ORGANOMETALLICS

Synthesis of Bis(N-heterocyclic carbene) Complexes of Iron(II) and Their Application in Hydrosilylation and Transfer Hydrogenation

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Supporting Information

ABSTRACT: N-heterocyclic carbene (NHC) adducts of iron dichloride, $(IMes)_2FeCl_2$ (1a; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and $(IEtPh^*)_2FeCl_2$ (1b; $IEtPh^* = 1,3$ -bis((R)-1'-phenylethyl)imidazol-2-ylidene), were prepared in good yields from the reactions of $Fe\{N(SiMe_3)_2\}_2$ with imidazolium salts. While the iron atom of 1a has a tetrahedral geometry, replacement of the chlorides by methyl groups via treatment of 1a with MeLi led to the formation of the square-planar complex *trans*-(IMes)_2FeMe_2 (2). The molecular



structures of complexes 1a,b and 2 were identified by means of single-crystal X-ray diffraction analysis. Complexes 1a,b and 2 are good catalyst precursors in the transfer hydrogenation of 2'-acetonaphthone, and complex 2 also efficiently catalyzes the hydrosilylation of 2'-acetonaphthone.

INTRODUCTION

N-heterocyclic carbenes (NHCs) constitute a growing class of ligands in organometallic chemistry (Figure 1).¹ While NHCs



Figure 1. NHCs and their abbreviations.

are often used as alternatives to well-known phosphines, their strong electron-donating ability leads to a more robust metal– ligand interaction. The strong binding of NHCs to various transition metals has been useful in homogeneous catalysis.^{11,2} A recent example is the enantioselective hydrogenation of substituted quinoxalines and benzofurans catalyzed by chiral NHC–ruthenium complexes.³ It is notable that NHCs have been mainly used as ligands for the second- and third-row transition metals, particularly noble metals. In comparison to generally toxic and costly noble metals typically used in catalysis, iron offers some advantages; iron is cheap, nontoxic, environmentally friendly, and abundant. Thus, there has been increasing attention paid to the catalytic application of iron in organic synthesis.⁴ However, details of the synthesis and catalytic applications of NHC–iron complexes remain scarce. $^{\rm 5-7}$

In this work, we have synthesized some simple iron(II) chloro and alkyl complexes having monodentate NHC ligands, and we have explored their catalytic applications in hydrogen transfer reactions and the hydrosilylation of 2'-acetonaphthone.

RESULTS AND DISCUSSION

Synthesis of NHC-Iron(II) Dichlorides. Two typical methods have been reported for the synthesis of NHC-iron halide complexes. One is the ligation of free NHC ligands to FeX₂.^{5c,6a,8} Iron(II) dihalide complexes with monodentate NHCs, (NHC)₂FeX₂, were synthesized by Grubbs et al.,^{6a} and this method was recently improved by Deng et al.,⁸ using 1,3-R₂-3,4-dimethylimidazol-2-ylidene (R = Me, Et, Pr^{i}). Another synthetic route is the metalation reaction, where the imidazolium salt is deprotonated by basic ligands in iron complexes; 6d,i,9,10 the silylamide $[N(SiMe_3)_2]^-$ is the most frequently employed basic ligand. Some bidentate or tridentate NHC-iron dihalide complexes^{6i,9} have been synthesized from $Fe{N(SiMe_3)_2}_{2}^{11}$ and we have synthesized $Cp^*Fe(IMes)Cl^{6d}$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) from the reaction of $Cp*Fe\{N(SiMe_3)_2\}^{12}$ with IMes·HCl. Recently, Danopoulos et al.¹⁰ have synthesized (SIPr')₂FeCl₂. (SIPr' = 1,3-bis(2-isopropylphenyl)imidazolin-2-ylidene) from the reaction of $Fe\{N(SiMe_3)_2\}_2$ with SIPr'·HCl.

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In this study, we chose a metalation reaction to synthesize the iron dichloride complexes. The reaction of $Fe\{N(SiMe_3)_2\}_2$ with 2 equiv of IMes·HCl¹³ in toluene afforded (IMes)₂FeCl₂ (1a)¹⁴ as a white crystalline powder in 89% yield (Scheme 1).



