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Yttrium-Alkyl Complexes Supported by a Ferrocene-Based Phosphinimine Ligand

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Abstract

The synthesis and characterization of two yttrium alkyl complexes supported by a bisphosphinimine ferrocene ligand, **NP^{fc}** (1,1'-di(2,4-di-*tert*-butyl-6-di-phenylphosphiniminophenoxy)ferrocene), were accomplished. Although **(NP^{fc})Y(CH$_2$Ph)** and **(NP^{fc})Y(CH$_2$SiMe$_3$)** could be structurally characterized, these compounds are thermally sensitive and decompose at ambient temperature within hours. Their characterization was accomplished by NMR spectroscopy, electrochemical measurements, and elemental analysis. Reactivity studies were also carried out, however, the lack of prolonged thermal stability at ambient temperature of these molecules led to decomposition before the clean formation of reaction products could be observed.

Introduction

Rare-earth alkyl complexes have been studied intensely because of their reactivity toward challenging substrates.[1-9] In 1983, Watson reported the first yttrium(III) monoalkyl metallocene complex;[10] that report was also the first to identify a ligand exchange reaction going through a four-membered transition state identified as σ-bond metathesis.[11-13] Although cyclopentadienyl ligands have dominated the chemistry of yttrium alkyl complexes for a long time,[3-5] recently, several groups have reported the synthesis of such compounds supported by non-cyclopentadienyl ligands.[14-16]

Our group has studied extensively the reactivity of group 3 metals and uranium alkyl complexes supported by diamide ligands towards heterocyclic aromatic compounds.[17-18] Benzyl complexes were found to ring open 1-methylimidazoles,[19-23] effect C–C coupling of pyridines,[24-25] and alkyl transfer to isoquinoline.[26-27] In those cases, the ligand framework was a ferrocene-diamide that could support a weak donor-acceptor interaction between the metal in the ligand.[18, 28-30] In another case, a pyridine-diamide ligand was prepared in order to probe the significance of this interaction; the resulting yttrium and lutetium complexes showed analogous reactivity toward aromatic N-heterocycles, but the reactions were less straightforward than in the case of complexes supported by ferrocene diamide ligands.[31] Other groups have prepared rare-earth metal complexes supported by pyridine-diamide ligands for the polymerization of ethylene and methyl methacrylate.[32]

In addition to diamide ligands, we also explored the use of ferrocene-derived Schiff base metal complexes for the ring-opening polymerization of cyclic esters.[17, 33-36] Schiff base metal complexes have found numerous uses in coordination chemistry and catalysis,[37-42] alkoxide yttrium complexes supported by such ligands being intensely researched as initiators for the ring-

opening polymerization of cyclic esters.[17, 35-36, 43-50] On the other hand, reports of structurally characterized alkyl or aryl rare earth complexes bearing an imine functionality in the backbone are rare,[51-52] the majority being represented by phosphinimine ligands.[53-60] In our lab, the synthesis of an electrophilic metal alkyl complex supported by a Schiff base ferrocene ligand would continually fail. Although a few examples of alkyl yttrium complexes supported by a ligand containing an imine group exist,[53, 61] in general, attempts to isolate such complexes resulted in the migration of the alkyl ligand to the imine group.[57, 62-63] We and others[64-65] have reasoned that replacing the imine with a phosphinimine backbone would increase the robustness of the resulting yttrium alkyl complexes. Herein, we report the synthesis, characterization, and reactivity of two yttrium alkyls supported by a ferrocene-based diphosphinimine ligand. These compounds were characterized by electrochemical measurements, elemental analysis, NMR spectroscopy, and X-ray crystallography. Reactivity studies were also carried out, however, the lack of prolonged thermal stability at ambient temperature of these molecules led to decomposition before the clean formation of reaction products could be observed.

