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# Synthesis of symmetrically and unsymmetrically 3,5-dimethylbenzyl-substituted 1,1'-ferrocene diamines

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# ABSTRACT

1,1'-Ferrocene diamides have shown remarkable efficacy as supporting ligands for electrophilic metal centers. While different substituents have been used, most ferrocene diamines are employed as dianionic precursors, thus limiting the possible scope and reactivity of these metal complexes. The use of a 3,5-dimethylbenzyl (xylyl) substituent allowed the successful synthesis of tri- and tetra-substituted ferrocene 1,1'-diamines, providing monoanionic and neutral pro-ligands. In addition, an unsymmetrically disubstituted 1,1'-ferrocene diamine was obtained containing both the 3,5-dimethylbenzyl and *t*-butyldimethylsilyl substituents.

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# 1. Introduction

The utilization of 1,1'-ferrocene diamides as supporting ligands for electrophilic metal centers has seen extensive exploration by several groups [1–32]. A variety of substituents, consisting mainly of silyl and aryl moieties, have often been attached to the nitrogen atoms of the 1,1'-ferrocene diamides. These ligands add to the number of excellent non-cyclopentadienyl alternatives for the ubiquitous cyclopentadienyl group 3 metal chemistry [33-36]. Ferrocene diamides have numerous advantages: (i) cis-coordination of the two amide donors is enforced, effectively blocking one side of the metal center; (ii) the ferrocene backbone can accommodate electron density changes at the metal center by varying the geometry around iron; (iii) other ligands and substrates coordinate perpendicularly to the plane formed by the two amide nitrogens, iron, and the metal, giving clear access to the electrophilic center; (iv) a weak interaction of donor-acceptor type between iron and the electrophilic metal center is possible and might influence the reactivity of the complex; (v) iron(II) can be oxidized to iron(III), potentially resulting in enhanced reactivity at the electrophilic metal center [7,16,37].

Previous research in our group has not only explored the use of these ligands with  $d^0f^n$  metals, but also variation of the nitrogen substituents [37]. While these substituents afford remarkable alterations in reactivity, solubility, electronic and steric properties,

thus far, the ferrocene-based ligands synthesized by our group have been limited to dianionic variants. Furthermore, all the pro-ligands have been symmetrical with respect to the nitrogen substituents. With this in mind, we report on achieving two goals: (1) the expansion of 1,1'-disubstituted ferrocene amides to neutral and monoanionic variations, and (2) the synthesis of an unsymmetrical dianionic precursor.

# 2. Results and discussion

#### 2.1. Formation of 1,1'-ferrocene dixylyl diamine

The synthetic procedure for the dixylyl-functionalized diamine  $fc(NHXy)_2$  (1, fc = 1,1'-ferrocenylene, Xy = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Eq. (1)) was adapted from a previously reported procedure employed for  $fc(NHMes)_2$  (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) [38]. The precursor  $fc(NH_2)_2$ reacted with 3,5-dimethylbromobenzene, NaO<sup>t</sup>Bu, and 1.75-4 mol% Pd(dba)(BINAP) (dba = dibenzylideneacetone, BINAP = 2,2'-bis (diphenylphosphino)-1,1'-binaphthyl) at 100 °C in toluene for 2 days under an inert atmosphere (Eq. (1)). The product was characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Figs. S1 and S2) as well as elemental analysis. Comparisons can be made between 1 and the previously characterized fc(NHSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub> or fc(NHMes)<sub>2</sub>. In the <sup>1</sup>H NMR spectrum of 1, the ferrocene protons are split into two broad peaks at 4.18 and 3.89 ppm, while the <sup>1</sup>H NMR spectrum of fc(NHSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub> shows two broad singlets at 3.84 and 3.82 ppm. The <sup>1</sup>H NMR spectrum of fc(NHMes)<sub>2</sub> is also similar, with the ferrocene protons located at 3.80 and 3.78 ppm. In compound 1, the





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amine protons are observed at 4.56 ppm, a significant downfield shift from the amine protons in  $fc(NHSi^{1}BuMe_{2})_{2}$ , observed at 2.07 ppm, but similar to the downfield shift of the amine protons in  $fc(NHMes)_{2}$ , which appear at 4.05 ppm. The methyl protons in **1** are found at 2.17 ppm, similar to the methyl protons in  $fc(NHMes)_{2}$ , which are found at 2.17 and 2.12 ppm. Overall, the <sup>1</sup>H NMR spectrum of **1** is similar to the closely related  $fc(NHMes)_{2}$ .



