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Reactions of Aromatic N-Heterocycles with Yttrium and Lutetium Benzyl Complexes Supported by a Pyridine-Diamide Ligand

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A comparison between the reactivity behavior of yttrium and lutetium benzyl complexes supported by a pyridine diamide, on one hand, and by a ferrocene diamide, on the other hand, toward aromatic N-heterocycles, such as 1-methylimidazole, isoquinoline, acridine, and 2-picoline, is presented. The ring opening of 1-methylimidazole by the pyridine-diamide complexes was observed, analogously to the ring opening of the same substrate by group 3 benzyl complexes supported by the ferrocene-diamide ligand. Also, analogous products were observed in the reactions with 2-picoline and isoquinoline. However, when acridine was employed, different products were obtained for the two metal centers: alkyl transfer for yttrium and ortho-metalation for lutetium.

Introduction

Interest in non-cyclopentadienyl group 3 metal complexes has been increasing in recent years[1−4] with the goal of expanding their reactivity toward challenging substrates, such as saturated[5] or unsaturated[6,7] hydrocarbons and polar molecules.[8−10] Owing to the electrophilic metal centers present even in neutral alkyl complexes, group 3 metal monoalkyl complexes supported by dianionic ancillary ligands engage in σ-bond metathesis reactions.[11−15]

The reactivity of group 3 metal alkyl compounds is a result of the metal's electrophilicity and of available coordination sites and can be substantially modulated by tuning the electronic and steric properties of the ancillary ligand framework. As a consequence, the design of new coordination environments is crucial in maintaining a balance between the kinetic stability and the high reactivity of the resulting complexes.[3,5,15] We have been interested in the reactivity of d^0f^n complexes supported by chelating-ferrocene ligands[16−21] and proposed that a weak interaction, of donor−acceptor type, between iron and the metal takes place in alkyl ferrocene-diamide (NN^{fc} = fc(NSi^{t}BuMe$_2$)$_2$) complexes.[22,23] According to our previous investigations, a substrate-dependent behavior was found with aromatic N-heterocycles: ring opening of 1-methylimidazole,[16,20] C−C coupling of pyridines,[19,20] and alkyl transfer to isoquinoline (Scheme 1).[24]

In order to probe the importance of the iron−metal interaction in determining the reactivity of the ferrocene-diamide alkyl complexes, we decided to employ a tridentate, dianionic, supporting ligand, 2,6-bis(2,6-di-*iso*-propylanilidomethyl)pyridine (NN^{py}), with which the metal center is likely to engage in a stronger interaction with the pyridine nitrogen than that with iron in the ferrocene ligands. The NN^{py} ligand coordinates exclusively in a meridional fashion to the metal center as a consequence of the high rigidity of its backbone

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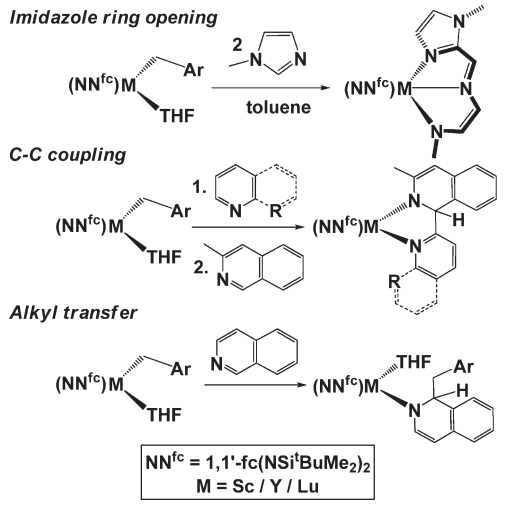
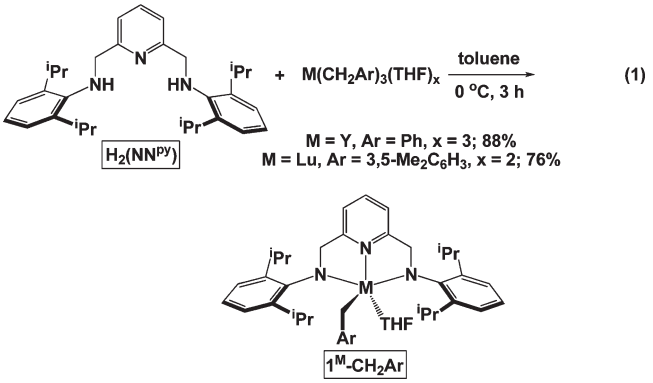
Scheme 1. Reactions of Group 3 Metal Benzyl Complexes Supported by a Ferrocene-Diamide Ligand with Aromatic N-Heterocycles



and, thus, mimics the coordination of the ferrocene-diamide ligand. Complexes of Ti(IV),[25−27] Zr(IV),[28−31] Ta(V),[32,33] lanthanides,[34−36] and Th(IV)[37,38] supported by pyridine-diamide ligands have been known. Herein we report the synthesis of yttrium and lutetium benzyl complexes bearing NN^{py} and their reactivity toward aromatic N-heterocycles.

Results and Discussion

Synthesis and Characterization of Benzyl Complexes. The benzyl diamidopyridine complexes $(NN^{py})M(CH_2Ar)(THF)$ (**1^{M}-CH_2Ar**; M = Y, Ar = Ph; M = Lu, Ar = 3,5-$Me_2C_6H_3$) were prepared by alkane elimination from $H_2(NN^{py})$ and $M(CH_2Ar)_3(THF)_x$ (M = Y, x = 3; M = Lu, x = 2)[19,20] in toluene, analogously to the route described by us for NN^{fc}-supported complexes (eq 1).[19,20] An instantaneous color change of the reaction mixture from colorless to orange evidenced the coordination of the pyridine-diamide ligand to the metal center. It was also noticed that the lutetium complex **1^{Lu}-CH_2Ar** had better solubility in hydrocarbon solvents than the yttrium congener **1^{Y}-CH_2Ph**, likely because of the increased hydrophobicity of the dimethyl-substituted benzyl group in **1^{Lu}-CH_2Ar**. The desired products were isolated in good yield after recrystallization.



The ^{1}H NMR spectrum of **1^{Y}-CH_2Ph** in C_6D_6 at ambient temperature showed a singlet at 4.78 ppm that was assigned to the methylene groups of NN^{py} and a doublet at 2.23 ppm that was assigned to the benzyl group. A multiplet at 3.83 ppm and a doublet at 1.33 ppm were assigned to the methine and methyl groups, respectively, of the four *iso*-propyl substituents. For the lutetium derivative **1^{Lu}-CH_2Ar**, two distinct doublets, at 5.09 and 4.48 ppm, were observed for the two methylene groups of NN^{py}, likely because of a lesser fluxional behavior shown by **1^{Lu}-CH_2Ar** than by **1^{Y}-CH_2Ph**, although the benzyl methylene appeared as a broad singlet at 2.16 ppm. Likewise, two multiplets for the methine and four doublets for the methyl groups were found for the *iso*-propyl substituents. A fluxional behavior was also observed for the yttrium and lutetium alkyl complexes **1^{M}-(CH_2SiMe_3)-**(THF).[34] Similar to the present case, it was reported that the fluxional behavior increased with the size of the metal center: the analogous scandium complex, **1^{Sc}-(CH_2SiMe_3)**, showed behavior similar to **1^{Lu}-CH_2Ar**, whereas the yttrium and lutetium complexes showed behavior similar to **1^{Y}-CH_2Ph**.

The thermal stability of **1^{Y}-CH_2Ph** was investigated by heating a C_6D_6 solution gradually to 70 °C for three days; under these conditions, **1^{Y}-CH_2Ph** was relatively stable. Total decomposition was observed only upon prolonged heating at 85 °C (3 days); attempts to identify the products were unsuccessful. The lutetium congener **1^{Lu}-CH_2Ar** showed similar behavior. The solids and solutions of **1^{Y}-CH_2Ph** and **1^{Lu}-CH_2Ar** could be stored at −35 °C in the glovebox for several weeks without decomposition.

