REVISED MANUSCRIPT

3 Schemes
3 Figures
1 Table

Mechanistic Studies of the Rhodium NHC Catalyzed Hydrodefluorination of Polyfluorotoluenes

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Abstract

The six-membered ring NHC complexes Rh(6-NHC)(PPh_3)$_2$H (6-NHC = 6-^{i}Pr, **1**; 6-Et, **2**; 6-Me, **3**) have been employed in the catalytic hydrodefluorination (HDF) of $C_6F_5CF_3$ and 2-$C_6F_4HCF_3$. Stoichiometric studies showed that **1** reacted with $C_6F_5CF_3$ at room temperature to afford cis- and trans-phsophine isomers of Rh(6-^{i}Pr)(PPh_3)$_2$F (**4**), which reform **1** upon heating with Et_3SiH. Although up to three consecutive HDF steps prove possible with $C_6F_5CF_3$, the ultimate effectiveness of the catalysts are limited by their propensity to undergo C-H activation of partially fluorinated toluenes to give, for example, Rh(6-^{i}Pr)(PPh_3)$_2$($C_6F_4CF_3$) (**7**), which was isolated and structurally characterized.

Introduction

The development of new routes for the synthesis of carbon-fluorine containing compounds is a topic of widespread interest because of the importance of such species in the pharmaceutical and agrochemical industries.[1] Figure 1 gives some selected examples of pharmaceuticals, all based upon partially fluorinated aromatic rings, with well-defined substitution patterns. The synthetic challenge is therefore to make C-F containing arenes, in a simple way that is also highly regio- and chemo-selective.[2]

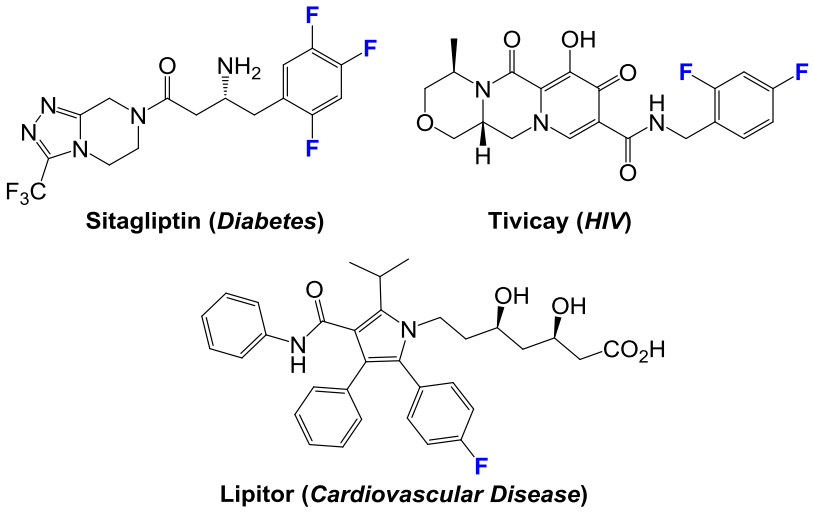


Figure 1. Examples of partially fluorinated compounds of pharmaceutical value.

One approach that is gaining in attention as a potential route for preparing partially fluorinated arenes is catalytic hydrodefluorination (HDF),[3] which involves the substitution of a fluorine atom in a readily available perfluoroarene by a hydrogen atom, most commonly under the action of a d-block metal catalyst.[4,5] However, before HDF can provide a route to the complicated partially fluorinated arenes, such as shown in Figure 1, there needs to be a much better mechanistic understanding of how to control the regio-

and chemo-selectivity of C-F activation, as well as the factors that govern catalyst activity and lifetime and pathways to catalyst decomposition.

In 2009, we reported the catalytic HDF of C_6F_5H by the N-heterocyclic carbene complexes $Ru(NHC)(PPh_3)_2(CO)H_2$ (NHC = IMes, IPr, SIMes, SIPr) in the presence of an alkylsilane.[6] These reactions took place with a remarkably high and quite atypical *ortho*-regioselectivity. DFT calculations revealed that this resulted from a novel nucleophilic hydride attack mechanism, which has been discussed in detail elsewhere.[7,8] The NHC ligands played a crucial role in the catalysis, helping to lower the energy of a key C-F bond breaking transition state by helping to stabilize C-H···F interactions. In contrast, the all-phosphine containing analogue, $Ru(PPh_3)_3(CO)H_2$, proved total inactive for HDF.

