211
#116	IMPREGNATION AND ACTIVATION OF CARBON AEROGELS MADE FROM 5-METHYLRESORCINOL AND FORMALDEHYDE. Perez-Caballero F. and Koel M., Tallinn University of Technology, Tallinn (Estonia) (PR)	212
#124	DINITROBENZENE DIFFUSION IN THE PAPER IN COMPRESSED CO₂. Dormidonova A., Shadrin A., Murzin A. and Shafikov D., Khlopin Radium Institute, St.-Petersburg (Russia) (PR)	213
#126	DECONTAMINATION OF SOILS IN LIQUID CO₂ AND IN OZONE FRIENDLY FREON HFC-134A. Shadrin A., Shafikov D., Murzin A., Dormidonova A. and Kamachev V., Khlopin Radium Institute, St.-Petersburg (Russia) (PR)	214
#127	NEW PERFLUORINATED BINAP-RHODIUM CATALYSTS AND ASYMMETRIC HYDROGENATION OF KETOESTER IN SUPERCRITICAL CO₂. Altinel H., Yilmaz M.-K., Arikaner S., Güzel B., Cukurova University, Adana (Turkey) and Avsar G., Mersin University, Mersin (Turkey) (PR)	215
#135	SEPARATION OF ALKANES AND ALCOHOLS WITH SUPERCRITICAL FLUIDS Schwarz C.-E., Bonthuys J.-H., Knoetze J.-H. and Burger A.-J., University of Stellenbosch (South Africa) (PR)	216
#148	SYNTHESIS OF SC CO₂ SOLUBLE FLUORINATED PHOSPHINOETHANE AND PHOSPHINOHYDRAZINE DERIVATIVES AND THEIR RHODIUM(I) COMPLEXES. Avsar G., Mersin University (Turkey), Altinel H., Yilmaz M.-K., Kicir N. and Güzel B., Cukurova University, Adana (Turkey) (PR)	217

#149	ANOMALOUS STABILITY OF "COLORED" FORM OF SPIROXAZINE PHOTOCROMS TRAPPED IN POLYCARBONATE MATRIX AFTER SUPERCRITICAL FLUID IMPREGNATION. Bagratashvili V., Timashev P.-S., Institute of Laser and Information Technologies RAS, Troitsk, Glagolev N.-N., Kotova A.-V., Solovyeva A.-B., and Zapadinskii B.-I., Institute of Chemical Physics, Moscow (Russia) (PR)	218
#151	CONTINUOUS HYDROTHERMAL SYNTHESIS OF IRON PHOSPHATE HYDROXIDE IN SUPERCRITICAL WATER. Liang M.-T., Wang S.-H., Tsai M.-H., I-Shou University (Taiwan) and Chang Y.-L., National Cheng Kung University, Tainan (Taiwan) (PR)	219
#153	RAMAN SPECTROSCOPIC STUDIES ON SPECIFIC INTERMOLECULAR INTERACTION OF URANYL β-DIKETONATO COMPLEX WITH B (C₆F₅)₂ UNDER SUPERCRITICAL CO₂. Kachi Y., Ikeda Y., Tokyo Institute of Technology and Tsukuhara T., The University of Tokyo (Japan) (PR)	220
#160	DESIGN AND COST STUDY OF A cGMP DELOS PLANT FOR DRUG MICRONIZATION. Cordoba A., Sala S., Ventosa N., Veciana J., ICMAB, Barcelona and Larrayoz M.-A., Universitat Politècnica de Catalunya, Barcelona (Spain) (PR)	221
#165	SYNTHESIS OF FUEL CELL CATALYSTS IN SUPERCRITICAL CARBON DIOXIDE AND THEIR STRUCTURE INVESTIGATION. Said-Galiyev E., Nikolaev A., Khokhlov A., A.N., Nesmeyanov Institut of Organoelement Compounds, Moscow, Gallyamov M., Abramchuk S. and Tsirlina G., M.V. Lomonosov Moscow State University (Russia) (PR)	222
#174	COMPARISON BETWEEN SC-CO₂ EXTRACTION AND SOLVENT EVAPORATION OF O/W EMULSIONS FOR DRUG-POLYMER MICROSPHERES PRODUCTION. Della Porta G., Scognamiglio M.-R. and Reverchon E., Università degli Studi di Salerno (Italy) (PR)	223
#176	FLUORINATED POLYMERIC BINAP LIGAND FOR ASYMMETRIC HYDROGENATION IN SC SO₂. Altinel H., Yilmaz M.-K., Erdem Ö., Guzel B., C.U. Science and Letters Faculty, Adana (Turkey) and Avsar G., M.U. Science and Letters Faculty, Mersin (Turkey) (PR)	224
#209	INVESTIGATION OF RESPONSE SURFACE OPTIMIZATION OF BENZOIN SYNTHESIS IN SUPERCRITICAL CARBON DIOXIDE. Celebi N., Baskent University, Ankara (Turkey) Yildiz N., Calimli A. Ankara University and Demir A.-S., Middle East Technical University, Ankara (Turkey) (PR)	225
#210	SYNTHESIS OF S-PENTANOL VIA LIPASE CATALYZED KINETIC RESOLUTION IN SUPERCRITICAL CARBON DIOXIDE. Özcan A., Yildiz N. and Calimli A., Ankara University (Turkey) (PR)	226
#242	MICROEMULSIONS GENERATING USING PGSS (Particle from Gas Saturated Solution) TECHNIQUE. Hanu L.-G., Kareth S., Kilzer A., Weidner E., Ruhr-University of Bochum (Germany) and Alessi P., University of Trieste (Italy) (PR)	227

