NEW FLUORINATED RHODIUM-PHOSPHINE COMPLEXES FOR HYDROGENATION IN SUPERCRITICAL CARBON DIOXIDE

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The different analogues of the well-known Wilkinson catalysts as $[(2\text{-}CF_3\text{-}Ph)_3P]_3$ RhCl , $[(2\text{-}CF_3\text{-}Ph)_3P]_3$RhBArF *"BArF = tetrakis[(3,5-bistrifluoromethyl)phenyl]borate"*, $[(4\text{-}CF_3\text{-}Ph)_3P]_3$RhCl, $[(4\text{-}CF_3\text{-}Ph)_3P]_3$Rh BArF have been synthesized. Structure of the synthesized catalysts were determined by using analytical and spectroscopic methods such as FT-IR, ^{1}H NMR, ^{31}P NMR, ^{19}F NMR and elemental analysis. The synthesized catalysts are soluble in supercritical carbondioxide and give effective results with hydrogenation of styrene. Hydrogenation reactions performed in $scCO_2$ by charging a cylindrical stainless steel reactor (80 ml capacity) with catalyst and substrate (s /c= 2000) followed by pressurization with hydrogen (200 psi).

INTRODUCTION

Chiral rhodium phosphine complexes have found important applications as catalysts in hydrogenation reactions. Chiral rhodium phosphine complexes have been synthesized to be used as ligands for transition-metal-catalysed homogeneous asymmetric synthesis [1,2].

In recent years, there has been increasing interest in using supercritical carbon dioxide ($scCO_2$) as the reaction medium for organic synthesis [3,4]. Use of a supercritical reaction medium, in addition to being an environmentally benign solvent, has other advantages. Supercritical fluids have density tunable physicochemical properties affecting reaction rates and selectivities. The mass transfer characteristics are superior in comparison to liquid reaction media due to high diffusion coefficients and low viscosities. Finally, $scCO_2$ is inert to most reactions, it is non-toxic, non-flammable, readily available, inexpensive and has rather mild critical properties.

Most homogeneous catalysts, however, are not soluble in $scCO_2$ without modification. It is well known that fluorine groups attached to ligands increase their solubility in $scCO_2$ [5]. Therefore, in this study, we used the sodium salt of tetrakis [(3,5-bistrifluoromethyl) phenyl] borate (NaBArF). The other studies reported that the selective as the BArF counterion in order to achieve solubility in supercritical carbon dioxide for use in asymmetric hydrogenation reactions [6, 7].

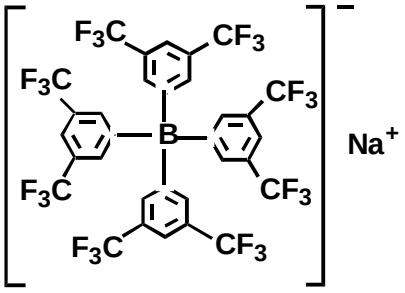


Fig. 1. The sodium salt of BArF

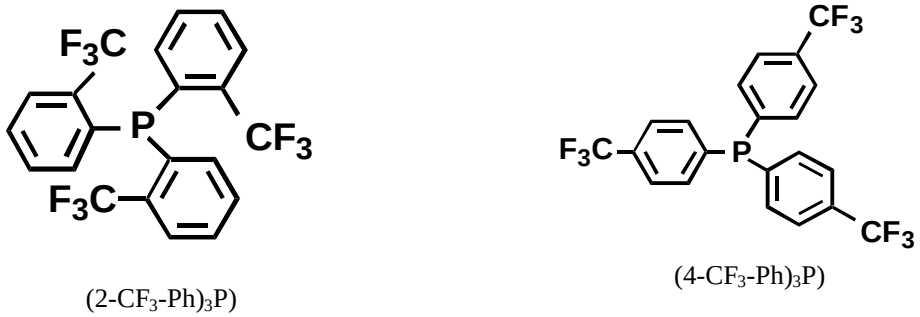
In this study, we report the synthesis and structural characterizarion of $[(2\text{-}CF_3\text{-}Ph)_3P]_3$Rh/Cl, $[(4\text{-}CF_3\text{-}Ph)_3P]_3$ Rh/Cl, $[(2\text{-}CF_3\text{-}Ph)_3P]_3$Rh/BArF, and $[(4\text{-}CF_3\text{-}Ph)_3P]_3$ Rh/BArF. The synthesis follows a different synthetic route than that reported by literatures methods.

