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Reactions of Aromatic Heterocycles with Uranium Alkyl Complexes

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The reactivity of a uranium dibenzyl complex supported by a ferrocenediamide ligand toward aromatic N-heterocycles was investigated. The uranium dibenzyl complex reacted with 1 equiv of pyridine or picoline to give the respective ortho-metalated product. In turn, the η^2-*N,C*-pyridyl complexes reacted with benzoxazole or benzothiazole, leading to a cascade of transformations that involves C−C coupling of the two heterocyclic rings, ring opening, and alkyl transfer. A similar cascade was previously reported for 1-methylimidazole. The present results provide support for the mechanism proposed earlier and attest to the generality of the reaction cascade described.

Introduction

Since the 1950s, the activation of strong, localized bonds, particularly C−H, C−N, and C−O, by transition metals has been researched intensively.[1,2] In the last 2 decades, the reactivity of f-block elements has been increasingly under scrutiny because of the unique chemical behavior of their complexes and potential to catalyze a wide range of transformations.[3−7] Aromatic heterocycles are substrates widely studied because they are important components of natural products and pharmaceuticals and are relevant to hydrodenitrogenation processes.[2,8−11] Complexes with d^0f^n metal−carbon bonds show diverse reactivity toward aromatic heterocycles, with both functionalization and ring-opening examples being reported.[2,8,12] Early-transition-metal, lanthanide, and actinide alkyl or hydride complexes often react with these substrates to produce ortho-metalated complexes that show subsequent transformations.[2,13−25]

We have been investigating the reactivity of group 3 metal[26−30] and uranium dialkyl[31,32] complexes supported by a 1,1′-ferrocenylenediamide ligand[33−35] toward aromatic N-heterocycles.[27,36−40] In particular, the reactivity of a uranium dibenzyl complex, $(NN^{fc})U(CH_2Ph)_2$ (**1-$(CH_2Ph)_2$**, where $NN^{fc} = fc(NSi^tBuMe_2)_2$ and fc = 1,1′-ferrocenylene),[31]

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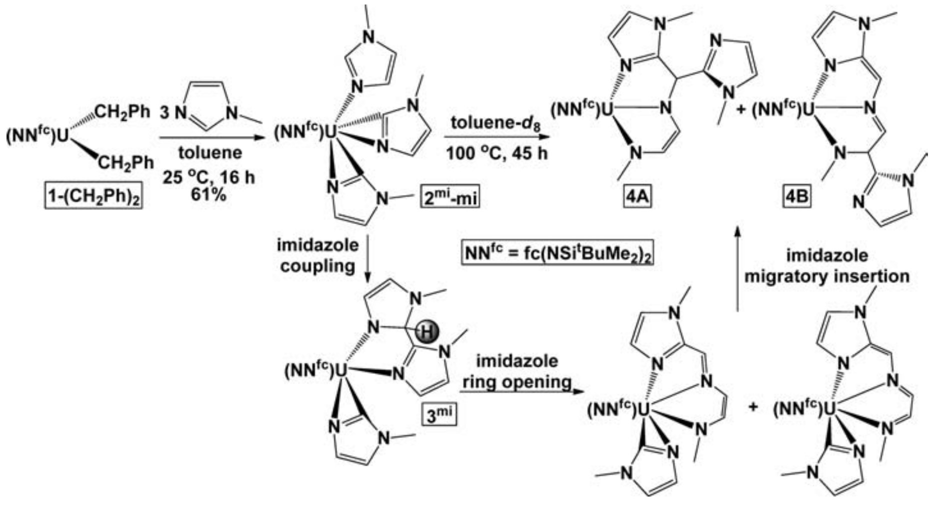
Scheme 1. Reactions of 1-Methylimidazole Mediated by **1-$(CH_2Ph)_2$**

