Inorganic Chemistry

ARTICLE

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Synthesis and Characterization of Cerium and Yttrium Alkoxide Complexes Supported by Ferrocene-Based Chelating Ligands

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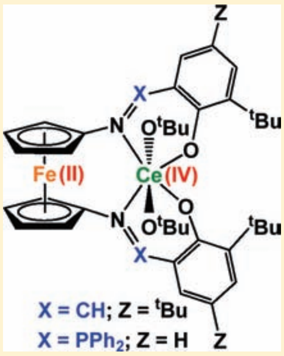
S Supporting Information

ABSTRACT: Two series of Schiff base metal complexes were investigated, where each series was supported by an ancillary ligand incorporating a ferrocene backbone and different N=X functionalities. One ligand is based on an imine, while the other is based on an iminophosphorane group. Cerium(IV), cerium(III), and yttrium(III) alkoxide complexes supported by the two ligands were synthesized. All metal complexes were characterized by cyclic voltammetry. Additionally, NMR, Mössbauer, X-ray absorption near-edge structure (XANES), and absorption spectroscopies were used. The experimental data indicate that iron remains in the +2 oxidation state and that cerium(IV) does not engage in a redox behavior with the ancillary ligand.



INTRODUCTION

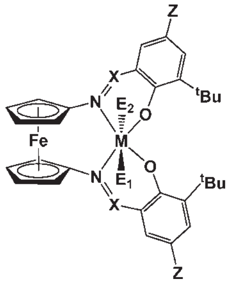
Ancillary ligand design in organometallic chemistry has recently taken on a new dimension as reports of modulated metal reactivity by direct ligand involvement in reactions are being demonstrated.[1−4] Redox-active ligands have been classified by Mirkin as follows: (1) substitutionally inert, redox-active ligands, (2) redox-switchable hemilabile ligands, and (3) redox-active ligands that are reactive (leaving) fragments in a metal complex.[5] We have been pursuing the study of 1,1′-disubstituted, ferrocene-based chelating ligands as versatile frameworks in supporting group 3 metal and uranium complexes.[6,7] Such ligands are substitutionally inert, redox-active ligands and open avenues in controlling the reactivity of a metal center by changing the oxidation state of ferrocene.[5,8−14]

Metallocene-based chelating ligands offer the possibility to engage a redox-active metal center in strong electronic communication, raising the possibility of redox isomerism.[15−17] To test if such a situation occurs between ferrocene and a lanthanide, cerium, we focused on Schiff bases incorporating ferrocene. 1,1′-Di(2,4-bis-*tert*-butyl-salicylimino)ferrocene (**1-H$_2$**, Chart 1) has already been used to generate various metal complexes; the Arnold group synthesized and characterized magnesium, titanium, and zirconium complexes,[18] while our group reported yttrium and cerium(IV) complexes.[19] The redox properties of those compounds were not investigated.

While complexes of transition metals have been targeted before to study redox isomerism,[15,18,20−24] lanthanide and actinide examples are still limited.[19,25] With a strongly oxidizing metal center like cerium(IV), there exists the potential for redox events to occur, effectively changing the ferrocene backbone of the ancillary ligand into ferrocenium upon complexation. Cerium(IV) is a good candidate for this process since it has a redox potential of 0.88 V in water, while ferrocene has a redox potential of 0.00 V (both measured versus Cp$_2$Fe/Cp$_2$Fe$^+$).[26] It is important to note that although the structures of Schiff base metal complexes have been thoroughly studied,[27] complexes of d^{0}f^n metals have not been the subject of electrochemical investigations, with the exception of some uranyl complexes.[28,29] Several studies of the electrochemical properties of Schiff base metal complexes were reported[30,31] and, in certain cases, ligand-based oxidations were identified.[32−43] Herein, we report the synthesis of cerium(IV) alkoxides supported by **1** to determine whether cerium(IV) could oxidize the ferrocene backbone or a different functionality of the ancillary ligand. For comparison, cerium(III) and yttrium(III) alkoxides were also synthesized (Chart 1). These complexes were characterized by cyclic voltammetry and NMR, Mössbauer, UV−vis−NIR, and X-ray absorption near-edge structure (XANES) spectroscopies. In addition, a new ferrocene diphosphazene proligand, 1,1′-di(2-*tert*-butyl-6-diphenylphosphiniminophenol)ferrocene (**2-H$_2$**), and its complexes

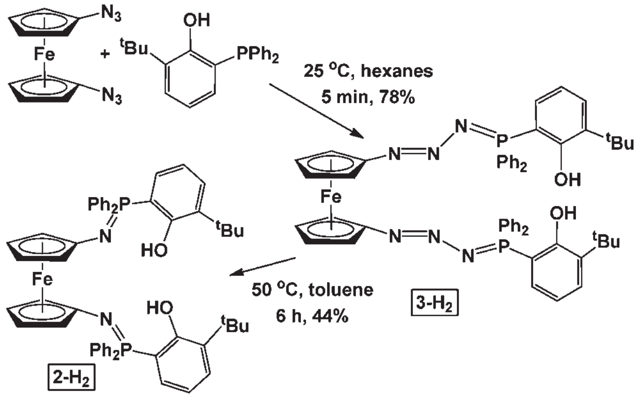
Received: October 13, 2010
Published: March 02, 2011

Chart 1. Cerium and Yttrium Alkoxide Complexes Discussed



M	E$_1$	E$_2$	X	Z	Label
Ce(IV)	O^{t}Bu	O^{t}Bu	CH	^{t}Bu	1-Ce(O^{t}Bu)$_2$
Ce(III)	O^{t}Bu	THF	CH	^{t}Bu	1-Ce(O^{t}Bu)(THF)
Ce(IV)	O^{t}Bu	O^{t}Bu	PPh$_2$	H	2-Ce(O^{t}Bu)$_2$
Ce(III)	O^{t}Bu	THF	PPh$_2$	H	2-Ce(O^{t}Bu)(THF)
Y(III)	O^{t}Bu	THF	CH	^{t}Bu	1-Y(O^{t}Bu)(THF)
Y(III)	O^{t}Bu	-	PPh$_2$	H	2-Y(O^{t}Bu)

Scheme 1. Synthesis of 2-H$_2$ and 3-H$_2$



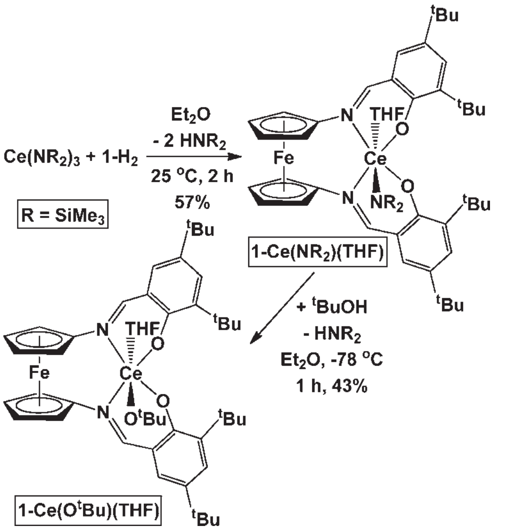
were synthesized and characterized to compare imine-derived contributions on their electronic properties.

RESULTS AND DISCUSSION

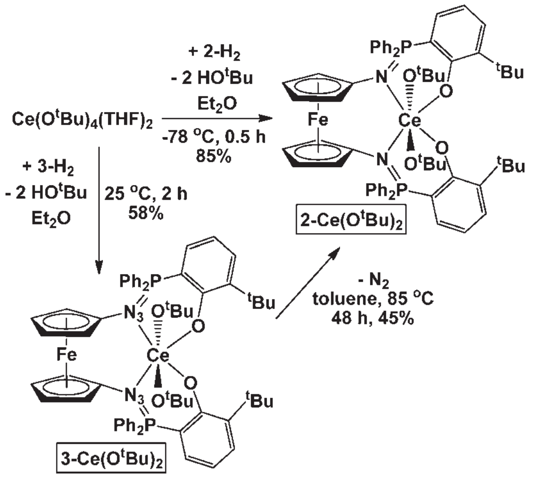
Synthesis of 2-H$_2$. The Staudinger reaction of 1,1′-diazoferrocene, fc(N$_3$)$_2$ (fc = 1,1′-ferrocenylene),[44] with 2-diphenylphosphino-6-*tert*-butylphenol[45,46] led to the formation of the bis(phosphazide) **3-H$_2$** as a red solid. The product **3-H$_2$** displayed an N−N stretch at 1417 cm^{-1} in its IR spectrum (CH$_2$Cl$_2$, 25 °C) and a ^{31}P chemical shift at 29.7 ppm (121 MHz, C$_6$D$_6$, 25 °C).[47−50] Heating **3-H$_2$** under an inert atmosphere in toluene at 50 °C for 6 h led to N$_2$ elimination to produce **2-H$_2$** (Scheme 1). The ^{31}P NMR (121 MHz, C$_6$D$_6$, 25 °C) spectrum of **2-H$_2$** revealed a peak at 27.1 ppm.[47,48,50,51] Free phosphinimines have been reported to have ^{31}P chemical shifts ranging from 12.4 ppm to 21.6 ppm, while free phosphazide ^{31}P chemical shifts have been reported within the range of 25 ppm to 52 ppm.[47−49] Phosphinimines tend to display ^{31}P chemical shifts upfield from the corresponding phosphazide,[47,48] a trend that we observed as well.

