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COMMUNICATION

Reactions of Zn bis-ferrocenyl-β-diketiminates with $[Ph_3C][B(C_6F_5)_4]$†

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The ZnMe complexes of bis-ferrocenyl-β-diketiminate ligands are prepared and the reactions with $[Ph_3C][B(C_6F_5)_4]$ are found to yield the salts $[H(Ph_3C)C(MeC(N(C_5H_4)FeCp)_2ZnMe][B(C_6F_5)_4]$ and $[CH_2{=}C(MeC(N(C_5H_4)FeCp)_2ZnMe][B(C_6F_5)_4]$, derived from electrophilic substitution and hydride abstraction.

The chemistry of β-diketiminate ligand complexes[1–3] has under gone a renaissance in the past decade. Part of the renewed interest has arisen as a result of the facile synthesis and the ease with which the ligand can be varied so as to tune the electronic and steric features. Numerous studies have described the use of these ligands targeting the development of reactive transition metal systems. Indeed, there are a number of systems that have been reported where these ligands act in an ancillary manner to stabilize unusually reactive metal fragments or provide species capable of catalyzing various processes.[4–8] On the other hand there are a number of reports in which the β-diketiminate ligands are not innocent observers of the chemistry at the metal, but rather undergo reactions on the ligand backbone.[9–12]

An interesting possibility for a substituent on a β-bis-ketiminate ligand is ferrocenyl as this is a robust, bulky yet electrochemically active fragment. However, in contrast to alkyl or aryl derivatives of β-diketiminates, generation of a species with ferrocenyl substituents is synthetically challenging. Indeed efforts to that end have yielded only ferrocenylimine-β-ketone derivatives.[13] In this communication we report the synthesis of such β-diketiminate ligands that have not been reported. These species are subsequently used to prepare Zn complexes. In contrast to Zn β-diketiminate complexes[14] that incorporate aryl substituents on N, the reactivity of these bis-ferrocenyl-β-ketiminate Zn species with $[Ph_3C][B(C_6F_5)_4]$ reveals unusual reactivity at the β-diketiminate ligands. This non-innocent behaviour of the ligand arises from hydride abstraction and electrophilic substitution.

Aminoferrocene was combined with 2,4-pentanedione in the presence of 3 Å molecular sieves and reacted overnight. Following work-up, dark orange needles of MeC(NH-(C_5H_4)FeCp)CHC(O)Me **1** were isolated in 89% yield. ^{1}H, ^{13}C NMR and mass spectral data were consistent with this formulation. In a similar fashion, MeC(NH(C_5H_4)FeCp)CMeC(O)Me **2**, was prepared in 63% yield. Compound **1** was heated at 130 °C for 4 days with additional aminoferrocene in the presence of 3 Å molecular sieves. Following work-up an orange solid **3** was isolated in 56% yield. The ^{1}H NMR spectrum showed a signal at 12.7 ppm attributable to an N–*H* fragment while signals at 4.68, 4.23, 4.20 and 3.91 ppm arise from CH, Cp and C_5H_4 fragments consistent with the formulation of **3** as MeC(NH(C_5H_4)FeCp)CHC(N(C_5H_4)FeCp)Me. In a similar fashion, reactions of **2** with additional aminoferrocene afforded MeC(NH(C_5H_4)FeCp)CMeC(N(C_5H_4)FeCp)Me **4** in 59% yield. The ^{1}H and ^{13}C NMR resonances observed as well as mass spectral data were consistent with this formulation. While this stepwise procedure affords the bis-ferrocenyldiketiminate precursors **3** and **4**, efforts to prepare these ligands directly *via* prolonged heating at 130 °C for 4 days of two equivalents of aminoferrocene with the corresponding acetylacetone resulted in the formation of a complex and inseparable mixture of products. Similarly, efforts to use conventional approaches such as acid catalysis or a Dean Stark apparatus to prepare these β-diketiminates were also unsuccessful. Nonetheless, the reasons for the success of the stepwise process remain unclear.

