Mechanistic Studies of the Rhodium NHC Catalyzed Hydrodefluorination of Polyfluorotoluenes

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Abstract

The six-membered ring NHC complexes Rh(6-NHC)(PPh3)2H (6-NHC = 6-Pr, 1; 6-Et, 2; 6-Me, 3) have been employed in the catalytic hydrodefluorination (HDF) of C6F5CF3 and 2-C6F4HCF3. Stoichiometric studies showed that 1 reacted with C6F5CF3 at room temperature to afford cis- and trans-phsophine isomers of Rh(6-Pr)(PPh3)2F (4), which reform 1 upon heating with Et3SiH. Although up to three consecutive HDF steps prove possible with C6F5CF3, the ultimate effectiveness of the catalysts are limited by their propensity to undergo C-H activation of partially fluorinated tolenes to give, for example, Rh(6-Pr)(PPh3)2(C6F4CF3) (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.\textsuperscript{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.\textsuperscript{2}

![Figure 1. Examples of partially fluorinated compounds of pharmaceutical value.](image)

One approach that is gaining in attention as a potential route for preparing partially fluorinated arenes is catalytic hydrodefluorination (HDF),\textsuperscript{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.\textsuperscript{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 C₆F₅H by the N-heterocyclic carbene complexes Ru(NHC)(PPh₃)₂(CO)H₂ (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(PPh₃)₃(CO)H₂, 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-PR₃ 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-PR₃ complexes, at least in stoichiometric C-F bond activation. Thus, the six-membered ring NHC complexes Rh(6-NHC)(PPh₃)₂H (6-NHC = 6-iPr, 1; 6-Et, 2; 6- Me, 3) activate hexafluopropene (F₂C=CFCF₃) to afford the corresponding fluoride complexes Rh(6-NHC)(PPh₃)₂F (6-NHC = 6-iPr, 4; 6-Et, 5; 6-Me, 6),¹⁰ which is quite surprising since most reactions of sp²-hybridized C-F bonds with rhodium phosphine complexes give only Rh-fluoroaryl or Rh-fluoroalkenyl products.⁹ In the case of C₆F₆, 1 does form the fluoroaryl complex Rh(6-iPr)(PPh₃)₂(C₆F₅) (7), although alongside 4.¹¹
We now wish to report mechanistic studies on the HDF of perfluorotoluene (C₆F₅CF₃) and polyfluorotoluenes of lower fluorine content, catalyzed by the Rh(6-NHC)(PPh₃)₂H complexes 1-3. Perfluorotoluene proved to be an excellent benchmark substrate, not only because of the electron-withdrawing ability of the CF₃ group, which facilitates the HDF reaction, but also because this group serves as a distinctive marker for HDF products in the ¹⁹F 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 (iPr, Et, Me) on the efficiency of the catalytic HDF reaction is described.

Results and Discussion

C-F Bond Activation of C₆F₅CF₃ by 1. Addition of 5 equiv of C₆F₅CF₃ to a benzene solution of Rh(6-iPr)(PPh₃)₂H (1) 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-C₆F₄HCF₃ (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, whereas the prior characterization of isomer 4b was much more tentative. 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, J_PRh = 175 Hz, J_PF = 27 Hz) in the ³¹P{¹H} NMR spectrum and the symmetry of the 6-iPr 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 $\delta$ -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)$^\circ$; cis-P-Rh-F 84.57(10)$^\circ$) with a level of distortion away from regular square-planar similar to that found in 4a (trans-C-Rh-P 166.43(8)$^\circ$; cis-P-Rh-F 83.27(5)$^\circ$).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-$^3$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 ($^\circ$): 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 $\text{C}_6\text{F}_5\text{CF}_3$ 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$_3$SiH (5 equiv) at room temperature to regenerate 1 (as well as Et$_3$SiF), 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$_3$SiH, as was independently verified by treatment of 1 with the silane (10 equiv) in C$_6$D$_6$ over 20 h at 90 °C.$^{13}$

![Scheme 1. Interconversion of Rh(6-iPr)(PPh$_3$)$_2$X (X = H, 1; F, 4).](image)

