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C–H Bond Activation/Borylation of Furans and Thiophenes Catalyzed by a Half-Sandwich Iron N-Heterocyclic Carbene Complex

Tsubasa Hatanaka, Yasuhiro Ohki,* and Kazuyuki Tatsumi*[a]

Abstract: A coordinatively unsaturated iron-methyl complex having an N-heterocyclic carbene ligand, [Cp*Fe(L^{Me})Me] (**1**; Cp* = η^5-C_5Me_5, L^{Me} = 1,3,4,5-tetramethyl-imidazol-2-ylidene), is synthesized from the reaction of [Cp*Fe(TMEDA)Cl] (TMEDA = N,N,N′,N′-tetramethylethylenediamine) with methyllithium and L^{Me}. Complex **1** is found to activate the C–H bonds of furan, thiophene, and benzene, giving rise to aryl complexes, [Cp*Fe(L^{Me})(aryl)] (aryl = 2-furyl (**2**), 2-thienyl (**3**), phenyl (**4**)). The C–H bond cleavage reactions are applied to the dehydrogenative coupling of furans or thiophenes with pinacolborane (HBpin) in the presence of *tert*-butylethylene and a catalytic amount of **1** (10 mol% to HBpin). The borylation of the furan/thiophene or 2-substituted furans/thiophenes occurs exclusively at the 2- or 5-positions, respectively, whereas that of 3-substituted furans/thiophenes takes place mainly at the 5-position and gives a mixture of regioisomers. Treatment of **2** with 2 equiv of HBpin results in the quantitative formation of 2-boryl-furan and the borohydride complex [Cp*Fe(L^{Me})(H_2Bpin)] (**5**). Heating a solution of **5** in the presence of *tert*-butylethylene led to the formation of an alkyl complex [Cp*Fe(L^{Me})CH_2CH_2tBu] (**6**), which was found to cleave the C–H bond of furan to produce **2**. On the basis of these results, a possible catalytic cycle is proposed.

Keywords: borylation · C–H activation · hydrocarbons · iron · N-heterocyclic carbenes

Introduction

The development of the efficient derivatization of hydrocarbons is one of the most important goals for chemistry.[1] In this regard, considerable attention has been paid to the activation of C–H bonds carried out by transition-metal complexes.[1,2] Although some interesting catalytic C–H bond activation reactions have been reported,[3] the first example of a highly efficient and selective C–H bond transformation was the ruthenium-catalyzed hydroarylation of olefins.[4] The vast majority of existing C–H bond activation catalysts use noble metals, such as Ru, Rh, Ir, Pd, and Pt. Thus the ability to use cheaper, less toxic, abundant metals, particularly Fe, remains an elusive challenge in this field.[5]

There are two notable examples of iron-catalyzed aromatic C–H bond activations. Jones et al. have reported that a zero-valent iron complex [$Fe(PMe_3)_2(CNCH_2t$Bu$)_3$] catalyzes the insertion of $CNCH_2t$Bu into a C–H bond of benzene under irradiation, resulting in the formation of aldimine PhCH=NCH_2tBu.[6] Nakamura et al. have recently achieved the direct arylation of phenyl pyridines or aryl imines catalyzed by [$Fe(acac)_3$] with chelating ligand (1,10-phenanthroline or 4,4′-di-*tert*-butyl-2,2′-bipyridine), although this reaction requires stoichiometric amounts of PhMgBr, $ZnCl_2$·TMEDA, and 1,2-dichloro-2-methylpropane.[7] In this paper, we report the catalytic C–H bond activation/borylation of furans and thiophenes carried out by a half-sandwich iron complex of the methyl-substituted N-heterocyclic carbene (denoted as L^{Me}). The catalyst is a newly synthesized coordinatively unsaturated iron complex, [Cp*Fe(L^{Me})Me] (**1**; Cp* = η^5-C_5Me_5, L^{Me} = 1,3,4,5-tetramethyl-imidazol-2-ylidene). This complex is related to complex **A** in Scheme 1, which we have previously reported as capable of the stoichiometric C–H bond activation and borylation of heteroarenes.[8] We have also conducted a series of reactions of the

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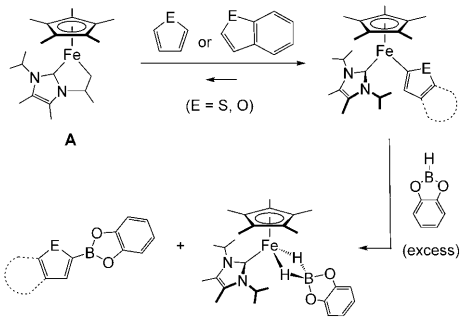


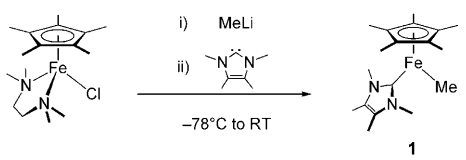
Scheme 1.

new iron complexes with nearly stoichiometric amount of substrate, to gain mechanistic insights.

Results and Discussion

Synthesis and Structure of [Cp*Fe(L^{Me})Me] (1)

The amide ligand, $N(SiMe_3)_2$, acts as a base, and we have previously demonstrated that $Fe\{N(SiMe_3)_2\}_2$ reacts readily with thiols and serves as a convenient precursor for the synthesis of iron bis-thiolate complexes and iron thiolate/sulfide clusters.[9] We have also reported that the reaction of [Cp*Fe{$N(SiMe_3)_2$}][10] with the mesityl-substituted imidazolium salt (HL^{Mes})(Cl) (L^{Mes} = 1,3-dimesityl-imidazol-2-ylidene) followed by treatment with methyllithium gives rise to [Cp*Fe(L^{Mes})Me].[8] However, an analogous reaction of [Cp*Fe{$N(SiMe_3)_2$}] with the methyl-substituted imidazolium salt, (HL^{Me})(Cl), resulted in the formation of a complex mixture, and this pathway did not appear promising for the synthesis of [Cp*Fe(L^{Me})Me] (**1**). Alternatively, the reaction of [Cp*Fe(TMEDA)Cl] (TMEDA = N,N,N′,N′-tetramethylethylenediamine)[11] with methyllithium at −78 °C followed by addition of L^{Me} at 0 °C led to the formation of a dark orange solution, from which **1** was isolated as orange crystals in 54 % yield (Scheme 2). Complex **1** is sensitive to air/moisture and, thus, needs to be handled under inert conditions. However **1** is thermally stable in solution and only gradually decomposes over several days in boiling [D_{18}]octane. The paramagnetic nature of **1** was indicated by the analysis of the ^{1}H NMR spectrum in which the methyl signals for Cp* and L^{Me} were observed at δ = 41.8 (Cp*), 8.4 (L^{Me}) and −47.5 ppm (L^{Me}). We were not able to find the signal assignable to Fe−CH_3 in the region from −500 to +500 ppm.



Scheme 2.

