Rhodium-Catalyzed Si-F Exchange Reaction between Fluorobenzenes and a Disilane. Catalytic Reaction Involving Cleavage of C-F Bonds

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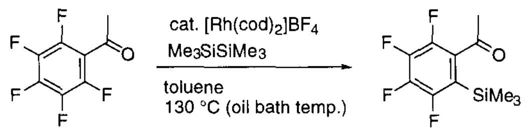
The reaction of functionalized fluorobenzenes, such as fluoroacetophenones and (fluorophenyl)oxazolines, with $Me_3SiSiMe_3$ in the presence of a catalytic amount of a rhodium complex results in a site-selective Si-F exchange to give *ortho*-(trimethylsilyl)fluorobenzenes. The reaction involves cleavage of C-F bonds.

The cleavage of unreactive chemical bonds such as C-H, C-C, C-O, and C-X bonds (X = Cl, F) by homogeneous transition metal complexes has been the subject of numerous attempts. In recent years, catalytic transformations involving cleavage of C-H,[1] C-C,[2] and C-Cl bonds,[3] have been developed and many reactions which are sufficiently useful for synthetic purpose have been reported. In contrast, the transformation involving the cleavage of C-F bonds remains still undeveloped due to the inert character of the C-F bond.[4] In 1994, Milstein reported a rhodium-catalyzed H-F exchange reaction between hexafluorobenzene and hydrosilanes.[5] Later, it was discovered that a similar H-F exchange reaction can be achieved with using H_2 in place of hydrosilanes.[6] Jones recently studied the mechanism of this exchange reaction in some detail.[7] Deacon reported an ytterbium-mediated H-F exchange in the reaction of pentafluorobenzoic acid with $Cp_2Yb(dme)$.[8] The addition of activated Mg into the reaction system provided for a catalytic reaction albeit in low catalytic turnover numbers. Richmond found that metallocene complexes, such as Cp_2TiF_2, Cp_2TiCl_2, and Cp_2ZrCl_2, catalyzed the defluorination of perfluorocycloalkanes to give perfluoroaromatic compounds in the presence of $Al/HgCl_2$.[9] Crabtree also reported the photoinduced Cp^*_2Fe-catalyzed defluorination of perfluoroalkanes to perfluoroalkenes.[10] We now wish to report some preliminary results on the rhodium-catalyzed Si-F exchange reaction between functionalized fluorobenzenes and $Me_3SiSiMe_3$.[11]

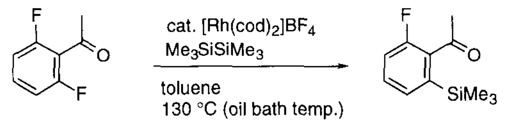


(1)

1 **2** 79-88%

The reaction of 2,3,4,5,6-pentafluoroacetophenone (**1**, 1 mmol) with $Me_3SiSiMe_3$ (10 mmol) in toluene (1 cm^3) at 130 °C (oil bath) in the presence of $[Rh(cod)_2]BF_4$ (0.1 mmol) for 20 h in a 50-cm^3 screw-capped pressure vial gave 2,3,4,5-tetrafluoro-6-(trimethylsilyl)acetophenone (**2**)[12] in 79% yield along with 7% of recovered **1** (eq 1). The replacement of F by $SiMe_3$ took place site-selectively at the *ortho*-position. The site-selectivity was confirmed as follows. The $^1H\{^{19}F\}$ NMR spectrum of **2** exhibited a doublet for an acetyl hydrogen (δ 2.58 ppm; d, J = 3.0 Hz), indicating the presence of one F atom at the *ortho* position in **2**. The site-selectivity was also confirmed by comparison of the ^1H NMR spectrum of the desilylprotonation product of **2** with that of an authentic sample.[13] While some other rhodium complexes such as $[RhCl(cod)]_2$ (43% yield) and $Rh(acac)(CO)_2$ (7% yield) showed catalytic activity, the $[RhCl(CO)_2]_2$ and $Rh_4(CO)_{12}$ complexes were not active. In the absence of rhodium complexes at 130 °C no reaction was observed.[14] Higher reaction temperatures are required for the reaction to proceed; at 110 °C (7% yield, 93% of recovered **1**) or 90 °C (0% yield, 98% of **1** recovered). The yield of **2** was improved up to 88% when the reaction of **1** with $Me_3SiSiMe_3$ was carried out in a 6-cm^3 stainless steel pressure-vial, which allowed a higher reaction temperature closer to that of the oil bath at 130 °C.

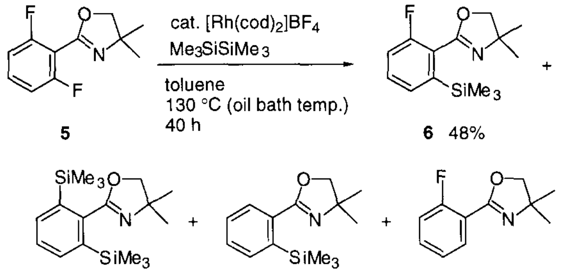
It was found that 2,6-difluoroacetophenone (**3**) is less reactive than **1**. The reaction of **3** with 10 equiv of $Me_3SiSiMe_3$ in a stainless steel pressure-vial at 130 °C for 20 h gave only a 33% yield of **4**,[15] 50% of **3** being recovered (eq 2). A prolonged reaction time (40 h) gave **4** in 48% yield, along with several unidentified byproducts.



