

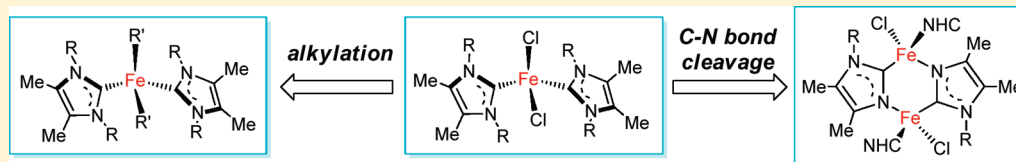
## Synthesis, Structure, and Reactivity of Organo-Iron(II) Complexes with N-Heterocyclic Carbene Ligation

Li Xiang, Jie Xiao, and Liang Deng\*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, People's Republic of China, 200032

## Supporting Information

## ABSTRACT:



The synthesis, structure, and reactivity of some organo-iron complexes with monodentate N-heterocyclic carbene (NHC) ligation were studied. Mononuclear ferrous complexes  $[(\text{IEt})_2\text{FeR}_2]$  ( $\text{IEt} = 2,5\text{-diethyl-3,4-dimethylimidazol-1-ylidene}$ ,  $\text{R} = \text{Me}$  (**2a**),  $\text{CH}_2\text{TMS}$  (**2b**)) and  $[(\text{IPr})\text{FeMe}_2]$  (**3**,  $\text{IPr} = 2,5\text{-diisopropyl-3,4-dimethylimidazol-1-ylidene}$ ) were prepared in good yields via salt elimination reactions of  $[(\text{NHC})_2\text{FeCl}_2]$  (**1**) with alkylation reagents. The interaction of **1** with  $\text{PhLi}$  gave a mixture of dinuclear complexes  $[\text{Cl}(\text{IEt})\text{Fe}(\text{IEt}')_2\text{Fe}(\text{IEt})\text{Cl}]$  (**4a**) and  $[\text{Ph}(\text{IEt})\text{Fe}(\text{IEt}')_2\text{Fe}(\text{IEt})\text{Ph}]$  (**4b**) ( $\text{IEt}' = 3\text{-Et-4,5-Me}_2\text{-2-ylideneimidazolyl anion}$ ), in which N–C(ethyl) bond cleavage of the NHC ligand was involved. Complexes **2a–4b** were characterized by  $^1\text{H}$  NMR, elemental analyses, and single-crystal X-ray diffraction studies. Solution magnetism measurement by Evan's method revealed the high-spin electronic configuration for the mononuclear organo-iron(II) complexes **2a**, **2b**, and **3**. Reactivity studies showed the tetrahedral complex **2a** was inert toward many unsaturated organic substrates, whereas the trigonal-planar complex **3** could react with CO and carbodiimide  $\text{Pr}^i\text{N}=\text{C}=\text{NPr}^i$  to yield dimesityl ketone and  $[(\text{IPr})\text{Fe}(\text{Mes})(\eta^2\text{-Pr}^i\text{NC}(\text{Mes})\text{NPr}^i)]$  (**5**), respectively. Relevant to iron-catalyzed Kumada couplings, both complexes **2b** and **3** were found reactive with  $\text{PhI}$  to yield the corresponding carbon–carbon bond formation products  $\text{Ph-CH}_2\text{TMS}$  and  $\text{Ph-Mes}$ .

## INTRODUCTION

Intrigued by its rich abundance and inexpensive, nontoxic, and environmentally benign features, iron has been subjected to extensive study in homogeneous catalysis.<sup>1</sup> Efforts in this area have led to not only the wide application of iron catalysis in organic chemistry<sup>1a,2</sup> but also the fast development of organo-iron chemistry, as evidenced by the emergence of a variety of new iron complexes in the recent years.<sup>3</sup> In addition to the continuing interest in classical cyclopentadienyl-, carbonyl-, phosphine-, and trispyrazolylborate-based iron complexes,<sup>3</sup> the introduction of new ligands, such as pyridine-diimine, diimine, diketimine, and N-heterocyclic carbene, in coordination chemistry has further enriched organo-iron chemistry.<sup>4</sup>

Among the above-mentioned ligands, N-heterocyclic carbenes (NHCs) have attracted much interest. As a unique type of carbon-based ligand, NHCs have been widely applied in transition metal chemistry.<sup>5</sup> An iron complex with NHC coordination was known as early as 1980s,<sup>6</sup> but little attention had been paid to this kind of complex in the last century. It is only in the last 10 years that iron–NHC complexes have garnered some attention. Up to now, a plethora of iron complexes bearing NHC moieties have been reported,<sup>7–10</sup> in which NHCs are either incorporated

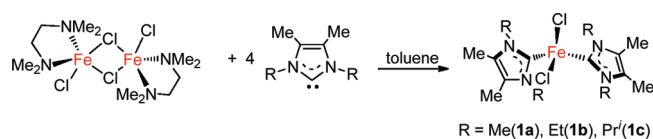
as ancillary ligands, as exemplified by monocyclopentadienyliron complexes  $\text{CpFeL}_n(\text{NHC})^8$  and diiron carbonyls  $\text{Fe}_2(\text{CO})_n(\text{SCH}_2\text{XCH}_2\text{S})\text{L}_n(\text{NHC})^9$  or functionalized into a multidentate ligand, such as 2,6-bis(imidazolylidene)pyridine,<sup>10c</sup> 2,2',2''-tris(imidazolylidene)triethylamine,<sup>10d</sup> and tris(imidazolylidene)borate.<sup>10e</sup> Studies on these NHC-containing iron complexes have demonstrated their versatile reactivity as well as catalytic applications in organic reactions.<sup>7–10</sup>

NHC ligands are generally known as strong  $\sigma$ -donors and weak  $\pi$ -acceptors and have tunable steric properties.<sup>11</sup> These structural and electronic features might endow their complexes unique reactivity. Inasmuch as most of the reported NHC-containing iron complexes bear complicated ligand environments,<sup>8–10</sup> and few of them have NHCs as the sole spectator ligands,<sup>7</sup> it is imperative for us to explore the chemistry of this type of iron–NHC complex. Pertinent to this goal, we report here the synthesis, structure, and reactivity study of some three- and four-coordinate aryl- and alkyl-iron(II) complexes with monodentate NHC ligation as shown below.

