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Group 3 Metal Complexes of Radical-Anionic 2,2′-Bipyridyl Ligands

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A new method for generating group 3 metal complexes containing radical-anionic 2,2′-bipyridyl (bipy) ligands is described that relies on hydrogen-atom abstraction from dearomatized biheterocyclic complexes. This method does not involve electron transfer to neutral 2,2′-bipyridyl or salt metathesis between the lithium salt of the 2,2′-bipyridyl radical anion and group 3 metal halides. The new metal complexes were characterized by single-crystal X-ray diffraction, electron paramagnetic resonance, and absorption spectroscopy. Density functional theory (DFT) calculations were used to probe the electronic structure of these compounds. All these methods support the radical-anionic character of bipy in all bipy compounds presented.

Introduction

Most metals are known to form complexes with 2,2′-bipyridyl (bipy).[1,2] For a low-valent, electropositive metal, the bipy ligand is commonly reduced to its corresponding radical anion, with the concomitant oxidation of the metal center. Examples of lanthanide and actinide complexes containing bipy as a radical-anionic ligand[3] have been reported increasingly in recent years: $(\mathrm{Me_5C_5})_2\mathrm{Yb(bipy)}$,[4−6] $\mathrm{YbI(bipy)(DME)_2}$ (DME = 1,2-dimethoxyethane),[7] $(\mathrm{Me_5C_5})_2\mathrm{Sm(bipy)}$,[8] $\mathrm{Eu(bipy)_4}$,[9] $[\mathrm{U(NCS)_5(bipy)_2}]^-$,[10] $\mathrm{(bipy)_2U(N^tBu[3,5\text{-}C_6H_3\text{-}Me_2])_2}$,[11] $\mathrm{(bipy)U(NAd[3,5\text{-}C_6H_3Me_2])_3}$ (Ad = 1-adamantyl),[11] $\mathrm{(bipy)_2U(NC^tBuMes)_3}$ (Mes = 2,4,6-$\mathrm{C_6H_2Me_3}$),[11] $\mathrm{Tp^*{}_2U(bipy)}$ (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate).[12]

It is interesting to note that the above complexes are synthesized via the direct reduction of neutral bipy by a low-valent, redox-active metal center, a reaction that requires that the redox potential of the metal is appropriate to effect the reduction of the bipy ligand. The same method was applied to the formation of metal complexes containing related nitrogen-based radical anions as ligands.[13−15] Redox processes were also involved in the synthesis of redox-inactive group 3 metal complexes containing a bipy radical anion. Examples include $\mathrm{LaI_2(bipy)(bipy)(DME)}$ and $[\mathrm{C_5H_4\text{-}(CH_2)_2\text{-}NMe_2}]\mathrm{Sc(bipy')_2}$ (bipy′ = 4,4′-dimethyl-bipy), which were formed by transferring an electron to neutral bipy from the reduced naphthalene ligand of $[\mathrm{LaI_2(THF)_3}]_2[\mathrm{C_{10}H_8}]$[16] and from the 2,3-dimethyl-1,3-butadiene dianion of $[\mathrm{C_5H_4\text{-}(CH_2)_2NMe_2}]\mathrm{Sc(C_6H_{10})}$, respectively.[17] Similarly, $\mathrm{Tp^*Y(bipy)(THF)_2}$ and $\mathrm{Tp^*{}_2La(bipy)}$ were obtained by the sodium-amalgam reduction of halide precursors.[18] Furthermore, the yttrium diazadiene complex Y(s,s′-*N*,*N*′-dab)$_3$ (dab = ^{t}Bu-N=CH—CH=N—^{t}Bu) was synthesized by the co-condensation of yttrium vapors with the diazadiene.[19]

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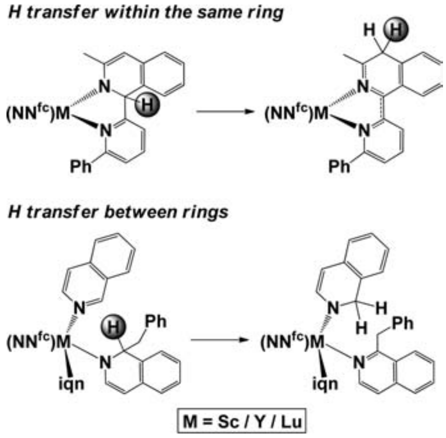
Scheme 1. Hydrogen-Transfer Processes in Dearomatized Heterocyclic Complexes of Group 3 Metals

