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# Reactivity of a Bis(amidinato)iron(II) Complex [Fe(MesC(NPr$^i$)$_2$)$_2$] toward Some Oxidizing Reagents

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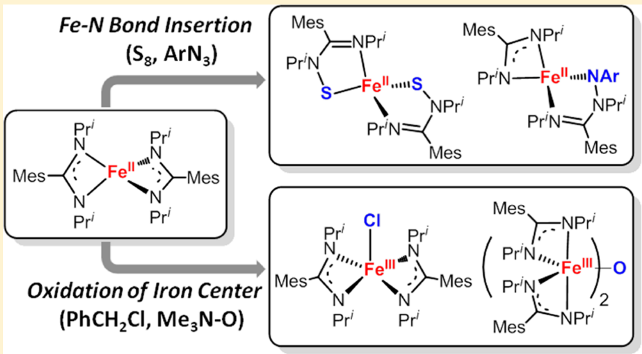
*Supporting Information*

**ABSTRACT:** A diversified reactivity of the mononuclear bis(amidinato)iron(II) complex [Fe(MesC(NPr$^i$)$_2$)$_2$] (**1**) toward oxidizing reagents has been disclosed. The bis(amidinato)iron(II) complex was synthesized from the reaction of [Fe(Mes)$_2$]$_2$ with 4 equiv of diisopropyl carbodiimide in good yield. Treatment of **1** with 1 equiv of benzyl chloride gives the high-spin ferric complex [FeCl(MesC(NPr$^i$)$_2$)$_2$] (**2**), with 0.25 equiv of $S_8$ affords the sulfur-insertion product [Fe(MesC(NPr$^i$)(NPr$^i$S))$_2$] (**3**), with 1 equiv of 3,5-dimethylphenyl azide or phenyl azide yields nitrene-insertion product [Fe(MesC(NPr$^i$)$_2$)(Pr$^i$NC(Mes)N(Pr$^i$)NAr)] (Ar = 3,5-dimethylphenyl, **4a**; phenyl, **4b**), and with 1 equiv of oxo-transfer reagent, trimethylamine oxide or 2,6-dichloropyridine oxide, generates the oxo-bridged diferric complex [(MesC(NPr$^i$)$_2$)$_2$FeOFe(MesC(NPr$^i$)$_2$)$_2$] (**5**). Complexes **1**−**3**, **4a**, and **5** have been characterized by $^1$H NMR, UV−vis, IR, elemental analysis, and single-crystal X-ray diffraction studies. The formations of these unusual sulfur- and nitrene-insertion products **3**, **4a**, and **4b**, can be explained by the sequential redox reaction between **1** and the oxidants, followed by migratory insertion steps.



## INTRODUCTION

The relevance of nonheme type high valent iron-oxo and -imido species to iron-mediated or -catalyzed organic transformations has stimulated contemporary research studies on their preparation, structure−reactivity relationship, as well as catalytic applications.[1−3] Because of their oxidizing nature, these iron-oxo and -imido species are usually very reactive. Hence, judicious design and selection of appropriate ligand systems are necessary to ensure their isolation. While studies have shown multidentate pyridine-,[4] amine-,[5] amide-,[6] pyrrolido-,[7] phosphine-,[8] and *N*-heterocyclic carbene-based[9] ligands are among the privileged for this task, recent endeavors revealed bidentate ligands, such as sterically encumbered $\beta$-diketiminates[10] and dipyrromethene anions,[11] are also effective in stabilizing iron-imido species. Prompted by these pioneering works, we are curious on the capability of amidinate ligands[12] in stabilizing high-valent iron-oxo, and -imido species.

In the recent years, elegant studies on the synthesis and structural characterization of amidinate iron(II) complexes have been reported.[13−18] But the reactivity of these iron amidinate compounds remains largely unknown. A few known explorations on this aspect include the complexation of CO and Lewis bases to [Fe(RC(NR′)$_2$)$_2$] (R = Bu$^t$, R′ = Cy, Pr$^i$),[14b] and [Fe$_2$(Me$_3$SiNCPhN)$_2$C$_6$H$_{10}$],[16] the CO-insertion reactions of [CpFe(FcC(NCy)$_2$)(CO)][14a] and [(PhC(NDipp)$_2$)$_2$Fe(THF)][15e] to afford carbamoyl compounds, the reduction of [FeBr(Bu$^t$C(NDipp)$_2$)]$_2$ to produce iron(I) complexes [(Bu$^t$C(NDipp)$_2$)Fe(toluene)] and [Fe$_2$(N$_2$)(DippNC(Bu$^t$)(NDipp))$_2$],[19] the oxidation of [Fe$_2$(HC(NPh)$_2$)$_3$] with air to yield [Fe$_4$O(HC(NPh)$_2$)$_6$],[13g] and the use of bis(amidinato)iron(III) alkoxides [Fe(OR)(PhC(NSiMe$_3$)$_2$)$_2$] (R = Et, CHPh$_2$) in polymerizations of $\varepsilon$-caprolactone and lactides.[20]

This status quo warrants further exploration on the reactivity of amidinate iron(II) complexes. With regard to this, we report herein the reactivity of a bis(amidinato)iron(II) complex [Fe(MesC(NPr$^i$)$_2$)$_2$] toward a series of oxidizing reagents including organic halides, elemental sulfur, aryl azides, trimethylamine oxide, and 2,6-dichloropyridine oxide. While no high-valent iron complex has yet been obtained, the isolation of the iron(III) compounds [FeCl(MesC(NPr$^i$)$_2$)$_2$] (**2**) and [(MesC(NPr$^i$)$_2$)$_2$FeOFe(MesC(NPr$^i$)$_2$)$_2$] (**5**), and the iron(II) compounds of sulfur- and nitrene-insertion reaction prodcuts [Fe(MesC(NPr$^i$)(NPr$^i$S))$_2$] (**3**) and [Fe(MesC(NPr$^i$)$_2$)(Pr$^i$NC(Mes)N(Pr$^i$)NAr)] (Ar = 3,5-dimethylphenyl, **4a**; phenyl, **4b**) has revealed the distinct reactivity of bis(amidinato)iron(II) complexes when compared with that

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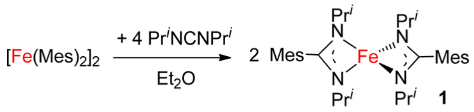
of other bis(amidinato) metal complexes or iron(II) complexes bearing other nitrogen-based ligands.

