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Selective C−F and C−H Activation of Fluoroarenes by $Fe(PMe_3)_4$ and Catalytic Performance of Iron Hydride in Hydrosilylation of Carbonyl Compounds

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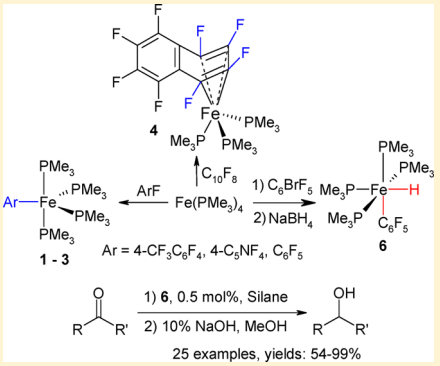
Supporting Information

ABSTRACT: The reactions of perfluorinated toluene ($CF_3C_6F_5$), pentafluoropyridine (C_5NF_5), and hexafluorobenzene (C_6F_6) with the iron(0) complex $Fe(PMe_3)_4$ were investigated. The Fe(I) complexes $(4\text{-}CF_3C_6F_4)Fe(PMe_3)_4$ (**1**), $(4\text{-}C_5NF_4)Fe(PMe_3)_4$ (**2**), and $(C_6F_5)Fe(PMe_3)_4$ (**3**) were obtained by selective activation of the C−F bonds. However, under similar reaction conditions, the reaction of $Fe(PMe_3)_4$ with perfluoronaphthalene ($C_{10}F_8$) afforded a π-coordinated Fe(0) complex, $(\eta^4\text{-}1,2,3,4\text{-}C_{10}F_8)Fe(PMe_3)_3$ (**4**), and the expected C−F bond activation reaction was not observed. The expected iron hydride $(C_6F_5)FeH(PMe_3)_4$ (**6**) could be obtained in a yield of 80% by the reaction of bromopentafluorobenzene with $Fe(PMe_3)_4$ and subsequent reduction with $NaBH_4$. The molecular structures of complexes **2**, **4**, and **6** were determined by single-crystal X-ray diffraction. Complexes **1**−**4** and **6** could be used as catalysts for the hydrosilylation of carbonyl compounds. Among them, complex **6** is the best catalyst. The selective reduction of carbonyl groups of α,β-unsaturated aldehydes and ketones was also realized with **6** as catalyst.



INTRODUCTION

In recent years, more and more methods have been developed for the preparation of organic fluorine compounds.[1−7] The comprehensive research on C−F bond activation by transition-metal complexes has provided a new way to explore the selective synthesis of new organic fluorides and to access novel methodologies for the defluorination of organic fluorides.[8−19] Nickel complexes were selected as catalysts in the $C(sp^2)$−F activation and functionalization of organic fluorides by Ackermann[19d,e] and Herrmann.[19f] However, there have been few reports on C−F bond activation and functionalization promoted by electron-rich low-valent iron complexes. Although Milstein in 1994 reported the C−F bond activation of pentafluorobenzene utilizing a rhodium complex as the catalyst at room temperature,[20] the first exmples of C−F bond activation by iron were published in 1997.[21]

We are interested in research on C−F bond activation and functionalization mediated by electron-rich iron, cobalt, and nickel complexes. Recently, we reported the synergistic effect of the complex tetrakis(trimethylphosphine)cobalt(0) and trimethylphosphine on selective C−F bond activation of fluoroarenes and catalytic hydrodefluorination of perfluoroarenes with sodium formate as the reducing agent under mild conditions.[22−24] We also demonstrated C−F bond activation by electron-rich cobalt and iron complexes using imine as an anchoring group.[25−27]

In this paper, we expand the scope of the C−F and C−H bond activation of perfluoroarenes and polyfluoroarenes with electron-rich low-valent iron complexes. The Fe(I) complexes **1**−**3** were formed by the reactions of tetrakis(trimethylphosphine)iron(0) with perfluorinated toluene, pyridine, and benzene via selective C−F bond cleavage. In the case of perfluoronaphthalene ($C_{10}F_8$), the π-coordinated Fe(0) complex **4** was formed by the reaction of $Fe(PMe_3)_4$ with perfluoronaphthalene. The novel iron(II) hydride **6** was synthesized and used as an efficient catalyst for the hydrosilylation of carbonyl compounds.

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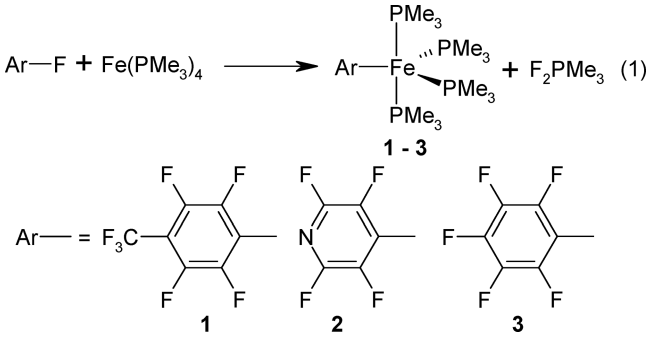
RESULTS AND DISCUSSION

Selective C−F Bond Activation of Perfluorinated Toluene, Pyridine, Benzene, and Naphthalene. Organocobalt(I) complexes could be obtained through selective C−F bond activation, while the reaction of perfluorotoluene with $Co(PMe_3)_4$ provided a cobalt benzyne complex via double C−F bond activation.[22,23] In place of $Co(PMe_3)_4$, the reactions of $Fe(PMe_3)_4$ with $CF_3C_6F_5$, C_5NF_5, and C_6F_6 were studied under similar reaction conditions. The three pentacoordinate iron(I) complexes **1**−**3** were isolated (eq 1). In the case of $CF_3C_6F_5$ and C_5NF_5, the C−F bond



activation occurred at the 4-position for both $Fe(PMe_3)_4$ and $Co(PMe_3)_4$.[22,23] In the IR spectra, the vibrations of the PMe_3 ligands were found at 938 (**1**), 933 (**2**) and 948 (**3**) cm^{-1}. Complexes **1**−**3** are paramagnetic because they have an iron(I) center with a d^7 configuration.