Reactions with 1-Methylimidazole. We had reported recently the unprecedented ring opening of 1-methylimidazole by scandium and yttrium complexes supported by NN^{fc}.[20] Because this reaction had not been observed with metallocene complexes, it was considered a good test to compare the reactivity of NN^{fc} and NN^{py} complexes. The reaction of a yellow toluene solution of **1^{Y}-CH_2Ph** or **1^{Lu}-CH_2Ar** with three equivalents of 1-methylimidazole resulted in the formation of a dark-red solution, after heating at 70 °C, from which a dark-red solid was isolated for either yttrium (**2^{Y}**) or lutetium (**2^{Lu}**) (Scheme 2). The products were analogous to those obtained for the NN^{fc}-based complexes, and we propose that a similar mechanism operates.[19,20]

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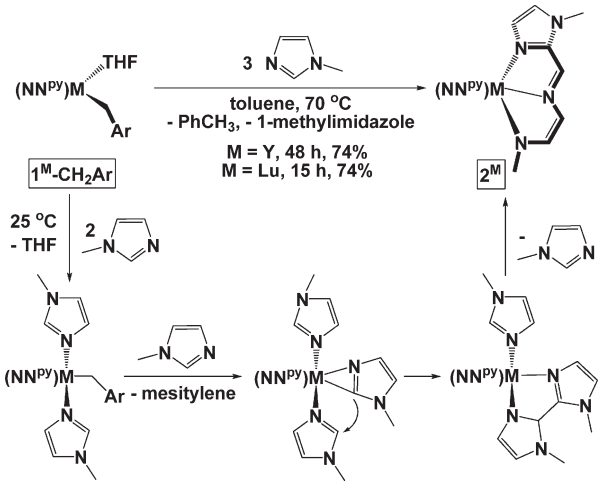
Scheme 2. Ring Opening of 1-Methylimidazole by 1^{M}-CH_2Ar (M = Y, Lu) and Proposed Mechanism



The reaction was faster for the lutetium complex (15 h) than for the yttrium one (48 h). The reaction of the yttrium complex was significantly slower for the NN^{py} than for the NN^{fc} complex (5 h).[20] DFT calculations established that, for the reaction of $(NN^{fc})Sc(CH_2Ar)(THF)$ with 1-methylimidazole, the step with the highest activation barrier, a rotation along the carbon−carbon bond between the two coupled rings to allow the coordination of the nitrogen bearing the methyl group, follows the coupling of the two imidazole rings.[19] It is possible that the much slower reaction of $\mathbf{1^{Y}\text{-}CH_2Ph}$ than of $(NN^{fc})Y(CH_2Ph)(THF)$ with 1-methylimidazole is a consequence of the increased steric crowding in $\mathbf{1^{Y}\text{-}CH_2Ph}$ that hinders this rotation, although other factors cannot be ruled out.

Single crystals suitable for X-ray diffraction analysis were obtained by the slow diffusion of *n*-pentane into a diethyl ether solution of $\mathbf{2^{Y}}$ at −35 °C. X-ray crystallography (Figure 1) revealed that the yttrium center is coordinated to six nitrogen atoms, three from the pyridine-diamide ligand and the other three from the imidazole-imine-amide fragment, which contains an open imidazole ring. Metrical parameters are consistent with the structure drawn in Scheme 2 (parameters for only one of the two independent molecules in the unit cell are discussed). For example, the N−C distances to the imine nitrogen are 1.3132(40) and 1.3414(41) Å, with the shortest distance corresponding to the N=C bond. In addition, the C−C distance corresponding to the C=C bond is 1.3972(48) Å. The sum of the angles around the imine-nitrogen atom of 359.9° with individual angles of 126.08(29)°, CNC, and 118.20(21) and 115.59(21)°, YNC, also supports the above structural assignment. The Y−N distances to the modified imidazole fragment are similar: 2.4454(27) Å for $Y-N_{im}$, 2.4942(26) Å for $Y-N_{imine}$, and 2.4218(27) Å for $Y-N_{amide}$. All these three distances are slightly longer than the $Y-N_{NNpy}$ distance of 2.3968(26) Å to the pyridine ring of the ancillary ligand and at least 0.15 Å longer than the $Y-N_{NNamide}$ distances of 2.2571(26) and 2.2666(26) Å to the ancillary ligand.

Reactions with 2-Picoline and Subsequent C−C Coupling Reactions with 3-Methylisoquinoline. The reactions of $\mathbf{1^{M}\text{-}CH_2Ar}$ with pyridines were investigated next since the ferrocene-diamide group 3 metal benzyl complexes can C−H activate substituted pyridines and effect their coupling.[19,20] The reaction between $\mathbf{1^{M}\text{-}CH_2Ar}$ and four equivalents of pyridine at 50 °C gave a mixture of products. Investigation of

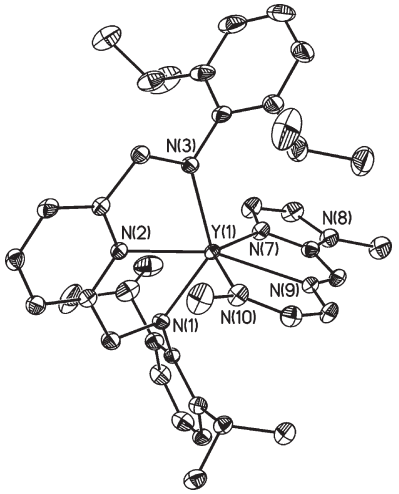
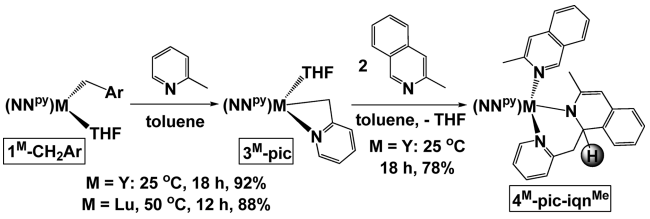


Figure 1. Thermal-ellipsoid (50% probability) representation of $\mathbf{2^{Y}}$. Hydrogen atoms were omitted for clarity. Only one of the two independent molecules present in the unit cell is shown.

Scheme 3. Reactions of 1^{M}-CH_2Ar with 2-Picoline and Subsequent C−C Coupling Reactions with 3-Methylisoquinoline



that mixture by ^{1}H NMR spectroscopy indicated the presence of olefinic peaks, similarly to what was observed when the corresponding ferrocene-diamide complexes were employed. On the basis of the reactivity behavior reported by us for substituted pyridines and isoquinoline,[19,20,24] we propose that multiple, competitive pathways are operative when pyridine is involved, leading to a mixture of products that proved intractable. However, when pyridine was replaced by 2-phenylpyridine or 8-methylquinoline, the products of the C−H activation reaction could be isolated and characterized.[19,20] Therefore, the reactions between $\mathbf{1^{M}\text{-}CH_2Ar}$ with 2-phenylpyridine or 8-methylquinoline were targeted, but in both cases a mixture of products was formed that proved intractable. These results indicate that 2-phenylpyridine and 8-methylquinoline behave like pyridine in the present reactions. It is possible that the aryl *iso*-propyl groups, which point toward the plane to be used by the substrate to coordinate, change some reaction profiles, making multiple pathways competitive; however, other factors may be operative.

Next, the reaction between $\mathbf{1^{M}\text{-}CH_2Ar}$ and 2-picoline was investigated. When one equivalent of 2-picoline was used, C−H activation of the methyl instead of the ortho-carbon was observed (Scheme 3), supported by the appearance in the ^{1}H NMR spectrum of $\mathbf{3^{M}\text{-}CH_2Ar}$ of a singlet at 2.30 ppm for the methylene group. The reaction proceeds at room temperature in 18 h for yttrium, but it requires heating to 50 °C overnight for lutetium. An analogous compound was isolated for yttrium supported by the ferrocene-diamide ligand.[39] Similar results have been reported for other yttrium[40] and thorium alkyl complexes.[41] DFT calculations

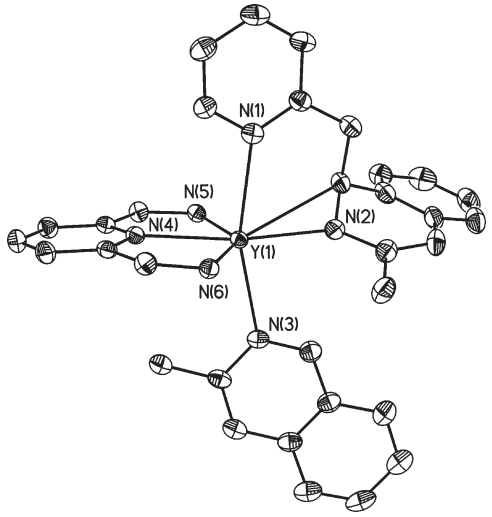
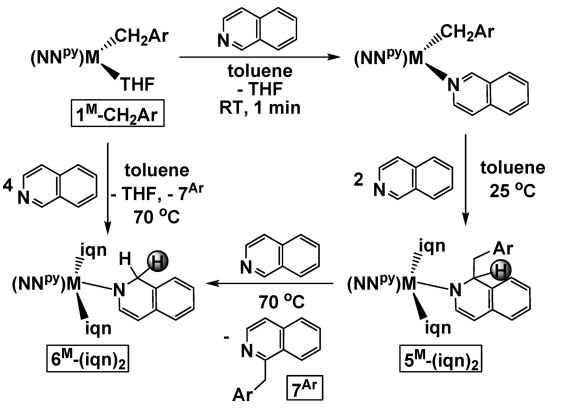


Figure 2. Thermal-ellipsoid (50% probability) representation of **4^{Y}-pic-iqn^{Me}**. Hydrogen atoms and 2,6-di-*iso*-propylphenyl groups were omitted for clarity.

were used to investigate which isomer of **3^{Y}-pic** is preferred and indicate that **3^{Y}-pic** is more stable by 1.3 kcal/mol than **3^{Y}-pic′**, in which the coordinated THF ligand points away from the methylene group. Although the energy difference between the two isomers is not large, the same isomer was identified for the analogous ferrocene-diamide complex.[39] Also, the preferential sp^3 C−H activation is supported by the fact that the two η^2-N,C-pyridyl isomers are less stable than **3^{Y}-pic** by as little as 3.2 kcal/mol and as much as 4.4 kcal/mol.

