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Monomeric Bis(anilido)iron(II) Complexes with *N*-Heterocyclic Carbene Ligation: Synthesis, Characterization, and Redox Reactivity toward Aryl Halides

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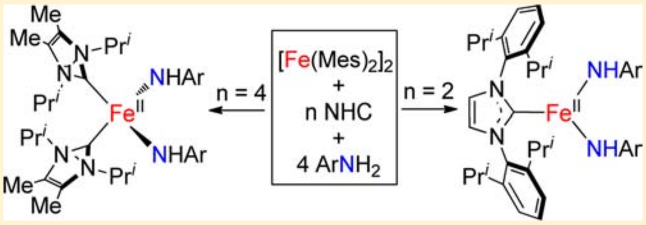
Supporting Information



ABSTRACT: Using monodentate *N*-heterocyclic carbenes as the ancillary ligands, seven monomeric bis(anilido)iron(II) complexes $[(IPr_2Me_2)_2Fe(NHAr)_2]$ (IPr_2Me_2 = 2,5-diisopropyl-3,4-dimethylimidazol-1-ylidene; Ar = Ph, C_6H_4-2-Pr^i, Mes, C_6H_3-2,6-Cl_2, Dipp) and $[(IPr)Fe(NHAr)_2]$ (IPr = 2,5-di(2,6-diisopropylphenyl)imidazol-1-ylidene; Ar = C_6H_3-2,6-Cl_2, Dipp) have been prepared by the one-pot reactions of $[Fe(Mes)_2]_2$ with the corresponding *N*-heterocyclic carbenes, and anilines. These high-spin diamido complexes have been fully characterized by ^{1}H NMR, solution magnetic susceptibility, UV−vis, IR, X-ray diffraction, cyclic voltammetry, as well as elemental analysis. The strong affinity of the *N*-heterocyclic carbene ligands toward ferrous centers, and the steric protection exerted by the NHC ligands are the key factors to stabilize these bis(anilido)iron complexes in a monomeric manner. Reactivity studies revealed the four-coordinate complex $[(IPr_2Me_2)_2Fe(NHMes)_2]$ can react with 1 equiv of 1-iodo-3,5-dimethylbenzene or 1-bromo-3,5-dimethylbenzene in C_6D_6 and THF-d_8 to furnish 1-C_6D_5-3,5-$Me_2C_6H_3$, and 5-D-1,3-$Me_2C_6H_3$, respectively. Under similar conditions, the three-coordinate compound $[(IPr)Fe(NHDipp)_2]$ is inert toward these halides.

INTRODUCTION

The relevance of iron amido species to important iron-mediated chemical transformations, such as dinitrogen reduction,[1] C−H bond amination,[2] and olefin hydroamination,[3] has spurred people's curiosities about the structure and reactivity properties of iron amido compounds,[4] particularly, those of the terminal type. Studies have shown simple amido anions display a strong tendency to bridge iron centers to form iron amido,[5] or even iron imido clusters,[6] rendering access to terminal type iron amide species difficult. In the case of some steric crowded amido anions, usually secondary amido anions like $[N(SiMe_3)_2]^-$, $[N(SiMe_2Ph)_2]^-$, $[NArBMes_2]^-$, $[NBu^t{}_2]^-$, $[NBu^t(C_6H_4\text{-}o\text{-}F)]^-$, and $[N(C_6F_5)_2]^-$, the aggregation tendency of iron amido moieties is alleviated, and monomeric iron amido complexes can be prepared.[5,7−13]

The preparation of the parent and primary amido-iron complexes is more challenging.[14] There are only two parent amido-iron complexes $[(dmpe)_2Fe(NH_2)H]$[15] and $[Fe(C_6H_3\text{-}2,6\text{-}Dipp_2)(NH_2)]_2$,[16] and a handful of primary amido-iron complexes are known. Power et al. reported the synthesis of the two-coordinate complexes $[Fe(NHAr^*)(Ar')]$ and $[Fe(NHAr^*)_2]$ (Ar^* = C_6H_3-2,6-Mes_2, C_6H_3-2,6-$(C_6H_3\text{-}2,4,6\text{-}Pr^i{}_3)_2$, Ar′ = C_6H_3-2,6-$Dipp_2$) by using the sterically congested terphenyl amido ligands.[17] Holland et al. achieved the preparation of some heteroleptic iron(II) amido complexes [(nacnac)Fe(NHR)] bearing bulky *β*-diketiminate ligands.[18] Caulton et al. prepared the four-coordinate complex $[(N(Bu^t{}_2PCH_2SiMe_2)_2)Fe(NHxyl)]$ featuring the bulky phosphine-amido ligand.[19] Besides these, the formation of iron amido complexes, such as $[(N(CH_2CONPr^i)(CH_2CH_2NCONHBu^t)_2)Fe(NHC_6H_4\text{-}p\text{-}Me)]$,[20] $[(Si(C_6H_4PPr^i{}_2)_3)Fe(NHC_6H_4\text{-}p\text{-}Me)]$, and $[(nacnac)Fe(NHAd)(py\text{-}Bu^t)]$, from the hydrogen abstraction reactions of iron imido species have also been noted.[20−23] Obviously, steric protection exerted by either the bulky substituents on the amido ligand or the multidentate ancillary ligands plays an important role in stabilizing these monomeric species.

In addition to this progress, we report herein that, by using monodentate *N*-heterocyclic carbene as the ancillary ligand, the monomeric bis(anilido)iron(II) complexes $[(IPr_2Me_2)_2Fe(NHAr)_2]$ (Ar = Ph, C_6H_4-2-Pr^i, Mes, C_6H_3-2,6-Cl_2, Dipp) and $[(IPr)Fe(NHAr)_2]$ (Ar = C_6H_3-2,6-Cl_2, Dipp) can be readily prepared via the reaction of $[Fe(Mes)_2]_2$ with the corresponding *N*-heterocyclic carbenes, and the anilines.[24] These compounds represent rare examples of iron complexes featuring two terminally bonded primary amido groups, and their molecular structures have been unequivocally established by single-crystal X-ray diffraction studies. Reactivity studies revealed the four-coordinate complex $[(IPr_2Me_2)_2Fe(NHMes)_2]$ can react with aryl iodide and bromide to furnish C(arene)-X bond cleavage products, whereas, the three-coordinate compound $[(IPr)Fe(NHDipp)_2]$ is inert toward these halides.