MATERIALS AND METHODS

All synthetic procedures were carried out under a nitrogen atmosphere using standard Schlenk and glove box techniques, and using flame-dried glassware. Diethyl ether (Et_2O), hexane, and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl under nitrogen before use. 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 sodium salt of tetrakis [(3,5-bistrifluoromethyl) phenyl] borate (NaBArF) and [bis-cycloocta-1,5-diene-rhodium(1)]$^+$BArF$^-$ [$(COD)_2$Rh-BArF] were prepared according to literatures methods [7, 8, 9]. NMR spectra were recorded on a Bruker-Avance DPX 400 spectrometer. Elemental analyses were recorded on a CHNS-932 (LECO) analyser.

Synthesis of Ligands:

The ligands were prepared by modified literature methods [10]. The CF_3-substituted ligands are tris(o-trifluoromethyl phenyl) phosphine ($2\text{-}CF_3\text{-}Ph)_3P$) and tris(p-trifluoro methyl phenyl) phosphine ($4\text{-}CF_3\text{-}Ph)_3P$) (Fig. 2.).



($2\text{-}CF_3\text{-}Ph)_3P$)

($4\text{-}CF_3\text{-}Ph)_3P$)

Fig. 2. The CF_3-substituted ligands

Synthesis of tris(o-trifluoromethyl) phenyl) phosphine *($2\text{-}CF_3\text{-}Ph)_3P$)* **(1) :** When a solution of n-butyllithium (6.6 ml, 0.01 mol) in diethyl ether was added dropwise to a solution of 2-bromobenzotrifluoride (2.35 g, 0.01 mol) in diethyl eter, the reaction mixture turned orange. After addition, the orange solution was stirred for 30 min and addition of a solution of phosphorus trichloride (0.48 g, 0.0035 mol) in diethyl ether coloured the reaction mixture to brown. After addition was complete, the brown solition was stirred for 20 min and filtered through anhdrous $MgSO_4$, to remove LiCl, and then added to hexane (30 mL) to give dark brown precipitate. The product was filtered off under nitrogen and recrystallized from hexane. The yield of the brown solid product was 75% (1.2 g), m.p.151-153 ^oC. Elemental analysis: Calc. for $C_{21}H_{12}F_9P$: C, 54.09; H, 2.59, found: C, 55.60; H, 2.85; FT-IR: 1443 cm^{-1} (Ar-P); ^{1}H-NMR (in $CDCI_3$, ppm): 6.8-7.6 m (12 H, C_6H_4); ^{31}P-NMR (161 MHz, $CDCI_3$): -16.75 d (q, $^4J_{P\text{-}P}$ = 55.3 Hz); ^{19}F-NMR (376 MHz, in $CDCI_3$): 57.75 ppm (s, 9 F, Ph).

Synthesis of tris(p-trifluoromethyl) phenyl) phosphine *($4\text{-}CF_3\text{-}Ph)_3P$)* **(2) :** When a solution of n-butyllithium (3.2 ml, 0.005 mol) in diethyl ether was added dropwise to a solution of 4-bromobenzo trifluoride (1.14 g, 0.0051 mol) in diethyl eter, the reaction mixture turned red. After addition, the red solution was stirred for 30 min and addition of a solution of phosphorus trichloride (0.48 g, 0.0035 mol) in diethyl ether caused the reaction mixture to turn orange. After addition was complete, the orange solition was stirred for 20 min and filtered through anhdrous $MgSO_4$, to remove LiCl, and then after removing diethyl ether to

give orange oily product. When the orange oily product was washed with hexane and cooled (-20 ^{o}C) an orange solid product precipitated. The yield of the product was 70 % (0.56 g). m.p.88-90 ^{o}C. Elemental analysis: Calc. for $C_{21}H_{12}F_9P$: C, 54.09; H, 2.59, found: C, 54.31; H, 2.80; FT-IR: 1444 cm^{-1} (Ar-P); ^{1}H-NMR (400 MHz, $CDCI_3$): 6.5-7.7 ppm (12 H, C_6H_4); ^{31}P-NMR (161 MHz, $CDCI_3$): 4.33 (s); ^{19}F-NMR (376 MHz $CDCI_3$): -63.77 ppm (s, 9 F, Ph).