Since a C−C coupling reaction between the ferrocene analogue of **3^{Y}-pic** and 3-methylisoquinoline was observed,[39] the reaction of **3^{Y}-pic** with the same substrate was also investigated. The two compounds reacted at room temperature to form the expected biheterocyclic product **4^{Y}-pic-iqn^{Me}**, in which the heterocyclic ring of 3-methylisoquinoline was dearomatized (Scheme 3). Single crystals of **4^{Y}-pic-iqn^{Me}** suitable for X-ray diffraction analysis were obtained by the slow diffusion of hexanes into an Et_2O solution of **4^{Y}-pic-iqn^{Me}** at −35 °C. The X-ray structure analysis (Figure 2) revealed that a 3-methylisoquinoline ligand was also coordinated to the yttrium center. The presence of a methylene group in the six-membered metallocycle allows a near-perpendicular orientation of the two heterocyclic rings. The complex **4^{Y}-pic-iqn^{Me}** features a short $Y-N_{amide}$ distance of 2.2772(20) Å to the dearomatized pyridine ring and two long $Y-N_{py}$ distances of 2.5505(20) and 2.5750(20) Å to the pyridine rings of 2-picoline and of 3-methylisoquinoline, respectively. The first distance, $Y-N_{amide}$, is comparable to the $Y-N_{NNamide}$ distances of 2.2890(19) and 2.3119(19) Å to the ancillary ligand, while the $Y-N_{py}$ distances are ca. 0.1 Å longer than the $Y-N_{NNpy}$ distance of 2.4533(19) Å to the pyridine ring of the ancillary ligand. A close contact to the sp^3-hybridized carbon atom of the dearomatized isoquinoline fragment is evidenced by a Y−C distance of 2.9590(24) Å (Figure 2). Metrical parameters

Scheme 4. Reactions of Isoquinoline Mediated by the Benzyl Complexes 1^{M}-CH$_2$Ar (M = Y, Lu)



are also consistent with the dearomatization of the pyridine ring in the coupled-isoquinoline fragment. For example, the N−C distances in the coordinated isoquinoline are 1.3304(32) and 1.3805(31) Å, while in the dearomatized fragment they are 1.3802(31) and 1.4821(31) Å, with the longest distance to the sp^3-carbon atom. In addition, C−C distances also reflect the dearomatization of the isoquinoline fragment: the values for the pyridine ring of the coordinated isoquinoline are 1.4115(35), 1.4004(36), 1.4159(36), and 1.3776(35) Å, while in the dearomatized one they are 1.3682(35), 1.4351(38), 1.4100(36), and 1.5177(34) Å, with the longest distance involving the sp^3-carbon atom. The NCC angle around the sp^3-carbon atom of 109.05(20)° and the CCC angle of 110.53(20)° also support the above structural assignment.

Reactions with Isoquinoline. The initial reaction between the benzyl complexes and 1-methylimidazole, after displacement of THF, is the C−H activation of the imidazole.[19,20] The same ortho-metalation reaction was observed when substituted pyridines were used as substrates.[19] If the substrate employed is changed to isoquinoline, C−H activation does not occur and, instead, alkyl migration takes place with the ferrocene-based group 3 metal complexes.[24] Therefore, we decided to investigate whether the same behavior will be observed with the present systems. The complexes **1^{M}-CH$_2$Ar** reacted with three equivalents of isoquinoline in toluene at room temperature to give a red solution, from which an orange solid was isolated (**5^{M}-(iqn)$_2$**, Scheme 4). The reaction is analogous to the one previously reported for ferrocene-diamide complexes.[24] According to ^{1}H NMR spectroscopy in C_6D_6, the benzyl group was transferred to the 1-position of isoquinoline with its concomitant dearomatization. Two other isoquinoline molecules were coordinated to the yttrium center to form **5^{Y}-(iqn)$_2$**. In the ^{1}H NMR spectrum of **5^{Y}-(iqn)$_2$**, two doublets, at 6.15 and 5.65 ppm, were assigned to the protons of the CH=CH bond in the dearomatized heterocycle. Because of the C1-stereogenic center, two distinct resonances for the CH_2 protons of the benzyl group were found, at 4.65 and 2.60 ppm, as a doublet of doublets. The triplet at 3.86 ppm revealed the presence of the proton on the newly sp^3-hybridized carbon in the dearomatized heterocycle.

When toluene solutions of **1^{M}-CH$_2$Ar** and four equivalents of isoquinoline were heated at 70 °C, their color changed gradually from orange to brown (Scheme 4). After workup, a new product, **6^{M}-(iqn)$_2$**, was identified together

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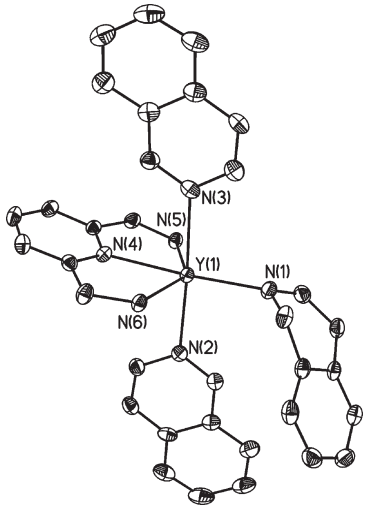


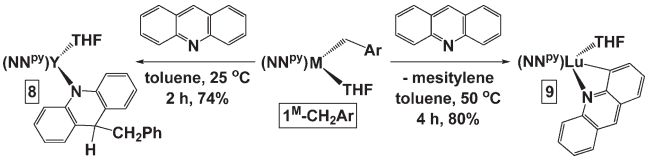
Figure 3. Thermal-ellipsoid (50% probability) representation of $\mathbf{6^{Y}\text{-}(iqn)_2}$. Hydrogen atoms and 2,6-di-*iso*-propylphenyl groups were omitted for clarity.

with 1-benzylisoquinoline ($\mathbf{7^{Ar}}$).[42] The conversion of the lutetium complex $\mathbf{1^{Lu}\text{-}CH_2Ar}$ to $\mathbf{6^{Lu}\text{-}(iqn)_2}$ was much slower (100 h) than that observed for the yttrium complex (24 h). The formation of $\mathbf{6^{Y}\text{-}(iqn)_2}$ was confirmed by the appearance in its ^{1}H NMR spectrum of a singlet at 4.35 ppm corresponding to the two protons of the methylene group in the dearomatized isoquinoline and by characteristic olefinic peaks at 6.60 and 5.70 ppm.

Single crystals of $\mathbf{6^{Y}\text{-}(iqn)_2}$ suitable for X-ray diffraction analysis were obtained by the slow diffusion of hexanes into an Et_2O/THF solution at −35 °C (Figure 3). The structure analysis revealed that two isoquinoline molecules were coordinated to the yttrium center in addition to the dearomatized ligand and that the geometry around the six-coordinate yttrium center can be described as distorted octahedral. Metrical parameters are consistent with the dearomatization of the pyridine ring in one of the isoquinoline ligands. For example, the N−C distances in the coordinated isoquinolines are 1.3204(30) and 1.3709(31) Å for one ligand and 1.3383(33) and 1.3680(33) Å for the other ligand, while in the dearomatized one they are 1.3623(33) and 1.4685(33) Å, with the longest distance to the sp^3-carbon atom. In addition, the C−C distances also reflect the dearomatization of one isoquinoline ligand: the values for the pyridine ring of the coordinated isoquinolines are 1.4084(34), 1.4204(37), 1.4093(36), and 1.3539(36) Å for one ligand and 1.4069(36), 1.4138(38), 1.4165(38), and 1.3651(36) Å for the other ligand, while in the dearomatized one they are 1.3675(35), 1.4508(35), 1.4101(34), and 1.5003(36) Å, with the longest distance involving the sp^3-carbon atom. The NCC angle around the sp^3-carbon atom of 112.96(21)° also supports the above structural assignment. The Y−N distance to the dearomatized isoquinoline (2.3099(21) Å) is shorter by ca. 0.2 Å than the Y−N distances (2.4987(21) and 2.5617(21) Å) to the aromatic, coordinated isoquinolines. The first distance, $Y-N_{amide}$, is comparable to the $Y-N_{NNamide}$ distances of 2.2790(20) and 2.2924(20) Å to the ancillary ligand, while the $Y-N_{py}$ distances are ca. 0.1 Å longer than the $Y-N_{NNpy}$ distance of 2.4173(20) Å to the pyridine ring of the ancillary ligand.