Chairpersons

Jaume Veciana, Lourdes Vega and Nora Ventosa

May 4 – 7, 2008
Barcelona (Spain)

Organization

Chairpersons

Jaume Veciana

ICMAB-CSIC, Barcelona, Spain

e-mail: vecianaj@icmab.es

Lourdes F. Vega

MATGAS, Barcelona, Spain

e-mail: vegal@matgas.com

Nora Ventosa

ICMAB-CSIC, Barcelona, Spain

e-mail: ventosa@icmab.es

Local Organizing Committee

Jordi Andreu (ICMAB-CSIC; MATGAS)

Santi Sala (CIBER-BBN/ICMAB-CSIC)

Jaume Veciana (ICMAB-CSIC)

Lourdes F. Vega (MATGAS)

Nora Ventosa (ICMAB-CSIC)

José Vidal (ICMAB-CSIC)

General Conference Secretary

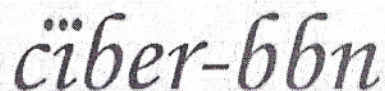
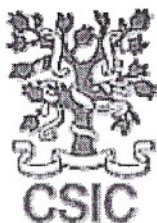
Françoise Brionne

ISASF-ENSIC, Nancy, France

e-mail: brionne@ensic.inpl-nancy.fr

Web master

José Antonio Gómez (ICMAB-CSIC)



Scientific Committees

Local Scientific Advisory Committee

José M^a Bayona (CID-CSIC, Barcelona)

Albertina Cabanas (UCM, Madrid)

Lourdes Calvo (UCM, Madrid)

M^a José Cocero (UVA, Valladolid)

Conchi Domingo (ICMAB-CSIC, Barcelona)

Elena Ibañez (IFI-CSIC, Madrid)

Guillermo Reglero (UAM, Madrid)

International Advisory Board

Gerd Brunner (T.U.-Harburg, Germany)

François Cansell (ICMCB-CNRS, France)

Ruben G. Carbonell (NSFSTC, USA)

Jacques Fages (Ecole des Mines d'Albi, France)

Ireneo Kikic (U. Trieste, Italy)

Manuel Nunes da Ponte (ITQB-UNL, Portugal)

Michel Perrut (SEPAREX, France)

Cor Peters (Delft U.T., Holland)

Martin Poliakoff (U. Nottingham, U.K.)

Anna Roig (ICMAB-CSIC, Spain)

SYNTHESIS OF SC CO₂ SOLUBLE FLUORINATED PHOSPHINOETHANE AND PHOSPHINOHYDRAZINE DERIVATIVES AND THEIR RHODIUM(I) COMPLEXES

G. Avşar¹, H. Altınel², M.K. Yılmaz², N. Kıcır² and B. Güzel^{2*}

¹Mersin University Sci. and Lett. Fac. Chemistry Department, 33342, Mersin, TURKEY

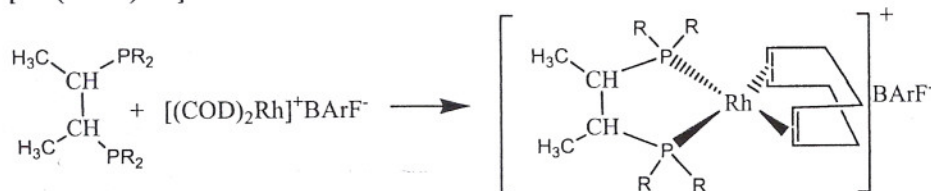
²Çukurova University Sci. and Lett. Fac. Chemistry Department, 01330, Adana, TURKEY

bilgehan@cu.edu.tr

Abstract

Derivatives of phosphine ligands and their rhodium complexes have found important applications as catalysts with high yields. In recent years there has been increasing interest in using supercritical carbon dioxide (sc CO₂) as the reaction medium for organic synthesis, because of the toxic effect of organic solvents [1,2]. It is well known that fluorine groups attached to ligands increase their solubility in sc CO₂ [3]. In this study, fluorinated derivatives of 1,2-bis(diphenylphosphino) ethane (Xn) and 1,2-bis(diphenylphosphino)hydrazine (Yn) containing 3,5-bis(trifluoromethyl)phenyl and meta-(1H,1H,2H,2H-perfluoroalkyl)phenyl functions were used in the synthesis of fluorinated derivatives of [Rh(COD)Xn]BARf and [Rh(COD)Yn]BARf, respectively (n:1 = 3,5-(CF₃)₂C₆H₃, n:2 = m-(1H,1H,2H,2H-perfluoroalkyl)phenyl), and characterized by using spectroscopic methods such as FT-IR, ¹H, ¹⁹F and ³¹P NMR. Solubility studies in sc CO₂ were performed at the conditions of 343°K, 2300 psi pressure.