Single crystals of **1** were grown from a concentrated hexane solution, and the molecular structure was determined by X-ray diffraction. There are two independent molecules in the asymmetric unit. Their structures are nearly identical, so that the following discussion is based on one molecule shown in Figure 1. Complex **1** is a 16-electron Fe^{II}

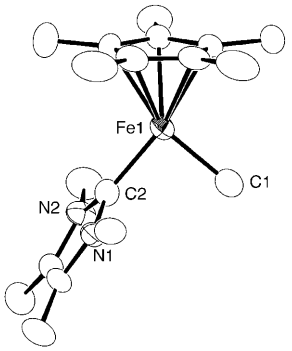
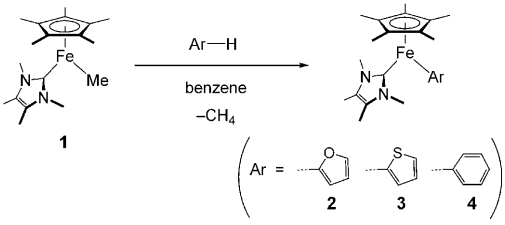


Figure 1. Molecular structure of **1** with thermal ellipsoids at the 50 % probability level. One of two molecules found in the asymmetric unit is shown. Selected bond distances (Å) and angles (°) for **1**: Fe(1)−C(1) = 1.978(5), Fe(1)−C(2) = 1.935(3), C(2)−N(1) = 1.363(5), C(2)−N(2) = 1.368(4), C(1)-Fe(1)-C(2) = 90.1(2), N(1)-C(2)-N(2) = 103.3(2).

complex coordinated by Cp*, L^{Me}, and CH_3 ligands. The plane consisting of the iron atom, methyl carbon, and carbene carbon of L^{Me}, is nearly perpendicular to the Cp* plane, with an inter-plane angle of 94.53(11)°. The Fe−C(L^{Me}) bond length of 1.935(3) Å and the Fe−CH_3 bond of 1.978(5) Å are comparable to those for the analogous complex [Cp*Fe(L^{Mes})Me] (Fe−C(L^{Mes}) 1.931(2) Å; Fe−CH_3 2.009(2) Å). On the other hand, they are slightly shorter than those for electronically saturated iron complexes, 1.949(10)–2.007(5) Å for Fe−C(L^{Me})[12] and 2.034(4)–2.130(6) Å for Fe−CH_3.[13]

C−H Bond Activation of Furan, Thiophene, and Benzene

Complex **1** was found to activate the C−H bonds of furan, thiophene, and benzene, providing the 2-furyl, 2-thienyl, and phenyl complexes **2**–**4**, respectively (Scheme 3). In the case of the reactions with furan and thiophene, complexes **2** and **3** were produced stoichiometrically at room temperature (**2**) or 60 °C (**3**) according to NMR, whereas the isolated crystalline yields were 74 % (**2**) and 53 % (**3**). However, the reaction with benzene required 7 days at 80 °C and gave the



Scheme 3.

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phenyl complex **4** in only 40% yield by NMR (36% isolated crystalline yield). Interestingly, the 2-furyl or 2-thienyl complexes **2** or **3** were selectively prepared from benzene solutions. This is indicative of much slower C–H bond activation of benzene than those of furan and thiophene. In the reactions illustrated in Scheme 3, the methyl ligand abstracts a hydrogen atom from the arenes, and is liberated as methane, which was detected in the ^{1}H NMR spectra of the reaction mixtures. The ^{1}H NMR spectra of complexes **2**–**4** are similar, exhibiting broad signals in the ranges of $\delta = 50.1$–47.0 (Cp*), 8.6–7.6 (L^{Me}), and -38.3–-42.4 ppm (L^{Me}). Interestingly, the NMR data demonstrates that complexes **2** and **3** were formed as single isomers, hence the regio-selective C–H bond activation of furan and thiophene occurred at the 2-position. The X-ray diffraction established the molecular structures of **3** and **4**, as shown in Figure 2 (selected bond distances and angles are listed in Table 1). A low quality

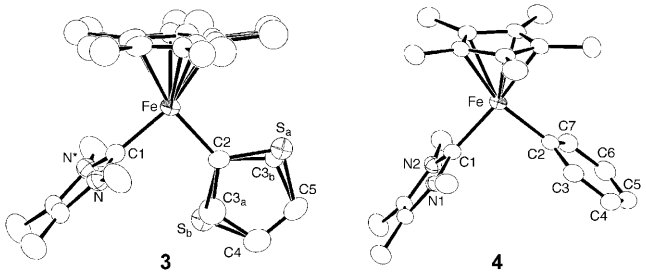
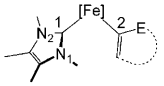


Figure 2. Molecular structures of **3** and **4** with thermal ellipsoids at the 50% probability level.

Table 1. Selected bond distances (Å) and angles (°) for complexes **3** and **4**.[a]

	3	**4**
Fe–C(1)	1.935(4)	1.9403(18)
Fe–C(2)	1.973(4)	1.9613(17)
C(1)–N(1)	1.360(3)	1.363(2)
C(1)–N(2)	–	1.359(2)
C(1)-Fe-C(2)	92.46(17)	92.64(7)
N(1)-C(1)-N(2)	103.3(3)	103.50(15)
	Dihedral Angle	
C(1)-Fe-C(2)/aryl	0	85.19(5)

[a] Labeling scheme as shown. [Fe] = Cp*Fe.



E = S (**3**), CH (**4**)

structure of **2** was also identified by X-ray analysis (see the Supporting Information). Complex **3** has crystallographic C_s symmetry, with the iron, the carbene carbon, and the 2-thienyl group on the mirror plane. In contrast, the phenyl group of **4** is close to perpendicular to the plane consisting of C(carbene)-Fe-C(Ph), with an inter-plane angle of 85.19(5)°. The Fe–C(aryl) (1.973(4) and 1.9613(17) Å) and Fe–C(L^{Me}) (1.935(4) and 1.9403(18) Å) bond lengths in **3** and **4** are close to the Fe–C(methyl) (1.978(5) Å) and Fe–C(L^{Me}) (1.935(3) Å) bond lengths in **1**, respectively.

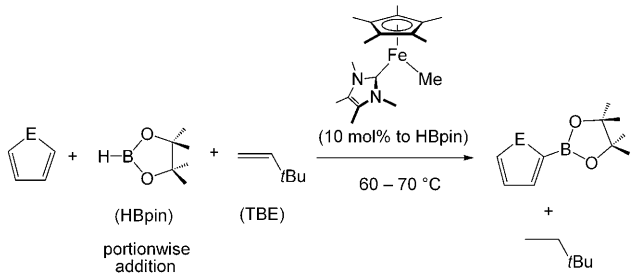
The reaction of **1** with 100 equiv of furan was found to obey pseudo-first-order kinetics with respect to the concentration of **1**. The kinetic data for the conversion of **1** into **2** were obtained by monitoring the decay of [**1**] by using ^{1}H NMR spectroscopy in the range of 10 to 50 °C, and an Eyring plot gave the activation parameters, $\Delta H^{\neq} = 9.3(2)$ kcal mol^{-1} and $\Delta S^{\neq} = -44.2(8)$ eu. The kinetic isotope effect (KIE) for this reaction was estimated to be $k_H/k_D = 3.8(2)$ at 25 °C, for which the rate constants k_H and k_D were determined from the reactions of **1** with furan and [D_4]furan, respectively. The KIE value and the large negative activation entropy of the reaction suggest that an intermolecular C–H bond cleaving process is involved in the rate-determining step.

