

# Silylated 1,1'-Diaminoferrrocene: Ti and Zr Complexes of a New Chelating Diamide Ligand

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Silylation of 1,1'-diaminoferrrocene afforded 1,1'-Fc(NHSiMe<sub>3</sub>)<sub>2</sub> (LH<sub>2</sub>) as red air-sensitive crystals. Reaction with M(CH<sub>2</sub>Ph)<sub>4</sub> (M = Ti, Zr) afforded the corresponding LM(CH<sub>2</sub>Ph)<sub>2</sub> (M = Zr; Ti), where the Fc(NSiMe<sub>3</sub>)<sub>2</sub><sup>2-</sup> group serves as a diamide ligand. Alternatively, the magnesium salt LMg(THF)<sub>2</sub> was reacted with TiCl<sub>4</sub>(THF)<sub>2</sub> to give LTiCl<sub>2</sub> as purple air-sensitive crystals. Methylation of the latter with MeLi affords LTiMe<sub>2</sub>.

## Introduction

In an effort to create electron-deficient group 4 transition metal centers for catalytic transformations, linked diamides have been considered by several researchers as alternatives to the ubiquitous metallocenes.<sup>1,2</sup> For example, silylated *o*-phenylenediamine has been used by Tilley and co-workers to prepare Ti and Zr complexes, where electron donation directly from the phenylene group compensates partly for the low electron count on the metal center.<sup>3</sup> In addition, a variety of diamide ligands based on naphthalene,<sup>4,5</sup> propylene,<sup>5,6</sup> and substituted propylene<sup>7</sup> diamines have been studied. McConville et al. reported propylenediamine-based Ti complexes that polymerize 1-hexene and, when activated with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, can do so in a "living" manner.<sup>8</sup> Schrock has reported using tridentate diamido/donor ligands for group IV-catalyzed 1-hexene polymerization.<sup>9</sup>

We recently described an improved synthesis of 1,1'-diaminoferrrocene<sup>10</sup> and were interested in incorporating this redox-active moiety into the backbone of a linked diamide system. Our interest in ferrocene containing ligands is twofold: first, ferrocene provides a unique geometry to the ligand environment, as demonstrated by the burgeoning use of its phosphine derivatives in transition metal chemistry.<sup>11,12</sup> Second, the possibility

of switching the redox state of the ferrocene backbone may provide another tool for controlling reactivity at a metal center. Here, in the first of a series of papers concerning functionalized ligands incorporating 1,1'-diaminoferrrocene, we describe the synthesis of a new silylated aminoferrrocene ligand and its use in the preparation of some Ti and Zr complexes.

## Results and Discussion

**Preparation of the Ligand.** Silylated diamines are often synthesized in a two-step process involving deprotonation with *n*-BuLi followed by treatment with an appropriate silylhalide.<sup>3–5,7,13</sup> In contrast, we found that a simple one-step silylation with Me<sub>3</sub>SiCl/Et<sub>3</sub>N in CH<sub>2</sub>Cl<sub>2</sub> afforded Fc(NHSiMe<sub>3</sub>)<sub>2</sub> (LH<sub>2</sub>) in nearly quantitative yields on small or large scales (Scheme 1).

The compound crystallizes from pentane as red air-sensitive crystals. Its <sup>1</sup>H NMR spectrum is typical for a 1,1'-substituted ferrocene, consisting of two ferrocene triplets, a broad NH resonance, and an SiMe<sub>3</sub> singlet, indicating an average C<sub>2v</sub> symmetry in solution. Cyclic voltammetry of the complex carried out in acetonitrile (0.1 M TBAPF<sub>6</sub>, glassy carbon electrode) shows a reversible oxidation wave with E<sub>1/2</sub> = -0.632 V vs Fc<sup>0/+</sup>. This is at even more negative potential than the analogous parameter found for the electron-rich unsubstituted diamine Fc(NH<sub>2</sub>)<sub>2</sub> (E<sub>1/2</sub> = -602 mV vs Fc<sup>0/+</sup>).<sup>10</sup>

**Lithium and Magnesium Complexes.** We sought to prepare Li and Mg derivatives of the ligand for use in subsequent salt metathesis reactions with metal halides. The Li salt was prepared by reacting LH<sub>2</sub> with 2 equiv of *n*-BuLi in Et<sub>2</sub>O (Scheme 2).

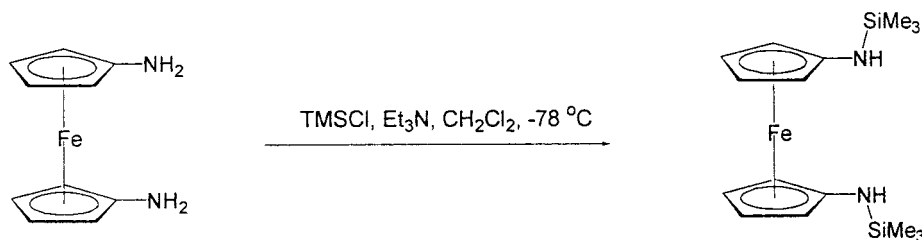
Upon crystallization, orange blocks of [Fc(NSiMe<sub>3</sub>)<sub>2</sub>]-Li<sub>2</sub>(Et<sub>2</sub>O)<sub>x</sub> (where *x* is 2.5–3.5) were obtained. The crystals desolvate quickly under vacuum, affording a yellow powder, for which *x* = 1.