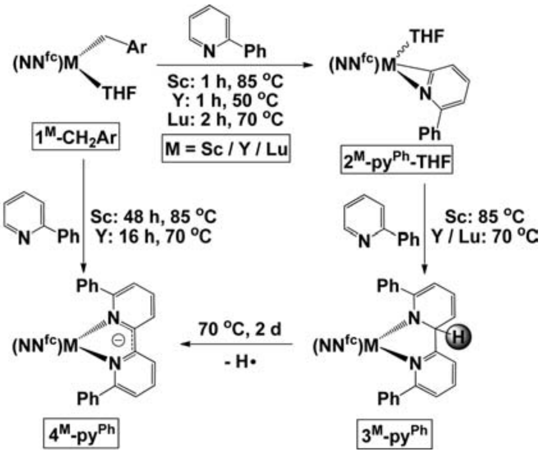


Synthetic methods that do not involve electron transfer are based on salt-metathesis reactions between the lithium salt of the bipy radical anion and group 3 metal halides.[20−22] Herein, we report the characterization of group 3 metal (scandium, yttrium, and lutetium) complexes containing radical-anionic bipy ligands; the synthesis of these complexes is based on H· abstraction from a dearomatized biheterocyclic ligand, which, in turn, is obtained by the C−C coupling of pyridines.

Results and Discussion

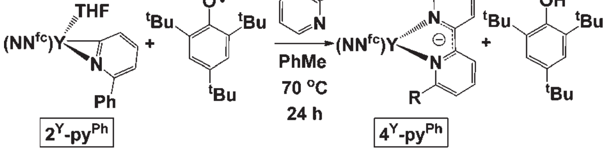
Synthesis of Complexes. Our group has been studying the reactivity of d^{0}f^n-metal complexes supported by ferrocene-based chelating ligands[23−29] toward aromatic N-heterocycles.[28−36] When ortho-substituted pyridines are employed, C−H activation and C−C coupling of the two heteroaromatic rings take place. The coupling reaction is accompanied by the dearomatization of one of the heterocycles.[26,29,37] In the case of isoquinoline and chelating pyridines, alkyl transfer was observed instead of C−H activation. The products of the C−C coupling or the alkyl-transfer reactions were found to undergo subsequent hydrogen transfers: within the same ring for the former and between two different heterocycles for the latter (Scheme 1).

Scheme 2. Synthesis of Group 3 Metal Complexes Containing Substituted, Radical-Anionic bipy Ligands



As reported earlier, the reaction between (NN^{fc})Sc(CH$_2$Ar)(THF) (**1^{Sc}-CH$_2$Ar**, NN^{fc} = 1,1′-fc(NSi^{t}BuMe$_2$)$_2$, Ar = 3,5-Me$_2$C$_6$H$_3$) and 2-phenylpyridine led to the C−H-activated product **2^{Sc}-py^{Ph}-THF**, which reacted with another equivalent of 2-phenylpyridine to give the coupling product **3^{Sc}-py^{Ph}** (Scheme 2).[26,29] The analogous reaction of the yttrium and lutetium complexes (NN^{fc})M(CH$_2$Ar)(THF) (M = Y, Ar = Ph: **1^{Y}-CH$_2$Ph**; M = Lu, Ar = 3,5-Me$_2$C$_6$H$_3$, **1^{Lu}-CH$_2$Ar**) produced the coupling products **3^{M}-py^{Ph}** in toluene after 6 h (Lu) or in C$_6$H$_6$ after 1 h (Y) at 70 °C, as established from monitoring the reaction mixtures by ^{1}H NMR spectroscopy (the conditions for these reactions are not shown in Scheme 2; the formation of **3^{M}-py^{Ph}** was assessed by comparing spectra of the reaction mixtures with those of other pyridine-coupling products).[37]

Surprisingly, crystals obtained after the workup of the yttrium and lutetium reaction mixtures suggested solid-state structures (**4^{M}-py^{Ph}**, Figure 1) that did not agree with the conclusions of the ^{1}H NMR spectroscopy experiments: the biheterocyclic fragment was symmetrical and no sp^3-hybridized carbon atom could be identified. It is likely that a mixture of **3^{M}-py^{Ph}** and **4^{M}-py^{Ph}** was present at the beginning of the crystallization process, but the presence of **4^{M}-py^{Ph}** could not be detected by ^{1}H NMR spectroscopy because of its paramagnetism (although some broad peaks are apparent in the spectra, they overlap with peaks corresponding to diamagnetic molecules).