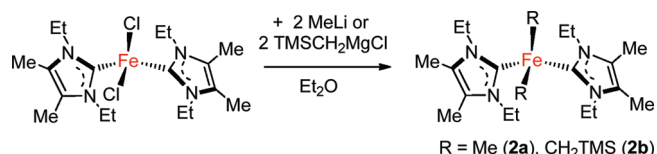
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### Scheme 1. Preparation of Bis(1,3-dialkyl-4,5-dimethylimidazolin-2-ylidene)iron Dichloride



### Scheme 2. Preparation of Mononuclear Dialkyl Iron Complexes with NHC Ligation

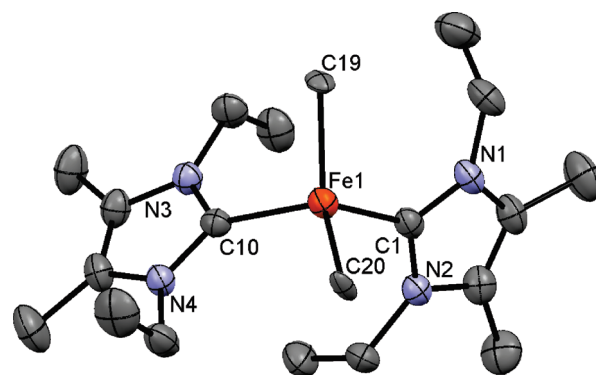


## RESULTS AND DISCUSSION

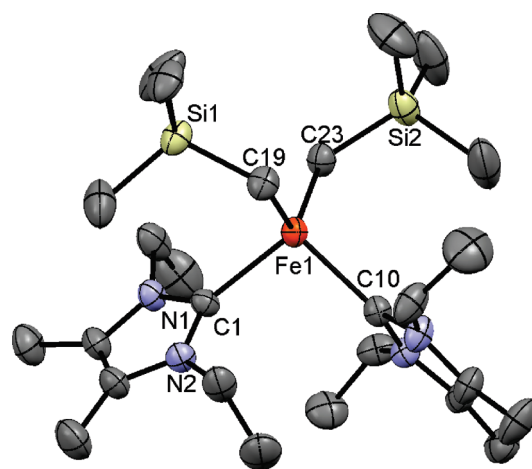
Among the many structurally characterized NHC-containing iron complexes, only few of them have monodentate NHCs as the sole spectator ligand.<sup>7</sup> In order to study the organometallic chemistry of this type of iron–NHC complex, we set out to prepare ferrous halides with NHC ligation.

**Iron(II)–NHC Dichlorides.** Applying the reported method,<sup>7a</sup> treatment of ferrous halide with two equivalents of IPr in toluene gave [(IPr)<sub>2</sub>FeCl<sub>2</sub>] in relatively low yield, which might result from the poor solubility of ferrous halides in toluene. As an improved method, [(TMEDA)FeCl<sub>2</sub>]<sub>2</sub><sup>12</sup> was used as the iron precursor. Reactions of [(TMEDA)FeCl<sub>2</sub>]<sub>2</sub> with four equivalents of free NHC ligands (IPr, IEt, and IMe)<sup>13,14</sup> in toluene, after filtration, afforded the corresponding ferrous complexes [(IPr)<sub>2</sub>FeCl<sub>2</sub>] (**1a**), [(IEt)<sub>2</sub>FeCl<sub>2</sub>] (**1b**), and [(IMe)<sub>2</sub>FeCl<sub>2</sub>] (**1c**) as colorless crystalline solids in good yields (80–84%) (Scheme 1). The compositions of these complexes were confirmed by elemental analysis. Unit cell check for a single crystal of **1a** showed identical cell parameters to the reported structure.<sup>7a</sup> Complexes **1a–c** are slightly soluble in toluene, diethyl ether, and THF. They are quite air- and moisture-sensitive both in solution and in the solid state. Under N<sub>2</sub> atmosphere, the crystalline solid can be preserved for several months at –20 °C, but decomposition, as evidenced by color change from colorless to yellow, can take place after the solids have stood at room temperature for several days.

**Iron(II)–NHC Alkyl Complexes.** The successful preparation of these halides paved the way to access alkyl complexes. Alkylation of [(IEt)<sub>2</sub>FeCl<sub>2</sub>] (**1b**) with two equivalents of MeLi or TMSCH<sub>2</sub>MgCl in Et<sub>2</sub>O, after workup, afforded the alkyl complex [(IEt)<sub>2</sub>FeMe<sub>2</sub>] (**2a**) or [(IEt)<sub>2</sub>Fe(CH<sub>2</sub>TMS)<sub>2</sub>] (**2b**), respectively, as yellow crystalline solids in high yield (Scheme 2). Similar alkylation reactions with ethyl, allyl, and benzyl Grignard reagents gave brown mixtures. Attempts to isolate alkylation products from these brown mixtures were unsuccessful. The alkyl complexes **2a** and **2b** are air- and moisture-sensitive and soluble in low-polar organic solvents such as *n*-hexane, Et<sub>2</sub>O, and THF. They were characterized by elemental analysis, magnetic susceptibility, and X-ray diffraction studies. In C<sub>6</sub>D<sub>6</sub>, both complexes show broad <sup>1</sup>H NMR peaks in the range 15 to –20 ppm, and the solution magnetic moment is 4.9 μB for **2a** and 4.8 μB



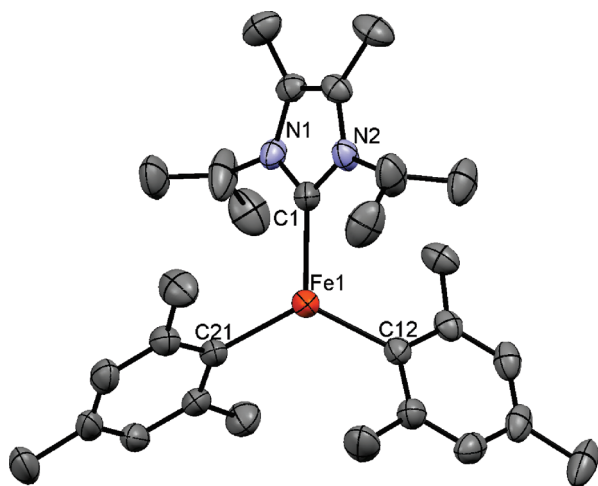
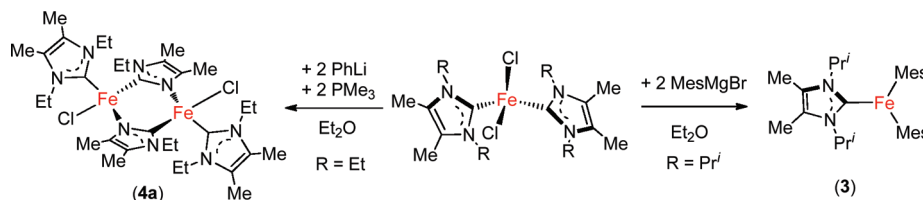
**Figure 1.** Molecular structure of [(IEt)<sub>2</sub>Fe(CH<sub>3</sub>)<sub>2</sub>] showing 30% probability ellipsoids and the atom-numbering scheme. Selected distances (Å) and angles (deg): Fe(1)–C(1) 2.132(3), Fe(1)–C(10) 2.140(3), Fe(1)–C(19) 2.168(3), Fe(1)–C(20) 2.166(3), C(1)–Fe(1)–C(10) 100.8(1), C(10)–Fe(1)–C(20) 114.2(1), C(20)–Fe(1)–C(19) 111.1(1).