Cerium Alkoxide Complexes. We previously reported the isolation of the cerium(IV) bis(*t*-butyloxide) complex **1-Ce(O^{t}Bu)$_2$** by the reaction of Ce(O^{t}Bu)$_4$(THF)$_2$ with **1-H$_2$**.[19] The cerium(III) alkoxide complex **1-Ce(O^{t}Bu)(THF)** was synthesized by the protonolysis reaction of Ce[N(SiMe$_3$)$_2$]$_3$ with **1-H$_2$** to produce **1-Ce[N(SiMe$_3$)$_2$](THF)** (Scheme 2). The amide ligand was exchanged for *tert*-butyloxide through the addition of ^{t}BuOH to **1-Ce[N(SiMe$_3$)$_2$](THF)**, in diethyl ether at −78 °C, to give **1-Ce(O^{t}Bu)(THF)** (Scheme 2). The complex **1-Ce(O^{t}Bu)(THF)** displays a paramagnetic ^{1}H NMR spectrum with broad peaks (see the Supporting Information): five characteristic peaks were found that account for the four *tert*-butyl groups of the ancillary ligand and the alkoxide group, indicating a desymmetrized structure in solution, unlike what was found for the analogous phosphinimine complex (see below).

Scheme 2. Synthesis of the Cerium(III) Alkoxide 1-Ce(O^{t}Bu)(THF)



Scheme 3. Syntheses of 2-Ce(O^{t}Bu)$_2$ and 3-Ce(O^{t}Bu)$_2$



Similarly to the preparation of **1-Ce(O^{t}Bu)$_2$**, the complex **2-Ce(O^{t}Bu)$_2$** was obtained from Ce(O^{t}Bu)$_4$(THF)$_2$ and **2-H$_2$** in tetrahydrofuran (THF) at room temperature (Scheme 3). The complex **2-Ce(O^{t}Bu)$_2$** was also independently synthesized from **3-Ce(O^{t}Bu)$_2$** by N$_2$ extrusion (Scheme 3). Interestingly, **3-Ce(O^{t}Bu)$_2$** represents the second lanthanide and one of the few d^{0}f^n-metal phosphazide complexes reported.[52,53] The complex **3-Ce(O^{t}Bu)$_2$** is diamagnetic, with a ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C) spectrum displaying two peaks for the ferrocene protons, at 4.00 and 4.97 ppm. The *tert*-butyl peaks of the phosphinimine ligand and alkoxides were found as two singlets at 0.83 and 2.00 ppm. The phosphine aryl protons were identified as multiplets between 6.50 and 7.82 ppm. The ^{31}P NMR spectrum of **3-Ce(O^{t}Bu)$_2$** displayed a peak at 34.6 ppm, comparable to values reported for analogous complexes.[54,55]

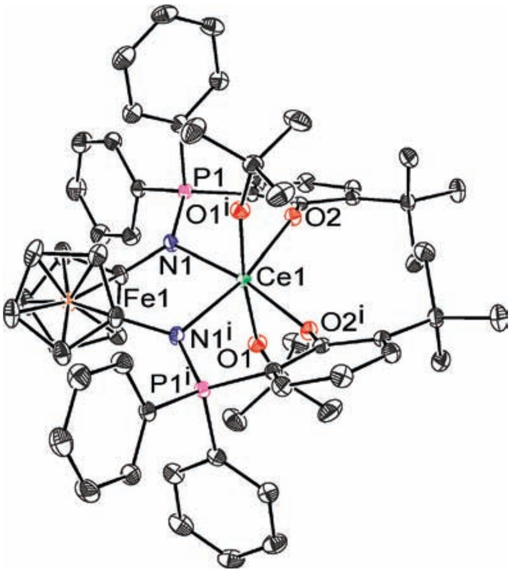


Figure 1. Thermal-ellipsoid (50% probability) representation of **2-Ce(O^{t}Bu)$_2$**; hydrogen and solvent atoms were removed for clarity. Selected metrical parameters for **2-Ce(O^{t}Bu)$_2$** (distances in Å and angles in deg): Ce(1)−O(1), 2.0932(11); Ce(1)−O(2), 2.2670(10); Ce(1)−N(1), 2.5183(12); N(1)−P(1), 1.5982(13); O(1)Ce(1)O(2), 90.03(4); O(1)Ce(1)N(1), 84.72(4).

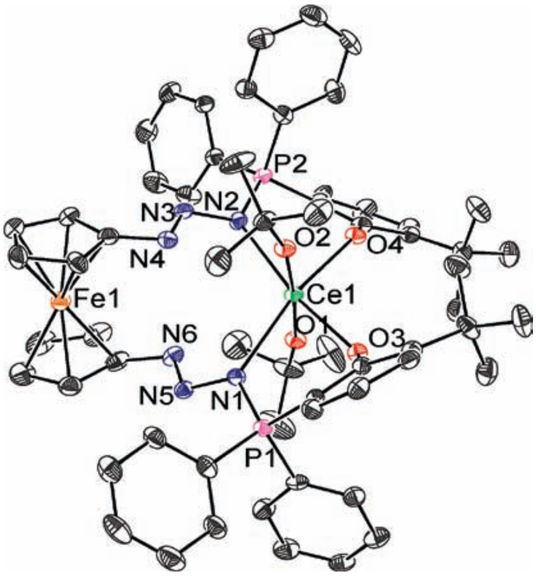
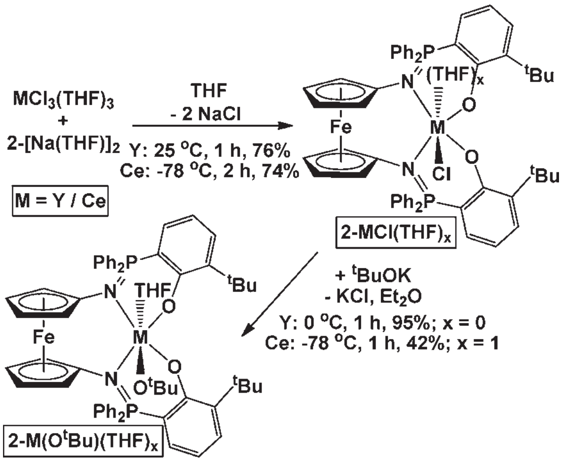


Figure 2. Thermal-ellipsoid (50% probability) representation of **3-Ce(O^{t}Bu)$_2$**; hydrogen and solvent atoms were removed for clarity. Selected metrical parameters for **3-Ce(O^{t}Bu)$_2$** (distances in Å and angles in deg): Ce(1)−O(1), 2.0691(29); Ce(1)−O(2), 2.0606(29); Ce(1)−O(3), 2.3237(30); Ce(1)−O(4), 2.3299(30); Ce(1)−N(1), 2.5523(36); Ce(1)−N(2), 2.5355(37); N(1)−P(1), 1.6350(37); N(1)−N(5), 1.3807(49); N(5)−N(6), 1.2636(47); N(2)−P(2), 1.6290(37); N(2)−N(3), 1.3746(48); N(3)−N(4), 1.2685(48); O(1)Ce(1)O(2), 175.24(12); O(1)Ce(1)O(3), 95.64(11); O(2)Ce(1)O(4), 98.19(11); O(1)Ce(1)N(1), 86.23(12); O(2)Ce(1)N(2), 88.88(12); N(1)N(5)N(6), 110.34(35); N(2)N(3)N(4), 110.88(35).