Catalytic Borylation of Furans and Thiophenes

Having achieved the successful C–H bond activation of arenes by **1**, we were motivated to try catalytic formation of aryl-boranes, which are useful building blocks for Suzuki–Miyaura coupling reactions (Scheme 4).[14]

In the presence of *tert*-butylethylene (TBE), a catalytic amount of **1** (10 mol% with respect to pinacolborane (HBpin)) was found to carry out the dehydrogenative coupling between furan/thiophene and HBpin at 60–70 °C (Scheme 4). For this reaction, it was necessary to keep the concentration of HBpin low in the reaction mixture. Thus 1 equiv of HBpin was divided into 10 portions, and each was added at intervals of 1 hour (see the Experimental Section). Experiments to optimize the conditions for the borylation of furan and thiophene are outlined in Table 2. The reaction using 1:1 ratio of HBpin and furan was found to give a 4:1 mixture of 2-boryl-furan and 2,5-di-boryl-furan (entry 1), whereas the selective formation of 2-boryl-furan was achieved with a 1:6 ratio of HBpin and furan (entry 2). In contrast, a 1:2 ratio of HBpin and thiophene was found to suppress the formation of 2,5-di-boryl-thiophene (entries 5–7). Whereas the yield of 2-boryl-thiophene was much lower than that of 2-boryl-furan, addition of excess *tert*-butylethylene was found to improve the yield (entries 6 and 7). The use of catecholborane (HBcat) instead of HBpin for borylation of furan and thiophene resulted in the formation of 2-boryl-furan in 6.2% yield and 2-boryl-thiophene in 3.9% yield under the same conditions for entries 2 and 6, respectively. Among the solvents employed, i.e., benzene, THF, fluorobenzene, good yields were attained if benzene or THF was used (entries 2, 3, 6, and 7), and thus the following catalytic reactions were carried out in benzene to facilitate the monitoring of the reactions by using NMR spectroscopy.

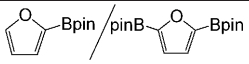
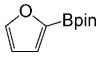
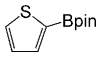
The catalytic borylation of furan derivatives and thiophene derivatives are summarized in Table 3. The product yield was determined by the ^{1}H NMR analysis of the reaction mixture using C_6Me_6 as an internal standard. All of the products were isolated by Kugelrohr distillation or column chromatography, and their isolated yields are given in paren-



Scheme 4.

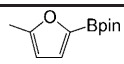
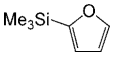
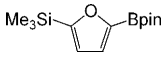
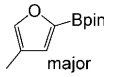
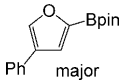
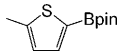
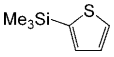
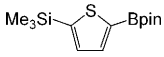
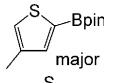
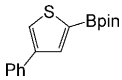
theses. The borylation of methylfurans and 2-trimethylsilylfuran gave good yields of boryl-furans (73–94% based on HBpin, entries 1–3). Regio-selective C–H bond cleavage provided only 5-borylated products from the reactions of 2-methyl- and 2-trimethylsilyl-furan. The borylation of 3-methylfuran took place mainly at the 5-position, and the product was a 92:8 mixture of 2-boryl-4-methylfuran and 2-boryl-3-methylfuran. These examples demonstrate that C–H bond activation is favored for the less hindered position neighboring the oxygen atom. The borylation of 3-phenylfuran (entry 4) gave a similar result to that of 3-methylfuran, while the yield was moderate (51%). Catalytic reactions using either 2-methoxyfuran or 2-cyanofuran gave no borylated product, and the stoichiometric reactions of **1** with these substrates did not provide characterizable iron species. While the borylation of 3-methylthiophene and 2-phenylthiophene (entries 7 and 8) yielded only 32% and 52% borylated products, analogous reactions with 2-methylthiophene and 2-trimethylsilylthiophene (entries 5 and 6) gave 5-boryl-thiophenes in good yields (88% and 90%).

Table 2. Optimization of the catalytic borylation reactions of furan or thiophene.[a]

Entry	Substrate	HBpin/arene/TBE[b]	Solvent	Product	T [°C]	t [h]	Yield by NMR [%][c]
1		1:1.1:2	benzene		60	11	41/10
2		1:6:2	benzene		60	11	75[d]
3		1:6:2	THF		60	11	74
4		1:6:2	C_6H_5F		60	11	54
5		1:2:2	benzene		70	11	13
6		1:2:10	benzene		70	11	24
7		1:2:10	THF		70	11	23

[a] The reactions were carried out with 0.58 mmol of HBpin, in the presence of a catalytic amount of **1** (10 mol% to HBpin, and 1.7–9.1 mol% for the substrates). 10×0.058 mmol of HBpin was added at 1 h intervals. [b] HBpin = pinacolborane (4,4,5,5-tetramethyl-1,3,2-dioxaborolane), TBE = *tert*-butylethylene (3,3-dimethyl-1-butene). [c] The yield based on HBpin was determined by ^{1}H NMR using C_6Me_6 as an internal standard. [d] The product was isolated in 66% yield by Kugelrohr distillation.

Table 3. Borylation of furan derivatives and thiophene derivatives catalyzed by **1**.[a]

Entry	Substrate	HBpin/arene/TBE	Product	T [°C]	t [h]	Yield by NMR [%][b]
1		1:6:2		70	11	94 (82)
2		1:2:2		70	11	73 (72)
3		1:6:2	 major	70	11	76 (70)[c]
4		1:2:2	 major	70	11	51 (46)[c]
5		1:3:10		70	11	88 (67)
6		1:3:10		70	11	90 (84)
7		1:3:10	 major	70	11	32 (30)[c]
8		1:1.5:10		70	11	52 (50)

[a] The reactions were carried out with 0.58 mmol of HBpin, in the presence of a catalytic amount of **1** (10 mol% to HBpin, and 1.7–9.1 mol% for the substrates). 10×0.058 mmol of HBpin was added at 1 h intervals. [b] The yield based on HBpin was determined by the ^{1}H NMR using C_6Me_6 as an internal standard. The yield of isolated product is given in parentheses. [c] The product was obtained as a mixture of the 5-borylated heteroarene (major) and the 2-borylated isomer (minor) in the ratios of 92:8 (entry 3), 90:10 (entry 4), or 96:4 (entry 7), respectively, based on the ^{1}H NMR analysis.

Mechanistic Investigation

To gain mechanistic insights into the catalytic borylation of furan, stepwise reactions using iron complexes, HBpin, *tert*-butylethylene, and furan, were carried out as follows.

*Reactions of Complexes **2**–**4** with Pinacolborane*

Treatment of the 2-furyl complex **2** with an excess of HBpin in C_6D_6 led to the formation of 2-boryl-furan and the borohydride complex [Cp*Fe(L^{Me})(H_2Bpin)] (**5**) (Scheme 5). Importantly, this reaction appeared not to be affected by the presence of *tert*-butylethylene and/or furan, indicating that this step accounts for the formation of boryl-furans during the catalytic reactions. In fact, complexes **2** and **5** were observed in the ^{1}H NMR spectra of the catalytic reaction mixture. In the reaction of **2** with HBpin, 2-boryl-furan and **5** were generated quantitatively according to analysis of the NMR spectra, whereas the relevant reactions of the 2-thienyl complex **3** or the phenyl com-

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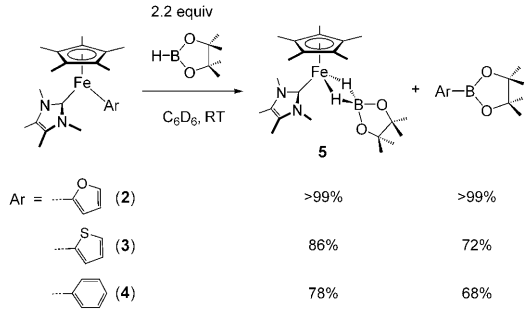
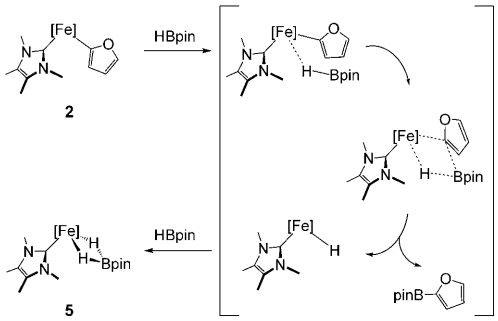


Scheme 5.



