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Hydrodefluorination of Fluorobenzene and 1,2-Difluorobenzene under Mild Conditions over Rhodium Pyridylphosphine and Bipyridyl Complexes Tethered on a Silica-Supported Palladium Catalyst

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*Summary: Fluorobenzene and 1,2-difluorobenzene are defluorinated under very mild conditions by H_2 (4 atm) at 70 °C in the presence of NaOAc. The heterogeneous catalysts for these reactions contain the rhodium pyridylphosphine (**1**) and bipyridyl (**2**) complexes [Rh(COD)(**1**)]BF_4 and [Rh(COD)(**2**)]BF_4 tethered to heterogeneous Pd−SiO_2.*

The C−F bond, which is the strongest bond that carbon can form,[1] is extremely reluctant to coordinate to metal centers and is resistant to chemical attack.[2] Although this lack of fluorocarbon reactivity has frequently been exploited in technological and medical applications, this chemical inertness also translates into environmental persistence since these compounds are quite difficult to degrade.[3] In the past decade, there have been several reports of organometallic complexes that are capable of promoting stoichiometric C−F bond activation under mild conditions,[4−8] but only recently have homogeneous metal complex-catalyzed hydrogenolyses of C−F bonds been reported.[9−11] Heterogeneously catalyzed hydrogenolyses of fluoroarenes are known; however, these reactions require very high temperatures.[3,12]

Recently, we discovered that rhodium complex catalysts tethered on a silica-supported palladium heterogeneous catalyst (Pd−SiO_2) are very active for the

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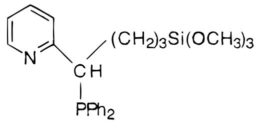
Table 1. Hydrodefluorination of Fluorobenzene[a]

catalyst	substrate/Rh[b] (mole ratio)	base	reaction time (h)	conversion (%)[c]	products (%)[d]	
					$C_6H_{11}F$	C_6H_{12}
Pd−SiO_2		NaOAc	23	17.8	1.1	16.7
Rh(N−P)[e]	250	NaOAc	21	36.1	7.1	29.0
Rh(N−N)[e]	250	NaOAc	20	28.5	2.4	26.1
Rh(N−P)/SiO_2[f]	540	NaOAc	5	0	0	0
Rh(N−N)/SiO_2[f]	1000	NaOAc	18	11.2	0.2	11.0
Rh(N−P)/Pd−SiO_2	850	NaOAc	15	46.7	0	46.7
Rh(N−N)/Pd−SiO_2	700	NaOAc	20	100	10.8	89.2
Rh(N−N)/Pd−SiO_2	700	$N(C_2H_5)_3$	6	13	2.0	11.0
Rh(N−N)/Pd−SiO_2	700	NaOH	2	0	0	0
Rh(N−P)/Pd−SiO_2[g]	760	none	12	100	88.3	11.7
Rh(N−N)/Pd−SiO_2[g]	700	none	12	100	85.2	14.8

[a] Reaction conditions: 50 mg of catalyst; 2.5 mmol of fluorobenzene; 2.5 mmol of base; 3 mL of heptane and 2 mL of ethanol as solvent; 4 atm of H_2, 70 °C. [b] Mole ratio of substrate to rhodium in 50 mg of catalyst. [c] Conversion determined by GC corresponds to the reaction time. [d] Yields of products determined by GC−MS. [e] 10 μmol of complex. [f] Rh(N−P)/SiO_2 (Rh content, 0.68 wt %) and Rh(N−N)/SiO_2 (Rh content, 0.95 wt %) were prepared in the same way as Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2, except SiO_2 was used instead of Pd−SiO_2. [g] 5.0 mL of heptane as solvent.

hydrogenation of arenes.[13] The high hydrogenation activity of these combined catalysts consisting of a tethered complex on a supported metal (TCSM) was attributed to the synergistic functioning of both catalyst components (tethered rhodium complex and supported palladium). In the present study, we apply the concept of TCSM catalysis to the hydrodefluorination of fluorobenzenes. We used TCSM catalysts consisting of tethered rhodium pyridylphosphine or bipyridyl complexes on SiO_2-supported palladium (Pd−SiO_2) for the hydrodefluorination of fluorobenzene and 1,2-difluorobenzene under the mild conditions of 70 °C and 4 atm of H_2. To our knowledge, these are the first examples of tethered metal complex catalysts that exhibit high activity for the hydrogenolysis of the C−F bond under mild conditions.