**Figure 2.** Molecular structure of [(IEt)<sub>2</sub>Fe(CH<sub>2</sub>TMS)<sub>2</sub>] showing 30% probability ellipsoids and the atom-numbering scheme. Selected distances (Å) and angles (deg): Fe(1)–C(1) 2.160(4), Fe(1)–C(10) 2.140(4), Fe(1)–C(19) 2.116(4), Fe(1)–C(23) 2.111(3), C(1)–Fe(1)–C(10) 99.0(2), C(19)–Fe(1)–C(23) 115.1(2), C(23)–Fe(1)–C(19) 115.1(2).

for **2b**,<sup>15</sup> respectively, indicating their high-spin electronic configurations.<sup>4c</sup>

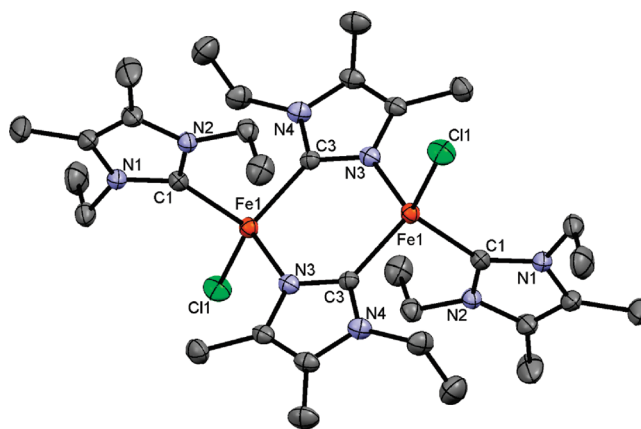
As shown in Figures 1 and 2, single-crystal X-ray analyses revealed that complexes **2a** and **2b** are isostructural, in which the distorted tetrahedral iron centers are coordinated with two carbene ligands and two alkyl groups with the C(carbene)–Fe–C(carbene) angles around 100° and the C(alkyl)–Fe–C(alkyl) angles about 110°. The Fe–C(carbene) separations are 2.132(3) and 2.140(3) Å in **2a** and 2.160(4) and 2.140(4) Å in **2b**, which are comparable to those of the four-coordinate high-spin Fe(II) complexes,<sup>7</sup> but much longer than those (ca. 1.95 Å) of the low-spin compounds.<sup>8,9</sup> The Fe–C(alkyl) bond distances in **2a** and **2b** are 2.168(3), 2.166(3) and 2.116(4), 2.111(3) Å, respectively, which are slightly longer than the ones in the reported tetrahedral ferrous complexes.<sup>16,17</sup> For examples, the Fe–Me bond distances are 2.095(4) Å in [(CH<sub>3</sub>)Fe(CH<sub>3</sub>)<sub>3</sub>–Li<sub>3</sub>(CH<sub>3</sub>)(OEt)<sub>2</sub>],<sup>16a</sup> 2.079(3) Å in [(CH<sub>3</sub>)Fe(PhTp)],<sup>16b</sup> and 2.084(6) Å in [(CH<sub>3</sub>)Fe(N(Ph-2,6-Me<sub>2</sub>)(TMS))(TMEDA)];<sup>16c</sup>

Scheme 3. Reactions of  $(\text{NHC})_2\text{FeCl}_2$  with PhLi and MesMgBr

**Figure 3.** Molecular structure of  $[(\text{IPr})\text{Fe}(\text{Mes})_2]$  showing 30% probability ellipsoids and the atom-numbering scheme. Selected distances (Å) and angles (deg):  $\text{Fe}(1)–\text{C}(1)$  2.125(3),  $\text{Fe}(1)–\text{C}(12)$  2.074(3),  $\text{Fe}(1)–\text{C}(21)$  2.072(3),  $\text{C}(1)–\text{Fe}(1)–\text{C}(12)$  116.5(1),  $\text{C}(1)–\text{Fe}(1)–\text{C}(21)$  118.9(1),  $\text{C}(12)–\text{Fe}(1)–\text{C}(21)$  124.3(1).

the  $\text{Fe}–\text{CH}_2\text{TMS}$  bond distances in the four-coordinate  $\text{Fe}(\text{II})$  complexes lie between 2.10 and 2.05 Å.<sup>17</sup> The elongation of  $\text{Fe}–\text{alkyl}$  bonds in **2a** and **2b** could be ascribed to the strong  $\sigma$ -donating property of NHCs, which makes the iron centers very electron-rich, weakening the  $\text{Fe}–\text{alkyl}$  interaction.

**Iron(II)–NHC Aryl Complexes.** Treatment of  $[(\text{IPr})_2\text{FeCl}_2]$  (**1a**) with two equivalents of MesMgBr (Mes = 2,4,6-trimethylphenyl) in  $\text{Et}_2\text{O}$ , after workup, yielded the diaryl complex  $[(\text{IPr})\text{Fe}(\text{Mes})_2]$  (**3**) as a pale yellow solid in 58% yield (Scheme 3). The formation of this three-coordinate complex rather than the four-coordinate  $(\text{IPr})_2\text{Fe}(\text{Mes})_2$  implies the dissociation of a IPr ligand in the reaction process. An alternative preparation by interaction of  $[\text{Fe}_2(\text{Mes})_4]$ <sup>18</sup> with two equivalents of IPr could yield **3** quantitatively. Complex **3** was fully characterized by  $^1\text{H}$  NMR, elemental analysis, magnetic susceptibility, and X-ray diffraction. The solution magnetic moment of **3** in  $\text{C}_6\text{D}_6$  is 5.4  $\mu\text{B}$ , indicating a high-spin ferrous center with  $S = 2$ .<sup>15,19</sup> X-ray diffraction study showed **3** adopts a propeller structure, in which the iron center has a trigonal-planar geometry via coordination with one IPr ligand and two mesityl groups (Figure 3). The sum of three  $\text{C}–\text{Fe}–\text{C}$  angles around the iron center is 359.7°. The  $\text{Fe}–\text{C}(\text{carbene})$  and  $\text{Fe}–\text{C}(\text{mesityl})$  bond distances are 2.125(3), 2.074(3), and 2.072(3) Å, respectively. The  $\text{Fe}–\text{C}(\text{mesityl})$  bond distances are close to the  $\text{Fe}–\text{C}(\text{aryl})$  bond distances in  $[(\text{nacnac})\text{FePh}]$ ,<sup>20a</sup>  $[(2,6\text{-Me}_2\text{Py})\text{Fe}(\text{Mes})_2]$ ,<sup>20b</sup> and  $[\text{Fe}_2(\text{Mes})_4]$ .<sup>20c</sup>