Scheme 6. A possible pathway for the formation of **5** and borylfuran ([Fe] = Cp*Fe, HBpin = pinacolborane.

plex **4** with HBpin in C_6D_6 provided 72% of 2-boryl-thiophene or 68% of borylbenzene, with concomitant formation of **5** in 86% (from **3**) or 78% (from **4**) yield.

The borohydride complex **5** is a diamagnetic 18e complex of Fe^{II}, and its ^1H NMR exhibited signals assignable to Cp* and Fe-*H*-B at $\delta = 1.96$ (15H) and -16.4 ppm (2H, $w_{1/2} = 175$ Hz), respectively. In the ^{11}B NMR spectrum, a resonance at $\delta = 36.3$ ppm appeared, which is characteristic for a borohydride group bound to a metal.[8,15] The crystal structure of **5** revealed that the H_2Bpin ligand coordinates to iron through Fe-H-B interactions (Figure 3). The Fe–B bond length of 2.0158(14) Å is in the range of known Fe-H-B complexes (1.855(2)–2.304(21) Å).[8,16] The Fe–C(carbene) bond length of **5** (1.9357(13) Å) is comparable to those for **1**, **3**, and **4** (1.935(4)–1.9403(18) Å).

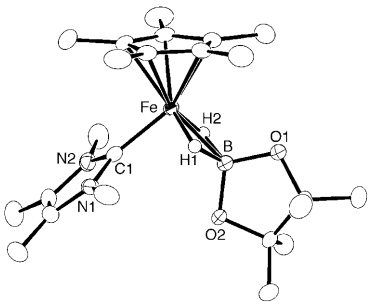
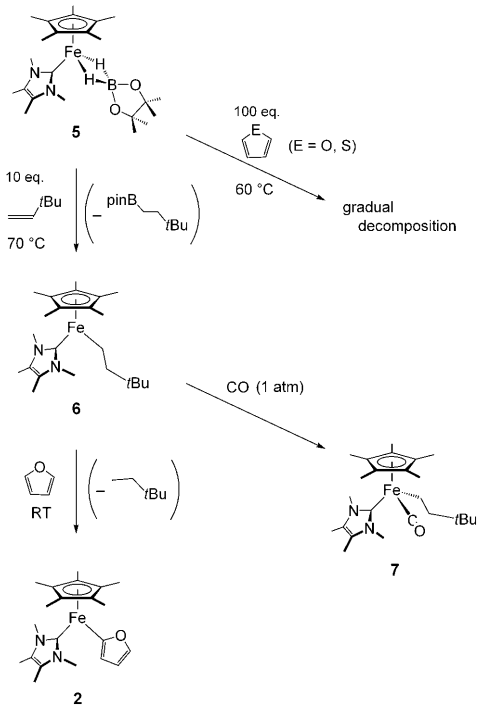


Figure 3. Molecular structure of **5** with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (°): Fe–B = 2.0158(14), Fe–C(1) = 1.9357(13), Fe–H(1) = 1.499(17), Fe–H(2) = 1.500(15), B–H(1) = 1.382(15), B–H(2) = 1.330(18), C(1)–N(1) = 1.3718(17), C(1)–N(2) = 1.3700(18), B-Fe-C(1) = 94.66(5), O(1)-B-O(2) = 108.73(10), B-Fe-H(1) = 43.3(5), B-Fe-H(2) = 41.3(6), Fe-B-H(1) = 48.0(7), Fe-B-H(2) = 48.1(6), N(1)-C(1)-N(2) = 102.32(11).

A possible pathway for the reaction of **2** with HBpin is shown in Scheme 6. We assume that this reaction proceeds with retention of the Fe^{II} oxidation state, because oxidative addition reaction is uncommon for Fe^{II} organo-iron complexes. As illustrated in the bracket in Scheme 6, we propose that the coordination of HBpin to iron would occur through an Fe-H-B interaction, resulting in close proximity between the boron atom and the furyl group. Sigma-bond metathesis between the Fe-(C_4H_3O) group and HBpin could occur to give 2-boryl-furan and a putative iron-hydride intermediate [Cp*Fe(L^{Me})H], and the hydride intermediate would react with another equivalent of HBpin to give **5**.

*Formation of the Furyl Complex **2** from the Borohydride Complex **5***

Treatment of a C_6D_6 solution of **5** with an excess of *tert*-butylethylene at 70 °C resulted in the formation of the borylalkane ($tBuCH_2CH_2Bpin$) and a new alkyl complex [Cp*Fe(L^{Me})CH_2CH_2tBu] (**6**) (Scheme 7). A new set of paramagnetic signals appeared in the ^1H NMR at $\delta = 42.5$ (Cp*), 7.6 (L^{Me}), and -43.5 ppm (L^{Me}), with chemical shifts similar to those for the Fe–CH_3 complex **1**. Despite efforts to use various conditions, isolation of **6** has been unsuccessful. However, we were able to convert **6** quantitatively into a stable CO adduct [Cp*Fe(L^{Me})(CO)CH_2CH_2tBu] (**7**), which was isolated in 92% yield based on **5**. The CO adduct **7** was characterized spectroscopically and by X-ray crystallograph-



Scheme 7.

ic analysis. ^{1}H NMR spectroscopy signals, characteristic for iron-bound methylene protons, registered at $\delta = 1.00$ and 0.86 ppm, and the alpha-methylene carbon signal was observed at $\delta = 4.7$ ppm in the $^{13}C\{^1H\}$ NMR spectrum. The CO stretching frequency of $\tilde{\nu} = 1855\ cm^{-1}$ in the IR spectrum is lower than those of the analogous complexes [Cp*Fe(L*i*Pr)(CO)(4-pyridyl)] ($\tilde{\nu} = 1889\ cm^{-1}$), [CpFe($L^{Mes}$)(CO)Me] ($\tilde{\nu} = 1886\ cm^{-1}$), and [CpFe($L^{Mes}$)(CO)I] ($\tilde{\nu} = 1938\ cm^{-1}$).[8,13n,17] Although the iron center is chiral, complex **7** crystallizes in a centric space group (*Pbca*) in a 50:50 enantiomeric mixture. Three independent molecules are found in the asymmetric unit, and one of these is shown in Figure 4. The Fe–CH_2 bond lengths range from 2.078(2) to 2.081(2) Å, and are comparable to the Fe–C(alkyl) bond lengths in [Cp*Fe($CO)_2$R] (2.057(3)–2.146(10) Å, R = C_3H_7, C_3H_6Br, CH_2SiMe_2OH, $(CH_2)_4OSiMe_2NPh_2$, η^1-C_5H_5).[18]