Synthesis of Complexes

Preparation of Tris[tris(o-triflouro methyl)phenyl)phosphino] rhodium(I)chloride [(2-CF_3 – Ph)$_3$P]$_3$ Rh/Cl **(3) :** Bis(cyclo-octa-1,5-diene) - μ,μ'- dichloro dirhodium, ([(COD)ClRh]$_2$) (0.03 g, 0.00005 mol) and (2-CF_3-Ph)$_3$P (0.15 g, 0.0003 mol) were dissolved in benzene in separate flasks. The ligand solution was added drop-wise to the solution of the rhodium compound. After addition, the orange solution was stirred for 24 hour and then reaction mixture turned brown. The product was filtered off under nitrogen and recrystallized from dichloromethane/hexan (1:1) The yield of the brown solid product was 80 % (0.12 g). m.p.147-148 ^{o}C. Elemental analysis: Calc. for $C_{63}H_{36}F_{27}P_3RhCl$: C, 49.23; H, 2.36. Found: C, 50.94; H, 3.48; FT-IR: 1445 cm^{-1} (Ar-P); ^{1}H-NMR (400 MHz, $CDCI_3$): 6.7-7.7 ppm (36 H, m, C_6H_4); ^{31}P-NMR (161 MHz $CDCI_3$): 36.5 (d, $^{1}J_{Rh\text{-}P}$ = 138 Hz); ^{19}F-NMR (376 MHz $CDCI_3$) 57.79 ppm (s, 27 F, Ph).

Preparation of Tris[tris(p-triflouro methyl)phenyl)phosphino] rhodium(I) chloride [(4-CF_3-Ph)$_3$P]$_3$ Rh/Cl **(4) :** A similar procedure as for **3** was used for **4.** Starting form [(COD)ClRh]$_2$ (0.0009 g, 0.00002 mol) and (4-CF_3-Ph)$_3$P (0.053 g, 0.00012 mol). The yield of the light brown solid product was 66 % (0.041 g). m.p.128-130 ^{o}C. Elemental analysis: Calc. for $C_{63}H_{36}F_{27}P_3RhCl$: C, 49.23; H, 2.36, found: C, 48.49; H, 3.64; FT-IR: 1440 cm^{-1} (Ar-P); ^{1}H-NMR (400 MHz, $CDCI_3$): 7.2-7.8 ppm (36 H, m, C_6H_4); ^{31}P-NMR (161 MHz, $CDCI_3$): 33.4 (2P, d, $^{1}J_{Rh\text{-}P}$ = 141 Hz) 47.0 (1P, d, $^{1}J_{Rh\text{-}P}$= 187 Hz,); ^{19}F-NMR (376 MHz $CDCI_3$): 63.76 ppm (s, 27 F, Ph).

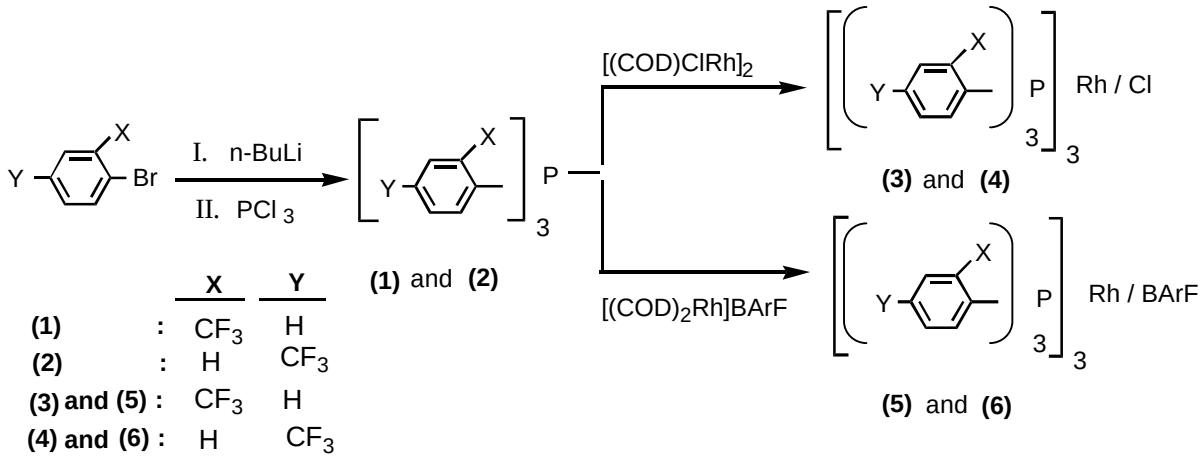
Preparation of Tris[tris(o-triflouro methyl)phenyl)phosphino] rhodium(I) BArF [(2-CF_3-Ph)$_3$P]$_3$ Rh/BArF **(5) :** A similar procedure as for **3** was used for **5.** Starting form [(COD)$_2$Rh-BArF] (0.13 g, 0.00011 mol) and (2-CF_3-Ph)$_3$P (0.15 g, 0.00032 mol). The yield of the dark brown solid product was 73 % (0.19 g). m.p.79-81^{o}C. Elemental analysis: Calc. for $C_{95}H_{48}F_{51}P_3BRh$: C, 48.24; H, 2.05. Found: C, 47.26; H, 2.32; FT-IR: 1450 cm^{-1} (Ar-P); ^{1}H-NMR (400 MHz, $CDCI_3$): 7.1-7.8 ppm (48 H, C_6H_4); ^{31}P-NMR (161 MHz $CDCI_3$): 40.99 (d, $^{1}J_{Rh\text{-}P}$ = 142 Hz); ^{19}F-NMR (376 MHz $CDCI_3$): 57.41 ppm (orto, s, 27 F, Ph), 62.92 ppm (1,3,5 trisubstutie benzene, s, 24 F, Ph).