In light of this enhancement at Ru brought about by the presence of an NHC, we became interested in looking for similar behaviour in Rh complexes, especially given that Rh-PR_3 hydride complexes are well-known in both stoichiometric and catalytic C-F activation.[9] Recent results from our laboratory have provided support for there being a difference in reactivity of Rh-NHC and Rh-PR_3 complexes, at least in stoichiometric C-F bond activation. Thus, the six-membered ring NHC complexes $Rh(6\text{-}NHC)(PPh_3)_2H$ (6-NHC = 6-^{i}Pr, **1**; 6-Et, **2**; 6-Me, **3**) activate hexafluopropene ($F_2C{=}CFCF_3$) to afford the corresponding fluoride complexes $Rh(6\text{-}NHC)(PPh_3)_2F$ (6-NHC = 6-^{i}Pr, **4**; 6-Et, **5**; 6-Me, **6**),[10] which is quite surprising since most reactions of sp^2-hybridized C-F bonds with rhodium phosphine complexes give only Rh-fluoroaryl or Rh-fluoroalkenyl products.[9t] In the case of C_6F_6, **1** does form the fluoroaryl complex $Rh(6\text{-}^iPr)(PPh_3)_2(C_6F_5)$ (**7**), although alongside **4**.[11]

We now wish to report mechanistic studies on the HDF of perfluorotoluene ($C_6F_5CF_3$) and polyfluorotoluenes of lower fluorine content, catalyzed by the Rh(6-NHC)$(PPh_3)_2H$ complexes **1**-**3**. Perfluorotoluene proved to be an excellent benchmark substrate, not only because of the electron-withdrawing ability of the CF_3 group, which facilitates the HDF reaction, but also because this group serves as a distinctive marker for HDF products in the ^{19}F NMR spectral analysis. The study of the consecutive steps of perfluorotoluene HDF reveals the mechanism of the catalytic reaction. In addition, the influence of the 6-NHC substituents (^{i}Pr, Et, Me) on the efficiency of the catalytic HDF reaction is described.

Results and Discussion

C-F Bond Activation of $C_6F_5CF_3$ by 1. Addition of 5 equiv of $C_6F_5CF_3$ to a benzene solution of Rh(6-^{i}Pr)$(PPh_3)_2H$ (**1**)[12] resulted in the slow (40 h) room temperature C-F activation of the substrate to generate the Rh-F complex **4** (Scheme 1), as a 4:1 mixture of the cis- and trans-phosphine isomers **4a** and **4b**, respectively. The only organofluorine product formed was 2,3,5,6-$C_6F_4HCF_3$ (Scheme 1), consistent with activation of the C-F bond exclusively in the *para*-position to the trifluoromethyl substituent.

Isomer **4a** was fully characterized in our previous studies,[10,11] whereas the prior characterization of isomer **4b** was much more tentative.[11] **4b** has now been completely characterized by a combination of multinuclear NMR spectroscopy and X-ray crystallography. The presence of a single resonance at δ 30.1 (dd, $^1J_{PRh}$ = 175 Hz, $^2J_{PF}$ = 27 Hz) in the $^{31}P\{^1H\}$ NMR spectrum and the symmetry of the 6-^{i}Pr substituents, observed in the ^1H NMR spectrum, indicated the trans arrangement of phosphines in **4b**.

The fluoride ligand (positioned trans to the NHC ligand) gave rise to a peak at δ -327.0 in the ^{19}F NMR spectrum with couplings of 70 and 29 Hz to ^{103}Rh and ^{31}P respectively. The X-ray structure of **4b** (Figure 2) confirmed the trans-phosphine arrangement and revealed a geometry (trans-P-Rh-P 168.77(6)°; cis-P-Rh-F 84.57(10)°) with a level of distortion away from regular square-planar similar to that found in **4a** (trans-C-Rh-P 166.43(8)°; cis-P-Rh-F 83.27(5)°).[11] Surprisingly, we observed no substantial difference between the Rh-F distances in the two isomers (**4a**: 2.088(2) Å; **4b**: 2.083(3) Å), despite the ligand positioned trans to fluoride, changing from PPh_3 in **4a** to an alkyl-substituted NHC ligand in **4b**.