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$_6$F$_5$CF$_3$ gave 2,3,5,6-C$_6$F$_4$HCF$_3$ and 2,3,4,5-C$_6$F$_4$HCF$_3$ 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). 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). 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$_3$)$_4$H catalyzes the HDF of $C_6F_6$, albeit under quite different reducing conditions (5.8 atm H$_2$, excess Et$_3$N), with a turnover of 3.4b
Table 1. Scope of catalytic Rh(6-NHC) Catalyzed HDF.\(^a\)

\[
\begin{align*}
\text{Entry} & \quad \text{Cat.} \quad \text{Substrate} \quad \text{Conv. (%)}^b \quad \text{Product distribution (%)}^c \quad \text{TON}^d \\
1 & 1 & \text{F}_{5-n}F_{n}^+ & 40 & 59 & 11 & 27 & 3 & 6 \\
2^e & 1 & \text{F}_{5-n}F_{n}^+ & 78 & - & - & 52 & 33 & 9 \\
3 & 2 & \text{F}_{5-n}F_{n}^+ & 35 & 83 & 8 & 9 & 0 & 4 \\
4 & 2 & \text{F}_{5-n}F_{n}^+ & 16 & - & - & 100 & 0 & 2 \\
5 & 3 & \text{F}_{5-n}F_{n}^+ & 22 & 93 & 0 & 7 & 0 & 2 \\
6 & 3 & \text{F}_{5-n}F_{n}^+ & 14 & - & - & 100 & 0 & 1
\end{align*}
\]

\(^a\)Conditions: 10 mol\% Rh, 0.19 mM substrate, 0.4 mL C\(_6\)D\(_6\), 20 h, 90 °C. \(^b\)Determined by integration of the \(^{19}\)F NMR spectra relative to a standard [C\(_6\)H\(_5\)CF\(_3\)] added at the end of
the reaction. Values are the average of 2 catalytic runs. °Determined by integration of the 19F NMR spectra. ‡TON = (moles of fluoroaromatic products x number of HDF steps)/moles of catalyst. °Traces of other, unidentified products account for the product distribution being < 100%.

**Deactivation of 1 by C-H activation.** 31P{1H} and 19F NMR spectra of the involatile material, left at the end of the catalytic HDF reaction of C6F5CF3 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-iPr)(PPh3)2(C6F4CF3) (7). As evidenced by the stoichiometric reaction described below, this compound is formed by the C-H activation of 2,3,5,6-C6F4HCF3, which is the major product of the catalytic HDF of C6F5CF3. When 1 was heated with an excess of 2,3,5,6-C6F4HCF3 at 90 °C, formation of 7 (60%) took place along with formation of 4 (40%) (Scheme 2), as evidenced by 31P{1H} and 19F NMR analyses.

As shown in Scheme 2, 2,3,5,6-C6F4HCF3 undergoes HDF ortho to the CF3 group, providing a pathway to the di-HDF product 2,3,5-C6F3H2CF3 under catalytic conditions. However, an additional pathway appears to involve C-H activation of 2,3,5,6-C6F4HCF3, which ultimately leads to the deactivation of the catalyst through formation of 7. We observed no further reaction of 7 with Et3SiH, indicating that this species once formed, is catalytically inactive. These findings help to rationalize the relatively low turnover numbers observed for catalysis with C6F5CF3 (Table 1), although it is worth commenting that the noticeably higher TON for 2,3,4,5-C6F4HCF3 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\(_6\)F\(_4\)HCF\(_3\).](image_url)

The fluoroaryl complex 7 was characterized by NMR spectroscopy and X-ray analysis. The presence of just a doublet resonance at \(\delta 29.3 (^{1}J_{PRh} = 170 \text{ Hz})\) in the \(^{31}\text{P}\{^{1}\text{H}\}\) spectrum indicates a trans-phosphine arrangement in 7. The \(^{19}\text{F}\) NMR spectrum shows three resonances in a 3:2:2 ratio between \(\delta -55\) 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-iPr ligands \((N(2)-C(1)-Rh(1) = 116.13(19)^{\circ}, N(1)-C(1)-Rh(1) = 126.9(2)^{\circ})\) are comparable to what is found in the Rh-C\(_6\)F\(_5\) 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. 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_N_Ar 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 \( \text{Rh}(6\text{-NHC})(\text{PPh}_3)_2\text{H} \) 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 \( \text{Rh}(\text{PMe}_3)_3(\text{fluoroaryl}) \) 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 \( \text{Et}_3\text{SiH} \).