Zn complexes of these ligands were readily prepared. Reaction of the **3** with $ZnMe_2$ proceeds with the evolution of methane and results in the formation of a red solid **5** isolated in 89% yield. The ^{1}H NMR spectrum of **5** shows resonances attributable to the β-diketeniminate ligand as well as a resonance at –0.18 ppm resulting from the presence of the Zn–*Me* fragment. The corresponding ^{13}C{^{1}H} NMR signal was observed at –7.8 ppm. These data together with mass spectral and analytical data were consistent with the formulation of **5** as HC(MeC(N(C_5H_4)FeCp)$_2$ZnMe. In a similar fashion, stoichiometric reaction of **3** with $Zn(N(SiMe_3)_2)_2$ proceeds with release of amine and formation of the red solid **6**. Similar to **5**, the NMR data for **6** was consistent with the presence of the anionic ligand in a 1 : 1 ratio with a $N(SiMe_3)_2$ fragment. The silyl-methyl groups give rise to resonances at 0.33 and 5.3 ppm in the ^{1}H and ^{13}C NMR spectrum, respectively. Thus, the formulation of **6** is (HC(MeC(N(C_5H_4)FeCp)$_2$ZnN$(SiMe_3)_2$. In an analogous manner, the ligand **4** was reacted with $ZnMe_2$ to give the analogous β-diketeniminate complex MeC(MeC(N(C_5H_4)FeCp)$_2$ZnMe **7**. This orange solid was isolated in 84% yield and showed NMR resonances analogous to **5** with the additional signal arising from the methyl group on the central carbon of the β-diketiminate ligand.

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Reaction of **5** with $[Ph_3C][B(C_6F_5)_4]$ proceeds in dichloromethane or bromobenzene, resulting in an immediate color change to dark purple. The product **8** was subsequently isolated as purple needle-like crystals in 90% yield. The observation of arene resonances in the ^{1}H NMR spectrum of **8** were consistent with the inclusion of the trityl fragment. In addition, the signals at 5.40, 4.10, 3.99 and 2.12 ppm were consistent with the presence of the intact diketiminate ligand. It is noteworthy that the ^{1}H signal arising from the C*H* signal in **8** is observed at 5.67 ppm, which is shifted dramatically from 4.65 ppm in **5**. As well, a signal at –0.72 ppm was attributed to the retained ZnMe unit. Similarly, the corresponding $^{13}C\{^1H\}$ resonances were observed with the Zn-methyl fragment giving rise to a signal at –8.9 ppm. ^{19}F and ^{11}B NMR data were consistent with the presence of the anion $[B(C_6F_5)_4]$ in **8**. These data infer the stoichiometric combination of **5** and $[Ph_3C][B(C_6F_5)_4]$. The precise nature of **8** was unambiguously determined by X-ray crystallography‡ (Fig. 1). These data revealed the formation of a new C–C bond between the trityl fragment and the central carbon of the β-diketiminate ligand. This confirms the formulation of **8** as $[H(Ph_3C)C(MeC(N(C_5H_4)FeCp)_2ZnMe][B(C_6F_5)_4]$. The cation thus contains a three coordinate Zn center with Zn–N distances of 2.0544(13) Å and 2.0654(12) Å, a Zn–C distance of 1.9567(16) Å and N–Zn–N and C–Zn–N angles of 92.72(5)°, 128.37(7)° and 133.90(6)°, respectively. The chelate ring on Zn adopts a puckered pseudo-boat configuration, with the trityl fragment in the axial position to accommodate the saturated central carbon. This distortion of the ligand backbone minimizes the interactions between the (C_5H_4)FeCp moieties and the Me substituents on the Zn and the ligand backbone. This orientation presents one of the arene rings in close proximity to the Zn with Zn–C distance of 2.577 Å (Zn–C36), suggesting a weak donation from the arene to the metal center. The ferrocenyl fragments on N are oriented in a pseudo-*transoid* disposition, presumably to minimize steric interactions with the trityl fragment.