In addition to being characterized in solution by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, **2-Ce(O^{t}Bu)$_2$** (Figure 1) and **3-Ce(O^{t}Bu)$_2$** (Figure 2) were characterized by single-crystal X-ray crystallography. Both complexes contain a pseudo-octahedral cerium ion, with the two *t*-butoxide ligands coordinated trans in the axial positions. Metrical parameters for the coordination environment of cerium in **2-Ce(O^{t}Bu)$_2$** and **3-Ce(O^{t}Bu)$_2$** are similar for the two complexes and compare well with those of **1-Ce(O^{t}Bu)$_2$**.[19] The main difference between the structures of **1-Ce(O^{t}Bu)$_2$** and **2-Ce(O^{t}Bu)$_2$** is the NCeOC torsion angles at the phenoxide oxygen: these values are 4.50(39) and 6.49(40)° for the nitrogen connected to the phenoxide and 159.56(69) and 139.48(63)° in **1-Ce(O^{t}Bu)$_2$**, while the corresponding values in **2-Ce(O^{t}Bu)$_2$** are 45.05(15)° and 116.47(23)°, respectively, indicating that there is a larger deviation from the planarity of the NCeO$_{\text{phenoxide}}$ arrangements in the latter compound. It is likely that this difference is a consequence of the more flexible P═N than C═N linkage found in **2-Ce(O^{t}Bu)$_2$**. The structure of **2-Ce(O^{t}Bu)$_2$** contains a mirror plane, indicating that this symmetry element is maintained in the solid state. The arrangement of the N$_3$ groups in **3-Ce(O^{t}Bu)$_2$** is s-trans and they are κ^1-N coordinated to the metal center. This coordination mode is likely a consequence of the steric properties of the supporting ligand, since the N$_3$ group is coordinated κ^2 and forms a four-member ring metallocycle in the other lanthanide phosphazide complex reported.[52]

The iminophosphorane cerium(III) alkoxide **2-Ce(O^{t}Bu)(THF)** was synthesized by the salt metathesis of **2-CeCl(THF)** with potassium *tert*-butoxide, in diethyl ether at −78 °C. The cerium(III) chloride **2-CeCl(THF)** was obtained from the reaction of CeCl$_3$(THF)$_3$ with **2-[Na(THF)]$_2$** in THF, at −78 °C (Scheme 4). The ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C) spectrum of **2-Ce(O^{t}Bu)(THF)** shows peaks characteristic for a paramagnetic compound. The *tert*-butyl protons of the ancillary ligand and the alkoxide group have chemical shifts of −5.06 and 6.40 ppm, respectively, indicating a C_s-symmetrical species in solution. Accordingly, the ^{31}P NMR (121 MHz, C$_6$D$_6$, 25 °C) spectrum of **2-Ce(O^{t}Bu)(THF)** shows a singlet at 45.1 ppm.

Scheme 4. Synthesis of 2-M(O^{t}Bu)(THF)$_x$ (M = Ce, x = 1; M = Y, x = 0)



Yttrium Alkoxide Complexes. The synthesis of **1-Y(O^{t}Bu)(THF)** was previously reported by our group;[19] a similar procedure was followed for the synthesis of **2-Y(O^{t}Bu)**. The salt metathesis reaction of YCl$_3$(THF)$_3$ and **2-[Na(THF)]$_2$** in THF, at room temperature, resulted in the formation of **2-YCl**, which reacted with potassium *tert*-butoxide in THF, at 0 °C, to yield the desired product, **2-Y(O^{t}Bu)** (Scheme 4). The ^{1}H NMR

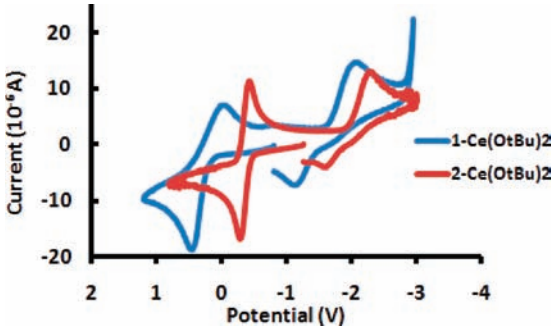


Figure 3. Cyclic voltammograms of **1-Ce(O^{t}Bu)$_2$** and **2-Ce(O^{t}Bu)$_2$** at 100 mV/s scan rate (1.5 mM in THF, 0.5 M [^{n}Pr$_4$N][BAr$^F{}_4$], Cp_2Fe/Cp_2Fe^+ corrected).

Table 1. Redox Events for the Compounds Discussed[a]

complex	$E_{1/2}$($Fe^{2+/3+}$) (V)	$E_{1/2}$($Ce^{3+/4+}$) (V)
1-H$_2$	0.29[b]	
2-H$_2$	−0.63[c]	
1-Y(O^{t}Bu)(THF)	0.09[c]	
2-Y(O^{t}Bu)	−0.29[b]	
1-Ce(O^{t}Bu)(THF)	E_{ox} = −0.21[c]	
	E_{red} = −1.05	
2-Ce(O^{t}Bu)(THF)	−0.57[b]	
1-Ce(O^{t}Bu)$_2$	−0.28[b]	E_{ox} = −1.01[b]
		E_{red} = −2.07
2-Ce(O^{t}Bu)$_2$	−0.38[b]	E_{ox} = −1.70[b]
		E_{red} = −2.39

[a] Numbers are from 250 mV/s scans. [b] 1.5 mM in THF, 0.5 M [^{n}Pr$_4$N][BAr$^F{}_4$], Cp_2Fe/Cp_2Fe^+ corrected. [c] 2.0 mM in THF, 0.5 M [^{n}Pr$_4$N][BAr$^F{}_4$], Cp_2Fe/Cp_2Fe^+ corrected.

(300 MHz, C_6D_6, 25 °C) spectrum of **2-Y(O^{t}Bu)** showed singlets at 1.61 and 1.55 ppm, which were assigned to the *tert*-butyl peaks of the ancillary ligand and the alkoxide, respectively. The ferrocene protons had chemical shifts at 5.09, 3.81, 3.58, and 3.53 ppm, while the phosphine aryl protons had chemical shifts between 6.53 and 7.95 ppm. The ^{31}P (121 MHz, C_6D_6, 25 °C) spectrum displayed a singlet at 32.6 ppm. The NMR spectroscopic data indicate that **2-Y(O^{t}Bu)**, like **2-Ce(O^{t}Bu)(THF)**, has pseudo-C_s symmetry in solution.

Cyclic Voltammetry. Cyclic-voltammetry studies were undertaken to probe the redox activity of cerium(IV) alkoxide complexes. Experiments were carried out using 1−2 mM THF solutions of the compound of interest, with [^{n}Pr$_4$N][BAr$^F{}_4$] (0.5 M, Ar^F = 3,5-$(CF_3)_2C_6H_3$) serving as the electrolyte (Figure 3 and Table 1). Cyclic voltammograms of the two proligands **1-H$_2$** and **2-H$_2$** revealed one redox event that was assigned to the $Fe^{2+/3+}$ couple (see the Supporting Information). Changing the imine with a phosphorimine functionality resulted in a more reducing potential for the $Fe^{2+/3+}$ event in **2-H$_2$** (−0.633 V) than in **1-H$_2$** (0.287 V). All metal complexes show a reversible (quasi-reversible for **1-Ce(O^{t}Bu)(THF)**), one-electron event that was assigned to the $Fe^{2+/3+}$ couple. In addition, the cerium (IV) complexes, **1-Ce(O^{t}Bu)$_2$** and **2-Ce(O^{t}Bu)$_2$**, show an irreversible reduction/oxidation event that was assigned to the $Ce^{4+/3+}$ couple (Figure 3). The oxidation of cerium in **1-Ce(O^{t}Bu)(THF)** and **2-Ce(O^{t}Bu)(THF)** was not observed (see the Supporting Information for details). Overall, we found that the oxidation of complexes based on the iminophosphorane (**2**) backbone is more facile than that of the complexes based on imine (**1**) and that there is more difficulty in reducing cerium(IV) to cerium(III) in **2-Ce(O^{t}Bu)$_2$** than in **1-Ce(O^{t}Bu)$_2$**.