## ■ RESULTS AND DISCUSSION

**Synthesis and Characterization of [Fe(MesC(NPr$^i$)$_2$)$_2$].** Our previous study has shown the reaction of the three-coordinate iron(II) complex [(IPr$_2$Me$_2$)Fe(Mes)$_2$] (IPr$_2$Me$_2$: 2,5-diisopropyl-3,4-dimethylimidazol-1-ylidene, Mes: 2,4,6-trimethylphenyl) with 1 or 2 equiv of Pr$^i$NCNPr$^i$ gives the mono(amidinato) complex [(IPr$_2$Me$_2$)Fe(Mes)(MesC(NPr$^i$)$_2$)], irrespective of the reaction stoichiometry.[21] In contrast with this, [Fe(Mes)$_2$]$_2$ can react with 4 equiv of Pr$^i$NCNPr$^i$ to yield the bis(amidinato)iron(II) complex [Fe(MesC(NPr$^i$)$_2$)$_2$] (**1**) in good yield (Scheme 1). Similar to its analogues [Fe(Bu$^t$C(NR)$_2$)$_2$] (R = Pr$^i$, Cy),[14b] complex **1** is air-, moisture-, and light-sensitive. It is quite soluble in benzene and diethyl ether, and slightly soluble in *n*-hexane. The $^1$H NMR spectra of **1** recorded in $C_6D_6$ and $d_8$-THF are close to each other.[22] Solution magnetic moment measurement in $C_6D_6$ revealed the iron(II) center in **1** has a high-spin electronic configuration ($\mu_{eff}$ = 5.5(1) $\mu$B).[23] The high sensitivity of this complex toward adventitious water or [Bu$^n_4$N][PF$_4$] made the attempts to measure its voltammogram unsuccessful.

**Scheme 1. Preparation of 1**



The molecular structure of **1** in solid state has been established by a single-crystal X-ray diffraction study. As shown in Figure 1, this molecule displays a crystallographically approximate $D_2$ symmetry in which two identical amidinato anions are coordinating to the iron(II) center in chelating fashion with the Fe–N distances of 2.025(1) and 2.036(1) Å, the N–C(amidinato) distances of 1.322(2) and 1.333(2) Å, and the dihedral angle between two chelating planes being 81.22 deg. These bond distances are found close to those of the known mononuclear bis(amidinato)iron(II) complexes, such as [Fe(FcC(NCy)$_2$)$_2$],[14a] [Fe(Bu$^t$C(NCy)$_2$)$_2$],[15a] [Fe(PhC(NDipp)$_2$)$_2$],[15b] and [Fe(MeC(NBu$^t$)$_2$)$_2$][18a] (Fc: ferrocenyl, Cy: cyclohexyl, Dipp: 2,6-diisopropylphenyl). Besides these, possibly because of steric congestion within the amidinato ligands, the methyl groups on the *iso*-propyl moieties in **1** are all pointing away from the mesityl group. This structural feature is also present in the structures of **2**–**5** (vide infra).

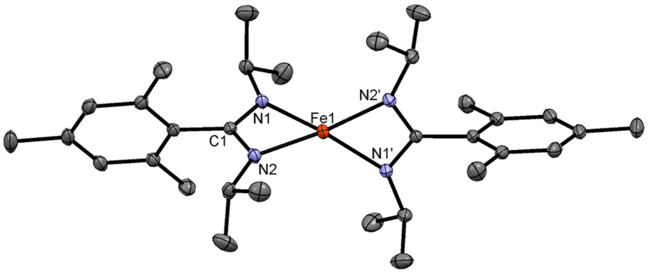
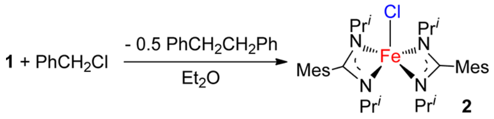


**Figure 1.** Molecular structure of [Fe(MesC(NPr$^i$)$_2$)$_2$] (**1**) showing 30% probability ellipsoids and the partial atom numbering schemes. Selected distances (Å) and angles (deg): Fe1–N1 2.036(1), Fe1–N2 2.025(1), C1–N1 1.322(2), C1–N2 1.333(2), N1–C1–N2 112.4(1), N1–Fe1–N2 65.8(5), N1–Fe1–N2′ 131.07(6).

**Reactions of [Fe(MesC(NPr$^i$)$_2$)$_2$] with Organic Halides.** Complex **1** can readily react with benzyl chloride to afford the iron(III) complex [FeCl(MesC(NPr$^i$)$_2$)$_2$] (**2**), but it is inert toward common alkyl and aryl halides at ambient temperature, such as dichloromethane, 1-bromooctane, and phenyl iodide. Treatment of **1** with 1 equiv of PhCH$_2$Cl in diethyl ether gives a dark green solution, from which **2** has been isolated as blue crystals in 68% yield, and 1,2-diphenylethane was identified as the byproduct by GC-MS analysis (Scheme 2). Complex **2** shows good solubility in low polar solvent such as benzene and diethyl ether, and solution magnetic moment measurement (Evans' method) has revealed its high-spin nature ($\mu_{eff}$ = 5.7(4) $\mu$B), consistent with that (5.8 $\mu$B) of its analogues [FeX(PhC(NSiMe$_3$)$_2$)$_2$] (X = OEt, OCHPh$_2$).[20]

**Scheme 2. Reaction of 1 with Benzyl Chloride**



The molecular structure of **2** in solid state shows a close resemblance to its congeners [FeX(PhC(NSiMe$_3$)$_2$)$_2$] (X = Cl, OEt, OCHPh$_2$)[13a,20] and [FeCl(Pr$^i$HNC(NPr$^i$)$_2$)$_2$].[24] As shown in Figure 2, this mononuclear iron(III) complex has a penta-coordinate iron center that is coordinating with one chloride and two chelating amidinates forming a distorted trigonal bipyramidal geometry with the Addison parameter $\tau$ = 0.66. The bonding of the amidinato ligands to the iron center is asymmetric as revealed by the different Fe–N bond distances within the four-membered metallocycles (2.118(1) and 1.993(1) Å for Fe1–N1 and Fe1–N2, and 2.092(1) and 2.013(1) Å for Fe1–N4 and Fe1–N3).

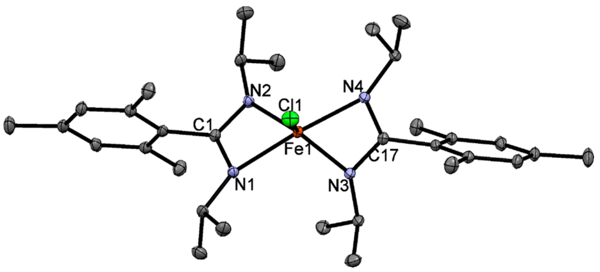
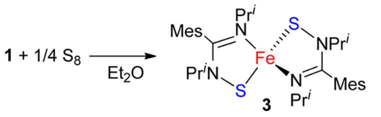


**Figure 2.** Molecular structure of [FeCl(MesC(NPr$^i$)$_2$)$_2$] (**2**) showing 30% probability ellipsoids and the partial atom numbering schemes. Selected distances (Å) and angles (deg): Fe1–N1 2.118(1), Fe1–N2 1.993(1), Fe1–N3 2.013(1), Fe1–N4 2.092(1), Fe1–Cl1 2.244(5), C1–N1 1.324(2), C1–N2 1.344(2), C17–N3 1.336(2), C17–N4 1.326(2), N1–C1–N2 112.3(1), N3–C17–N4 111.8(1), N1–Fe1–N2 65.1(5), N3–Fe1–N4 64.9(5), N2–Fe1–N3 118.3(6), N2–Fe1–N4 108.3(6), N1–Fe1–Cl1 96.5(4), N3–Fe1–Cl1 124.7(4).