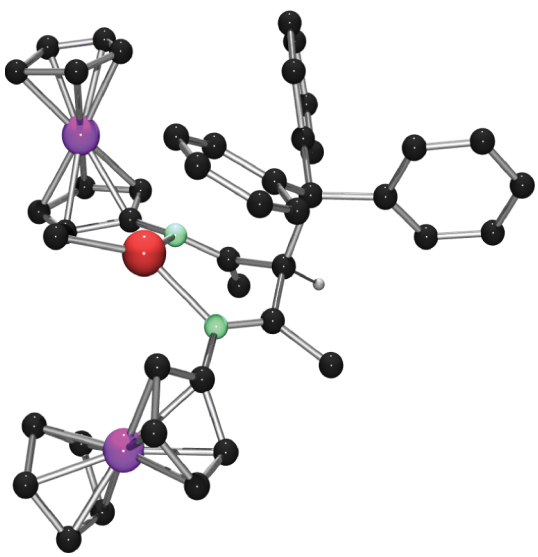
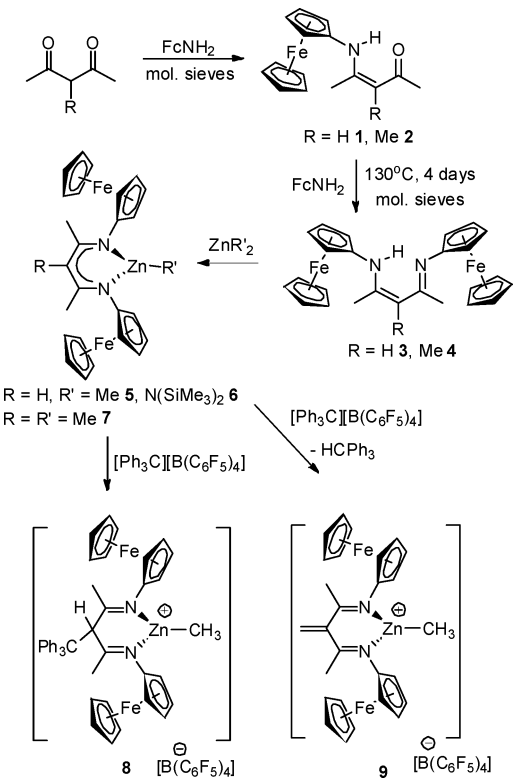


Fig. 1 POV-Ray rendering of ORTEP depictions of the cation of **8**.

In a similar fashion the species **7** reacted with $[Ph_3C][B(C_6F_5)_4]$ to give a dark purple solution from which purple crystals of **9** were isolated in 85% yield. In this case, monitoring the reaction



Scheme 1 Synthesis of **1–9**.

by NMR spectroscopy confirmed the formation of Ph_3CH as a by-product. The species **9** gives rise to new ^{1}H NMR resonances at 5.82 ppm attributable to olefinic protons resulting from hydride removal from the central methyl fragment of **7**. The corresponding ^{13}C resonances were observed at 171.5 ppm. Resonances corresponding to the remainder of the β-diketiminate ligand were observed in addition to the ^{1}H singlet at 0.05 ppm and ^{13}C resonance at –9.4 ppm resulting from the Zn-bound methyl group. These data are consistent the formulation of **9** as $[CH_2{=}C(MeC(N(C_5H_4)FeCp)_2ZnMe]\ [B(C_6F_5)_4]$.

While a trityl cation often reacts with metal alkyl species resulting in alkyl-abstraction and generation of a coordinatively unsaturated metal center, the formation of **8** and **9** is consistent with the non-innocent behaviour of β-diketiminate ligands. Moreover, these observations suggest the possibility that the ferrocenyl substituents sterically block reactivity of the Zn-methyl fragment prompting reaction at the ligand backbone.