Table 2. Mössbauer Parameters for the Compounds Discussed

complex	δ [mm s^{-1}]	ΔE_Q [mm s^{-1}]	G_{FWHM} [mm s^{-1}]
1-Y(O^{t}Bu)(THF)	0.61(1)	2.55(1)	0.26(1)
2-Y(O^{t}Bu)	0.52(1)	2.42(1)	0.27(1)
1-Ce(O^{t}Bu)(THF)	0.53(1)	2.42(1)	0.28(1)
2-Ce(O^{t}Bu)(THF)	0.54(1)	2.48(1)	0.28(1)
1-Ce(O^{t}Bu)$_2$	0.60(1)	2.51(1)	0.26(1)
2-Ce(O^{t}Bu)$_2$	0.53(1)	2.48(1)	0.28(1)

Mössbauer Spectroscopy. Mössbauer spectroscopy was used to probe the electronic structure of the ferrocene backbone in all metal complexes (Table 2). The yttrium complexes were used as an iron(II) standard, since no electron-transfer processes were expected to occur between the ferrocene backbone and the yttrium. All cerium complexes have similar isomer shifts and quadrupole splittings, indicating that iron is found as iron(II) in all complexes.

XANES Spectroscopy. To probe whether cerium engaged in redox events with other parts of the ancillary ligands, X-ray absorption near-edge structure (XANES) spectroscopic studies were undertaken. Fe K-edge measurements corroborated the results of Mössbauer spectroscopy showing that the data for all the cerium and yttrium complexes are similar to each other and ferrocene. Ce L_3-edge measurements (Figure 4) indicated that **1-Ce(O^{t}Bu)$_2$** and **2-Ce(O^{t}Bu)$_2$** have similar spectra to cerium(IV) standards, while **1-Ce(O^{t}Bu)(THF)** and **2-Ce(O^{t}Bu)(THF)** have similar characteristics to the cerium(III) standard $CeCl_3$ (the shoulder observed for **1-Ce(O^{t}Bu)(THF)** is assigned to a cerium(IV) impurity). The XANES data suggest that cerium(IV) is not reduced to cerium(III) by the oxidation of iron or any other functionality of the ancillary ligands.

UV−vis−NIR spectroscopy. The cerium and yttrium alkoxide complexes were further characterized by UV−vis−NIR spectroscopy (see the Supporting Information for spectra). The metal complexes supported by **1** have molar absorptivities between 20000 and 40000 M^{-1} cm^{-1} that consist of two peaks between 290 and 590 nm. The metal complexes supported by **2** have molar absorptivities between 10000 and 40000 M^{-1} cm^{-1} that consist of one peak between 290 and 590 nm. The f-f transitions were not observed for the cerium(III) complexes.[56]

Reactivity Studies. To investigate whether redox events would occur at the ancillary ligands in solution, the reactivity of the cerium alkoxide complexes toward electron-transfer reagents was probed. The complexes **1-Ce(O^{t}Bu)(THF)** and **2-Ce(O^{t}Bu)(THF)** were converted to **1-Ce(O^{t}Bu)I** and **2-Ce(O^{t}Bu)I**, respectively, by the addition of I_2 in toluene (Scheme 5). After 1 h, ^{1}H NMR spectroscopy indicated the formation of diamagnetic species. Salt-metathesis reactions of the alkoxide-iodide compounds with KO^{t}Bu in THF afforded **1-Ce(O^{t}Bu)$_2$** and **2-Ce(O^{t}Bu)$_2$**.

Cerium(IV) complexes could be converted, in turn, to the corresponding cerium(III) complexes (eq 1). To reduce the occurrence of unwanted side products, **1-Ce(O^{t}Bu)$_2$** was first transformed to **1-Ce(O^{t}Bu)Cl** with 1 equiv of lutidinium chloride. The complex **1-Ce(O^{t}Bu)Cl** was reduced by KC_8 after 16 h at room temperature in toluene to form **1-Ce(O^{t}Bu)(THF)**,

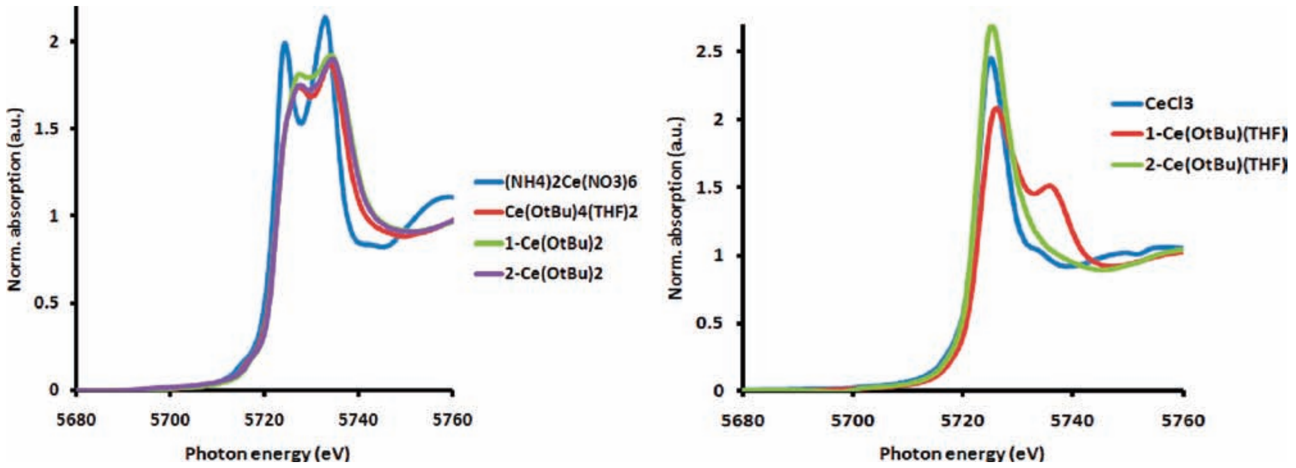
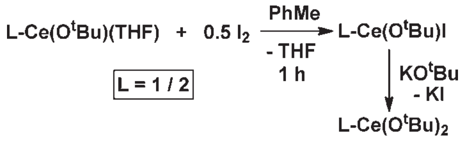


Figure 4. Ce L_3-edge XANES spectra for cerium(IV) (left) and cerium(III) (right) complexes.

Scheme 5. Transformation of Cerium(III) into Cerium(IV) Complexes



isolated in a 56% yield. The alkoxide-iodide **2-Ce(O^{t}Bu)I** reacted with KC_8 in THF at room temperature within minutes to form **2-Ce(O^{t}Bu)(THF)**, which was isolated in a 68% yield.

$$\text{L-Ce(O}^t\text{Bu)X} + \text{KC}_8 \longrightarrow \text{L-Ce(O}^t\text{Bu)(THF)} \quad (1)$$

L = 1: X = Cl, toluene, 16 h, 56%
L = 2: X = I, THF, 5 min, 68%

Conclusions. Two series of ferrocene-based metal complexes supported by a Schiff base or an analogue ligand were investigated. The two ancillary ligands differ by the type of the N=X functionality that they incorporate: one ligand is based on an imine, whereas the other is based on an iminophosphorane group. The characterization of the resulting cerium(IV) bis(alkoxide) complexes was targeted to determine whether the presence of a strongly oxidizing metal center will give rise to non-innocent redox behavior in the supporting ligands. For comparison, the corresponding cerium(III) and yttrium(III) alkoxide complexes were also synthesized. All the metal complexes were characterized by cyclic voltammetry and NMR, Mössbauer, X-ray absorption near-edge structure (XANES), and absorption spectroscopies. The experimental data indicate that iron remains in the +2 oxidation state and that cerium(IV) does not engage any part of the ancillary ligand in redox behavior. The ancillary ligand containing the iminophosphorane group was more easily oxidized than the ligand with the imine group. Since the ligand does not engage cerium into a redox behavior, more investigation is needed to utilize the redox behavior of these complexes to gain new reactivity.