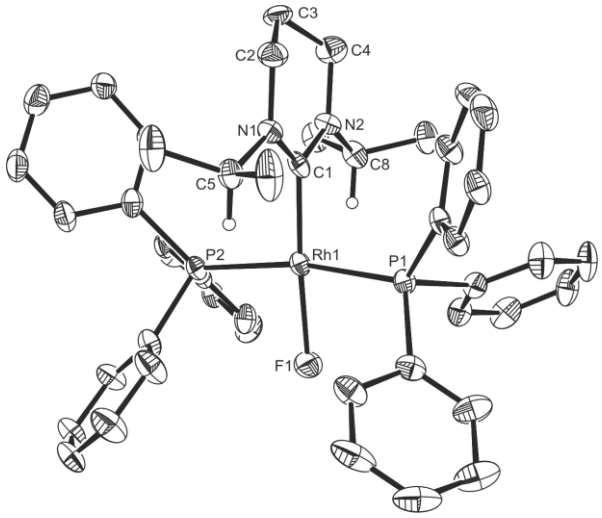
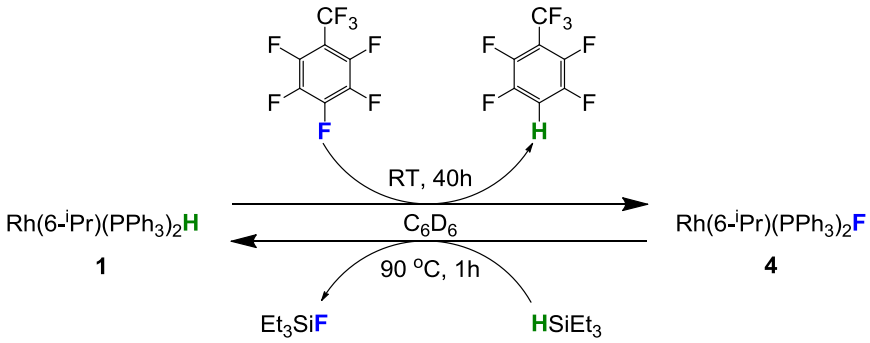


Figure 2. Molecular structure of trans-Rh(6-^{i}Pr)(PPh_3)$_2$F (**4b**). Ellipsoids are shown at the 30% level with all hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): Rh(1)-P(1) 2.2987(16), Rh(1)-P(2) 2.2961(16), Rh(1)-C(1) 1.973(6), Rh(1)-F(1) 2.083(3), P(1)-Rh(1)-C(1) 94.13(16), P(2)-Rh(1)-C(1) 95.88(16), P(1)-Rh(1)-P(2) 168.77(6), P(1)-Rh(1)-F(1) 84.57(10), P(2)-Rh(1)-F(1) 85.94(10), C(1)-Rh(1)-F(1) 174.5(2).

Catalytic HDF of $C_6F_5CF_3$ with 1-3. In order for the Rh-H complexes **1-3** to show catalytic HDF properties, the Rh-F complexes **4-6** must be able to reform the hydride complexes in presence of a hydrogen source. This was probed through stoichiometric studies on **4**, which showed reaction with Et_3SiH (5 equiv) at room temperature to regenerate **1** (as well as Et_3SiF), but only very slowly (ca. 50% conversion after 140 h). Raising the temperature to 90 °C consumed all of the remaining starting material in < 1h (Scheme 1). There was no side reaction of **1** with Et_3SiH, as was independently verified by treatment of **1** with the silane (10 equiv) in C_6D_6 over 20 h at 90 °C.[13]



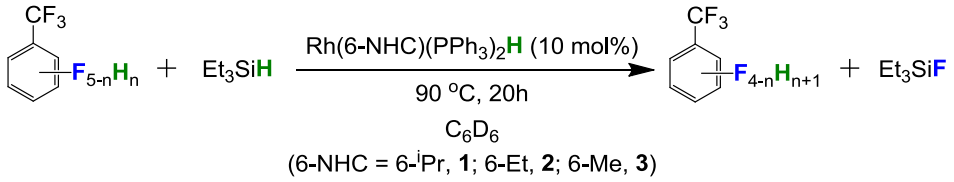
Scheme 1. Interconversion of $Rh(6\text{-}^{i}Pr)(PPh_3)_2X$ (X = H, **1**; F, **4**).