To further probe this aspect, DFT calculation were performed on **7**. The energy minimized structure showed a distortion in the ligand backbone providing C_2 symmetry with C=N–Zn–N=C dihedral angle of 10.4° (Fig.2) and a *transoid* disposition of the ferrocenyl fragments. The computed distortion of the *transoid* conformation presumably results from the minimization of the interactions between the ferrocenyl moieties with the methyl substituents on the Zn and the β-diketiminate ligand. Interestingly, efforts to locate a minimum energy conformation of the corresponding conformation of **7** in which the ferrocenyl groups adopt a *cisoid* disposition were unsuccessful. In contrast similar calculations for the Zn complex $HC(MeC(N(C_6H_4iPr_2)_2ZnMe$ revealed a minimum energy conformation in which the ligand-Zn geometry is completely planar. Nonetheless, both **7** and

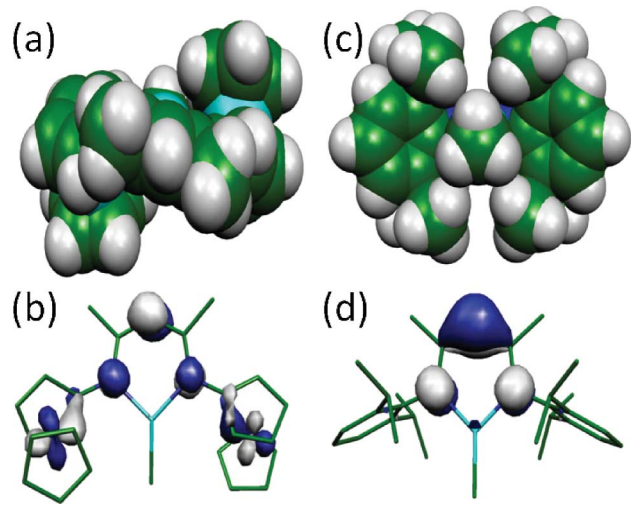


Fig. 2 (a) Space filling view of the DFT calculated energy minimized structure of **7**, the view is from the ligand side of the coordination plane. (b) Depiction of the HOMO of **7**. (c) and (d) Analogous drawings for HC(MeC(N(C_6H_4*i*Pr_2)$_2$ZnMe.

HC(MeC(N(C_6H_4*i*Pr_2)$_2$ZnMe exhibit highest occupied molecular orbitals (HOMO) that have significant components residing on the central carbon of the β-diketiminate ligand. This presumably accounts for the electrophilic attack by the trityl cation. The *transoid* disposition of the ferrocenyl ligand in **7** occupies space above and below the plane of the diketiminate ligand in a dissymmetric fashion so as to provide access of the trityl cation to the HOMO. In contrast, the symmetric conformation of HC(MeC(N(C_6H_4*i*Pr_2)$_2$ZnMe blocks entry to the central position on the ligand backbone. A number of reports have shown the non-innocence of the ligand in β-diketiminate complexes.[9–12] Indeed, hydride removal from the methyl groups on the carbons alpha to the imine is well documented. Thus, the formation of **9** is perhaps less surprising. However the formation of **8** provides a rare example in which alkylation occurs with a sterically demanding electrophile.

Experimental

Synthesis of MeC(N(C_5H_4)FeCp)CHC(O)Me (1) and MeC(N(C_5H_4)FeCp)CMeC(O)Me (2)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. Aminoferrocene (0.232 g, 1.15 mmol), 2,4-pentanedione (0.115 g, 1.15 mmol) and approximately 0.25 g of 3 Å molecular sieves were combined in 10 mL of dichloromethane (or diethyl ether) and stirred overnight. The reaction was filtered through a plug of Celite (to remove residue from molecular sieves) and dried *in vacuo* to an orange solid. The solid was recrystallized two times from pentane (cooling to −30 °C each time) affording 0.327 g (89% yield) of dark orange needles.