Results and discussion

Synthesis and characterization of yttrium alkyl complexes. The synthesis of 1,1'-di(2-*tert*-butyl-6-di(phenylphosphiniminophenol))ferrocene, (phosfen)H_2, was previously reported by our group.[33] In an attempt to optimize its synthesis and explore other derivatives, we observed that substitution of the *para*-phenolic hydrogen with a *tert*-butyl group led to better solubility properties and ease of isolation. A similar procedure as that used for the synthesis of (phosfen)H_2 was followed for the synthesis of **(NP^{fc})H$_2$** (**NP^{fc}** = 1,1'-di(2,4-di-*tert*-butyl-6-di-phenylphosphiniminophenol)ferrocene). The corresponding sodium salt was prepared in situ by

treating **(NP^{fc})H$_2$** with an excess of NaH. This salt was immediately used in a reaction with $YCl_3(THF)_{3.5}$ in THF yielding **(NP^{fc})YCl** as a pale yellow powder (Scheme 1). Finally, this precursor allowed the preparation of **(NP^{fc})Y(CH$_2$Ph)** and **(NP^{fc})Y(CH$_2$SiMe$_3$)** via another salt metathesis reaction with KCH_2Ph or $LiCH_2SiMe_3$, respectively (Scheme 1).

The ^{1}H NMR spectrum of **(NP^{fc})Y(CH$_2$Ph)** in C_6D_6 at ambient temperature showed a doublet at 2.44 ppm that was assigned to the methylene group of the benzyl ligand. The ^{31}P NMR spectrum of **(NP^{fc})Y(CH$_2$Ph)** shows a singlet at 32.16 ppm. For the neosilyl derivative, **(NP^{fc})Y(CH$_2$SiMe$_3$)**, the methylene protons appeared at 0.23 ppm as a doublet and the trimethylsilyl group appeared at 0.34 ppm as a singlet; additionally, there is a singlet in the ^{31}P NMR spectrum at 34.06 ppm.

Scheme 1. Synthesis of yttrium alkyl complexes.

In addition to being characterized in solution by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, both **(NP^{fc})Y(CH$_2$Ph)** and **(NP^{fc})Y(CH$_2$SiMe$_3$)** were characterized by single-crystal X-ray diffraction. The solid-state molecular structures (Figure 1) of the two compounds show a pseudo-square pyramidal yttrium center with the alkyl ligand in the apical position. The Y-CH$_2$ distances are 2.485(7) and 2.399(3) Å for **(NP^{fc})Y(CH$_2$Ph)** and **(NP^{fc})Y(CH$_2$SiMe$_3$)**, respectively. The Fe-Y distances of 3.95 Å (**(NP^{fc})Y(CH$_2$Ph)**) and 4.06 Å (**(NP^{fc})Y(CH$_2$SiMe$_3$)**) are outside the range of an iron-yttrium interaction, the sum of the covalent radii of the two atoms being 3.22 Å.[66]