[Rh(COD)Xn]BARf:

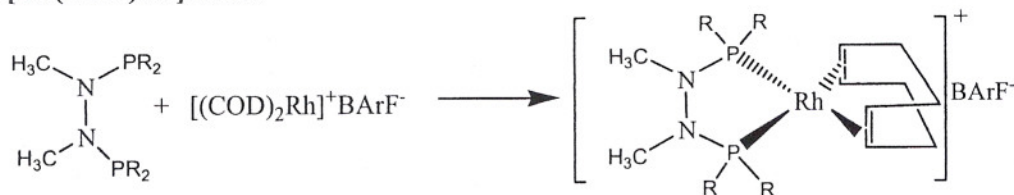


BARf: Tetrakis(bis 3,5-ditri fluoromethyl phenyl)borat

R----- Xn : (n:1) = 3,5-(CF₃)₂C₆H₃
(n:2) = m-(1H,1H,2H,2H-perfluoroalkyl)phenyl

Bis-arylphosphinoethane

[Rh(COD)Yn]BARf:



BARf: Tetrakis(bis 3,5-ditri fluoromethyl phenyl)borat

R----- Yn: (n:1) = 3,5-(CF₃)₂C₆H₃
(n:2) = m-(1H,1H,2H,2H-perfluoroalkyl)phenyl

Bis-arylphosphinohydrazine

[1] S. Haji, and C. Erkey, *Tetrahedron*. **2002**, 58, 3929 - 3941.

[2] G. Francio, W. Leitner, *Journal of Organometallic Chem.* **2001**, 621, 130 - 142.

[3] B. Güzel, M.A. Omary, J.P. Fackler, A. Akgerman, *Inorg. Chem. Acta.* **2001**, 325, 45 - 50.

SYNTHESIS OF SC CO₂ SOLUBLE FLUORINATED PHOSPHINOETHANE AND PHOSPHINOHYDRAZINE DERIVATIVES AND THEIR RHODIUM(I) COMPLEXES

Gokturk Avşar¹, Huseyin Altinel², M.Kemal Yılmaz², Nur Kıcırcı² and Bilgehan Güzel^{2*}

¹Mersin University Sci. and Lett. Fac. Chemistry Department, 33342, Mersin, TURKEY

²Çukurova University Sci. and Lett. Fac. Chemistry Department, 01330, Adana, TURKEY

bilgehan@cu.edu.tr; Fax: +90.322.3386070

The fluorus derivatives of 1,2-bis(diphenylphosphino)ethane and 1,2-bis(diphenylphosphino)hydrazine ligands and their cationic Rh(I) complexes have been synthesized and characterized by using spectroscopic methods such as FT-IR, ¹H, ¹⁹F and ³¹P NMR. Catalytic efficiency of synthesized complexes was performed on hydrogenation of styrene in supercritical carbon dioxide at the conditions of 363.15°K and a total pressure of 1750 psi.

INTRODUCTION

Catalysis by metal complexes in homogenous solution has undergone important developments in nontraditional reaction media such as water, fluorus solvents, ionic liquids and supercritical carbon dioxide (scCO₂). On the other hand, the design of stereoselective reactions remains an important challenge in modern organic chemistry and plays a critical role in both pharmaceutical and agrochemical industries. Synthesis of many specialty chemicals in this area involves use of organic solvents. The solvents used are coming under close scrutiny because of environmental regulatory restrictions due to their toxicity. There is a great push in industry today to replace these solvents with environmentally benign solvents, such as water based solvents. However, most of the catalytic materials used in organic synthesis are not soluble in aqueous media. Furthermore, even if water-soluble catalyst is synthesized, the organic reactants and products may not be soluble in water and may be decompose, because of their sensitivity to water.

A unique advantageous characteristic of scCO₂ are that their density, polarity, viscosity, diffusivity and overall solvent strength can be dramatically varied by relatively small changes in pressure and/or temperature. On the other hand the use of scCO₂ as a reaction media offers the opportunity to optimize and potentially control effect that solvent properties can have on selectivity. In addition, scCO₂ is inert to most reaction, cheap, readily available and non-flammable. It is well known that fluorine groups attached to ligands increase their solubility in scCO₂. To increase the solubility of transition metal catalysts in scCO₂, Leitner and co workers used the perfluoroalkyl attached ligands and they observed 150 times higher solubility than unfluorinated alkylphosphane complexes [1]. Most of the fluorus metal catalysts developed to date feature fluorous phosphine. This has in turn required syntheses of new phosphines and the development of methodologies that practical on larger scales [2]. Several other groups have already made significant contribution to this subject, and we wish to place our work in context of these earlier reports at our set. A related research direction has been the

synthesis of perfluorinated alkyl hydrazine derivatives bidentate phosphines to enhance catalyst solubility in $scCO_2$.