(2)

3 **4** 33-48%

The presence of a ketone carbonyl group is essential for the Si-F exchange reaction to proceed. Hexafluorobenzene gave only a trace amount of the monosilylated product. Pentafluorobenzoic acid methyl ester and pentafluorobenzaldehyde failed to react with $Me_3SiSiMe_3$ under the same reaction conditions. We found that the oxazoline ring also promotes the Si-F exchange reaction. Although the reaction was more complicate than that of the ketones described above, the total yield of the products arising from the Si-F exchange was as high as 80% (eq 3).

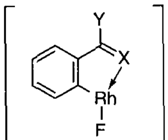


(3)

7 10% **8** 10% **9** 12%

Thus, the reaction of 2-(2,6-difluorophenyl)-4,4-dimethyl-1,3-oxazoline (**5**) with 5 equiv of $Me_3SiSiMe_3$ in the presence of 10 mol% of $[Rh(cod)_2]BF_4$ for 40 h gave four products including the monosilylation product **6**[16] in 48% yield and the disilylation product **7** in 10%. The byproducts **8** and **9** are probably formed through the in situ hydrolysis of **7** and **6**, by traces of moisture which are present.

In summary, we have demonstrated the first catalytic Si-F exchange reaction between functionalized fluorobenzenes and $Me_3SiSiMe_3$. Studies which take advantage of chelation assistance such as for the case of **10** are now in progress.[17]



10

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References and Notes

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11 Matsumoto and Nagai reported the Pd-catalyzed Si-Cl exchange reaction between chloronitrobenzenes and $Me_3SiSiMe_3$. H. Matsumoto, K. Shono, and Y. Nagai, *J. Organomet. Chem.*, **208**, 145 (1981) and references cited therein. Later, Hiyama found that the Si-I exchange reaction proceeds smoothly under mild reaction conditions when F^- is added as a promoter in the Pd-catalyzed coupling of iodobenzenes with $Me_3SiSiMe_3$. Y. Hatanaka and T. Hiyama, *Tetrahedron Lett.*, **28**, 4715 (1987). For information on Si-H exchange reactions using $Me_3SiSiMe_3$, see: N. A. Williams, Y. Uchimaru, and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1995**, 1129.

12 2,3,4,5-Tetrafluoro-6-(trimethylsilyl)acetophenone (**2**). Colorless oil; ^1H NMR ($CDCl_3$) δ 0.30 (d, J = 2.3 Hz, 9H), 2.58 (d, J = 3.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 0.74 (d, J = 4.8 Hz), 32.36 (d, J = 3.7 Hz), 121-153 (numerous overlapping multiplets), 199.02 (s); IR (neat) 1711, 1502, 1436, 1363, 1335, 1253, 1180, 1098, 1041 cm^{-1}; MS, *m/z* (rel intensity) 264 (M^+, 1), 249 (M^+-Me, 100). Anal. Calcd for $C_{11}H_{12}F_4OSi$: C, 49.99; H, 4.58. Found: C, 50.08; H, 4.63.

13 2,3,4,5-Tetrafluoroacetophenone is commercially available from Aldrich Chemical Co.

14 When the reaction of **1** with $Me_3SiSiMe_3$ in the presence of $NaBF_4$ was run at 130 °C, no reaction was observed. This experiment shows that BF_4^- has no catalytic activity.

15 (**4**). Colorless oil; ^1H NMR ($CDCl_3$) δ 0.28 (s, 9H), 2.62 (d, J = 4.6 Hz, 3H), 7.06-7.13 (m, 1H), 7.37-7.44 (c, 2H); ^{13}C NMR ($CDCl_3$) δ 0.25 (s), 31.99 (d, J = 7.4 Hz), 116.76 (d, J = 23 Hz), 131.11 (d, J = 3.6 Hz), 131.98 (d, J = 8.6 Hz), 132.69 (d, J = 12 Hz), 143.77 (s), 161.28 (d, J = 252 Hz), 201.06 (s); IR (neat) 1695, 1250, 1228, 1139 cm^{-1}; MS, *m/z* (rel intensity) 195 (M^+-Me, 100). Anal. Calcd for $C_{11}H_{15}FOSi$: C, 62.82; H, 7.19. Found: C, 62.80; H, 7.22.

16 (**6**). Colorless oil; ^1H NMR ($CDCl_3$) δ 0.31 (s, 9H), 1.41 (s, 6H), 4.11 (s, 2H), 7.03-7.11 (m, 1H), 7.31-7.39 (c, 2H); ^{13}C NMR ($CDCl_3$) δ -0.02 (s), 28.39 (s), 68.29 (s), 78.96 (s), 116.32 (d, J = 22 Hz), 122.56 (d, J = 11 Hz), 129.96 (d, J = 3.6 Hz), 130.75 (d, J = 7.4 Hz), 142.59 (s), 158.96 (s), 160.92 (d, J = 239 Hz); IR (neat) 1666, 1292, 1037 cm^{-1}; MS, *m/z* (rel intensity) 265 (M^+, 12), 250 (M^+-Me, 100). Anal. Calcd for $C_{14}H_{20}FNOSi$: C, 63.36; H, 7.60; N, 5.28. Found: C, 63.53; H, 7.68; N, 5.37.

17 Several unsuccessful attempts were made to form C-C bond using organosilicon reagents, such as allylsilane, enol silyl ethers, ketene silyl acetals, and silyl cyanide.