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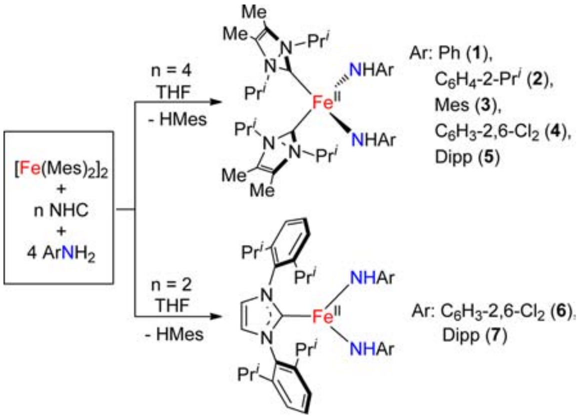
RESULTS AND DISCUSSION

Preparation and Characterization of the Bis(anilido) Iron Complexes. Treatment of $[Fe(Mes)_2]_2$[25] with 4 equiv of IPr_2Me_2,[26] and 4 equiv of anilines in tetrahydrofuran (THF) gave a yellow-brown solution; after workup, the four-coordinate bis(anilido)iron(II) complexes $[(IPr_2Me_2)_2Fe(NHAr)_2]$ (Ar = Ph, **1**; C_6H_4-2-Pr^i, **2**; Mes, **3**; C_6H_3-2,6-Cl_2, **4**; Dipp, **5**) were isolated as yellow crystals in moderate yields (41%-73%). In a similar manner, the three-coordinate complexes $[(IPr)Fe(NHAr)_2]$ (Ar = C_6H_3-2,6-Cl_2, **6**; Dipp, **7**) have also been prepared when using $[Fe(Mes)_2]_2$, IPr, and the corresponding anilines in a 1:2:4 ratio (Scheme 1). The attempts to prepare three-coordinate complexes $(IPr)Fe(NHAr)_2$ employing the less bulky anilines, $PhNH_2$, 2-Pr^i-$C_6H_4NH_2$, gave brown, oily materials that could not be identified.

Scheme 1. Preparation of the Diamido Iron Complexes



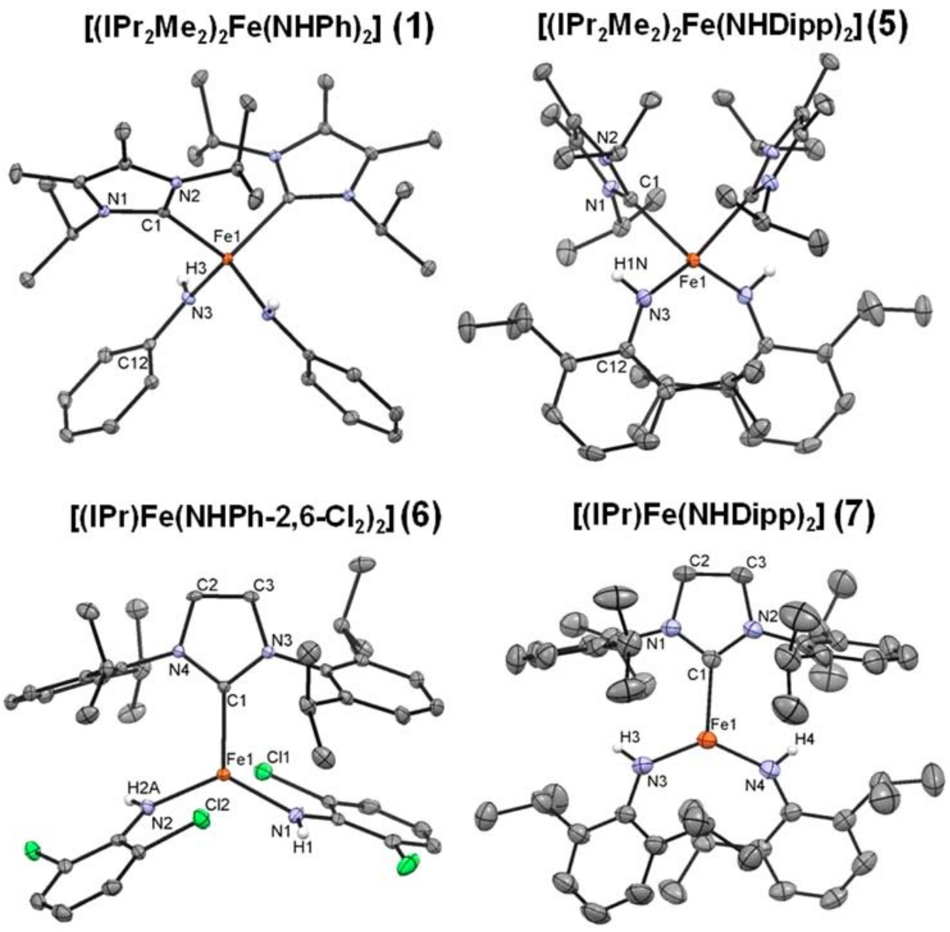
Complexes **1**−**7** are air- and moisture-sensitive and soluble in benzene, Et_2O, and THF. They were fully characterized by ^1H NMR, solution magnetic susceptibility, UV−vis, IR, elemental analysis, X-ray diffraction study, and cyclic voltammetry. Differing from $[(NHC)Fe(N(SiMe_3)_2)_2]$ (NHC = IPr, IMes) which dissociate their free carbene ligands in toluene,[8] the carbene ligands in **1**−**7** are more strongly bonded to the iron centers as (1) their ^1H NMR spectra in C_6D_6 acquired at room temperature only feature broad ^1H NMR peaks and no noticeable peak arising from free NHCs, (2) the ^1H NMR spectra of **3** recorded in C_6D_6 and THF-d_8 display resonances at similar positions indicating the same species is observed, and (3) the addition of 10 equiv of IPr_2Me_2 to a solution of **3** in C_6D_6 did not cause the shift of the paramagnetic signals. The magnetic moments of **2**−**7** measured by Evans method range from 4.6 to 5.4 μB, suggesting their high spin electronic configurations.[27] Dissolution of the complexes in THF develops pale yellow solutions, and only shoulder bands near 300 nm caused by LMCT were observed in their UV−vis absorption spectra (Supporting Information, Figure s1). Since at very low concentration these complexes might undergo decomposition (see electrochemical studies, vide infra), these absorptions might not directly come from **1**−**7** themselves. Characteristic N−H stretching vibrations around 3350 cm^{-1} have been found in their IR spectra.