**Reactions of [Fe(MesC(NPr$^i$)$_2$)$_2$] with $S_8$ and Se.** Treatment of **1** with 0.25 equiv of $S_8$ in diethyl ether at −78 °C produced a yellow solution whose color slowly changed to brown then raised to room temperature. After workup a yellow complex [Fe(MesC(NPr$^i$)(NPr$^i$S))$_2$] (**3**) has been isolated in 62% yield (Scheme 3). Complex **1** is unreactive toward Se in $C_6D_6$ as suggested by NMR scale reactions at room temperature and 70 °C. Complex **3** has been characterized by

**Scheme 3. Reaction of 1 with $S_8$**



$^1$H NMR, IR, elemental analysis, and single-crystal X-ray diffraction study. The paramagnetic complex has a magnetic moment of 4.5(1) $\mu$B (in $C_6D_6$ at room temperature) that is slightly lower than the spin-only value expected for high-spin ferrous complexes, but comparable to that of 4.4 $\mu$B observed for the tetrahedral complexes (dmpe)Fe(Mes)$_2$ and (depe)Fe(Mes)$_2$ reported by Chirik.[25] The unusual low magnetic moment value spurred us to investigate the variable temperature magnetic susceptibility of **3** in d$_8$-THF which indicates its solution magnetic moments varied in a narrow range (from 4.6 to 4.9 $\mu$B) when the temperature changed from 295 to 195 K (Supporting Information, Figure S4), meanwhile the $^1$H NMR peaks showed peak-shifting phenomenon, but no peak-coalescence (Supporting Information, Figure S3). These observations suggest the low magnetic moment value might not come from the geometry equilibrium between tetrahedral and square planar geometry.

Single-crystal X-ray crystallography has revealed **3** is an iron(II) compound featuring two unique bidentate imidoyl aminothiolato ligands, [MesC(NPr$^i$)(NPr$^i$S)]$^-$ (Figure 3). The coordination of these two chelates to the iron center renders it a distorted tetrahedral geometry as the angles surrounding the iron center spanning in a broad range from 84.8(6) to 127.9(3) deg. The Fe−S distances (2.283(8) and 2.272(8) Å) and Fe−N distances (2.036(2) and 2.030(2) Å) are consistent with the corresponding ones in neutral iron(II) compounds containing tetrahedral $FeS_2N_2$ units, such as [Fe(SDipp)$_2$(1-MeIm)$_2$] (1-MeIm: 1-methylimidazole),[26] and [Fe(STipp)$_2$(btmgp)] (Tipp: 2,4,6-trisiopropylphenyl, btmgp: 1,3-bis(*N,N,N′N′*-tetramethylguanidino)propane).[27] The structures of the two imidoyl aminothiolato ligands, [MesC(NPr$^i$)(NPr$^i$S)]$^-$, are nearly identical, and both of them possess planar N−C−N-S alignments, long S−N bonds (1.755(2) Å), and narrow N−C distance distribution (1.318(3) to 1.348(3) Å), suggesting the contributions of both canonical forms (Chart 1).

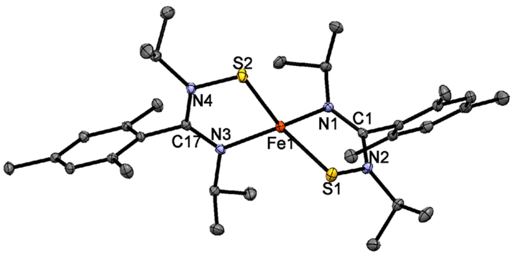
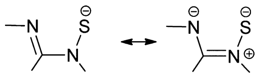


**Figure 3.** Molecular structure of [Fe(MesC(NPr$^i$)(NPr$^i$S))$_2$] (**3**) showing 30% probability ellipsoids and the partial atom numbering schemes. Selected distances (Å) and angles (deg): Fe1−S1 2.283(8), Fe1−S2 2.272(8), Fe1−N1 2.036(2), Fe1−N3 2.030(2), S1−N2 1.755(2), S2−N4 1.755(2), C1−N1 1.318(3), C1−N2 1.348(3), C17−N3 1.321(3), C17−N4 1.344(3), S1−Fe1−S2 127.9(3), N1−Fe1−N3 124.7(8), N1−Fe1−S1 84.8(6), N3−Fe1−S2 85.2(6), N1−Fe1−S2 119.6(6), N3−Fe1−S1 119.6(6), N1−C1−N2 119.8(2), N3−C17−N4 120.3(2).

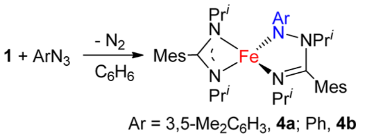
**Chart 1. Canonical Structures of Imidoyl Aminothiolato Ligand**



The isolation of this imidoyl aminothiolato complex demonstrates the distinct reactivity of the bis(amidinato)iron(II) complex when compared with other amidinates complexes and iron(II) amides. For examples, the bis(amidinato)titanium(II) complex [{(PhC(NSiMe$_3$)$_2$)$_2$Ti}$_2$(N$_2$)] is known to react with $S_8$ to yield disulfido complex [(PhC(NSiMe$_3$)$_2$)$_2$Ti(S$_2$)],[28] the reaction of mono(amidinato)germanium(II) [(PhC(NBu$^t$)$_2$)GeCl] with $S_8$ and KC$_8$ gives germanium sulfide [(PhC(NBu$^t$)$_2$)GeSGe(PhC(NBu$^t$)$_2$)],[29] and the interaction of [Fe(N(SiMe$_3$)$_2$)$_2$]$_2$ or Fe(N(SiMe$_3$)$_2$)(NHBu$^t$) with $S_8$ also produces sulfide compound [Fe$_4$S$_4$(N(SiMe$_3$)$_2$)$_4$],[30] or [Fe$_2$($\mu$-S)($\mu$-NHBu$^t$)$_2$(N(SiMe$_3$)$_2$)$_2$],[31] respectively. In light of these, we propose the formation of **3** might entail transient iron sulfide intermediates (MesC(NPr$^i$)$_2$)$_2$FeSFe(MesC(NPr$^i$)$_2$)$_2$, (MesC(NPr$^i$)$_2$)$_2$Fe(S$_2$), or (MesC(NPr$^i$)$_2$)$_2$Fe(S). But, because of the nucleophilicity of the amidinato ligand (as demonstrated by the aforementioned CO-insertion reactions of iron(II) amidinates),[14a,15e] these intermediates might be unstable and could convert to imidoyl aminothiolato complexes upon migratory insertion steps.