An analogous complex with chiral NHC ligands, (IEtPh*)₂FeCl₂ (**1b**; IEtPh* = 1,3-bis((*R*)-1'-phenylethyl)imidazol-2-ylidene)), was obtained in 86% yield from Fe{N-(SiMe₃)₂}₂ and IEtPh*·HCl.¹⁵ Further attempts to synthesize (IPrⁱ)₂FeCl₂ (IPrⁱ = 1,3-bis(2,6-diisopropylphenyl)imidazol-2ylidene) by the metalation method was not successful and gave (IPrⁱ)FeCl{N(SiMe₃)₂}.¹⁰

Complexes **1a,b** are air and moisture sensitive both in solution and in the solid state. These complexes are paramagnetic, and their ¹H NMR spectra exhibited broad signals in the ranges of 27.8–2.2 ppm (**1a**) and 37–4.2 ppm (**1b**). Their solution magnetic moments were determined by the Evans method¹⁶ as 5.1 $\mu_{\rm B}$ at 296 K (**1a**) and 5.2 $\mu_{\rm B}$ at 297 K (**1b**), respectively. These values are close to the spin-only value for an S = 2 state (4.90 $\mu_{\rm B}$) and are consistent with a high-spin electronic configuration for tetrahedral d⁶ complexes.¹⁷

The molecular structures of 1a,b were determined by X-ray diffraction and are shown in Figures 2 and 3, respectively.



Figure 2. Molecular structure of $(IMes)_2FeCl_2$ (1a) with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Fe-C1 = 2.140(4), Fe-C22 = 2.144(3), Fe-Cl1 = 2.2796(17), Fe-Cl2 = 2.2998(16); C1-Fe-C22 = 126.09(14), C1-Fe-Cl1 = 99.74(9), C1-Fe-Cl2 = 115.77(10), C22-Fe-Cl1 = 112.46(11), C22-Fe-Cl2 = 94.97(10), C11-Fe-Cl2 = 107.28(7).

There are two independent molecules in the asymmetric unit of **1b**. As they are very similar to each other, the following discussion is based on one of the molecules. In complexes **1a**,**b**, the iron atom has a distorted-tetrahedral geometry with two NHC ligands and two chlorides. The Fe–C(carbene) distacnes are 2.140(4) and 2.144(3) Å in **1a** and 2.148(4) and 2.124(4) Å in **1b**, which are comparable to those in other tetrahedral Fe(II) bis-carbene chloride complexes (2.1298(16) - 2.1363(15) Å).^{6a,10} The C(carbene)–Fe–C(carbene) angle of **1a** $(126.09(14)^{\circ})$ is notably larger than those for $(SIPr')_2FeCl_2$ $(103.33(13)^{\circ})$,¹⁰ **1b** $(104.13(14)^{\circ})$, and $(IPr)_2FeCl_2$



Figure 3. Molecular structure of $(IEtPh^*)_2FeCl_2$ (**1b**) with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Fe-C1 = 2.148(4), Fe-C20 = 2.124(4), Fe-Cl1 = 2.2812(12), Fe-Cl2 = 2.3073(12); C1-Fe-C20 = 104.13(14), C1-Fe-Cl1 = 116.56(11), C1-Fe-Cl2 = 105.14(11), C20-Fe-Cl1 = 108.39(11), C20-Fe-Cl2 = 116.58(11), C1-Fe-Cl2 = 106.46(5).

 $(102.05(6)^{\circ};$ IPr = 2,5-diisopropyl-3,4-dimethylimidazol-2ylidene).^{6a} The large C(carbene)-Fe-C(carbene) angle of 1a is due to the steric congestion between the IMes ligands, and this congestion may also lead to the narrow C22-Fe-Cl2 angle (94.97(10)°).