The Mg salt was obtained in a related fashion by reacting LH<sub>2</sub> with Me<sub>2</sub>Mg or Bu<sub>2</sub>Mg in THF. Addition of pentane and cooling the solution to -40 °C resulted in the formation of yellow crystals of [Fc(NSiMe<sub>3</sub>)<sub>2</sub>]Mg-(THF)<sub>2</sub> in 83% yield. The solid-state structure shows the Mg to be coordinated by a chelating Fc(NSiMe<sub>3</sub>)<sub>2</sub><sup>2-</sup>

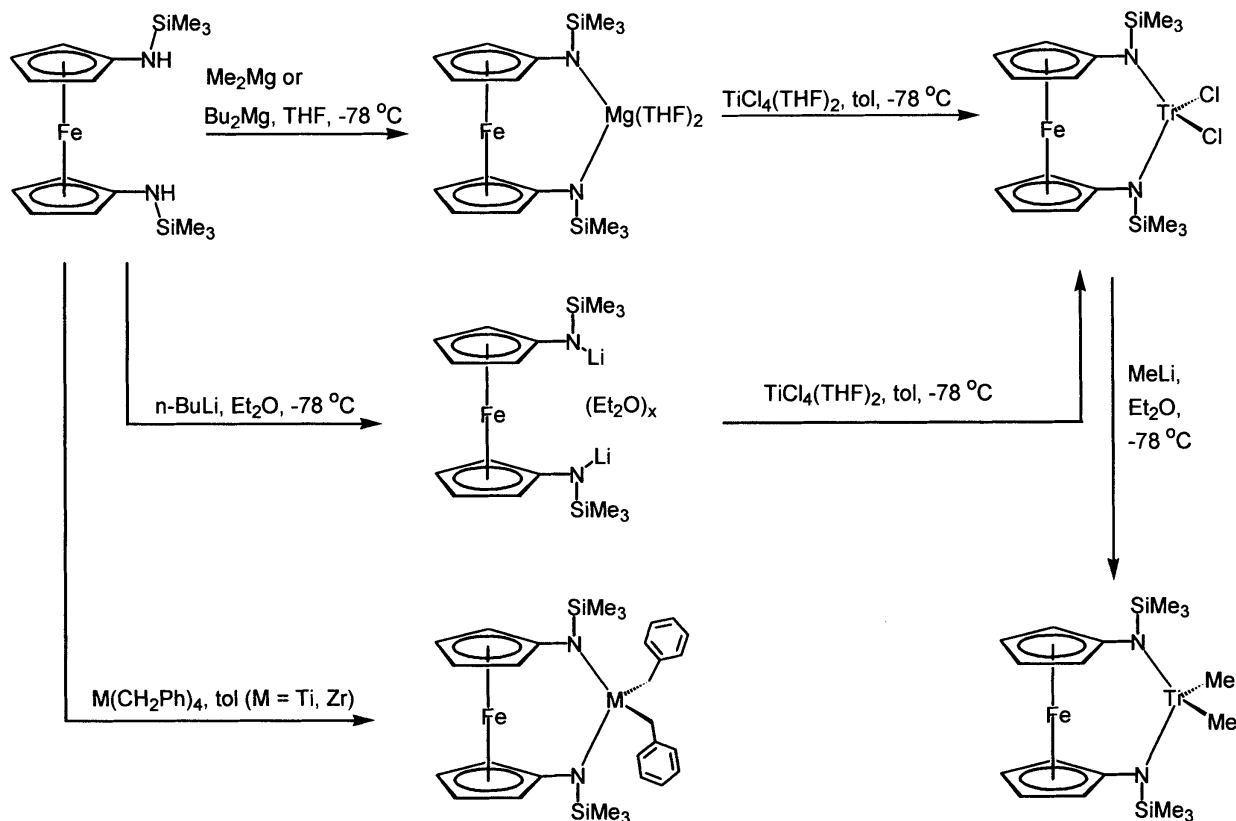
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Scheme 1