The molecular structure of complex **2** is shown in Figure 1. In complex **2** the iron atom is located at the center of a

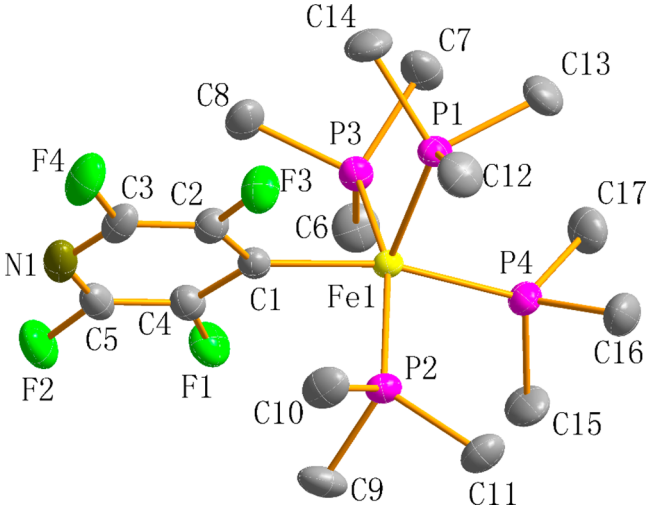


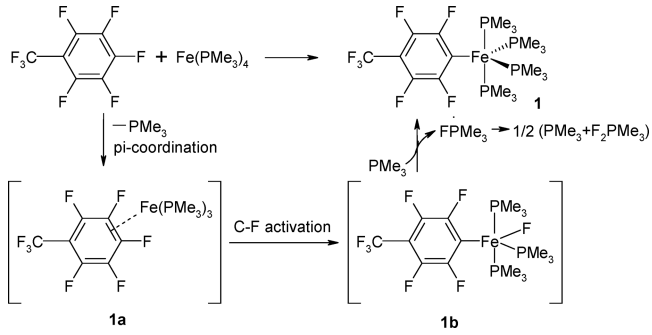
Figure 1. Molecular structure of **2** (all of the hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Fe1−C1 2.031(2), Fe1−P3 2.2251(6), Fe1−P4 2.2291(6), Fe1−P2 2.2441(6), Fe1−P1 2.2656(8); C1−Fe1−P3 87.27(5), C1−Fe1−P4 164.83(5), P3−Fe1−P4 93.78(3), C1−Fe1−P2 81.64(5), P3−Fe1−P2 158.09(2), P4−Fe1−P2 92.17(3), C1−Fe1−P1 99.46(5), P3−Fe1−P1 95.52(2), P4−Fe1−P1 95.51(2), P2−Fe1−P1 104.88(2).

tetragonal pyramid with the P1 atom at the vertex position. The Fe1−C1 bond distance in complex **2** is 2.031(2) Å. All of the Fe−P bond distances are in the normal range. In complex **2** the aromatic plane is almost perpendicular to the corresponding square plane.

The molecular structures of complexes **1** and **3** are similar to that of complex **2**. Although the structures of complexes **1** and **3** were also supported by single-crystal X-ray diffraction, the poor crystallographic data prevent their publication. The ball and stick representations of these two structures along with their Cartesian coordinates are provided in the Supporting Information.

On the basis of the similar chemistry on cobalt,[22] a proposed mechanism for the formation of complexes **1**−**3** is given with complex **1** as an example (Scheme 1). The precoordination of

Scheme 1. Proposed Mechanism of Formation of Complex 1



the aromatic ring to the Fe(0) center to form the intermediate **1a** with an η^2-coordinated perfluorotoluene ligand[23] under elimination of a trimethylphosphine ligand is the first possible step. The C−F bond activation is promoted by the nucleophilicity of the active electron-rich low-valent $Fe(PMe_3)_3$. Selective oxidative addition of the C−F bond of perfluorotoluene at the *para* position at the Fe(0) center occurs to give rise to intermediate **1b**. The radical $FPMe_3$ formed through one-electron reductive elimination disproportionates to PMe_3 and F_2PMe_3 with the formation of the final product **1**. The calculation showed that this process is thermodynamically favorable.[28] The formation of F_2PMe_3 in solution was confirmed via ^{19}F and ^{31}P NMR.[29]