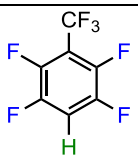
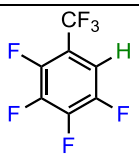
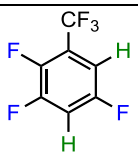
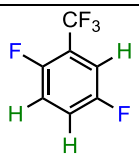
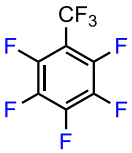
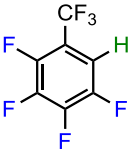
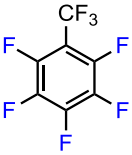
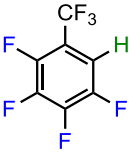
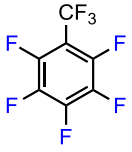
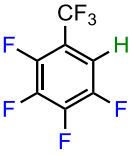
To allow both the forward and the reverse steps of an HDF cycle to proceed on a reasonable timescale, catalysis was performed at 90 °C with 10 mol% of catalyst **1** (Table 1). Under these conditions perfluorotoluene underwent mono-, di- and even tri-HDF at the aryl ring, while leaving the benzylic fluorines intact (Table 1, entry 1). The mono-HDF of $C_6F_5CF_3$ gave 2,3,5,6-$C_6F_4HCF_3$ and 2,3,4,5-$C_6F_4HCF_3$ as a result of C-F activation both *para* and *ortho* to the CF_3 group, respectively (Table 1, entry 1). The activation at both *para* and *ortho* positions takes place only at a higher temperature (90

°C), as compared with the room temperature stoichiometric reaction of $C_6F_5CF_3$ and **1**, which gave only to the *para*-C-F activation (Scheme 1). Of particular note was the formation of a relatively large amount of the di-HDF product 2,3,5-$C_6F_3H_2CF_3$, which results from consecutive HDF events (Table 1, entry 1). To probe this further, 2,3,4,5-$C_6F_4HCF_3$ was employed as the substrate, which led to formation of the di-HDF species 2,3,5-$C_6F_3H_2CF_3$ as the major product, alongside a noticeable amount of the tri-HDF product 2,5-$C_6F_2H_3CF_3$ (Table 1, entry 2).[14] Interestingly, the first HDF event of 2,3,4,5-$C_6F_4HCF_3$ occurs *para* to the CF_3 group to give 2,3,5-$C_6F_3H_2CF_3$, while the second HDF event occurs *meta* to give 2,5-$C_6F_2H_3CF_3$.

Performing HDF of $C_6F_5CF_3$ and 2,3,4,5-$C_6F_4HCF_3$ with catalysts **1**-**3** (10 mol% loading) under the same conditions, clearly showed that the catalytic activity decreases upon going from **1** to **3** (Table 1, entries 1-6).[15] **1** exhibits the highest activity, with 9 turnovers (Table 1, entry 2), while **2** and **3** have lower activity with up to 4 and 2 turnovers, respectively. In comparison, it is worth noting that $Rh(PPh_3)_4H$ catalyzes the HDF of C_6F_6, albeit under quite different reducing conditions (5.8 atm H_2, excess Et_3N), with a turnover of 3.[4b]

Table 1. Scope of catalytic Rh(6-NHC) Catalyzed HDF.[a]



Entry	Cat.	Substrate	Conv. (%)[b]	Product distribution (%)[c]				TON[d]
								
1	**1**		40	59	11	27	3	6
2[e]	**1**		78	-	-	52	33	9
3	**2**		35	83	8	9	0	4
4	**2**		16	-	-	100	0	2
5	**3**		22	93	0	7	0	2
6	**3**		14	-	-	100	0	1

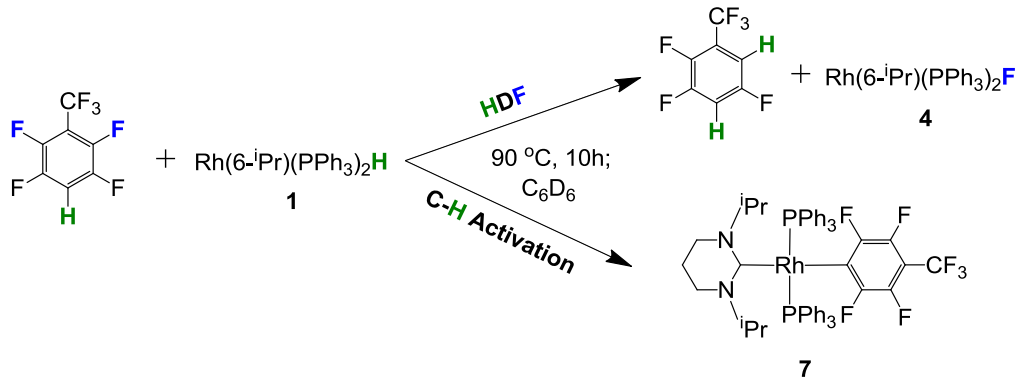
[a]Conditions: 10 mol% Rh, 0.19 mM substrate, 0.4 mL C_6D_6, 20 h, 90 °C. [b]Determined by integration of the ^{19}F NMR spectra relative to a standard [$C_6H_5CF_3$] added at the end of