The two TCSM catalysts were prepared by tethering the rhodium pyridylphosphine (**1**)[14] and bipyridyl (**2**)[15] complexes $[Rh(COD)(\mathbf{1})]BF_4$ and $[Rh(COD)(\mathbf{2})]BF_4$ to silica-supported palladium (Pd−SiO_2). The rhodium complexes $[Rh(COD)(\mathbf{1})]BF_4$ (Rh(N−P))[16] and $[Rh(COD)(\mathbf{2})]BF_4$ (Rh(N−N))[17] were prepared by reaction of $[Rh(COD)(THF)_2]BF_4$ (which was prepared by the reaction of $[Rh(COD)Cl]_2$ with 2 equiv of $AgBF_4$ in THF at room temperature) with 1 equiv of **1** or **2** in THF at −40 °C. After the reaction mixture was stirred for 1 h at −40 °C and then 3 h at room temperature, the solvent was removed under vacuum and the residue was washed with ethyl ether (2 × 10 mL) to give the complexes $[Rh(COD)(\mathbf{1})]BF_4$ and $[Rh(COD)(\mathbf{2})]BF_4$. The TCSM catalysts were prepared by stirring the Rh complexes, Rh(N−P) and Rh(N−N), with Pd−SiO_2[18] in CH_2Cl_2 at room temperature overnight. After filtration, the solids were washed with CH_2Cl_2 and then dried in a vacuum at room temperature to give the tethered catalysts, Rh(N−N)/Pd−SiO_2 (Rh content, 0.71 wt %) and Rh(N−P)/Pd−SiO_2 (Rh content, 0.6 wt %). The solid-state ^{31}P NMR spectrum of the Rh(N−P)/Pd−SiO_2 catalyst showed a peak at 48.4 ppm, which is similar to that (47.6 ppm, in $CDCl_3$ solvent) of the untethered Rh(N−P) complex. When Rh(N−N)/Pd−SiO_2 was stirred in CH_2Cl_2 under a CO atmosphere at room temperature overnight, the diffuse reflectance IR spectrum (DRIFTS) of the resulting sample exhibited four ν(CO) bands at 2104(s), 2090(w, sh), 2045(s), and 2022(w, sh) cm^{-1}, which are similar to those (2099(s), 2088(w, sh), 2040(s), and 2016(w, sh) cm^{-1} in CH_2Cl_2) of the sample obtained from the reaction of Rh(N−N) and CO in CH_2Cl_2 under the same conditions. These characterizations suggest that the structures of the tethered Rh(N−P) and Rh(N−N) complexes on the surface of Pd−SiO_2 are similar to those of the untethered complexes.



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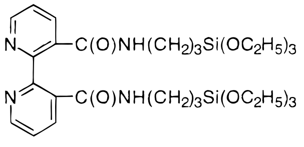