1: ^{1}H NMR (C_6D_6): 12.5 (s, 1H, N–*H*), 4.99 (s, 1H, MeCC(*H*)CMe), 4.05 (s, 5H, *Cp*), 3.95 (broad t, 2H, $^3J_{H-H}$ = 2.0 Hz, $H_{2,5}$-C_5H_4), 3.71 (broad t, 2H, $^3J_{H-H}$ = 2.0 Hz, $H_{3,4}$-C_5H_4), 2.05 (s, 3H, *Me*C(NH)), 1.54 (s, 3H, C(O)C*Me*). ^{13}C{^{1}H} (C_6D_6): 195.4 (*C*═O), 161.4 (Me*C*(N(C_5H_4)FeCp)), 97.0 (MeC*C*(H)CMe), 94.9 (C_1-C_5H_4), 70.0 (C_5H_5-Fe), 65.98 ($C_{2,5}$-C_5H_4), 65.93($C_{3,4}$-C_5H_4), 29.2 (C(O)C*Me*), 19.0 (*Me*C(NH)). MS(EI): 283 [M$^+$]. Anal. calcd for $C_{15}H_{17}$FeNO: C 63.63, H 6.05, N 4.95. Found: C 63.27, H 5.92, N 4.80.

2: 0.278 g (63% yield) of dark orange needles. ^{1}H NMR (C_6D_6): 13.5 (s, 1H, N–*H*), 4.13 (s, 5H, *Cp*), 4.01 (broad t, 2H, $^3J_{H-H}$ = 2.0 Hz, $H_{2,5}$-C_5H_4), 3.76 (broad t, 2H, $^3J_{H-H}$ = 2.0 Hz, $H_{3,4}$-C_5H_4), 2.13 (s, 3H, MeCC(*Me*)CMe), 1.64 (s, 3H, *Me*C(NH)), 1.59 (s, 3H, C(O)C*Me*). ^{13}C{^{1}H} (C_6D_6): 195.9 (*C*═O), 159.6 (Me*C*(N(C_5H_4)FeCp)), 100.0 (MeC*C*(Me)CMe), 95.5 (C_1-C_5H_4), 70.0 (C_5H_5-Fe), 66.6 ($C_{2,5}$-C_5H_4), 65.9 ($C_{3,4}$-C_5H_4), 28.6 (C(O)C*Me*), 15.9 (*Me*C(NH)), 11.7 (MeCC(*Me*)CMe). Anal. calcd for $C_{16}H_{19}$FeNO: C 64.67, H 6.44, N 4.71. Found: C 62.50, H 6.10, N 4.74.

Synthesis of HC(MeC(N(C_5H_4)FeCp)$_2$ (3)

In a Teflon-sealed flask, **1** (0.363 g, 1.28 mmol), aminoferrocene (0.257 g, 1.28 mmol), approximately 0.25 g of 3 Å molecular sieves and a mechanical stirring bar were combined in 10 mL of toluene. The flask was sealed and the reaction mixture was stirred and heated at 130 °C for 4 d. The flask was brought into an inert atmosphere glovebox, where the reaction was filtered through a plug of Celite (to remove sieves) and dried *in vacuo* to give an orange solid. The residual material was washed 3 × 5 mL dry hexanes to give a clean orange solid (0.337 g, 56% yield). ^{1}H NMR (C_6D_6): 12.7 (s, 1H, N–*H*), 4.68 (s, 1H, MeCC(*H*)CMe), 4.23 (s, 10H, *Cp*), 4.20 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{2,5}$-C_5H_4), 3.91 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{3,4}$-C_5H_4), 1.84 (s, 6H, *Me*CC(H)C*Me*). ^{13}C{^{1}H} (C_6D_6): 160.5 (Me*C*(H)CMe), 102.2 (MeC*C*(H)CMe), 98.3 (C_1-C_5H_4), 69.9 (C_5H_5-Fe), 65.0 ($C_{2,5}$-C_5H_4), 64.8 ($C_{3,4}$-C_5H_4), 21.1 (*Me*CC(H)C*Me*). MS(EI): 466 [M$^+$]. Anal. calcd for $C_{25}H_{26}Fe_2N_2$: C 64.41, H 5.62, N 6.01. Found: C 63.94, H 5.76, N 6.08.