the reaction. Values are the average of 2 catalytic runs. [c]Determined by integration of the ^{19}F NMR spectra. [d]TON = (moles of fluoroaromatic products x number of HDF steps)/moles of catalyst. [e]Traces of other, unidentified products account for the product distribution being < 100%.

Deactivation of 1 by C-H activation. $^{31}P\{^{1}H\}$ and ^{19}F NMR spectra of the involatile material, left at the end of the catalytic HDF reaction of $C_6F_5CF_3$ with **1** (Table 1, Entry 1) showed the presence of a single new rhodium containing product, which was identified as the fluoroaryl complex $Rh(6\text{-}^{i}Pr)(PPh_3)_2(C_6F_4CF_3)$ (**7**). As evidenced by the stoichiometric reaction described below, this compound is formed by the C-H activation of 2,3,5,6-$C_6F_4HCF_3$, which is the major product of the catalytic HDF of $C_6F_5CF_3$. When **1** was heated with an excess of 2,3,5,6-$C_6F_4HCF_3$ at 90 °C, formation of **7** (60%) took place along with formation of **4** (40%) (Scheme 2), as evidenced by $^{31}P\{^{1}H\}$ and ^{19}F NMR analyses .

As shown in Scheme 2, 2,3,5,6-$C_6F_4HCF_3$ undergoes HDF *ortho* to the CF_3 group, providing a pathway to the di-HDF product 2,3,5-$C_6F_3H_2CF_3$ under catalytic conditions. However, an additional pathway appears to involve C-H activation of 2,3,5,6-$C_6F_4HCF_3$, which ultimately leads to the deactivation of the catalyst through formation of **7**. We observed no further reaction of **7** with Et_3SiH, indicating that this species once formed, is catalytically inactive. These findings help to rationalize the relatively low turnover numbers observed for catalysis with $C_6F_5CF_3$ (Table 1), although it is worth commenting that the noticeably higher TON for 2,3,4,5-$C_6F_4HCF_3$ with **1** (Table 1, entry

2) implies that 2,3,5-$C_6F_3H_2CF_3$ is less prone to activation of the C-H bond para to the CF_3 group than 2,3,5,6-$C_6F_4HCF_3$.



Scheme 2. Competing C-F and C-H activation pathways of **1** with 2,3,5,6-$C_6F_4HCF_3$.

The fluoroaryl complex **7** was characterized by NMR spectroscopy and X-ray analysis. The presence of just a doublet resonance at δ 29.3 ($^1J_{PRh}$ = 170 Hz) in the $^{31}P\{^1H\}$ spectrum indicates a trans-phosphine arrangement in **7**. The ^{19}F NMR spectrum shows three resonances in a 3:2:2 ratio between δ -55 and -146, consistent with the benzylic and two types of aryl fluorines. The distortion away from a square-planar geometry in the X-ray crystal structure (Figure 3) and asymmetric orientation of the 6-^{i}Pr ligands (N(2)-C(1)-Rh(1) = 116.13(19)°, N(1)-C(1)-Rh(1) = 126.9(2)°) are comparable to what is found in the Rh-C_6F_5 analogue.[11]