**Reactions of [Fe(MesC(NPr$^i$)$_2$)$_2$] with Aryl Azides.** To examining whether the bis(amidinato)iron scaffold can support imido species, the reactions of **1** with aryl azides, 3,5-dimethylphenyl azide, and phenyl azide, have been attempted. Addition of 1 equiv of 3,5-dimethylphenyl azide, 3,5-Me$_2$C$_6$H$_3$N$_3$, to a solution of **1** in benzene at room temperature led to an instant color change from colorless to brown with concomitant $N_2$ gas evolution. $^1$H NMR analyses suggested the formation of new paramagnetic species, and recrystallization on the reaction mixture has led to the isolation of [Fe(MesC(NPr$^i$)(NPr$^i$NC$_6$H$_3$-3,5-Me$_2$))(MesC(NPr$^i$)$_2$)] (**4a**) as yellow crystals in 47% yield (Scheme 4). Complex **4a** has been fully characterized by $^1$H NMR, IR, elemental analysis, and single-crystal X-ray diffraction study, and solution magnetic moment measurement indicated its high spin nature ($\mu_{\mathrm{eff}}$ = 5.1(1) $\mu$B). The reaction of **1** with PhN$_3$ gave new paramagnetic species with similar $^1$H NMR spectrum as that of **4a.**[22] Though our attempts to isolate the product upon recrystallization were unsuccessful, column chromatographic separation on the quenched reaction mixture yielded MesC(NPr$^i$)(NPr$^i$NHPh) and MesC(NPr$^i$)(NPr$^i$H) in an 1:1 ratio. Thus, the paramagnetic product can be formulated as [Fe(MesC(NPr$^i$)(NPr$^i$NPh))(MesC(NPr$^i$)$_2$)] (**4b**). Notably, despite the presence of the [Fe(MesC(NPr$^i$)$_2$)] fragments in **4a** and **4b,** they are found inert when treated with the second equivalent of the corresponding azide.

**Scheme 4. Reactions of 1 with the Aryl Azides**



As shown in Figure 4, complex **4a** is a mono(amidinato)iron(II) complex bearing a bidentate imidoyl hydrazido ligand, [MesC(NPr$^i$)(NPr$^i$NC$_6$H$_3$-3,5-Me$_2$)]$^-$. The chelation of the imidoyl hydrazido ligand to the iron center gives a five-

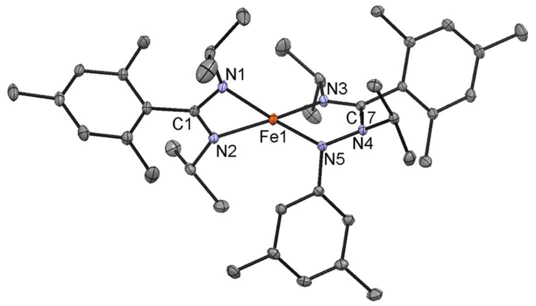
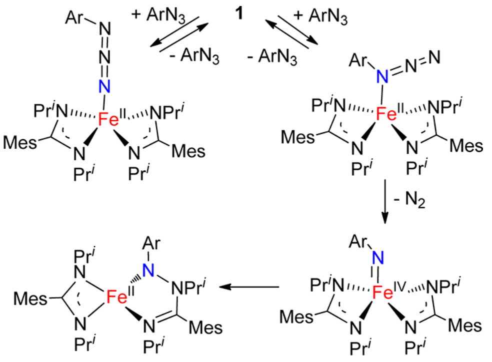


**Figure 4.** Molecular structure of [Fe(MesC(NPr$^i$)(NPr$^i$NC$_6$H$_3$-3,5-Me$_2$))(MesC(NPr$^i$)$_2$)] (**4a**) showing 30% probability ellipsoids and the partial atom numbering schemes. Selected distances (Å) and angles (deg): Fe1–N1 2.038(2), Fe1–N2 2.059(2), Fe1–N3 2.044(2), Fe1–N5 2.004(2), C1–N1 1.338(3), C1–N2 1.326(3), C17–N3 1.302(2), C17–N4 1.370(2), N4–N5 1.433(2), N1–Fe1–N2 65.5(7), N3–Fe1–N5 80.3(6), N1–Fe1–N5 125.8(7), N2–Fe1–N3 124.2(7), N1–C1–N2 112.6(2), N3–C17–N4 118.7(2), C17–N4–N5 115.3(2).

membered Fe–N–N–C–N metallocycle with the sequential N–N (1.433(2) Å), N–C (1.370(2) Å), and C–N (1.302(2) Å) connections being single, single, and double bonds in character. Consistent with this, both nitrogen atoms of the hydrazido moiety, N5 and N4, display a trigonal pyramidal geometry with the 3,5-dimethylphenyl and *iso*-propyl substituents on them being a transoid arrangement. The nonplanar geometry observed for the two hydrazido nitrogen atoms, which might be caused by steric congestion and the stereochemically active property of N(sp$^3$) atoms, signifies the distinction of this imidoyl hydrazido ligand when compared with those in [(*p*-cymene)Ru(PhC(NMe)(NHNMe$_2$))Cl]Cl,[32] and [Ti(PhC(NC$_6$H$_3$-2,6-Me$_2$)(NMeO))$_2$Cl$_2$].[33] In addition, the Fe–N bond distances ranging from 2.004(2) to 2.059(2) Å in **4a** are found close to those of the aforementioned bis(amidonato)iron(II) complexes,[14a,15a,b,18a] and the metric data of the [Fe(MesC(NPr$^i$)$_2$)] fragment are in line with those observed in **1**.

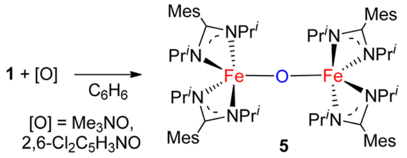
The evident formation of the imidoyl hydrazido ligand in the structure of **4a** points out iron(IV)-imido or iron(II)-nitrene species might be involved in the reaction of **1** with the aryl azide (Scheme 5), though other reaction mechanisms cannot be excluded. As our control experiments showed the amidinato anion Li[MesC(NPr$^i$)$_2$)$_2$] is inert toward 3,5-dimethylphenyl azide, we propose the reaction should proceed by the coordination of one azide molecule with the iron center in **1** to give terminal or internal organic azide adduct (MesC(NPr$^i$)$_2$)$_2$Fe(N$_3$Ar). While the terminal azide adduct might not be amenable to eliminate N$_2$, it could convert back to **1** upon dissociation of the azide.[2c,10b] On the other hand, the internal organic azide adduct could eliminate a N$_2$ molecule to afford an iron(IV)-imido or iron(II)-nitrene species (MesC(NPr$^i$)$_2$)$_2$Fe(NAr).[34] A subsequent step of nitrene-insertion into an Fe–N(amidinato) bond within the intermediate could then afford the imidoyl hydrazido complex. The reactivity of nitrene-insertion into an Fe–N(amidinato) bond is hitherto unknown. However, it is apparent this conversion parallels that of the aforementioned CO- and sulfur-insertion reactions, and also the reported reactions of nitrene-insertion into metal-pyrrole nitrogen bonds of metalloporphyrins.[35]

**Scheme 5. Possible Mechanism for the Formations of 4a**



**Reactions of [Fe(MesC(NPr$^i$)$_2$)$_2$] with Oxo-Transfer Reagents.** Prompted by the imido/nitrene-insertion reactions, we further investigated the reactions of **1** with 1 equiv of oxo-transfer reagents, trimethylamine oxide, and 2,6-dichloropyridine oxide in benzene, both of which, however, afforded a dinuclear iron(III) complex [(MesC(NPr$^i$)$_2$)$_2$FeOFe(MesC(NPr$^i$)$_2$)$_2$] (**5**), rather than the oxygen-insertion analogue of **4a** (Scheme 6). The addition sequence of the reagents and the reaction stoichiometry show no apparent effect on the reaction outcome as either adding a solution of **1** (1 or 2 equiv) in benzene to a solution of 2,6-dichloropyridine oxide, or with the reversed addition sequence all afforded **5** in comparable yields. Moreover, GC-MS analyses on the quenched reaction mixtures indicated the absence of hydroxylamine MesC(NPr$^i$)(NPr$^i$OH).