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(14) **1** was prepared as follows: To a diethyl ether solution (20 mL) of 2-[(diphenylphosphino)methyl]pyridine (1.10 g, 4.0 mmol) (Alvarez, M.; Lugan, N.; Mathieu, R. *J. Chem. Soc., Dalton Trans.* **1994**, 2755) was added 2.5 mL of a 1.6 M hexane solution of *n*-butyllithium (4.0 mmol) at −40 °C. The solution was stirred for 1 h at −40 °C. Then, 1.15 g (4.0 mmol) of (3-iodopropyl)trimethoxysilane (Ahmed, I.; Parish, R. V. *J. Organomet. Chem.* **1993**, *452*, 23) was slowly added, and the solution was stirred for 3 h while the temperature was allowed to increase to room temperature. The solvents were removed under vacuum, and the crude product was purified by column (3 × 5 cm) chromatography on silica gel using a CH_2Cl_2/Et_2O (4:1) mixture as eluant. The ligand **1** was obtained in 53% yield as a yellow oil. ^1H NMR ($CDCl_3$): δ 8.47 (m, 1H, C_5H_4N), 7.01−7.65 (m, 13H, $2C_6H_5$ and C_5H_4N), 3.66 (m, 1H, PCH), 3.43 (s, 9H, 3 OCH_3), 2.12 (m, AB, $1H_a$, $CH\mathit{CH_2}$), 1.71 (m, AB, $1H_b$, $CH\mathit{CH_2}$), 1.27 (m, 2H, $CHCH_2\mathit{CH_2}$), 0.57 (m, 2H, $CHCH_2CH_2\mathit{CH_2}$). ^{31}P {H}NMR ($CDCl_3$): δ −1.69 (s). Anal. Calcd for $C_{24}H_{30}NO_3PSi$: C, 65.57; H, 6.89; N, 3.19. Found: C, 65.32; H, 6.71; N, 3.04.

(15) **2** was prepared as follows: To a suspension of 1.39 g (5.1 mmol) of 2,2′-bipyridyl-3,3′-dicarboxylic acid (Dholakia, S.; Gillard, R. D.; Wimmer, F. L. *Polyhedron* **1985**, *4*, 791) in 40 mL of dichloromethane was added 2.10 g (10.2 mmol) of 1,3-dicyclohexylcarbodiimide (DCC), and then 2.4 mL (10.2 mmol) of $H_2NCH_2CH_2CH_2Si(OEt)_3$ was slowly added. The mixture was stirred at room temperature overnight. Then, the solution was washed with water (3 × 50 mL). After the solvents were removed under vacuum, the residue was purified by column (3 × 5 cm) chromatography on silica gel using ethanol as eluant. The bipyridyl ligand **2** was isolated as an orange-red oil (2.7 g, yield 82%). ^1H NMR ($CDCl_3$): δ 8.54 (m, 2H, $2C_5H_3N$), 7.88 (m, 2H, $2C_5H_3N$), 7.58 (m, 2H, $2C_5H_3N$), 7.18 (s, broad, 2H, 2NH), 3.74 (q, 12H, $6O\mathit{CH_2}CH_3$ $J_{HH} = 6.9$ Hz), 3.10 (m, 4H, $2NH\mathit{CH_2}$), 1.31 (m, 4H, $2NHCH_2\mathit{CH_2}$), 1.16 (t, 18H, $6OCH_2\mathit{CH_3}$ $J_{HH} = 6.9$ Hz), 0.40 (m, 4H, $2NHCH_2CH_2\mathit{CH_2}$). ^{13}C NMR ($CDCl_3$): δ 168 (s, C=O), 156.5 (s, C_5H_3N), 149.5 (s, C_5H_3N), 135.7 (s, C_5H_3N), 132.4 (s, C_5H_3N), 123.1 (s, C_5H_3N), 58.4 (s, $O\mathit{CH_2}CH_3$), 42.4 (s, $NHCH_2$), 22.7 (s, $NHCH_2\mathit{CH_2}$), 18.3 (s, $OCH_2\mathit{CH_3}$), 7.7 (s, $NHCH_2CH_2\mathit{CH_2}$).