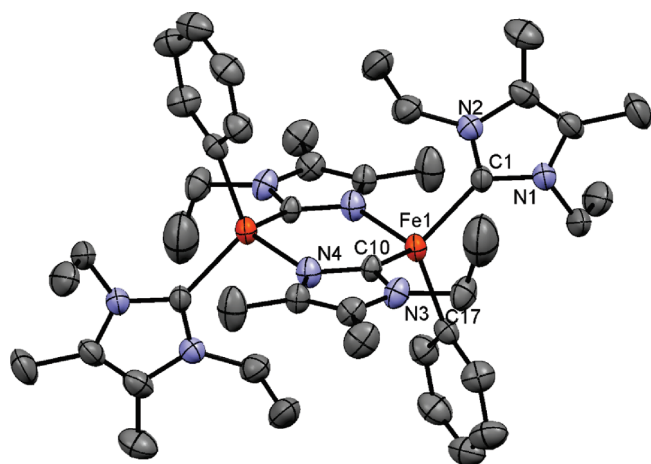


**Figure 4.** Molecular structure of  $[(\text{IEt})(\text{Cl})\text{Fe}(\text{IEt}')_2\text{Fe}(\text{Cl})(\text{IEt})]$  showing 30% probability ellipsoids and the atom-numbering scheme. The molecule has crystallographically imposed  $C_i$  symmetry. Selected distances (Å) and angles (deg):  $\text{Fe}(1)–\text{C}(1)$  2.116(4),  $\text{Fe}(1)–\text{C}(3)$  2.087(3),  $\text{Fe}(1)–\text{N}(3)$  2.045(3),  $\text{Fe}(1)–\text{Cl}(1)$  2.311(1),  $\text{C}(1)–\text{Fe}(1)–\text{C}(3)$  105.5(1),  $\text{C}(3)–\text{Fe}(1)–\text{N}(3)$  110.5(1).

The interaction of iron halides with PhLi gave distinct results. Reaction of  $[(\text{IEt})_2\text{FeCl}_2]$  (**1b**) with two equivalents of PhLi afforded a brown mixture, from which yellow complexes  $[\text{Cl}(\text{IEt})\text{Fe}(\text{IEt}')_2\text{Fe}(\text{IEt})\text{Cl}]$  (**4a**) and  $[\text{Ph}(\text{IEt})\text{Fe}(\text{IEt}')_2\text{Fe}(\text{IEt})\text{Ph}]$  (**4b**) were isolated in low yields ( $\text{IEt}' = 3\text{-Et-4,5-Me}_2\text{-2-ylidene-imidazolyl anion}$ ). The yield of **4a** could be improved to 25% when **1b** was reacted with one equivalent of PhLi in the presence of  $\text{PMe}_3$  (Scheme 3). Complexes **4a** and **4b** have been characterized by an X-ray diffraction study. As shown in Figures 4 and 5, the  $C_i$  symmetric complexes **4a** and **4b** are isostructural, in which the  $\text{Fe}(\text{II})$  sites are tetrahedrally coordinated with one intact carbene ligand, the ylidene carbon of one imidazolyl anion, the amide nitrogen of the other imidazolyl anion, and the chloro or phenyl group in **4a** or **4b**, respectively. The  $\mu_2$ -bridge moieties (3-Et-4,5-Me<sub>2</sub>-2-ylidene-imidazolyl anion) are bound with the two iron centers with distances of 2.087(3) Å for  $\text{Fe}–\text{C}(\text{IEt}')$ , 2.045(3) Å for  $\text{Fe}–\text{N}(\text{IEt}')$  in **4a**, and 2.071(3) Å for  $\text{Fe}–\text{C}(\text{IEt}')$ , 2.075(3) Å for  $\text{Fe}–\text{N}(\text{IEt}')$  in **4b**, respectively. The bond distances of  $\text{Fe}–\text{C}(\text{IEt})$ ,  $\text{Fe}–\text{C}(\text{Ph})$ , and  $\text{Fe}–\text{Cl}$  are typical for tetrahedral  $\text{Fe}(\text{II})$  complexes.<sup>7a,21</sup>

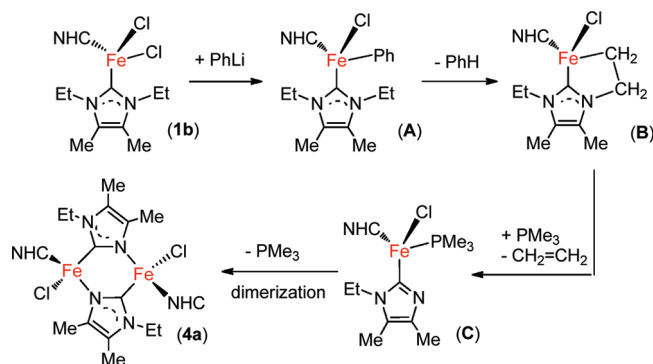
The observation of this novel imidazolyl bridge in **4a** and **4b** indicates that a  $\text{C}–\text{N}$  bond cleavage process had taken place. Although the mechanism for this  $\text{C}–\text{N}$  bond cleavage is unclear, the following observations are worth noting: (1) no  $\text{Ph}–\text{Et}$  was observed in the reaction mixture of **1b** with PhLi according to GC-MS analysis, (2) no Diels–Alder addition product 9,10-dihydro-9,10-[1,2]-benzenoanthracene was observed when





**Figure 5.** Molecular structure of  $[(\text{Iet})(\text{Ph})\text{Fe}(\text{Iet}')_2\text{Fe}(\text{Ph})(\text{Iet})]$  showing 30% probability ellipsoids and the atom-numbering scheme. The molecule has crystallographically imposed  $C_i$  symmetry. Selected distances (Å) and angles (deg):  $\text{Fe}(1)–\text{C}(1)$  2.123(4),  $\text{Fe}(1)–\text{C}(10)$  2.071(3),  $\text{Fe}(1)–\text{N}(4\text{A})$  2.075(3),  $\text{Fe}(1)–\text{C}(17)$  2.102(4),  $\text{C}(1)–\text{Fe}(1)–\text{C}(10)$  104.1(2),  $\text{C}(17)–\text{Fe}(1)–\text{N}(4\text{A})$  109.2 (1).