The molecular structures of **1**−**7** have been determined by single-crystal X-ray diffraction studies. Figure 1 shows the molecular structures of **1**, **5**, **6**, and **7** as the representatives. Table 1 lists the key bond lengths and angles. The iron centers in **1**−**5** are tetrahedrally coordinated with two IPr_2Me_2 and two anilido ligands. Examining the metrical data around their FeC_2N_2 units (Table 1) revealed the steric bulkiness of the anilido ligands, as reflected by their Fe−N(amido)−C(aryl) and N(amido)−Fe−N(amido) angles that deviate from angles for idealized tetrahedral geometry, induces distortion of the FeC_2N_2 unit. The FeC_2N_2 unit in $[(IPr_2Me_2)_2Fe(NHPh)_2]$ (**1**) exhibits the least distortion with the interatomic angles within the FeC_2N_2 unit ranging from 107.0(1) to 114.4(1) degrees, whereas, the FeC_2N_2 core in $[(IPr_2Me_2)_2Fe(NHDipp)_2]$ (**5**) is the most distorted one with the angles spanning between 93.61(8) and 128.1(1) degrees. Overall, the deviation of the FeC_2N_2 units from tetrahedral geometry shows a trend of $\mathbf{1} < \mathbf{2} < \mathbf{3} \le \mathbf{4} < \mathbf{5}$, which accords well with the bulkiness of their anilido ligands. In addition to the bond angles, a stepwise elongation of the Fe−C(carbene) bonds from 2.148(1) to 2.210(2) Å is also observed in **1**−**5**, which again could be ascribed to the steric effect of the anilido ligands. The bond lengths of the Fe−N(amido) moieties in **1**−**5** are close to each other (1.986(2)−2.019(2) Å), but are longer than those of the known iron(II) amido complexes such as $[Fe(NHC_6H_3\text{-}2,6\text{-}Mes_2)_2]$ (1.909(3) Å),[17a] [(nacnac)Fe(NHDipp)(py-*p*-Bu^t)] (1.949(2) Å),[18a] $[(N(Bu^t{}_2PCH_2SiMe_2)_2)Fe(NHxyl)]$ (1.951(2) Å),[19] and $[(PhBP_3)Fe(NH\text{-}p\text{-}tolyl)]$ (1.913(2) Å).[21a] The elongation could be due to the stronger σ-donating property of the *N*-heterocyclic carbene ligand over the phosphine and nacnac ligands.

As shown in Figure 1, the coordination of the sterically demanding IPr ligand in **6** and **7** allows the formation of the three-coordinate complexes, in which the Fe center is nearly coplanar with the C(carbene) and the two N(amido) atoms. As listed in Table 1, the Fe−C(carbene) bond distances in **6** and **7** are 2.104(2) and 2.142(2) Å, respectively. These distances are shorter than those of the Fe−C(carbene) bonds in $[(IPr_2Me_2)_2Fe(NHC_6H_3\text{-}2,6\text{-}Cl_2)_2]$ (**4**) $[(IPr_2Me_2)_2Fe(NHDipp)_2]$ (**5**), and $[(IPr)Fe(N(SiMe_3)_2)_2]$ (**8**).[8] The Fe−N(amido) separations in **6** and **7** (1.969 (2) and 1.922(2) Å on average) are also the shorter Fe−N(amido) bonds among **1**−**8** (Table 1), but longer than those of the three-coordinate iron(II) amides [(nacnac)Fe(NHR)] (1.79−1.91 Å).[18a] It is noteworthy that although the molecular structures of **6** and **7** exhibit a close resemblance, **6** features weak interactions between its iron center and the peripheral chlorine atoms (Cl(1) and Cl(2)) with the Fe−Cl separations being 2.717(1) and 2.732(1) Å. These weak interactions cause the near vertical arrangement of the anilido ligands toward the coordination plane in **6**, sharply contrasting with the near coplanar aryl groups in **7** (Figure 1).

Reactions of the Bis(anilido) Iron Complexes with Aryl Halides. The redox properties of **1**−**7** have been examined by cyclic voltammetry and open circuit potential studies (Supporting Information, Figures s2−s9). In general these voltammograms are dominated by irreversible redox waves which is in sharp contrast to the quasi-reversible one of $[(IMes)_2FeCl_2]^{0/1+}$.[28] Because the peak current intensities of the quasi-reversible waves with very negative half-wave potentials in these voltammograms increased when more scans were performed, we refrain from assigning chemical events for these voltammograms.

As mentioned above, iron amido moieties are prone to aggregation; the successful preparation of these monomeric primary amido-iron compounds clearly indicates the strong affinity of NHCs toward ferrous centers, which had also been demonstrated by the isolation of the stable all-ferrous iron−


[(IPr$_2$Me$_2$)$_2$Fe(NHPh)$_2$] (1)

[(IPr$_2$Me$_2$)$_2$Fe(NHDipp)$_2$] (5)

[(IPr)Fe(NHPh-2,6-Cl$_2$)$_2$] (6)

[(IPr)Fe(NHDipp)$_2$] (7)

Figure 1. Molecular Structures of **1**, **5**, **6**, and **7**, showing 30% probability ellipsoids and the partial atom numbering scheme.