#### 2.2. 1,1'-Ferrocene tetraxylyl diamine

Small amounts of byproducts present during the synthesis of **1** suggested that the amine nitrogens may be substituted with additional xylyl groups. Indeed, from **1**, an additional 2 equivalents of 3,5-dimethylbromobenzene, 3 equivalents of NaO<sup>t</sup>Bu, and 1.75–4 mol% Pd(dba)(BINAP) yielded fc(NXy<sub>2</sub>)(NXy<sub>2</sub>), **2**, in 68% yield (Eq. (2)). Compound **2** was characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Figs. S3 and S4); while the proton resonances in the <sup>1</sup>H NMR spectrum appear to be similar to those of **1**, there are noticeable shifts of the ferrocene signals from 4.17 and 3.89 ppm in **1** to 4.26 and 4.07 ppm in **2**, and the *o,o'*-xylyl-*H* signals shift from 6.52 ppm in **1** to 7.23 ppm in **2**. Additionally, the disappearance of the amine proton resonance supports the formation of **2**.



#### 2.3. 1,1'-Ferrocene trixylyl diamine

During one of the reactions to form **2**, an intermediate, the trixylyl species fc(NHXy)(NXy<sub>2</sub>), **3**, was observed. Separately, the formation of **3** from **1** was monitored via <sup>1</sup>H NMR spectroscopy, by which it was determined that there was a 75% conversion from **1** after 8 days (Eq. (3)). Attempts to optimize the reaction conditions by varying the amount of Pd(dba)(BINAP) did not increase conversion, while additional equivalents of NaO<sup>t</sup>Bu led to the formation of **2**. Fortunately, **3** is sparingly soluble in hexanes, unlike **1**; as a consequence, **3** was easily isolated in 56% yield. As expected, a reduction of symmetry was observed in the <sup>1</sup>H NMR spectrum of **3** compared to **1** and **2** (Fig. S5): the ferrocene proton signals have increased from 2 peaks (4.17 and 3.89 ppm) to 4 peaks (4.31, 4.17, 4.01, and 3.92 ppm). Additionally, separate resonances are observed for the aromatic xylyl and amine (NH) protons (6.51, 6.44, and 4.75 ppm) and the corresponding  $N(Xy)_2$  protons (7.21 and 6.60 ppm).



#### 2.4. 1,1'-Ferrocene monoxylyl diamine

The successful isolation and characterization of **3** led us to investigate whether 1,1'-ferrocene monoxylyl diamine, **4**, could be synthesized and isolated (Scheme 1). From  $fc(NH_2)_2$ , 1 equivalent of both 3,5-dimethylbromobenzene and NaO<sup>t</sup>Bu in the presence of 1.75–4 mol% Pd(dba) (BINAP) led to the formation of **4**. Similar to the incomplete conversion of **1** to **3**, the formation of **4** stopped after 70% of the initial ferrocene diamine was consumed, as assessed by <sup>1</sup>H NMR spectroscopy. However, much like **3**, solubility differences allowed the separation of **1** and **4**, leading to the isolation of **4** in 51% yield. As with **3**, there is a reduction of symmetry observed in the <sup>1</sup>H NMR spectrum of **4** when compared to the starting material. The number of peaks for the ferrocene protons increases from 2 to 4 (3.74 and 3.66 ppm in  $fc(NH_2)_2$  to 4.19, 3.91, 3.73, and 3.62 ppm in **4**, Fig. S10).