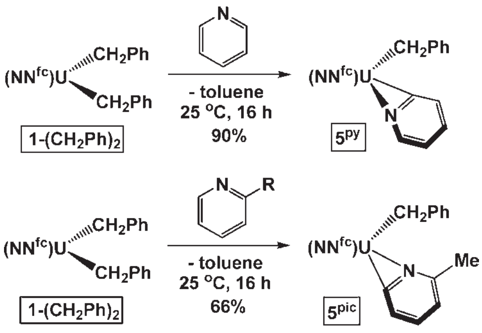


has held our attention because it has two alkyl groups that can both react with substrates. For example, we recently reported a novel C−H activation by **1-$(CH_2Ph)_2$** showing that both benzyl ligands engaged an sp^2 C−H bond of 1-methylimidazole (mi) to give **2^{mi}-mi** (Scheme 1).[36,41] In addition to the double C−H activation, an interesting cascade of functionalization reactions was induced thermally. Specifically, upon heating, one of the η^2-*N*,*C*-imidazolyl and coordinated imidazole ligands in **2^{mi}-mi** underwent C−C coupling to give **3^{mi}**, a process followed by the ring opening of the dearomatized ring and the migratory insertion of the remaining imidazolyl ligand, ultimately leading to an isomeric mixture of **4A** and **4B** (Scheme 1).[36] This cascade of reactions represented the first example of aromatic N-heterocycle cleavage by actinide complexes in which no oxygen atoms[42] or redox processes[43] were involved. At the time when we reported our initial findings, the mechanistic proposal was based on the isolation of the 1-methylbenzimidazole (mbi) analogue of the proposed intermediate **3^{mi}**.[36] We decided to investigate the generality of this reactivity behavior in order to find support for the pathway proposed. Herein we report the reactions of **1-$(CH_2Ph)_2$** with other aromatic heterocycles. Substrates analogous to imidazole, such as benzoxazole and benzothiazole, as well as pyridine substrates were studied. The products of the reactions discussed attest to the generality of the reaction cascade proposed in Scheme 1.

Results and Discussion

Reactions between **1-$(CH_2Ph)_2$** and 1 equiv of pyridine or picoline (Scheme 2) led to the corresponding ortho-metalated products $(NN^{fc})U(CH_2Ph)(\eta^2$-*N*,*C*-pyridyl) (**$5^{py}$**) or $(NN^{fc})U(CH_2Ph)$(6-Me-η^2-*N*,*C*-pyridyl) (**5^{pic}**), with one benzyl group engaging in C−H activation. These reactions are analogous to the formation of the imidazolyl complexes $(NN^{fc})U(CH_2Ph)(\eta^2$-*N*,*C*-1-methylimidazolyl) (**5^{mi}**) and $(NN^{fc})U(CH_2Ph)(\eta^2$-*N*,*C*-1-methylbenzimidazolyl) (**5^{mbi}**) from **1-$(CH_2Ph)_2$** and 1 equiv of mi or mbi, respectively.[41] Similar observations were made by the Kiplinger group when starting from $Cp^*{}_2AnR_2$ ($Cp^* = C_5Me_5$, An = Th, U; R = Me, Ph, CH_2Ph)[19,21,22] and by the Dormond[16] and the Scott groups[14] using cyclometalated amide thorium and/or uranium complexes and pyridine substrates. The reaction of pyridine with **1-$(CH_2Ph)_2$** (16 h) was 3 times faster than the analogous reaction with $Cp^*{}_2UMe_2$ (reported to take place in 48 h).[22]

Scheme 2. Reactions of **1-$(CH_2Ph)_2$** with Pyridine and 2-Picoline



Although two isomers are possible for the η^2-*N*,*C*-pyridyl complexes **5^{py}** and **5^{pic}**, only one was observed in each case. For **5^{pic}**, the isomer featuring the methyl group and the nitrogen donor of the picolyl ligand pointing toward the benzyl ligand is analogous to the isomer reported by the Kiplinger group for $Cp^*{}_2AnMe[\eta^2$-*N*,*C*-6-$CH_3NC_5H_3]$ (An = Th, U).[21] The other isomer was isolated, however, for **5^{py}** (Figure 1). Switching the identity of the nitrogen, N(3), and carbon, C(29), atoms for **5^{py}** during the refinement process resulted in unstable situations.

The solid-state structures of the newly synthesized η^2-*N*,*C*-pyridyl complexes (Figure 1) are not unusual and compare well to those of analogous uranium complexes. For example, the $U-N_{py}$ distances of 2.3700(40) Å in **5^{py}** and 2.3932(25) Å in **5^{pic}**, although relatively short, are in the range exhibited by other pyridyl complexes.[14,21,22,41] A similar situation is encountered for the $U-C_{py}$ distances of 2.4059(46) Å in **5^{py}** and 2.3967(30) Å in **5^{pic}**. The X-ray crystal structures also reveal an η^2 coordination of the benzyl ligands with U−C distances of 2.5076(52) Å [U−C(33)] and 2.8433(48) Å [U−C(22)] in **5^{py}** and 2.5215(30) Å [U−C(17)] and 2.8558(30) Å [U−C(18)] in **5^{pic}** and U−C−C angles of 87.60(30)° in **5^{py}** and 87.52(18)° in **5^{pic}**.