Table 1. Selected Bond Distances (Å) and Angles (degree) in 1−8[a]

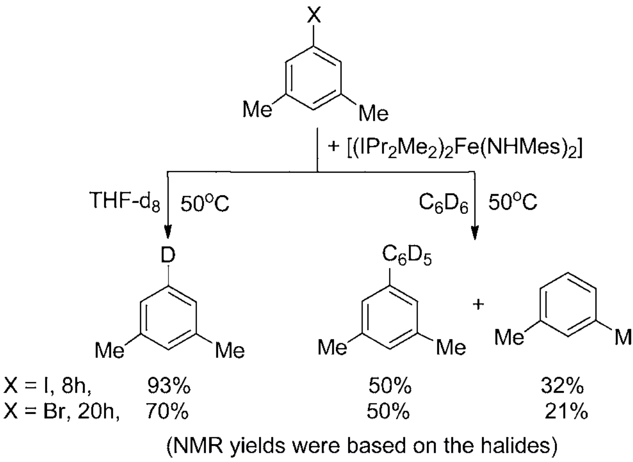
	1	2	3	4	5	6	7	8
Fe−C	2.148(1)	2.150(2)	2.172(2)	2.175(2)	2.210(2)	2.104(2)	2.142(2)	2.182(2)
			2.174(2)	2.185(2)				
Fe−N	1.999(1)	1.986(2)	2.006(2)	2.005(1)	1.985(2)	1.967(2)	1.921(2)	1.982(2)
								1.979(2)
			2.019(2)	2.007(1)		1.971(2)	1.924(2)	
C−Fe−C	108.5(1)	105.0(1)	97.77(8)	96.05(6)	93.61(8)			
N−Fe−N	114.4(1)	117.4(1)	126.4(1)	128.4(1)	128.1(1)	127.4(1)	135.4(1)	124.3(1)
C−Fe−N	107.0(1)	112.2(1)	110.4(1)	113.4(1)	97.28(6)	114.4(1)	112.6(1)	117.1(1)
	109.9(1)	104.5(1)						118.6(1)
			103.0(1)	100.4(1)	118.2(1)	118.1(1)	111.9(1)	
			110.6(1)	112.4(1)				
			105.1(1)	101.9(1)				
Fe−N−C(aryl)	125.5(1)	127.0(2)	137.6(2)	139.0(1)	143.9(1)	130.7(2)	132.8(2)	
			142.1(2)	138.8(1)		128.8(2)	144.3(2)	

[a]For [(IPr)Fe(N(SiMe$_3$)$_2$)$_2$] (**8**), see ref 8.

sulfur cubane [Fe$_4$S$_4$(IPr$_2$Me$_2$)$_4$],[29] and the dimethyl iron(II) complex [(IEt$_2$Me$_2$)$_2$Fe(CH$_3$)$_2$][30] in our previous studies. With these diamido iron(II) compounds in hand, we have performed some preliminary reactivity investigations to examine the potential application of these iron anilido complexes in carbon−nitrogen bond construction.[31]

NMR assays in C$_6$D$_6$ indicated [(IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$] (**3**) can slowly react with 1-iodo-3,5-dimethylbenzene (1 equiv) at room temperature (less than 5% conversion of the iodide in 3 h). When the temperature was raised to 50 °C, slow color change from pale yellow to dark brown occurred. After 8 h, ^{1}H NMR spectrum analyses indicated the full consumptions of the start materials, and the formations of 1-(C$_6$D$_5$)-3,5-Me$_2$C$_6$H$_3$ (50% NMR yield), 1,3-Me$_2$C$_6$H$_4$ (32% NMR yield), and new paramagnetic species (Scheme 2). Interestingly, when the reaction was conducted in THF-d$_8$, the aryl iodide was converted to 5-D-1,3-Me$_2$C$_6$H$_3$ (93% NMR yield) exclusively. The identities of the two deuterated arenes were confirmed by

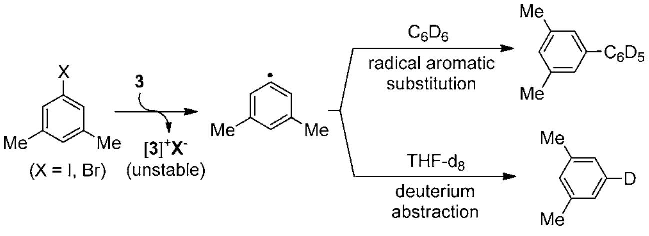
Scheme 2. Reactions of 3 with Aryl Halides



NMR and GC-MS analyses. Attempts to isolate the paramagnetic species by recrystallization were unsuccessful. Similar products were obtained when **3** was treated with 1-bromo-3,5-dimethylbenzene, but no reaction took place when 1-chloro-3,5-dimethylbenzene was used. Different from the observed reactivity of **3**, the three-coordinate complex [(IPr)Fe(NHDipp)$_2$] (**7**) was inert toward these aryl halides.

The formation of 1-(C_6D_5)-3,5-$Me_2C_6H_3$ and 5-D-1,3-$Me_2C_6H_3$ clearly demonstrates iron complex-mediated C-(arene)-X (X = Br, I) bond cleavage reaction has taken place. On the basis of the observed products pattern, we propose the reaction between **3** and the aryl halides might proceed in a single-electron transfer mechanism to generate a transient species $[3]^+[X]^-$ and an aryl radical Ar$^{\bullet}$.[30,32] In deuterobenzene, the aryl radical might react with a deuterobenzene molecule to generate a σ-complex which might then be oxidized by $[3]^+[X]^-$ or other species to produce 1-(C_6D_5)-3,5-$Me_2C_6H_3$ (Scheme 3).[33] In the case with THF-d_8 as solvent, deuterium-atom-abstraction reaction between the aryl radical with a THF-d_8 molecule might occur to yield 5-D-1,3-$Me_2C_6H_3$. The failure to achieve coupling between the anilido ligand and the aryl halides in these trials should be due to the outer-sphere character of the single-electron transfer step that should produce aryl radicals surrounded by solvent molecules and subsequently make the access of the aryl radicals toward the anilido moiety difficulty.