Synthesis of MeC(MeC(N(C_5H_4)FeCp)$_2$ (4)

Synthesized in the same manner as compound **4**, using **2** (0.333 g, 1.12 mmol), aminoferrocene (0.225 g, 1.12 mmol), and approximately 0.25 g of 3 Å molecular sieves. The residual material was washed with 3 × 5 mL dry hexanes to give a clean orange solid (0.317 g, 59% yield). ^{1}H NMR (C_6D_6): 13.8 (s, 1H, N–*H*), 4.26 (s, 10H, *Cp*), 4.20 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{2,5}$-C_5H_4), 3.94 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{3,4}$-C_5H_4), 1.91 (s, 6H, *Me*CC(Me)C*Me*), 1.72 (s, 3H, MeCC(*Me*)CMe). ^{13}C{^{1}H} (C_6D_6): 160.3 (Me*C*C(Me)*C*Me), 102.8 (MeC*C*(Me)CMe), 99.6 (C_1-C_5H_4), 69.8 (C_5H_5-Fe), 65.3 ($C_{2,5}$-C_5H_4), 64.6 ($C_{3,4}$-C_5H_4), 18.3 (*Me*CC(Me)C*Me*), 15.8 (MeCC(*Me*)CMe). MS(EI): 480 [M$^+$]. Anal. calcd for $C_{26}H_{28}Fe_2N_2$: C 65.03, H 5.88, N 5.83. Found: C 64.59, H 6.33, N 6.26. E-Chem: $E_{1/2}$ (CH_2Cl_2) = 768 mV, −13.5 mV, −226 mV

Synthesis of HC(MeC(N(C_5H_4)FeCp)$_2$ZnMe (5), of (HC(MeC(N(C_5H_4)FeCp)$_2$ZnN(SiMe$_3$)$_2$ (6) and MeC(MeC(N(C_5H_4)FeCp)$_2$ZnMe (7)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. In an inert atmosphere glovebox, **4** (60 mg, 0.128 mmol) was dissolved in 5 mL dry toluene and cooled to −30 °C while stirring. $ZnMe_2$ solution (10% w/v in hexanes, 0.12 mL, 0.126 mmol) was added dropwise. The

reaction was stirred overnight, and a red solid was isolated by drying *in vacuo* and washing 2 × 5 mL with pentane (61 mg, 89%).

5: ^{1}H NMR (C_6D_6): 4.60 (s, 1H, MeCC(*H*)CMe), 4.16 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{2,5}$-C_5H_4), 4.12 (s, 10H, *Cp*), 3.88 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{3,4}$-C_5H_4), 1.92 (s, 6H, *Me*CC(H)C*Me*), 0.16 (s, 3H, Zn–*Me*). ^{1}H NMR (CD_2Cl_2): 4.65 (s, 1H, MeCC(*H*)CMe), 4.24 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{2,5}$-C_5H_4), 4.17 (s, 10H, *Cp*), 4.08 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{3,4}$-C_5H_4), 2.06 (s, 6H, *Me*CC(H)C*Me*), –0.18 (s, 3H, Zn–*Me*). ^{13}C{^{1}H} (C_6D_6): 166.6 (Me*C*C(H)CMe), 108.1 (MeC*C*(H)CMe), 100.0 (C_1-C_5H_4), 70.2 (C_5H_5-Fe), 65.2 ($C_{2,5}$-C_5H_4), 65.0 ($C_{3,4}$-C_5H_4), 24.3 (*Me*CC(H)C*Me*), –7.8 (Zn-Me). MS(EI): 529 [M$^+$ – Me]. Anal. calcd for $C_{26}H_{28}Fe_2N_2Zn$: C 57.23, H 5.17, N 5.13. Found: C 56.34, H 5.28, N 5.06. E-Chem: $E_{1/2}$ (CH_2Cl_2) = 829 mV, –42 mV, –163 mV.