It is important to note that the *para* C−F bond was activated for both perfluorotoluene and perfluoropyridine. This is consistent with our early reports on C−F bond activation with $Co(PMe_3)_4$.[22,24] Because the C−F bond activation is realized by nucleophilic attack by $Fe(PMe_3)_3$ with the assistance of PMe_3, the C−F bond activation occurs only at the *ortho* or *para* position in both perfluorotoluene and perfluoropyridine with electron-withdrawing groups (CF_3 group in perfluorotoluene and N atom in pyridine). Obviously, the 3,4-position π-coordination is better than 1,2-position π coordination in terms of both electronegativity and stereochemistry. In addition, the DFT calculations on the mechanism of the C−F bond activation of perfluorotoluene by $Co(PMe_3)_4$ indicated that *para* C−F bond activation is preferred.[28]

Interestingly, the reaction of perfluoronaphthalene with $Fe(PMe_3)_4$ is completely different from the aforementioned reactions (eq 1). Under similar reaction conditions, a π-coordinated Fe(0) complex, $(\eta^4\text{-}1,2,3,4\text{-}C_{10}F_8)Fe(PMe_3)_3$ (**4**), was confirmed (eq 2). Complex **4** is stable in air for more than 1/2 h. The expected C−F bond activation product was not found on extending the reaction time (48 h) or increasing the reaction temperature (50 °C). The 18-valence-electron configuration of penta-coordinate iron(0) species confers upon complex **4** this stability. In the infrared spectrum of complex **4** the characteristic $\rho(PMe_3)$ band was recorded at 948

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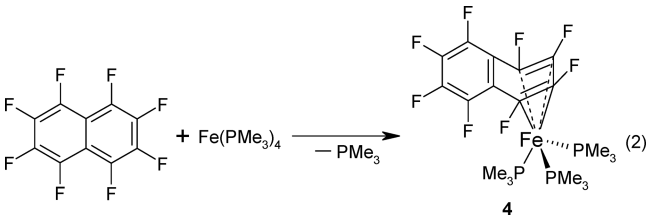

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cm^{-1}. In the ^{1}H NMR spectrum, the proton resonances of the PMe_3 groups were recorded at 1.31 ppm as a pseudotriplet and 1.40 ppm as a doublet in the ratio of 2:1. The ^{31}P NMR signals are observed at 18.3 and 20.1 ppm as multiplets with an integration ratio of 2:1. In the ^{19}F NMR spectra the resonances at −200.5, −195.6, −163.8, and −154.4 ppm were registered in the integration ratio of 1:1:1:1. This indicates that the eight fluorine atoms of perfluoronaphthalene are divided into four types after η^4-coordination. However, in free perfluoronaphthalene there are two types of fluorine atoms.

In the molecular structure of complex **4** the iron atom is coordinated with a η^4-1,2,3,4-perfluoronaphthalene molecule and three trimethylphosphine ligands (Figure 2). The

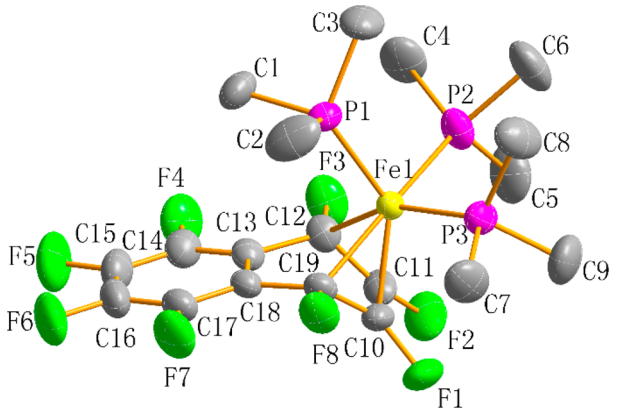
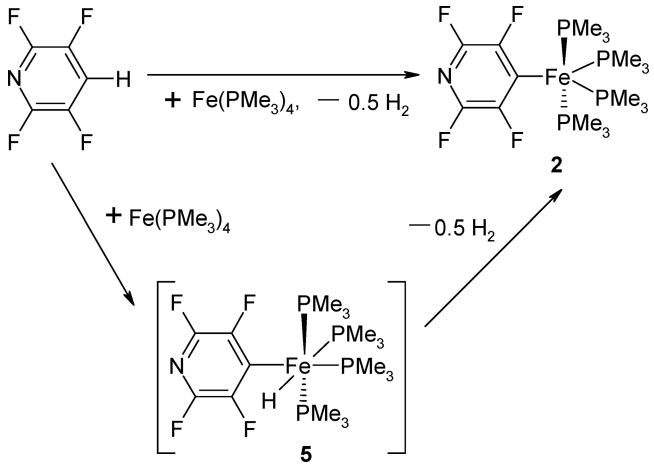


Figure 2. Molecular structure of **4** (all of the hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Fe1−C10 2.003(2), Fe1−C11 1.994(2), Fe1−C12 2.068(2), Fe1−C19 2.075(2), Fe1−P1 2.2231(6), Fe1−P3 2.2398(6), Fe1−P2 2.2536(6); C11−Fe1−P1 141.03(7), C19−Fe1−P1 90.90(6), C11−Fe1−P3 116.83(7), C19−Fe1−P3 97.85(6), P1−Fe1−P3 99.01(2), C11−Fe1−P2 95.89(7), P1−Fe1−P2 96.83(3), P3−Fe1−P2 93.31(2).