Scheme 3. Possible Pathways for the Formation of the Deuterated Arenes



■ CONCLUSION

In summary, we have prepared a series of monomeric primary amido iron(II) complexes bearing monodentate NHC ligation via the one pot reactions of [Fe(Mes)$_2$]$_2$ with NHCs and primary anilines. The reactions using the less steric demanding NHC ligand afforded four-coordinate complexes [(IPr$_2$Me$_2$)$_2$Fe(NHAr)$_2$] (Ar = Ph, C_6H_4-2-Pr^i, Mes, C_6H_3-2,6-Cl_2, Dipp), whereas, the three-coordinate compounds [(IPr)Fe(NHAr)$_2$] (Ar = C_6H_3-2,6-Cl_2, Dipp) were obtained with the more steric demanding IPr. These bis(anilido)iron(II) complexes have a high-spin electronic configuration and were characterized by various spectroscopic methods. Reactivity studies have revealed the four-coordinate complex [(IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$] can react with 1-iodo-3,5-dimethylbenzene or 1-bromo-3,5-dimethylbenzene, possibly via single-electron transfer mechanism, to give 1-C_6D_5-3,5-$Me_2C_6H_3$ in deuterated benzene, and 5-D-1,3-$Me_2C_6H_3$ in THF-d_8. Under similar conditions, the three-coordinate compound [(IPr)Fe(NHDipp)$_2$] is inert toward these halides.

■ EXPERIMENTAL SECTION

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. [Fe(Mes)$_2$]$_2$,[25] 2,5-diisopropyl-3,4-dimethylimidazol-1-ylidene (IPr$_2$Me$_2$),[26] 2,5-di(2,6-diisopropylphenyl)imidazol-1-ylidene-(IPr)[34] were prepared according to literature methods. All chemicals were purchased from either Strem or J&K Chemical Co. and used as received unless otherwise noted. ^{1}H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer. All chemical shifts were reported in δ units with references to the residual protons of the deuterated solvents for proton chemical shifts. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). Magnetic moments were measured at 23 °C by the method originally described by Evans with stock and experimental solutions containing a known amount of a $(CH_3)_3SiOSi(CH_3)_3$ standard.[27] GC-MS analyses were performed on a Shimadzu GCMS-QP 2010 Spectrometer. UV−vis spectra were recorded with a Shimadzu UV-3600 spectrophotometer. IR spectra were recorded with a NICOLET AVATAR 330 FT-IR spectrophotometer. Electrochemical studies were made with a CHI 600D potentiostation in THF solutions using a glassy carbon working electrode, 0.1 M $(Bu_4N)(PF_6)$ supporting electrolyte, and a SCE reference electrode. A sweep rate of 50 mV/s was used for the cyclic voltammetry measurements. Under these conditions, $E_{1/2}$ = 0.55 V for the $[Cp_2Fe]^{0,1+}$ couple.

Preparation of (IPr$_2$Me$_2$)$_2$Fe(NHPh)$_2$ (1). To a red-brown solution of [(IPr$_2$Me$_2$)Fe(Mes)$_2$] prepared by mixing [Fe(Mes)$_2$]$_2$ (122.9 mg, 0.20 mmol) and IPr$_2$Me$_2$ (155.1 mg, 0.80 mmol) in 5.0 mL of THF was slowly added a solution of $PhNH_2$ (85.1 mg, 0.80 mmol) in THF (3 mL) at room temperature. After stirring for 16 h, lots of yellow solids precipitated out from the solution. The suspension was then filtrated to give some yellow solid and a brown mother solution. The solid was washed with a small amount of THF (3 mL), and dried under vacuum, to afford **1** as a yellow powder (146.6 mg, yield: 61%). Yellow-green crystals of **1** suitable for X-ray crystallography were obtained by adding a small portion of toluene (1 mL) to the brown mother solution and then evaporating THF at room temperature for 5 days. The ^{1}H NMR spectra of the yellow powder and the yellow-green crystal are identical. ^{1}H NMR (400 MHz, C_6D_6): δ 41.09(2H, *m-CH* on the phenyl rings), 11.46(6H, =CCH_3), 8.67(12H, NCH(CH_3)$_2$), −64.90(1H, *p-CH* on the phenyl rings). The signals of the *ortho-CH* on the phenyl rings, the NCH(CH_3)$_2$, or NHAr was not observed. Anal. Calcd for $C_{34}H_{52}FeN_6$: C, 67.99; H, 8.73; N, 13.99. Found: C, 68.10; H, 8.59; N, 14.00. IR (KBr, cm^{-1}): υ_{N-H} 3321.7. Because of the low solubility of **1** in C_6D_6, its solution magnetic moment has not been measured.

Preparation of (IPr$_2$Me$_2$)$_2$Fe(NHC$_6$H$_4$-2-Pr^i)$_2$ (2). To a red-brown solution of [(IPr$_2$Me$_2$)Fe(Mes)$_2$] prepared by mixing [Fe(Mes)$_2$]$_2$ (122.9 mg, 0.20 mmol) and IPr$_2$Me$_2$ (155.1 mg, 0.80 mmol) in 5.0 mL of THF was slowly added a solution of 2-Pr^i-$C_6H_4NH_2$ (109.1 mg, 0.80 mmol) in THF (3 mL) at room temperature. After stirring for 18 h, the color of the mixture changed to green-brown, and then all the volatiles were removed under vacuum to give a brown residue. The residue was redissolved in THF (7 mL). After filtration, the filtrate was concentrated to about 5 mL, and toluene (1 mL) was added. Slow evaporation of THF afforded the product as yellow crystals. Yield: 199.0 mg, 73%. ^{1}H NMR (300 MHz, C_6D_6): δ 48.41(1H, *m*-C*H* on the phenyl rings), 38.15(br, *m*-C*H* on the phenyl rings), 30.49(br, *o*-C*H* on the phenyl rings), 8.88(12H, NCH(CH_3)$_2$), 7.63(6H, =CCH_3 or CCH(CH_3)$_2$), 6.41(6H, =CCH_3 or CCH(CH_3)$_2$), −62.72(1H, *p*-C*H* on the phenyl rings). The signals of C*H*(CH$_3$)$_2$ or N*H*Ar were not observed. Anal. Calcd for $C_{40}H_{64}FeN_6$: C, 70.15; H, 9.42; N, 12.27. Found: C, 70.01; H, 9.58; N, 12.19. Magnetic susceptibility: μ_{eff} = 4.6(1) μ_B. IR (KBr, cm^{-1}): υ_{N-H} 3378.9.