(1)

It is reasonable that to obtain **4^{M}-py^{Ph}** from **3^{M}-py^{Ph}** (M = Y, Lu), an H·acceptor has to be present during the transformation. The moderate yields (47% for yttrium and 46% for lutetium) and the presence of unidentified

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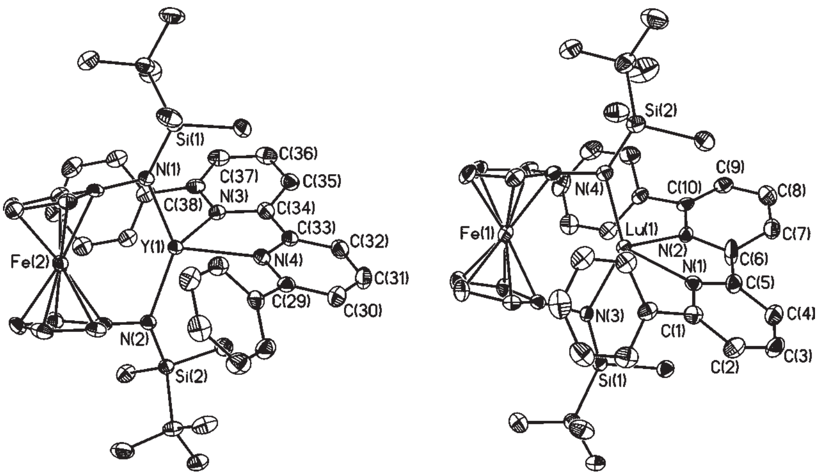
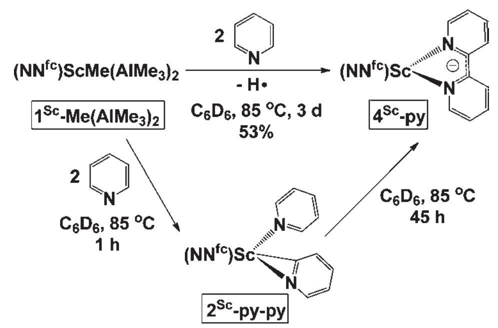


Figure 1. Thermal-ellipsoid (50% probability) representation of $\mathbf{4^{Y}}$**-py**$^{\mathbf{Ph}}$ (left) and $\mathbf{4^{Lu}}$**-py**$^{\mathbf{Ph}}$ (right); hydrogen atoms were removed for clarity. Selected metrical parameters for $\mathbf{4^{Y}}$**-py**$^{\mathbf{Ph}}$ (distances in Å and angles in deg): Y(1)−N(1), 2.2197(20); Y(1)−N(2), 2.2115(20); Y(1)−N(3), 2.3706(22); Y(1)−N(4), 2.3787(21); N(1)Y(1)N(2), 135.75(8); N(1)Y(1)N(3), 99.26(7); N(1)Y(1)N(4), 112.00(7); N(2)Y(1)N(3), 116.59(7); N(2)Y(1)N(4), 104.50(7); N(3)Y(1)N(4), 69.84(7). Selected metrical parameters for $\mathbf{4^{Lu}}$**-py**$^{\mathbf{Ph}}$ (distances in Å and angles in deg): Lu(1)−N(1), 2.3403(32); Lu(1)−N(2), 2.2478(32); Lu(1)−N(3), 2.1739(31); Lu(1)−N(4), 2.1864(31); N(1)Lu(1)N(2), 72.24(11); N(1)Lu(1)N(3), 96.63(11); N(1)Lu(1)N(4), 115.65(12); N(2)Lu(1)N(3), 112.82(12); N(2)Lu(1)N(4), 103.50(12); N(3)Lu(1)N(4), 137.37(12).

byproducts are consistent with this interpretation. To increase the yield and to verify the above hypothesis, the reaction of $\mathbf{2^{Y}}$**-py**$^{\mathbf{Ph}}$ with 2-phenylpyridine was carried out in the presence of 2,4,6-tri-*t*-butylphenoxyl[38] (eq 1). The use of the phenoxyl radical led to high conversions (76% after recrystallization) and almost no byproduct formation. Surprisingly, when $\mathbf{4^{Lu}}$**-py**$^{\mathbf{Ph}}$ was obtained from $\mathbf{1^{Lu}}$**-CH**$_{\mathbf{2}}$**Ar** in the presence of $AlMe_3$, the yield was 72%. Methylaluminoxane and trialkyl aluminum complexes have been reported to act as co-catalysts in the dehydrogenation of cyclooctane by group 4 metal compounds.[39] This report highlights that the dehydrogenation reactions occur in the absence of a hydrogen acceptor; those results suggested to us that the co-catalyst may fulfill its function, as observed with the formation of $\mathbf{4^{Lu}}$**-py**$^{\mathbf{Ph}}$ in the presence of $AlMe_3$.