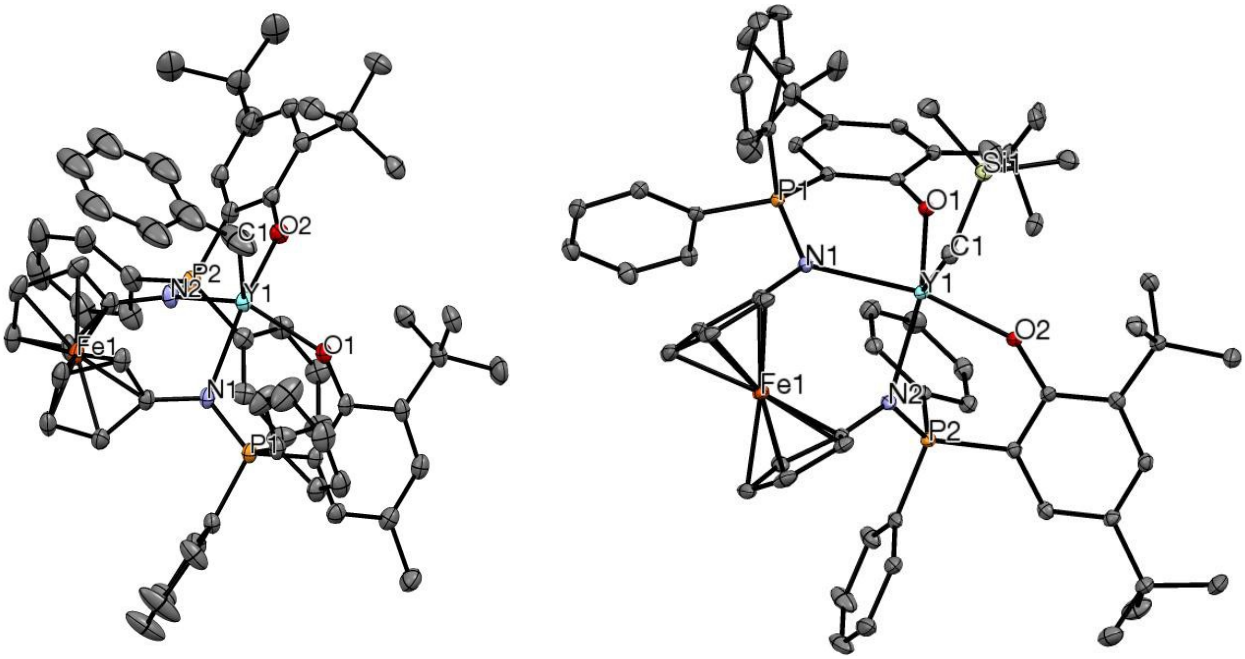

Figure 1. Thermal-ellipsoid (35% probability) representation of **(NP^{fc})Y(CH$_2$Ph)** (left) and **(NP^{fc})Y(CH$_2$SiMe$_3$)** (right); hydrogen, disordered counterparts, and solvent atoms were removed for clarity. Selected distances (Å) and angles (°) for **(NP^{fc})Y(CH$_2$Ph)**: Y(1)-C(1), 2.485(7); Y(1)-O(1), 2.139(3); Y(1)-O(2), 2.169(3); Y(1)-N(1), 2.388(3); Y(1)-N(2), 2.359(3); P(1)-N(1), 1.619(3); P(2)-N(2), 1.607(3); O(1)-Y(1)-O(2), 94.52(10); N(2)-Y(1)-N(1), 88.25(11); O(1)-

Y(1)-C(1), 109.8(2); O(2)-Y(1)-C(1), 97.0(2); N(1)-Y(1)-C(1), 107.0(2); N(2)-Y(1)-C(1), 121.7(2). For **(NP^{fc})Y(CH$_2$SiMe$_3$)**: Y(1)-C(1), 2.399(3); Y(1)-O(1), 2.128(2); Y(1)-O(2), 2.1822(19); Y(1)-N(1), 2.429(2); Y(1)-N(2), 2.371(2); P(1)-N(1), 1.616(2); P(2)-N(2), 1.600(2); O(1)-Y(1)-O(2), 98.78(7); N(2)-Y(1)-N(1), 85.92(8); O(1)-Y(1)-C(1), 106.53(9); O(2)-Y(1)-C(1), 99.86(9); N(1)-Y(1)-C(1), 103.84(9); N(2)-Y(1)-C(1), 121.52(9).

Cyclic voltammetry studies were performed with a glassy carbon electrode in 1,2-difluorobenzene containing 0.1 M [^{n}Pr$_4$N][BAr$^F{}_4$] in order to assess the redox activity of the yttrium complexes. It was imperative to employ a non-coordinating solvent and electrolyte in order to obtain this data[67] since other conditions led to the decomposition of the yttrium benzyl complex. The cyclic voltammogram of **(NP^{fc})Y(CH$_2$Ph)** recorded at 100 mV s^{-1} (Figure 2) indicates a quasi-reversible one-electron redox couple, with anodic and cathodic peak potentials of –0.28 and –0.49 V, respectively. This redox event is assigned to the ferrocene-ferrocenium oxidation in **(NP^{fc})Y(CH$_2$Ph)**. Unfortunately, when attempting the chemical oxidation of **(NP^{fc})Y(CH$_2$Ph)**, formation of bibenzyl was observed and the yttrium product could not be isolated and characterized. Cyclic voltammetry studies of **(NP^{fc})H$_2$** and **(NP^{fc})YCl** (Table 1) were also performed and show that, as expected, while **(NP^{fc})H$_2$** ($E_{1/2}$ = –0.74 V, Figure S65) is easier to oxidize than **(NP^{fc})Y(CH$_2$Ph)**, **(NP^{fc})YCl** is slightly more difficult to oxidize ($E_{1/2}$ = –0.22 V, Figure S67) than **(NP^{fc})Y(CH$_2$Ph)**. Using the same conditions as for **(NP^{fc})Y(CH$_2$Ph)**, two oxidations events were found for **(NP^{fc})Y(CH$_2$SiMe$_3$)** at –0.24 and –0.04 V and one reduction at –0.29 V (Figure S69); a rate study (Figure S71) indicated that these redox events are irreversible.