6: (127 mg, 92%). ^{1}H NMR (C_6D_6): 4.82 (s, 1H, MeCC(*H*)CMe), 4.52 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{2,5}$-C_5H_4), 4.02 (s, 10H, *Cp*), 3.97 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{3,4}$-C_5H_4), 2.46 (s, 6H, *Me*CC(H)C*Me*), 0.33 (s, 18H, NSi*Me*$_3$). ^{13}C{^{1}H} (C_6D_5Br): 167.0 (Me*C*C(H)*C*Me), 105.4 (MeC*C*(H)CMe), 101.3 (C_1-C_5H_4), 69.6 (C_5H_5-Fe), 65.6 ($C_{2,5}$-C_5H_4), 65.5 ($C_{3,4}$-C_5H_4), 24.8 (*Me*CC(H)C*Me*), 5.3 (NSi*Me*$_3$). MS(EI): 689 [M$^+$]. Anal. calcd for $C_{31}H_{43}Fe_2N_3Si_2Zn$: C 53.89, H 6.27, N 6.08. Found: C 53.18, H 6.16, N 6.12.

7: (68 mg, 84%). ^{1}H NMR (C_6D_6): 4.16 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{2,5}$-C_5H_4), 4.14 (s, 10H, *Cp*), 3.89 (t, 4H, $^3J_{H-H}$ = 2.0 Hz, $H_{3,4}$-C_5H_4), 2.02 (s, 6H, *Me*CC(Me)C*Me*), 1.74 (s, 3H, MeCC(*Me*)CMe), 0.17 (s, 3H, Zn–*Me*). ^{13}C{^{1}H} (C_6D_6): 166.6 (Me*C*C(Me)CMe), 109.0 (MeC*C*(Me)CMe), 101.2 (C_1-C_5H_4), 70.2 (C_5H_5-Fe), 65.1 ($C_{2,5}$-C_5H_4), 65.0 ($C_{3,4}$-C_5H_4), 22.1 (*Me*CC(Me)C*Me*), 18.9 (MeCC(*Me*)CMe), –8.8 (Zn–*C*H$_3$). MS(EI): 480 [M$^+$ – ZnMe]. Anal. calcd for $C_{27}H_{30}Fe_2N_2Zn$: C 57.95, H 5.40, N 5.01. Found: C 52.89, H 5.10, N 4.84.

Synthesis of [H(Ph$_3$C)C(MeC(N(C$_5$H$_4$)FeCp)$_2$ ZnMe][B(C$_6$F$_5$)$_4$] (8)

A solution of [CPh$_3$][B(C$_6$F$_5$)$_4$] (20 mg, 0.022 mmol) in deuterated or non-deuterated dichloromethane (or bromobenzene) was added to compound **4** (12 mg, 0.022 mmol). The solution immediately turned a dark purple colour. The product was isolated by layering hexanes over the reaction mixture and leaving at room temperature for 18 h, upon which time purple needle-like crystals formed (29 mg, 90% yield). ^{1}H NMR (C_6D_5Br): 7.20–7.07 (m, 15H, C*Ph*$_3$), 5.40 (s, 2H, MeCC(*H*)CPh$_3$), 4.10 (m, 8H, C$_5$*H*$_4$), 3.99 (s, 10H, *Cp*), 2.12 (s, 6H, *Me*CC(*H*)C), –0.72 (s, 3H, Zn*Me*). ^{1}H NMR (CD_2Cl_2): 7.47 (m, *m*-CH*Ph*$_3$), 7.20 (m, *o*,*p*-CH*Ph*$_3$), 5.67 (s, 1H, MeC C(*H*)CPh$_3$CMe), 4.42 (m, 4H, $H_{2,5}$-C_5H_4), 4.32 (m, 4H, $H_{3,4}$-C_5H_4), 4.16 (s, 10H, *Cp*), 2.48 (s, 6H, *Me*C C(H)CPh$_3$C*Me*), –0.07 (s, 3H, Zn*Me*). ^{13}C{^{1}H} (C_6D_5Br): 177.3 (Me*C*C(H)CPh$_3$*C*Me), 149.8, 147.4 (C_6F_5), 140.5 (*o*-CH*Ph*$_3$), 137.8, 135.3 (C_6F_5), 128.3 (*p*-CH*Ph*$_3$), 99.6 (C_1-C_5H_4), 70.1 (C_5H_5-Fe), 68.4 ($C_{2,5}$-C_5H_4), 66.2 ($C_{3,4}$-C_5H_4), 65.4 (MeC*C*(H)CPh$_3$CMe), 28.7 (*Me*CC(H)CPh$_3$C*Me*), –8.9 (Zn*Me*). Anal. calcd for $C_{69}H_{43}BF_{24}Fe_2N_2Zn$: C 53.68, H 2.81, N 1.81. Found: C 53.89, H 2.70, N 1.84.