Scheme 2



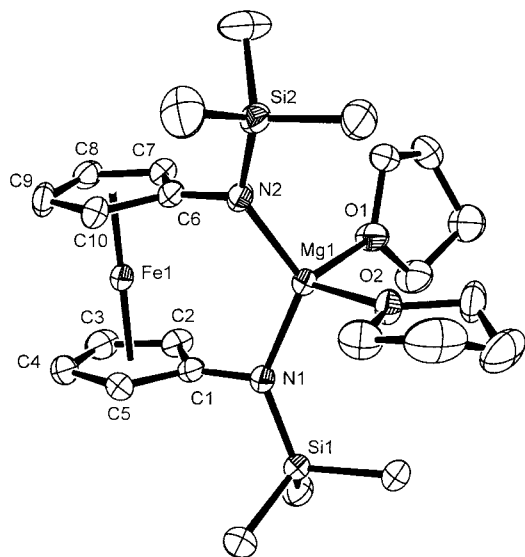
ligand and two THF molecules (Figure 1). The geometry around Mg is roughly tetrahedral, but the Mg center is sitting 0.5 Å out of the plane formed by Fe1, N1, and N2 atoms; the nitrogen atoms are trigonal planar. The  $^1\text{H}$  NMR spectrum of the complex is consistent with an average  $C_{2v}$  symmetry in solution, showing two ferrocene triplets, a silyl resonance, and a set of bound THF resonances.

**Titanium and Zirconium Complexes.** Two strategies were employed in obtaining Ti and Zr complexes (Scheme 2). The Mg or Li salts of the ligand were used to generate  $[\text{Fc}(\text{NSiMe}_3)_2]\text{TiCl}_2$  through salt metathesis with  $\text{TiCl}_4(\text{THF})_2$ . Alternatively, direct reaction of the neutral ligand with homoleptic metal alkyls led to the formation of the corresponding metal complexes via alkane elimination.

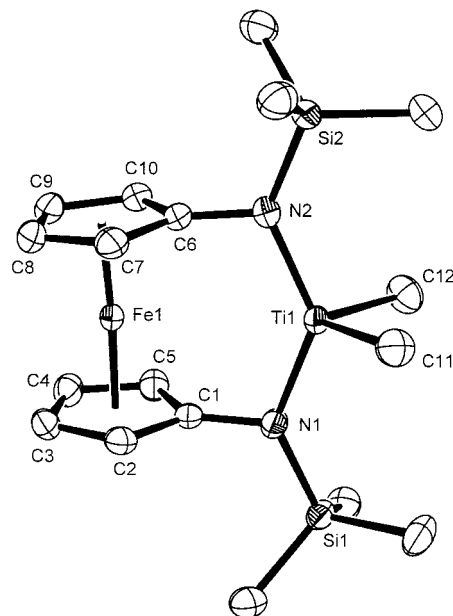
Reaction of  $[\text{Fc}(\text{NSiMe}_3)_2]\text{Mg}(\text{THF})_2$  with a slurry of  $\text{TiCl}_4(\text{THF})_2$  in toluene was accompanied by the immediate darkening of the reaction mixture to dark purple. Extraction of the residue into pentane followed by crystallization afforded  $\text{Fc}(\text{NSiMe}_3)_2\text{TiCl}_2$  in 69% yield as dark purple crystals. The compound was also prepared from  $[\text{Fc}(\text{NSiMe}_3)_2]\text{Li}_2(\text{Et}_2\text{O})_x$  in an analogous manner, although the yields were somewhat lower. The

$^1\text{H}$  NMR spectrum is also consistent with  $C_{2v}$  symmetry in solution, showing two ferrocene resonances and a single silyl resonance. The  $C_{2v}$  symmetry (noncrystallographic) is also found in the solid state (Figure 2). The Cp groups are eclipsed, and the Fe–N1–N2–Ti plane is roughly orthogonal to the Ti–Cl1–Cl2 plane. The Ti–N distances of 1.891(2) and 1.895(2) Å are similar to those reported for related compounds,<sup>3,4,7,8</sup> but the N–Ti–N angle of 134.01(9)° is significantly larger than the tetrahedral angle usually found in these compounds (ranges from 97° to 109°). The N atoms are  $\text{sp}^2$  hybridized, as evidenced by the average sum of angles around nitrogen atoms being 359.5°. The Fe–C distances in the ferrocene backbone are quite normal, and the dihedral angle between the Cp rings is 4.30°.

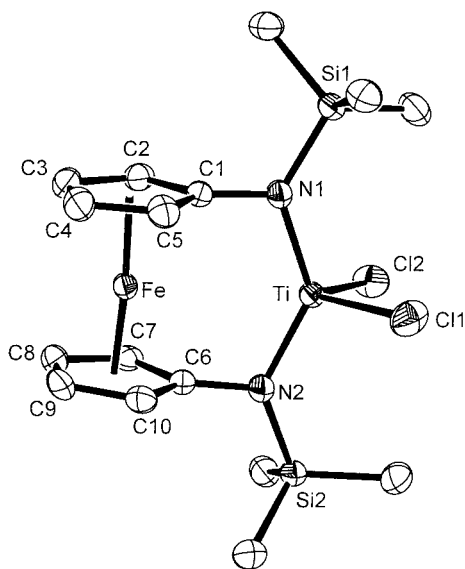
Methylation of  $[\text{Fc}(\text{NSiMe}_3)_2]\text{TiCl}_2$  with 2 equiv of MeLi proceeded smoothly in  $\text{Et}_2\text{O}$  at  $-60^\circ\text{C}$  and was accompanied by a color change from deep purple to orange. The resulting dimethyl species,  $[\text{Fc}(\text{NSiMe}_3)_2]\text{TiMe}_2$ , was isolated from pentane as red crystals in 75% yield. Its  $^1\text{H}$  NMR spectrum in  $\text{C}_6\text{D}_6$  is similar to that of the dichloride precursor with the addition of a methyl resonance at 1.09 ppm integrating to 6 H. The solid-state structure, determined by X-ray crystallography,