The following mechanistic scenario is proposed that is consistent with the data described above (Scheme 2). The observation of $\mathbf{3^{M}}$**-py**$^{\mathbf{Ph}}$ in the ^{1}H NMR spectra of the crude reaction mixtures indicates that this complex is a possible intermediate. In addition, the radical-anionic bipy complexes $\mathbf{4^{M}}$**-py**$^{\mathbf{Ph}}$ are likely more stable than $\mathbf{3^{M}}$**-py**$^{\mathbf{Ph}}$. It is possible that H· forms H_2 (although it was not observed by ^{1}H NMR spectroscopy) and/or impurities formed in the original reaction mixtures act as hydrogen acceptors in the initial stages of generating $\mathbf{4^{M}}$**-py**$^{\mathbf{Ph}}$. The byproducts of these reactions may decompose and provide other sources of hydrogen acceptors or act as hydrogen acceptors themselves. Given the prolonged reaction times and high temperatures, the decomposition of the starting material and/or the product may also occur. This proposal is consistent with the moderate yield observed and its increase when a hydrogen acceptor was added at the beginning of the reaction (eq 1).

Scheme 3. Synthesis of $\mathbf{4^{Sc}}$**-py**



We became interested in determining whether the formation of an analogous scandium bipy complex, $\mathbf{4^{Sc}}$**-py**$^{\mathbf{Ph}}$ was possible. By heating a solution of $\mathbf{2^{Sc}}$**-py**$^{\mathbf{Ph}}$ and phenylpyridine or carrying out the direct reaction of $\mathbf{1^{Sc}}$**-CH**$_{\mathbf{2}}$**Ar** with excess 2-phenylpyridine, the scandium complex $\mathbf{4^{Sc}}$**-py**$^{\mathbf{Ph}}$ was also isolated (Scheme 2). Interestingly, the parent scandium bipy radical-anion complex, $\mathbf{4^{Sc}}$**-py**, could be obtained by a different method (Scheme 3). In this process, the scandium η^2-N,C-pyridyl pyridine complex, (NN^{fc})Sc(η^2-N,C-py)py ($\mathbf{2^{Sc}}$**-py-py**),[23] was generated from the scandium methyl precursors (NN^{fc})ScMe(AlMe$_3$)$_2$ ($\mathbf{1^{Sc}}$**-Me(AlMe**$_{\mathbf{3}}$**)**$_{\mathbf{2}}$) or (NN^{fc})ScMe(THF)$_2$ ($\mathbf{1^{Sc}}$**-Me**).[40] Heating $\mathbf{2^{Sc}}$**-py-py** led to the formation of $\mathbf{4^{Sc}}$**-py**. The complex $\mathbf{4^{Sc}}$**-py** was isolated in 53% yield from the direct reaction of $\mathbf{1^{Sc}}$**-Me(AlMe**$_{\mathbf{3}}$**)**$_{\mathbf{2}}$ and pyridine (Scheme 3).

Structural Characterization. The X-ray crystal structures of $\mathbf{4^{Y}}$**-py**$^{\mathbf{Ph}}$ and $\mathbf{4^{Lu}}$**-py**$^{\mathbf{Ph}}$ were determined and confirmed the radical-anionic character of the bipyridyl ligand. Since the lowest unoccupied molecular orbital (LUMO) of bipy has a π bond between the carbon atoms connecting the aromatic rings, shortening of the bond between these atoms and enhanced coplanarity of the two rings are signatures that the bipy ligand is coordinated as

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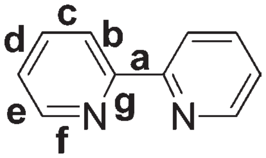
Table 1. Comparison of Distances (Å) in bipy and in Discussed Complexes



bond	bipy[10]	$\mathbf{4^{Y}\text{-}py^{Ph}}$	$\mathbf{4^{Lu}\text{-}py^{Ph}}$
a	1.490(3)	1.4208(36)	1.4678(58)
b	1.394(2)	1.4214(36)	1.3971(56)
		1.4105(36)	1.4091(58)
c	1.385(2)	1.3677(39)	1.3669(58)
		1.3637(39)	1.3684(61)
d	1.383(3)	1.3991(40)	1.3844(59)
		1.4110(41)	1.4134(60)
e	1.384(2)	1.3717(37)	1.3871(55)
		1.3744(36)	1.3628(55)
f	1.341(2)	1.3725(31)	1.3661(48)
		1.3721(32)	1.3797(47)
g	1.346(2)	1.3904(32)	1.3729(49)
		1.3898(33)	1.3797(47)