**Scheme 6. Reactions of 1 with the Oxo-Transfer Reagents**



Single-crystal X-ray diffraction study has shown the dinuclear complex **5** possesses a $\mu_2$-oxo bridge that connects two (MesC(NPr$^i$)$_2$)$_2$Fe$^{III}$ fragments with the Fe–O–Fe angle of 176.5(1) deg (Figure 5). The bond distances and angles of the

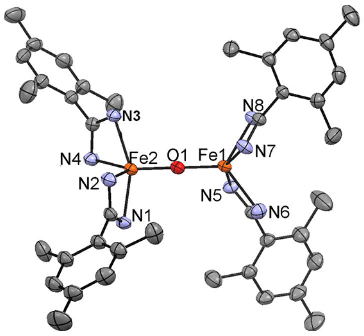


**Figure 5.** Molecular structure of [(MesC(NPr$^i$)$_2$)$_2$FeOFe(MesC(NPr$^i$)$_2$)$_2$] (**5**) showing 30% probability ellipsoids and the partial atom numbering schemes. For simplicity, the *iso*-propyl groups are omited. Selected distances (Å) and angles (deg): Fe1–O1 1.795(2), Fe2–O1 1.797(2), Fe1–N5 2.127(3), Fe1–N6 2.137(3), Fe1–N7 2.129(3), Fe1–N8 2.100(3), Fe2–N1 2.112(3), Fe2–N2 2.127(3), Fe2–N3 2.128(3), Fe2–N4 2.106(3), Fe1–O1–Fe2 176.5(1), N5–Fe1–N6 61.8(1), N7–Fe1–N8 62.7(1), N1–Fe2–N2 62.7(1), N3–Fe2–N4 62.7(1).

(MesC(NPr$^i$)$_2$)$_2$Fe units are close to each other, and accord well with those of the aforementioned high-spin bis(amidinato)iron(III) complexes.[13a,20] Similar to many of the known oxo-bridged dinuclear iron(III) complexes, **5** is diamagnetic and its $^1$H NMR spectrum features resonances in the range 1.0 to 8.0 ppm suggesting strong antiferromagnetic coupling between the two iron(III) centers.[36]

**Reactivity Patterns of [Fe(MesC(NPr$^i$)$_2$)$_2$] with the Oxidizing Reagents.** The current study has now revealed two reactivity patterns of the bis(amidinato)iron(II) complex toward oxidizing reagents: oxidation of the iron(II) center to give bis(amidinato)iron(III) complex (**2** and **5**), and "oxidation" of the ligand to give iron(II) complex (**3** and **4a**). The latter type of reactivity can be viewed as the insertion of a six-electron fragment, S or [NAr]$^0$, into an Fe−N(amidinato) bond. With the establishment of these distinct reactivity patterns, it is now appropriate to discuss their underlying causes.

Among these oxidizing reagents, benzyl chloride is a well-known single-electron oxidant for high-spin iron(II) complexes,[37] and the formation of **2** from the reaction of **1** with benzyl chloride is straightforward and not unusual. Sulfur, *N*-oxides, and organic azides are two-electron oxidants, and their interaction with **1** should initially give iron(III)−sulfur species [(MesC(NPr$^i$)$_2$)$_2$Fe]$_2$S (or (MesC(NPr$^i$)$_2$)$_2$Fe(S$_2$)) and the formal iron(IV) intermediates (MesC(NPr$^i$)$_2$)$_2$FeX (X = S, O, NAr) via two-electron redox processes. Once these formal iron(III, IV) species are formed, the electronic properties of the X groups should then affect their fates. The smaller electronegativity values of sulfur and nitrogen atoms,[38] compared with oxygen, might render the X (X = S, NAr) moieties in [(MesC(NPr$^i$)$_2$)$_2$Fe]$_2$S (or (MesC(NPr$^i$)$_2$)$_2$Fe(S$_2$) and (MesC(NPr$^i$)$_2$)$_2$Fe(S)) and (MesC(NPr$^i$)$_2$)$_2$FeNAr electron-deficient (or electrophilic), and trigger subsequent migratory insertion reactions to produce the imidoyl aminothiolato and imidoyl hydrazido ligands in **3** and **4a**. In contrast, the largest electronegativity value of oxygen among these X fragments would make the oxygen in (MesC(NPr$^i$)$_2$)$_2$FeO less electron-deficient or even nucleophlic, facilitating its interaction with another bis(amidinato)iron(II) molecule to afford the oxo-bridged diferric complex **5**. It should be mentioned, besides these factors, the affinity of sulfur and nitrogen anions toward iron(II) center and that of oxo toward iron(III) ion governed by their hard/soft characters, as well as the thermodynamic driving force of forming five-membered chelate rings from four-membered rings should also play important roles for the distinct reactivity patterns observed in these group-transfer reactions. With these understanding, we are now modifying the amidinato ligand aiming to reduce its nucleophilicity.

## ■ CONCLUSION

The following are the principal results and conclusions of this investigation.

(1) The monomeric bis(amidinato)iron(II) complex [Fe(MesC(NPr$^i$)$_2$)$_2$] has been prepared in good yield by the reaction of [Fe(Mes)$_2$]$_2$ with 4 equiv of Pr$^i$NCNPr$^i$. The ferrous complex has a high-spin electron configuration and has been fully characterized by various spectroscopic methods.

(2) The bis(amidinato)iron(II) complex can react with benzyl chloride via a single-electron redox process to afford the mononuclear ferric compound [FeCl(MesC(NPr$^i$)$_2$)$_2$] and diphenylethane. Its reaction with S$_8$, however, gives the iron(II) complex [Fe(MesC(NPr$^i$)(NPr$^i$S))$_2$] featuring the unprecedented imidoyl aminothiolato ligand. The formation of this imidoyl aminothiolato ligand is explained by migratory insertion reactions of bis(amidinato)iron-sulfide or -disulfide intermediate.

(3) The reactions of [Fe(MesC(NPr$^i$)$_2$)$_2$] with phenyl azides give iron(II) complexes [Fe(MesC(NPr$^i$)(NPr$^i$NAr))(MesC(NPr$^i$)$_2$)]. Iron(IV)-imido or iron(II)-nitrene intermediates are proposed as the key intermediates for these reactions. In contrast, the interactions of [Fe(MesC(NPr$^i$)$_2$)$_2$] with the oxo-transfer reagents, trimethylamine oxide, and 2,6-dichloropyridine oxide, give the diferric complex [(MesC(NPr$^i$)$_2$)$_2$FeOFe(MesC(NPr$^i$)$_2$)$_2$]. The different outcome of these two reactions indicates the distinct property of the oxo- and imido-moieties on the bis(amidinato)iron(IV) platform.