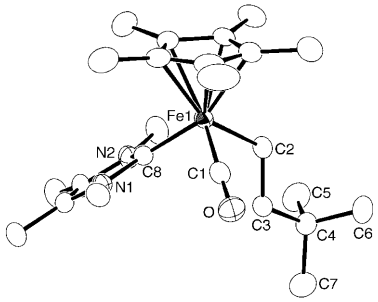


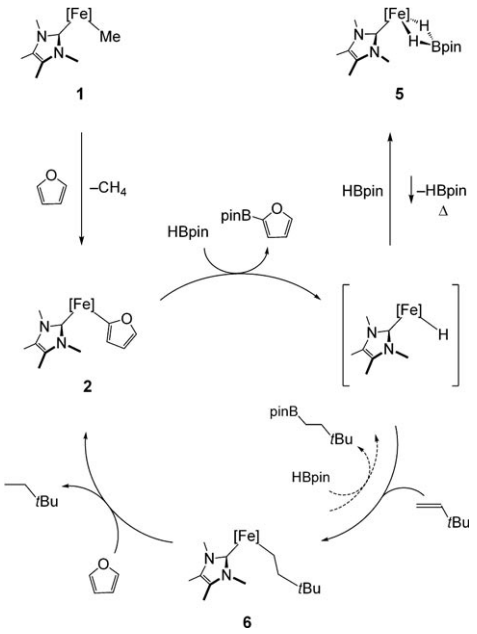
Figure 4. Molecular structure of **7** with thermal ellipsoids at the 50% probability level. One of three molecules found in an asymmetric unit is shown. Selected bond distances (Å) and angles (°): Fe(1)–C(1) = 1.710(2), C(1)–O(1) = 1.170(3), Fe(1)–C(2) = 2.081(2), C(2)–C(3) = 1.525(3), Fe(1)–C(8) = 1.953(2), C(8)–N(1) = 1.376(2), C(8)–N(2) = 1.368(2), C(1)-Fe(1)-C(2) = 86.16(10), C(2)-Fe(1)-C(8) = 95.91(9), C(8)-Fe(1)-C(1) = 94.11(8), Fe(1)-C(1)-O(1) = 179.1(2), N(1)-C(8)-N(2) = 102.13(18).

The alkyl complex **6** was probably formed by means of dissociation of HBpin from **5** to generate the iron-hydride intermediate [Cp*Fe(L^{Me})H], followed by the insertion of *tert*-butylethylene into the Fe–H bond. The liberated HBpin would react with **6** to provide the alkylborane (tBuCH$_2$CH$_2$Bpin) and iron-hydride [Cp*Fe(L^{Me})H]. The iron-hydride species is again transformed into **6** in the presence of excess *tert*-butylethylene. As one can expect, treatment of **6** with excess HBpin resulted in the formation of **5** and alkylborane (tBuCH$_2$CH$_2$Bpin).

Complex **6**, generated from **5** and *tert*-butylethylene, was found to promote the C–H bond cleavage of furan at room temperature to give rise to complex **2** and 2,2-dimethylbutane (Scheme 7). The sequential formation of **2** from **5**, by way of **6**, suggests that *tert*-butylethylene serves not only as a hydrogen scavenger, but also as the source for the iron-alkyl group in **6**, which is responsible for the C–H bond activation of furan. In contrast to the facile formation of **2** from the alkyl complex **6**, treatment of a C_6D_6 solution of the borohydride complex **5** with 100 equiv of furan or thiophene at 60 °C led to gradual decomposition of the iron complex into multiple species. These results and the reactions of **1** with arenes (Scheme 3) indicate that the iron-alkyl group is crucial for C–H bond activation.

A Possible Pathway for Catalytic Borylation

On the basis of the above results, we propose a possible catalytic cycle in Scheme 8. One step in this proposed catalytic cycle is the borylation of an iron-furyl group in **2** with



Scheme 8. A possible catalytic cycle ([Fe] = Cp*Fe, HBpin = pinacolborane).

HBpin, and formation of an iron-hydride intermediate [Cp*Fe(L^{Me})H]. This is followed by the insertion of *tert*-butylethylene into the Fe–H bond of the iron-hydride. The resulting Fe-alkyl complex **6** abstracts a proton from the 2-position of furan to regenerate complex **2**, which restarts the cycle. Although we have not been able to observe [Cp*Fe(L^{Me})H], generation of this intermediate is in agreement with the formation of **5** from **2**+HBpin and the formation of **6** from **5**+*tert*-butylethylene. The Fe-alkyl complex **6** promotes the C–H bond activation of furan, as shown in Scheme 7, whereas the borohydride complex **5** does not activate the C–H bond of furan, but gradually decomposes upon heating with excess furan.

Borohydride complex **5** is more stable than [Cp*Fe(L^{Me})H], and the iron-hydride intermediate opts for complexation with HBpin to form **5** rather than the reaction with TBE to generate **6**. Thus, to facilitate the formation of **6** from **5**, which is essential for the catalytic cycle, the concentration of HBpin needs to be low, as was described earlier in this paper. A low concentration of HBpin is also important to reduce the reaction between **6** and HBpin that wastes both *tert*-butylethylene and HBpin by hydroborylation.

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Conclusions

A coordinatively unsaturated Cp*Fe complex **1** was found to catalyze the dehydrogenative coupling of furans/thiophenes with pinacolborane (HBpin) in the presence of *tert*-butylethylene. Although Ir[19], Rh[19b,19i,20], and Re[21] catalysts have been reported, this is the first example of an iron-catalyzed borylation of aromatic C–H bonds. The borylation of furans and thiophenes occurred regio-selectively at the less hindered 2- or 5-positions. The N-heterocyclic carbene ligand remained intact during the course of the catalytic processes. An advantage of N-heterocyclic carbene ligands is their strong σ-donating ability, which leads to strong bonding between various metals.[22]

A series of reactions, including complexes **1** and **6** with furan, complex **2** with HBpin, and complex **5** with *tert*-butylethylene under heating, have provided insight into the catalytic pathway: a) The iron complexes responsible for C–H bond activation are the Fe-alkyl complexes **1** and **6**. b) The reactions of the Fe-aryl complexes with HBpin provide boryl-arenes and the hydride intermediate [Cp*Fe(L^{Me})H], which is trapped by HBpin to form the borohydride complex **5**. c) The additive *tert*-butylethylene serves not only as a hydrogen scavenger, but also as the source for the alkyl group in **6**, which is generated by means of insertion of *tert*-butylethylene into the Fe–H bond of [Cp*Fe(L^{Me})H].

Experimental Section

General Procedures

All manipulation was carried out under a nitrogen or argon atmosphere by using standard Schlenk techniques and/or in a glove box. THF, toluene, Et_2O, benzene, and hexane were purified by the method of Grubbs,[23] by which the solvents were passed over columns of activated alumina and a supported copper catalyst supplied by Hansen & Co. Ltd. Fluorobenzene was dried over calcium hydride, and distilled prior to use. Deuterated benzene (C_6D_6) was vacuum-transferred from sodium prior to use. ^{1}H, ^{11}B{^{1}H}, and ^{13}C{^{1}H} NMR spectra were acquired by using a JEOL ECA-600. The ^{1}H NMR signals were referenced to the residual proton peak of the deuterated solvent. The ^{11}B chemical shift was measured relative to an external reference of (Me_3N)BH_3 in C_6D_6 ($\delta = -9.1$ ppm). The ^{13}C chemical shifts were measured relative to the carbon signals for the deuterated solvents. Infrared spectra were recorded by using a JASCO A3 spectrometer. Elemental analyses were performed by using a LECO-CHNS-932 elemental analyzer in which the air-sensitive crystalline samples were sealed in silver capsules under nitrogen. X-ray diffraction data were collected by using a Rigaku AFC8 or a Rigaku FR-E equipped with a CCD area detector using graphite-monochromated $Mo_{K\alpha}$ radiation. [Cp*Fe(TMEDA)Cl] [11] and L^{Me} (1,3,4,5-tetramethylimidazol-2-ylidene)[24] were prepared according to literature procedures.