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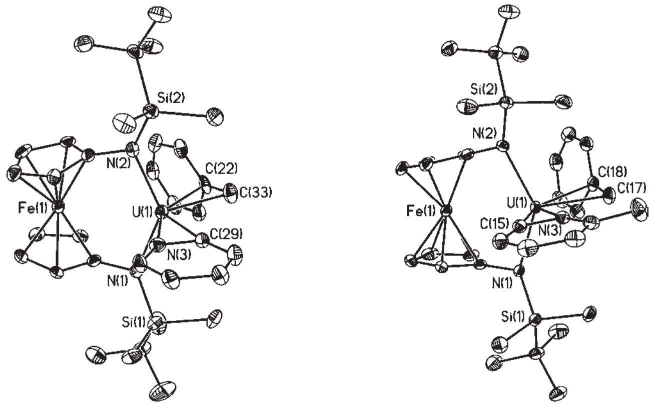
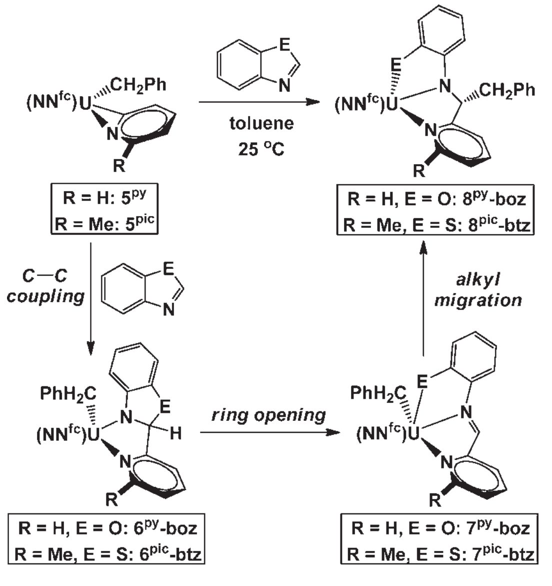


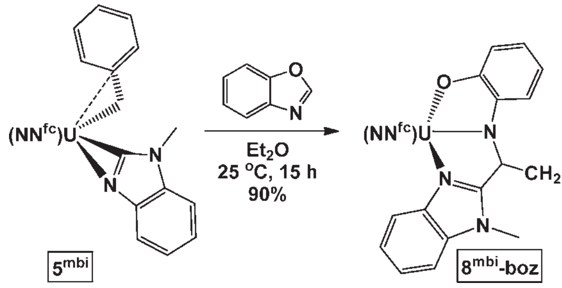
Figure 1. Thermal ellipsoid (50% probability) representation of 5^{py} (left) and 5^{pic} (right). Hydrogen atoms were removed for clarity. Selected metrical parameters for 5^{py} (distances in Å and angles in deg): U(1)−N(1), 2.2273(38); U(1)−N(2), 2.2388(39); U(1)−N(3), 2.3700(40); U(1)−C(29), 2.4059(46); U(1)−C(22), 2.8433(48); U(1)−C(33), 2.5076(52); N(3)−C(29), 1.3388(59); C(22)−C(33), 1.4019(69); U(1)−C(33)−C(22), 87.60(30); N(1)−U(1)−N(2), 135.77(14); N(1)−U(1)−N(3), 90.91(14); N(2)−U(1)−N(3), 89.65(13). Selected metrical parameters for 5^{pic} (distances in Å and angles in deg): U(1)−N(1), 2.2343(24); U(1)−N(2), 2.2342(25); U(1)−N(3), 2.3932(25) Å; U(1)−C(15), 2.3967(30); U(1)−C(17), 2.5215(30); U(1)−C(18), 2.8558(30); N(3)−C(15), 1.3398(37); C(17)−C(18), 1.4546(42); U(1)−C(17)−C(18), 87.52(18); N(1)−U(1)−N(2), 136.08(8); N(1)−U(1)−N(3), 102.81(9); N(2)−U(1)−N(3), 102.49(8).