a radical anion.[41,42] The C−C distance between the two pyridine rings is 1.4208(36) Å in $\mathbf{4^{Y}\text{-}py^{Ph}}$ and 1.4678(58) Å in $\mathbf{4^{Lu}\text{-}py^{Ph}}$ (vs 1.490(3) Å in bipy, Table 1) respectively, while the corresponding torsion angles (NCCN and CCCC) are 14.11(34) and 19.07(39)° in $\mathbf{4^{Y}\text{-}py^{Ph}}$ and 13.97(62) and 40.71(70)° in $\mathbf{4^{Lu}\text{-}py^{Ph}}$, respectively. The C−C distance and the CCCC torsion angle in $\mathbf{4^{Lu}\text{-}py^{Ph}}$ are rather large compared to the same values in $\mathbf{4^{Y}\text{-}py^{Ph}}$, but other parameters are comparable for the two complexes (Figure 1 and Table 1). It is possible that the difference in the torsion angles of the two complexes is a consequence of crystal-packing effects. The other bipy C−C and C−N distances found in $\mathbf{4^{Y}\text{-}py^{Ph}}$ and $\mathbf{4^{Lu}\text{-}py^{Ph}}$ are also in agreement with the radical-anionic character of the bipy ligand (Table 1). Acceptance of an electron into the LUMO of bipy causes the bonds (Table 1) **a**, **c**, and **e** to shorten and the bonds **b**, **d**, **f**, and **g** to lengthen,[4] as was observed for $\mathbf{4^{Y}\text{-}py^{Ph}}$ and $\mathbf{4^{Lu}\text{-}py^{Ph}}$.

Spectroscopical Characterization. The radical-anionic character of the bipyridyl ligand was confirmed by electron paramagnetic resonance (EPR, Figure 2) and UV−vis−NIR spectroscopy (Figure 3). For $\mathbf{4^{Y}\text{-}py^{Ph}}$, the EPR spectrum (see the Supporting Information for spectra of the other bipy complexes) collected at 190 K showed a single feature, with a hyperfine structure and a *g* value of 2.0048. A simulation of the spectrum led to the following coupling constants: 5.33 G for ^{89}Y, 3.91 G for ^{1}H, 1.34 G for ^{14}N, and 1.16 G for ^{13}C, also consistent with the presence of an organic radical.

The bipy radical anion has a diagnostic optical spectrum with three intense ($\varepsilon \approx 10^3$ M^{-1} cm^{-1}) absorption bands in the 700−1000 nm region.[4] Absorption spectra of $\mathbf{4^{Y}\text{-}py^{Ph}}$ in toluene solutions at 25 °C are shown in Figure 3. Bands present in the UV region (200−400 nm) were assigned to $\pi \rightarrow \pi^*$ transitions of the arene rings or to ligand to metal charge transfer because of their high intensity ($\varepsilon \approx 10^5$ M^{-1} cm^{-1}, see the Supporting Information for details). The bands at 601 (1842 M^{-1} cm^{-1}) and 850 nm (763 M^{-1} cm^{-1}) were attributed to the bipy radical anion. Absorption bands that have $\varepsilon \approx 10^3$ M^{-1} cm^{-1} and are present in the visible region (400−800 nm) could also be charge-transfer transitions, and they may overlap with transitions due to the radical-anionic bipy ligand.

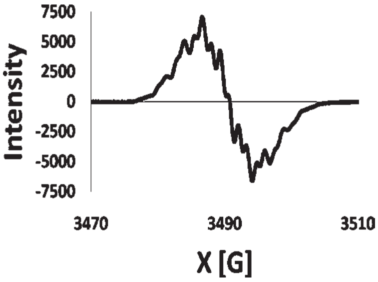


Figure 2. EPR spectrum (toluene, 190 K) of $\mathbf{4^{Y}\text{-}py^{Ph}}$.

Density Functional Theory (DFT) Calculations. DFT calculations were carried out with ADF2009.01[43−45] to probe the electronic structure of $\mathbf{4^{M}\text{-}py^{Ph}}$. Calculations were performed on the full molecule for $\mathbf{4^{Y}\text{-}py^{Ph}}$. Geometry optimizations were carried out with relativistic corrections, and the results indicated that the model showed similar metrical parameters to those obtained from the X-ray crystal structures for $\mathbf{4^{Y}\text{-}py^{Ph}}$ (Table 2).

The agreement between the calculated metrical parameters and those obtained from crystallography indicates that the computational model may be used to probe the electronic structure of $\mathbf{4^{Y}\text{-}py^{Ph}}$. The frontier molecular orbitals of $\mathbf{4^{Y}\text{-}py^{Ph}}$ were inspected (Figure 4). Both SOMO (defined as the highest singly occupied molecular orbital with spin α) and LUMO (defined as the lowest unoccupied molecular orbital with spin α) are bipy based with almost no contribution from the metal. The DFT calculations confirmed the assignment of the bipy ligand in $\mathbf{4^{Y}\text{-}py^{Ph}}$ as a radical anion since the unpaired electron was found in a molecular orbital corresponding to the LUMO of free bipy.

Conclusions. A new method for generating group 3 metal complexes containing radical-anionic 2,2′-bipyridyl ligands is reported. This method relies on hydrogen-atom abstraction from dearomatized biheterocyclic complexes, which can be obtained by coupling two pyridine substrates. The new bipy metal complexes were characterized by single-crystal X-ray diffraction, EPR, and absorption spectroscopy. DFT calculations were used to probe the electronic structure of these compounds. All these methods support the radical-anionic character of bipy in the newly synthesized complexes.