Synthesis of [Cp*Fe(L^{Me})Me] (**1**): An Et_2O solution of methyllithium (0.96 M, 1.15 mL, 1.10 mmol) was added to a THF (40 mL) solution of [Cp*Fe(TMEDA)Cl] (380 mg, 1.11 mmol) at −78 °C. The reaction mixture was allowed to warm gradually to 0 °C with stirring, producing a dark-bluish-green solution. A THF (8 mL) solution of L^{Me} (138 mg, 1.11 mmol) was added to the reaction mixture. After warming to room temperature, the reaction mixture was stirred for several hours. The solvent was removed under reduced pressure, and the residue was extracted with hexane (40 mL) and centrifuged. The solution was concentrated to ≈15 mL, and cooled at −30 °C to give [Cp*Fe(L^{Me})Me] (**1**) as orange crystals (199 mg, 0.60 mmol, 54 % yield). ^{1}H NMR (C_6D_6): $\delta = 41.8$ (15H, Cp*), 8.4 (6H, L^{Me}), −47.5 ppm (6H, L^{Me}); elemental analysis (%) calcd for $C_{18}H_{30}N_2Fe$: C 65.46, H 9.16, N 8.48; found: C 65.83, H 8.97, N 8.35.

Synthesis of [Cp*Fe(L^{Me})(2-C_4H_3O)] (**2**): A toluene (7 mL) solution of **1** (56 mg, 0.17 mmol) and furan (49 μL, 0.67 mmol) was stirred at room temperature for 1 day. The solvent was removed under reduced pressure, and the residue was extracted with hexane/Et_2O (12:3 mL) and centrifuged. The solution was concentrated to ≈1 mL, and cooled at −30 °C to give [Cp*Fe(L^{Me})(2-C_4H_3O)] (**2**) as brownish-green crystals (48 mg, 0.13 mmol, 74 %). ^{1}H NMR (C_6D_6): $\delta = 47.0$ (15H, Cp*), 38.0 (1H, C_4H_3O), 7.6 (6H, L^{Me}), −38.3 (6H, L^{Me}), −69.4 (1H, C_4H_3O), −93.0 ppm (1H, C_4H_3O); elemental analysis (%) calcd for $C_{21}H_{30}N_2OFe$: C 65.97, H 7.91, N 7.33; found: C 65.65, H 8.02, N 7.27.

Synthesis of [Cp*Fe(L^{Me})(2-C_4H_3S)] (**3**): The synthetic procedure is analogous to that for **2**. The reaction of **1** (66 mg, 0.20 mmol) with thiophene (32 μL, 0.40 mmol) at 60 °C for 3 days gave [Cp*Fe(L^{Me})(2-C_4H_3S)] (**3**) as brownish-green crystals (42 mg, 0.11 mmol, 53 % yield). ^{1}H NMR (C_6D_6): $\delta = 47.0$ (15H, Cp*), 20.3 (1H, C_4H_3S), 8.6 (6H, L^{Me}), −21.5 (1H, C_4H_3S), −38.8 (6H, L^{Me}), −66.1 ppm (1H, C_4H_3S); elemental analysis (%) calcd for $C_{21}H_{30}N_2SFe$: C 63.31, H 7.59, N 7.03, S 8.05; found: C 63.20, H 7.544, N 7.07, S 7.57.

Synthesis of [Cp*Fe(L^{Me})Ph] (**4**): Method A, the reaction of **1** with benzene: A benzene (10 mL, 0.11 mol) solution of **1** (65 mg, 0.20 mmol) was stirred at 80 °C for 7 days. The solvent was removed under reduced pressure, and the residue was extracted with Et_2O (7 mL) and centrifuged. The solution was concentrated to ca. 1 mL, and cooled at −30 °C to give [Cp*FeL^{Me}Ph] (**4**) as reddish-orange crystals (28 mg, 0.071 mmol, 36 % yield). ^{1}H NMR (C_6D_6): $\delta = 50.1$ (15H, Ph), 15.0 (1H, Ph), 7.9 (6H, L^{Me}), 2.8 (2H, Ph), −9.4 (2H, Ph), −42.4 ppm (6H, L^{Me}); elemental analysis (%) calcd for $C_{34}H_{40}N_2Fe$: C 70.41, H 8.22, N 7.14; found: C 70.81, H 8.45, N 7.21 ppm. Method B, the reaction of [Cp*Fe(TMEDA)Cl] with phenyllithium: Analogous to the synthesis of **1**, the reaction of [Cp*Fe(TMEDA)Cl] (475 mg, 1.39 mmol) with a Bu_2O solution of phenyllithium (1.9 M, 0.73 mL, 1.39 mmol) and L^{Me} (172 mg, 1.38 mmol) in toluene (50 mL) yielded **4** (183 mg, 0.47 mmol, 34 %) as reddish-orange crystals.

*Kinetic Study of the Reaction of **1** with Furan*

Furan (900 μL, 12.4 mmol) was added to a C_6D_6 (4.0 mL) solution of **1** (41 mg, 0.12 mmol) and C_6Me_6 (20 mg, 0.12 mmol, internal standard). Portions of this solution were charged into seven NMR tubes, and the tubes were capped with a J-Young valve. The Cp* signal of **1** (δ 41.8 at 25 °C) was monitored by ^{1}H NMR spectroscopy at 10–50 °C and was integrated at intervals. Rate constants k were determined to be $8.93(13)\times10^{-5}$ (10 °C), $1.20(15)\times10^{-4}$ (15 °C), $1.50(4)\times10^{-4}$ (20 °C), $2.27(8)\times10^{-4}$ (25 °C), $2.93(5)\times10^{-4}$ (30 °C), $4.84(8)\times10^{-4}$ (40 °C), and $7.60(12)\times10^{-4}$ (50 °C). An Eyring plot (see the Supporting Information) yielded the activation parameters, $\Delta H^{\neq} = 9.3(2)$ kcal mol^{-1} and $\Delta S^{\neq} = -44.2(8)$ eu.

*Kinetic Isotope Effect (KIE) for the Reaction of **1** with Furan*

Deuterated furan (178 μL, 2.45 mmol) was added to an NMR tube containing a C_6D_6 (0.80 mL) solution of **1** (8.1 mg, 0.025 mmol) and C_6Me_6 (4.0 mg, 0.025 mmol, internal standard). The Cp* signal of **1** was monitored periodically by ^{1}H NMR at 25 °C, and the rate constant was obtained as $k_D = 5.97(7)\times10^{-5}$ (25 °C). k_H/k_D was found to be 3.8(2).

Typical Procedure for the Catalytic Dehydrogenative Coupling between Furans/Thiophenes and Pinacolborane

A benzene (8 mL) solution containing **1** (19 mg, 0.058 mmol), furans or thiophenes, *tert*-butylethylene, and C_6Me_6 (19 mg, 0.12 mmol, as an internal standard), was charged into a Schlenk tube with a J-Young valve. The reaction mixture was stirred for 1 hour at 60 or 70 °C before addition of the first portion (500 μL) of a benzene (5.0 mL) solution containing pinacolborane (83.5 μL, 0.58 mmol). The remaining nine portions (9 × 500 μL) of pinacolborane solution were added successively at 1 hour intervals. The reaction mixture was further stirred for 1 h at 60 or 70 °C after completion of the addition of pinacolborane, and thus the total reaction time was 11 h. The volatiles were removed under reduced pressure, and the residue was dissolved in C_6D_6. The product yield was determined by ^{1}H NMR spectroscopy, using C_6Me_6 as an internal standard. The product

was isolated by Kugelrohr distillation or by column chromatography on silica gel eluted with CH_2Cl_2. Known organic products were identified by comparison of the NMR signals with those for authentic samples,[19f-h,j,25] and unreported compounds were characterized based by using NMR spectroscopy, EI-MS, and elemental analysis. Detailed procedures and characterization of compounds are found in the Supporting Information.