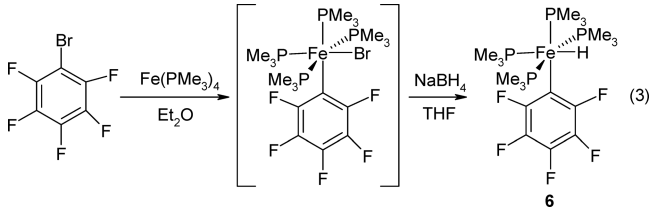
configuration of complex **4** can be considered as a distorted-trigonal-bipyramidal coordination geometry with P2 and the midpoint of the C10−C19 bond in the axial positions, while P1, P3, and the midpoint of the C11−C12 bond are in the triangular plane. Owing to the η^4-coordination, the deviation of the plane [C19−C10−C11−C12] from the original naphthylene ring is 44.97(9)°. The distance from the central iron atom to this plane is 1.6047 Å. Owing to the η^4-1,2,3,4-coordination of the naphthylene molecule the corresponding four C−F bonds (F1−C10 = 1.363(3), F2−C11 = 1.367(2), F3−C12 = 1.392(2), and F8−C19 = 1.380(2) Å) are longer than the other four C−F bonds (F4−C14 = 1.349(3), F5−C15 = 1.346(3), F6−C16 = 1.346(3), and F7−C17 = 1.348(3) Å). For the same reasons, the bond distances C10−C11 (1.373(3) Å), C11−C12 (1.429(3) Å), C12−C13 (1.481(3) Å), C18−C19 (1.482(3) Å), and C10−C19 (1.425(3) Å) are longer than the related bond distances C15−C16 (1.356(4) Å), C14−C15 (1.380(3) Å), C13−C14 (1.379(3) Å), C17−C18 (1.376(3) Å), and C16−C17 (1.385(3) Å). According to this configuration, the eight fluorine atoms can actually be divided into four different types: F1 and F2; F3 and F8; F4 and F7; F5 and F6. This result is consistent with the analysis of NMR data. Owing to this η^4-coordination the four C−F bonds C10−F1 (1.363(3) Å), C11−F2 (1.367(2) Å), C12−F3 (1.392(2) Å), and C19−F8 (1.380(2) Å) were activated because they are obviously longer than the other four C−F bonds C14−F4 (1.349(3) Å), C15−F5 (1.346(3) Å), C16−F6 (1.346(3) Å), and C17−F7 (1.348(3) Å). The Fe−P and Fe−C distances are both in the normal regions.

Selective C−H Bond Activation of 2,3,5,6-Tetrafluoropyridine. The reaction of $Fe(PMe_3)_4$ with 2,3,5,6-tetrafluoropyridine (pK_a = −10.94) in pentane at room temperature selectively gave rise to the C−H bond activation product **2** with release of hydrogen (Scheme 2). Hydride complex **5** as the expected intermediate was not isolated.

Scheme 2



Synthesis of Pentafluorophenyl Iron Hydride Complex 6. The reaction of pentafluorobenzene with $Fe(PMe_3)_4$ also failed to give the corresponding hydrido iron complex **6**. A hydrido cobalt intermediate as a possible C−H bond activation product in the study of selective C−F/C−H bond activation of C_6F_5H with $Co(PMe_3)_4$ was proposed on the basis of the observation of *in situ* IR and ^{1}H NMR spectra, but an experiment to isolate the hydrido cobalt intermediate also failed.[23] Except for the C−H activation pathway, direct reduction is also feasible in synthesizing metal hydrides according to refs 30 and 31. The reaction of bromopentafluorobenzene with $Fe(PMe_3)_4$ in diethyl ether at room temperature gave a red solution. The solvent was then changed to THF, and $NaBH_4$ was added. Yellow crystals of complex **6** could be obtained from pentane at −20 °C in a yield of 80% (eq 3).



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The ν(Fe−H) stretching band of complex **6** was found at 1952 cm^{-1} in the IR spectrum, and the hydrido signal as a multiplet was found at −12.94 ppm in the ^{1}H NMR spectrum. Three ^{31}P NMR resonances (22.9, 19.3, and 5.98 ppm) showed the four PMe_3 ligands in a ratio of 2:1:1. In the ^{19}F NMR spectrum, four signals (−95.40, −99.35, −163.99, and −164.80 ppm) in a ratio of 1:1:2:1 indicate the five fluorine atoms.

The molecular structure of complex **6** confirms a hexacoordinate octahedral geometry in the crystals (Figure 3). The iron atom is located at the center of the octahedron.

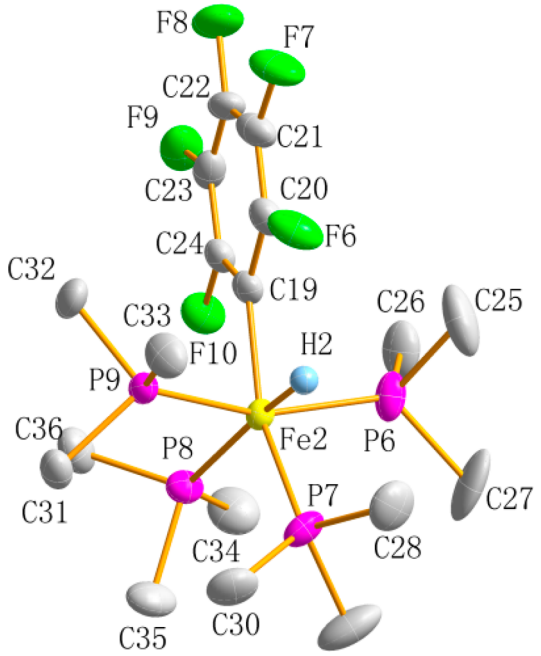


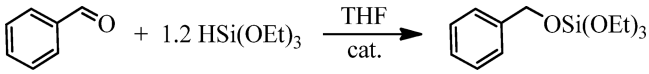
Figure 3. Molecular structure of **6** (most of the hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Fe2−P6 2.231(2), Fe2−P7 2.212(1), Fe2−P9 2.227(1), Fe2−P8 2.257(2), Fe2−C19 2.055(4), Fe2−H2 1.42(4); P8−Fe2−H2 170.5(14), P9−Fe2−P6 160.02(5), C19−Fe2−P7 160.06(12), C19−Fe2−H2 85.8(13), C9−Fe2−H2 81.9(14), C6−Fe2−H2 82.8(14).