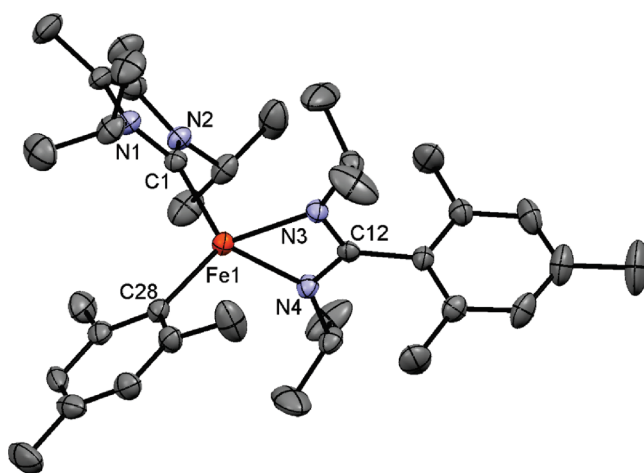
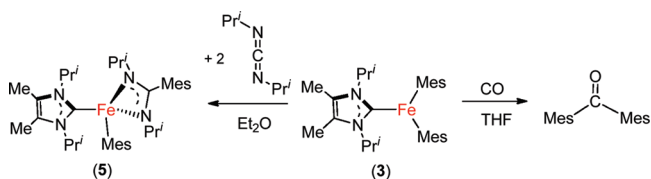
**Scheme 4.** Proposed Mechanism of the Conversion from  $\text{Iet}$  to  $\text{Iet}'$



anthracene was added to the reaction of **1b** with  $\text{PhLi}$ , (**3**) addition of trimethylphosphine results in higher yield,<sup>22</sup> (**4**) a similar reaction using  $\text{MesMgBr}$  as the arylation reagent gave only **3** (*vide supra*), and (**5**) the reaction of **1b** with one equivalent of  $\text{Bu}^n\text{Li}$  and  $\text{PMe}_3$  also yielded **4a**. According to these observations, a mechanism shown in Scheme 4 was postulated. The reaction of **1b** with  $\text{PhLi}$  gave  $(\text{Iet})_2\text{FeCl}(\text{Ph})$  (**A**), which could eliminate benzene via intramolecular C–H activation<sup>8f</sup> to form the metallacyclopentane intermediate **B**. The coordination of  $\text{PMe}_3$  and concomitant elimination of ethylene from **B** could afford  $(\text{Iet})\text{FeCl}(\text{Iet}')(\text{PMe}_3)$  (**C**). Intermediate **C** might then dissociate  $\text{PMe}_3$  and undergo dimerization to form **4a**. Notably, C–N bond cleavage of NHCs has been observed in ruthenium, palladium, nickel, and zirconium complexes,<sup>23</sup> and similar metallacyclopentane intermediates have been proposed in the C–N bond cleavage reactions of ruthenium, nickel, and zirconium complexes.<sup>23a,b,g,h</sup>

**Reactivity of the Alkyl and Aryl Complexes.** To examine the reactivity of these NHC-bound iron alkyls and aryls, their reactions with some unsaturated organic substrates were tested.

**Scheme 5.** Reactions of  $(\text{NHC})\text{Fe}(\text{Mes})_2$  with CO and Carbodiimide

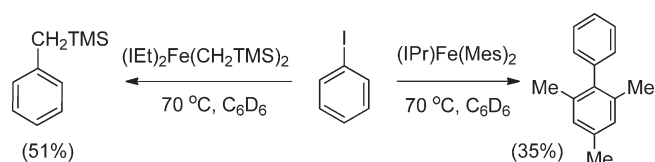


**Figure 6.** Molecular structure of  $[(\text{IPr})\text{Fe}(\text{Mes})(\text{Pr}^i\text{NC}(\text{Mes})\text{NPr}^i)]$  showing 30% probability ellipsoids and the atom-numbering scheme. Selected distances (Å) and angles (deg):  $\text{Fe}(1)–\text{C}(1)$  2.132(3),  $\text{Fe}(1)–\text{C}(28)$  2.084(3),  $\text{Fe}(1)–\text{N}(3)$  2.118(2),  $\text{Fe}(1)–\text{N}(4)$  2.112(2),  $\text{C}(1)–\text{Fe}(1)–\text{C}(28)$  114.4(1),  $\text{N}(3)–\text{Fe}(1)–\text{N}(4)$  63.05(9).

The four-coordinate complex **2a** was found inert toward 3-hexyne, phenyl nitrile, and diisopropylcarbodiimide ( $\text{Pr}^i\text{N}=\text{C}=\text{NPr}^i$ ), whereas its interaction with  $\text{H}_2$ , CO, and 2,6-dimethylphenyl isocyanide gave mixtures hard to identify. The reactions of the three-coordinate complex **3** with unsaturated substrates were also investigated. Though most were unsuccessful, its reactions with CO and  $\text{Pr}^i\text{N}=\text{C}=\text{NPr}^i$  did lead to the isolation of dimesityl ketone and  $[(\text{IPr})\text{Fe}(\text{Mes})(\eta^2\text{-Pr}^i\text{NC}(\text{Mes})\text{NPr}^i)]$  (**5**), respectively (Scheme 5). Dimesityl ketone was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and mass spectra that are consistent with the reported data.<sup>24</sup> Its formation could be explained by a consecutive insertion–reductive elimination mechanism as proposed in other carbonylation reactions of iron alkyls.<sup>17a,25</sup> Attempts to isolate the presumable iron-containing product  $(\text{IPr})\text{Fe}(\text{CO})_4$  were unsuccessful. The carbodiimide insertion product **5** was identified by elemental analysis. Its structure in the solid state was confirmed by single-crystal X-ray analysis. As shown in Figure 6, **5** has pseudoplanar structure, in which the ferrous iron center is trigonally bound with the IPr, mesityl, and  $\eta^2$ -amidinate groups with the  $\text{Fe}–\text{C}(\text{carbene})$  distance of 2.132(3) Å,  $\text{Fe}–\text{C}(\text{mesityl})$  distance of 2.084(3) Å, and  $\text{Fe}–\text{N}(\text{amidinate})$  distances of 2.118(2) and 2.112(2) Å, respectively. It should be mentioned that despite the presence of a  $\text{Fe}–\text{C}(\text{mesityl})$  bond in **5**, no further insertion reaction took place when it was treated with  $\text{Pr}^i\text{N}=\text{C}=\text{NPr}^i$ .