Synthesis of [CH$_2$=C(MeC(N(C$_5$H$_4$)FeCp)$_2$ZnMe][B(C$_6$F$_5$)$_4$] (9)

Synthesized in the same manner as for compound **8**, using **7** (10 mg, 0.018 mmol) and [CPh$_3$][B(C$_6$F$_5$)$_4$] (17 mg, 0.018 mmol). A dark purple solid was isolated by layering the reaction mixture with hexanes and leaving for 18 h at room temperature, decanting the residual liquid and drying *in vacuo* (20 mg, 85% yield). ^{1}H NMR (C_6D_5Br): 5.82 (s, 2H, MeCC(=C*H*$_2$)CMe), 5.44 (s, 1H, C*H*Ph$_3$), 4.28 (broad s, 4H, $H_{2,5}$-C_5H_4), 4.18 (broad s, 4H, $H_{3,4}$-C_5H_4), 4.06 (s, 10H, *Cp*), 2.16 (s, 6H, *Me*CC(=CH$_2$)C*Me*), 0.05 (s, 3H, Zn*Me*). ^{1}H NMR (CD_2Cl_2): 7.29 (t, $^3J_{H-H}$ = 7 Hz, *m*-CH*Ph*$_3$), 7.21 (m, *p*-CH*Ph*$_3$), 7.13 (d, $^3J_{H-H}$ = 7 Hz, *o*-CH*Ph*$_3$), 6.45 (s, 2H, MeCC(=C*H*$_2$)CMe), 5.56 (s, 1H, C*H*Ph$_3$), 4.58 (t, 4H, $^3J_{H-H}$ = 2 Hz, $H_{2,5}$-C_5H_4), 4.52 (t, 4H, $^3J_{H-H}$ = 2 Hz, $H_{3,4}$-C_5H_4), 4.30 (s, 10H, *Cp*), 2.64 (s, 6H, *Me*CC(=CH$_2$)C*Me*), 0.06 (s, 3H, Zn*Me*). ^{13}C{^{1}H} (C_6D_6): 171.5 (Me*C*C(=CH$_2$)*C*Me), 98.5 (C_1-C_5H_4), 69.8 (C_5H_5-Fe), 68.6 ($C_{2,5}$-C_5H_4), 65.6 ($C_{3,4}$-C_5H_4), 22.4 (*Me*CC(=CH$_2$)C*Me*), –9.4 (Zn*Me*). Anal. calcd for $C_{27}H_{30}Fe_2N_2Zn$ $C_{51}H_{29}BF_{20}Fe_2N_2Zn$: C 49.49, H 2.36, N 2.26. Found: C 49.32, H 2.22, N 2.14.

X-Ray data collection, reduction, solution and refinement

Single crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an N_2 stream. The data were collected on a Bruker Apex II diffractometer. The data were collected at 150(±2) K. Data reduction was performed using the SAINT software package and an absorption correction applied using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least-squares on F^2 using XL as implemented in the SHELXTL suite of programs.[15] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.

Computational studies

All calculated structures were minimized using the Gaussian 03 program[16] at the B3LYP/6-31g(d) level of theory. All minimized structures were found to contain no imaginary frequencies, unless otherwise noted.

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Notes and references

‡ Crystallographic data: space group = triclinic, $P\bar{1}$; Z = 2, a = 12.8817(6) Å, b = 15.2658(7) Å, c = 17.4986(8) Å, α = 75.639(2)°, β = 68.973(2)°, γ = 68.653(2)°, V = 2964.2(2) Å3, μ = 0.994, data = 21 171, variables = 901, R ($>3\sigma$) = 0.0379, wR_2 = 0.1062, GOF = 1.046.

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