Scheme 3. Reactions of Uranium η^2-*N*,*C*-Pyridyl Complexes with Benzoxazole and Benzothiazole and the Proposed Mechanism



We decided to determine whether the C−C coupling and heterocycle ring-opening reactions observed for mi (Scheme 1) would be observed for other aromatic heterocycles as well. The reaction between 5^{py} and benzoxazole (2 equiv) or between 5^{pic} and benzothiazole (1 or 2 equiv), substrates analogous to imidazoles, led to products reminiscent of **4A** and **4B** (Scheme 3). We propose that steps similar to those described in Scheme 1 also take place in the present cases (Scheme 3): the coordination of benzoxazole or benzothiazole is followed by C−C coupling to the pyridyl ligand with concomitant dearomatization of the diheteroatom ring (**6^{py}-boz** or **6^{pic}-btz**). This intermediate undergoes ring opening of the dearomatized heterocycle to form **7^{py}-boz** or **7^{pic}-btz**. The imine functionality is still reactive and engages the benzyl ligand in a migratory insertion to form the final product, **8^{py}-boz** or **8^{pic}-btz**.

The products **8^{py}-boz** and **8^{pic}-btz** were both characterized by X-ray crystallography; the structure of **8^{py}-boz**, however, showed a high degree of thermal disorder and is only included in the Supporting Information to show atom connectivity (Figure SX4). The complex **8^{pic}-btz** (Figure 2) features metrical parameters consistent with the structure proposed in Scheme 3. For example, the U−N$_{amide}$ distance of 2.3534(36) Å is longer by ca. 0.1 Å than the U−N$_{fc}$ distances of 2.2406(36) and 2.2421(38) Å. The U−S distance of 2.6914(12) Å is in the range reported for other U−S distances in terminal thiolate complexes.[44−47] The other distances also support the above structural assignment. For example, the C−N$_{amide}$ distances are 1.4665(55) and 1.5074(63) Å, and the N−C−C and C−C−C angles around C6 are 110.85(38), 112.05(36), and 110.54(38)°.



(1)

The reaction observed between 5^{py} and benzoxazole or between 5^{pic} and benzothiazole was extended to 5^{mbi} and benzoxazole (eq 1). The isolation of **8^{mbi}-boz** in 90% yield, together with the above reactions, attests to the generality of the sequence proposed to occur for these transformations. The complex **8^{mbi}-boz** was characterized by ^{1}H NMR spectroscopy and elemental analysis; a comparison of its ^{1}H NMR spectrum with those of **8^{py}-boz** and **8^{pic}-btz** showed analogous features.

Conclusions

We have shown that uranium alkyl complexes mediate various reactions with aromatic N-heterocycles. The reactions between the uranium dibenzyl complex **1-(CH$_2$Ph)$_2$** and one equivalent of pyridine or 2-picoline led to the formation of alkyl-η^2-N,C-pyridyl complexes through C−H activation. These ortho-metalated complexes engage in complex reactions with benzoxazole or benzothiazole. The reaction sequence proposed to explain the formation of the final products is reminiscent of the previously reported transformation of the uranium bis(η^2-N,C-imidazolyl) complex **2^{mi}** into **4A** and **4B**. The intimate reaction steps are based on C−C coupling, heterocycle ring-opening, and alkyl transfer. The reactions reported herein provide support for the mechanism proposed earlier for 1-methylimidazole and attest to the generality of the reaction cascade described.

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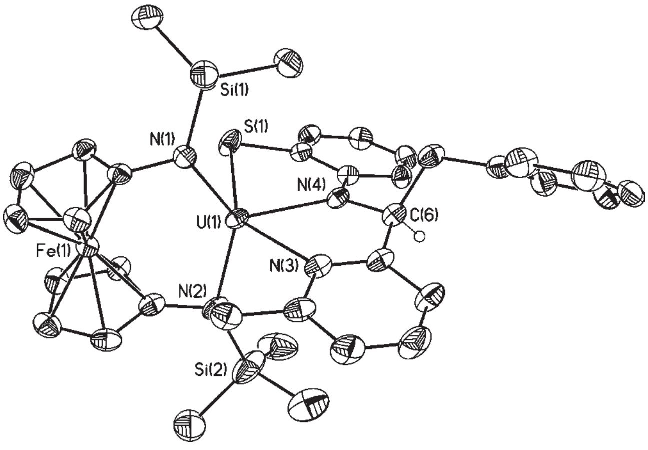