Synthesis of an NHC–Iron(II) Dimethyl Complex. Fourcoordinate, tetrahedral NHC–iron(II) alkyl complexes, (IEt)₂FeR₂ (IEt = 1,3-diethyl-3,4-dimethylimidazol-2-ylidene, R = Me, CH₂TMS), were synthesized by Deng et al.⁸ from the reactions of (IEt)₂FeCl₂ with 2 equiv of MeLi or TMSCH₂MgCl. From an analogous reaction of (IMes)₂FeCl₂ (1a) with 2 equiv of MeLi in THF, the square-planar complex *trans*-(IMes)₂FeMe₂ (2) was isolated in 86% yield as an air- and moisture-sensitive reddish orange powder (Scheme 2). We also



attempted to synthesize (IEtPh*)₂FeMe₂ from **1b** and MeLi. The ¹H NMR measurement of the reaction mixture revealed the disappearance of **1b** and the formation of a new iron complex, but its isolation was unsuccessful. Complex **2** is paramagnetic, as evidenced by the solution magnetic moment of 3.5 $\mu_{\rm B}$ at 296 K. The temperature-dependent magnetic susceptibility in the solid state (Figure 4) also exhibited $\mu_{\rm eff}$ values ranging from 2.74 to 3.24 $\mu_{\rm B}$ at 30–300 K, which are comparable to the spin-only value for an S = 1 state (2.83 $\mu_{\rm B}$). When the magnetic moment and the square-planar structure are taken into account, complex **2** can be assigned as an intermediate-spin S = 1 state with an unoccupied $d_{x^2-y^2}$ orbital.¹⁷

Complex **2** was structurally identified by an X-ray diffraction study. There are two independent molecules in the asymmetric



Figure 4. Temperature-dependent magnetic susceptibility of 2 in the solid state.

unit of 2, and one of these is shown in Figure 5. The iron atom is coordinated by two IMes ligands in trans positions and two



Figure 5. Molecular structure of $(IMes)_2FeMe_2$ (2) with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Fe-C1 = 2.125(5), Fe-C2 = 1.959(5); C1-Fe-C2 = 90.69(19), C1-Fe-C2* = 89.30(19).

methyl groups, and the four carbon atoms bound to iron are crystallographically coplanar with iron. From Figures 2 and 5, one can see that the replacement of chlorides in 1a by methyl groups induces a geometric change. This change is probably caused by both steric and electronic factors. The square-planar geometry with trans IMes ligands is suitable for reducing the steric congestion between the mesityl groups of the IMes ligands, and the two IMes ligands are twisted against each other with a torsion angle of $57.3(2)^{\circ}$ between the N-containing fivemembered rings. The strong σ -donating properties of IMes and methyl ligands lead to a strong ligand field, enabling the squareplanar configuration for four-coordinate complex 2 with an efficiently destabilized antibonding $d_{x^2-y^2}$ orbital. The Fe-C(carbene) bond length is 1.959(5) Å, which is shorter than those of tetrahedral Fe(II) bis-carbene complexes $(2.075(4) - 2.1363(15) \text{ Å})^{6a,c,i,8,9c,10}$ and is comparable to those of reported square planar Fe(II) bis-carbene complexes (1.801(9)-2.010(9) Å).^{9c,18} The Fe–CH₃ bond length of 2.125(5) Å is longer than those reported for the square-planar Fe complexes ${\rm Li(THF)_4}[({\rm PDI}){\rm FeMe}]^{19a}$ (2.013(9) Å, PDI = {2,6-[2,6-(*i*-Pr)₂PhN=C(CH₃)]₂}(C₃H₃N)), (PDI){\rm FeMe}^{19b} (2.001(6) Å), and [(PDI)FeMe](BPh₄) (2.006(4) Å).^{19c} The long Fe-CH₃

distance in **2** is possibly due to the strong trans influence of CH_3 groups.

Catalytic Reduction of 2'-Acetonaphthone via Transfer Hydrogenation and Hydrosilylation. Recently, several groups have reported iron(II) NHC complexes which catalyze the hydrogenation/hydrosilylation of carbonyl compounds.⁷ For example, Royo et al. reported cyclopentadienyl-functionalized NHC-Fe complexes for the transfer hydrogenation of ketones,^{7a} and Darcel et al. reported cyclopentadienyl NHC-Fe complexes for the hydrosilylation of aldehydes and ketones under visible light irradiation.7b With new NHC-FeII complexes in hand, we also examined the catalytic reduction of 2'-acetonaphthone (3) via transfer hydrogenation and hydrosilylation.²⁰ The progress of the reactions was monitored by GC-MS or ¹H NMR signals of the corresponding alcohol or silvl ether. In the transfer hydrogenation reactions, 2-propanol was used as the hydrogen source, and the results are summarized in Table 1. In the presence of t-BuOK as a base