Organo–iron–NHC complexes have been proposed as key intermediates in some iron-catalyzed Kumada couplings, in

### Scheme 6. Reactions of Aryl- and Alkyl-Iron Complexes with Iodobenzene



which the iron–NHC catalysts were generated *in situ* and the catalytic mechanisms are unclear.<sup>7e,26</sup> Relevant to those catalytic reactions, the reactions of our well-defined organo–iron–NHC complexes with iodobenzene were studied. As shown in Scheme 6, the reactions of **2b** or **3** with one equivalent of iodobenzene in deuterated benzene were run at 70 °C in NMR scale. After hydrolysis, <sup>1</sup>H NMR and GC–MS analysis clearly showed the formation of TMSCH<sub>2</sub>Ph and Ph–Mes in 51% and 35% yields, respectively. The presence of these coupling products indicates that the reaction of organo–iron(II)–NHC species with organic halides might be the C–C bond formation step in the Kumada couplings, although the involvement of low-valent iron species could not be excluded.<sup>16a</sup> Methodology studies with these well-defined iron(II)–NHC complexes as catalysts are currently under way.

## SUMMARY

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

- (1) Ligand substitution reactions of TMEDA in [(TMEDA)<sub>2</sub>Fe<sub>2</sub>Cl<sub>4</sub>] by monodentate NHCs afford monomeric iron(II) complexes [(NHC)<sub>2</sub>FeCl<sub>2</sub>] in high yields, which provides a convenient way to access iron complexes with NHC ligation.
- (2) Tetrahedral ferrous complexes [(IEt)<sub>2</sub>Fe(Me)<sub>2</sub>] and [(IEt)<sub>2</sub>Fe(CH<sub>2</sub>TMS)<sub>2</sub>] have been prepared by alkylation of the halide. Arylation of [(IPr)<sub>2</sub>FeCl<sub>2</sub>] with the bulky Grignard reagent MesMgBr yields the trigonal-planar complex [(IPr)Fe(Mes)<sub>2</sub>].
- (3) Unusual C–N bond cleavage of the NHC ligand has been observed in the reactions of [(IEt)<sub>2</sub>FeCl<sub>2</sub>] with PhLi or Bu<sup>n</sup>Li, yielding the ferrous complex [Cl(IEt)Fe(IEt')<sub>2</sub>Fe(IEt)Cl]. The dinuclear complex features the unique η<sup>2</sup>-2-ylideneimidazolyl anionic ligand.
- (4) The tetrahedral dialkyl complex [(IEt)<sub>2</sub>Fe(Me)<sub>2</sub>] is not reactive toward some unsaturated organic substrates. The trigonal-planar complex [(IPr)Fe(Mes)<sub>2</sub>] can react with CO and Pr<sup>n</sup>N=C=NPr<sup>i</sup> to afford dimesityl ketone and [(IPr)Fe(Mes)(η<sup>2</sup>-Pr<sup>i</sup>NC(Mes)NPr<sup>i</sup>)], respectively.
- (5) Relevant to iron–NHC-catalyzed Kumada couplings, both the alkyl and aryl iron(II) complexes are found to be reactive with PhI to give C–C bond formation products, revealing that organo–iron(II)–NHC species might be involved in the C–C bond formation step in the Kumada couplings.

## 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. All organic

solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. [(TMEDA)FeCl<sub>2</sub>]<sub>2</sub>,<sup>12</sup> 2,5-diisopropyl-3,4-dimethylimidazol-1-ylidene (IPr),<sup>13</sup> 2,5-diethyl-3,4-dimethylimidazol-1-ylidene (IEt),<sup>13</sup> 2,3,4,5-tetramethylimidazol-1-ylidene (IMe),<sup>13</sup> and [Fe(Mes)<sub>2</sub>]<sub>2</sub><sup>18</sup> 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. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 300 or 400 MHz spectrometer. All chemical shifts were reported in δ units with references to the residual protons of the deuterated solvents for proton chemical shifts and the <sup>13</sup>C of deuterated solvents for carbon chemical shifts. Mass spectra were recorded with a HP-5989 instrument. 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 23 °C by the method originally described by Evans with stock and experimental solutions containing a known amount of a (CH<sub>3</sub>)<sub>3</sub>SiOSi(CH<sub>3</sub>)<sub>3</sub> standard.<sup>15</sup>

**[(IPr)<sub>2</sub>FeCl<sub>2</sub>] (1a).** The complexes were prepared using a modified method originally described by Grubbs et al.<sup>7a</sup> To a toluene (10 mL) solution of 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene (0.720 g, 4.0 mmol) was added [(TMEDA)FeCl<sub>2</sub>]<sub>2</sub> (0.486 g, 1.0 mmol) at room temperature. The reaction mixture was stirred overnight and filtered. The solid was washed with *n*-hexane (5 mL) and dried under vacuum for 2 h, giving **1a** as an off-white crystalline solid (0.620 g, 80%). X-ray diffraction-quality crystals were obtained by vapor diffusion of *n*-hexane into the benzene solution. Unit cell check of a single crystal of **1a** showed identical cell parameters to those reported.<sup>7a</sup>

**[(IEt)<sub>2</sub>FeCl<sub>2</sub>] (1b).** This complex was obtained (1.45 g, 84%) as an off-white crystalline solid by the reaction of 1,3-diethyl-4,5-dimethylimidazolin-2-ylidene (1.218 g, 8.0 mmol) with [(TMEDA)FeCl<sub>2</sub>]<sub>2</sub> (0.972 g, 2.0 mmol) in toluene (10 mL) using the procedures similar to those for **1a**. Anal. Calcd for C<sub>18</sub>H<sub>32</sub>Cl<sub>2</sub>FeN<sub>4</sub>: C, 50.13; H, 7.48; N, 12.99. Found: C, 49.57; H, 7.57; N, 12.47.

**[(IMe)<sub>2</sub>FeCl<sub>2</sub>] (1c).** This complex was obtained (0.620 g, 83%) as an off-white crystalline solid by the reaction of 1,3-dimethyl-4,5-dimethylimidazolin-2-ylidene (0.500 g, 4.0 mmol) with [(TMEDA)FeCl<sub>2</sub>]<sub>2</sub> (0.486 g, 1.0 mmol) in toluene (10 mL) using the procedures similar to that for **1a**. Anal. Calcd for C<sub>14</sub>H<sub>24</sub>Cl<sub>2</sub>FeN<sub>4</sub>: C, 44.83; H, 6.45; N, 14.94. Found: C, 45.30; H, 6.57; N, 14.12.