■ 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[57] and transferred to the glovebox without exposure to air. $CeCl_3$ and $(NH_4)_2Ce(NO_3)_4$ were purchased from Alfa Aesar, and KO^{t}Bu and $NaN(SiMe_3)_2$ were purchased from Sigma-Aldrich. All reagents were used as received. Ce(O^{t}Bu)$_4$(THF)$_2$,[58] $Ce[N(SiMe_3)_2]_3$,[59] **1-H$_2$**,[18] 1,1′-diazoferrocene,[44] 2-(diphenyl)phosphino-6-*tert*-butylphenol,[45,46] and $[{}^nPr_4N][BAr^F{}_4]$[60] were synthesized according to published procedures. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. ^1H NMR spectra were recorded on Bruker300 or Bruker500 spectrometers at room temperature in C_6D_6 (the UCLA NMR spectrometers are supported by the NSF Grant CHE-9974928). Chemical shifts are reported with respect to internal solvent, 7.16 ppm (C_6D_6) for ^1H NMR spectra. For ^{31}P NMR spectra, chemical shifts are reported with respect to an external standard, 121 ppm (1% trimethylphosphite in C_6D_6). UV−vis−NIR spectra were recorded on a Varian Carey 5000 spectrophotometer from 200 to 1800 nm using matched, 1-cm quartz cells; all spectra were obtained using a solvent reference blank in a cuvette fitted with an air-free Teflon adapter. Cyclic voltammetry data were obtained in an MBraun glovebox system equipped with binding posts; all data were collected using a Princeton Applied Research Corp. (PARC) Model 263A potentiostat under computer control with PARC Model 270 software. XANES experiments at both Fe K-edge and Ce L_3-edge were performed at the Materials Research Collaborative Access Team (MRCAT) beamline (10-BM) at the Advanced Photon Source, Argonne National Laboratory. CHN analyses were performed by Midwest Microlabs, LLC, 7212 N. Shadeland Ave Suite 110, Indianapolis, IN 46250.

3-H$_2$. 1,1′-diazoferrocene (0.9352 g, 3.49 mmol) dissolved in hexanes was added to a stirring solution of 2-(diphenyl)phosphino-6-*tert*-butylphenol (2.333 g, 6.97 mmol) in hexanes at room temperature to yield a red precipitate within minutes. The solid was collected, washed thoroughly with hexanes, and dried in vacuo producing a bright-red powder. Yield: 2.551 g, 78.1%. ^1H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 1.59 (s, 18H, CCH_3), 3.82 (s, 4H, C_5H_4), 4.48 (s, 4H, C_5H_4), 6.56(m, 2H, C_6H_3), 6.85 (m, 2H, C_6H_3), 7.01 (m, 12H, $P(C_6H_5)_2$), 7.37 (d, 2H, C_6H_3), 7.71 (m, 8H, $P(C_6H_5)_2$). ^{13}C NMR (75 MHz, 25 °C, C_6D_6), δ (ppm): 29.8, 35.7, 63.9, 68.9, 106.5, 118.4, 128.8, 131.5, 131.7, 132.3, 133.7, 139.9, 164.5. ^{31}P NMR (121 MHz, 25 °C, C_6D_6), δ (ppm): 29.7 (s). The protons for the OH group were not observed in the spectrum. Elemental analysis could not be performed on this compound because upon solvation the compound begins to convert to **2-H$_2$**.

2-H$_2$. In toluene, **3-H$_2$** was heated at 50 °C for 6 h. The volatiles were removed, and the product was washed with hexanes and diethyl ether resulting in a dull-yellow powder. The product was recrystallized from a concentrated THF solution layered with *n*-pentane at −36 °C. Yield: 1.35 g, 43.6%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 1.77 (s, 18H, CCH_3), 3.53 (s, 4H, C_5H_4), 4.23 (s, 4H, C_5H_4), 6.50 (m, 2H, C_6H_3), 6.86 (m, 12H, $P(C_6H_5)_2$), 6.98 (m, 2H, C_6H_3), 7.55 (d, 2H, C_6H_3), 7.77 (m, 8H, $P(C_6H_5)_2$), 13.00 (br s, 2H, OH). ^{13}C NMR (75 MHz, 25 °C, C_6D_6), δ (ppm): 29.8, 35.6, 65.3, 131.7, 132.3, 133.1, 140.9. ^{31}P NMR (121 MHz, 25 °C, C_6D_6), δ (ppm): 27.1 (s). Anal. for $C_{54}FeH_{54}N_2O_2P_2$. Calcd: C, 73.63%; H, 6.18%; N, 3.18%. Found: C, 73.58%; H, 6.25%; N, 2.96%.

1-Ce[N(SiMe$_3$)$_2$](THF). A diethyl ether solution of **1-H$_2$** (0.215 g, 0.331 mmol) was added to a diethyl ether solution of Ce[N(SiMe$_3$)$_2$]$_3$ (0.257 g, 0.414 mmol), and the mixture was stirred at room temperature for 2 h. The volatiles were removed, and the product was washed with hexanes and then extracted with diethyl ether. The volatiles were removed again producing a gold powder. The product was recrystallized from a concentrated toluene solution layered with *n*-pentane at −36 °C. Yield: 0.180 g, 57.5%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): −17.74 (s, 2H, C_5H_4, OC_6H_2, or NCH), −5.00 (s, 2H, C_5H_4 or OC_6H_2or NCH), −3.69 (s, 18H, $SiCH_3$ or CCH_3), −3.38 (s, 1H, C_5H_4, OC_6H_2, or NCH), −3.07 (s, 2H, C_5H_4, OC_6H_2, or NCH), −1.79 (s, 2H, C_5H_4, OC_6H_2, or NCH), 2.08 (s, 18H, $SiCH_3$ or CCH_3), 3.60 (s, 18H, $SiCH_3$ or CCH_3), 11.14 (s, 2H, C_5H_4, OC_6H_2, or NCH), 14.84 (s, 2H, C_5H_4 or OC_6H_2or NCH), 22.06 (s, 2H, C_5H_4, OC_6H_2, or NCH). Note: Attempts were made to acquire elemental analysis data for **1-Ce[N(SiMe$_3$)$_2$](THF)**. The compound could be shipped, but its static nature prevented the precise measurement of small amounts required for analysis.

1-Ce(O^{t}Bu)(THF). A diethyl ether solution of ^{t}BuOH (0.020 g, 0.267 mmol) was added to a diethyl ether solution of **1-Ce[N(SiMe$_3$)$_2$](THF)** (0.253 g, 0.267 mmol) at −78 °C. After stirring for 1 h at −78 °C, the volatiles were removed, and the solid was extracted into hexanes. The volatiles were removed yielding an orange powder. The product was recrystallized from concentrated hexanes. Yield: 0.100 g, 43.3%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): −12.97 (s, 9H, CCH_3 or OCH_3), −7.49 (s, 1H, C_5H_4, OC_6H_2, or NCH), −5.06 (s, 1H, C_5H_4, OC_6H_2, or NCH), −2.83 (s, 2H, C_5H_4, OC_6H_2, or NCH), −1.29 (s, 9H, CCH_3 or OCH_3), 1.53 (s, 9H, CCH_3 or OCH_3), 2.79 (s, 9H, CCH_3 or OCH_3), 3.20 (s, 1H, C_5H_4, OC_6H_2, or NCH), 4.85 (s, 9H, CCH_3 or OCH_3), 8.58 (s, 1H, C_5H_4, OC_6H_2, or NCH), 9.83 (s, 1H, C_5H_4, OC_6H_2, or NCH), 10.44 (s, 1H, C_5H_4, OC_6H_2, or NCH), 12.14 (s, 1H, C_5H_4, OC_6H_2, or NCH), 12.31 (s, 1H, C_5H_4, OC_6H_2, or NCH), 13.47 (s, 1H, C_5H_4, OC_6H_2, or NCH), 17.81 (s, 1H, C_5H_4, OC_6H_2, or NCH). Anal. for $CeC_{44}H_{59}FeN_2O_3(C_6H_{14})$. Calcd: C, 63.47%; H, 7.78%; N, 2.96%. Found: C, 63.21%; H, 7.62%; N, 2.79%.

3-Ce(O^{t}Bu)$_2$. In diethyl ether, **3-H$_2$** (0.391 g, 0.417 mmol) was added to Ce(O^{t}Bu)$_4$(THF)$_2$ (0.240 g, 0.417 mmol). After stirring at room temperature for 2 h, solvent was removed. The product was washed with hexanes and extracted with diethyl ether. The product was recrystallized from concentrated toluene layered with pentane at −36 °C. Yield: 0.293 g, 57.6%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 0.83 (s, 18H, CCH_3), 2.00 (s, 18H, CCH_3), 4.00 (s, 4H, C_5H_4), 4.97 (s, 4H, C_5H_4), 6.50 (m, 2H, OC_6H_3), 6.88 (m, 2H, OC_6H_3), 7.07 (m, 12H, $P(C_6H_5)_2$), 7.63 (d, 2H,OC_6H_3), 7.82 (m, 8H, $P(C_6H_5)_2$). ^{13}C NMR (75 MHz, 25 °C, C_6D_6), δ (ppm): 31.4, 33.1, 36.3, 64.7, 68.7, 86.9, 108.9, 115.2, 129.6, 130.3, 131.7, 131.8, 132.4, 131.2, 139.5. ^{31}P NMR (121 MHz, 25 °C, C_6D_6), δ (ppm): 34.6 (s). Anal. for $C_{54}FeH_{54}N_6O_2P_2$. Calcd: C, 64.32%; H, 6.09%; N, 7.26%. Found: C, 64.58%; H, 6.14%; N, 6.90%.