Table 1. Transfer Hydrogenation of 2'-Acetonaphthone $(3)^a$

		Fe catalyst PrOLi (1.2 eq) i-PrOH	C	H \
	(3)		(4)	
entry	cat. (amt (mol %))	$T (^{\circ}C)/t (h)$	yield (%) ^b	ee (%)
1^c	1a (1.0)	80/6	48	
2^{c}	2 (1.0)	80/6	55	
3	1a (1.0)	80/3	98	
4	2 (1.0)	80/3	97	
5^d	1a (1.0)	80/3	10	
6 ^e	none	80/3	9	
7	1a (1.0)	70/3	97	
8	2 (1.0)	70/3	97	
9	1a (1.0)	50/5	52	
10	1a (1.0)	25/12	0	
11^{f}	1a (0.1)	70/3	(92) ^g	
12^{f}	1b (0.1)	70/3	(91) ^g	<5

^{*a*}The reactions were carried out using 3 (0.20 mmol), Fe catalyst, *i*-PrOLi (0.24 mmol), and *i*-PrOH (2.0 mL) under Ar. ^{*b*}Yield determined by ¹H NMR spectroscopy. ^{*c*}*t*-BuOK was used as a base. ^{*d*}The reaction was carried out with *i*-PrOLi (0.015 mmol). ^{*e*}The reaction was carried out without Fe catalyst. ^{*f*}The reaction was conducted on a 5-fold scale (1.0 mmol of 3). ^{*g*}The yield of the isolated product is given in parentheses.

(1.2 equiv to 3), complexes 1a and 2 (1.0 mol %) catalyzed the hydrogenation of 3 at 80 °C to give the desired alcohol 4 in moderate yields (entries 1 and 2). The product yields became excellent upon changing the base to *i*-PrOLi (entries 3 and 4). However, a catalytic amount of *i*-PrOLi (7.5 mol %) was insufficient, and only a 10% yield of 4 was obtained (entry 5). Adolfsson et al.²¹ reported that *i*-PrOLi works as an efficient catalyst for the transfer hydrogenation of ketones at high temperature (i.e. i-PrOLi (6 mol %), 180 °C, 20 min for acetophenone, 94% yield); however, the Fe catalyst appeared to be necessary for the quantitative conversion of the substrate in our reaction (entry $\hat{6}$). The reaction proceeds smoothly at 70 °C (entries 7 and 8), whereas a lower reaction temperature (50 or 25 °C) results in a drop of the yield (entries 9 and 10). Interestingly, a 5-fold increase of the reaction scale (1.0 mmol of 3) with 0.1 mol % of 1a afforded the desired alcohol 4 in 92% isolated yield (entry 11). Complex **1b**, having chiral NHC ligands, was also highly active in catalyzing the transfer hydrogenation of **3** (entry 12), while the enantioselectivity of **4** was almost negligible. The catalytic performances of **1a**,**b** are significant, as a product yield of >90% at 70 °C with a catalyst loading as low as 0.1 mol % (entries 11 and 12) is comparable to the results for the best iron catalysts thus far reported.^{7a,22,23}

The results of the catalytic hydrosilylation of 3 are summarized in Table 2. In the presence of 1a (5 mol %), the



	(3)	Fe catalyst Silane THF then KF, TBAF	(4)	OH
entry	cat (amt (mol %))	silane (amt (equiv))	$T(^{\circ}C)/t(h)$	yield $(\%)^b$
1	1a (5.0)	(EtO) ₃ SiH (2.0)	80/5	0
2^{c}	1a (2.0)	(EtO) ₃ SiH (1.5)	50/10	0
3	2 (5.0)	(EtO) ₃ SiH (2.0)	80/5	99
4	2 (1.2)	(EtO) ₃ SiH (1.1)	25/5	99
5	2 (1.2)	$Ph_{2}SiH_{2}$ (1.1)	40/5	99
6	2 (1.2)	Et ₃ SiH (1.1)	40/10	0
7^d	2 (0.1)	(EtO) ₃ SiH (1.1)	25/5	$(91)^{e}$
8^d	2 (0.1)	Ph_2SiH_2 (1.1)	40/5	$(96)^{e}$