Figure 2. Thermal ellipsoid (50% probability) representation of **8^{pic}-btz**. Irrelevant hydrogen atoms and *tert*-butylmethyl groups were removed for clarity. Selected metrical parameters for **8^{pic}-btz** (distances in Å and angles in deg): U(1)−N(1), 2.2406(36); U(1)−N(2), 2.2421(38); U(1)−N(3), 2.5026(37) Å; U(1)−N(4), 2.3534(36) Å; U(1)−S(1), 2.6914(12); N(4)−C(6), 1.4665(55); N(1)−U(1)−N(2), 132.80(14); N(1)−U(1)−S(1), 96.55(10); N(2)−U(1)−S(1), 103.37(10); N(3)−U(1)−S(1), 140.60(9); N(4)−U(1)−S(1), 74.07(9).

Experimental Section

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs[48] 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. Uranium turnings were purchased from Argonne National Laboratories. Compounds **1-(CH_2Ph)$_2$**[31] and **5^{mbi}**[41] were prepared following published procedures. The aromatic heterocycles were distilled or recrystallized before use; all other materials were used as received. ^{1}H NMR spectra were recorded on a Bruker 300 or Bruker 500 spectrometer (supported by NSF Grant CHE-9974928) at room temperature in C_6D_6 unless otherwise specified. Chemical shifts are reported with respect to the solvent residual peak, 7.16 ppm (C_6D_6). CHN analyses were performed by the UC Berkeley Micro-Mass facility, 8 Lewis Hall, College of Chemistry, University of California, Berkeley, CA 94720.

Synthesis of 5^{py}. Pyridine (0.0264 g in ~3 mL of toluene, 2 equiv) was added dropwise to a stirring toluene solution (5 mL) of 1-(CH_2Ph)$_2$ (0.1441 g, 0.167 mmol) in a 20-mL scintillation vial and allowed to stir vigorously at room temperature for 16 h. The solvent was removed under reduced pressure, and the dried product was extracted with hexanes and filtered through Celite. The filtrate was dried under reduced pressure, and the above extraction/filtration procedure was repeated. The filtrate was concentrated and placed in a −35 °C freezer. Crystals formed overnight (crop 1: 0.0572 g, 40%). The mother liquor was decanted and placed back in the freezer. Two additional crops of crystals were obtained in this manner. Total yield of the three crops: 0.1257 g, 89%. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 21.97 and 18.87 (s, 12H, $SiCH_3$), 17.13 [s, 18H, $SiC(CH_3)_3$], 3.33, 0.09, −9.83, −11.94, −13.23, and −32.69 (s, 2H each, $CH_2C_6H_5$ or C_5H_4), 7.40, 3.53, −3.67, −4.82, and −20.06 (s, 1H each, C_5H_4 or NC_5H_4), −82.52 (s, 2H, $CH_2C_6H_5$). Anal. Calcd for $C_{34}H_{49}FeN_3Si_2U$: C, 48.05; H, 5.81; N, 4.94. Found: C, 47.68; H, 5.81; N, 4.93.

Synthesis of 5^{pic}. 2-Picoline (2 mL of a 0.116 M solution in hexanes, 0.232 mmol, 2 equiv) was added dropwise to a stirring solution of **1-(CH_2Ph)$_2$** (100 mg in 5 mL of hexanes, 0.116 mmol) in a 12-mL Schlenk tube. The reaction mixture was stirred at room temperature for 30 h. The solvent was removed under reduced pressure, and the dried product was extracted in hexanes, filtered through Celite, concentrated, and placed in a −35 °C freezer. Yield: 66 mg, 66%. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ −71.13 (s, 2H, $CH_2C_6H_5$), 18.80 and 14.96 (s, 12H, $SiCH_3$), 15.23 [s, 18H, $SiC(CH_3)_3$], 1.91, −13.09, −24.35, and −32.42 (s, 2H each, $CH_2C_6H_5$ or C_5H_4), 9.98, 8.70, −2.12, and −9.53 (s, 1H each, C_5H_4 or NC_5H_4), −9.53 (s, 3H, $NCCH_3$). Anal. Calcd for $C_{35}H_{51}FeN_3Si_2U$: C, 48.66; H, 5.95; N, 4.86. Found: C, 48.46; H, 6.04; N, 4.77.