Synthesis of [Cp*Fe(L^{Me})(H_2Bpin)] (**5**): Method A, from **1** and pinacolborane: Pinacolborane (109 μL, 75 mmol) was added to a THF (10 mL) solution of **1** (83 mg, 0.25 mmol) at room temperature. After stirring for 1 hour, the solvent was removed under reduced pressure. The residue was extracted with hexane (15 mL) and centrifuged. The solution was concentrated to ≈5 mL, and cooled at 0°C to give [Cp*Fe(L^{Me})(H_2Bpin)] (**5**) as purple crystals (90 mg, 0.20 mmol, 81% yield). ^{1}H NMR (C_6D_6): δ = 3.64 (s, 6H, L^{Me}), 1.96 (s, 15H, Cp*), 1.43 (s, 6H, L^{Me}), 1.33 (s, 6H, Bpin), 1.04 (s, 6H, Bpin), −16.4 ppm (br, $w_{1/2}$ = 175 Hz, 2H, Fe-H-B); ^{11}B{^{1}H} NMR (C_6D_6): δ = 36.3 ppm ($w_{1/2}$ = 190 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ = 203.6 ($CN_2C_2Me_2$), 125.1 ($CN_2C_2Me_2$), 82.9 (C_5Me_5), 81.0, 80.2 (Bpin), 36.3 ($CN_2(Me)_2C_2Me_2$), 25.5, 25.3 (Bpin), 12.3 (C_5Me_5), 9.7 ppm ($CN_2C_2Me_2$); elemental analysis (%) calcd for $C_{23}H_{41}BN_2O_2Fe$: C 62.18, H 9.30, N 6.31; found: C 62.30, H 8.82, N 6.31.

Method B, from **2** and pinacolborane in an NMR tube: The reaction of **2** (5.2 mg, 0.014 mmol) with pinacolborane (8.0 μL, 0.030 mmol) in C_6D_6 (0.6 mL, with 4 mg of C_6Me_6 (0.025 mmol) as an internal standard) yielded 2-borylfuran and **5** in >99% and >99%, respectively.

Method C, from **3** and pinacolborane in an NMR tube: The reaction of **3** (10 mg, 0.025 mmol) with pinacolborane (8.0 μL, 0.055 mmol) in C_6D_6 (0.6 mL, with 4 mg of C_6Me_6 (0.025 mmol) as an internal standard) gave 2-borylthiophene and **5** in 72% and 86%, respectively. Method D, from **4** and pinacolborane in an NMR tube: The reaction of **4** (12 mg, 0.031 mmol) with pinacollborane (9.5 μL, 0.065 mmol) in C_6D_6 (0.6 mL, with 4 mg of C_6Me_6 (0.025 mmol) as an internal standard) yielded borylbenzene and **5** in 68% and 78% yields, respectively.

NMR Observation of Iron Complexes in the Catalytic Reaction Mixture

As described in the procedure for catalytic reactions, a C_6D_6 (8 mL) solution containing **1** (19 mg, 0.058 mmol), furan (251 μL, 3.45 mmol), *tert*-butylethylene (148 μL, 1.15 mmol), and C_6Me_6 (19 mg, 0.12 mmol, internal standard), was charged into a Schlenk tube, and the solution was stirred for 1 hour at 60°C. After addition of 500 μL of a benzene (5.0 mL) solution containing pinacolborane (83.5 μL, 0.58 mmol), the solution was again stirred at 60°C. Portions of the reaction mixture were periodically taken out and were subjected to NMR analysis. Complexes **2** and **5** were observed in the ^{1}H NMR. Their ratios after addition of pinacolborane were as follows: **2**:**5** = 1.8:1 (3 min), 2.4:1 (10 min), 5.6:1 (25 min), 12.3:1 (50 min).

Formation of [Cp*Fe(L^{Me})CH_2CH_2tBu] (**6**) from **5** and *tert*-butylethylene: A C_6D_6 solution (0.60 mL) containing **5** (10 mg, 0.023 mmol) and *tert*-butylethylene (29 μL, 0.23 mmol) was charged into an NMR tube, and a glass capillary containing a C_6D_6 solution of ferrocene (0.25 M) was inserted as an internal standard. The NMR tube was heated at 70°C for 3 h. Analysis of the ^{1}H NMR spectra revealed one set of paramagnetic signals assignable to [Cp*Fe(L^{Me})CH_2CH_2tBu] (**6**) at δ = 42.5 (15H, Cp*), 14.0 (9H, *t*Bu), 7.6 (6H, L^{Me}), 1.79 (2H, CH_2CH_2tBu), and −43.5 ppm (6H, L^{Me}), although we were not able to observe the signal for Fe−CH_2 group. The signals for alkylborane (tBuCH$_2$CH$_2$Bpin) were observed at δ = 1.07 (12H, Bpin), 1.02 (2H, CH_2), 0.86 (9H, *t*Bu), 0.83 ppm (2H, CH_2). The yields of **6** and tBuCH$_2$CH$_2$Bpin in these NMR experiments were determined, as 90% and 97%, respectively.

Reaction of **6** with furan: Furan (6.5 μL, 0.089 mmol) was added to the NMR tube used for the formation of **6**. The tube was stood for 2 days at room temperature, and the furyl complex **2** and 2,2-dimethylbutane were formed in 90% and 99% yields, respectively, based on **6**. The ^{1}H NMR signals for 2,2-dimethylbutane were observed at δ = 1.17 (q, 2H, CH_2), 0.84 (s, 9H, *t*Bu), 0.80 ppm (t, 3H, CH_3).

Reaction of **6** with pinacolborane: Complex **6** was generated from **5** (10 mg, 0.023 mmol) and *tert*-butylethylene (29 μL, 0.23 mmol) in C_6D_6 (0.60 mL, with 4 mg of C_6Me_6 (0.025 mmol) as an internal standard), as described above. This solution was transferred to a Schlenk tube and was evaporated under reduced pressure to remove unreacted *tert*-butylethylene. The residue was again dissolved in C_6D_6 (0.6 mL), and the solution was charged into an NMR tube. Addition of pinacolborane (6.5 μL, 0.045 mmol) gave **5** and tBuCH$_2$CH$_2$Bpin in >99% and 81% yields, respectively, based on **6**.