2-Ce(O^{t}Bu)$_2$. *Method A (from **2-H$_2$**).* A diethyl ether solution of **2-H$_2$** (0.423 g, 0.417 mmol) was added to Ce(O^{t}Bu)$_4$(THF)$_2$ (0.240 g, 0.417 mmol) at −78 °C. The reaction was stirred for 0.5 h at room temperature then the volatiles were removed. The product was washed with hexanes, ether, and a small amount of toluene to yield a brown powder. The product was recrystallized from concentrated toluene layered with pentane at −36 °C. Yield: 0.375 g, 84.8%.

*Method B (from **3-Ce(O^{t}Bu)$_2$**).* **3-Ce(O^{t}Bu)$_2$** (0.140 g, 0.115 mmol) was heated at 85 °C in toluene for 48 h. The volatiles were removed under reduced pressure, and the product was washed with hexanes and diethyl ether. The product was extracted with toluene and recrystallized from a concentrated toluene solution layered with *n*-pentane at −36 °C. Yield: 0.061 g, 45.50%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 1.11 (s, 18H, CCH_3), 1.97 (s, 18H, CCH_3), 3.88 (s, 4H, C_5H_4), 4.43 (s, 4H, C_5H_4), 6.46 (m, 2H, OC_6H_3), 6.77(m, 2H, OC_6H_3), 7.02 (m, 12H, $P(C_6H_5)_2$), 7.59 (d, 2H, OC_6H_3), 7.71 (m, 8H, $P(C_6H_5)_2$). ^{13}C NMR (75 MHz, 25 °C, C_6D_6), δ (ppm): 31.6, 33.5, 65.6, 66.8, 127.1, 131.6, 131.8, 134.0. ^{31}P NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 30.8 (s). Anal. for $C_{62}CeFeH_{70}N_2O_4P_2 \cdot C_7H_8$. Calcd: C, 65.91%; H, 6.41%; N, 2.23%. Found: C, 65.73%; H, 6.12%; N, 2.11%.

2-CeCl(THF). In THF, at −78 °C, **2-Na$_2$(THF)$_2$** (0.251 g, 0.235 mmol) was added to CeCl$_3$(THF)$_3$ (0.108 g, 0.235 mmol). After 2 h of stirring at −78 °C, the volatiles were removed. The product was washed with hexanes, and extracted with diethyl ether. The volatiles were removed, and the product was recrystallized from a concentrated toluene solution layered with *n*-pentane at −36 °C. Yield: 0.183 g, 74.0%. This paramagnetic complex has no identifiable peaks by ^{1}H or ^{31}P NMR spectroscopy. Anal. for $C_{58}H_{60}FeN_2O_3P_2CeCl$. Calcd: C, 61.84%; H, 5.33%; N, 2.49%. Found: C, 62.08%; H, 5.31%; N, 2.24%.

2-Ce(O^{t}Bu)(THF). A diethyl ether solution of KO^{t}Bu (0.030 g, 0.273 mmol) was added to an ether slurry of **2-CeCl(THF)** (0.288 g, 0.273 mmol) at −78 °C. After 1 h of stirring at −78 °C, the volatiles were removed. The product was extracted with toluene, and the resulting solution was then concentrated and layered with *n*-pentane to yield a yellow precipitate at −36 °C. Yield: 0.135 g, 42.5%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 13.74 (s, 2H, C_5H_4), 10.82 (broad s, 3H, $P(C_6H_5)_2$ or OC_6H_3), 10.10 (s, 2H, C_5H_4), 9.77 (s, 2H, C_5H_4), 7.44 (s, 5H, $P(C_6H_5)_2$ or OC_6H_3), 6.40 (s, 9H, CCH_3), 3.60 (s, 12H, $P(C_6H_5)_2$ or OC_6H_3), 1.36 (s, 12H, $P(C_6H_5)_2$ or OC_6H_3), −4.01 (br s, 2H, C_5H_4), −5.06 (s, 18H, CCH_3). ^{31}P NMR (121 MHz, 25 °C, C_6D_6), δ (ppm): 45.1 (s). Anal. for $C_{62}H_{69}FeN_2O_4P_2Ce$. Calcd: C, 63.97%; H, 5.97%; N, 2.41%. Found: C, 64.06%; H, 6.09%; N, 2.40%.

1-Ce(O^{t}Bu)Cl. Lutidinium chloride (0.017 g, 0.121 mmol) was added to **1-Ce(O^{t}Bu)$_2$** (0.113 g, 0.121 mmol) in THF at room temperature. After stirring for 1.5 h, the volatiles were removed, and the product was extracted with hexanes and diethyl ether. The product was recrystallized from a concentrated diethyl ether solution at −36 °C. Yield: 0.080 g, 74.0%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 1.09 (s, 9H, CCH_3), 1.29 (s, 18H, CCH_3), 1.88 (s, 18H, CCH_3), 4.03 (s, 2H, C_5H_4), 4.11 (s, 2H, C_5H_4), 4.22 (s, 2H, C_5H_4), 4.67 (s, 2H, C_5H_4), 6.94 (s, 2H, OC_6H_2), 7.82 (s, 2H, OC_6H_2), 8.25 (s, 2H, OC_6H_2). ^{13}C NMR (75 MHz, 25 °C, C_6D_6), δ (ppm): 30.6, 31.6, 33.3, 36.1, 64.9, 67.1, 68.7, 69.7, 126.1, 129.9, 131.3, 137.2, 140.0, 167.0, 169.7. Anal. for $C_{44}CeFeH_{59}N_2O_3Cl$. Calcd: C, 59.02%; H, 6.64%; N, 3.13%. Found: C, 58.85%; H, 6.44%; N, 3.10%.

1-Ce(O^{t}Bu)I. Iodine (0.018 g, 0.071 mmol) was added to a THF solution of **1-Ce(O^{t}Bu)(THF)** (0.122 g, 0.141 mmol) at room temperature. After stirring for 1 h, the volatiles were removed, and the product was extracted with hexanes and diethyl ether at −36 °C. The product was recrystallized from a concentrated diethyl ether solution. Yield: 0.090 g, 65.0%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 1.01 (s, 9H, CCH_3), 1.27 (s, 18H, CCH_3), 1.91 (s, 18H, CCH_3), 4.02 (s, 2H, C_5H_4), 4.07 (s, 2H, C_5H_4), 4.13 (s, 2H, C_5H_4), 4.80 (s, 2H, C_5H_4), 6.96 (s, 2H, OC_6H_2), 7.85 (s, 2H, OC_6H_2), 8.44 (s, 2H, OC_6H_2). ^{13}C NMR (75 MHz, 25 °C, C_6D_6), δ (ppm): 30.7, 31.6, 33.3, 34.1, 36.1, 65.0, 68.5, 68.8, 70.1, 126.9, 129.9, 131.5, 167.5, 170.2. Anal. for $C_{44}CeFeH_{59}N_2O_3I$. Calcd: C, 53.55%; H, 6.03%; N, 2.84%. Found: C, 53.23%; H, 5.91%; N, 2.99%.

2-Ce(O^{t}Bu)I. Iodine (0.013 g, 0.053 mmol) was added to a THF solution of **2-Ce(O^{t}Bu)(THF)** (0.115 g, 0.105 mmol) at room temperature. After stirring for 1 h, the volatiles were removed, and the product was extracted with hexanes and diethyl ether. The product was recrystallized from a toluene solution layered with hexanes at −36 °C. Yield: 0.093 g, 90.3%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 1.19 (s, 9H, CCH_3), 1.93 (s, 18H, CCH_3), 3.79 (s, 4H, C_5H_4), 4.26 (s, 4H, C_5H_4), 6.49 (m, 2H, $P(C_6H_5)_2$), 6.87(m, 2H, $P(C_6H_5)_2$), 7.00 (m, 12H, $P(C_6H_5)_2$), 7.60 (m, 6H, OC_6H_3), 8.06 (m, 4H, $P(C_6H_5)_2$). ^{31}P NMR (121 MHz, 25 °C, C_6D_6), δ (ppm): 33.1 (m). A ^{13}C NMR spectrum for **2-Ce(O^{t}Bu)I** could not be obtained because of its low solubility in regular deuterated solvents. Anal. for $C_{58}CeFeH_{61}N_2O_3P_2I$. Calcd: C, 57.15%; H, 5.04%; N, 2.29%. Found: C, 57.45%; H, 5.15%; N, 2.01%.