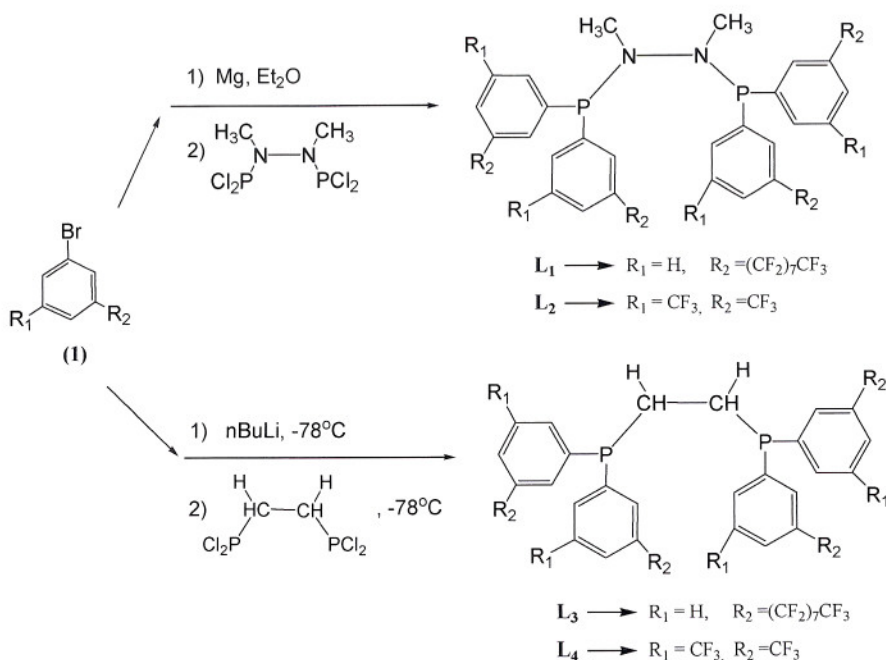
In this project we synthesized fluorinated derivatives of phosphine ligands and their rhodium complexes which are soluble and active catalyst for homogeneous reactions in $scCO_2$. Solubility of synthesized compounds in $scCO_2$ was measured at a pressure range of 1700 - 1900 psi in the temperature range of 313.15 – 363.15°K in windowed reactor. Hydrogenation reactions were performed in $scCO_2$ by charging a cylindrical stainless steel reactor (80 mL and 100 mL capacity) with catalyst and substrate (substrate/catalyst = 250) followed by pressurization with hydrogen gas (10 bar) and CO_2 (total pressure of 1750 psi) in the reaction period range of 3 hours.

RESULTS AND DISCUSSION

Synthesis of Ligands and Complexes:

The L_{1-4} ligands were prepared by reaction of lithiation or an excess of Grignard reagent as described previous studies [3-6]. The general methods of synthesis for ligands and complexes are given in Scheme 1 and Scheme 2, respectively. Analytical and spectroscopic data details can be found in experimental section. Reduction procedure of perfluorinated ligands are given in ref.7.

Rhodium-phosphorus NMR coupling has been reviewed by several authors. The values are normally in the range of 80-150 Hz [8,9].



Scheme 1

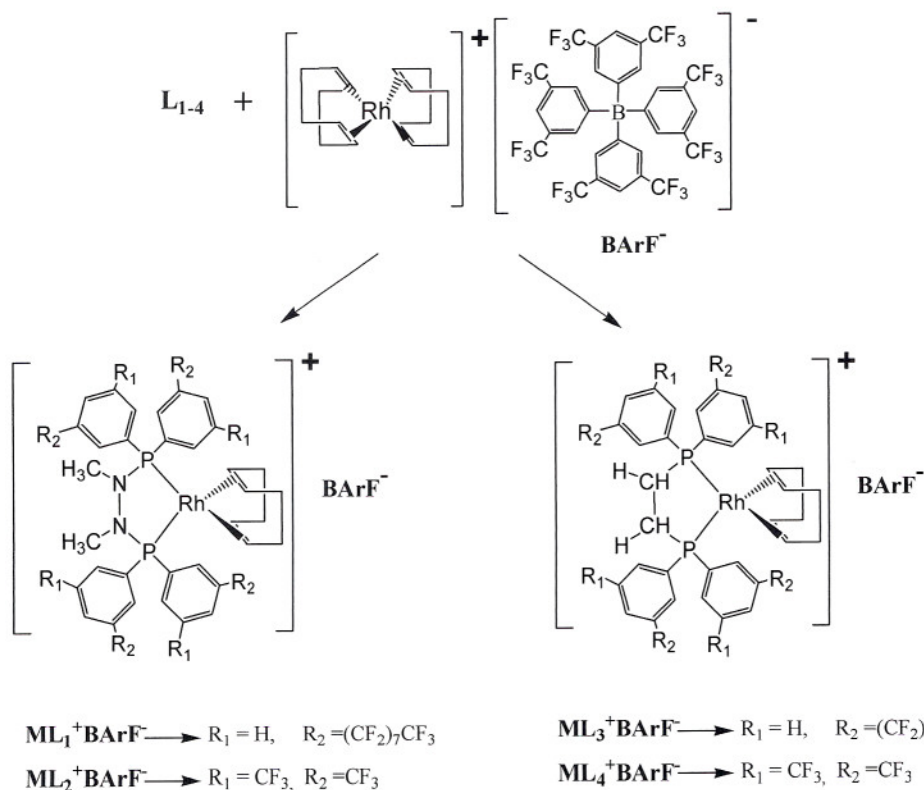
In the synthesis of **1** to obtain perfluoroalkyl ligand derivatives (L_1 and L_3), copper catalysed reaction of $CF_3(CF_2)_7I$ with the Grignard reagent from *meta*-dibromo-benzene provides the *meta*-perfluoroalkyl-substituted arylbromide [1,6,10]. In the second step, by using lithiation reaction, we observed monophosphine hydrazine derivatives from NMR results. Therefore, although lithiation is a good choice for synthesis of phosphinoethane