(42) Uff, B. C.; Kershaw, J. R. *J. Chem. Soc.* (*C*) **1969**, 666–668.

Scheme 5. Reactions of $\mathbf{1^{M}\text{-}CH_2Ar}$ (M = Y, Lu) with Acridine



Reactions with Acridine. The reactivity behavior of $\mathbf{1^{M}\text{-}CH_2Ar}$ toward acridine was also investigated in order to determine whether C−H activation or alkyl transfer would occur.[24,39] The reaction between $\mathbf{1^{Y}\text{-}CH_2Ph}$ and one equivalent of acridine in toluene at room temperature led to the alkyl-transfer product **8** (Scheme 5), in which the benzyl group migrated from the yttrium center to the 9-position of acridine and the heterocycle was dearomatized. This reaction is similar to the benzyl-transfer reaction observed for scandium and lutetium benzyl complexes supported by the ferrocene-diamide ligand and 2,2′-bipyridine.[24] However, the reaction of the same scandium benzyl complex and acridine resulted in the C−H activation of acridine. The formulation of **8** was based on its ^{1}H NMR spectrum since protons for two equivalent phenyl groups were identified for the acridine fragment. A triplet at 4.30 ppm corresponding to one proton was assigned to the 9-position of acridine, and a doublet at 3.11 ppm corresponding to two protons was assigned to the methylene group of the benzyl substituent. These chemical shifts are comparable to those reported for 9-benzyl-9,10-dihydroacridine (4.15 and 2.82 ppm).[43]

The reaction between $\mathbf{1^{Lu}\text{-}CH_2Ar}$ and one equivalent of acridine in C_6D_6 was very slow at room temperature, so the reaction mixture was heated at 50 °C for 4 h. Surprisingly, a different product than **8** was isolated (**9**, Scheme 5). The identity of **9** was established by analyzing the ^{1}H NMR spectrum of the reaction mixture that indicated mesitylene formation and two different sets of peaks for the two phenyl rings in acridine. As mentioned earlier, the scandium benzyl complex supported by NN^{fc} leads to the formation of an analogous product.[39] DFT calculations support the proposal that the structure drawn for **9** in Scheme 5 is preferred by 1.4 kcal/mol to the isomer in which THF was coordinated next to the acridine-nitrogen atom. Although this value is small, the analogous complex was also identified for scandium supported by the the ferrocene-diamide ligand.

Conclusions

The synthesis and characterization of yttrium and lutetium benzyl complexes supported by a pyridine-diamide ligand were accomplished. The reactions of these benzyl complexes with aromatic heterocycles, such as 1-methylimidazole, 2-picoline, isoquinoline, and acridine, were investigated and the results compared to those obtained when benzyl complexes supported by a ferrocene-diamide ligand were employed. Similar behavior for the two classes of complexes was observed when 1-methylimidazole, 2-picoline, and isoquinoline were used. In the case of acridine, the yttrium and lutetium benzyl complexes $\mathbf{1^{M}\text{-}CH_2Ar}$ led to the formation of different products: that of alkyl transfer for yttrium and that of sp^2 C−H activation for lutetium. The difference between the two classes of complexes was

(43) Noyori, R.; Katô, M.; Kawanisi, M.; Nozaki, H. *Tetrahedron* **1969**, *25*, 1125–1136.

manifested in the reactions with 2-phenylpyridine and 8-methylisoquinoline, which were too complex and did not allow the isolation of single products for the pyridine-diamide complexes. This difference notwithstanding, the behavior of yttrium and lutetium benzyl complexes supported by the pyridine-diamide ligand is similar to that of the analogous complexes supported by the ferrocene-diamide ligand. It is likely that the dominant features in predicting the reactivity behavior of these complexes are (1) the presence of a diamide donor set and (2) the geometry imposed by the rigid backbone of the ligands. The results presented herein also suggest that the interaction between iron from the ferrocene ligand and the group 3 metal center is as relevant in determining the reactivity behavior of the corresponding benzyl complexes as is the interaction between the pyridine nitrogen of the pyridine diamide and group 3 metal centers. In order to determine whether the presence of this interaction is important, an analogue of the pyridine-diamide ligand, in which pyridine is replaced by benzene, is currently under study.

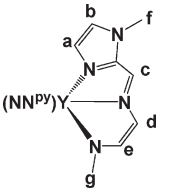
Experimental Section

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[44] 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. Yttrium and lutetium oxides were purchased from Stanford Materials Corporation (Aliso Viejo, CA) and used as received. $H_2(NN^{py})$,[28] $Y(CH_2Ph)_3(THF)_3$,[20] and $Lu(CH_2\text{-}3,5\text{-}Me_2C_6H_3)_3(THF)_2$[19] were prepared according to published procedures. The aromatic N-heterocycles were distilled or recrystallized before use; all other materials were used as received. ^{1}H NMR spectra were recorded on Bruker500 spectrometers (work supported by the NSF grants CHE-9974928 and CHE-0116853) at room temperature in C_6D_6 unless otherwise specified. Chemical shifts are reported with respect to internal solvent, 7.16 ppm (C_6D_6). CHN analyses were performed by UC Berkeley Micro-Mass Facility, College of Chemistry, University of California, Berkeley, CA.

Synthesis of 1^{Y}-CH_2Ph. $Y(CH_2Ph)_3(THF)_3$ (184.6 mg, 0.32 mmol) and $H_2(NN^{py})$ (146.1 mg, 0.32 mmol) were cooled in 4 and 2 mL of toluene, respectively, to 0 °C and then combined. The reaction mixture was stirred for 3 h at 0 °C. The resulting orange solution was concentrated to ca. 2 mL and filtered through Celite. The filtrate was layered with *n*-pentane to yield a yellow solid. Yield: 198.2 mg, 88%. ^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 7.23−7.14 (m, 5 H, $CH_2C_6H_5$), 6.96−6.87 (m, 6 H, NC_6H_3), 6.56 (d, J = 7.5 Hz, 2 H, NC_5H_3), 6.25 (t, 1 H, J = 7.0 Hz, NC_5H_3), 4.78 (s, 4 H, NCH_2), 3.83 (sept, J = 6.0 Hz, 4 H, $CH(CH_3)_2$), 3.10 (m, 4 H, OCH_2CH_2), 2.23 (d, J = 4.0 Hz, 2 H, CH_2Ph), 1.33 (d, J = 6.0 Hz, 24 H, $CH(CH_3)_2$), 0.98 (m, 4 H, OCH_2CH_2). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 164.9 (py-*ortho*), 152.6, 151.3, 146.8, 136.6, 129.7, 123.7, 123.2, 122.8, and 117.2 (aromatic-*C*), 69.8 (OCH_2CH_2), 65.3 (NCH_2), 50.0 (d, J_{Y-C} = 30.4 Hz, Y-CH_2), 28.1, 26.9, 25.0, and 24.8 ($CHMe_2$, $CH(CH_3)_2$ and OCH_2CH_2). Anal. (%) Calcd for $C_{42}H_{56}N_3OY$ (707.82): C, 71.27; H, 7.97; N, 5.94. Found: C, 70.86; H, 7.76; N, 5.72.