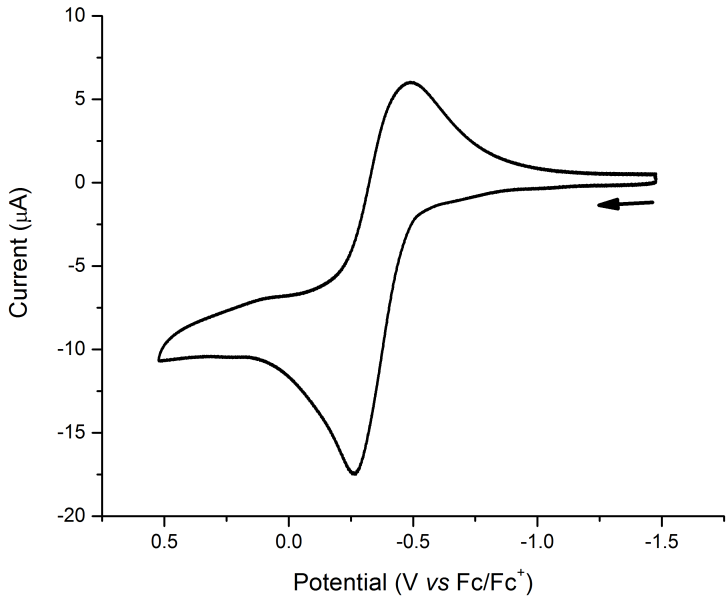

Figure 2. Cyclic voltammogram of a 1,2-difluorobenzene solution of 2.5 mM **(NP^{fc})Y(CH$_2$Ph)** recorded at 100 mV s^{-1} with a freshly polished glassy carbon working electrode and 100 mM [^{n}Pr$_4$N][BAr$^F{}_4$].

Table 1. Redox potentials for **(NP^{fc})H$_2$**, **(NP^{fc})YCl**, and **(NP^{fc})Y(CH$_2$Ph)**.

Compound	$E_{1/2}$ **(V)**	i_{pc}/i_{pa}
(NP^{fc})H$_2$	–0.74	1.04
(NP^{fc})YCl	–0.22	0.98
(NP^{fc})Y(CH$_2$Ph)	–0.39	0.72

Reactivity studies. The thermal stability of **(NP^{fc})Y(CH$_2$Ph)** was investigated by heating a C_6D_6 solution to 50 ºC for three hours; under these conditions, **(NP^{fc})Y(CH$_2$Ph)** completely decomposed. Attempts to identify the products were unsuccessful. The thermal stability of **(NP^{fc})Y(CH$_2$SiMe$_3$)** was also investigated by letting a C_6D_6 solution stand for two hours in a J. Young tube with a trimethoxybenzene internal standard and it was found that 35% starting

material was still present (Figures S43–S45). Additionally, heating a solution of **(NP^{fc})Y(CH$_2$SiMe$_3$)** in C_6D_6 for one hour at 50 ºC showed complete decomposition.. In an attempt to increase the thermal stability of **(NP^{fc})Y(CH$_2$SiMe$_3$)**, donor molecules such as THF, PPh_3, and DMAP (4-dimethylaminopyridine) were introduced; however, it did not result in the stabilization of this complex. Introducing 10 equivalents of THF or PPh_3, showed decomposition and 29 or 42%, respectively, of (NP^{fc})Y(CH$_2$SiMe$_3$) still present after 2 h at ambient temperature (Figures S46-S48 and S49-S51). Finally, reacting 10 equivalents of DMAP with (NP^{fc})Y(CH$_2$SiMe$_3$) showed conversion to an intractable mixture of products in 15 min.