^{*a*}The reactions were carried out using 3 (0.20 mmol), Fe catalyst, silane, and THF (2.0 mL) under Ar. ^{*b*}Yield determined by GC-MS. ^{*c*}Na(acac) (5.0 mol %) was added. ^{*d*}The reaction was conducted on a 5-fold scale (1.0 mmol of 3). ^{*c*}The yield of the isolated product is given in parentheses.

hydrosilylation of 3 did not proceed at all (entry 1). Nishiyama et al.²⁴¹ reported the positive effect of Na(acac) in ironcatalyzed hydrosilylation; however, the addition of Na(acac) (5.0 mol %) did not change the outcome (entry 2). In contrast to the unsuccessful reactions with 1a, complex 2 (5.0 mol %) was found to efficiently catalyze the hydrosilylation of 3 in THF at 80 °C, in the presence of 2 equiv of (EtO)₃SiH (entry 3). Even under more challenging conditions, with 1.1 equiv of (EtO)₃SiH and a reduced amount of 2 (1.2 mol %), the hydrosilylation of 3 proceeded quantitatively at 25 °C (entry 4). The hydrosilylation of **3** also took place with Ph_2SiH_2 (entry 5), whereas Et_3SiH was not applicable in this system (entry 6). Only 0.1 mol % of 2 was enough for the reactions on a 5-fold scale (1.0 mmol of 3) in the presence of 1.1 equiv of hydrosilanes ((EtO)₃SiH or Ph_2SiH_2) at room temperature, and the isolated yields of 4 were 91-96% (entries 7 and 8). The catalytic performance of 2 in hydrosilylation can be compared with those of the good iron catalysts thus far reported.22,24,25

CONCLUDING REMARKS

In this study, the two NHC-Fe^{II} chloride complexes $(IMes)_2FeCl_2$ (1a) and $(IEtPh^*)_2FeCl_2$ (1b) were synthesized from the reactions of Fe{N(SiMe₃)₂}₂ with imidazolium salts. Treatment of $(IMes)_2FeCl_2$ with MeLi resulted in the formation of the square-planar complex $(IMes)_2FeMe_2$ (2). Complexes 1a,b and 2 revealed high catalytic activities in the hydrogen transfer reaction of 2'-acetonaphthone. Complex 2 was also found to serve as a good catalyst for the hydrosilylation of 2'-acetonaphthone. Remarkably, only 0.1 mol % catalyst

loading appeared to be sufficient for the transfer hydrogenation catalyzed by **1a**,**b** and the hydrosilylation catalyzed by **2**.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out using standard Schlenk techniques and a glovebox under a nitrogen or an argon atmosphere. Toluene, diethyl ether, THF, and hexane were purified by the method of Grubbs,²⁶ where the solvents were passed over columns of activated alumina and a supported copper catalyst supplied by Hansen & Co. Ltd. Other solvents were degassed and distilled from sodium benzophenone ketyl. Deuterated solvents, C₆D₆ and d₈-THF, were dried by sodium and distilled prior to use. The ¹H and ${}^{13}C{}^{1}H{}$ NMR spectra were recorded on a JEOL ECA-600 spectrometer. The signals were referenced to the residual peak of the deuterated solvent. Solid magnetic susceptibility was measured using a Quantum Design MPMS-XL SQUID-type magnetometer, and the crystalline samples were sealed in quartz tubes. Solution magnetic susceptibilities were determined by the Evans method, using C_6D_6 /hexamethylbenzene or d_8 -THF/hexamethylbenzene solutions.¹⁶ GC-MS spectra were recorded on an Agilent Technologies 7890A GC system with Agilent 5975C VL MSD or 5975 inert mass selective detector (EI) on a HP-5MS column (0.25 mm \times 30 m, film 0.25 μ m). Elemental analyses were performed on a LECO CHNS-932 microanalyzer, where the samples were sealed into silver capsules in a glovebox. X-ray diffraction data were collected on a Rigaku AFC8 or a Rigaku RA-Micro7 equipped with a CCD area detector by using graphite-monochromated Mo K α radiation. Fe{N(SiMe₃)₂}₂,¹¹ IMes·HCl (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene),¹³ and IEtPh*·HCl (IEtPh* = 1,3-bis $((\hat{R})$ -1'-phenylethyl)imidazol-2-ylidene)¹⁵ were prepared according to literature procedures.