#### 2.5. Unsymmetrically substituted 1,1'-ferrocene diamine

With the successful isolation of 4, the isolation of an unsymmetrically substituted 1.1'-ferrocene diamine was explored. Compound **4** was combined with triethylamine and <sup>t</sup>BuMe<sub>2</sub>SiCl in dichloromethane for 14 h at room temperature to generate fc(NHXy)(NHSi<sup>t</sup>BuMe<sub>2</sub>) (5) in 60% yield (Scheme 1). Analysis of the <sup>1</sup>H and <sup>13</sup>C NMR spectra confirms the formation of **5** (Figs. S12 and S13): the NH<sub>2</sub> protons at 1.62 ppm in **4** are replaced by the amine proton signal at 1.84 ppm and the *t*-butyl and methyl protons of the *t*-butyldimethylsilyl substituent are found at 0.85 and 0.12 ppm, respectively. These signals exhibit an upfield shift with respect to fc(NHSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub> (amine proton signal at 2.08 ppm and *t*-butyl and methyl signals at 0.93 and 0.17 ppm, respectively). In addition, the signals for the xylyl and xylyl amine protons have shifted with respect to the starting compound 4; while the aryl and methyl peaks have hardly shifted from 6.64, 6.46, and 2.22 ppm in 4 to 6.64, 6.45, and 2.21 ppm in 5, the amine proton has moved upfield from 5.68 ppm in **4** to 5.05 ppm in **5**.



Scheme 1. Synthesis of 4 and 5.

# 3. Conclusions

The use of a xylyl substituent allowed the successful synthesis of a series of 1,1'-ferrocene diamines. Characterization by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy indicates that the amine proton peaks of fc(NHXy)<sub>2</sub> (**1**) appear more downfield than those of the previously reported fc(NHSi<sup>f</sup>BuMe<sub>2</sub>)<sub>2</sub>. Further variations from **1** led to fc(NXy<sub>2</sub>)<sub>2</sub> (**2**) and fc(NHXy)(NXy<sub>2</sub>) (**3**), while reactions carried out from fc(NH<sub>2</sub>)<sub>2</sub> led to the formation of fc(NH<sub>2</sub>)(NHXy) **4**. Compound **4** was reacted with *t*-butyldimethylsilylchloride to produce fc(NHXy)(NHSi<sup>f</sup>BuMe<sub>2</sub>) **5**, an unsymmetrically substituent and the standard *t*-butyldimethylsilyl substituent commonly used in our research. Reactivity studies with a variety of metal centers are currently in progress.

#### 4. Experimental

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in an MBraun inertgas glovebox. Solvents were purified using a two-column solidstate purification system by the method of Grubbs [39] and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use.  $fc(NH_2)_2$  was prepared following published procedures [40], <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker300 or Bruker500 spectrometers (supported by the NSF grant CHE-9974928) at room temperature in  $C_6D_6$  unless otherwise specified. Chemical shifts are reported with respect to solvent residual peak, 7.16 ppm ( $C_6D_6$ ). CHN analyses were performed on an Exeter Analytical, Inc. CE-440 Elemental Analyzer.

## 4.1. Synthesis of 1

fc(NH<sub>2</sub>)<sub>2</sub> (200.0 mg, 0.925 mmol) was combined with 3 equiv of NaO<sup>t</sup>Bu (266.8 mg, 2.776 mmol), 2.5 equiv of 3,5dimethylbromobenzene (428.2 mg, 2.314 mmol), and 2.4 mol% of Pd(dba)BINAP (21.8 mg, 0.0226 mmol) in 20 mL of toluene in a 50 mL Schlenk tube equipped with a magnetic stir bar. The solution was heated and stirred at 100 °C for 48 h. The volatiles were then removed under reduced pressure; the resulting orange solid was extracted with hexanes and filtered through Celite. The filtrate was reduced to dryness and the resulting solid was taken up in a minimal amount of ether to obtain a concentrated solution. The solution was then placed in a freezer at -35 °C. The product obtained from crystallization was a yellow-orange flaky solid in 91% yield (360.2 mg, 0.844 mmol).