As mentioned earlier, our group has found interesting reactivity for group 3 metal benzyl complexes with aromatic N-heterocycles. The reactions of (NN^{fc})Y(CH$_2$Ph) (NN^{fc} = fc(NSi^{t}BuMe$_2$)$_2$, fc = 1,1'-ferrocenediyl) with 2-phenylpyridine[25] and 1-methylimidazole[20] showed C–C coupling of pyridine and ring opening of the imidazole. We proposed at the time that the diverse reactions observed with the alkyl complexes supported by ferrocene diamide ligands is a consequence of the fact that the group 3 metals have the possibility to engage in a weak interaction with iron.[18] Since the distance between yttrium and iron in **(NP^{fc})Y(CH$_2$Ph)** and **(NP^{fc})Y(CH$_2$SiMe$_3$)** is outside the range of a metal-metal interaction, we became interested to compare the reactivity of the new compounds with that of those previously reported. When treating **(NP^{fc})Y(CH$_2$Ph)** with 1-methylimidazole in Et_2O or C_6D_6 at ambient temperature, a reaction occurred but we observed the formation of a mixture of unidentifiable products. Attempts with other substrates such as 1-methylbenzimidazole and benzoxazole also led to mixtures of products. Furthermore, treating **(NP^{fc})Y(CH$_2$Ph)** with pyridine in Et_2O or C_6D_6 produced similar outcomes. Replacing pyridine with 2-phenylpyridine led to no reaction at ambient temperature. Other reactivity studies toward this substrate were not pursued since

(NP^{fc})Y(CH$_2$Ph) shows complete decomposition at 50 ºC after three hours and the C-C coupling of a bulky pyridine required a prolonged heating even for the ferrocene diamide complexes,[24] which are more sterically accessible than **(NP^{fc})Y(CH$_2$Ph)**.

Scheme 2. Reactions of **(NP^{fc})Y(CH$_2$SiMe$_3$)** with silanes.

Because those reactions did not yield fruitful results, we decided to pursue the formation of a yttrium hydride complex in order to determine if the phosphinimine architecture is compatible with the hydride ligand, especially since examples of non-metallocene hydride complexes are not numerous.[68] Initially, we used a mild hydride source, Me_2PhSiH, with **(NP^{fc})Y(CH$_2$SiMe$_3$)** in C_6D_6 at ambient temperature. The reaction was monitored over the course of three hours before decomposition of the starting material occurred. An analogous reaction using Ph_2SiH_2 was also carried out. Before a significant reaction to produce a clean product could be observed, the decomposition of **(NP^{fc})Y(CH$_2$SiMe$_3$)** occurred again. Lastly, **(NP^{fc})Y(CH$_2$SiMe$_3$)** was treated with $PhSiH_3$ in C_6D_6. This was done initially on an NMR scale by freezing a 0.5 mL C_6D_6 solution of **(NP^{fc})Y(CH$_2$SiMe$_3$)** in the glove box and adding 5 equivalents of $PhSiH_3$ to this solution. The NMR tube was taken immediately to the spectrometer and the reaction was warmed gently until the mixture melted; NMR spectra were recorded immediately. A relatively clean reaction was observed and four new *tert*-butyl peaks appeared at 1.72, 1.56, 1.39, and 1.26 ppm assigned to a product that we label **A**; **(NP^{fc})Y(CH$_2$SiMe$_3$)** shows

only two *tert*-butyl peaks. The reaction was repeated in Et_2O at –78 ºC on a larger scale and the formation of the same product **A** was observed (Scheme 2). Attempts to isolate this product proved unsuccessful due to its insolubility in ethereal solvents, hexanes, *n*-pentane, and dichloromethane. Compound **(NP^{fc})Y(CH$_2$Ph)** did not react cleanly with $PhSiH_3$. We propose that **A** is a polymeric species formed from an intermediate yttrium hydride.[69] Reactions with unsaturated substrates, diphenylacetylene, azobenzene, or *trans*-stilbene, and **A** were carried out in an effort to find more information about the nature of **A**. Unfortunately, no reaction was observed in either case after four hours at ambient temperature. In addition, the reaction with an electrophile, dicyclohexylcarbodiimide (DCC), was carried out and aliquots were taken at 15 min, 60 min, and 24 h; monitoring by ^{1}H NMR spectroscopy showed no reaction with DCC. However, a new ^{31}P resonance was observed in the corresponding ^{31}P NMR spectra with the same relative intensity across all three spectra. Upon further investigation, we realized that **A** slowly reacts with C_6D_6 over time. Unfortunately, the isolation of the observed product was not possible because its formation was always accompanied by the formation of other products (Figure S60).