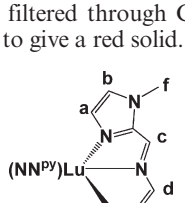
Synthesis of 1^{Lu}-CH_2Ar. $Lu(CH_2\text{-}3,5\text{-}Me_2C_6H_3)_3(THF)_2$ (243.8 mg, 0.36 mmol) and $H_2(NN^{py})$ (165.2 mg, 0.36 mmol) were cooled in 4 and 2 mL of toluene, respectively, to 0 °C and then combined. The reaction mixture was stirred for 3 h at 0 °C. The volatiles were removed under reduced pressure, and the residue was dissolved in hexanes and filtered through Celite. The solution was concentrated and cooled at −35 °C to give a yellow crystalline solid. Yield: 223.7 mg, 76%. ^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 7.25−7.10 (m, 6 H, NC_6H_3), 6.93 (s, 2 H, *o*-3,5-$Me_2C_6H_3$), 6.85 (t, J = 8.0 Hz, 1 H, NC_5H_3), 6.49 (d, J = 8.0 Hz, 2 H, NC_5H_3), 5.94 (s, 1 H, *p*-3,5-$Me_2C_6H_3$), 5.09 (d, J = 19.0 Hz, 2 H, NCH_2), 4.73 (m, 2 H, $CH(CH_3)_2$), 4.48 (d, J = 19.0 Hz, 2 H, NCH_2), 3.37 (m, 2 H, $CH(CH_3)_2$), 2.95 (m, 4 H, OCH_2CH_2), 2.17 (s, 2 H, CH_2Ar), 2.15 (s, 6 H, 3,5-$(CH_3)_2C_6H_3$), 1.60 (d, J = 6.0 Hz, 6 H, $CH(CH_3)_2$), 1.48 (d, J = 6.0 Hz, 6 H, $CH(CH_3)_2$), 1.17 (d, J = 6.0 Hz, 6 H, $CH(CH_3)_2$), 1.12 (d, 6 H, J = 6.0 Hz, $CH(CH_3)_2$), 0.77 (m, 4 H, OCH_2CH_2). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 164.1 (py-*ortho*), 153.7, 149.8, 136.8, 136.4, 128.5, 123.6, 123.0, 122.5, 120.8, 116.7 (aromatic-*C*), 70.1 (OCH_2CH_2), 65.2 (NCH_2), 52.9 (Lu-CH_2), 28.0, 25.1, 24.7, and 21.9 ($CHMe_2$, $CH(CH_3)_2$, Ar-CH_3, and OCH_2CH_2). Anal. (%) Calcd for $C_{44}H_{60}LuN_3O$ (821.93): C, 64.30; H, 7.36; N, 5.11. Found: C, 63.72; H, 7.23; N, 4.91.

Synthesis of 2^{Y}. 1^{Y}-CH_2Ph (90.0 mg, 0.13 mmol) and 3 equiv of 1-methylimidazole (32.5 mg, 0.39 mmol) were combined in 6 mL of toluene in a Schlenk tube. The reaction mixture was heated at 70 °C for 48 h. After the volatiles were removed under reduced pressure, the residue was extracted with diethyl ether and filtered through Celite. The filtrate was layered with *n*-pentane to give a red crystalline solid. Yield: 63.5 mg, 74%.



^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 7.17−7.02 (m, 7 H, NC_6H_3 and NC_5H_3), 6.85 (s, 1 H, *a*), 6.72 (d, J = 7.5 Hz, 2 H, NC_5H_3), 6.39 (s, 1 H, *b*), 6.18, 6.09, and 5.47 (s, 1 H each, *c*, *d*, or *e*), 5.13 (d, J = 20.0 Hz, 2 H, NCH_2), 4.89 (d, J = 20.0 Hz, 2 H, NCH_2), 3.85 (sept, J = 6.5 Hz, 2 H, $CH(CH_3)_2$), 3.70 (sept, J = 6.5 Hz, 2 H, $CH(CH_3)_2$), 2.76 (s, 3 H, *f*), 1.95 (s, 3 H, *g*), 1.41 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 1.34 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 1.28 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 1.24 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 165.6 (py-*ortho*), 161.5 (N*C*), 152.1 (N*C*H, *e*), 153.8, 146.4, 145.9, 136.6, 123.4, 123.3, 122.5, and 117.1 (aromatic-*C*), 126.7 (N*C*H, *b*), 118.2 (N*C*H, *a*), 110.4, and 109.3 (N*C*H, *c* and *d*), 66.2 (NCH_2), 43.5 (NCH_3, *g*), 31.0 (NCH_3, *f*), 27.7, 27.6, 27.2, 26.7, 24.6, 24.4 ($CHMe_2$ and $CH(CH_3)_2$). Anal. (%) Calcd for $C_{39}H_{52}N_7Y$ (707.78): C, 66.18; H, 7.41; N, 13.85. Found: C, 65.79; H, 7.25; N, 13.56.

Synthesis of 2^{Lu}. 1^{Lu}-CH_2Ar (116.9 mg, 0.14 mmol) and 3 equiv of 1-methylimidazole (35.5 mg, 0.43 mmol) were combined in 6 mL of toluene in a Schlenk tube. The reaction mixture was heated at 70 °C for 15 h to yield a deep-red solution. After the volatiles were removed under reduced pressure, the residue was extracted with diethyl ether and filtered through Celite. The filtrate was layered with *n*-pentane to give a red solid. Yield: 83.9 mg, 74%.



^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 7.17−7.13 (m, 4 H, NC_6H_3), 7.07 (t, J = 7.5 Hz, 1 H, NC_5H_3), 7.01 (t, J = 7.0 Hz,

(44) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

2 H, NC_6H_3), 6.90 (s, 1 H, *a*), 6.71 (d, J = 7.5 Hz, 2 H, NC_5H_3), 6.34 (s, 1 H, *b*), 6.25, 6.14, 5.47 (s, 1 H each, *c*, *d*, or *e*), 5.19 (d, J = 20.0 Hz, 2 H, NCH_2), 4.98 (d, J = 20.0 Hz, 2 H, NCH_2), 3.85 (sept, J = 6.5 Hz, 2 H, $CH(CH_3)_2$), 3.70 (sept, J = 6.5 Hz, 2 H, $CH(CH_3)_2$), 2.70 (s, 3 H, *f*), 1.98 (s, 3 H, *g*), 1.40 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 1.32 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 1.27 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 1.24 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 165.8 (py-*ortho*), 162.0 (N*C*), 152.6 (N*C*H, e), 154.9, 146.5, 146.0, 136.6, 123.3, 123.2, 122.3, and 117.0 (aromatic-*C*), 127.1 (N*C*H, *b*), 118.3 (N*C*H, *a*), 110.7, and 109.5 (N*C*H, *c* and *d*), 66.2 (NCH_2), 43.8 (NCH_3, *g*), 31.1 (NCH_3, *f*), 27.6, 27.5, 27.3, 26.9, 24.4, and 24.1 ($CHMe_2$ and $CH(CH_3)_2$). Anal. (%) Calcd for $C_{39}H_{52}LuN_7$ (793.84): C, 59.01; H, 6.60; N, 12.35. Found: C, 58.20; H, 6.62; N, 12.06.

Synthesis of 3^{Y}-pic. 1^{Y}-CH_2Ph (126.0 mg, 0.18 mmol) and 1 equiv of 2-picoline (16.4 mg, 0.18 mmol) were combined in 5 mL of toluene, and the reaction mixture was stirred at room temperature for 18 h. The volatiles were removed under reduced pressure, and the residue was filtered through Celite in diethyl ether and hexanes. The filtrate was stored in the −35 °C freezer to give a yellow crystalline solid. Yield: 115.1 mg, 92%. ^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 7.19−7.09 (m, 6 H, NC_6H_3), 7.02 (t, J = 7.5 Hz, 1 H, NC_5H_3), 6.93 (d, J = 5.5 Hz, 1H, pic-C*H*), 6.71 (t, J = 7.5 Hz, 1 H, pic-C*H*), 6.68 (d, J = 7.5 Hz, 2 H, NC_5H_3), 6.56 (d, J = 8.5 Hz, 1 H, pic-C*H*), 5.73 (t, J = 6.0 Hz, 1 H, pic-C*H*), 4.83 (br s, 4 H, NCH_2), 3.68 (m, 4 H, $CH(CH_3)_2$), 3.15 (m, 4 H, OCH_2CH_2), 2.30 (s, 2 H, pic-CH_2), 1.27 (d, J = 7.0 Hz, 24 H, $CH(CH_3)_2$), 1.02 (br s, 4 H, OCH_2CH_2). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 167.5 and 165.2 (py-*ortho* and pic-2-*C*), 153.7, 146.8, 145.8, 136.7, 135.3, 123.6, 122.9, 119.6, 117.1, and 107.7 (aromatic *C*), 70.3 (OCH_2CH_2), 65.5 (NCH_2), 51.1 (Y-CH_2), 27.9, 26.9, 24.9, and 24.6 ($CHMe_2$, $CH(CH_3)_2$, and OCH_2CH_2). Anal. (%) Calcd for $C_{41}H_{55}N_4OY$ (708.81): C, 69.47; H, 7.82; N, 7.90. Found: C, 69.42; H, 8.03; N, 7.68.