ligand derivatives (L_3 and L_4), we decided to use Grignard reagent to synthesize the phosphinohydrazine ligands (L_1, L_2) instead of lithiation reaction [11,12].

A major problem associated with the most homogenous catalyst systems is the separation of the designed perfluoroalkyl products from the reaction media. To work out this problem, we used Fluoroflash® chromatography using fluorus solvents (*tetradecafluorohexane*, etc.) instead of conventional techniques.

Solubility Properties:

Increasing the solubility of the desired products is the other aim of our project. The unsubstituted bis(arylphosphine)complex $[\text{Rh}(\text{COD})(\text{dppe})]^+\text{BArF}^-$ is insoluble in pure scCO_2 even at high. As expected the 3,5-bistrifluorophenyl analogue is show low solubility. After using 0.5 mL methanol as co-solvent, the solubility was increased. For fluorus bidantate phosphine complexes, it was noted that at least eight perfluoroalkyl tails are necessary to achieve good solubility in fluorus solvents and scCO_2 [1,13,14]. The perfluorinated derivatives of ligands provide significantly higher solubility in scCO_2 compared to the insoluble parent compounds. Therefore, fluorinated derivatives of the well-known hydrazine and arylphosphine compounds will be used as ligands for homogeneous catalysis in scCO_2 .



Scheme 2

Hydrogenation:

The synthesized catalysts give effective results with hydrogenation of styrene. Hydrogenation reactions were performed in scCO_2 a stirred stainless steel reactor (100 mL) with catalyst and substrate followed by pressurization with hydrogen (P_{total} , 1750 psi). The efficiencies of catalysts on hydrogenation of styrene are given in Table 1.

Table 1. Catalytic efficiency of synthesized complexes on hydrogenation of styrene in scCO₂^a.

Entry	Catalyst	% Conversion ^b	TON ^c	TOF ^d (h ⁻¹)	Product
1	ML ₁ ⁺ BArF ⁻	41	102.5	>34	Ethylbenzene
2	ML ₂ ⁺ BArF ⁻	77	192.5	>64	Ethylbenzene
3	ML ₃ ⁺ BArF ⁻	24	60	20	Ethylbenzene
4	ML ₄ ⁺ BArF ⁻	38	95	>32	Ethylbenzene

^a Reaction conditions: T: 363,15 °K, pH₂: 10 bar, P_{total}: 1750 psi, time: 3 h, Substrate/catalyst = 250.

^b % conversion of styrene after 3 h; ^c mol of product / mol of catalyst; ^d TOF after 3 h.

EXPERIMENTAL

General

All synthetic procedures were carried out under an inert argon or nitrogen atmosphere using standard Schlenk techniques and glove box, and using flame-dried glassware. Diethyl ether (Et₂O), hexane, and tetrahydrofuran (THF) were distilled from sodium benzophenone kettle under nitrogen. Methylene chloride (CH₂Cl₂) was distilled from CaH₂. All other chemicals were of reagent grade quality and were used without further purification.

The ¹H NMR spectra were obtained on a Bruker-Advance DPX 400 spectrometer in CDCl₃. IR spectra were recorded on a Perkin Elmer Mattson 1000 FT-IR spectrometer by using KBr pellets in the range of 4000-400 cm⁻¹. Elemental analyses were recorded on a LECO CHNS-932 analyzer. Melting point was determined on a Gallenkamp apparatus in a sealed capillary and is uncorrected. Thermal behaviour of the complexes were recorded on Perkin Elmer Pyris DSC instrument. CO₂ with a purity of 99.99% was supplied by BOS Company (Adana, Turkey). The solubility and catalytic studies were performed with stainless steel batch reactor (PARR, 50 ml, windowed and autoclave engineering stirred reactor 100 mL) and syringe pump (ISCO, series D) in scCO₂.