Conclusions

The synthesis and characterization of yttrium alkyl complexes supported by a bisphosphinimine ferrocene ligand were accomplished. Although **(NP^{fc})Y(CH$_2$Ph)** and **(NP^{fc})Y(CH$_2$SiMe$_3$)** could be structurally characterized, these compounds are thermally sensitive and decompose at ambient temperature within hours. This instability prevented an extensive reactivity study since decomposition of the starting materials was apparent before a reaction with the substrate of interest could occur. When treating **(NP^{fc})Y(CH$_2$SiMe$_3$)** with 5 equivalents of

$PhSiH_3$, a new product is obtained. The identity of this product could not be established, but it is likely a polymeric species formed from a transient, reactive hydride intermediate.

Experimental

General considerations. All reactions were performed using standard Schlenk techniques or in an MBraun drybox (<1 ppm O_2/H_2O) unless noted otherwise. All glassware, cannulae, and Celite were stored in an oven at > 425 K before being brought into the drybox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs[70] 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. NMR spectra were recorded at ambient temperature on Bruker AV-300, AV-400, AV-500, and DRX-500 spectrometers unless otherwise noted. Proton and carbon chemical shifts are given relative to residual solvent peaks. Phosphorus chemical shifts are given relative to the external standard H_3PO_4. Unless otherwise noted, all reagents were acquired from commercial sources and used as received. Elemental analyses were performed on an Exeter Analytical, Inc. CE-440 Elemental Analyzer.

Synthesis of $(NP^{fc})H_2$. Compound 1,1'-di(2,4-di-*tert*-butyl-6-di-phenylphosphazidophenoxy)ferrocene[33] (2.21 g, 2.11 mmol, 1 equiv) was dissolved in 18 mL of toluene and transferred to a Schlenk tube and removed from the glove box. The solution was heated at 50 ºC for 6 h. The reaction mixture was brought back into the glove box, filtered over a medium frit and washed with cold toluene (3 x 5 mL) to yield an orange powder. Yield: 1.64 g, 74.7%. ^{1}H NMR (500 MHz, 25 ºC, C_6D_6), δ (ppm): 1.15 (s, 18H, CCH_3), 1.72 (s, 18H, CCH_3), 3.55 (s, 4H, C_5H_4), 3.98 (s, 4H, C_5H_4), 6.96 (m, 12H, $P(C_6H_5)_2$), 7.03 (d, 2H, C_6H_2), 7.67 (s, 2H,

C_6H_2), 7.76 (m, 8H, $P(C_6H_5)_2$), 15.31 (s, 2H, O*H*). ^{13}C NMR (126 MHz, 25 ºC, C_6D_6), δ (ppm): 30.00, 31.59, 34.25, 34.93, 62.98, 63.07, 65.76, 131.89, 133.31, 133.40. ^{31}P NMR (121 MHz, 25 ºC, C_6D_6) δ 23.74 ppm. Anal. for $C_{62}H_{70}FeN_2O_2P_2$: Calcd: C, 74.99%; H, 7.11%; N 2.82%. Found: C, 75.45%, H, 6.87%, N, 2.44%.