Synthesis of [Cp*FeL^{Me}(CO)(CH_2CH_2tBu)] (**7**). A toluene solution (10 mL) of **5** (82 mg, 0.19 mmol) and *tert*-butylethylene (1.2 mL, 9.3 mmol) was stirred for 4 h at 70°C. After cooling to room temperature, the reaction mixture was exposed to 1 atm of CO. The color of solution became orange. After stirring for 2 h, the volatile materials were removed under reduced pressure. Column chromatography on neutral alumina, eluted with hexane under an argon atmosphere, provided an orange eluent of [Cp*FeL^{Me}(CO)(CH_2CH_2tBu)] (**7**). Complex **7** was isolated as an orange powder (73 mg, 0.17 mmol, 92% yield). Orange crystals of **7** were obtained from a hexane solution stored at −20°C (25 mg, 31% yield). ^{1}H NMR (C_6D_6): δ = 3.55 (s, 3H, L^{Me}), 3.39 (s, 3H, L^{Me}), 1.62 (s, 15H, Cp*), 1.54 (dt, J_{HH} = 7.7, 4.1 Hz, 1H, *t*Bu-CH_2-), 1.49 (s, 3H, L^{Me}), 1.33 (s, 3H, L^{Me}), 1.08 (dt, J_{HH} = 7.7, 4.1 Hz, 1H, *t*Bu-CH_2-), 1.00 (ddd, J_{HH} = 13.1, 7.7, 4.1 Hz, 1H, Fe-CH_2-), 0.86 ppm (ddd, J_{HH} = 13.1, 7.7, 4.1 Hz, 1H, Fe-CH_2-); ^{13}C{^{1}H} NMR (C_6D_6): δ = 228.3 (CO), 199.7 (CN_2C_2), 125.9 (CN_2C_2), 125.4 (CN_2C_2), 89.9 (C_5Me_5), 52.1 (CMe_3), 35.9 ($CN_2(Me)_2C_2(Me)_2$), 34.9 ($CN_2(Me)_2C_2(Me)_2$), 32.2 (*t*Bu-CH_2), 30.6 (CMe_3), 10.5 (C_5Me_5), 9.8 ($CN_2(Me)_2C_2(Me)_2$), 9.5 ($CN_2(Me)_2C_2(Me)_2$), 4.7 ppm (Fe-CH_2); IR (KBr): $\tilde{\nu}$ = 1855 cm^{-1} (s, CO); elemental analysis (%) calcd for $C_{24}H_{40}N_2OFe$: C 67.28, H 9.41, N 6.54; found: C 66.85, H 9.29, N 6.32.

*Degradation of **5** in the Presence of Furan or Thiophene*

Furan (164 μL, 2.26 mmol) was added to a C_6D_6 (1.6 mL) solution of **5** (10 mg, 0.023 mmol) and hexamethylbenzene (2.5 mg, 0.015 mmol, internal standard), and a portion of this solution was charged into an NMR tube. A C_6D_6 (1.6 mL) solution containing **5** (10 mg), thiophene (180 μL, 2.25 mmol), and C_6Me_6 (2.5 mg) was prepared in a similar manner, and was also introduced into an NMR tube. The tubes were kept at 60°C in the NMR probe. The reaction mixtures gradually exhibited unassigned signals in the ^{1}H NMR, indicating degradation of the iron complex. The half-lives ($t_{1/2}$) of **5** were 22 min (with furan) and 139 min (with thiophene).

X-ray Crystal Structure Determination

Crystal data and refinement parameters for **1**, **3**--**5**, and **7** are summarized in Table 4. Preliminary crystallographic study on **2** is given in the Supporting Information. Single crystals were coated with oil (Immersion Oil, type B: Code 1248, Cargille Laboratories, Inc.) and mounted on loops. Diffraction data were collected at −100°C under a cold nitrogen stream by using a Rigaku AFC8 equipped with a Saturn70 CCD detector or on a Rigaku FR-E equipped with a Saturn70 CCD detector using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.710690 Å). Six preliminary data frames were measured at 0.5° increments of ω, to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at 0.5° intervals of ω. The frame data were integrated using the CrystalClear program package, and the data sets were corrected for absorption using a REQAB program. The calculations were performed with the CrystalStructure program package. All structures were solved by direct methods, and refined by full-matrix least squares. Anisotropic refinement was applied to all non-hydrogen atoms except for disordered groups in **1**, **3**, and **7** (refined isotropically), and all hydrogen atoms were put at calculated positions. In the asymmetric unit of **1**, there are two crystallographically independent molecules. The iron-bound methyl group of one of these molecules is disordered over two positions, with 50:50 occupancy. The Cp* ligand in **3** is disordered over two equally occupied positions. The thienyl group in **3** is disordered over two positions, with occupancy factors of 60:40. In an asymmetric unit of **7**, there are three crystallographically independent molecules. The Cp* ligand of one of these molecules is disordered over two positions, with occupancy factors of 50:50. The *t*Bu group in a different molecule is disordered over two positions, with occupancy factors of 50:50. The atomic coordinates for complexes for complexes **1**, **3**–**5**, and **7** have been deposited with the

Table 4. Crystal data for [Cp*Fe(L^{Me})Me] (**1**), [Cp*Fe(L^{Me})(2-C_4H_3S)] (**3**), [Cp*Fe(L^{Me})Ph] (**4**), [Cp*Fe(L^{Me})(H_2Bpin)] (**5**), and [Cp*Fe(L^{Me})(CO)(CH_2CH_2tBu)] (**7**).

	1	**3**	**4**	**5**	**7**
formula	$C_{18}H_{30}N_2Fe$	$C_{21}H_{30}N_2SFe$	$C_{23}H_{32}N_2Fe$	$C_{23}H_{41}BN_2O_2Fe$	$C_{24}H_{40}N_2OFe$
M_w [g mol^{-1}]	330.29	398.39	392.37	444.25	428.44
crystal system	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$ (#2)	*Pnma* (#62)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	*Pbca* (#61)
crystal color	orange	yellowish green	yellowish brown	reddish purple	orange
crystal size [mm]	0.2×0.08×0.02	0.1×0.05×0.05	0.1×0.1×0.07	0.1×0.1×0.03	0.2×0.2×0.03
a [Å]	10.618(3)	19.803(3)	10.517(2)	11.7529(18)	14.8602(16)
b [Å]	12.191(3)	11.6494(17)	14.033(3)	10.8939(15)	20.808(2)
c [Å]	14.535(4)	9.3090(12)	15.043(3)	18.858(3)	46.856(5)
α [°]	90.417(6)				
β [°]	91.075(5)		107.427(3)	96.122(2)	
γ [°]	101.695(5)				
V [Å^3]	1842.0(9)	2147.5(5)	2118.2(7)	2400.6(6)	14488(3)
Z	4	4	4	4	24
ρ_{calc} [g cm^{-3}]	1.191	1.232	1.230	1.229	1.178
$\mu(Mo_{K\alpha})$ [cm^{-1}]	8.15	8.04	7.20	6.48	6.39
$2\theta_{max}$ [°]	54.8	54.9	55.0	55.0	55.0
no. of measured rflns	22215	16673	16794	18612	128198
no. of unique rflns	8317	2529	4802	5359	16510
no. of variables	435	126	267	309	750
$R1$[a]	0.098	0.077	0.046	0.036	0.065
wR_2[b]	0.181	0.237	0.080	0.088	0.163
GOF[c]	1.01	1.19	1.04	1.01	1.07

[a] $I>2\sigma(I)$, $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] Refined with all data, $wR2=[\{\Sigma w(F_o^2-F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$. [c] GOF$=[\{\Sigma w(F_o^2-F_c^2)^2\}/(N_o-N_p)]^{1/2}$, where N_o and N_p denote the numbers of reflection data and parameters.

Cambridge Crystallographic Data Centre, Cambridge CB2 1EK, UK , respectively). CCDC 766277 (**1**), CCDC 766282 (**2**), CCDC 766278 (**3**), CCDC 766279 (**4**), CCDC 766280 (**5**), and CCDC 766281 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif

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