When P8−Fe2−H2 (170.5(14)°) is designated as the axial direction, iron and the four atoms [C19−P9−P7−P6] are in the equatorial plane. The Fe1−H1 distance (1.42 Å) is in the normal region,[32] and the Fe−H bond lies in the plane of the pentafluorobenzene. Fe2−P8 (2.257(2) Å) is slightly longer than the other three Fe−P bonds (Fe2−P6 = 2.231(2), Fe2−P7 = 2.212(1), Fe2−P9 = 2.227(1) Å) because of the strong *trans*-influence of the hydrido ligand.

Catalytic Application of Complexes 1−4 and 6 in Hydrosilylation of Aldehydes and Ketones. Iron complexes, especially iron hydrides, are involved in many chemical processes, such as polymerization, insertion, addition, and reduction. Recently, there have been some examples of iron hydrides as catalysts in reduction reactions.[33−36] Guan reported a catalytic hydrosilylation of carbonyl compounds by hydrido [PCP]-pincer iron complexes.[37] The hydrogenation of ketones by an iron catalyst under low hydrogen pressure with high chemoselectivity at room temperature was disclosed by Casey.[38] The selective hydrogenation of alkyne to *trans*-alkene and selective reduction of the carbonyl group of α,β-unsaturated ketones were realized with iron hydries by Bianchini's group.[39,40] Several reports on hydrosilylation with iron hydrides as catalysts were published.[41] Recently, we have found that several pincer iron(II) hydrides and bidentate iron(II) hydrides can be used as catalysts in the reduction of carbonyl groups with triethyloxysilane as the reduction reagent.[42−47] As a continuation of our study in this direction, complexes **1**−**4** and **6** were used as catalysts to explore their performance in the hydrosilylation of carbonyl compounds.

It can be seen from Table 1 that with complex **6** as catalyst $(EtO)_3SiH$ is the best hydrogen source among the tested

Table 1. Different Silanes as Hydrogen Sources with 1−4 and 6 as Catalysts[a]



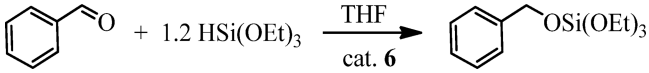
entry	cat.	hydrogen source	time (h)	*yield*[b] (%)
1	**6**	$(EtO)_3SiH$	3	94
2	**6**	Et_3SiH	3	37
3	**6**	Ph_3SiH	3	0
4	**6**	Me_2PhSiH	3	0
5	**6**	Ph_2SiH_2	3	71
6	**6**	$PhSiH_3$	3	89
7	**6**	TMDS	3	23
8	**6**	PMHS	3	0
9	**1**	$(EtO)_3SiH$	3	48
10	**1**	$(EtO)_3SiH$	7	93
11	**2**	$(EtO)_3SiH$	3	33
12	**2**	$(EtO)_3SiH$	12	98
13	**3**	$(EtO)_3SiH$	3	33
14	**3**	$(EtO)_3SiH$	10	93
15	**4**	$(EtO)_3SiH$	3	83
16	**4**	$(EtO)_3SiH$	20	94

[a]Catalytic reaction conditions: PhCHO (1.0 mmol), $(EtO)_3SiH$ (1.2 mmol), *n*-dodecane (internal standard) (1.0 mmol), THF (2 mL), catalyst (0.5 mol %). [b]Determined by GC analysis.

silanes. Although complexes **1**−**4** could also catalyze this process, their activities are relatively weak because the transformation needed a longer time.

As shown in Table 2, the reaction conditions of hydrosilylation reactions catalyzed by iron hydrido complex **6** were

Table 2. Optimization of Reaction Conditions for Hydrosilylation[a]



entry	amt of cat. (mol %)	*T* (°C)	conversion (%)[b]
1	1	60	>99
2	1	40	>99
3	0.5	40	>99
4	0.3	40	96
5	0.1	40	25

[a]Reaction conditions: 0.5 mmol of benzaldehyde, 0.6 mmol of $HSi(OEt)_3$, 2 mL of THF, 3 h. [b]GC conversion.

optimized. With a 0.5 mol % catalyst loading of **6**, the reaction was complete in 3 h in THF at 40 °C (entry 3). Further decrease of the catalyst loading reduced the conversion (entries 4 and 5).