Synthesis of (NP^{fc})YCl. (NP^{fc})H$_2$ (1.48 g, 1.49 mmol, 1 equiv) was dissolved in 30 mL of THF and transferred to a stirring slurry of excess NaH (0.358 g, 14.9 mmol, 10 equiv) in 10 mL of THF. This solution was stirred for 2 h before filtering over Celite. The red solution was then added to a stirring slurry of YCl_3•$THF_{3.5}$ (0.734 g, 1.64 mmol, 1.10 equiv) and stirred for 2 h. The volatiles were removed under vacuum and the remaining solids were dissolved in toluene and filtered over Celite. The volatiles from the toluene extract were removed, and the remaining solids were put into hexanes and stirred for 15 min. This yellow slurry was filtered over a medium frit and the solids were collected and isolated as **(NP^{fc})YCl**. The product was crystallized from a concentrated toluene solution layered with hexanes at –40 ºC. Yield: (1.21 g, 73%). ^{1}H NMR (500 MHz, 25 ºC, C_6D_6), δ (ppm): 1.20 (s, 18H, CCH_3), 1.59 (s, 18H, CCH_3), 3.48 (s, 2H, C_5H_4), 3.53 (s, 2H, C_5H_4), 3.70 (s, 2H, C_5H_4), 5.02 (s, 2H, C_5H_4), 6.98 (m, 14H, $P(C_6H_5)_2$), 7.82 (m, 4H, C_6H_2), 7.76 (m, 6H, $P(C_6H_5)_2$). ^{13}C NMR (126 MHz, 25 ºC, C_6D_6), δ (ppm) 31.04, 32.31, 34.82, 36.42, 66.08, 66.76, 67.53, 68.13, 102.60, 112.50, 113.38, 132.73, 132.84, 134.23, 134.30, 137.06, 137.18, 140.91, 140.97, 168.33. ^{31}P NMR (121 MHz, 25 ºC, C_6D_6) δ 31.63 ppm. Anal. for $C_{62}H_{68}FeN_2O_2P_2YCl$: Calcd: C, 66.76%; H, 6.15%; N 2.51%. Found: C, 66.30; H, 6.05%; N, 2.76%.

Synthesis of (NP^{fc})Y(CH$_2$Ph). A diethyl ether solution (3 mL) of **(NP^{fc})YCl** (132 mg, 0.118 mmol, 1 equiv) was prepared inside the glove box in a scintillation vial and chilled to –78 ºC for 15 min. A slurry of KCH_2Ph (16.2 mg, 0.124 mmol, and 1.05) in Et_2O (2 mL) was added

dropwise to the stirring solution of **(NP^{fc})YCl** and stirred for 2 h at –78 ºC. The reaction was filtered over Celite to remove excess KCH_2Ph. The volatiles were removed from this solution and the solids were dissolved in toluene and filtered over Celite to remove any remaining salts. Next, the volatiles of the toluene solution were removed. The product was crystallized from diethyl ether and *n*-pentane at –40 ºC. Yield (80.3 mg, 58%). ^{1}H NMR (500 MHz, 25 ºC, C_6D_6), δ (ppm): 1.19 (s, 18H, CCH_3), 1.63 (s, 18H, CCH_3), 2.44 (d, 2H, YCH_2), 3.56 (s, 4H, C_5H_4), 3.71 (s, 2H, C_5H_4), 3.49 (s, 2H, C_5H_4), 6.75 (m, 2H, C_6H_2), 6.93 (m, 8H, $P(C_6H_5)_2$), 7.05 (m, 12H, $P(C_6H_5)_2$), 7.31 (br, 2H, C_6H_5), 7.46 (d, 2H, C_6H_2), 7.83 (br, 3H, C_6H_5) ^{13}C NMR (75 MHz, 25 ºC, C_6D_6), δ (ppm) 31.15, 32.33, 43.81, 36.45, 66.03, 103.60, 125.05, 132.66, 134.34. 140.51. ^{31}P NMR (121 MHz, 25 ºC, C_6D_6) δ 32.17 ppm. Anal. for $C_{69}H_{75}FeN_2O_2P_2Y$: Calcd: C, 70.77%; H, 6.46%; N 2.39%. Found: C, 70.32%; H, 6.03%, N, 2.68%.