Preparation of (IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$ (3). This complex was obtained as yellow crystals by the reaction of [Fe(Mes)$_2$]$_2$ (116.5 mg, 0.20 mmol) with IPr$_2$Me$_2$ (146.8 mg, 0.80 mmol) and MesNH$_2$ (109.3 mg, 0.80 mmol) in 8 mL of THF using procedures similar to that of **2**. Yield: 112.0 mg, 41%. ^{1}H NMR (300 MHz, C_6D_6): δ 97.00(br, *o*-CH_3 on the mesityl group), 80.77(3H, *p*-CH_3 of the mesityl group), 45.47(2H, *m*-C*H* of the mesityl group), 7.38(12H, NCH(CH_3)$_2$), 3.63(6H, =CCH_3). ^{1}H NMR (400 MHz, THF-d_8): δ 95.67(br, *o*-CH_3 on the mesityl group), 79.27(3H, *p*-CH_3 of the mesityl group), 44.33(2H, *m*-C*H* of the mesityl group), 7.97(12H, NCH(CH_3)$_2$), 4.27(6H, =CCH_3). The signals of C*H*(CH$_3$)$_2$ or N*H*Ar was not observed. Anal. Calcd for $C_{40}H_{64}FeN_6$: C, 70.15; H, 9.42; N, 12.27. Found: C, 70.23; H, 9.55; N, 12.51. Magnetic susceptibility: μ_{eff} = 4.8(1) μ_B. IR (KBr, cm^{-1}): υ_{N-H} 3349.6.

Preparation of (IPr$_2$Me$_2$)$_2$Fe(NHC$_6$H$_3$-2,6-Cl$_2$)$_2$ (4). This complex was obtained as yellow crystals by the reaction of [Fe(Mes)$_2$]$_2$ (118.4 mg, 0.20 mmol) with IPr$_2$Me$_2$ (150.1 mg, 0.80 mmol) and 2,6-Cl$_2$−C$_6$H$_3$NH$_2$ (129.2 mg, 0.80 mmol) in 8 mL of THF using procedures similar to that of **2**. Yield: 132.0 mg, 45%. ^{1}H NMR (300 MHz, C_6D_6): δ 9.30(6H, =CCH_3), 6.77(12H, NCH(CH_3)$_2$), −59.90(1H, *p*-C*H* on the phenyl rings). The signals of *m*-C*H* on the phenyl rings, C*H*(CH$_3$)$_2$, or N*H*Ar was not observed. Anal. Calcd for $C_{34}H_{48}Cl_4FeN_6$: C, 55.30; H, 6.55; N, 11.38. Found: C, 55.38; H, 6.31; N, 11.42. Magnetic susceptibility: μ_{eff} = 4.7(1) μ_B. IR (KBr, cm^{-1}): υ_{N-H} 3334.7.

Preparation of (IPr$_2$Me$_2$)$_2$Fe(NHDipp)$_2$ (5). This complex was obtained as yellow crystals by the reaction of [Fe(Mes)$_2$]$_2$ (118.2 mg, 0.20 mmol) with IPr$_2$Me$_2$ (151.1 mg, 0.80 mmol) and DippNH$_2$ (149.1 mg, 0.80 mmol) in 8 mL of THF using procedures similar to that of **2**. Yield: 218.0 mg, 71%. ^{1}H NMR (300 MHz, C_6D_6): δ 44.53(2H, *m*-C*H* of the phenyl rings), 9.41(12H, CH(CH_3)$_2$), 6.41(br, CH(CH_3)$_2$ or =CCH_3), 5.50(br, CH(CH_3)$_2$ or =CCH_3), −62.00(1H, *p*-C*H* on the phenyl rings). The signals of C*H*(CH$_3$)$_2$ or N*H*Ar was not observed. Anal. Calcd for $C_{46}H_{76}FeN_6$: C, 71.85; H, 9.96; N, 10.93. Found: C, 71.83; H, 9.88; N, 11.09. Magnetic susceptibility: μ_{eff} = 4.8(1) μ_B. IR (KBr, cm^{-1}): υ_{N-H} 3340.9.

Preparation of (IPr)Fe(NHC$_6$H$_3$-2,6-Cl$_2$)$_2$ (6). To a solution of [Fe(Mes)$_2$]$_2$ (117.8 mg, 0.20 mmol) in THF (7 mL) was added IPr (156.1 mg, 0.40 mmol) at room temperature. After stirring for 1 h, a yellow suspension was formed. Then a solution of 2,6-Cl$_2$−C$_6$H$_3$NH$_2$ (131.2 mg, 0.8 mmol) in THF (3 mL) was slowly added to the suspension, and the mixture was further stirred for 8 h. Removal of the volatiles under vacuum gave a yellow solid, which was redissolved in diethyl ether (10 mL) and filtrated. The filtrate was concentrated to about 5 mL and *n*-hexane (1 mL) was added. Slow evaporation of Et$_2$O afforded the product as yellow crystals. Yield: 110.0 mg, 36%. ^{1}H NMR (300 MHz, C_6D_6): δ 60.15(2H), 27.91(1H), 12.20(2H), 9.25(6H), 1.20(1H), −3.20(6H), −10.11(2H), −62.72(1H). Anal. Calcd for $C_{39}H_{45}Cl_4FeN_4$: C, 61.03; H, 5.91; N, 7.30. Found: C, 61.23; H, 5.95; N, 7.48. Magnetic susceptibility: μ_{eff} = 5.4(2) μ_B. IR (KBr, cm^{-1}): υ_{N-H} 3390.7.