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[46]

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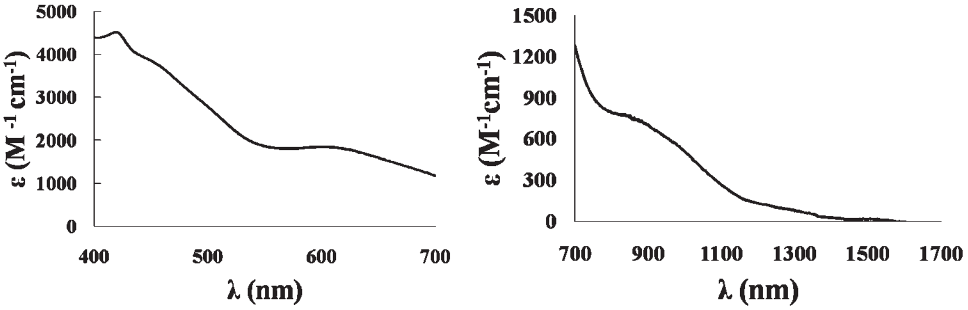
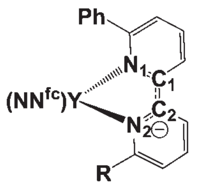


Figure 3. Absorption spectra (toluene, 25 °C) of **4^{Y}-py^{Ph}**: left, 0.5 mM, and right, 5 mM.

Table 2. Comparison of Metrical Parameters from Calculated (ADF) and X-ray Crystal Structures (Experimental) for **4^{Y}-py^{Ph}**

Complex	Parameter	ADF	Experimental
	Y−N_{fc}	2.26 Å	2.21 Å
	Y−N_{fc}	2.26 Å	2.22 Å
	Y−N1	2.39 Å	2.37 Å
	Y−N2	2.40 Å	2.38 Å
	C1−C2	1.44 Å	1.42 Å
	N1−C1	1.41 Å	1.39 Å
	N2−C2	1.41 Å	1.39 Å
	N1YN2	70.0°	69.8°
	N1C1C2N2	11.7°	14.1°
	$N_{fc}YN_{fc}$	134.7°	135.7°

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. Scandium, yttrium, and lutetium oxides were purchased from Stanford Materials Corporation, 4 Meadowpoint, Aliso Viejo, CA 92656, and used as received. K(CH_2Xy-3,5), KCH_2Ph, **1^{M}-CH_2Ar**, **1^{Sc}-Me**, **1^{Sc}-Me($AlMe_3$)$_2$**, and **2^{M}-py^{Ph}-THF** were prepared following published procedures.[26,29,40] Complexes **4^{M}** show only broad peaks in their NMR spectra. EPR spectra were collected on a BrukerEMX EPR spectrometer. UV−vis−NIR spectra were recorded on a Shimadzu UV-3101PC UV−vis−NIR scanning spectrophotometer from 200 to 1600 nm using matched 1 cm quartz cells; all spectra were obtained using a solvent reference blank in a cuvette with an air-free Teflon adapter. CHN analyses were performed by Midwest Microlab, LLC, 7212 N. Shadeland Avenue, Suite 110, Indianapolis, IN 46250.

Synthesis of 4^{Y}-py^{Ph}. **1^{Y}-CH_2Ph** (124.0 mg, 0.181 mmol) was combined with 2 equiv of 2-phenylpyridine (56.1 mg, 0.361 mmol) in toluene (5 mL). The mixture was stirred in a Schlenk tube for 16 h at 50 °C. Removal of the volatiles under reduced pressure led to a black solid, which was dissolved in hexanes. Cooling to −35 °C overnight afforded black crystals. Yield: 71.5 mg, 47.2%. Compound **4^{Y}-py^{Ph}** could also be obtained directly from the compound **2^{Y}-py^{Ph}-THF** with 1 equiv 2-phenylpyridine (2 d, 70 °C, 36.3%). UV (toluene, 0.05 mM, 25 °C), λ in nm (ε in M^{-1} cm^{-1}): 310 (8078). Vis (toluene 0.5 mM, 25 °C) λ in nm (ε in M^{-1} cm^{-1}): 419 (4514), 601 (1842). NIR (toluene, 5 mM, 25 °C), λ in nm (ε in M^{-1} cm^{-1}): 850 (763). Anal. (%): Calcd. for $C_{44}H_{54}N_4FeSi_2Y$: C, 57.20; H, 6.48; N, 5.00. Found: C, 57.69; H, 6.20; N, 5.32.