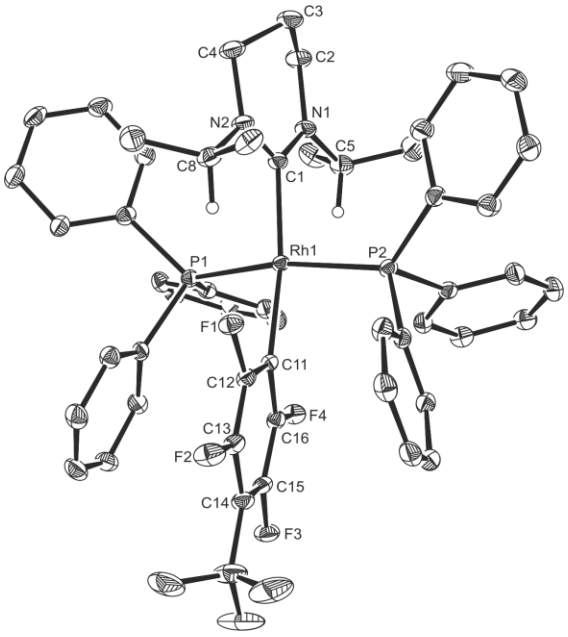
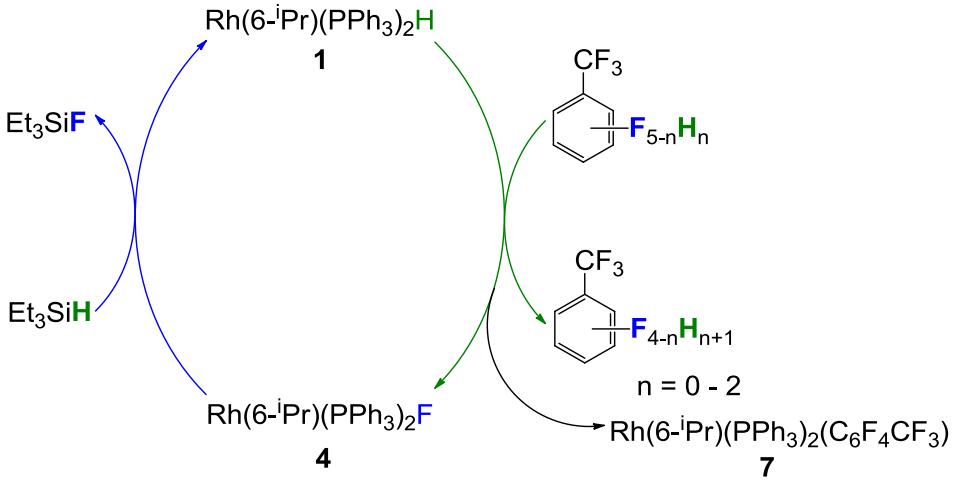


Figure 3. Molecular structure of **7**. Ellipsoids are shown at the 30% level with all hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): Rh(1)-P(1) 2.2965(7), Rh(1)-P(2) 2.3329(17), Rh(1)-C(1) 2.081(3), Rh(1)-C(11) 2.078(2), P(1)-Rh(1)-P(2) 165.64(2), C(1)-Rh(1)-C(11) 167.81(10), P(1)-Rh(1)-C(1) 91.94(8).

Proposed Catalytic Cycle for HDF. A catalytic cycle for the HDF of polyfluorotoluenes by **1** involving direct reaction of a substrate with the rhodium hydride precursor, followed by reaction of the resulting Rh-F species with silane to reform Rh-H is shown in Scheme 3. Such a mechanism was proposed a number of years ago by Holland to rationalize the Fe(β-diketiminate) catalyzed HDF of fluororoaromatics.[4d] We have now established direct experimental evidence of such a simple, two-step pathway. The C-F bond activation most probably takes place by S_NAr substitution, since the regioselectivity of the HDF events is primarily dictated by the electronics of polyfluoroarene.

Despite the presence of the strongly donating NHC ligands, the catalytic effectiveness of the Rh(6-NHC)(PPh_3)$_2$H systems is not that high, presumably because they are prone to deactivation by C-H bond activation, combined with the unreactivity of the resulting fluoroaryl products (e.g.**7**, Scheme 3) towards Si-H bonds. Interestingly, this behavior is quite different to that reported by Milstein for Rh(PMe_3)$_3$(fluoroaryl) complexes, which react with silane by Si-H oxidative addition followed by C-H reductive elimination to actually afford the HDF product.[4a]



Scheme 3. Catalytic cycle for the rhodium catalyzed HDF of polyfluorotoluenes in the presence of Et_3SiH.

Summary

The interconversion of Rh-H (**1**) and Rh-F (**4**) complexes lies at the basis of the catalytic HDF of polyfluorotoluenes. The stoichiometric mono-HDF of perfluorotoluene by **1** takes place readily at room temperature and leads to exclusive formation of 2,3,5,6-$HC_6F_4CF_3$ and **4**, which can be reconverted back to **1** by treatment with triethylsilane.