Synthesis of 3^{Lu}-pic. 1^{Lu}-CH_2Ar (109.3 mg, 0.13 mmol) and 1 equiv of 2-picoline (12.2 mg, 0.13 mmol) were combined in 5 mL of toluene. The reaction mixture was stirred at 50 °C for 12 h. The volatiles were removed under reduced pressure, and the residue was extracted in diethyl ether and hexanes. The filtrate was concentrated and cooled at −35 °C overnight to give a yellow crystalline solid. Yield: 108.7 mg, 88%. ^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 7.20−7.10 (m, 6 H, NC_6H_3), 7.03 (t, J = 7.5 Hz, 1 H, NC_5H_3), 6.81 (d, J = 6.0 Hz, 1 H, pic-C*H*), 6.74 (t, J = 7.5 Hz, 1 H, pic-C*H*), 6.68 (d, J = 7.5 Hz, 2 H, NC_5H_3), 6.63 (d, J = 8.0 Hz, 1 H, pic-C*H*), 5.79 (t, J = 6.0 Hz, 1 H, pic-C*H*), 4.86 (br s, 4 H, NCH_2), 3.73 (m, 4 H, $CH(CH_3)_2$), 3.17 (m, 4 H, OCH_2CH_2), 2.36 (s, 2 H, pic-CH_2), 1.26 (d, J = 6.5 Hz, 24 H, $CH(CH_3)_2$), 1.00 (m, 4 H, OCH_2CH_2). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 169.8 and 165.1 (py-*ortho* and pic-2-*C*), 155.0, 147.0, 146.0, 136.7, 136.2, 123.5, 122.8, 119.7, 116.9, and 108.7 (aromatic-*C*), 70.6 (OCH_2CH_2), 65.5 (NCH_2), 49.2 (Lu-CH_2), 27.8, 27.0, 24.8, and 24.5 ($CHMe_2$, $CH(CH_3)_2$, and OCH_2CH_2). Anal. (%) Calcd for $C_{41}H_{55}LuN_4O$ (794.87): C, 61.95; H, 6.97; N, 7.05. Found: C, 61.80; H, 7.05; N, 6.97.

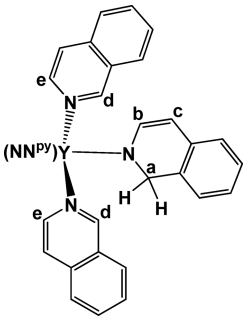
Synthesis of 4^{Y}-pic-iqn^{Me}. 1^{Y}-CH_2Ph (120.0 mg, 0.17 mmol) and 1 equiv of 2-picoline (15.8 mg, 0.17 mmol) were combined in 5 mL of toluene, and the reaction mixture was stirred at room temperature for 18 h. The formation of **3^{Y}-pic** was considered complete by checking an aliquot of the reaction mixture by ^{1}H NMR spectroscopy. Then, 3-methylisoquinoline (50.0 mg, 0.34 mmol) in 2 mL of toluene was added, and the reaction mixture was stirred at room temperature for another 1 h. The volatiles were removed under reduced pressure, the residue was extracted with THF, and the resulting solution was filtered through Celite. After THF was removed under reduced pressure, diethyl ether was added to give an orange crystalline solid. Yield: 122.6 mg, 78%. ^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 9.60 (br s, 1 H, iqn-1-C*H*N), 8.16 (d, J = 5.5 Hz, 1 H, iqn-3-C*H*N), 7.66 (br s, 1 H, aromatic-C*H*), 7.25−7.07 (m, 10 H, aromatic-C*H*), 7.01 (s, 1 H, aromatic-C*H*), 6.93−6.89 (m, 3 H, aromatic-C*H*), 6.82 (d, J = 8.0 Hz, 1 H, aromatic-C*H*), 6.79 (d, J = 8.0 Hz, 1 H, aromatic-C*H*), 6.74 (t, J = 8.0 Hz, 1 H, aromatic-C*H*), 6.34−6.30 (m, 2 H, aromatic-C*H*), 5.68 (d, J = 7.0 Hz, 1 H, aromatic-C*H*), 5.62 (s, 1 H, iqn-NC(CH_3)C*H*), 5.27−5.16 (m, 3 H, NCH_2 and pic-CH_2), 4.96 (d, J = 21.0 Hz, 1 H, NCH_2), 4.86 (d, J = 21.0 Hz, 1 H, NCH_2), 4.09 (dd, J_1 = 18.5 Hz, J_2 = 9.5 Hz, 1 H, N*C*HCH_2), 3.52 (sept, J = 7.0 Hz, 1 H, $CH(CH_3)_2$), 3.34 (sept, J = 7.0 Hz, 1 H, $CH(CH_3)_2$), 3.14 (sept, J = 7.0 Hz, 1 H, $CH(CH_3)_2$), 3.01 (sept, J = 7.0 Hz, 1 H, $CH(CH_3)_2$), 2.46 (s, 3 H, $NC(CH_3)$), 2.22 (d, J = 18.5 Hz, 1 H, pic-CH_2), 1.37 (s, 3 H, iqn-CH_3), 1.27 (d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$), 1.16 (d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$), 1.12 (d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$), 0.83 (d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$), 0.54 (d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$), 0.31 (d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$), −0.00 (d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$), −0.06 (d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 166.2, 165.6, and 164.9 (py-*ortho* and pic-2-*C*), 156.5, 154.6, 151.8, 147.5, 147.0, 146.9, 146.5, 145.9, 143.0, 137.6, 137.4, 136.9, 136.6, 126.5, 126.4, 124.6, 124.2, 123.9, 123.7, 123.4, 122.7, 122.1, 120.5, 119.5, 117.6, and 117.5 (aromatic-*C* and iqn*-3-*C*), 93.7 (iqn*-4-*C*), 68.0 (NCH_2), 67.7 (NCH_2), 52.7 (iqn*-1-*C*), 42.0 (pic-CH_2), 27.9, 27.7, 27.5, 27.3, 27.2, 26.9, 26.8, 26.6, 24.4, 24.3, 23.8, 22.7 ($CHMe_2$, $CH(CH_3)_2$, iqn-CH_3, and iqn*-CH_3). Anal. (%) Calcd for $C_{57}H_{65}N_6Y$ (923.07): C, 74.17; H, 7.10; N, 9.10. Found: C, 73.95; H, 7.26; N, 8.81.

Synthesis of 5^{Y}-(iqn)$_2$. 1^{Y}-CH_2Ph (107.8 mg, 0.15 mmol) and 3 equiv of isoquinoline (59.2 mg, 0.46 mmol) were combined in 6 mL of toluene to give a red solution. The reaction mixture was stirred at ambient temperature for 3 h. The volatiles were removed under reduced pressure, and the residue was extracted in diethyl ether and filtered through Celite. The filtrate was layered with hexanes to give an orange solid. Yield: 90.5 mg, 58%. ^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 9.55 (s, 2 H, iqn-1-C*H*), 8.08 (br s, 2 H, iqn-4-C*H*), 7.25−6.98 (m, 21 H, aromatic-C*H*), 6.95 (d, J = 6.0 Hz, 2 H, aromatic-C*H*), 6.88 (d, J = 8.0 Hz, 2 H, aromatic-C*H*), 6.68 (t, J = 7.5 Hz, 1 H, aromatic-C*H*), 6.57 (d, J = 7.5 Hz, 2 H, aromatic-C*H*), 6.15 (d, J = 7.5 Hz, 1 H, NC(CH_3)C*H*), 5.65 (d, J = 6.5 Hz, 1 H, aromatic-C*H*), 5.11 (q, J = 21.0 Hz, 4 H, NCH_2), 4.65 (dd, J_1 = 10.0 Hz, J_2 = 4.5 Hz, 1 H, CH_2Ph), 3.86 (t, J = 11.0 Hz, 1 H, N*C*HCH_2), 3.21 (m, 4 H, $CH(CH_3)_2$), 2.60 (dd, J_1 = 11.5 Hz, J_2 = 4.5 Hz, 1 H, CH_2Ph), 1.00 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 0.91 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 0.35 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 0.23 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 166.3 (py-*ortho*), 156.3, 153.8, 147.3, 147.0, 142.2, 141.2, 139.5, 137.3, 136.9, 135.9, 132.0, 130.7, 129.2, 129.1, 128.5, 127.2, 126.5, 125.9, 125.3, 124.1, 124.0, 123.4, 121.5, 121.1, 120.7, and 117.7 (aromatic-*C* and iqn*-3-*C*), 94.8 (iqn*-4-*C*), 67.1 (NCH_2), 62.0 (iqn*-1-*C*), 40.7 (CH_2Ph), 27.7, 27.4, 27.3, 27.2, 23.8, and 23.7 ($CHMe_2$ and $CH(CH_3)_2$). Anal. (%) Calcd for $C_{65}H_{69}N_6Y$ (1023.19): C, 76.30; H, 6.80; N, 8.21. Found: C, 75.73; H, 6.82; N, 7.98.