Synthesis of (IMes)₂FeCl₂ (1a). Fe{N(SiMe₃)₂)₂ (1.00 g, 2.67 mmol) and IMes·HCl (1.82 g, 5.33 mmol) were charged into a 100 mL flask, and toluene (60 mL) was added at room temperature. The mixture was stirred overnight. The resulting brown solution was concentrated under reduced pressure, during which time a white crystalline powder of 1a appeared. The crystalline powder was collected, washed with hexane, and dried under vacuum (1.75 g, 89%). Single crystals suitable for crystallography were obtained from a toluene solution at -30 °C. ¹H NMR (600 MHz, C₆D₆): δ 27.8 (4H), 5.66 (8H), 3.75 (24H), 2.22 (12H). Magnetic susceptibility (C₆D₆, 296 K): $\mu_{\text{eff}} = 5.1 \mu_{\text{B}}$. Anal. Calcd for C₄₂H₄₈N₄FeCl₂: C, 68.58; H, 6.58; N, 7.62. Found: C, 68.14; H, 6.76; N, 7.36.

Synthesis of (IEtPh*)₂FeCl₂ (1b). Fe{N(SiMe₃)₂}₂ (350 mg, 0.929 mmol) and IEtPh*·HCl (585 mg, 1.87 mmol) were charged into a 100 mL flask, and toluene (30 mL) was added at room temperature. The mixture was stirred overnight. The resulting white suspension was evaporated until dryness, and the white residue was washed with hexane. After extraction with THF (40 mL), the extract was centrifuged to remove a small amount of insoluble solid, and the THF solution was evaporated under reduced pressure. The white solid was washed with hexane to afford a white powder of 1b (544 mg, 86%). Single crystals suitable for crystallography were obtained from a toluene/THF solution at room temperature. ¹H NMR (600 MHz, d_8 -THF): δ 37.0 (4H), 7.54 (8H), 6.89 (4H), 6.23 (8H), 4.22 (12H). Magnetic susceptibility (d_8 -THF, 297 K): $\mu_{eff} = 5.2 \mu_{B}$. Anal. Calcd for C₃₈H₄₀N₄FeCl₂: C, 67.17; H, 5.93; N, 8.25. Found: C, 67.17; H, 6.21; N, 7.92.

Synthesis of (IMes)₂FeMe₂ (2). An Et₂O solution of MeLi (1.06 M, 1.40 mL, 1.48 mmol) was added to a THF (12 mL) solution of 1a (501 mg, 0.68 mmol) at -78 °C. The mixture was gradually warmed to room temperature and was stirred overnight. The resulting orange solution was evaporated until dryness. After it was washed with hexane, the residue was extracted with toluene (20 mL) and the extract was centrifuged to remove LiCl. The solution was evaporated under reduced pressure to afford 2 as a reddish orange powder (405 mg, 86%). Single crystals suitable for crystallography were obtained from a toluene solution at -30 °C. ¹H NMR (600 MHz, C_6D_6): δ 2.09, -2,20, -2,61, -3.59, -32.0. Magnetic susceptibility (C_6D_6 , 296 K):

Organometallics

 μ_{eff} = 3.5 μ_{B} . Anal. Calcd for C₄₄H₅₄N₄Fe: C, 76.06; H, 7.83; N, 8.06. Found: C, 76.15; H, 7.99; N, 7.57.

Typical Procedure for Transfer Hydrogenation of 2'-Acetonaphthone (3). (IMes)₂FeCl₂ (1a; 1.0 mg, 1.4×10^{-3} mol), 2'-acetonaphthone (3; 170 mg, 1.0 mmol), and *i*-PrOLi (79.2 mg, 1.2 mmol) were charged into a 10 mL J. Young tube. Under an argon atmosphere, *i*-PrOH (3.0 mL) was added, and the mixture was stirred for 3 h at 70 °C. The consumption of 3 was monitored by GC-MS. The reaction mixture was filtered through a plug of silica. The filtrate was evaporated until dryness. The residue was purified by silica gel column chromatography (with ethyl acetate/pentane 1/1 as eluent) to give the desired alcohol 4 (159 mg, 0.92 mmol) in 92% yield. The product was analyzed by ¹H and ¹³C NMR.