In accord with the optimized reaction conditions, complex **6** was chosen as the catalyst. The scope of the reduction of

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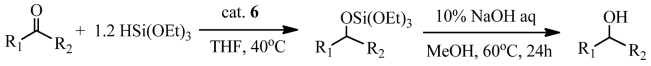
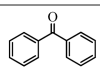
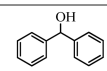
aldehydes and ketones is shown in Table 3. With aldehydes as substrates, the yields are good. The molecules containing

Table 3. Scope of Hydrosilylation Reactions[a]



Entry	Substrates	Products	Cat./mol%	t/h	Yields/%[b]
1			0.5	3	92
2			0.5	3	95
3			0.5	6	94
4			0.5	6	99
5			3	3	85
6			3	3	90
7			3	7	97
8			3	7	95
9			3	7	91
10			3	7	81
11			3	7	83
12			3	24	55[c]
13			3	24	80
14			3	24	64
15			3	24	68[c]
16			3	24	54

[a]Reaction conditions: 0.5 mmol of substrate, 0.6 mmol of $HSi(OEt)_3$, 2 mL of THF, reacted at 40 °C. Then 3 mL of methanol and 1 mL of 10% NaOH(aq) were added, reacted at 60 °C for 24 h. [b]Isolated yields. [c]GC yields.

electron-withdrawing groups need longer reaction times (entries 3 and 4) or higher catalyst loadings (entries 6–8). For ketones, even with 3 mol % of catalyst and reaction for 24 h, the yields are still moderate. This catalytic system is also suitable for an aliphatic aldehyde (entry 5), but the yield is moderate. The scope of this catalytic system could be extended to other aromatic compounds bearing functional reducible groups, such as nitro, nitrile, ester, etc. (entries 9–11).

α,β-Unsaturated aldehydes and ketones are also applicable to this catalytic system (Table 4). An electron-withdrawing group on the benzene ring influenced the reaction negatively (entry 6). These results showed that the reductions occurred selectively at the carbonyl groups and the C═C bond remained unchanged. The selectivity of the reduction of C═C and C═O bonds is always regarded as a challenge for *α,β*-

Table 4. Hydrosilylation of Unsaturated Aldehydes[a]

Entry	Substrates	Products	Yields/%[b]
1			88
2			85
3			87
4			82
5			85
6			73
7[c]			81
8[d]			79
9[e]			90

[a]Reaction conditions unless specified otherwise: 0.5 mmol of substrate, 0.6 mmol of $HSi(OEt)_3$, 2 mL of THF, catalyst loading 2 mol %, 3 h, at 40 °C. Then 3 mL of methanol and 1 mL of 10% NaOH(aq) were added, reacted at 60 °C for 24 h. [b]Isolated yields. [c]With *α*-bromocinnamaldehyde as substrate, the product is 3-phenyl-2-propyn-1-ol because the elimination of HBr occurred during the basic hydrolysis. [d]Catalyst loading 3 mol %, 24 h, at 40 °C. [e]Catalyst loading 3 mol %, 24 h, at 40 °C, GC yield.

unsaturated aldehydes and ketones. In the literature,[48] most reports on the reduction of *α,β*-unsaturated aldehydes and ketones detail the selective reduction of the C═C bonds with the C═O bonds unchanged. Obviously, complex **6** is a good catalyst for the selective reduction of C═O bonds of *α,β*-unsaturated aldehydes and ketones. This selectivity is similar to that of our earlier reported system.[46] Regrettably, the yields (Table 4) are not as good as those of Beller with fluoro(tris(2-(diphenylphosphino)phenyl)phosphino)iron tetrafluoroborate as catalyst.[49]

CONCLUSIONS

In summary, the three novel perfluorinated aryl iron(I) complexes **1**–**3** were synthesized through C–F bond activation by the reaction of perfluorinated toluene, pyridine, and benzene with $Fe(PMe_3)_4$. Under similar reaction conditions, the reaction of $Fe(PMe_3)_4$ with perfluoronaphthalene ($C_{10}F_8$) afforded a stable *π*-coordinated Fe(0) complex, (η^4-1,2,3,4-$C_{10}F_8$)$Fe(PMe_3)_3$ (**4**). The expected C–F bond cleavage reaction was not observed. The complex (4-C_5NF_4)$Fe(PMe_3)_4$ (**2**) could also be obtained from the selective C–H bond activation of 2,3,5,6-pentafluoropyridine with $Fe(PMe_3)_4$. The iron hydride (C_6F_5)$FeH(PMe_3)_4$ (**6**) could be obtained from the reaction of pentafluorophenyl bromide with $Fe(PMe_3)_4$ in

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the presence of $NaBH_4$ in a yield of 80%. Complexes **1**−**4** and **6** could be used as catalysts for the hydrosilylation of carbonyl compounds. Among them, complex **6** is the best catalyst. The selective reduction of the carbonyl groups of α,β-unsaturated aldehydes and ketones was also realized with **6** as catalyst.

EXPERIMENTAL SECTION

General Procedures and Materials. Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Solvents were dried by known procedures and distilled under nitrogen before use. Literature methods were used in the preparation of $Fe(PMe_3)_4$.[50] $CF_3C_6F_5$, C_5NF_5, C_6F_6, and $C_{10}F_8$ were obtained from ABCR. All other chemicals were used as purchased. Infrared spectra (4000−400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker ALPHA FT-IR spectrometer. The *in situ* IR was carried out on a METTLER TOLEDO React IR IC 15 instrument. ^1H, ^{31}P, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker Avance 300, Bruker Avance 400, and Bruker Avance 500 MHz spectrometers. ^{31}P and ^{13}C NMR resonances were obtained with broad-band proton decoupling. Elemental analyses were carried out on an Elementar Vario EL III instrument. GC-MS were recorded on a TRACE-DSQ instrument.