Synthesis of 5^{Lu}-(iqn)$_2$. 1^{Lu}-CH_2Ar (106.1 mg, 0.13 mmol) and 3 equiv of isoquinoline (54.2 mg, 0.42 mmol) were combined in 6 mL of toluene to give a red solution. The reaction mixture was stirred at ambient temperature for 3 h. The volatiles were removed under reduced pressure, and the residue was extracted in diethyl ether and filtered through Celite. The filtrate was layered with *n*-pentane to give an orange solid. Yield: 124.0 mg, 85%. ^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 9.52 (br s, 2 H, iqn-1-C*H*), 7.96 (br s, 2 H, iqn-3-C*H*), 7.23−6.93 (m, 20 H, aromatic-C*H*), 6.86 (d, J = 8.0 Hz, 2 H, aromatic-C*H*), 6.68 (m, 2 H, aromatic-C*H*), 6.29 (s, 2 H, *o*-$Me_2C_6H_3$), 6.19 (d, J = 7.0 Hz, 1 H, NC(CH_3)C*H*), 5.66 (d, J = 7.0 Hz, 1 H, aromatic-C*H*), 5.18 (q, J = 21.0 Hz, 4 H, NCH_2), 4.57 (dd, J_1 = 10.5 Hz, J_2 = 4.5 Hz, 1 H, CH_2-C_6H_3), 3.88 (t, J = 11.0 Hz, 1 H, N*C*HCH_2), 3.19 (m, 2 H, $CH(CH_3)_2$), 3.13 (m, 2 H, $CH(CH_3)_2$), 2.56 (dd, J_1 = 11.0 Hz, J_2 = 4.5 Hz, 1 H, CH_2-C_6H_3), 2.17 (s, 6 H, CH_3-C_6H_3), 1.02 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 0.94 (d, J = 6.5 Hz, 6 H,

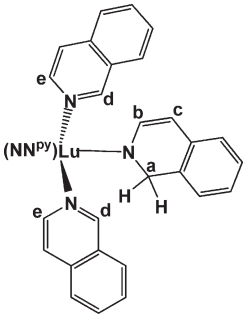
$CH(CH_3)_2$), 0.43 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 0.34 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 166.5 (py-*ortho*), 156.3, 154.5, 147.7, 147.3, 142.1, 141.2, 139.2, 137.4, 136.8, 136.4, 135.9, 132.1, 129.3, 129.2, 128.6, 127.5, 127.1, 126.4, 125.9, 124.1, 123.9, 123.6, 121.6, 120.9, 120.5, and 117.7 (aromatic-*C* and iqn*-3-*C*), 95.0 (iqn*-4-*C*), 67.2 (NCH_2), 62.0 (iqn*-1-*C*), 39.9 (CH_2Ar), 27.6, 27.4, 27.2, 24.1, 24.0, and 21.3 ($CHMe_2$, $CH(CH_3)_2$, and Ar-CH_3).

Synthesis of 6^{Y}-(iqn)$_2$. 1^{Y}-CH_2Ph (107.8 mg, 0.15 mmol) and 4 equiv of isoquinoline (77.8 mg, 0.60 mmol) were combined in 6 mL of toluene to give a red solution. The reaction mixture was stirred at 70 °C for 24 h. The volatiles were removed under reduced pressure, and the residue was extracted with diethyl ether and filtered through Celite. The filtrate was layered with hexanes. The product was isolated as a brown solid and dried under vacuum. Yield: 83.9 mg, 59%.



^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 9.34 (s, 2 H, *d*), 8.09 (br s, 2 H, *e*), 7.23−6.95 (m, 21H, aromatic-C*H*), 6.87 (d, J = 8.0 Hz, 2 H, aromatic-C*H*), 6.60 (d, J = 7.0 Hz, 1 H, *b*), 5.70 (d, J = 6.5 Hz, 1H, *c*), 5.13 (s, 4 H, NCH_2), 4.35 (s, 2 H, *a*), 3.17 (sept, J = 7.0 Hz, 4 H, $CH(CH_3)_2$), 0.95 (d, J = 7.0 Hz, 12 H, $CH(CH_3)_2$), 0.26 (d, J = 7.0 Hz, 12 H, $CH(CH_3)_2$). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 166.5 (py-*ortho*), 156.0, 153.3, 147.0, 141.3, 138.7, 137.2, 135.9, 131.9, 129.3, 129.1, 126.7, 125.9, 125.7, 125.5, 123.8, 123.0, 122.3, 121.5, 119.8, and 117.6 (aromatic-*C* and iqn*-3-*C*), 96.0 (iqn*-4-*C*), 67.0 (NCH_2), 50.6 (iqn*-NCH_2), 27.6, 27.2, and 23.6 ($CHMe_2$ and $CH(CH_3)_2$). Anal. (%) Calcd for $C_{58}H_{63}N_6Y$ (933.07): C, 74.66; H, 6.81; N, 9.01. Found: C, 74.61; H, 6.50; N, 8.96.

Synthesis of 6^{Lu}-(iqn)$_2$. 1^{Lu}-CH_2Ar (100.7 mg, 0.12 mmol) and 4 equiv of isoquinoline (63.3 mg, 0.49 mmol) were combined in 6 mL of toluene to give a red solution. The reaction mixture was stirred at 70 °C for 100 h. The volatiles were removed under reduced pressure, and the residue was extracted in diethyl ether and filtered through Celite. The filtrate was layered with *n*-pentane to give a brown solid. Yield: 95.4 mg, 76%.



^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 9.37 (br s, 2 H, *d*), 7.99 (br s, 2 H, *e*), 7.22−6.82 (m, 23 H, aromatic-C*H*), 6.59 (d, J = 7.0 Hz, 1 H, *b*), 5.73 (d, J = 7.0 Hz, 1 H, *c*), 5.19 (s, 4 H, NCH_2), 4.28 (s, 2 H, *a*), 3.13 (sept, J = 7.0 Hz, 4 H, $CH(CH_3)_2$), 0.94 (d, J = 7.0 Hz, 12 H, $CH(CH_3)_2$), 0.31 (d, J = 7.0 Hz, 12 H, $CH(CH_3)_2$). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 166.7 (py-*ortho*), 156.1, 154.1, 147.4, 147.3, 141.2, 138.6, 137.2, 135.9, 132.0, 129.4, 129.2, 126.8, 125.9, 125.8, 123.8, 123.4, 122.4, 121.6, 119.8, and 117.6 (aromatic-*C* and iqn*-3-*C*), 96.8 (iqn*-4-*C*), 67.3 (NCH_2), 50.7 (iqn*-NCH_2), 27.5, 27.2, and 23.7 ($CHMe_2$ and $CH(CH_3)_2$). Anal. (%) Calcd for $C_{58}H_{63}LuN_6$ (1019.13): C, 68.35; H, 6.23; N, 8.25. Found: C, 68.01; H, 6.10; N, 7.98.

Synthesis of 8. 1^{Y}-CH_2Ph (104.9 mg, 0.15 mmol) and 1 equiv of acridine (26.2 mg, 0.15 mmol) were combined in 6 mL of toluene. The reaction mixture was stirred at room temperature for 2 h. The volatiles were removed under reduced pressure, and the residue was dissolved in diethyl ether and filtered through Celite. The filtrate was layered with hexanes and stored in a −35 °C freezer to give a yellow solid. Yield: 96.3 mg, 74%. ^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 7.13−7.05 (m, 9 H, aromatic-C*H*), 6.99 (t, J = 8.0 Hz, 1 H, aromatic-C*H*), 6.89 (d, J = 7.0 Hz, 2 H, aromatic-C*H*), 6.85 (d, J = 7.5 Hz, 2 H, aromatic-C*H*), 6.74 (t, J = 7.0 Hz, 2 H, acr), 6.64 (t, J = 7.5 Hz, 2 H, acr), 6.61 (d, J = 7.5 Hz, 2 H, aromatic-C*H*), 6.48 (d, J = 7.5 Hz, 2 H, aromatic-C*H*), 5.37 (d, J = 20.0 Hz, 2 H, NCH_2), 4.57 (d, J = 20.0 Hz, 2 H, NCH_2), 4.30 (t, J = 7.0 Hz, 1 H, acr-9-C*H*), 3.93 (m, 2 H, $CH(CH_3)_2$), 3.43 (m, 2 H, $CH(CH_3)_2$), 3.11 (d, J = 7.0 Hz, 2 H, CH_2Ph), 3.07 (m, 4 H, OCH_2CH_2), 1.21 (m, 18 H, $CH(CH_3)_2$), 1.04 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 0.86 (m, 4 H, OCH_2CH_2). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 165.3 (py-*ortho*), 153.1, 148.1, 147.8, 145.6, 140.5, 137.4, 130.5, 130.3, 126.8, 126.0, 125.2, 124.1, 123.4, 123.2, 117.9, 117.4, and 114.3 (aromatic-*C*), 70.8 (OCH_2CH_2), 65.3 (NCH_2), 48.4 ($CHCH_2Ph$), 46.2 (CH_2Ph), 28.8, 28.2, 27.7, 26.3, 24.8, 24.7, and 23.9 ($CHMe_2$, $CH(CH_3)_2$, and OCH_2CH_2). Anal. (%) Calcd for $C_{55}H_{65}N_4OY$ (887.04): C, 74.47; H, 7.39; N, 6.32. Found: C, 74.21; H, 7.35; N, 6.53.