## ■ 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 cannula techniques, or in a glovebox. Organic solvents were dried with a solvent purification system (Innovative Technology) and bubbled with dry N$_2$ gas prior to use. [Fe(Mes)$_2$]$_2$[39] and the phenyl azides[40] were prepared according to literature methods. All other chemicals were purchased from either Strem or J&K Chemical Co. and used as received unless otherwise noted. $^1$H and $^{13}$C NMR spectra were recorded on a VARIAN Mercury 300 or 400 MHz spectrometer. Variable temperature NMR study was performed on a VARIAN Mercury 500 MHz spectrometer. All chemical shifts were reported in $\delta$ units with references to the residual protons of the deuterated solvents for proton chemical shifts and the $^{13}$C of deuterated solvents for carbon chemical shifts. IR spectra were recorded with a NICOLET AVATAR 330 FT-IR spectrophotometer. Absorption spectra were recorded with a HITACHI U-3310 UV−vis spectrophotometer. Mass spectra were recorded with a Waters Micromass GCT instruments for EI-MS, and IonSpec 4.7 T FTMS for MALDI/DHB. GC/MS was performed on a Shimadzu GCMS-QP2010 Plus spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). Magnetic moments were measured at room temperature by the method originally described by Evans with stock and experimental solutions containing a known amount of a (CH$_3$)$_3$SiOSi(CH$_3$)$_3$ standard.[23]

**Preparation of [Fe(MesC(NPr$^i$)$_2$)$_2$] (1).** To a solution of Fe$_2$(Mes)$_4$ (588 mg, 1.00 mmol) in Et$_2$O (10 mL) was added a solution of *N,N′*-diisopropylcarbodiimide (505 mg, 4.00 mmol) in Et$_2$O (5 mL) at −78 °C. The color of solution changed to dark-brown quickly, and the reaction mixture was warmed to room temperature and further stirred for 8 h. After removal of the solvent under vacuum, the brown residue was extracted with Et$_2$O (20 mL) and filtered. Slow evaporation of Et$_2$O at room temperature afforded **1** as a colorless crystalline solid. Yield: 837 mg, 76%. $^1$H NMR (300 MHz, C$_6$D$_6$, 298 K): $\delta$ (ppm) 14.54 (br, 2H, Mes-CH), 6.59 (br, 3H, *p*-Mes-CH$_3$), 4.15 (br, 18H, *o*-Mes-CH$_3$ + Pr$^i$-CH$_3$), −130.3 (br, 2H, Pr$^i$-CH). $^1$H NMR (300 MHz, d$_8$-THF, 298 K): $\delta$ (ppm) 14.91 (s, 2H, Mes-CH), 7.00 (s, 3H, *p*-Mes-CH$_3$), 4.70 (br, 6H, *o*-Mes-CH$_3$), 3.18 (br, 12H, Pr$^i$-CH$_3$), −129.45 (br, 2H, Pr$^i$-CH). $^1$H NMR (400 MHz, C$_6$D$_6$, 298 K): $\delta$ (ppm) 169.4 (br, 2H, Pr$^i$-CH), 14.51 (br, 2H, Mes-CH), 6.58 (br, 3H, *p*-Mes-CH$_3$), 4.16 (br, 18H, *o*-Mes-CH$_3$ + Pr$^i$-CH$_3$). $^1$H NMR (400 MHz, d$_8$-THF, 298 K): $\delta$ (ppm) 172.28 (br, 2H, Pr$^i$-CH), 14.96 (s, 2H, Mes-CH), 7.04 (s, 3H, *p*-Mes-CH$_3$), 4.76 (br, 6H, *o*-Mes-CH$_3$), 3.22 (br, 12H, Pr$^i$-CH$_3$). Anal. Calcd for C$_{32}$H$_{50}$FeN$_4$: C 70.31, H 9.22, N 10.25; Found: C 70.43, H 9.31, N 10.08. Magnetic susceptibility (C$_6$D$_6$, 302 K): $\mu_{\mathrm{eff}}$ = 5.5(1) $\mu_{\mathrm{B}}$. Absorption spectrum (C$_6$H$_6$): $\lambda_{\max}$ ($\varepsilon_{\mathrm{M}}$) 267 (5700), 353(3000) nm. IR (KBr, cm$^{-1}$): $\upsilon$ = 2963.6 (s), 2923.5 (s), 2864.8 (s), 1634.8 (s), 1612.8 (s), 1479.2 (s), 1451.0 (s), 1378.3 (m), 1358.7 (m), 1316.2 (m), 1267.5 (m), 1177.2 (s), 1140.2 (w), 1125.2 (w), 1012.4 (w), 852.3 (m), 764.5 (w), 690.0 (w), 482.5 (w).

**Preparation of [FeCl(MesC(NPr$^i$)$_2$)$_2$] (2).** To a solution of **1** (109 mg, 0.2 mmol) in $Et_2O$ (10 mL) was added a solution of benzyl chloride (25.3 mg, 0.20 mmol) in $Et_2O$ (1.0 mL) at −78 °C. The color of solution changed to green quickly, and the reaction mixture was warmed to room temperature and further stirred for 8 h. After removal of the solvent under vacuum, the green residue was extracted with $Et_2O$ (5.0 mL) and filtered. Slow evaporation of $Et_2O$ at room temperature afforded **2** as a green-blue crystalline solid. Yield: 79.2 mg, 68%. $^1$H NMR (300 MHz, $C_6D_6$, 298 K): $\delta$ (ppm) 21.90 (br, 6H, *p*-Mes-$CH_3$), 13.63 (br, 12H, Pr$^i$-$CH_3$). Anal. Calcd for $C_{32}H_{50}ClFeN_4$: C 66.03, H 8.66, N 9.63; Found: C 66.07, H 8.95, N 9.75. Magnetic susceptibility ($C_6D_6$, 302 K): $\mu_{eff}$ = 5.7(4) $\mu_B$. Absorption spectrum ($C_6H_6$): $\lambda_{max}$ ($\varepsilon_M$) 397 (sh, 1700), 637(2800) nm. IR (KBr, cm$^{-1}$): $\upsilon$ = 2964.0 (s), 2925.3 (s), 2868.8 (s), 1634.8 (s), 1612.3 (s), 1435.4 (s), 1379.4 (s), 1360.2 (s), 1333.1 (s), 1268.3 (w), 1222.3 (m), 1173.8 (m), 1138.8 (m), 1121.2 (m), 1013.6 (m), 942.4 (w), 850.6 (s), 761.5 (w), 727.5 (w), 692.2 (w), 552.8 (w), 489.9 (w), 425.9 (w), 404.9 (w).