<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ , ppm: 6.52 (s, 4H, d), 6.46 (s, 2H, a), 4.56 (s, 2H, f), 4.17 (t, 4H, h), 3.89 (t, 4H, i), 2.17 (s, 12H, b). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ , ppm: 146.1 (e), 138.3 (c), 120.7 (a), 113.0 (d), 100.5 (g), 64.8 (i), 62.8 (h), and 21.2 (b). Anal. (%) for C<sub>26</sub>H<sub>28</sub>FeN<sub>2</sub> Calcd: C, 73.59; H, 6.65; N, 6.60; Found: C, 73.86; H, 6.44; N, 6.42.

#### 4.2. Synthesis of 2

In a glove box, **1** (194.9 mg, 0.459 mmol) was dissolved in ~10 mL toluene. To this solution, 3,5-dimethylbromobenzene (0.187 mL, 1.38 mmol), NaO<sup>t</sup>Bu (133 mg, 1.38 mmol) and Pd(dba) BINAP (32.1 mg, 3 mol%) were added and the solution was transferred to a Schlenk tube. The solution was stirred and heated at 100 °C for 14 h, after which the tube was brought back into the glove box and solvent was removed under reduced pressure. The crude solid was redissolved in diethyl ether and filtered through Celite. The filtrate was collected, solvent was removed, and the resulting solid was dissolved in a minimal amount of hexanes. The solution was stored at -35 °C overnight, which afforded the product as a red solid; the solid was separated by filtration, dried under reduced pressure, and determined to be **2** via NMR spectroscopy. Yield: 196.6 mg, 67.7%.



<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ, ppm: 7.23 (s, 8H, d), 6.59 (s, 4H, a), 4.26 (m, 4H, *f*), 4.07 (m, 4H, g), 2.06 (s, 24H, b). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>): δ, ppm: 148.1 (e), 138.3 (c), 124.8 (a), 122.7 (d), 108.5 (h), 64.8 (g), 61.1 (f), and 20.9 (b). Anal. (%): Calcd. for C<sub>42</sub>H<sub>44</sub>FeN<sub>2</sub>: C, 79.74; H, 7.01; N, 4.43. Found: C, 79.52; H 7.05; N 3.99.

#### 4.3. Synthesis of **3**

In a glove box, **1** (150.2 mg, 0.354 mmol) was dissolved in  $\sim$ 7 mL toluene. To this solution, 3,5-dimethylbromobenzene (0.048 mL, 0.353 mmol), NaO<sup>t</sup>Bu (33.9 mg, 0.353 mmol) and Pd(dba)BINAP (9.8 mg, 3 mol%) were added and the solution was transferred to a Schlenk tube. The solution was stirred and heated at 100 °C for 8 days, at which time it was determined via NMR spectroscopy that the reaction could not be pushed further. The Schlenk tube was brought back into the glove box and the volatiles were then removed under reduced pressure. The crude solid was redissolved in diethyl ether and filtered through Celite. The filtrate was collected, solvent was removed, and the resulting solid was stored at -35 °C overnight, which afforded the product as a redorange solid; the solid was separated by filtration, dried under

reduced pressure, and determined to be **3** via NMR. Yield: 105.0 mg, 56.2%.



<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ , ppm: 7.21 (s, 4H, d), 6.60 (s, 2H, a), 6.51 (s, 2H, j), 6.44 (s, 1H, g), 4.75 (s, 1H, f), 4.31 (br s, 2H, m), 4.17 (br s, 2H, o), 4.02 (br s, 2H, n), 3.92 (br s, 2H, p), 2.15 (s, 6H, h), 2.09 (s, 12H, b). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ , ppm: 147.7 (e), 146.7 (k), 138.5 (c), 138.1 (i), 125.0 (a), 122.7 (d), 120.4 (g), 112.7 (j), 100.5 (l), 65.3 (n), 64.5 (p), 64.1 (m), 60.4 (o), 21.2 (h), and 21.0 (b). Anal. (%): Calcd. for C<sub>34</sub>H<sub>36</sub>FeN<sub>2</sub>: C, 77.27; H, 6.87; N, 5.30. Found: C, 77.76; H 6.94; N 5.08.