**Figure 1.** ORTEP diagram of  $\text{Fc}(\text{NSiMe}_3)_2\text{Mg}(\text{THF})_2$  drawn with 50% thermal ellipsoids. Selected bond distances (Å):  $\text{Mg1-N1}$  1.983(2),  $\text{Mg1-N2}$  1.988(2),  $\text{Mg1-O1}$  2.042(2),  $\text{Mg1-O2}$  2.049(2),  $\text{Fe1-C1}$  2.095(2),  $\text{Fe1-C2}$  2.052(2),  $\text{Fe1-C3}$  2.039(2),  $\text{Fe1-C4}$  2.033(2),  $\text{Fe1-C5}$  2.050(2),  $\text{Fe1-C6}$  2.090(2),  $\text{Fe1-C7}$  2.056(2),  $\text{Fe1-C8}$  2.036(2),  $\text{Fe1-C9}$  2.039(2),  $\text{Fe1-C10}$  2.041(2),  $\text{N1-C1}$  1.413(2),  $\text{N2-C6}$  1.415(2). Selected bond angles (deg):  $\text{N1-Mg1-N2}$  123.18(7),  $\text{O1-Mg1-O2}$  96.79(7).



**Figure 3.** ORTEP diagram of  $\text{Fc}(\text{NSiMe}_3)_2\text{Ti}(\text{CH}_3)_2$  drawn with 50% thermal ellipsoids. Selected bond distances (Å):  $\text{Ti1-N1}$  1.921(2),  $\text{Ti1-N2}$  1.918(2),  $\text{Ti1-C11}$  2.091(2),  $\text{Ti1-C12}$  2.092(2),  $\text{Fe1-C1}$  2.059(2),  $\text{Fe1-C2}$  2.044(2),  $\text{Fe1-C3}$  2.047(2),  $\text{Fe1-C4}$  2.045(2),  $\text{Fe1-C5}$  2.049(2),  $\text{Fe1-C6}$  2.061(2),  $\text{Fe1-C7}$  2.050(2),  $\text{Fe1-C8}$  2.046(2),  $\text{Fe1-C10}$  2.042(2),  $\text{N1-C1}$  1.417(2),  $\text{N2-C6}$  1.418(2). Selected bond angles (deg):  $\text{N1-Ti1-N2}$  134.71(7),  $\text{C11-Ti1-C12}$  100.80(9).



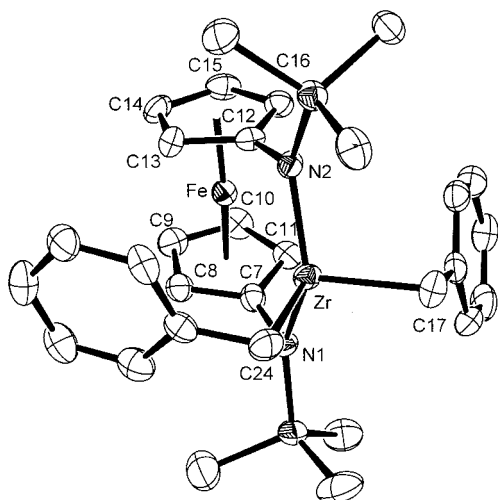
**Figure 2.** ORTEP diagram of  $\text{Fc}(\text{NSiMe}_3)_2\text{TiCl}_2$  drawn with 50% thermal ellipsoids. Selected bond distances (Å):  $\text{Ti-N1}$  1.891(2),  $\text{Ti-N2}$  1.895(2),  $\text{Ti-Cl1}$  2.2546(8),  $\text{Ti-Cl2}$  2.2499(8),  $\text{Fe-C1}$  2.044(2),  $\text{Fe-C2}$  2.042(3),  $\text{Fe-C3}$  2.040(3),  $\text{Fe-C4}$  2.041(3),  $\text{Fe-C5}$  2.045(2),  $\text{Fe-C6}$  2.039(3),  $\text{Fe-C7}$  2.047(2),  $\text{Fe-C8}$  2.046(3),  $\text{Fe-C9}$  2.040(3),  $\text{Fe-C10}$  2.040(3),  $\text{N1-C1}$  1.414(3),  $\text{N2-C6}$  1.411(3). Selected bond angles (deg):  $\text{N1-Ti-N2}$  134.01(9),  $\text{Cl1-Ti-Cl2}$  103.81(3).

again closely resembles that of the dichloride (Figure 3). Both compounds crystallize in space group  $P1$ , have very similar unit cell dimensions, and exhibit the same type of crystal packing.  $\text{Ti-N}$  and  $\text{Ti-C}$  distances are as expected, but the  $\text{N-Ti-N}$  angle is again unusually large:  $134.71^\circ$ . The dihedral angle between the Cp rings is  $4.07^\circ$ .