Preparation of Tris[tris(p-triflouro methyl)phenyl)phosphino] rhodium(I) BArF [(4-CF_3-Ph)$_3$P]$_3$ Rh/BArF **(6) :** A similar procedure as for **3** was used for **6.** Starting form [(COD)$_2$Rh-BArF] (0.048 g, 0.00004 mol) and (4-CF_3-Ph)$_3$P (0.057 g, 0.00013 mol). The yield of the dark brown solid product was 62 % (0.059 g). m.p.122-124 ^{o}C. Elemental analysis: Calc. for $C_{95}H_{48}F_{51}P_3BRh$: C, 48.24; H, 2.05. Found: C, 47.38; H, 3.26; FT-IR: 1444 cm^{-1} (Ar-P); ^{1}H-NMR (400 MHz, $CDCI_3$): 7.1-7.8 ppm (48 H, C_6H_4); ^{31}P-NMR (161 MHz $CDCI_3$): 31 (2P, d, $^{1}J_{Rh\text{-}P}$ = 144 Hz) 49.0 (1P, d, $^{1}J_{Rh\text{-}P}$ = 188 Hz); ^{19}F-NMR (376 MHz $CDCI_3$): 63.92 ppm (para, s, 27 F, Ph), 62.85 ppm (1,3,5 trisubstutie benzene, s, 24 F, Ph).

Hydrogenation : The synthesized catalysts are soluble in supercritical carbondioxide and give effective results with hydrogenation of styrene. Hydrogenation reactions performed in $scCO_2$ by charging a cylindrical stainless steel reactor (80 ml capacity) with catalyst and substrate (substrate / catalyst = 2000) followed by pressurization with hydrogen (200 psi).

CONCLUSION

The general method of synthesis is given in Scheme 1. Analytical and spectroscopik data can be found in detail in experimental section.



Scheme 1. Synthesis reaction of complexes

The results of the elemental analysis of synthesized compounds are in agreement with the theoritical values. The ^{19}F NMR spectras (in $CDCI_3$) of compounds 1,2,3, and 4 show a singlet, 5 and 6 shows two singlet in a agreement with the literature. Rhodium-phosphorus NMR coupling has been reviewed by several authors. The values are normally in range of 81-150 Hz [13]. The peaks at 36.5 ppm (d, $^1J_{Rh\text{-}P}$ = 138 Hz) for **3**; at 33.4 ppm (2P, d, $^1J_{Rh\text{-}P}$ = 141 Hz), 47.0 (1P, d, $^1J_{Rh\text{-}P}$ = 187 Hz,) for **4**; at 40.99 ppm (d, $^1J_{Rh\text{-}P}$ = 142 Hz) for **5**; at 31ppm (2P, d, $^1J_{Rh\text{-}P}$ = 144 Hz,) 49.0 (1P, d, $^1J_{Rh\text{-}P}$ = 188 Hz) for **6**; in the ^{31}P NMR spectras (in $CDCI_3$) are therefore, consistent with the literature. All the peaks of 1,2,3,4 obtained by ^1H NMR spectras were consistent with the literature.

Choosing the CF_3 groups as the CO_2–philic solubilizers results only in a small structural modification of the donor group. The synthesised fluorus catalyst show high activity in the hydrogenation of styrene (99%). The results of the hydrogenation studies illustrate the remarkable potantial of orto and para CF_3 substitue Wilkinson catalysts as a homogeneous catalysts for asymmetric hydrogenation studies.

Acknowledgements

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