**Preparation of [Fe(MesC(NPr$^i$)(NPr$^i$S)$_2$)$_2$] (3).** To a solution of **1** (109 mg, 0.20 mmol) in $Et_2O$ (10 mL) was added $S_8$ (12.8 mg, 0.05 mmol) at −78 °C. The color of solution changed to brown slowly, and the reaction mixture was warmed to room temperature and further stirred for 8 h. After removal of the solvent under vacuum, the brown residue was extracted with $Et_2O$ (10 mL) and filtered. Slow evaporation of $Et_2O$ at room temperature afforded **3** as a yellow crystalline solid. Yield: 71.6 mg, 62%. The $^1$H NMR spectrum of this paramagnetic complex displayed four broad peaks in the range −150 to 150 ppm. Attempts to assign them have not been made. $^1$H NMR (300 MHz, $C_6D_6$, 298 K): $\delta$ (ppm) 11.07 (br), 9.30 (br), 6.74 (br), 2.96 (br). $^1$H NMR (300 MHz, $d_8$-THF, 298 K): $\delta$ (ppm) 11.32 (br), 8.25 (br), 6.79 (br), 2.31 (br). Anal. Calcd for $C_{32}H_{50}FeN_4S_2$: C 62.93, H 8.25, N 9.17; Found: C 62.66, H 8.26, N 8.81. Magnetic susceptibility (302 K): $\mu_{eff}$ = 4.5(1) $\mu_B$ in $C_6D_6$, 4.7(1) $\mu_B$ in THF-$d_8$. IR (KBr, cm$^{-1}$): $\upsilon$ = 2967.3 (s), 2922.3 (s), 2866.5 (m), 1634.3 (m), 1611.4 (m), 1498.3 (s), 1478.8 (s), 1399.5 (m), 1379.3 (m), 1360.5 (m), 1336.0 (m), 1173.9 (m), 1127.4 (m), 1012.9 (m), 858.1 (m), 775.5 (w), 738.4 (w), 670.8 (w), 555.3 (w), 526.4 (w), 485.8 (w), 442.9 (w), 416.4 (w).

**Preparation of [Fe(MesC(NPr$^i$)(NPr$^i$NC$_6$H$_3$-3,5-Me$_2$)(MesC(NPr$^i$)$_2$)] (4a).** To a solution of **1** (164 mg, 0.30 mmol) in benzene (10 mL) was added a solution of 3,5-dimethylphenyl azide (44.1 mg, 0.3 mmol) in benzene (5 mL) at room temperature. $N_2$ bubbles were released quickly, and the color of solution changed to dark brown. The mixture was further stirred at room temperature for 8 h. After removal of the solvent, the residue was extracted with $Et_2O$ (5.0 mL) and filtered. Slow evaporation of $Et_2O$ at room temperature afforded **4a** as a yellow crystalline solid. Yield: 93.8 mg, 47%. The $^1$H NMR spectrum of this paramagnetic complex displayed 15 characteristic peaks in the range −150 to 150 ppm. Attempts to assign them have not been made. $^1$H NMR (300 MHz, $C_6D_6$, 298 K): $\delta$ (ppm) 53.11, 29.16, 28.80, 26.28, 21.21, 16.83, 14.83, 11.99, 10.54, −9.74, −15.08, −22.38, −35.97, −68.26, −95.86. Anal. Calcd for $C_{40}H_{59}FeN_5$: C 72.16, H 8.93, N 10.52; Found: C 72.11, H 9.17, N 10.47. Magnetic susceptibility ($C_6D_6$, 302 K): $\mu_{eff}$ = 5.1(1) $\mu_B$. IR (KBr, cm$^{-1}$): $\upsilon$ = 2954.8 (s), 2917.8 (s), 2864.4 (m), 1630.8 (m), 1611.6 (s), 1583.9 (s), 1534.4 (s), 1447.8 (s), 1378.2 (s), 1357.9 (s), 1327.7 (s), 1314.7 (s), 1232.2 (w), 1177.2 (m), 1156.9 (m), 1139.2 (m), 1121.7 (m), 1015.8 (m), 985.3 (w), 851.9, 817.0, 765.1 (w), 708.5 (w), 693.6 (w), 588.9 (w), 564.4 (w), 534.6 (w), 522.1 (w), 483.6 (w), 440.0 (w).

**Reaction of [Fe(MesC(NPr$^i$)$_2$)$_2$] with PhN$_3$.** To a solution of **1** (273 mg, 0.50 mmol) in benzene (10 mL) was added a solution of phenyl azide (60 mg, 0.50 mmol) in benzene (5 mL) at room temperature. $N_2$ bubbles were released quickly, and the color of solution changed to dark brown. $^1$H NMR of this mixture displayed 14 characteristic peaks in the range −150 to 150 ppm. Attempts to assign them have not been made. $^1$H NMR (300 MHz, $C_6D_6$, 298 K): $\delta$ (ppm) 49.90, 28.09, 28.00, 23.65, 19.58, 16.32, 14.15, 11.16, 10.13, −7.24, −12.40, −33.93, −69.08, −98.68. The mixture was further stirred at room temperature for 8 h and then quenched with aq. $NH_4Cl$ (6.8 M, 5 mL). After extraction with $Et_2O$ (2 × 10 mL), the combined organic layers were dried over magnesium sulfate and filter. Removal of all the volatiles under vacuum gave deep brownish oil. Chromatographic separation ($SiO_2$, 300−400 mesh, *n*-hexane/EtOAc (1/1)) afforded the protonated ligand MesC(NPr$^i$)(NHPr$^i$) (59.1 mg, 48%) and the imidoyl hydrazine compound [(NPr$^i$)MesC(NPr$^i$NHPh)] (67.8 mg, 40%) both as colorless solid. For MesC(NPr$^i$)(NHPr$^i$): $^1$H NMR (300 MHz, $CDCl_3$, 298 K): $\delta$ (ppm) 6.92 (s, 2H, Mes-CH), 3.05 (m, 2H, Pr$^i$-CH), 2.25 (s, 3H, *p*-Mes-$CH_3$), 2.18 (s, 6H, *o*-Mes-$CH_3$), 1.12 (d, 12H, Pr$^i$-$CH_3$). The signal of NH proton has not been observed. $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): $\delta$ (ppm) 163.85 (C═N), 141.36, 134.36, 129.24, 122.55, 47.18 (CH-Pr$^i$), 45.78 (CH-Pr$^i$), 23.10 ($CH_3$-Mes), 21.07 ($CH_3$-Mes), 19.13 ($CH_3$-Pr$^i$), 8.62 ($CH_3$-Pr$^i$). HRMS-TOF (*m*/*z*): $[M+H]^+$ calcd for $C_{16}H_{26}N_2$, 247.2174; Found, 247.2177. IR (KBr, cm$^{-1}$): $\upsilon$ = 2974.4 (s), 2925.2 (m), 2873.9 (m), 1613.5 (s), 1445.5 (m), 1395.9 (m), 1369.4 (m), 1327.7 (w), 11160.1 (m), 1131.3 (m), 1035.5 (w), 853.8 (m), 806.0 (w), 730.2 (m), 697.5 (w), 649.3 (w), 612.6 (w). The streching resonance of N−H has not been observed. For (NPr$^i$)MesC(NPr$^i$NHPh): $^1$H NMR (300 MHz, $CDCl_3$, 298 K): $\delta$ (ppm) 7.27−7.21 (m, 2H, Ph−CH), 7.07 (br, 2H, Mes-CH), 6.91−6.87 (m, 3H, Ph−CH), 3.70 (br, NH), 2.99 (quintet, 1H, Pr$^i$-CH), 2.34 (s, 6H, *o*-Mes-$CH_3$), 2.28 (s, 3H, *p*-Mes-$CH_3$), 1.21 (s, 6H, Pr$^i$-$CH_3$), 1.09 (s, 3H, Pr$^i$-$CH_3$), 0.69 (s, 3H, Pr$^i$-$CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): $\delta$ (ppm) 157.8 (C═N), 151.0 (C-Mes), 137.4, 135.2, 130.4, 129.1, 128.1, 119.5, 115.3, 50.34, 49.79, 24.62, 22.19, 20.89, 20.20, 19.46. HRMS-TOF (*m*/*z*): $[M+H]^+$ calcd for $C_{22}H_{31}N_3$, 338.2596; Found, 338.2583. IR (KBr, cm$^{-1}$): $\upsilon$ = 3256.4 (w, NH), 2965.3 (s), 2925.8 (m), 2868.3 (w), 1612.9 (s), 1598.3 (s), 1494.2 (s), 1440.9 (w), 1377.6 (m), 1359.6 (m), 1340.4 (w), 1285.2 (s), 1245.1 (m), 1188.5 (w), 1154.6 (m), 1109.4 (m), 1080.9 (m), 1058.2 (m), 1025.2 (w), 980.4 (w), 945.8 (w), 884.9 (w), 852.6 (m), 752.6 (s), 692.5 (s), 664.0 (w), 622.9 (w).