Zirconium dialkyl complexes were prepared using an alternate synthetic route involving alkane elimination. Thus, reaction of  $\text{LH}_2$  with 1 equiv of  $\text{Zr}(\text{CH}_2\text{Ph})_4$  in toluene led to the clean formation of  $[\text{Fc}(\text{NSiMe}_3)_2]\text{Zr}(\text{CH}_2\text{Ph})_2$  and 2 equiv of toluene; the dibenzyl complex was isolated from  $\text{Et}_2\text{O}$  in 65% yield as yellow crystals. The solid-state structure of this complex (Figure 4) displays features similar to those of  $\text{LTiCl}_2$  and  $\text{LtiMe}_2$ . The Zr center is coordinated by two amido nitrogen atoms of the  $\text{Fc}(\text{NSiMe}_3)_2^{2-}$  ligand and by two benzylic carbon atoms. The symmetry of the molecule, however, is reduced from  $C_{2v}$  to  $C_2$  (noncrystallographic) due to the twist in the benzyl groups. The  $\text{Zr-N}$  distances are 2.082(3) and 2.074(3) Å, and the  $\text{N-Zr-N}$  angle is  $138.6(1)^\circ$ . The dihedral angle between the Cp rings is  $10.13^\circ$ , and the nitrogen atoms are essentially trigonal planar.

Although in the solid state the molecule only has a noncrystallographic  $C_2$  symmetry, the  $^1\text{H}$  NMR is consistent with  $C_{2v}$  symmetry in solution, showing equivalent phenyl groups, two triplets for the Cp resonances, one benzylic  $\text{CH}_2$  resonance, and a single silyl resonance. Additionally, although in the solid state the average  $\text{Zr-C-C}(\text{Ph})$  angle of  $98.9^\circ$  is less than that expected for an  $\text{sp}^3$  carbon, no evidence for any  $\eta^2$  interaction in solution was found spectroscopically. Interestingly, the Cp protons *ortho* to the amido groups have an unusually large upfield shift and appear at 2.57 ppm (compared to a normal shift of 3.5–4.5 ppm for ferrocene derivatives). This shift is attributed to the ring current effect of the phenyl groups, which, at least in the solid state, are bent toward the ferrocene moiety. The compound is thermally robust, showing no signs of





**Figure 4.** ORTEP diagram of  $\text{Fc}(\text{NSiMe}_3)_2\text{Zr}(\text{CH}_2\text{Ph})_2$  drawn with 50% thermal ellipsoids. Selected bond distances (Å): Zr(1)–N(1) 2.082(3), Zr(1)–N(2) 2.074(3), Zr(1)–C(17) 2.263(4), Zr(1)–C(24) 2.261(5), Fe(1)–C(7) 2.0889(4), Fe(1)–C(8) 2.052(4), Fe(1)–C(9) 2.043(4), Fe(1)–C(10) 2.042(5), Fe(1)–C(11) 2.061(4), Fe(1)–C(12) 2.086(4), Fe(1)–C(13) 2.067(4), Fe(1)–C(14) 2.038(4), Fe(1)–C(15) 2.036(4), Fe(1)–C(16) 2.051(4). Selected bond angles (deg): N(1)–Zr(1)–N(2) 138.6(1), C(17)–Zr(1)–C(24) 97.3(2), Zr(1)–C(17)–C(18) 99.3(3), Zr(1)–C(24)–C(25) 98.5(3).

decomposition upon heating a  $\text{C}_6\text{D}_6$  solution to 100 °C for 12 h.

$\text{Ti}(\text{CH}_2\text{Ph})_4$  reacted with  $\text{LH}_2$  in an analogous fashion, producing  $[\text{Fc}(\text{NSiMe}_3)_2]\text{Ti}(\text{CH}_2\text{Ph})_2$  in 46% yield as dark red needles. The  $^1\text{H}$  NMR spectrum of this derivative closely resembles that of the Zr analogue, suggesting that the compounds have the same basic structure in solution. The only significant change in the  $^1\text{H}$  NMR spectrum comes in the position of the benzylic resonance, which moves from 2.99 ppm in the Zr complex to 3.51 ppm in  $[\text{Fc}(\text{NSiMe}_3)_2]\text{Ti}(\text{CH}_2\text{Ph})_2$ .

We are in the process of investigating the reactivity of these complexes, in particular their use in olefin polymerizations. Preliminary results show that when activated with perfluoroarylborane reagents, the dialkyls catalyze polymerization of  $\alpha$ -olefins. This work, and details of electrochemical studies, will be the subject of forthcoming accounts.