Typical Procedure for Hydrosilylation of 2'-Acetonaphthone (3). (IMes)₂FeMe₂ (2; 1.0 mg, 1.4×10^{-3} mol), 2'acetonaphthone (3; 170 mg, 1.0 mmol), and THF (3.0 mL) were charged into a 10 mL J. Young tube. Under an argon atmosphere, (EtO)₃SiH (0.21 mL, 1.1 mmol) was added, and the mixture was stirred for 5 h at room temperature. The consumption of 3 was monitored by GC-MS. A THF solution of tetrabutylammonium fluoride (TBAF, 1.0 M, 2.0 mL), KF (116 mg), MeOH (1.0 mL), and H₂O (1.0 mL) was added at 0 °C. The mixture was extracted with ethyl acetate (30.0 mL) and was washed with water (5.0 mL) and brine (5.0 mL). The combined organic layer was dried over anhydrous MgSO₄ and was evaporated until dryness, and then the residue was purified by silica gel column chromatography (with ethyl acetate/ pentane 1/1 as eluent) to give the desired alcohol 4 (156 mg, 0.91 mmol) in 91% yield.

Table 3. Crystal Data for $(IMes)_2FeCl_2$ (1a), $(IEtPh^*)_2FeCl_2$ (1b), and $(IMes)_2FeMe_2$ (2)

	1a	$1b^{-1}/_{2}C_{4}H_{8}O$	2				
formula	$\mathrm{C}_{42}\mathrm{H}_{48}\mathrm{Cl}_{2}\mathrm{FeN}_{4}$	$C_{40}H_{44}Cl_2FeN_4O_{0.5}$	$\mathrm{C}_{44}\mathrm{H}_{54}\mathrm{FeN}_4$				
fw	735.62	715.56	694.78				
temp (°C)	-100	-100	-160				
cryst syst	triclinic	orthorhombic	monoclinic				
space group	P-1 (#2)	$P2_12_12_1$ (#19)	C2/c (#15)				
a (Å)	9.797(6)	9.117(2)	20.835(7)				
b (Å)	10.669(7)	25.346(4)	20.799(6)				
c (Å)	20.094(13)	32.221(6)	18.861(6)				
α (deg)	79.27(3)						
β (deg)	79.53(3)		107.613(4)				
γ (deg)	69.92(3)						
V (Å ³)	1922(2)	7446(3)	7790(5)				
Z	2	8	8				
$D_{\rm calcd}~({\rm g/cm^3})$	1.271	1.277	1.185				
max 2θ (deg)	50.6	55.0	50.7				
R1 ^a	0.0489	0.0605	0.0737				
$wR2^{b}$	0.1050	0.1238	0.1703				
GOF^{c}	1.002	1.007	1.004				
${}^{a}R1 = \sum F_{o} - F_{c} / \sum F_{o} (I > 2\sigma(I)). {}^{b}wR2 = [(\sum (w(F_{o} - F_{c})^{2} / (W(F_{o} $							
$\sum w F_o^2 \overline{)}^{1/2}$ (all reflections). GOF = $\left[\sum w (F_o - F_c)^2 / (N_o - N_v)\right]^{1/2}$							
(where $N_o =$ number of observations, $\overline{N}_v =$ number of variables).							

X-ray Crystal Structure Determination. Crystal data and refinement parameters for **1a,b** and **2** are summarized in Table 3. 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 or -160 °C under a cold nitrogen stream on a Rigaku RA-Micro7 instrument equipped with a Saturn70 CCD detector, using graphite-monochromated Mo K α radiation ($\lambda = 0.710$ 690 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 atoms (refined isotropically), and all hydrogen atoms were placed at calculated positions. In the asymmetric unit of **1b**, there are two crystallographically independent molecules. Three phenyl groups of the IEtPh* ligand of **1b** are disordered over two positions in 2/3, 1/1, and 2/3 ratios, respectively. In the asymmetric unit of **2**, there are two crystallographically independent molecules. The hydrogen atoms of one of the Fe– CH_3 groups are disordered over two positions in a 1/1 ratio. Additional data are available as Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

CIF files giving X-ray crystallographic data for the structures of **1a**,**b** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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