Preparation of (IPr)Fe(NHDipp)$_2$ (7). To a solution of [Fe(Mes)$_2$]$_2$ (441.3 mg, 0.75 mmol) in THF (15 mL) was added IPr (582.9 mg, 1.5 mmol) at room temperature. After stirring for 1 h, a yellow suspension was formed. Then a solution of DippNH$_2$ (531.8 mg, 3.0 mmol) in THF (5 mL) was slowly added to the suspension, and the mixture was further stirred for 19 h, during which the color of the mixture changed to yellow-brown. Removal of the volatiles under vacuum gave a yellow solid, which was redissolved in diethyl ether (10 mL) and filtrated. The filtrate was concentrated to about 7 mL, and *n*-hexane (1 mL) was added. Slow evaporation of Et$_2$O afforded the product as yellow crystals. Yield: 900.0 mg, 75%. ^{1}H NMR (300 MHz, C_6D_6): δ 52.33(br), 34.88(br), 1.10(br), −1.16(br), −11.01(br). Because of the large width of the peaks, integration was not performed. Anal. Calcd for $C_{51}H_{72}FeN_4$: C, 76.86; H, 9.11; N, 7.03. Found: C, 76.10; H, 9.13; N, 7.02. Magnetic susceptibility: μ_{eff} = 5.1(2) μ_B. IR (KBr, cm^{-1}): υ_{N-H} 3337.9.

Reaction of (IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$ (3) with 1-Iodo-3,5-dimethylbenzene in C$_6$D$_6$. To a solution of (IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$ (24.2 mg, 0.040 mmol) in C_6D_6 (1 mL) in a J. Young NMR tube was added 1-iodo-3,5-dimethylbenzene (9.5 mg, 0.041 mmol), and 1,3,5-trimethoxybenzene (8.2 mg, 0.049 mmol) as internal standard. The reaction was monitored by ^{1}H NMR, and it proceeded very slowly at room temperature. Then the mixture was heated to 50 °C. After 8 h, the color of the solution turned into dark brown, and ^{1}H NMR spectrum analyses on the mixture indicated the full consumptions of the two start materials, and the formations of 1-(C_6D_5)-3,5-Me$_2$C$_6$H$_3$ and 1,3-Me$_2$C$_6$H$_4$ in 50% and 32% yields, respectively, in addition with new paramagnetic species. The identities of these two products were confirmed by ^{1}H NMR and GC-MS analyses. Attempts to isolate the paramagnetic species by recrystallization were unsuccessful. For 1-(C_6D_5)-3,5-Me$_2$C$_6$H$_3$, ^{1}H NMR (300 MHz, C_6D_6): δ 2.14 (s, 6H, CH_3), 6.78 (s, 1H, *p*-C$_6H_3$), 7.14 (s, 2H, *o*-C$_6H_3$); GC-MS: calcd for $C_{14}H_9D_5^+$: 187; Found: 187. For 1,3-Me$_2$C$_6$H$_4$, ^{1}H NMR (300 MHz, C_6D_6): δ 2.09 (s, 6H, CH_3), 6.80(s, 1H), 6.84−6.85 (d, 2H), 7.03−7.06 (m, 1H).

Reaction of (IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$ (3) with 1-Iodo-3,5-dimethylbenzene in C$_6$H$_6$. In C_6H_6 (5.0 mL), (IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$ (273.7 mg, 0.40 mmol) was reacted with 1-iodo-3,5-dimethylbenzene (92.8 mg, 0.40 mmol) at 50 °C overnight. The mixture was then quenched with saturated aqueous NaHCO$_3$ solution (20 mL) and extracted with ether (3 × 10 mL). The organic phase was separated and dried with MgSO$_4$. Removal of the volatiles afforded a yellow oily material, which was subjected to column chromatographic separation (SiO$_2$, 300−400 mesh) to give 1-phenyl-3,5-dimethylbenzene (49.7 mg, 66% yield) as a colorless solid. ^{1}H NMR (300 MHz, C_6D_6): δ: 2.42 (s, 6H, CH_3), 7.03 (s, 1H, *p*-C$_6H_3$), 7.25 (s, 2H, *o*-C$_6H_3$), 7.34−7.38 (m, 1H, *p*-C$_6H_5$), 7.43−7.47 (m, 2H, C$_6H_5$), 7.60−7.62 (m, 2H, C$_6H_5$). ^{13}C NMR (300 MHz, C_6D_6): δ 21.42, 125.09, 127.06, 127.17, 128.62, 128.87, 138.24, 141.23, 141.43. The NMR spectra are idential to those reported in literature.[35]

Reaction of (IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$ (3) with 1-Iodo-3,5-dimethylbenzene in THF-d$_8$. The reaction between (IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$ (25.0 mg, 0.036 mmol) and 1-iodo-3,5-dimethylbenzene (8.5 mg, 0.036 mmol) with 1,3,5-trimethoxybenzene (6.0 mg, 0.032 mmol) as the internal standard was performed in THF-d_8 (1 mL). After being heated at 50 °C for 8 h, the color of the solution turned to dark brown, and ^{1}H NMR spectrum analyses indicated the full conversion of 1-iodo-3,5-dimethylbenzene to 5-D-1,3-Me$_2$C$_6$H$_3$ in 93% NMR yield. For 5-D-1,3-Me$_2$C$_6$H$_3$, ^{1}H NMR (300 MHz, C_6D_6): δ 2.22(s, 6H), 6.90(s, 2H), 6.95(s, 1H); GC-MS: calcd for $C_8H_9D^+$: 107; Found: 107. Paramagnetically shifted ^{1}H NMR signals with similar chemical shifts as those observed in the reaction conducted in C_6D_6 were also observed in the ^{1}H NMR spectrum.

Reaction of (IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$ (3) with 1-Bromo-3,5-dimethylbenzene in C$_6$D$_6$. In a J. Young NMR tube, the reaction mixture of (IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$ (18.0 mg, 0.026 mmol), 1-bromo-3,5-dimethylbenzene (4.7 mg, 0.025 mmol), and 1,3,5-trimethoxybenzene (4.4 mg, 0.026 mmol) in C_6D_6 (1 mL) was heated at 50 °C. After 20 h, ^{1}H NMR spectrum analyses indicated the retention of 1-bromo-3,5-dimethylbenzene (6%), and the formations of 1-(C_6D_5)-3,5-Me$_2$C$_6$H$_3$, and 1,3-Me$_2$C$_6$H$_4$ in 50% and 21% yields, respectively, in addition with unknown paramagnetic species. Attempts to isolate the paramagnetic species by recrystallization were unsuccessful.