Synthesis of 1,2-bis(bis(3-heksadekafluorooktilphenyl)phosphino)-1,2-dimethylhydrazine (L₁): A solution of (**1**) (9.2 g, 16 mmol) in Et₂O (10 ml) was added drop wise under stirring to Mg turnings (0.431 g, 0.018 mol) in Et₂O (15 ml). The rate of addition was adjusted to maintain the solution under gentle reflux. The resulting mixture 3-C₈F₁₇-PhMgCl was stirred for 3 d at room temperature. A solution of 1,2-bis(dichlorophosphino)-1,2-dimethylhydrazine (1.05 g, 4 mmol) in THF (15 ml) was added drop wise a solution of 3-C₈F₁₇-PhMgCl (16 mmol) also in THF (25 ml) at -7 °C with constant stirring. Stirring was continued for further 4 h while allowing the reaction mixture to warm to room temperature. The magnesium chloride was filtered off. 10 mL of 10% NaOH aqueous solution was added and extracted three times with 10 mL ether. Organic layer was separated and dried on MgSO₄ and filtered off again. Evaporation of the solvent in vacuo gave colorless oil L₁, 73% (6.1 g) yield. Anal. Calcd for C₅₈H₂₂F₆₈N₂P₂: C, 33.16; H, 1.06; N, 1.33 %. Found: C, 32.87; H, 1.13; N, 1.29 %; ¹H NMR (CDCl₃), δ ppm: 2.72 (t, ³J_{PH} + ⁴J_{PH} = 1.10 Hz, 6H, NCH₃), 7.23 (m, 16H, Ph); ³¹P NMR, δ (s). 62.5 ppm; ¹⁹F{¹H} NMR (282,4 MHz, CDCl₃, 29°C): δ = -89,9 (m, 3F, F₃C8), -123.1 (m, 2F, F₂C7), -127.3 (m, 2F, F₂C6), -133.2 (m, 2F, F₂C5), -133.5 (m, 2F, F₂C4), -134.6 (m, 2F, F₂C3), -138.1 (m, 2F, F₂C2), -139.0 (m, 2F, F₂C1); ν(P-N): 922 cm⁻¹

Synthesis of 1,2-bis(bis(3,5-bis(trifluoromethyl)phenyl)phosphino)-1,2-dimethylhydrazine (L₂): This was prepared in the same way as for L₁. Anal. Calcd for C₃₄H₁₈F₂₄N₂P₂: C, 41.99; H, 1.87; N, 2.88. Found: C, 41.08; H, 1.84; N, 2.74 %; ¹H NMR (TMS, CDCl₃), δ ppm: 2.81 (t, ³J_{PH} + ⁴J_{PH} = 1.10 Hz, 6H, NCH₃), 6,8-7,7 (m, 12H, Ph), ³¹P NMR: δ (s) 62.7 ppm; ¹⁹F{¹H} NMR (282, 4 MHz, CDCl₃, 29°C): δ = -62.3 ppm (s, 24F, PPh(CF₃)₂); ν(P-N): 929cm⁻¹

Synthesis of 1,2-bis(bis(3-hekzadecafluorooctylphenyl)phosphino)ethane (L₃): To a solution of (1) (9.95 g, 17.3 mmol) in Et₂O (10 ml) with a three necked flask, nBuLi (7.34 g, 17.5 mmol) in 15 mL Et₂O was added dropwise at -78°C under stirring for about 1 h. After stirring further 1 hour, the mixture was allowed to heat up to 0°C. And after cooling -78°C, 1,2-bis(dichlorophosphino)ethane (1.01 g, 4.3 mmol) in 15 mL Et₂O was added dropwise from a second funnel to the cooled mixture in 1 h with a continuous stirring. After further stirring 2 h, the mixture was allowed to heat up to the room temperature and stirred for 12 h more. The resulting mixture was filtered off. 20 mL aqueous solution of 10% NaOH was added to the solution and extracted three times with 10 mL Et₂O. Organic layer was separated and dried on MgSO₄ and filtered off. After filtration, the solution was concentrated in vacuo, and purified by using Fluoroflash chromatography with FC-72/Et₂O (2mL/20mL) elution. After purification and the eluant was distilled under reduced pressure. And the product was solved in 10 mL Et₂O again and 10 ml of n-hexane was added. The resulting solution was cooled at 0°C for 8 h, to afford the white crystalline powder of L₃ in 67% (5.98 g) yield. Anal. Calcd for C₅₈H₂₀F₆₈P₂: C, 33.64; H, 0.97. Found: C, 33.21; H, 1.02 %; ¹H NMR (TMS, CDCl₃), δ ppm: δ_H 7.29 – 6.87 (br m, 16H), 2.13 (s, 4H, CH₂); ³¹P NMR: δ (s) -12.5 ppm; ¹⁹F {¹H} NMR (282,4 MHz, CDCl₃, 29°C): δ_F = -91,2 (m, 3F, F₃C8), -123.6 (m, 2F, F₂C7), -127.4 (m, 2F, F₂C6), -133.6 (m, 2F, F₂C5), -134.3 (m, 2F, F₂C4), -135 (m, 2F, F₂C3), -138 (m, 2F, F₂C2), -138.2 (m, 2F, F₂C1).