## Experimental Section

**General Considerations.** Standard Schlenk-line and glove-box techniques were used unless otherwise indicated. All solvents were purified by passage through a column of activated alumina and degassed with argon prior to use.  $\text{Fc}(\text{NH}_2)_2$ ,<sup>10</sup>  $\text{Zr}(\text{CH}_2\text{Ph})_4$ ,<sup>14</sup> and  $\text{Ti}(\text{CH}_2\text{Ph})_4$ <sup>15</sup> were prepared according to published procedures.  $\text{MeLi}$  and  $\text{Bu}_2\text{Mg}$  were purchased from Aldrich.  $n\text{-BuLi}$  was purchased from Alfa-Aesar.  $\text{NET}_3$  was purchased from Aldrich and distilled from Na prior to use.  $\text{Me}_3\text{SiCl}$  was purchased from Aldrich and distilled from  $\text{CaH}_2$  prior to use.  $\text{C}_6\text{D}_6$  was vacuum transferred from sodium/benzophenone. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded at ambient

temperature on a Bruker AM-300 or DRX-500 spectrometer.  $^1\text{H}$  NMR chemical shifts are given relative to  $\text{C}_6\text{D}_5\text{H}$  (7.16 ppm) and  $\text{CHCl}_3$  (7.26 ppm).  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra are relative to  $\text{C}_6\text{D}_6$  (128.3 ppm). Electrochemical measurements were performed using a BAS-100b electrochemical analyzer with a BAS C3 cell stand mounted inside an inert atmosphere glovebox. Elemental analyses were determined at the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley. Single-crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley.

**$\text{Fc}(\text{NSiMe}_3)_2(\text{LH}_2)$ .** A solution of 1,1'-diaminoferrrocene (1.50 g, 6.9 mmol) in 100 mL of  $\text{CH}_2\text{Cl}_2$  was cooled to  $-60$  °C.  $\text{NET}_3$  (2.2 mL, 15.8 mmol) and  $(\text{CH}_3)_3\text{SiCl}$  (2.6 mL, 20.4 mmol) were added via syringe. The mixture was allowed to warm to ambient temperature and stored for 10 h. The volatile fraction was removed under reduced pressure, and the resulting dark solid was extracted with pentane. The dark red extract was filtered, concentrated, and cooled to  $-30$  °C, resulting in red crystals (2.1 g, 85%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.82 (t,  $J = 1.8$  Hz, 4H, Cp), 3.78 (t,  $J = 1.8$  Hz, 4H, Cp), 2.03 (s, br, 2H, NH), 0.16 (s, 18H, SiMe<sub>3</sub>) ppm. Mp: 50.3–51.0 °C. Anal. Calcd for  $\text{C}_{16}\text{H}_{28}\text{N}_2\text{FeSi}_2$ : C, 53.32; H, 7.83; N, 7.77. Found: C, 53.45; H, 7.82; N, 7.92.

**$\text{LLi}_2(\text{Et}_2\text{O})_x(\text{LH}_2)$ .**  $\text{LH}_2$  (250 mg, 0.7 mmol) was dissolved in 15 mL of  $\text{Et}_2\text{O}$ , cooled to  $-60$  °C, and treated with  $n\text{-BuLi}$  (1.54 mmol). The reaction was kept at this temperature for 20 min, then allowed to warm to ambient temperature and stirred for an additional hour. At this point the solution was filtered, concentrated to 4 mL, treated with 8 mL of pentane, and cooled to  $-40$  °C. Golden crystals were isolated (243 mg), which powdered upon drying. Anal. Calcd for ( $x = 1$ )  $\text{C}_{20}\text{H}_{36}\text{N}_2\text{FeLi}_2\text{OSi}_2$ : C, 53.81; H, 8.13; N, 6.28. Found: C, 53.58; H, 7.94; N, 6.08.

**$\text{LMg}(\text{THF})_2(\text{LH}_2)$ .**  $\text{LH}_2$  (3.60 g, 10.0 mmol) was dissolved in 40 mL of THF, cooled to  $-60$  °C, and treated with a  $\text{Bu}_2\text{Mg}$  solution (10.0 mL; 1.0 M in heptane, 10.0 mmol). The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h, at which point it was filtered. The dark red solution was concentrated, treated with pentane, and cooled to  $-40$  °C, resulting in yellow crystals (4.25 g, 81%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.04 (t,  $J = 1.8$  Hz, 4H, Cp), 3.91 (t,  $J = 1.8$  Hz, 4H, Cp), 3.70 (m, 8H, THF), 1.33 (m, 8H, THF), 0.20 (s, 18H, SiMe<sub>3</sub>) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  113.5, 69.6, 67.2, 63.6, 25.6, 3.0 ppm. Anal. Calcd for  $\text{C}_{24}\text{H}_{42}\text{N}_2\text{O}_2\text{Si}_2\text{MgFe}$ : C, 54.71; H, 8.03; N, 5.32. Found: C, 54.37; H, 8.03; N, 5.32.