Reaction of (IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$ (3) with 1-Bromo-3,5-dimethylbenzene in THF-d$_8$. In a J. Young NMR tube, the reaction mixture of (IPr$_2$Me$_2$)$_2$Fe(NHMes)$_2$ (30.9 mg, 0.045 mmol), 1-bromo-

Table 2. Crystal Data and Summary of Data Collection and Refinement for **1**−**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_{34}H_{52}FeN_6$	$C_{40}H_{64}FeN_6$	$C_{40}H_{64}FeN_6$	$C_{34}H_{48}Cl_4FeN_6$	$C_{46}H_{76}FeN_6$	$C_{39}H_{44}Cl_4FeN_4$	$C_{51}H_{72}FeN_4$
crystal size (mm)	0.341 × 0.211 × 0.169	0.25 × 0.23 × 0.18	0.25 × 0.22 × 0.14	0.30 × 0.18 × 0.11	0.35 × 0.30 × 0.20	0.35 × 0.25 × 0.14	0.370 × 0.350 × 0.321
fw	600.67	684.82	684.82	738.43	768.98	766.43	796.98
crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	*C*2/*c*	*P*2/*n*	*P*2(1)/*c*	$P\bar{1}$	*C*2/*c*	*Cc*	$P\bar{1}$
a, Å	17.095(2)	21.079(2)	11.097(2)	10.7210(1)	25.435(3)	10.281(1)	11.141(7)
b, Å	9.450(1)	9.236(1)	22.560(2)	12.184(1)	11.582(1)	22,888(3)	13.530(1)
c, Å	20.360(2)	21.123(2)	16.012(1)	15.355(2)	18.907(4)	16.865(2)	18.027(0)
α, deg	90	90	90	96.194(1)	90	90	101.373(1)
β, deg	100.219(2)	107.531(2)	103.916(1)	102.035(2)	126.605(1)	99.463(3)	91.985(1)
γ, deg	90	90	90	106.672(1)	90	90	114.128(1)
V, Å^3	3236.9(7)	3921.4(7)	3891.1(4)	1848.8(3)	4471.1(1)	3914.7(9)	2411.0(3)
Z	4	4	4	2	4	4	2
D_{calcd}, Mg/m^3	1.233	1.160	1.169	1.326	1.142	1.300	1.098
radiation (*λ*), Å	Mo K*α* (0.71073)	Mo K*α* (0.71073)	Mo K*α* (0.71073)	Mo K*α* (0.71073)	Mo K*α* (0.71073)	Mo K*α* (0.71073)	Mo K*α* (0.71073)
2*θ* range, deg	4.06 to 52.00	3.26 to 53.98	3.18 to 51.00	3.54 to 54.00	3.98 to 60.00	4.32 to 59.04	3.40 to 52.00
μ, mm^{-1}	0.498	0.419	0.422	0.729	0.374	0.690	0.348
F(000)	1296	1488	1488	776	1680	1600	864
no. of obsd reflns	11156	27589	26529	14177	20930	17743	13266
no. of params refnd	197	441	442	418	250	441	550
goodness of fit	1.068	0.974	0.992	1.026	1.032	0.999	1.001
R1	0.0269	0.0451	0.0396	0.0312	0.0469	0.0434	0.0492
*w*R2	0.0733	0.1048	0.0952	0.0837	0.1256	0.0903	0.1113

3,5-dimethylbenzene (7.5 mg, 0.041 mmol), and 1,3,5-trimethoxybenzene (5.7 mg, 0.034 mmol) in THF-d_8 (1 mL) was heated at 50 °C. After 20 h, ^{1}H NMR spectrum analyses indicated the retention of 1-bromo-3,5-dimethylbenzene (30%), and the formation of 5-D-1,3-$Me_2C_6H_3$ in 70% NMR yield. Paramagnetically shifted ^{1}H NMR signals with similar chemical shifts as those observed in the reaction conducted in C_6D_6 were also observed in the ^{1}H NMR spectrum.

X-ray Structure Determinations. The structures of the seven compounds in Supporting Information, Table S1 were determined. Crystallizations were performed at room temperature. Crystals were coated with Paratone-N oil and mounted on a Bruker APEX CCD-based diffractometer equipped with an Oxford low-temperature apparatus. Data were collected with scans of 0.3 s/frame for 30 s. Cell parameters were retrieved with SMART software and refined using SAINT software on all reflections. Data integration was performed with SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS.[36] Space groups were assigned unambiguously by analysis of symmetry and systematic absences determined by XPREP. All structures were solved and refined using SHELXTL.[37] Metal and first coordination sphere atoms were located from direct-method E-maps; other non-hydrogen atoms were found in alternating difference Fourier synthesis and least-squares refinement cycles, and during final cycles were refined anisotropically. All the hydrogen atoms were placed in calculated positions employing a riding model. Final crystal parameters and agreement factors are reported in Table 2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format, UV−vis absorption spectra, and cyclic voltammograms, and ^{1}H NMR spectra for complexes **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

NHC, *N*-heterocyclic carbene; IPr_2Me_2, 2,5-diisopropyl-3,4-dimethylimidazol-1-ylidene; IEt_2Me_2, 2,5-diethyl-3,4-dimethylimidazol-1-ylidene; IPr, 2,5-di(2,6-diisopropylphenyl)imidazol-1-ylidene; IMes, 2,5-di(1,3,5-trimethylphenyl)imidazol-1-ylidene; sIPr, 2,5-di(2,6-diisopropylphenyl)-3,4-dihydroimidazol-1-ylidene; Mes, 2,4,6-trimethylphenyl; Dipp, 2,6-diisopropylphenyl; Cp, cyclopentadienyl

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