Synthesis of 8^{py}-boz. A 2-mL benzene solution of benzoxazole (13 mg, 0.11 mmol) was slowly added to a 2-mL benzene solution of **5^{py}** (43 mg, 0.051 mmol). The reaction mixture was stirred at room temperature for 12 h. The volatiles were removed under reduced pressure, and the resulting dark-red powder was dissolved in diethyl ether. The solution was filtered through Celite, concentrated, and stored at −35 °C. X-ray-quality crystals formed overnight. Yield: 30.1 mg, 61%. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 51.22, 40.27, 39.62, and 31.57 (s, 3H each, $SiCH_3$), 28.01 and 27.15 [s, 9H each, $SiC(CH_3)_3$], 1.85 (t, 2H, CH_2Ph), 2.89, −1.25, −2.28, −2.90, −10.38, and −12.38 (t, 1H each, C_5H_4, aromatic CH, or NC_5H_3), −3.81, −15.08, −17.41, −17.79, −19.19, −22.19, and −25.13 (d, 1H each, C_5H_4, aromatic CH, or NC_5H_3), −3.88, −11.42, −13.17, −13.39, −13.95, −27.80, −38.07, −46.63, and −73.03 (s, 1H each, C_5H_4, aromatic CH, or NC_5H_3). Anal. Calcd for $C_{41}H_{55}FeN_4OSi_2U$ (970): C, 50.77; H, 5.72; N, 5.78. Found: C, 50.53; H, 5.73; N, 5.53.

Synthesis of 8^{pic}-btz. A 2-mL pentane solution of benzothiazole (72.7 mg, 0.522 mmol) was slowly added to a 2-mL *n*-pentane solution of **5^{pic}** (347 mg, 0.401 mmol). The reaction mixture was left at room temperature without stirring. The pink precipitate that formed after 10 h (yield: 217.5 mg, 54%) was separated, dried, dissolved in diethyl ether, filtered through Celite, and stored at −35 °C. X-ray-quality crystals formed overnight. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 49.38, 27.51, 25.17, and 18.45 (s, 3H each, $SiCH_3$), 27.06 and 24.32 [s, 9H each, $SiC(CH_3)_3$], −12.14 (s, 2H, CH_2Ph), 10.08, 9.58, 3.47, 2.77, 2.49, −1.08, and −30.98 (t, 1H each, C_5H_4, aromatic CH, or NC_5H_3), −3.44, −16.94, and −26.17 (d, 1H each, C_5H_4, aromatic CH, or NC_5H_3), 12.17, −1.76, −3.15, −4.44, −4.77, −12.70, −17.61, −29.59, and −62.44 (s, 1H each, C_5H_4, aromatic CH, or NC_5H_3), −70.70 (s, 3H, $NCCH_3$). Anal. Calcd for $C_{42}H_{57}FeN_4SSi_2U[(C_7H_8)_{1/3}]$ (1030): C, 51.64; H, 5.83; N, 5.44. Found: C, 51.66; H, 5.78; N, 5.63.

Synthesis of 8^{mbi}-boz. Benzoxazole (7.9 mg, 0.066 mmol) was dissolved in 2 mL of diethyl ether and added to a 2-mL diethyl ether solution of **5^{mbi}** (58.6 mg, 0.065 mmol). The reaction mixture was stirred at room temperature for 15 h. The volatiles were removed under reduced pressure, and the dried product was extracted with hexanes, filtered through Celite, and dried again. The pale-orange powder (crude yield of 59.9 mg, 90%, pure by ^{1}H NMR spectroscopy) was dissolved in fresh hexanes, passed through Celite, and stored at −35 °C. Clumps of dark-red needles embedded in salmon-pink powder formed after 48 h. The product is stable in solution at room temperature indefinitely. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 47.41, 42.06, 39.67, and 32.26 (s, 3H each, $SiCH_3$), 28.31 and 26.45 [s, 9H each, $SiC(CH_3)_3$], 2.43, −0.06, −2.27, −2.92, −4.08, −20.44, −23.24, and −25.15 (t, 1H each, C_5H_4, aromatic CH, or NC_5H_3), −6.44 (d, 2H, CH_2Ph), −10.22 (s, 3H, $NCCH_3$), −19.09, −20.78, and −41.10 (d, 1H each, C_5H_4, aromatic CH, or NC_5H_3), −12.63, −13.59, −15.12, −17.82, −18.02, −27.40, −40.29, and −51.89 (s, 1H each, C_5H_4, aromatic CH, or NC_5H_3). Anal. Calcd for $C_{44}H_{57}FeN_5OSi_2U$ (1021): C, 51.71; H, 5.62; N, 6.85. Found: C, 52.01; H, 5.70; N, 6.57.