**$\text{LTiCl}_2$ .** A slurry of  $\text{TiCl}_4(\text{THF})_2$  (1.90 g, 5.70 mmol) in toluene (50 mL) was cooled to  $-60$  °C and treated with a toluene (20 mL) solution of  $\text{LMg}(\text{THF})_2$  (3.00 g, 5.70 mmol). The dark purple mixture was stirred for 20 min at  $-60$  °C and then for 2 h at ambient temperature. The volatile fraction was removed under vacuo, and the resulting solid was extracted with pentane ( $3 \times 60$  mL). The dark red extract was filtered, concentrated to 50 mL, and cooled to  $-40$  °C, resulting in dark purple crystals (1.88 g, 69%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.08 (t,  $J = 1.8$  Hz, 4H, Cp), 3.17 (t,  $J = 1.8$  Hz, 4H, Cp), 0.50 (s, 18H, SiMe<sub>3</sub>) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  83.9 (ipso-Cp), 74.4 (Cp), 69.2 (Cp), 0.8 ppm (SiMe<sub>3</sub>). Anal. Calcd for  $\text{C}_{16}\text{H}_{26}\text{N}_2\text{Cl}_2\text{Si}_2\text{FeTi}$ : C, 40.27; H, 5.49; N, 5.87. Found: C, 40.39; H, 5.55; N, 5.53.

**$\text{LTiMe}_2$ .** To a dark purple solution of  $\text{LTiCl}_2$  (0.950 g, 2.00 mmol) in  $\text{Et}_2\text{O}$  cooled to  $-60$  °C was added a solution of  $\text{MeLi}$  (5.0 mL, 1.0 M in  $\text{Et}_2\text{O}$ ) via syringe. The resulting yellow mixture was allowed to stir for 30 min, then warmed to ambient temperature and allowed to react for an additional 2 h before removing the solvent under reduced pressure. The resulting yellow solid was extracted with pentane, filtered, concentrated, and cooled to  $-40$  °C. Yellow crystals were isolated (0.740 g, 85%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.99 (t,  $J = 1.9$  Hz, 4H, Cp), 3.03 (t,  $J = 1.9$  Hz, 4H, Cp), 1.09 (s, 6H, TiMe<sub>2</sub>), 0.53 (s, 18H, SiMe<sub>3</sub>) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  86.5 (ipso-Cp), 71.4

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Table 1. Crystallographic Data

	LMg(THF) <sub>2</sub>	LTiCl <sub>2</sub>	LTi(CH <sub>3</sub> ) <sub>2</sub>	LZr(CH <sub>2</sub> Ph) <sub>2</sub>
molecular formula	C <sub>24</sub> H <sub>42</sub> N <sub>2</sub> Si <sub>2</sub> O <sub>2</sub> FeMg	C <sub>18</sub> H <sub>26</sub> N <sub>2</sub> Si <sub>2</sub> TiFeCl <sub>2</sub>	C <sub>18</sub> H <sub>32</sub> N <sub>2</sub> Si <sub>2</sub> TiFe	ZrFeSi <sub>2</sub> N <sub>2</sub> C <sub>30</sub> H <sub>40</sub>
fw	526.93	477.22	436.38	631.90
cryst color, habit	yellow block	purple block	red block	yellow block
cryst size (mm)	0.48 × 0.48 × 0.32	0.26 × 0.15 × 0.07	0.43 × 0.25 × 0.18	0.23 × 0.20 × 0.11
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	9.7711(2)	9.5286(4)	9.649(1)	20.1832(3)
<i>b</i> (Å)	9.8978(3)	10.6963(5)	10.877(1)	15.7034(3)
<i>c</i> (Å)	15.1255(3)	12.4076(6)	12.322(1)	19.1485(4)
α, deg	99.665(1)	72.005(1)	76.309(2)	90
β, deg	98.642(1)	74.412(1)	69.552(1)	90.471(1)
γ, deg	102.706(1)	64.254(1)	63.658(2)	90
<i>V</i> (Å <sup>3</sup> )	1380.90(6)	1069.90(8)	1082.5(2)	6068.8(2)
<i>Z</i>	2	2	2	8
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.267	1.481	1.339	1.383
temp, °C	-106	-107	-102	-106
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
μ, cm <sup>-1</sup>	6.77	14.13	11.52	9.21
<i>T</i> <sub>max</sub> , <i>T</i> <sub>min</sub>	0.838, 0.730	0.951, 0.814	0.940, 0.889	0.898, 0.721
<i>R</i> <sub>merge</sub>	0.029	0.022	0.022	0.030
<i>R</i> , <i>R</i> <sub>w</sub>	0.031, 0.048	0.024, 0.028	0.024, 0.033	0.050, 0.078
GOF	1.76	0.88	1.41	3.26
largest shift/err	0.00	0.00	0.00	0.00
max, min, e Å <sup>-3</sup>	0.34, -0.41	0.29, -0.22	0.36, -0.29	0.57, -1.67

(Cp), 68.5 (Cp), 57.2 (TiMe<sub>2</sub>), 1.4 (SiMe<sub>3</sub>) ppm. Anal. Calcd for C<sub>18</sub>H<sub>32</sub>N<sub>2</sub>Si<sub>2</sub>TiFe: C, 49.55; H, 7.39; N, 6.42. Found: C, 49.75; H, 7.55; N, 6.41.