**[(IEt)<sub>2</sub>FeMe<sub>2</sub>] (2a).** To a Et<sub>2</sub>O (15 mL) suspension of [(IEt)<sub>2</sub>FeCl<sub>2</sub>] (0.323 g, 0.75 mmol) was slowly added MeLi (0.94 mL, 1.6 M in Et<sub>2</sub>O, 1.5 mmol) at –78 °C. The resulting mixture was allowed to warm to room temperature, stirred overnight, and filtered. The filtrate was concentrated to about 5 mL, and 1 mL of *n*-hexane was added. Slow evaporation of Et<sub>2</sub>O afforded the product as a yellow, crystalline solid (0.190 g, 65%). The <sup>1</sup>H NMR spectrum of this paramagnetic complex displayed only two characteristic peaks in the range –100 to 100 ppm. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 5.89(3H), 10.24(3H). Magnetic susceptibility (C<sub>6</sub>D<sub>6</sub>): μ<sub>eff</sub> = 4.9 μ<sub>B</sub>. Anal. Calcd for C<sub>20</sub>H<sub>38</sub>FeN<sub>4</sub>: C, 61.53; H, 9.81; N, 14.35. Found: C, 61.63; H, 9.78; N, 14.34.

**[(IEt)<sub>2</sub>Fe(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] (2b).** To a Et<sub>2</sub>O (15 mL) suspension of [(IEt)<sub>2</sub>FeCl<sub>2</sub>] (0.114 g, 0.26 mmol) was slowly added ClMgCH<sub>2</sub>SiMe<sub>3</sub> (0.41 mL, 1.3 M in THF, 0.52 mmol) at –78 °C. The resulting mixture was allowed to warm to room temperature and stirred overnight. After the addition of dioxane (2 mL), the mixture was stirred for another day and filtered. The filtrate was concentrated to about 5 mL, and 1 mL of *n*-hexane was added. Slow evaporation of Et<sub>2</sub>O afforded the product as yellow crystals (0.067 g, 48%). The <sup>1</sup>H NMR spectrum of this paramagnetic complex displayed three characteristic peaks in the range –100 to 100 ppm. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 4.30(3H), 11.59(3H), 14.05(2H). Magnetic susceptibility (C<sub>6</sub>D<sub>6</sub>): μ<sub>eff</sub> = 4.8 μ<sub>B</sub>. Anal. Calcd for C<sub>26</sub>H<sub>54</sub>FeN<sub>4</sub>Si<sub>2</sub>: C, 58.40; H, 10.18; N, 10.48. Found: C, 57.84; H, 10.08; N, 10.20.

Table 1. Crystal Data and Summary of Data Collection and Refinement for Complexes 2a–5<sup>a</sup>

	2a	2b	3	4a	4b	5
formula	C <sub>20</sub> H <sub>38</sub> FeN <sub>4</sub>	C <sub>26</sub> H <sub>54</sub> FeN <sub>4</sub> Si <sub>2</sub>	C <sub>29</sub> H <sub>42</sub> FeN <sub>2</sub>	C <sub>32</sub> H <sub>54</sub> Cl <sub>2</sub> Fe <sub>2</sub> N <sub>8</sub>	C <sub>44</sub> H <sub>64</sub> Fe <sub>2</sub> N <sub>8</sub>	C <sub>36</sub> H <sub>56</sub> FeN <sub>4</sub>
fw	390.39	543.76	474.50	733.43	816.73	600.70
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)	<i>P</i> ca2(1)	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> , Å	15.346(1)	10.214(1)	16.639(1)	13.009(1)	12.744(1)	18.333(2)
<i>b</i> , Å	9.339(1)	13.270(2)	8.652(1)	10.266(1)	13.515(1)	9.438(1)
<i>c</i> , Å	16.820(1)	12.683(2)	19.516(1)	19.250(1)	12.757(1)	21.373(2)
α, deg	90	90	90	90	90	90
β, deg	108.806(1)	101.870(2)	90	131.847(4)	93.899(2)	102.741(2)
γ, deg	90	90	90	90	90	90
<i>V</i> , Å <sup>3</sup>	2281.9(3)	1682.1(4)	2809.5(1)	1915.0(3)	2192.2(4)	3607.1(6)
<i>Z</i>	4	2	4	2	2	4
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.136	1.056	1.122	1.272	1.237	1.106
2θ range, deg	3.1 to 52.0	3.2–54.0	4.2–50.1	4.2–50.0	4.4–52.0	2.3–54.0
GOF ( <i>F</i> <sup>2</sup> )	0.997	0.874	1.056	1.066	0.943	0.878
R1 <sup>b</sup>	0.0622, <sup>d</sup> 0.0798 <sup>e</sup>	0.0511, <sup>d</sup> 0.0768 <sup>e</sup>	0.0405, <sup>d</sup> 0.0483 <sup>e</sup>	0.0446, <sup>d</sup> 0.0660 <sup>e</sup>	0.0581, <sup>d</sup> 0.0850 <sup>e</sup>	0.0525, <sup>d</sup> 0.0992 <sup>e</sup>
wR2 <sup>c</sup>	0.1861, <sup>d</sup> 0.1970 <sup>e</sup>	0.0947, <sup>d</sup> 0.1031 <sup>e</sup>	0.0991, <sup>d</sup> 0.1061 <sup>e</sup>	0.1155, <sup>d</sup> 0.1320 <sup>e</sup>	0.1628, <sup>d</sup> 0.1775 <sup>e</sup>	0.1091, <sup>d</sup> 0.1324 <sup>e</sup>

<sup>a</sup> Collected using Mo Kα radiation ( $\lambda = 0.71073$  Å). <sup>b</sup> R1 =  $\Sigma[(F_o - F_c)]/\Sigma(F_o)$ . <sup>c</sup> wR2 =  $\{\Sigma[w(F_o^2 - F_c^2)]^2/\Sigma[w(F_o^2)]^2\}^{1/2}$ . <sup>d</sup>  $I > 2\sigma(I)$ . <sup>e</sup> All data.

**[(IPr)Fe(Mes)<sub>2</sub>] (3).** To a Et<sub>2</sub>O (10 mL) solution of [FeMes<sub>2</sub>]<sub>2</sub> (0.235 g, 0.4 mmol) was added 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene (0.144 g, 0.8 mmol) at room temperature. The resulting mixture was stirred overnight and filtered. The filtrate was concentrated to about 5 mL, and 2 mL of *n*-hexane was added. Slow evaporation of Et<sub>2</sub>O afforded the product as colorless crystals (0.334 g, 88%). The <sup>1</sup>H NMR spectrum of this paramagnetic complex displayed five characteristic peaks in the range –100 to 100 ppm. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  –55.87(6H), –27.60(3H), 5.65(3H), 24.15(2H), 33.85(3H). Magnetic susceptibility (C<sub>6</sub>D<sub>6</sub>):  $\mu_{\text{eff}} = 5.4 \mu_B$ . Anal. Calcd for C<sub>29</sub>H<sub>42</sub>FeN<sub>2</sub>: C, 73.41; H, 8.92; N, 5.90. Found: C, 72.78; H, 9.06; N, 6.36.