#### 4.4. Synthesis of 4

In a glove box, fc(NH<sub>2</sub>)<sub>2</sub> (250 mg, 1.146 mmol) was dissolved in ~10 mL toluene. To this solution, 3,5-dimethylbromobenzene (0.171 mL, 1.261 mmol), NaO<sup>t</sup>Bu (110.1 mg, 1.146 mmol), and Pd(dba)BINAP (32.1 mg, 3 mol%) were added and the solution was transferred to a Schlenk tube. The solution was stirred and heated at 100 °C for 48 h, after which the tube was brought back into the glove box and the volatiles were then removed under reduced pressure. The crude solid was redissolved in diethyl ether and filtered through Celite. The filtrate was collected, volatiles were removed, and the resulting solid was dissolved in a minimal amount of hexanes. The solution was stored at -35 °C overnight, which afforded the product as a yellow solid; the solid was separated by filtration, dried under reduced pressure, and determined to be **4** via NMR spectroscopy. Yield: 187.0 mg, 50.8%.



<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ , ppm: 6.64 (s, 2H, d), 6.46 (s, 1H, a), 5.68 (s, 1H, *f*), 4.19 (br s, 2H, *k*), 3.91 (br s, 2H, *l*), 3.73 (br s, 2H, *i*), 3.62 (br s, 2H, *j*), 2.22 (s, 6H, *b*), 1.62 (s, 2H, g). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ , ppm: 148.3 (e), 138.2 (c), 119.6 (a), 112.0 (d), 95.6 (h), 66.7 (l), 65.7 (*k*), 63.8 (*j*), 59.3 (*i*), and 21.2 (*b*). Anal. (%): Calcd. for C<sub>18</sub>H<sub>20</sub>FeN<sub>2</sub>: C, 67.52; H, 6.30; N, 8.75. Found: C, 67.92; H 6.30; N 8.74.

#### 4.5. Synthesis of 5

In a glove box, **4**(101.1 mg, 0.314 mmol) was dissolved in ~7 mL dichloromethane in a 20 mL vial. In a separate vial, triethylamine (0.044 mL, 0.314 mmol) and *t*-butyldimethylsilylchloride (43.5 mg, 0.314 mmol) were combined and dissolved in ~5 mL dichloromethane. The solutions were combined and stirred at room temperature for 14 h, after which the volatiles were then removed under reduced pressure. The crude solid was suspended in hexanes, filtered through Celite, and dried, whereupon ~1 mL hexanes was added to form a concentrated solution and stored overnight at -35 °C. An orange-yellow crystalline material was collected via filtration, dried under reduced pressure, and identified via NMR spectroscopy. Yield: 81.9 mg, 60.1%.



<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ , ppm: 6.64 (s, 2H, d), 6.45 (s, 1H, a), 5.05 (s, 1H, *f*), 4.20 (d, 2H, h), 3.94 (d, 2H, *i*), 3.77 (m, 4H, *j*,*k*), 2.21 (s, 6H, *b*), 1.84 (s, 2H, *m*), 0.85 (s, 9H, *p*), 0.12 (d, 6H, *n*). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ , ppm: 147.9 (*e*), 138.2 (*c*), 119.9 (*a*), 112.1 (*d*), 106.3 (*l*), 96.6 (g), 65.9 (*j*), 65.7 (*k*), 63.7 (*i*), 59.8 (*h*), 26.1 (*p*), 21.2 (*b*), 17.9 (*o*), and -4.5 (*n*). Anal. (%): Calcd. for C<sub>24</sub>H<sub>34</sub>FeN<sub>2</sub>Si: C, 66.35; H, 7.89; N, 6.45. Found: C, 66.04; H 7.43; N 6.41.

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#### Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jorganchem.2011.06.043.

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