(16) Selected data for $[Rh(COD)(\mathbf{1})]BF_4$: ^1H NMR ($CDCl_3$): δ 8.26 (m, 1H, C_5H_4N), 7.81−7.42 (m, 13H, $2C_6H_5$ and C_5H_4N), 5.52 (s, 2H, COD), 4.36 (m, 1H, PCH), 4.16 (m, 2H, COD), 3.50 (s, 9H, $3OCH_3$), 2.18−2.56 (m, 10H, COD and $CH\mathit{CH_2}$), 1.64 (m, 2H, $CHCH_2\mathit{CH_2}$), 0.68 (m, 2H, $CHCH_2CH_2\mathit{CH_2}$). $^{31}P\{H\}$ NMR ($CDCl_3$): δ 47.6 (d, $J_{P-Rh} = 149.7$ Hz). Anal. Calcd for $C_{32}H_{42}BF_4NO_3PRhSi$: C, 52.11; H, 5.75; N, 1.90. Found: C, 51.46; H, 5.65; N, 1.85.

Activities of the TCSM catalysts Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2 in the hydrodefluorination of fluorobenzene are compared with other catalysts in Table 1. The reactions were conducted at 70 °C under 4 atm of H_2 in heptane/ethanol solvent while being stirred; fluorocyclohexane and cyclohexane were the only detected products. From the data in Table 1, it is evident that the TCSM catalysts, Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2, in the presence of sodium acetate are much more effective for the hydrodefluorination of fluorobenzene than the simple heterogeneous SiO_2-supported Pd catalyst (Pd−SiO_2), the Rh(N−P) and Rh(N−N) complexes tethered to just SiO_2 (Rh(N−P)/SiO_2 and Rh(N−N)/SiO_2), or the untethered Rh(N−P) and Rh(N−N) complexes. With the Rh(N−P)/Pd−SiO_2 catalyst, in the presence of NaOAc, fluorobenzene was defluorinated within 15 h to cyclohexane in 46.7% yield as the only product. With the Rh(N−N)/Pd−SiO_2 catalyst, fluorobenzene reacted completely to give the hydrodefluorination product cyclohexane in 89.2% yield along with 10.8% fluorocyclohexane. In this latter reaction, 620 fluorines are removed per rhodium center; that is, the turnover of the Rh(N−N)/Pd−SiO_2 catalyst is 620 mol of fluorine removed/1 mol rhodium. This result compares with those of Milstein et al.,[9b] who used $L_3RhC_6F_5$ or L_4RhH (L = Me_3P) to catalyze the hydrogenolysis of C_6F_6 and C_6F_5H to produce C_6F_5H and $C_6F_4H_2$ at 95−100 °C under 85 psi of H_2; after 36 h, their highest turnover number was 114 mol of fluorine removed/1 mol Rh. Young and Grushin[10a] used $(Cy_3P)_2Rh(H)Cl_2$ to generate homogeneous and heterogeneous catalysts that defluorinated monofluoroarenes at 95 °C under 40−130 psi of H_2 in the presence of NaOH, but the turnover numbers were only 38−150. The transition metallocenes Cp_2TiF_2 and Cp_2ZrF_2 were used to catalyze the reductive defluorination of perfluorodecalin to perfluoronaphthalene in the presence of excess Al/$HgCl_2$ at room temperature and gave a turnover number of 120 (moles of fluorine removed/mole metal) during a period of 24 h.[11a] Prior to our present report, no tethered transition metal complex-catalyzed hydrodefluorination reactions have been described.

The importance of the NaOAc base is shown by the fact that the hydrodefluorination of fluorobenzene using the Rh(N−N)/Pd−SiO_2 catalyst with NaOAc is much more efficient than the catalyst with $N(C_2H_5)_3$ (Table 1). In fact, the $N(C_2H_5)_3$ reduces the rate of reaction below that of Rh(N−N)/Pd−SiO_2 in the absence of base, which gives primarily fluorocyclohexane (85.2%). The Rh(N−N)/Pd−SiO_2 catalyst is completely inactive when NaOH was used as the base. The effect of NaOAc on the selectivity of the reaction is illustrated by the fact that the Rh(N−P)/Pd−SiO_2- and Rh(N−N)/Pd−SiO_2-catalyzed reactions with no base give primarily the arene hydrogenation product fluorocyclohexane, but in the presence of NaOAc these catalysts yield predominantly the hydrodefluorination product cyclohexane. Although the acetate ion is a possible ligand for the Rh complex, NaOAc could promote the hydrodefluorination reaction in several different ways.

