SYNTHESIS OF SC CO_2 SOLUBLE FLUORINATED PHOSPHINOETHANE AND PHOSPHINOHYDRAZINE DERIVATIVES AND THEIR RHODIUM(I) COMPLEXES

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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, ^{1}H, ^{19}F and ^{31}P NMR..Catalytic efficiency of synthesized complexes was performed on hydrogenation of styrene in supercritical carbon dioxide at the conditions of 363.15^{o}K and a total pressure of 1750 psi.

INTRODUCTION

Catalysis by metal complexes in homogenous solution has undergo important developments in nontraditional reaction media such as water, fluorus solvents, ionic liquids and supercritical carbon dioxide ($scCO_2$). 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 $scCO_2$ 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 $scCO_2$ as a reaction media offers the opportunity to optimize and potantionally control effect that solvent properties can have on selectivity. In addition, $scCO_2$ 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 $scCO_2$. To increase the solubility of transition metal catalysts in $scCO_2$, 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 out set. A related research direction has been the

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

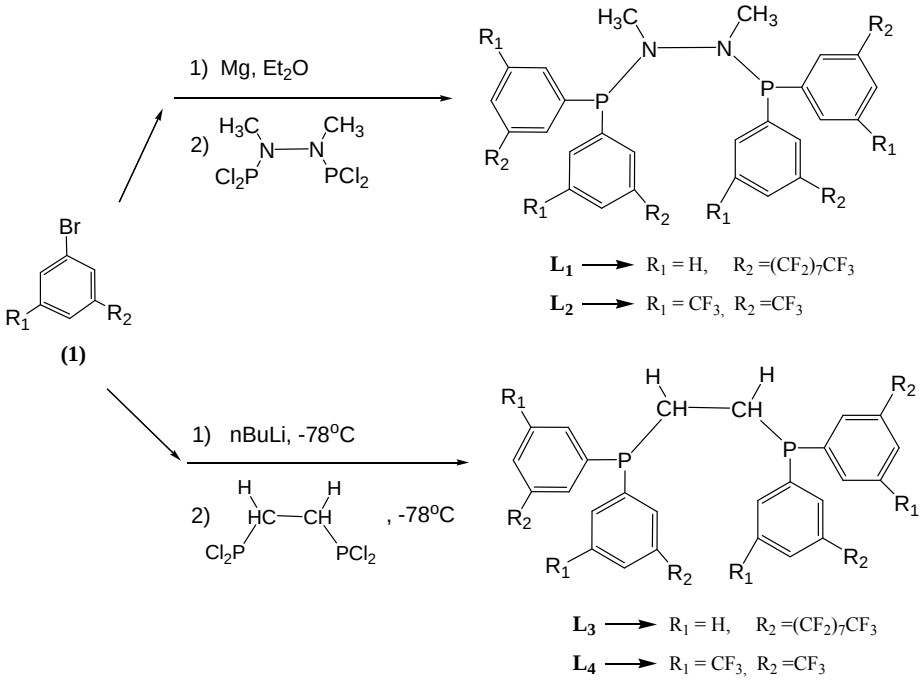
In this project we synthesized fluorinated derivatives of phosphine ligands and their rhodium complexes which are soluble and active catalyst for homogeneous reactions in $scCO_2$. Solubility of synthesized compounds in $scCO_2$ was measured at a pressure range of 1700 - 1900 psi in the temperature range of 313.15 – 363.15^oK 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