Caution! $(EtO)_3SiH$ is flammable and highly toxic by inhalation and may cause skin irritation and blindness. Even though during our studies on the dehydration of amides we used it without incident, triethoxysilane should be used with precaution. Indeed, due to possible silane disproportionation, the formation of an extremely pyrophoric gas (possibly SiH_4) has led to several fires and explosions, as reported in the literature.[51]

Synthesis of Complex 1. A solution of $Fe(PMe_3)_4$ (1.00 g, 2.70 mmol) in 50 mL of pentane was combined with a solution of $CF_3C_6F_5$ (0.63 g, 2.70 mmol) in pentane (30 mL) at −80 °C. The reaction mixture was warmed to ambient temperature and stirred for 18 h. During this period the pale yellow mixture turned brown-yellow. The reaction mixture was filtered. Crystallization from pentane at −4 °C afforded red single crystals of **1** (0.75 g, 48%). Anal. Found (calcd) for **1**, $C_{19}H_{36}FeF_7P_4$, 577.21 g/mol: C, 39.33 (39.54); H, 5.99 (6.29). IR (Nujol, cm^{-1}): 1609, 1561 ν(C═C); 938 $\rho(PMe_3)$.

Synthesis of Complex 2. A solution of $Fe(PMe_3)_4$ (1.20 g, 3.30 mmol) in 50 mL of pentane was combined with a solution of C_5NF_5 (0.55 g, 3.30 mmol) in pentane (30 mL) at −80 °C. The reaction mixture was warmed to ambient temperature and stirred for 18 h. During this period the pale yellow mixture turned brown-yellow. The reaction mixture was filtered. Crystallization from pentane at −4 °C afforded red single crystals of **2** (0.89 g, 53%). Anal. Found (calcd) for **2**, $C_{17}H_{36}FeF_4P_4$, 510.20 g/mol: C, 39.77 (40.02); H, 7.00 (7.11); N, 2.70 (2.75). IR (Nujol, cm^{-1}): 1607, 1589 ν(C═C); 933 $\rho(PMe_3)$.

Synthesis of Complex 3. A solution of $Fe(PMe_3)_4$ (1.10 g, 3.00 mmol) in 50 mL of pentane was combined with a solution of C_6F_6 (0.60 g, 3.00 mmol) in pentane (30 mL) at −80 °C. The reaction mixture was warmed to ambient temperature and stirred for 18 h. During this period the pale yellow mixture turned brown-yellow. The reaction mixture was filtered. Crystallization from pentane at −4 °C afforded red single crystals of **3** (0.40 g, 25%). Anal. Found (calcd) for **3**, $C_{18}H_{36}FeF_5P_4$, 527.20 g/mol: C, 41.20 (41.01); H, 6.72 (6.88). IR (Nujol, cm^{-1}): 1555 ν(C═C); 948 $\rho(PMe_3)$.

Synthesis of Complex 4. A solution of $Fe(PMe_3)_4$ (0.60 g, 1.70 mmol) in 50 mL of pentane was combined with a solution of $C_{10}F_8$ (0.50 g, 1.70 mmol) in pentane (30 mL) at −80 °C. The reaction mixture was warmed to ambient temperature and stirred for 18 h. During this period the pale yellow mixture turned brown-yellow. The reaction mixture was filtered. Crystallization from pentane at −4 °C afforded red single crystals of **4** (0.60 g, 62%). Anal. Found (calcd) for **4**, $C_{19}H_{27}FeF_8P_3$, 556.17 g/mol: C, 41.22 (41.03); H, 4.97 (4.89). IR (Nujol, cm^{-1}): 1625 ν(C═C); 948 $\rho(PMe_3)$. ^1H NMR (300 MHz, acetone-d_6, 300 K): δ 1.31 (t′, 18H, $|^2J(PH) + {}^4J(PH)|$ = 6 Hz, PCH_3), 1.40 (d, $^2J(PH)$ = 6 Hz, 9H, PCH_3). ^{31}P NMR (121.4 MHz, acetone-d_6, 297 K): δ 18.3 (m, 2P, PCH_3), 20.1 (m, 1P, PCH_3). ^{19}F NMR (282 MHz, acetone-d_6, 300 K): δ −154.4 (m, 2F, CF_{arom}), −163.8 (m, 2F, CF_{arom}), −195.6 (m, 2F, CF_{arom}), −200.5 (m, 2F, CF_{arom}). ^{13}C NMR (100 MHz, $(CD_3)_2CO$, 298 K): δ 20.78 (dt, $^1J(PC)$ = 23 Hz, $^3J(PC)$ = 2 Hz, PCH_3), 21.84 (t′, $|^1J(PC) + {}^3J(PC)|$ = 24 Hz, PCH_3), 93.34 (m, $^1J(FC)$ = 194 Hz, Ar−C), 120.14 (m, $^1J(FC)$ = 242 Hz, Ar−C), 125.04 (m, Ar−C), 135.73 (m, $^1J(FC)$ = 232 Hz, Ar−C), 140.58 (m, $^1J(FC)$ = 229 Hz, Ar−C).