Synthesis of 4^{Lu}-py^{Ph}. Method A. This method describes how the crystals of **4^{Lu}-py^{Ph}** were obtained originally. **1^{Lu}-CH_2Ar** (196.2 mg, 0.243 mmol) was measured. Next, 4 equiv of 2-phenylpyridine (150.6 mg, 0.970 mmol) was measured. The reagents were combined in approximately 5 mL of toluene in a Schlenk tube equipped with a magnetic stir bar. The solution was heated and stirred at 70 °C for 6 h. The volatiles were removed under reduced pressure, giving a dark solid. To the solid was then added 3 mL of *n*-pentane, and the suspension filtered through Celite. The remaining solid was then extracted with toluene into a separate vial. The toluene portion was dried under reduced pressure, and the resulting solid was taken up in a minimal amount of hexanes. Cooling to −35 °C overnight afforded black crystals. Yield: 72.2 mg, 45.7%.

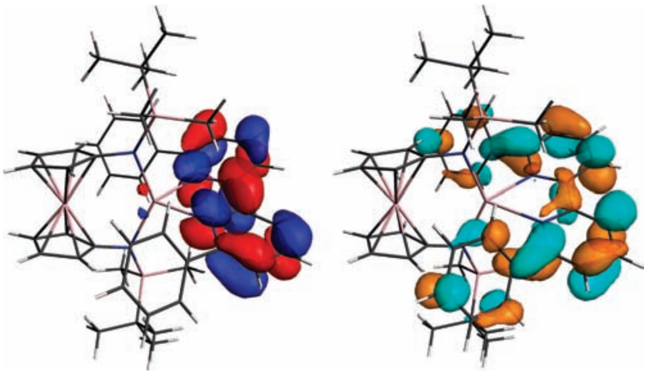


Figure 4. SOMO (left) and LUMO (right) of **4^{Y}-py^{Ph}**.

Method B. This method describes how **4^{Lu}-py^{Ph}** was obtained on a preparative scale. The use of $AlMe_3$ increased the yield of the desired product. Two reactions were done in parallel and later combined. **1^{Lu}-CH_2Ar** (100.0 mg each, 0.124 mmol each) was measured into two separate vials and dissolved into approximately 1 mL of toluene. To each vial, 3 equiv of $AlMe_3$ (26.8 mg, 0.371 mmol) was added. The solutions were stirred for 10 min. Next, 6 equiv of 2-phenylpyridine (115.1 mg, 0.742 mmol) was added to each vial. The orange solutions were transferred to a Schlenk tube and diluted to ~5 mL of toluene. The Schlenk tubes were sealed and heated to 85 °C while stirring. After a day of stirring, the solutions were black. The solutions were allowed to stir for 11 days total at 85 °C. At this point, the solutions were combined and dried under reduced pressure. The product was washed through Celite over a glass frit with five separate 1 mL portions of *n*-pentane. The remaining solid was washed into a separate flask with toluene. The pentane solution, which contained aluminum byproducts, was discarded. The toluene portion was concentrated under vacuum and layered with *n*-pentane. Cooling this solution to −35 °C allowed the formation of black crystals of **4^{Lu}-py^{Ph}**. Yield: 176.5 mg, 72.1%. The lutetium complex could not be purified to obtain satisfactory analytical data. Because of its paramagnetism, it was difficult to assess whether it decomposes readily or it could not be purified. The results of one analytical sample are included. Anal. (%): Calcd. for $C_{44}H_{54}N_4FeSi_2Lu$: C, 57.08; H, 5.88; N, 6.05. Found: C, 55.67; H, 5.62; N, 5.27.

Synthesis of 4^{Sc}-py^{Ph}. Compound **1^{Sc}-CH_2Ar** (35.0 mg, 0.0516 mmol) was dissolved in C_6D_6 and then 2-phenylpyridine (17.0 mg, 0.110 mmol) was added. The mixture was heated at 85 °C for 2 d. The color changed from yellow to red, then green (coupling product **3^{Sc}-py^{Ph}**), and finally to dark. The volatiles were removed under reduced pressure and the resulting dark solid was extracted into hexanes and the solution filtered through Celite. Greenish-black crystals formed from concentrated hexanes at −35 °C. Yield: 28.8 mg, 70.2%.

Reaction of 2^{Y}-py^{Ph}-THF with 2,4,6-Tri-*t*-butylphenoxyl. **2^{Y}-py^{Ph}-THF** (26.7 mg, 0.0352 mmol) was combined with 1 equiv of 2-phenylpyridine (5.5 mg, 0.0354 mmol) and 1 equiv of 2,4,6-tri^{t}Bu-phenoxyl (9.3 mg, 0.0356 mmol) dissolved in C_6D_6 (1.5 mL). The solution was then heated in a J-Young NMR tube at 70 °C for 24 h. An ^{1}H NMR spectrum taken at this time confirmed the formation of 2,4,6-tri-^{t}Bu-phenol, after which the solution was dried under reduced pressure. Dissolving the solid in hexanes and cooling to −35 °C afforded a black powder. **4^{Y}-py^{Ph}** was obtained by repeated crystallizations until no impurities were evidenced in its ^{1}H NMR spectrum (under the consideration that the impurities were diamagnetic; the same method was used to purify the compound for elemental analysis). Yield: 22.4 mg, 75.8%.