X-ray Crystal Structures. X-ray-quality crystals were obtained from various concentrated solutions placed in a −35 °C freezer in the glovebox. Inside the glovebox, the crystals were

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[48] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

coated with oil (STP Oil Treatment) on a microscope slide, which was brought outside the glovebox. The X-ray data collections were carried out on a Bruker AXS single-crystal X-ray diffractometer using Mo Kα radiation and a SMART APEX CCD detector. The data were reduced by *SAINT+*, and an empirical absorption correction was applied using the package *SADABS*. The structures were solved and refined using *SHELXTL* (Bruker 1998, SMART, *SAINT*, *XPREP*, and *SHELXTL*, Bruker AXS Inc., Madison, WI). All atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions unless specified otherwise. Tables with atomic coordinates and equivalent isotropic displacement parameters, with all of the bond lengths and angles, and with anisotropic displacement parameters are listed in the CIF in the Supporting Information.

X-ray Crystal Structure of 5^{py}. X-ray-quality crystals were obtained from a concentrated Et_2O solution. A total of 8332 reflections ($-13 \leq h \leq 13$, $-15 \leq k \leq 15$, and $-23 \leq l \leq 23$) were collected at T = 100(2) K with $2\theta_{max}$ = 56.24°, of which 6737 were unique (R_{int} = 0.0406). The residual peak and hole electron densities were +1.47 and −2.35 e A^{-3}. The least-squares refinement converged normally with residuals of R1 = 0.0593 and GOF = 1.043. Crystal and refinement data for 5^{py}: formula $C_{34}H_{49}N_3Si_2FeU$, space group $P\bar{1}$, a = 9.8710(16) Å, b = 11.7017(19) Å, c = 17.624(3) Å, α = 76.825(2)°, β = 74.133(2)°, γ = 65.740(2)°, V = 1769.7(5) $Å^3$, Z = 2, μ = 5.07 mm^{-1}, $F(000)$ = 840, R1 = 0.0412 and wR2 = 0.0759 (based on all 8332 data).

X-ray Crystal Structure of 5^{pic}. X-ray-quality crystals were obtained from a concentrated hexanes solution. A total of 9077 reflections ($-13 \leq h \leq 13$, $-15 \leq k \leq 15$, and $-24 \leq l \leq 24$) were collected at T = 100(2) K with $2\theta_{max}$ = 57.43°, of which 8169 were unique (R_{int} = 0.0221). The residual peak and hole electron densities were +1.44 and −0.81 e A^{-3}. The least-squares refinement converged normally with residuals of R1 = 0.0253 and GOF = 1.021. Crystal and refinement data for 5^{pic}: formula $C_{35}H_{51}N_3Si_2FeU$, space group $P\bar{1}$, a = 9.805(4) Å, b = 11.590(5) Å, c = 18.359(8) Å, α = 73.400(4)°, β = 87.716(4)°, γ = 66.498(4)°, V = 1826.9(13) $Å^3$, Z = 2, μ = 4.92 mm^{-1}, $F(000)$ = 856, R1 = 0.0299 and wR2 = 0.0555 (based on all 9077 data).

X-ray Crystal Structure of 8^{pic}-btz. X-ray-quality crystals were obtained from a concentrated *n*-pentane solution. A total of 41 865 reflections ($-32 \leq h \leq 33$, $-24 \leq k \leq 24$, and $-31 \leq l \leq 32$) were collected at T = 100(2) K with θ_{max} = 30.77°, of which 12 252 were unique (R_{int} = 0.0361). The residual peak and hole electron densities were +3.00 and −2.61 e A^{-3}. The least-squares refinement converged normally with residuals of R1 = 0.0408 and GOF = 1.034. Crystal and refinement data for **8^{pic}-btz**: formula $C_{42}H_{56}N_4Si_2FeSU$, space group $C2/c$, a = 23.049(2) Å, b = 17.1069(16) Å, c = 22.439(2) Å, β = 109.840(1)°, V = 8322.7(14) $Å^3$, Z = 8, μ = 4.377 mm^{-1}, $F(000)$ = 3984, R1 = 0.0599 and wR2 = 0.1052 (based on all 12 252 data).

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Supporting Information Available: Experimental details for compound characterization and full crystallographic descriptions in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.