**Summary**

The interconversion of \( \text{Rh-H} (1) \) and \( \text{Rh-F} (4) \) 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 \( 2,3,5,6-\text{HC}_6\text{F}_4\text{CF}_3 \) 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 (iPr > 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 PR3 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 C6D5H at δ 7.15. 1H resonances for the PPh3 ligands are only given when they could be assigned unequivocally. 31P{1H} and 19F spectra were referenced externally to 85% H3PO4 (85%) and CFCl3 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-iPr)(PPh3)2F (4b)**. A J. Youngs NMR tube containing a C6D6 (0.5 mL) solution of 1 (40 mg, 0.050 mmol) and C6F5CF3 (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\(_6\)D\(_6\), 25 °C):\(^*\) \(\delta\) 7.89 (sept, \(^3\)J\(_{HH}\) = 6.88 Hz, 2H, NCH(CH\(_3\))\(_2\)), 2.44 (t, \(^3\)J\(_{HH}\) = 5.90 Hz, 4H, NCH\(_2\)), 1.39 (br quint, 2H, NCH\(_2\)CH\(_2\)), 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\(_6\)D\(_6\), 25 °C): \(\delta\) 30.1 (dd, \(^1\)J\(_{PRh}\) = 175 Hz, \(^2\)J\(_{PF}\) = 27 Hz). \(^{19}\)F NMR (470 MHz, C\(_6\)D\(_6\), 25 °C): \(\delta\) -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\(_2\)FP\(_2\)Rh (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\(_6\)D\(_6\), C\(_6\)F\(_5\)CF\(_3\) (27 \(\mu\)L, 0.19 mmol) and Et\(_3\)SiH (150 \(\mu\)L, 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 \(\alpha,\alpha,\alpha\)-trifluorotoluene was added as an internal reference for \(^{19}\)F NMR analysis.
**Rh(6-Pr)(PPh$_3$)$_2$(C$_6$F$_4$CF$_3$)** (7). A C$_6$H$_6$ (2.5 mL) solution of 1 (35 mg, 0.044 mmol) and 2,3,5,6-C$_6$F$_4$HCF$_3$ (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$_6$D$_6$ (0.5 mL). $^{31}$P{$_1$H} 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. $^1$H NMR (500 MHz, C$_6$D$_6$, 25 °C): δ 9.67-9.33 (br, 12H, PC$_6$H$_5$ + 2 x NCH(CH$_3$)$_2$), 8.91-8.76 (br s, 20H, PC$_6$H$_5$), 2.53 (m, 4H, NCH$_2$H$_2$), 1.52 (m, 2H, NCH$_2$CH$_2$), 0.48 (d, 12H, $^3$J$_{HH}$ = 6.8 Hz, NCH(CH$_3$)$_2$). $^{31}$P{$_1$H} NMR (202 MHz, C$_6$D$_6$, 25 °C): δ 29.3 (d, $^1$J$_{PRh}$ = 170 Hz). $^{19}$F NMR (470 MHz, C$_6$D$_6$, 25 °C): δ -55.3 (t, $^4$J$_{FF}$ = 18.8 Hz, 3F, CF$_3$), -107.6 (m, 2F, Rh-o-C$_6$F$_4$CF$_3$), -146.1 (m, 2F, Rh-m-C$_6$F$_4$CF$_3$). Anal. calcd for C$_{53}$H$_{50}$N$_2$F$_7$P$_2$Rh (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 and refined using full-matrix least squares in SHELXL-97. 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].

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**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.

**References**


6. Reade, S. P.; Mahon, M. F.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2009**, *131*, 1847. IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene; SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene.


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 PPh₃ and O=PPh₃ and other signals of unknown origin in the $^{31}$P{$^{1}$H} NMR spectrum.

14. Assigned by comparison to the $^{19}$F NMR spectrum of an authentic sample (C₆D₆, 376 MHz, 25 °C: δ -61.95 (d, $^4$$^4$J$_{FH}$ = 12.4 Hz, 3F, CF₃), -117.02 (m, 1F), -120.62 (m, 1F)). The $^{19}$F NMR spectrum of the alternative product, 2,3-C₆F₂H₃CF₃, is very different (C₆D₆, 376 MHz, 25 °C: δ -61.16 (d, $^4$$^4$J$_{FH}$ = 11.7 Hz, 3F, CF₃), -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 Et₃SiH to either (EtO)₃SiH or Ph₂SiH₂.

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