**Preparation of [(MesC(NPr$^i$)$_2$)$_2$FeOFe(MesC(NPr$^i$)$_2$)$_2$] (5).** To a solution of **1** (109 mg, 0.20 mmol) in benzene (10 mL) was added trimethylamine *N*-oxide (15.0 mg, 0.20 mmol) at −78 °C. The color of solution changed to red quickly, and the reaction mixture was warmed to room temperature and further stirred for 8 h. After removal of the solvent under vacuum, the red residue was extracted with $Et_2O$ (5 mL) and filtered. Slow evaporation of $Et_2O$ at room temperature afforded **5** as a red crystalline solid. Yield: 34.3 mg, 31%. $^1$H NMR (300 MHz, $C_6D_6$, 298 K): $\delta$ (ppm) 6.75 (s, 4H, Mes-CH), 4.43 (br, 2H, Pr$^i$-CH), 3.21 (br, 1H, Pr$^i$-CH), 3.02 (br, 1H, Pr$^i$-CH), 2.24 (s, 12H, *o*-Mes-$CH_3$), 2.15 (s, 6H, *p*-Mes-$CH_3$), 1.22 (d, 12H, Pr$^i$-$CH_3$), 1.02 (d, 12H, Pr$^i$-$CH_3$). Anal. Calcd for $C_{64}H_{100}Fe_2N_8O$: C 69.30, H 9.09, N 10.10; Found: C 70.02, H 9.25, N 10.01. IR (KBr, cm$^{-1}$): $\nu$ = 2963.6 (s), 2925.6 (s), 2865.2 (s), 1635.4 (s), 1612.3 (s), 1480.4 (s), 1451.9 (s), 1378.4 (m), 1359.8 (m), 1316.7 (m), 1267.0 (m), 1177.1 (m), 1125.1 (w), 1033.7 (w), 977.4 (w), 852.6 (m), 802.6 (w), 742.7 (w). Alternatively, complex **5** can also be prepared from the reaction of **1** (109 mg, 0.20 mmol) with 2,6-dichloropyridine *N*-oxide (16.4 mg, 0.10 mmol) in benzene using similar procedures described above (yield: 20.0 mg, 18%). The reaction of **1** with dioxygen in benzene furnished **5** in trace amount.

**X-ray Structure Determinations.** The structures of the five compounds were determined. Diffraction-quality crystals were obtained as [Fe(MesC(NPr$^i$)$_2$)$_2$] (**1**), [FeCl(MesC(NPr$^i$)$_2$)$_2$] (**2**), [Fe(MesC(NPr$^i$)(NPr$^i$S)$_2$)$_2$] (**3**), [Fe(MesC(NPr$^i$)(NPr$^i$NC$_6$H$_3$-3,5-Me$_2$)(MesC(NPr$^i$)$_2$)] (**4a**), and [(MesC(NPr$^i$)$_2$)$_2$FeOFe(MesC(NPr$^i$)$_2$)$_2$] (**5**) in diethyl ether. 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. 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.[41] Space groups were assigned unambiguously by analysis of symmetry and systematic absences determined by XPREP. All structures were solved and refined using SHELXTL.[42] Metal and first coordination sphere atoms were located from direct-methods E-maps; other non-hydrogen atoms were found in alternating difference Fourier synthesis and least-squares refinement

**Table 1. Crystal Data and Summary of Data Collection and Refinement for 1−3, 4a, and 5[a]**

|  | 1 | 2 | 3 | 4a | 5 |
|---|---|---|---|---|---|
| formula | $C_{32}H_{50}FeN_4$ | $C_{32}H_{50}ClFeN_4$ | $C_{32}H_{50}FeN_4S_2$ | $C_{40}H_{59}FeN_5$ | $C_{64}H_{100}Fe_2N_8O$ |
| fw | 546.61 | 582.06 | 610.73 | 665.77 | 1109.22 |
| crystal system | orthorhombic | monoclinic | triclinic | triclinic | monoclinic |
| space group | *Pbcn* | *P*2(1)/*c* | $P\bar{1}$ | $P\bar{1}$ | *P*2(1)/*c* |
| *a*, Å | 19.494(6) | 12.070(1) | 9.522(2) | 8.569(1) | 10.948(1) |
| *b*, Å | 7.970(3) | 12.678(1) | 11.688(2) | 12.400(2) | 27.900(1) |
| *c*, Å | 21.069(7) | 22.399(2) | 15.649(2) | 19.574(3) | 21.949(1) |
| $\alpha$, deg | 90.00 | 90.00 | 98.99(3) | 101.18(2) | 90.00 |
| $\beta$, deg | 90.00 | 104.87(2) | 98.09(3) | 90.96(2) | 103.65(1) |
| $\gamma$, deg | 90.00 | 90.00 | 101.00(3) | 108.06(2) | 90.00 |
| *V*, Å$^3$/Z | 3273.1(2)/4 | 3312.9(6)/4 | 1662.2(4)/2 | 1933.4(5)/2 | 6514.8(3)/4 |
| $d_{calcd}$, g/cm$^3$ | 1.109 | 1.167 | 1.220 | 1.144 | 1.131 |
| $2\theta$ range, deg | 3.8−50.0 | 3.5−60.4 | 4.1−59.4 | 3.5−60.2 | 2.4−51.0 |
| GOF ($F^2$) | 1.280 | 1.015 | 0.986 | 1.096 | 0.982 |
| $R_1$[b] | 0.0346,[d] | 0.0396,[d] | 0.0510,[d] | 0.0569,[d] | 0.0515,[d] |
|  | 0.0402[e] | 0.0663[e] | 0.1043[e] | 0.0761[e] | 0.0951[e] |
| $wR_2$[c] | 0.1329,[d] | 0.0948,[d] | 0.0978,[d] | 0.1699,[d] | 0.1277,[d] |
|  | 0.1453[e] | 0.1063[e] | 0.1164[e] | 0.1821[e] | 0.1589[e] |

[a]Collected using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). [b]$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c]$wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [d]$I > 2\sigma(I)$. [e]All data.

cycles and during final cycles were refined anisotropically. Hydrogen atoms were placed in calculated positions employing a riding model. Final crystal parameters and agreement factors are reported in Table 1.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Crystallographic data in CIF format, UV−vis, and NMR spectra for complexes **1**−**5**. 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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