**LZr(CH<sub>2</sub>Ph)<sub>2</sub>.** To a flask containing LH<sub>2</sub> (253 mg, 0.70 mmol) and Zr(CH<sub>2</sub>Ph)<sub>4</sub> (325 mg, 0.71 mmol) was added 15 mL of toluene, and the resulting dark solution was stored at 55 °C in the dark for 24 h. The solvent was then removed under reduced pressure, and the resulting dark solid was extracted with pentane. The extract was filtered, concentrated, and cooled to -30 °C. After 12 h yellow crystals were isolated (215 mg, 48%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.00–6.90 (m, 8H, o-Ph and m-Ph), 6.72 (tt, 2H, p-Ph), 3.84 (t, *J* = 1.9 Hz, 4H, Cp), 2.99 (s, 4H, CH<sub>2</sub>Ph), 2.57 (t, *J* = 1.9 Hz, 4H, Cp), 0.42 (s, 18H, SiMe<sub>3</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 141.9 (ipso-Ph), 129.3 and 129.0 (o- and m-Ph), 122.3 (p-Ph), 89.9 (ipso-Cp), 71.4 (Cp), 69.1 (CH<sub>2</sub>Ph), 68.9 (Cp), 1.2 (SiMe<sub>3</sub>) ppm. Anal. Calcd for C<sub>30</sub>H<sub>40</sub>N<sub>2</sub>Si<sub>2</sub>ZrFe: C, 57.02; H, 6.38; N, 4.43. Found: C, 56.89; H, 6.38; N, 4.37.

**LTi(CH<sub>2</sub>Ph)<sub>2</sub>.** LH<sub>2</sub> (204 mg, 0.57 mmol) and Ti(CH<sub>2</sub>Ph)<sub>4</sub> (250 mg, 0.61 mmol) were combined in a flask, 15 mL of toluene was added, and the solution was heated to 37 °C for 16 h. The solvent was removed under reduced pressure, and the residue was extracted with 2 × 40 mL of hexanes. The red solution was concentrated to 8 mL and cooled to -30 °C. Dark red crystals were isolated (156 mg, 46%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 6.97–6.91 (m, 8H, o-Ph and m-Ph), 6.69 (tt, 2H, p-Ph), 3.84 (t, *J* = 1.9 Hz, 4H, Cp), 3.51 (s, 4H, CH<sub>2</sub>Ph), 2.55 (t, *J* = 1.9 Hz, 4H, Cp), 0.60 (s, 18H, SiMe<sub>3</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 144.5 (ipso-Ph), 129.2 and 128.2 (o- and m-Ph), 122.5 (p-Ph), 88.5 (ipso-Cp), 86.0 (CH<sub>2</sub>Ph), 72.2 (Cp), 69.2 (Cp), 1.7 (SiMe<sub>3</sub>) ppm. Anal. Calcd for C<sub>30</sub>H<sub>40</sub>N<sub>2</sub>Si<sub>2</sub>ZrFe: C, 61.22; H, 6.85; N, 4.76. Found: C, 60.13; H, 7.17; N, 4.56.

**General Procedures X-ray Crystallography.** Pertinent details for the individual compounds can be found in Table 1. Crystals suitable for X-ray diffraction were grown at -40 °C from THF/pentane (LMg(THF)<sub>2</sub>), pentane (LTiCl<sub>2</sub> and LTiMe<sub>2</sub>), and Et<sub>2</sub>O (LZr(CH<sub>2</sub>Ph)<sub>2</sub>). A crystal of appropriate size was mounted on a glass capillary using Paratone-N hydrocarbon

oil. The crystal was transferred to a Siemens SMART diffractometer/CCD area detector,<sup>16</sup> centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrix and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. An arbitrary hemisphere of data was collected, and the raw data were integrated using SAINT.<sup>17</sup> Cell dimensions reported in Table 1 were calculated from all reflections with *I* > 10σ. Data analysis and absorption correction were performed using Siemens XPREP.<sup>18</sup> The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. The structures were solved and refined with the teXsan software package.<sup>19</sup> All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included as fixed contributions. ORTEP diagrams were created using the ORTEP-3 software package.<sup>20</sup>

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**Supporting Information Available:** Tables of positional and thermal parameters, bond distances and angles, and ORTEP diagrams for crystal structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) SAINT: SAX Area Detector Integration Program; Madison, WI, 1995.

(18) XPREP: Part of SHELXTL Crystal Structure Determination Package; Madison, WI, 1995.

(19) TeXsan: Crystal Structure Analysis Software Package; Molecular Structure Corp.: The Woodlands, TX, 1992.

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