To determine whether fluorocyclohexane was an intermediate in the reactions that give cyclohexane as the product, the hydrodefluorination of fluorocyclohexane using the Rh(N−N)/Pd−SiO_2 catalyst and NaOAc was attempted under the conditions in Table 1 for 20 h. However, no defluorination product cyclohexane was detected. This result suggests that in the hydrodefluorination of fluorobenzene over the Rh(N−N)/Pd−SiO_2 catalyst the fluorine is removed before the benzene ring is hydrogenated.

The two TCSM catalysts, Rh(N−P)/Pd−SiO_2, and Rh(N−N)/Pd−SiO_2, are also active for the hydrodefluorination of 1,2-difluorobenzene under the reaction conditions in Table 1. The reaction of 2.5 mmol of 1,2-difluorobenzene with 50 mg of Rh(N−N)/Pd−SiO_2 in the presence of NaOAc (5.0 mmol) performed for 20 h gave a 63.7% conversion of 1,2-difluorobenzene to cyclohexane (43.2%), fluorocyclohexane (5.6%), and fluorobenzene (14.9%). Under the same conditions, the reaction with the Rh(N−P)/Pd−SiO_2 catalyst for 20 h led to a 63.6% conversion of 1,2-difluorobenzene to cyclohexane (48.3%), fluorocyclohexane (3.3%), and fluorobenzene (12.0%). Thus, 750 and 850 fluorines are removed per rhodium center using the Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2 catalysts, respectively.

In conclusion, we report here that catalysts prepared by tethering transition metal complexes on Pd−SiO_2 promote the hydrogenolysis of the strong C−F bond under mild conditions. Whether the rhodium remains coordinated to the N−P and N−N ligands during the catalysis is not known. The TCSM catalysts, Rh(N−P)/Pd−SiO_2 and Rh(N−N)/Pd−SiO_2, not only give high turnover numbers (moles of fluorine removed/mole Rh) for the hydrodefluorination of fluorobenzene and 1,2-difluorobenzene but are also easily separated from the reaction mixtures.

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(17) Selected data for [Rh(COD)(**2**)]BF_4: ^1H NMR ($CDCl_3$): δ 8.22 (m, 2H, $2C_5H_3N$), 7.84 (m, 2H, $2C_5H_3N$), 7.58 (m, 2H, $2C_5H_3N$), 7.18 (s, broad, 2H, 2NH), 4.38−4.66 (m, 4H, COD), 3.79 (q, 12H, $6OCH_2$ J_{H-H} = 6.9 Hz), 3.22 (m, 4H, $NHCH_2$), 4.38−4.66 (m, 8H, COD), 1.80−2.31 (m, 8H, COD), 1.65 (m, 4H, $2NHCH_2CH_2$), 1.18 (t, 18H, $6OCH_2CH_3$ J_{H-H} = 6.9 Hz), 0.45 (s, broad, 4H, $2NHCH_2CH_2CH_2$). Anal. Calcd for $C_{38}H_{62}BF_4N_4O_8RhSi_2$: C, 48.10; H, 6.59; N, 5.90. Found: C, 48.87; H, 6.41; N, 6.34.

(18) Pd−SiO_2 was prepared by the incipient wetness method (Kazi, A. M.; Chen, B.; Goodwin, J. G., Jr.; Marcelin, G.; Rodriguez, N.; Baker, R. T. K. *J. Catal.* **1995**, *157*, 1) by impregnation of SiO_2 (7.0 g) using an aqueous solution of H_2PdCl_4 (which was prepared by dissolving 1.2 g of $PdCl_2$ in 50 mL of aqueous HCl (0.2 M)), calcining at 500 °C for 4 h, and reducing with H_2 at 380 °C.