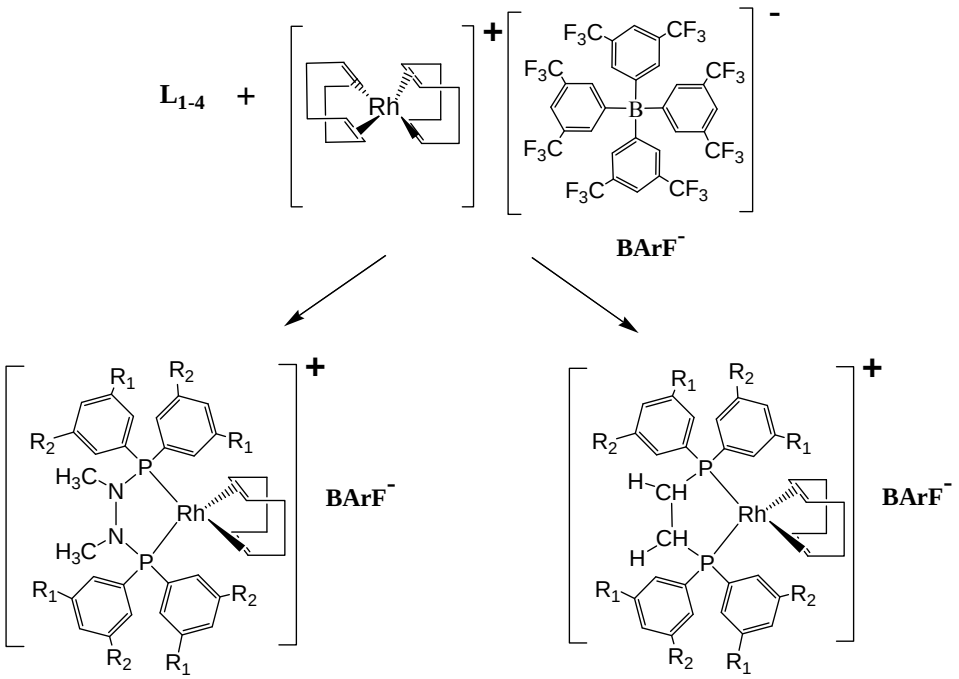
In the synthesis of **1** to obtain perfluoroalkyl ligand derivatives (L_1 and L_3), copper catalysed reaction of $CF_3(CF_2)_7I$ with the Grignard reagent from *meta-dibromo-benzene* provides the *meta-perfluoroalkyl-substituted arylbromide* [1,6,10]. In the second step, by using lithiation reaction, 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 $[Rh(COD)(dppe)]^+BArF^-$ 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 fluorous 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 $scCO_2$.



$ML_1^+BArF^-$ ⟶ $R_1 = H$, $R_2 = (CF_2)_7CF_3$

$ML_2^+BArF^-$ ⟶ $R_1 = CF_3$, $R_2 = CF_3$

$ML_3^+BArF^-$ ⟶ $R_1 = H$, $R_2 = (CF_2)_7CF_3$

$ML_4^+BArF^-$ ⟶ $R_1 = CF_3$, $R_2 = CF_3$

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 $scCO_2$[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 ^oK, pH_2: 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 (Et_2O), hexane, and tetrahydrofuran (THF) were distilled from sodium benzophenone kettle under nitrogen. Methylene chloride (CH_2Cl_2) was distilled from CaH_2. 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 $CDCL_3$. 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. CO_2 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 $scCO_2$.

***Synthesis of 1,2-bis(bis(3-hekzadekafluorooktilphenyl)phosphino)-1,2-dimethylhydrazine* (L_1):** A solution of **(1)** (9.2 g, 16 mmol) in Et_2O (10 ml) was added drop wise under stirring to Mg turnings (0.431 g, 0.018 mol) in Et_2O (15 ml). The rate of addition was adjusted to maintain the solution under gentle reflux. The resulting mixture 3-C_8F_{17}-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-C_8F_{17}-PhMgCl (16 mmol) also in THF (25 ml) at -7 ^oC 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 $MgSO_4$ and filtered off again. Evaporation of the solvent in vacuo gave colorless oil **L_1,** 73% (6.1 g) yield. Anal. Calcd for $C_{58}H_{22}F_{68}N_2P_2$: C, 33.16; H, 1.06; N, 1.33 %. Found: C, 32.87; H, 1.13; N, 1.29 %; ^1H NMR ($CDCl_3$), δ ppm: 2.72 (t, $^3J_{PH}$ + $^4J_{PH}$ = 1.10 Hz, 6H, NCH_3), 7.23 (m, 16H, Ph); ^{31}P NMR, δ (s). 62.5 ppm; $^{19}F\{^1H\}$ NMR (282,4 MHz,$CDCl_3$, 29°C): δ= -89,9 (m, 3F, F_3C8), -123.1 (m, 2F, F_2C7), -127.3 (m, 2F, F_2C6), -133.2 (m, 2F, F_2C5), -133.5 (m, 2F, F_2C4), -134.6 (m, 2F, F_2C3), -138.1 (m, 2F, F_2C2), -139.0 (m, 2F, F_2C1); ν(P-N): 922 cm^{-1}