2-YCl. In THF, at room temperature, **2-Na$_2$(THF)$_2$** (0.223 g, 0.209 mmol) was added to $YCl_3(THF)_3$ (0.086 g, 0.209 mmol). The reaction was stirred for 1 h, then the volatiles were removed. The product was washed with hexanes and ether, then extracted with toluene. The volatiles were removed from the resulting solution yielding a yellow powder, which was recrystallized from a concentrated toluene solution layered with *n*-pentane at −36 °C. Yield: 0.160 g, 76.0%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 1.51 (s, 18H, CCH_3),3.42 (s, 2H, C_5H_4), 3.54 (s, 2H, C_5H_4), 3.71 (s, 2H, C_5H_4), 4.98 (s, 2H, C_5H_4), 6.54 (m, 2H, OC_6H_3), 6.84 (m, 2H, OC_6H_3), 6.98 (m, 12H, $P(C_6H_5)_2$), 7.47 (d, 2H, OC_6H_3), 7.68 (m, 8H, $P(C_6H_5)_2$). ^{31}P NMR (121 MHz, 25 °C, C_6D_6), δ (ppm): 30.7 (s). A ^{13}C NMR spectrum for **2-YCl** could not be obtained because of its low solubility in regular deuterated solvents. Anal. for $C_{54}ClFeH_{52}N_2O_2P_2Y$. Calcd: C, 64.66%; H, 5.29%; N, 2.79%. Found: C, 64.83%; H, 5.68%; N, 2.50%.

2-Y(O^{t}Bu). A diethyl ether solution of KO^{t}Bu (0.020 g, 0.182 mmol) was added to a diethyl ether slurry of **2-YCl** (0.183 g, 0.182 mmol) at 0 °C. After stirring for 1 h at 0 °C, solvent was removed, and the product was washed with hexanes then extracted with toluene. The product was recrystallized from a concentrated toluene solution layered with *n*-pentane at −36 °C. Yield: 0.180 g, 95.0%. ^{1}H NMR (300 MHz, 25 °C, C_6D_6), δ (ppm): 1.51 (s, 9H, CCH_3), 1.60 (s, 18H, CCH_3), 3.53 (s, 2H, C_5H_4), 3.58 (s, 2H, C_5H_4), 3.81 (s, 2H, C_5H_4), 5.09 (s, 2H, C_5H_4), 6.53 (m, 2H, OC_6H_3), 6.73 (m, 2H, OC_6H_3), 6.94 (m, 12H, $P(C_6H_5)_2$), 7.31 (m, 3H, $P(C_6H_5)_2$), 7.59 (d, 2H, $P(C_6H_5)_2$), 7.9 5 (m, 3H, $P(C_6H_5)_2$). ^{13}C NMR (75 MHz, 25 °C, C_6D_6), δ (ppm): 25.8, 30.6, 34.8, 35.6, 64.7, 66.4, 67.7, 67.8, 71.5, 105.1, 114.2, 131.6, 131.9, 133.8, 140.9, 170.3. ^{31}P NMR (121 MHz, 25 °C, C_6D_6), δ (ppm): 32.6 (s). Anal. for $C_{58}FeH_{61}N_2O_3P_2Y$. Calcd: C, 66.93%; H, 5.90%, N, 2.69%. Found: C, 66.53%, H, 5.84%, N, 2.63%.

XANES Measurements. The setup used was similar to that outlined by Castagnola et al.[61] In an argon-filled Vacuum Atmospheres glovebox with a large-capacity recirculator (0.25 ppm of O_2 and 0.5 ppm of H_2O), a predetermined amount of each sample was loaded as a self-supporting wafer without binder in the channels (i.d. = 4 mm) of a stainless steel multisample holder. The sample holder was then placed in the center of a quartz tube, which was equipped with gas and thermocouple ports and Kapton windows. After the whole setup was purged with dry He, it was transferred into the experiment hutch. The quartz tube was mounted on a positioning platform. The beam was set to scan the sample cell holder by manipulating the position of the platform. Once the sample positions were fine-tuned, the XAS spectra were recorded in transmission mode at room temperature. The energy calibration and background removal were performed with Athena.

Mössbauer Spectroscopy. ^{57}Fe Mössbauer spectra were recorded on a WissEl Mössbauer spectrometer (MRG-500) at 77 K in constant acceleration mode. ^{57}Co/Rh was used as the radiation source. WinNormos for Igor Pro software has been used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.21 mm s^{-1}. The temperature of the samples was controlled by an MBBC-HE0106 MÖSSBAUER He/N_2 cryostat within an accuracy of ±0.3 K. Isomer shifts were determined relative to α-iron at 298 K.

Cyclic Voltammetry. Solutions were contained in PARC Model K0264 microcells consisting of a glassy carbon working electrode, a 1 mm diameter Pt wire counter electrode, and a silver-wire quasi-reference electrode. Scan rates from 50 to 1000 mV/s were employed to assess the chemical and electrochemical reversibility of the observed redox transformations. Potential calibrations were performed in situ for all samples at the end of each data collection cycle by addition of 1 equiv of ferrocene per complex and the use of the ferrocenium/ferrocene couple as an internal potential standard.

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, Wisconsin, U.S.A.). 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.

X-ray Crystal Structure of 2-Ce(O^{t}Bu)$_2$. X-ray quality crystals were obtained from a concentrated toluene solution layered with *n*-pentane. A total of 9462 reflections ($-40 \le h \le 39$, $-21 \le k \le 20$, $-24 \le l \le 23$) were collected at $T = 100(2)$ K with $2\theta_{max} = 61.57°$, of which 8218 were unique ($R_{int} = 0.0301$). The residual peak and hole electron density were 0.69 and −0.36 e A^{-3}. The least-squares refinement converged normally with residuals of $R_1 = 0.0257$ and GOF = 1.012. Crystal and refinement data for **2-Ce(O^{t}Bu)$_2$**: formula $C_{62}H_{70}N_6O_4P_2FeCe$, triclinic, space group *C*2/*c*, $a = 28.326(3)$ Å, $b = 14.7583$ Å, $c = 16.8906(16)$ Å, $\beta = 114.249(1)°$, $V = 6438.1(10)$ Å^3, $Z = 4$, $\mu = 1.351$ mm^{-1}, $F(000) = 2728$, $R_1 = 0.0327$, w$R_2 = 0.0623$ (for all data).

X-ray Crystal Structure of 3-Ce(O^{t}Bu)$_2$. X-ray quality crystals were obtained from a concentrated toluene solution layered with *n*-pentane. A total of 19129 reflections ($-18 \le h \le 18$, $-18 \le k \le 18$, $-29 \le l \le 29$) was collected at $T = 100(2)$ K with $2\theta_{max} = 61.01°$, of which 13408 were unique ($R_{int} = 0.0501$). The unit cell contains two molecules of toluene, of which one was disordered. That disorder was not modeled; instead the aromatic carbons were constrained to fit a benzene ring and to have the same value thermal ellipsoids. Because of these constraints and disorder, the CCC angle made by the methyl group and the ring is different than the expected value and one of its hydrogen atoms is too close to one of the aromatic hydrogens. This disorder was not solved. The residual peak and hole electron density were 2.58 and −1.80 e A^{-3}. The least-squares refinement converged normally with residuals of $R_1 = 0.0621$ and GOF = 1.051. Crystal and refinement data for **3-Ce(O^{t}Bu)$_2$**: formula $C_{62}H_{70}N_6O_4P_2FeCe$, triclinic, space group $P\bar{1}$, $a = 13.104(4)$ Å, $b = 13.120(4)$ Å, $c = 21.294(7)$ Å, $\alpha = 93.180(3)°$, $\beta = 103.069(3)°$, $\gamma = 103.040(3)°$, $V = 3452(2)$ Å^3, $Z = 2$, $\mu = 0.961$ mm^{-1}, $F(000) = 1460$, $R_1 = 0.0962$, w$R_2 = 0.1606$ (for all data).

ASSOCIATED CONTENT

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

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ACKNOWLEDGMENT

This work was supported by the UCLA, DOE (Grant ER15984), Sloan Foundation, the University of Erlangen-Nuremburg, DFG, and the Bavarian California Technology Center (BaCaTec). The use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. MRCAT (Sector 10) operations are supported by the Department of Energy and the MRCAT member institutions.