Synthesis of 4^{Sc}-py. Method A. Compound **1^{Sc}-Me(AlMe$_3$)$_2$** (223.5 mg, 0.346 mmol) was dissolved in 5 mL of toluene and then pyridine (210 mg, 2.655 mmol) was added. The mixture was heated at 85 °C. The color changed from yellow to dark red after one day, but the reaction mixture was kept on 85 °C for two more days. The volatiles were removed under reduced pressure, the resulting dark solid was extracted into hexanes, and the solution filtered through Celite. Black crystals formed from concentrated hexanes at −35 °C. Yield: 118.7 mg, 53.3%. Anal. (%): Calcd. for $C_{32}H_{46}N_4FeSi_2Sc$ (MW = 643.721) C, 59.71; H, 7.20; N 8.70. Found: C, 59.98; H, 7.44; N, 8.72.

Method B. Compound **1^{Sc}-Me** (75.0 mg, 0.116 mmol) was dissolved in 5 mL of toluene and then pyridine (46.0 mg, 0.582 mmol) was added. The mixture was heated at 85 °C for 3 days. The volatiles were removed under reduced pressure, the resulting dark solid was extracted into hexanes, and the solution filtered through Celite. Black crystals formed from concentrated hexanes at −35 °C. Yield: 19.5 mg, 26.1%. Attempts to get more crystals out from the mother liquor failed even with using *n*-pentane as a solvent.

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 MoK$_{\alpha}$ radiation and a SMART APEX CCD detector. The data was 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). 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 the bond lengths and angles, and with anisotropic displacement parameters are listed in the cifs in the Supporting Information.

X-ray Crystal Structure of 4^{Y}-py^{Ph}. X-ray quality crystals were obtained from a concentrated hexanes solution. A total of 10663 reflections ($-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-25 \leq l \leq 24$) was collected at T = 100(2) K with $2\theta_{max}$ = 56.63°, of which 8016 were unique (R_{int} = 0.0344). The residual peak and hole electron density were 0.49 and −0.43 e A^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0422 and GOF = 1.015. Crystal and refinement data for **4^{Y}-py^{Ph}**: formula $C_{44}H_{54}N_4Si_2YFe \cdot 0.5(C_6H_{14})$, triclinic, space group $P\bar{1}$, a = 10.995(2) Å, b = 11.243(2) Å, c = 18.766(4) Å, α = 80.676(2)°, β = 75.471(2)°, γ = 84.537(2)°, V = 2212.3(8) Å^3, Z = 2, μ = 1.724 mm^{-1}, F(000) = 928, R_1 = 0.0610, wR_2 = 0.0992 (for all data).

X-ray Crystal Structure of 4^{Lu}-py^{Ph}. X-ray quality crystals were obtained from a concentrated *n*-pentane solution. A total of 10934 reflections ($-23 \leq h \leq 23$, $-14 \leq k \leq 15$, $-30 \leq l \leq 29$) was collected at T = 100(2) K with $2\theta_{max}$ = 56.50°, of which 7763 were unique (R_{int} = 0.0677). The residual peak and hole electron density were 1.47 and −0.83 e A^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0389 and GOF = 1.009. Crystal and refinement data for **4^{Lu}-py^{Ph}**: formula $2(C_{44}H_{54}N_4Si_2LuFe) \cdot C_5H_6$, monoclinic, space group $P2_1/c$, a = 17.541(2) Å, b = 11.3868(14) Å, c = 22.597(3) Å, β = 99.954(1)°, V = 4445.6(10) Å^3, Z = 2, μ = 2.624 mm^{-1}, F(000) = 1956, R_1 = 0.0675, wR_2 = 0.0842 (for all data).

DFT Calculations. The Amsterdam Density Functional (ADF) package (version ADF2009.01)[43−45] was used to do geometry optimizations on Cartesian coordinates obtained from the crystal structure of **4^{Y}-py^{Ph}**. For the yttrium 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-4d (Y), and 1s (C, N, O) electrons treated as frozen cores. The local density approximation (LDA) by Becke-Perdew was used together with the exchange and correlation corrections that are employed by default by the ADF2009.01 program suite. Calculations were carried out using the spin-unrestricted, scalar spin−orbit relativistic formalism.

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Supporting Information Available: Experimental details for compound characterizations and DFT calculations, and full crystallographic descriptions (as cif). This material is available free of charge via the Internet at http://pubs.acs.org.