***Synthesis of 1,2-bis(bis(3,5-bis(trifluoromethyl)phenyl)phosphino)-1,2-dimethylhydrazine* (L_2):** This was prepared in the same way as for L_1. Anal. Calcd for $C_{34}H_{18}F_{24}N_2P_2$: C, 41.99; H, 1.87; N, 2.88. Found: C, 41.08; H, 1.84; N, 2.74 %; ^1H NMR (TMS, $CDCl_3$), δ ppm: 2.81 (t, $^3J_{PH}$ + $^4J_{PH}$ = 1.10 Hz, 6H, NCH_3), 6,8-7,7 (m, 12H, Ph), ^{31}P NMR: δ (s) 62.7 ppm; $^{19}F\{^1H\}$ NMR (282, 4 MHz, $CDCl_3$, 29°C): δ = -62.3 ppm (s, 24F, $PPh(CF_3)_2$); ν(P-N): 929cm^{-1}

***Synthesis of 1,2-bis(bis(3-hekzadecafluorooctylphenyl)phosphino)ethane* (L_3):** To a solution of **(1)** (9.95 g, 17.3 mmol) in Et_2O (10 ml) with a three necked flask, nBuLi (7.34 g, 17.5 mmol) in 15 mL Et_2O 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 Et_2O 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 Et_2O. Organic layer was separated and dried on $MgSO_4$ and filtered off. After filtration, the solution was concentrated in vacuo, and purified by using Fluoroflash chromatography with FC-72/Et_2O (2mL/20mL) elution. After purification and the eluant was distilled under reduced pressure. And the product was solved in 10 mL Et_2O 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 $\mathbf{L_3}$ in 67% (5.98 g) yield. Anal. Calcd for $C_{58}H_{20}F_{68}P_2$: C, 33.64; H, 0.97. Found: C, 33.21; H, 1.02 %; ^{1}H NMR (TMS, $CDCl_3$), δ ppm: δ_H 7.29 – 6.87 (br m, 16H), 2.13 (s, 4H, CH_2); ^{31}P NMR: δ (s) -12.5 ppm; ^{19}F{^{1}H} NMR (282,4 MHz,$CDCl_3$, 29°C): δ_F = -91,2 (m, 3F, F_3C8), -123.6 (m, 2F, F_2C7), -127.4 (m, 2F, F_2C6), -133.6 (m, 2F, F_2C5), -134.3 (m, 2F, F_2C4), -135 (m, 2F, F_2C3), -138 (m, 2F, F_2C2), -138.2 (m, 2F, F_2C1).

***Synthesis of 1,2-bis(bis(3,5-bis(trifluoromethyl)phenyl)phosphino)ethane* (L_4):** This was prepared in the same way as for $\mathbf{L_3}$. Anal. Calcd for $C_{34}H_{16}F_{24}P_2$: C, 43.33; H, 1.71. Found: C, 42.68; H, 1,59 % ; ^{1}H NMR (TMS, $CDCl_3$), δ ppm: 7,75 - 6,81 (br m, 12H, Ph), 2.01 (s, 4H, CH_2); ^{31}P NMR: δ (s) -12.7 ppm; ^{19}F{^{1}H} NMR (282, 4 MHz, CDCl3, 29°C): δ_F = -64.2 ppm (s, 24F, $PPh(CF_3)_2$).

***Synthesis of [(1,2-bis(bis(3-hekzadecafluorooctylphenyl)phospino)-1,2-dimethylhydrazine) rhodium(I)(cyclo-octadiene)]$^+$ BArF$^-$* ($\mathbf{ML_1^+BArF^-}$):** A modification of the procedure reported by Guzel et al. was used for the preparation of $\mathbf{ML_1^+BArF^-}$ [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 L_1 (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 $C_{98}H_{46}F_{92}N_2P_2Rh$: C, 37.20; H, 1.47; N, 0.89. Found: C, 36.85; H, 1.51; N, 0.83 % ; ^{1}H NMR (TMS, $CDCl_3$), δ ppm: 2.1 (m, COD-CH_2), 2.2 - 2.7 (m, 12H, COD-CH_2 and CH-CH_2), 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, NCH_3); ^{31}P NMR (300MHz, $CDCl_3$): 69.7 ppm (J_{RH-P} = 147 Hz); ^{19}F NMR (300MHz, $CDCl_3$): δ = -81.9 (m, 3F, F_3C8), -113.3 (m, 2F, F_2C7), -115.4 (m, 2F, F_2C6), -121.9 (m, 2F, F_2C5), -122.7 (m, 2F, F_2C4), -123.7 (m, 2F, F_2C3), -124.3 (m, 2F, F_2C2), -127.0 (m, 2F, F_2C1), -62.3 ppm (s, 24F, $BPh(CF_3)_2$).