Synthesis of Complex 6. A solution of $Fe(PMe_3)_4$ (0.77 g, 2.1 mmol) in 30 mL of diethyl ether was combined with a solution of bromopentafluorobenzene (0.39 g, 2.1 mmol) in diethyl ether (20 mL) at room temperature. The reaction mixture was stirred for 3 h. Then the solvent was changed to THF and $NaBH_4$ (0.19 g, 5 mmol) was added. During this period the red solution turned light yellow. The THF was removed, and the solid was extracted by pentane. Crystallization from pentane at −20 °C afforded yellow single crystals of **6** (0.89 g, 80%). Anal. Found (calcd) for **6**, $C_{18}H_{37}FeF_5P_4$, 528.21 g/mol: C, 41.27 (40.93); H, 6.89 (7.06). IR (Nujol, cm^{-1}): 1952, ν(Fe−H); 1614, 1585 ν(C═C); 940, $\rho(PMe_3)$. ^1H NMR (300 MHz, benzene-d_6, 300 K): δ −12.94 (m, 1H, Fe-*H*), 0.97 (s, 18H, PCH_3), 1.13 (s, 9H, PCH_3), 1.26 (s, 9H, PCH_3). ^{31}P NMR (121.4 MHz, benzene-d_6, 300 K): δ 22.9 (t, $^2J_{PP}$ = 40 Hz, 2P, PCH_3), 19.3 (s, 1P, PCH_3), 5.98 (m, 1P, PCH_3). ^{19}F NMR (282 MHz, benzene-d_6, 300 K): δ −95.40 (1F, CF_{arom}), −99.35 (1F, CF_{arom}), −163.99 (2F, CF_{arom}), −164.80 (1F, CF_{arom}).

General Procedure for the Catalytic Hydrosilylation of Aldehydes and Ketones. By standard Schlenk techniques, the aldehyde or ketone (0.5 mmol), $(EtO)_3SiH$ (0.6 mmol), and the corresponding amount of complex **6** in THF were combined. Then 2 mL of THF was added. The reaction mixture was stirred at 40 °C. To the reaction mixture was then added MeOH (3 mL) and a 10% aqueous solution of NaOH (1 mL) with vigorous stirring at 60 °C for about 24 h. The organic product was extracted with Et_2O (15 mL × 3), dried over anhydrous $MgSO_4$, and concentrated under vacuum. The alcohol product was further purified by silica column chromatography (with petroleum/ethyl acetate 10/1 as eluent). Finally, all products were confirmed by ^1H NMR.

X-ray Structure Determinations. Intensity data were collected on a STOE STADI VARI diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic. Each hydride was located directly from the difference map and the position refined. The remaining H atoms were either located or calculated and subsequently treated with a riding model. CCDC-946453 (**2**), CCDC-871948 (**4**), and CCDC-1483882 (**6**) contain supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax(+44)1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

Crystallographic data of complex **2**: $C_{17}H_{36}F_4FeNP_4$, 510.20 g/mol, 0.22 × 0.20 × 0.18 mm, monoclinic, $P2_1/n$, a = 9.3973(19) Å, b = 16.146(3) Å, c = 15.785(3) Å, β = 91.16(3)°, V = 2394.6(8) Å^3, T = 293(2) K, Z = 4, D_{calc} = 1.415 Mg/m^3, μ = 0.931 mm^{-1}, data collection range 2.50 < 2θ < 27.54°, $-12 \le h \le 12$, $-19 \le k \le 20$, $-20 \le l \le 20$, no. of unique data 5470 (R(int) = 0.0210), parameters 256, GOF on F^2 1.041, R1 ($I > 2\sigma(I)$) = 0.0293, wR2 = 0.0821 (all data).

Crystallographic data of complex **4**: $C_{19}H_{27}F_8FeP_3$, 556.17 g/mol, 0.15 × 0.12 × 0.10 mm, orthorhombic, *Pbca*, a = 12.8431(8) Å, b = 11.9957(7) Å, c = 30.6007(19) Å, V = 4714.4(5) Å^3, T = 273(2) K, Z = 8, D_{calc} = 1.567 Mg/m^3, μ = 0.911 mm^{-1}, data collection range 1.33< 2θ < 25.05°, $-15 \le h \le 15$, $-14 \le k \le 14$, $-36 \le l \le 34$, no. of unique data 4180 (R(int) = 0.0262), parameters 281, GOF on F^2 1.079, R1 ($I > 2\sigma(I)$) = 0.0279, wR2 = 0.0745 (all data).

Crystallographic data of complex **6**: $C_{18}H_{37}F_5FeP_4$, 528.21 g/mol, 0.15 × 0.10 × 0.08 mm, monoclinic, $P2_1/c$, a = 23.694(8) Å, b = 12.609(3) Å, c = 18.059(5) Å, β = 112.301(2)°, V = 4992(2) Å^3, T = 173(2) K, Z = 8, D_{calc} = 1.406 Mg/m^3, μ = 0.900 mm^{-1}, data collection range 2.78< 2θ < 27.46°, $-27 \le h \le 28$, $-14 \le k \le 14$, $-21 \le l \le 21$, no. of unique data 8621 (R(int) = 0.0483), parameters 534, GOF on F^2 1.043, R1 ($I > 2\sigma(I)$) = 0.0397, wR2 = 0.0929 (all data).

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00546.

Original IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and ^{19}F NMR spectra of the complexes and the catalytic products (alcohols) and ball and stick representations of complexes **1** and **3** (PDF)

Cartesian coordinates of complexes **1** and **3** (XYZ)

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Notes

The authors declare no competing financial interest.

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