Catalysts **1-3** have proven capable not only of mono-HDF, but also of di-HDF and even tri-HDF of the benchmark substrate perfluorotoluene, giving access to polyfluorotoluenes with lower fluorine content. The relative activity of the catalysts decreases as the N‑alkyl substituents get smaller (^{i}Pr > Et, > Me), while the HDF sequence is ultimately interfered with by C-H activation of lower HDF products, to give irreversible formation of fluoroaryl complexes, exemplified by **7**.

Our results suggest that while the presence of a strongly donating NHC ligand enhances the activity of Rh complexes as HDF catalysts, the remaining cast of supporting ligands is not sufficient to prevent C-H activation. Further studies are focused on fine-tuning the balance between NHC and PR_3 ligands in an effort to shut down this deactivation pathway.

Experimental

All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of purified argon and using dried and degassed solvents. NMR spectra were referenced to residual C_6D_5H at δ 7.15. ^{1}H resonances for the PPh_3 ligands are only given when they could be assigned unequivocally. $^{31}P\{^{1}H\}$ and ^{19}F spectra were referenced externally to 85% H_3PO_4 (85%) and $CFCl_3$ respectively (both δ = 0.0). Elemental analyses were performed by the Elemental Analysis Service, London Metropolitan University, London, UK. Complexes **1-3** were prepared according to the literature procedure.[10,11]

trans-Rh(6-^{i}Pr)(PPh$_3$)$_2$F (4b). A J. Youngs NMR tube containing a C_6D_6 (0.5 mL) solution of **1** (40 mg, 0.050 mmol) and $C_6F_5CF_3$ (50 μL, 0.251 mmol) was prepared

inside a glovebox and monitored periodically by NMR spectroscopy over 40 h at room temperature, until all of the Rh-H starting material had reacted. The resulting yellow solution was then evaporated to dryness and the residue washed with hexane (3 mL) and dried under vacuum to give 29 mg of a 4:1 mixture of **4a** and **4b**, respectively (72% yield). Both isomers are partially soluble in hexane, and thus cooling the hexane washings to -35 °C, afforded a small number of X-ray quality crystals of each isomer. Manual separation allowed isolation of the orange crystals of **4b** from the yellow crystals of **4a**. While characterization of isomer **4a** has been reported previously,[11] characterization of isomer **4b** is as follows: ^{1}H NMR (500 MHz, C_6D_6, 25 °C):* δ 7.89 (sept, $^{3}J_{HH}$ = 6.88 Hz, 2H, NC*H*$(CH_3)_2$), 2.44 (t, $^{3}J_{HH}$ = 5.90 Hz, 4H, NC*H*$_2$), 1.39 (br quint, 2H, NCH_2CH_2), 0.48 (d, 12H, $^{3}J_{HH}$ = 6.88 Hz, $NCH(CH_3)_2$).* Assignments based on TOCSY and COSY analysis. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 25 °C): δ 30.1 (dd, $^{1}J_{PRh}$ = 175 Hz, $^{2}J_{PF}$ = 27 Hz). ^{19}F NMR (470 MHz, C_6D_6, 25 °C): δ -327.0 (dt, $^{1}J_{FRh}$ = 69.6 Hz, $^{2}J_{FP}$ = 28.5 Hz, Rh-F). Anal. calcd for $C_{46}H_{50}N_2FP_2Rh$ (814.71),%: C, 67.81; H, 6.19; N, 3.44. Found, %: C, 67.98; H, 5.95; N, 3.81.

Catalytic HDF Procedure. Loadings were all carried out inside a glovebox with a representative procedure described. To a sample vial containing 15 mg of **1** (0.019 mmol), were added 0.4 mL C_6D_6, $C_6F_5CF_3$ (27 μL, 0.19 mmol) and Et_3SiH (150 μL, 0.94 mmol). The reaction solution was stirred and transferred to a J. Young's resealable NMR tube. The sealed tube was removed from the glovebox and heated for 20 h at 90 °C in an oil bath. After cooling to room temperature, the tube was opened and 5 mL α,α,α,-trifluorotoluene was added as an internal reference for ^{19}F NMR analysis.