Synthesis of 1,2-bis(bis(3,5-bis(trifluoromethyl)phenyl)phosphino)ethane (L₄): This was prepared in the same way as for L₃. Anal. Calcd for C₃₄H₁₆F₂₄P₂: C, 43.33; H, 1.71. Found: C, 42.68; H, 1,59 % ; ¹H NMR (TMS, CDCl₃), δ ppm: 7,75 - 6,81 (br m, 12H, Ph), 2.01 (s, 4H, CH₂); ³¹P NMR: δ (s) -12.7 ppm; ¹⁹F {¹H} NMR (282, 4 MHz, CDCl₃, 29°C): δ_F = -64.2 ppm (s, 24F, PPh(CF₃)₂).

Synthesis of [(1,2-bis(bis(3-hekzadecafluorooctylphenyl)phospino)-1,2-dimethylhydrazine)rhodium(I)(cyclo-octadiene)]⁺BARF⁻ (ML₁⁺BARF⁻): A modification of the procedure reported by Guzel et al. was used for the preparation of ML₁⁺BARF⁻ [8]. A solution of [Rh(COD)₂]⁺BARF⁻ (500 mg, 0.42 mmol) in 15 ml of THF at 25 °C was added drop wise to a solution of L₁ (0.882 mg, 0.42 mmol) in 8 ml of THF. The color of the solution and after that the THF was removed under reduced pressure precipitating an orange-red crystalline product. The product was dissolved in methylene chloride (7 ml), and hexane (40 ml) was added slowly to crystallize the product as an orange crystalline solid, in 62% (0.374 g) yield. Anal. Calcd for C₉₈H₄₆F₉₂N₂P₂Rh: C, 37.20; H, 1.47; N, 0.89. Found: C, 36.85; H, 1.51; N, 0.83 % ; ¹H NMR (TMS, CDCl₃), δ ppm: 2.1 (m, COD-CH₂), 2.2 - 2.7 (m, 12H, COD-CH₂ and CH-CH₂), 4.85 (s, 2H, COD-CH), 5.5 (s, 2H, COD-CH), 7.74 (s, 8H, BPh), - 7.57 (s, 4H, BPh), 2.88 (t, 6H, NCH₃); ³¹P NMR (300MHz, CDCl₃): 69.7 ppm (J_{RH-P} = 147 Hz); ¹⁹F NMR (300MHz, CDCl₃): δ = -81.9 (m, 3F, F₃C8), -113.3 (m, 2F, F₂C7), -115.4 (m, 2F, F₂C6), -121.9 (m, 2F, F₂C5), -122.7 (m, 2F, F₂C4), -123.7 (m, 2F, F₂C3), -124.3 (m, 2F, F₂C2), -127.0 (m, 2F, F₂C1), -62.3 ppm (s, 24F, BPh(CF₃)₂).

Synthesis of [(1,2-bis(bis(3,5-bis(trifluoromethyl)phenyl)phosphino)-1,2-dimethylhydrazine)rhodium(I) (cyclooctadiene)]⁺BARF⁻ (ML₂⁺BARF⁻): This was prepared in the same way as for ML₁⁺BARF⁻. Anal. Calcd for C₇₄H₄₂F₄₈N₂P₂Rh: C, 43.66; H, 2.08; N, 1.38. Found: C, 42.93; H, 2.15; N, 1.33 %; ¹H NMR (TMS, CDCl₃), δ ppm: 2.01 ppm (m, COD-CH₂), 2.21-2.69 ppm (m, 12H, COD-CH₂ and CH-CH₂), 4.85 ppm (s, 2H, COD-CH), 5.52 ppm (s, 2H, COD-CH), 2.9 (t, 6H, NCH₃); ³¹P NMR (300MHz, CDCl₃): 69.8 ppm (J_{RH-P} = 148 Hz); ¹⁹F NMR (300MHz, CDCl₃): -64.3 ppm (s, 24F, BPh (CF₃)₂), -63.4 ppm (s, 24F, PPh(CF₃)₂).

Synthesis of [(1,2-bis(bis(3-hekzadecafluorooctylphenyl)phosphino)ethane)rhodium(I) (cyclo octadiene)]⁺BARF⁻ (ML₃⁺BARF⁻): This was prepared in the same way as for ML₁⁺BARF⁻. Anal. Calcd for C₉₈H₄₄F₉₂P₂Rh: C, 37.56; H, 1.41. Found: C, 35.25; H, 1.46 %; ¹H NMR (TMS, CDCl₃), δ ppm: 2.1 ppm (m, COD-CH₂), 2.2-2.7 (m, 12H, COD-CH₂ and CH-CH₂), 4.87 ppm

(s, 2H, COD-CH), 5.5 ppm (s, 2H, COD-CH), 2.08 (s, 4H, CH₂); ³¹P NMR (300MHz, CDCl₃): 69.7 ppm (*J*_{RH-P} = 147 Hz); ¹⁹F NMR (300MHz, CDCl₃): δ = -93.4 (m, 3F, F₃C8), -113.5 (m, 2F, F₂C7), -115.7 (m, 2F; F₂C6), -122.1 (m, 2F, F₂C5), -123 (m, 2F, F₂C4), -123.5 (m, 2F, F₂C3), -124.1 (m, 2F, F₂C2), -127.1 (m, 2F, F₂C1), -62.3 ppm (s, 24F, BPh(CF₃)₂).