**[Cl(IET)Fe(IET')<sub>2</sub>Fe(IET)Cl] (4a).** Method A. To a Et<sub>2</sub>O (15 mL) suspension of [(IET)<sub>2</sub>FeCl<sub>2</sub>] (0.100 g, 0.23 mmol) and PMe<sub>3</sub> (2 mL, 0.3 M in *n*-hexane, 0.60 mmol) was slowly added *n*-BuLi (0.15 mL, 1.6 M in *n*-hexane, 0.23 mmol) at –78 °C. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. After filtration, the filtrate was concentrated to about 5 mL, and 2 mL of *n*-hexane was added. Slow evaporation of Et<sub>2</sub>O afforded the product as a yellow crystalline solid (0.021 g, 25%). The <sup>1</sup>H NMR spectrum of this paramagnetic complex displayed many peaks in the range –100 to 100 ppm. Anal. Calcd for C<sub>32</sub>H<sub>54</sub>Cl<sub>2</sub>Fe<sub>2</sub>N<sub>8</sub>: C, 52.40; H, 7.42. Found: C, 52.60; H, 7.95. Satisfactory data for nitrogen analysis have not been obtained.

Method B. To a Et<sub>2</sub>O (15 mL) suspension of [(IET)<sub>2</sub>FeCl<sub>2</sub>] (0.097 g, 0.22 mmol) and PMe<sub>3</sub> (1.5 mL, 0.3 M in *n*-hexane, 0.45 mmol) was slowly added PhLi (0.22 mL, 2.0 M in Bu<sub>2</sub>O, 0.44 mmol) at –78 °C. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. After filtration, the filtrate was concentrated to about 5 mL, and 2 mL of *n*-hexane was added. Slow evaporation of Et<sub>2</sub>O afforded 4a as yellow, crystalline solids. A small amount of orange plate-like crystals was also obtained from the bulk sample and shown by an X-ray structure determination to be [Ph(IET)Fe(IET')<sub>2</sub>Fe(IET)Ph] (4b).

**[(IPr)Fe(Mes)( $\eta^2$ -Pr'NC(Mes)NPr')] (5).** To a Et<sub>2</sub>O (10 mL) solution of 3 (0.095 g, 0.2 mmol) was slowly added 'PrN=C=N'Pr (0.050 g, 0.4 mmol) at –78 °C. The resulting mixture was allowed to warm to room temperature and stirred overnight. After filtration, the filtrate was concentrated to about 5 mL, and 1 mL of *n*-hexane was added. Slow evaporation of Et<sub>2</sub>O afforded the product as yellow crystals (0.078 g, 65%). The <sup>1</sup>H NMR spectrum of this paramagnetic complex displayed many peaks in the range –100 to 100 ppm. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):

$\delta$  –68.04, –32.41, –7.82, –1.63, 8.27, 11.84, 14.82, 21.70, 28.13, 50.32, 56.25, 98.35. Anal. Calcd for C<sub>36</sub>H<sub>56</sub>FeN<sub>4</sub>: C, 71.98; H, 9.40; N, 9.33. Found: C, 72.50; H, 9.36; N, 9.75.

**Reaction of 3 with CO.** A solution of 3 (0.22 g, 0.46 mmol) in THF (10 mL) was cooled with liquid N<sub>2</sub>, and then 1 atm of CO was added via a CO balloon. The mixture was allowed to warm to room temperature and stirred for 30 min, giving a dark brown solution. After removal of the solvent, the brown residue was subjected to flash column chromatography (SiO<sub>2</sub>, 200–300 mesh, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, 1:1, as eluent). Dimesityl ketone (0.058 g, 47%) was isolated as a white solid. <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>):  $\delta$  2.12 (s, 12H, *o*-CH<sub>3</sub>), 2.29 (s, 6H, *p*-CH<sub>3</sub>), 6.84 (s, 4H, *m*-C<sub>6</sub>H<sub>2</sub>). <sup>13</sup>C NMR (300 MHz CDCl<sub>3</sub>):  $\delta$  20.64 (*o*-CH<sub>3</sub>), 21.07 (*p*-CH<sub>3</sub>), 129.71 (phenyl C), 136.52 (phenyl C), 138.35 (phenyl C), 139.90 (phenyl C), 202.60 (C=O). MS: *m/z* calcd for C<sub>19</sub>H<sub>22</sub>O<sup>+</sup> 266, found 266. These data are consistent with those reported in the literature.<sup>23</sup>

**Reactions of 2b and 3 with PhI.** In a J. Young NMR tube, 2b (30.5 mg, 0.057 mmol) or 3 (19.1 mg, 0.040 mmol) was dissolved in C<sub>6</sub>D<sub>6</sub> (0.5 mL). Iodobenzene (11.6 mg, 0.057 mmol for 2b; 8.2 mg, 0.04 mmol for 3, respectively) was added to this solution. The mixture was kept at 70 °C. The reaction process was followed by <sup>1</sup>H NMR until 2b or 3 was consumed. After quenching with one drop of aqueous HCl (3 N) and drying over MgSO<sub>4</sub> powder, the organic phase was analyzed by GC-MS. The yields of arenes were determined by GC analysis with *n*-dodecane (4.8 mg, 0.029 mmol for 2b; 6.8 mg, 0.04 mmol for 3, respectively) as an internal standard. The reaction of 2b with PhI yielded (determined by GC) PhCH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub> (51%). The reaction of 3 with PhI yielded (determined by GC) 2-phenyl-1,3,5-trimethylbenzene (35%), mesityl–mesityl (35%), and 1,3,5-trimethylbenzene (30%).

**X-ray Structure Determination.** All single crystals were immersed in Paratone-N oil and sealed under N<sub>2</sub> in thin-walled glass capillaries. Data were collected at 293 K on a Bruker AXSD8 X-ray diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.<sup>27</sup> All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on *F*<sup>2</sup> using the SHELXTL program package.<sup>28</sup> All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 1.



## ■ ASSOCIATED CONTENT

**S Supporting Information.** X-ray crystallographic files in CIF format for the six compounds in Table 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

## Corresponding Author

\*E-mail: [deng@sioc.ac.cn](mailto:deng@sioc.ac.cn).

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