Rh(6-^{i}Pr)(PPh$_3$)$_2$(C$_6$F$_4$CF$_3$) (7). A C_6H_6 (2.5 mL) solution of **1** (35 mg, 0.044 mmol) and 2,3,5,6-$C_6F_4HCF_3$ (100 μL, 0.740 mmol) was stirred and heated at 90 °C for 37 h, in a J. Youngs ampule. The solvent was removed from the reaction solution under vacuum and the residue was redissolved in C_6D_6 (0.5 mL). $^{31}P\{^1H\}$ NMR analysis revealed formation of **7** (60%) and **4** (40%). Layering the benzene solution with hexane afforded 16 mg of **7** (34% yield) in the form of X-ray quality orange crystals. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 9.67-9.33 (br, 12H, PC_6H_5 + 2 x $NCH(CH_3)_2$), 8.91-8.76 (br s, 20H, PC_6H_5), 2.53 (m, 4H, NCH_2), 1.52 (m, 2H, NCH_2CH_2), 0.48 (d, 12H, $^3J_{HH}$ = 6.8 Hz, $NCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 25 °C): δ 29.3 (d, $^1J_{PRh}$ = 170 Hz). ^{19}F NMR (470 MHz, C_6D_6, 25 °C): δ -55.3 (t, $^4J_{FF}$ = 18.8 Hz, 3F, CF_3), -107.6 (m, 2F, Rh-*o*-$C_6F_4CF_3$), -146.1 (m, 2F, Rh-*m*-$C_6F_4CF_3$). Anal. calcd for $C_{53}H_{50}N_2F_7P_2Rh$ (1012.78),%: C, 62.84; H, 4.98; N, 2.74. Found, %: C, 62.99; H, 4.91; N, 2.87.

X-ray crystallography. Single crystals of compounds for **4b** and **7** were analyzed on station I19 at the Diamond light source and a Nonius Kappa CCD diffractometer, respectively. Both data sets were collected at -123 °C, and details of the data collections, solutions and refinements are given in Table S1 (see ESI). The structures were solved using SHELXS-97[21] and refined using full-matrix least squares in SHELXL-97.[16]

The crystal sample for **4b** was very small and it exhibited significant diffraction fall-off at higher Bragg angles. For compound **7**, the asymmetric unit was seen to comprize one molecule of the rhodium complex, half of a molecule of benzene (proximate to an inversion centre) and an additional very disordered region of solvent which has been treated via PLATON SQUEEZE. Based on the SQUEEZE findings for the latter, in conjunction with the height of the electron density peaks prior to application of this

algorithm, an allowance of half of a benzene molecule per asymmetric unit has been made in the formula presented herein.

Crystallographic data for compounds **4b** and **7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1012004 and 1012005, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements. We acknowledge financial support from the EPSRC (LS) and the University of Bath (RCP). We thank Johnson Matthey plc for the loan of hydrated $RhCl_3$.

Supporting Information Available: Table S1. CIF files giving X-ray crystallographic data for **4b** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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12. As previously reported (ref 11), **1** exists in solution as 1:2 mixture of the cis- and trans-phosphine isomers **1a** and **1b**, respectively.
13. This experiment revealed that the 1:2 ratio of cis: trans-phosphine isomers **1a** and **1b** was unchanged even after 20 h at 90 °C. Upon increasing the temperature to

110 °C for a further 3 days, there was significant decomposition of both isomers, leading to the appearance of PPh_3 and $O{=}PPh_3$ and other signals of unknown origin in the $^{31}P\{^1H\}$ NMR spectrum.

14. Assigned by comparison to the ^{19}F NMR spectrum of an authentic sample (C_6D_6, 376 MHz, 25 °C: δ -61.95 (d, $^4J_{FH}$ = 12.4 Hz, 3F, CF_3), -117.02 (m, 1F), -120.62 (m, 1F)). The ^{19}F NMR spectrum of the alternative product, 2,3-$C_6F_2H_3CF_3$, is very different (C_6D_6, 376 MHz, 25 °C: δ -61.16 (d, $^4J_{FH}$ = 11.7 Hz, 3F, CF_3), -136.12 (m, 1F), -139.97 (m, 1F)), making the two isomers easy to differentiate

15. There was no enhancement in the activity of **1** upon changing Et_3SiH to either $(EtO)_3SiH$ or Ph_2SiH_2.

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Mechanistic Studies of the Rhodium NHC Catalyzed Hydrodefluorination of Polyfluorotoluenes

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