Synthesis of [(1,2-bis(bis(3,5-bis(trifluoromethyl)phenyl)phosphino)ethane) rhodium(I) (cyclo octadiene)]⁺ BArF⁻ (ML₄⁺BArF⁻): This was prepared in the same way as for ML₁⁺BArF⁻. Anal. Calcd for C₇₄H₄₀F₄₈P₂Rh: C, 45.00; H, 2.04. Found: C, 44.35; H, 2.12 %; ¹H NMR (TMS, CDCl₃), δ ppm: 2.1 (m, COD-CH₂), 2.2-2.7 (m, 12H, COD-CH₂ and CH-CH₂), 4.85 (s, 2H, COD-CH), 5.5 (s, 2H, COD-CH), 2.06 (s, 4H, CH₂); ³¹P NMR (300MHz, CDCl₃): 70.1 ppm (*J*_{RH-P} = 148 Hz); ¹⁹F NMR (300MHz, CDCl₃): -63.1 ppm (s, 24F, BPh (CF₃)₂), -62.7 ppm (s, 24F, PPh(CF₃)₂).

Hydrogenation: Hydrogenation experiments were carried out in a window-equipped stainless-steel high-pressure reactor (80 and 100 mL). The reactor was charged with 3.46 x 10⁻⁶ mol complexes and 8.65 x 10⁻⁴ mol styrene (1μL) to adjust the desired ratio of 250 for S/C. Hydrogenation reaction conditions were performed at a temperature of 363,15 °K, and a pressure of 10 bar for H₂ and 1750 psi for the total pressure (pCO₂+pH₂) with stirring for 3 h.

CONCLUSION

The effect of alkyl and hydrazine backbone on catalytic efficiency and solubility properties of fluoro methyl and perfluoroalkyl were investigated. As expected, the perfluorinated complexes show more solubility than fluorinated complexes in scCO₂, but they show low catalytic activity. The complexes that have hydrazine backbone shows more catalytic activity than alkyl derivatives due to the P-N bonds. The efficiency of catalysts are given with their entry numbers in the decreasing order: **2 > 1 > 4 > 3**.

ACKNOWLEDGEMENTS

We thank to Çukurova University Research Foundation for financial support (FEF2004D12).

REFERENCES

- [1] S.Kainz, D.Koch, W. Baumann, and W. Leitner, *Angew Chem.Int.Ed.Engl.*36,**1997**, 1628.
- [2] T. Soos, B.L. Bennet, D. Rutherford, L.P. Barthei-Rosai, and J.A. Gladsz, *Organometallics* 20, **2001**, 3079 - 3086.
- [3] M. Brookhart, B. Grant, A.F. Volpe, *Organometallics* 11, **1992**, 3920.
- [4] H. Nishida, N. Takada, M. Yashimura, *Bull. Chem. Soc. Jpn.* 57, **1984**, 2600.
- [5] S. Haji, and C. Erkey, *Tetrahedron.* 58, **2002**, 3929 - 3941.
- [6] G. Francio, W. Leitner, *Journal of Organometallic Chem.* 621, **2001**, 130 - 142.
- [7] L.C. Baldwin, M.J. Fink, *Journal of Organometallic Chemistry* 646, **2002**, 230 - 238.
- [8] B. Güzel, M.A. Omary, J.P. Fackler, A. Akgerman, *Inorg. Chem. Acta.* 325, **2001**, 45 - 50.
- [9] R. Harris, B.E. Mann, *NMR in the Periodic Table, Academic Press, London*, **1978**, 249.
- [10] S. Kainz, Z. Luo, D.P. Curran, W. Leitner, *Synthesis*, **1998**, 1425.
- [11] P. Bhattacharyya, D. Gudmunsen, E. Hope, R.D.W. Kemmitt, D.R. Paige and A.M. Stuart, *J. Chem., Perkin Trans. 1*, **1997**, 3609 – 3612.
- [12] V.S. Reddy and K.V. Katty, *Inorg. Chem.* 33, **1994**, 2695 – 2696.
- [13] E. Wolf, A.L. Spek, B.W.M. Kuipers, A.P. Philipse, J.D. Meeldijk, P.H.H. Bomans, P.M.Frederik, B.J. Deelman, and G. Koten, *Tetrahedron*, 56, **2002**, 3911 – 3922.
- [14] E.G. Hope, R.D.W. Kemmitt, A.M. Stuart, *J. Chem. Soc., Dalton Trans.* **1998**, 3765.

11th European Meeting on Supercritical Fluids

**New Perspectives in
Supercritical Fluids:
Nanoscience, Materials and
Processing**

May 4-7 2008
Barcelona, Spain



INTERNATIONAL SOCIETY FOR THE
ADVANCEMENT OF SUPERCRITICAL FLUIDS