REFERENCES

(1) Chirik, P. J.; Wieghardt, K. *Science* **2010**, *327*, 794.

(2) van der Vlugt, J. I.; Reek, J. N. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 8832.

(3) Ray, K.; Petrenko, T.; Wieghardt, K.; Neese, F. *Dalton Trans.* **2007**, 1552.

(4) Kohl, S. W.; Weiner, L.; Schwartsburd, L.; Konstantinovski, L.; Shimon, L. J. W.; Ben-David, Y.; Iron, M. A.; Milstein, D. *Science* **2009**, *324*, 74.

(5) Allgeier, A. M.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 894.

(6) Diaconescu, P. L. *Acc. Chem. Res.* **2010**, *43*, 1352.

(7) Diaconescu, P. L. *Comments Inorg. Chem.* **2010**, *31*, 196.

(8) Gregson, C. K. A.; Gibson, V. C.; Long, N. J.; Marshall, E. L.; Oxford, P. J.; White, A. J. P. *J. Am. Chem. Soc.* **2006**, *128*, 7410.

(9) Süss;ner, M.; Plenio, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 6885.

(10) Liu, G.; He, H.; Wang, J. *Adv. Synth. Catal.* **2009**, *351*, 1610.

(11) Ringenberg, M. R.; Kokatam, S. L.; Heiden, Z. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2007**, *130*, 788.

(12) Slone, C. S.; Mirkin, C. A.; Yap, G. P. A.; Guzei, I. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 10743.

(13) Tennyson, A. G.; Lynch, V. M.; Bielawski, C. W. *J. Am. Chem. Soc.* **2010**, *132*, 9420.

(14) Ringenberg, M. R.; Nilges, M. J.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **2010**, *29*, 1956.

(15) Sixt, T.; Sieger, M.; Krafft, M. J.; Bubrin, D.; Fiedler, J.; Kaim, W. *Organometallics* **2010**, *29*, 5511.

(16) Kaim, W.; Lahiri, G. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 1778.

(17) Poneti, G.; Mannini, M.; Sorace, L.; Sainctavit, P.; Arrio, M.-A.; Otero, E.; Criginski Cezar, J.; Dei, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 1954.

(18) Shafir, A.; Fiedler, D.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2002**, 555.

(19) Broderick, E. M.; Diaconescu, P. L. *Inorg. Chem.* **2009**, *48*, 4701.

(20) Kaim, W.; Sixt, T.; Weber, M.; Fiedler, J. *J. Organomet. Chem.* **2001**, *637*–*639*, 167.

(21) Sixt, T.; Fiedler, J.; Kaim, W. *Inorg. Chem. Commun.* **2000**, *3*, 80.

(22) Shaw, A. P.; Norton, J. R.; Buccella, D.; Sites, L. A.; Kleinbach, S. S.; Jarem, D. A.; Bocage, K. M.; Nataro, C. *Organometallics* **2009**, *28*, 3804.

(23) Paim, L.; Batista, A.; Dias, F.; Golfeto, C.; Ellena, J.; Siebald, H.; Ardisson, J. *Transition Met. Chem.* **2009**, *34*, 949.

(24) Gibson, V. C.; Gregson, C. K. A.; Halliwell, C. M.; Long, N. J.; Oxford, P. J.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **2005**, *690*, 6271.

(25) Monreal, M. J.; Carver, C. T.; Diaconescu, P. L. *Inorg. Chem.* **2007**, *46*, 7226.

(26) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(27) Holm, R. H.; Everett, J., G. W.; Chakravorty, A. In *Progress in Inorganic Chemisrty*; Cotton, F. A., Ed.; Wiley: New York, 2007; p 83.

(28) Mizuoka, K.; Kim, S.-Y.; Hasegawa, M.; Hoshi, T.; Uchiyama, G.; Ikeda, Y. *Inorg. Chem.* **2003**, *42*, 1031.

(29) Mizuoka, K.; Ikeda, Y. *Inorg. Chem.* **2003**, *42*, 3396.

(30) Kapturkiewicz, A.; Behr, B. *Inorg. Chim. Acta* **1983**, *69*, 247.

(31) Zanello, P.; Cinquantini, A. *Trans. Met. Chem.* **1985**, *10*, 370.

(32) Roy, N.; Sproules, S.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2009**, *48*, 3783.

(33) De Castro, B.; Freire, C. *Inorg. Chem.* **1990**, *29*, 5113.

(34) Vilas-Boas, M.; Freire, C.; de Castro, B.; Christensen, P. A.; Hillman, A. R. *Inorg. Chem.* **1997**, *36*, 4919.

(35) de Castro, B.; Freire, C.; Pereira, E. *J. Chem. Soc., Dalton Trans.* **1994**, 571.

(36) Freire, C.; de Castro, B. *J. Chem. Soc., Dalton Trans.* **1998**, 1491.

(37) de C.T. Carrondo, M. A. A. F.; de Castro, B.; Coelho, A. M.; Domingues, D.; Freire, C.; Morais, J. *Inorg. Chim. Acta* **1993**, *205*, 157.

(38) Goldsby, K. A.; Blaho, J. K.; Hoferkamp, L. A. *Polyhedron* **1989**, *8*, 113.

(39) Azevedo, F.; de C. T. Carrondo, M. A. A. F.; de Castro, B.; Convery, M.; Domingues, D.; Freire, C.; Duarte, M. T.; Nielsen, K.; Santos, I. C. *Inorg. Chim. Acta* **1994**, *219*, 43.

(40) Shimazaki, Y.; Tani, F.; Fukui, K.i.; Naruta, Y.; Yamauchi, O. *J. Am. Chem. Soc.* **2003**, *125*, 10512.

(41) Shimazaki, Y.; Yajima, T.; Tani, F.; Karasawa, S.; Fukui, K.; Naruta, Y.; Yamauchi, O. *J. Am. Chem. Soc.* **2007**, *129*, 2559.

(42) Orio, M.; Jarjayes, O.; Kanso, H.; Philouze, C.; Neese, F.; Thomas, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 4989.

(43) Meleshonkova, N. N.; Shpakovsky, D. B.; Fionov, A. V.; Dolganov, A. V.; Magdesieva, T. V.; Milaeva, E. R. *J. Organomet. Chem.* **2007**, *692*, 5339.

(44) Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. *Organometallics* **2000**, *19*, 3978.

(45) Pearson, D. E.; Wysong, R. D.; Breder, C. V. *J. Org. Chem.* **1967**, *32*, 2358.

(46) Willoughby, C. A.; Duff, R. R.; Davis, W. M.; Buchwald, S. L. *Organometallics* **1996**, *19*, 472.

(47) Shalev, D. E.; Chiacchiera, S. M.; Radkowsky, A. E.; Kosower, E. M. *J. Org. Chem.* **1996**, *61*, 1689.

(48) Molina, P.; López-Leonardo, C.; Llamas-Botía, J.; Foces-Foces, C.; Fernández-Castaño, C. *Tetrahedron* **1996**, *52*, 9629.

(49) Goerlich, J. R.; Farkens, M.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **1994**, *620*, 707.

(50) Liu, X.; Thirupathi, N.; Guzei, I. A.; Verkade, J. G. *Inorg. Chem.* **2004**, *43*, 7431.

(51) Liu, C.-Y.; Chen, D.-Y.; Cheng, M.-C.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1995**, *14*, 1983.

(52) Liu, B.; Cui, D. *Dalton Trans.* **2009**, 550.

(53) Bebbington, M. W. P.; Bourissou, D. *Coord. Chem. Rev.* **2009**, *253*, 1248.

(54) Hillhouse, G. L.; Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1982**, *21*, 2064.

(55) Cadierno, V.; Zablocka, M.; Donnadieu, B.; Igau, A.; Majoral, J. P.; Skowronska, A. *Chem.—Eur. J.* **2000**, *6*, 345.

(56) Buchler, J. W.; Dippell, T. *Eur. J. Inorg. Chem.* **1998**, *1998*, 445.

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

(58) Evans, W. J.; Deming, T. J.; Olofson, J. M.; Ziller, J. W. *Inorg. Chem.* **1989**, *28*, 4027.

(59) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021.

(60) Thomson, R. K.; Scott, B. L.; Morris, D. E.; Kiplinger, J. L. *Compt. Rend. Chim.* **2010**, *13*, 790.

(61) Castagnola, N. B.; Kropf, A. J.; Marshall, C. L. *Appl. Catal., A* **2005**, *290*, 110.