Synthesis of 9. 1^{Lu}-CH_2Ar (108.0 mg, 0.13 mmol) and 1 equiv of acridine (23.4 mg, 0.13 mmol) were combined in 6 mL of toluene. The reaction mixture was stirred under heating at 50 °C for 4 h. The volatiles were removed under reduced pressure, and the residue was washed with small amount of diethyl ether and hexanes. A bright yellow solid was obtained. Yield: 91.9 mg, 80%. ^{1}H NMR (500 MHz, C_6D_6), δ (ppm): 8.35 (s, 1 H, acr), 8.11 (d, J = 6.0 Hz, 1 H, acr), 7.67 (d, J = 8.0 Hz, 1 H, acr), 7.59 (d, J = 8.0 Hz, 1 H, acr), 7.48 (t, J = 7.5 Hz, 1 H, acr), 7.26 (t, J = 7.5 Hz, 1 H, acr), 7.18−6.97 (m, 8 H, aromatic-C*H*), 6.86 (d, J = 7.5 Hz, 2 H, NC_5H_3), 6.59 (d, J = 7.5 Hz, 1 H, acr), 5.31 (d, J = 20.0 Hz, 2 H, NCH_2), 4.88 (d, J = 20.0 Hz, 2 H, NCH_2), 3.66 (sept, J = 6.5 Hz, 2 H, $CH(CH_3)_2$), 3.57 (m, 4 H, OCH_2CH_2), 3.41 (sept, J = 6.5 Hz, 2 H, $CH(CH_3)_2$), 1.33 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 1.24 (m, 4 H, OCH_2CH_2), 1.20 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 0.60 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$), 0.34 (d, J = 6.5 Hz, 6 H, $CH(CH_3)_2$). ^{13}C NMR (126 MHz, C_6D_6), δ (ppm): 166.5 (py-*ortho*), 161.7, 155.0, 147.4, 146.4, 146.2, 140.2, 138.2, 137.0, 129.5, 129.1, 126.9, 126.6, 126.2, 125.5, 124.2, 123.8, 123.1, 123.0, 122.6, and 117.5 (aromatic-*C*), 70.3 (OCH_2CH_2), 66.5 (NCH_2), 27.9, 27.5, 27.1, 26.6, 25.3, 24.7, and 22.4 ($CHMe_2$, $CH(CH_3)_2$, and OCH_2CH_2). Anal. (%) Calcd for $C_{48}H_{57}LuN_4O$ (880.96): C, 65.44; H, 6.52; N, 6.36. Found: C, 65.10; H, 6.40; N, 6.25.

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 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 SAINTPLUS, 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).[45] All atoms were refined anisotropically, and hydrogen atoms were placed in calculated

(45) Sheldrick, G. *Acta Crystallogr. A* **2008**, *64*, 112–122.

positions unless specified otherwise. Tables with atomic coordinates and equivalent isotropic displacement parameters, with all the bond lengths and angles and with anisotropic displacement parameters, are listed in the cifs.

X-ray Crystal Structure of 2^{Y}. X-ray quality crystals were obtained by slow diffusion of *n*-pentane into a diethyl ether solution of $\mathbf{2^{Y}}$ placed in a −35 °C freezer in the glovebox. A total of 38 525 reflections ($-20 \le h \le 20$, $-21 \le k \le 21$, $-24 \le l \le 25$) were collected at $T = 100(2)$ K with $2\theta_{max} = 56.66°$, of which 20 595 were unique ($R_{int} = 0.0459$). The residual peak and hole electron density were 2.54 and −0.84 e Å^{-3}. The unit cell contains two independent molecules of $\mathbf{2^{Y}}$ and two molecules of *n*-pentane solvent. Some methyl groups and solvent atoms were slightly disordered; this disorder was not modeled. The least-squares refinement converged normally with residuals of $R_1 = 0.0565$ and GOF = 1.026. Crystal and refinement data for $\mathbf{2^{Y}}$: formula $C_{44}H_{64}N_7Y$, space group $P\bar{1}$, $a = 15.316(3)$ Å, $b = 16.488(4)$ Å, $c = 18.773(4)$ Å, $\alpha = 68.659(2)°$, $\beta = 78.608(2)°$, $\gamma = 76.991(2)°$, $V = 4267.5(16)$ Å^3, $Z = 4$, $\mu = 1.404$ mm^{-1}, $F(000) = 1664$, $R_1 = 0.0984$ and $wR_2 = 0.1450$ (based on all 20 595 data, $I > 2\sigma(I)$).

X-ray Crystal Structure of 4^{Y}-pic-iqn^{Me}. X-ray quality crystals were obtained by the slow diffusion of hexanes into an Et_2O solution of $\mathbf{4^{Y}}$-pic-iqn^{Me} placed in a −35 °C freezer in the glovebox. A total of 46 597 reflections ($-26 \le h \le 26$, $-18 \le k \le 18$, $-27 \le l \le 28$) were collected at $T = 100(2)$ K with $2\theta_{max} = 58.36°$, of which 12 971 were unique ($R_{int} = 0.0667$). The residual peak and hole electron density were 0.72 and −0.56 e Å^{-3}. The least-squares refinement converged normally with residuals of $R_1 = 0.0476$ and GOF = 1.012. Crystal and refinement data for $\mathbf{4^{Y}}$-pic-iqn^{Me}: formula $C_{57}H_{65}N_6Y$, space group $P2_1/c$, $a = 19.098(3)$ Å, $b = 13.646(2)$ Å, $c = 20.466(3)$ Å, $\beta = 114.859(2)°$, $V = 4839.4(12)$ Å^3, $Z = 4$, $\mu = 1.249$ mm^{-1}, $F(000) = 1952$, $R_1 = 0.0845$ and $wR_2 = 0.1180$ (based on all 12 971 data, $I > 2\sigma(I)$).

X-ray Crystal Structure of 6^{Y}-(iqn)$_2$. X-ray quality crystals were obtained by the slow diffusion of hexanes into an Et_2O/THF solution of $\mathbf{6^{Y}}$-(iqn)$_2$ placed in a −35 °C freezer in the glovebox. A total of 44 508 reflections ($-24 \le h \le 24$, $-15 \le k \le 15$, $-31 \le l \le 30$) were collected at $T = 100(2)$ K with $2\theta_{max} = 56.38°$, of which 12 043 were unique ($R_{int} = 0.0771$). The residual peak and hole electron density were 0.38 and −0.42 e Å^{-3}. The least-squares refinement converged normally with residuals of $R_1 = 0.0476$ and GOF = 1.008. Crystal and refinement data for $\mathbf{6^{Y}}$-(iqn)$_2$: formula $C_{58}H_{63}N_6Y$, space group $P2_1/n$, $a = 18.347(3)$ Å, $b = 11.7235(17)$ Å, $c = 23.396(4)$ Å, $\beta = 99.929(2)°$, $V = 4956.9(13)$ Å^3, $Z = 4$, $\mu = 1.220$ mm^{-1}, $F(000) = 1968$, $R_1 = 0.0884$ and $wR_2 = 0.1047$ (based on all 12 043 data, $I > 2\sigma(I)$).

DFT Calculations. The Amsterdam Density Functional (ADF) package (version ADF2008.01) was used to perform geometry optimizations on Cartesian coordinates of the model compounds specified in the text. For the yttrium, silicon, and iron atoms, standard triple-ζ STA basis sets from the ADF database ZORA TZP were employed with 1s-2p (Si), 1s-3p (Fe), and 1s-4p (Y) electrons treated as frozen cores. For all the other elements, standard double-ζ STA basis sets from the ADF database ZORA DZP were used, with the 1s electrons treated as a frozen core for non-hydrogen atoms. The local density approximation (LDA) by Becke−Perdew was used together with the exchange and correlation corrections that are employed by default by the ADF2008.01 program suite. Calculations for all model compounds were carried out using the spin-unrestricted, scalar spin−orbit relativistic formalism.

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Supporting Information Available: Details of the NMR spectroscopy experiments, DFT calculations, and full crystallographic descriptions (as cif) are available free of charge via the Internet at http://pubs.acs.org. CCDC numbers for $\mathbf{2^{Y}}$, $\mathbf{4^{Y}}$-pic-iqn^{Me}, and $\mathbf{6^{Y}}$-(iqn)$_2$ are 756843, 756844, and 756845, respectively.