***Synthesis of [(1,2-bis(bis(3,5-bis(trifluoromethyl)phenyl)phosphino)-1,2-dimethylhydrazine) rhodium(I) (cyclooctadiene)]$^+$ BArF$^-$* ($\mathbf{ML_2^+BArF^-}$):** This was prepared in the same way as for $\mathbf{ML_1^+BArF^-}$. Anal. Calcd for $C_{74}H_{42}F_{48}N_2P_2Rh$: C, 43.66; H, 2.08; N, 1.38. Found: C, 42.93; H, 2.15; N, 1.33 %; ^{1}H NMR (TMS, $CDCl_3$), δ ppm: 2.01 ppm (m, COD-CH_2), 2.21-2.69 ppm (m, 12H, COD-CH_2 and CH-CH_2), 4.85 ppm (s, 2H, COD-CH), 5.52 ppm (s, 2H, COD-CH), 2.9 (t, 6H, NCH_3); ^{31}P NMR (300MHz, $CDCl_3$): 69.8 ppm (J_{RH-P} = 148 Hz); ^{19}F NMR (300MHz, $CDCl_3$): -64.3 ppm (s, 24F, BPh $(CF_3)_2$), -63.4 ppm (s, 24F, $PPh(CF_3)_2$).

***Synthesis of [(1,2-bis(bis(3-hekzadecafluorooctylphenyl)phosphino)ethane) rhodium(I) (cyclo octadiene)]$^+$ BArF$^-$* ($\mathbf{ML_3^+BArF^-}$):** This was prepared in the same way as for $\mathbf{ML_1^+BArF^-}$. Anal. Calcd for $C_{98}H_{44}F_{92}P_2Rh$: C, 37.56; H, 1.41. Found: C, 35.25; H, 1.46 %; ^{1}H NMR (TMS, $CDCl_3$), δ ppm: 2.1 ppm (m, COD-CH_2), 2.2-2.7 (m, 12H, COD-CH_2 and CH-CH_2), 4.87 ppm

(s, 2H, COD-CH), 5.5 ppm (s, 2H, COD-CH), 2.08 (s, 4H, CH_2); ^{31}P NMR (300MHz, $CDCl_3$): 69.7 ppm (J_{RH-P} = 147 Hz); ^{19}F NMR (300MHz, $CDCl_3$): δ = -93.4 (m, 3F, F_3C8), -113.5 (m, 2F, F_2C7), -115.7 (m, 2F; F_2C6), -122.1 (m, 2F, F_2C5), -123 (m, 2F, F_2C4), -123.5 (m, 2F, F_2C3), -124.1 (m, 2F, F_2C2), -127.1 (m, 2F, F_2C1), -62.3 ppm (s, 24F, $BPh(CF_3)_2$).

Synthesis of [(1,2-bis(bis(3,5-bis(trifluoromethyl)phenyl)phosphino)ethane) rhodium(I) (cyclo octadiene)]$^+$ BArF$^-$ ($ML_4^+BArF^-$): This was prepared in the same way as for $ML_1^+BArF^-$. Anal. Calcd for $C_{74}H_{40}F_{48}P_2Rh$: C, 45.00; H, 2.04. Found: C, 44.35; H, 2.12 %; ^{1}H NMR (TMS, $CDCl_3$), δ ppm: 2.1 (m, COD-CH_2), 2.2-2.7 (m, 12H, COD-CH_2 and CH-CH_2), 4.85 (s, 2H, COD-CH), 5.5 (s, 2H, COD-CH), 2.06 (s, 4H, CH_2); ^{31}P NMR (300MHz, $CDCl_3$): 70.1 ppm (J_{RH-P} = 148 Hz); ^{19}F NMR (300MHz, $CDCl_3$): -63.1 ppm (s, 24F, BPh $(CF_3)_2$), -62.7 ppm (s, 24F, $PPh(CF_3)_2$).

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 ^{o}K, and a pressure of 10 bar for H_2 and 1750 psi for the total pressure (pCO_2+pH_2) 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 $scCO_2$, 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).

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