Synthesis of (NP^{fc})Y(CH_2SiMe_3). A diethyl ether solution (4 mL) of **(NP^{fc})YCl** (177 mg, 0.158 mmol, 1 equiv) was inside the glove box in a scintillation vial and chilled to –78 ºC for 15 min. A 0.7 M solution of $LiCH_2SiMe_3$ (0.25 mL, 0.174 mmol, 1.1 equiv) was added dropwise to the stirring solution of (NP^{fc})YCl and stirred for 2 h at –78 ºC. The solution was filtered over a medium frit and the solids were washed with cold (–40 ºC) diethyl ether (2 x 2 mL). These solids yielded pure **(NP^{fc})Y(CH_2SiMe_3)** as a pale yellow solid, which could be crystallized from toluene and *n*-pentane. Yield: 111 mg, 60%. ^{1}H NMR (500 MHz, 25 ºC, C_6D_6), δ (ppm): 0.23 (d, 2H, YCH_2), 0.34 (s, 9H, $Si(CH_3)_3$) 1.18 (s, 18H, CCH_3), 1.68 (s, 18H, CCH_3), 3.50 (s, 2H, C_5H_4), 3.53 (s, 2H, C_5H_4), 3.76 (s, 2H, C_5H_4), 4.84 (s, 2H, C_5H_4), 6.75 (d, 2H, C_6H_2), 6.99 (m, 12H, $P(C_6H_5)_2$), 7.33 (m, 4H, $P(C_6H_5)_2$), 7.72 (d, 2H, C_6H_2), 7.99 (m, 4H, $P(C_6H_5)_2$). ^{13}C NMR (126 MHz, 25 ºC, C_6D_6), δ (ppm): 5.40, 16.12, 31.37, 32.27, 34.75, 36.53, 65.31, 65.63, 66.45, 68.11, 68.79, 104.71, 132.56, 134.18, 134.26, 134.39, 134.46, 136.63, 136.75, 140.71, 140.77, 168.61. ^{31}P

NMR (121 MHz, 25 ºC, C_6D_6) δ 34.07 ppm. Anal. for $C_{66}H_{79}FeN_2O_2P_2SiY$: Calcd: C, 67.92%; H, 6.82%; N 2.40%. Found: C, 67.51%; H, 6.43%; N, 2.71%.

Synthesis of A. A diethyl ether solution (5 mL) of **(NP^{fc})Y(CH$_2$SiMe$_3$)** (156 mg, 0.134 mmol, 1.0 equiv) was cooled to 0 ºC inside the glove box in a scintillation vial for 10 min. Using a microliter syringe, $PhSiH_3$ (83 µL, 0.669 mmol, 5.0 equiv) was added to the stirring solution of **(NP^{fc})Y(CH$_2$SiMe$_3$)** and the resulting mixture stirred for 2 h at 0 ºC. The solution was filtered over a medium frit and the solids were washed with cold (0 ºC) hexanes (2 x 2 mL). These solids yielded **A** as a bright yellow powder. Yield: 65.4 mg. Elemental Analysis for **A**: Found: C, 71.25%; H, 8.97%; N, 2.08%.

Cyclic Voltammetry. Cyclic voltammetric studies were carried out in a 20 mL scintillation vial with electrodes fixed in position by rubber stopper. A glassy carbon working electrode with planar circular area of 0.071 cm^2, a platinum reference electrode with planar circular area of 0.031 cm^2, and a silver-wire reference electrode all purchased from CH Instruments. Before each cyclic voltammogram was recorded, the working and auxiliary electrodes were polished with an aqueous suspension of 0.05 µm alumina on a Microcloth polishing pad, after which the electrodes were rinsed with water and blotted dry with a Kimwipe. The electrodes were then brought into the glovebox overnight under vacuum. Cyclic voltammograms were acquired with a CH Instruments potentiostat (model CHI630D). All potentials in this report are given with respect to the ferrocenium-ferrocene couple. This potential was determined after the experiment by adding approximately an equimolar amount of ferrocene per analyte.

X-ray crystal Structures. X-ray quality crystals were obtained from various concentrated solutions placed in a –40 ºC 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_{α} 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 distances and angles, and with anisotropic displacement parameters are listed in the cifs.

X-ray Crystal Structure of (NP^{fc})Y(CH_2Ph). Crystal data for $C_{76}H_{83}FeN_2O_2P_2Y$; M_r = 1263.14; triclinic; space group P-1; *a* = 12.716(6) Å; *b* = 13.305(6) Å; *c* = 21.743(9) Å; α = 82.290(5)°; β = 76.846(5)°; γ = 87.007(5)°; V = 3549(3) $Å^3$; Z = 2; T = 100(2) K; λ = 0.71073 Å; μ = 1.107 mm^{-1}; d_{calc} = 1.182 $g.cm^{-3}$; 34079 reflections collected; 12361 unique (R_{int} = 0.0317); R_1 = 0.0611, wR_2 = 0.1739 for 9979 data with [I>2σ(I)] and R_1 = 0.0749, wR_2 = 0.1823 for all 12361 data. Residual electron density ($e^{-}.Å^{-3}$) max/min: 3.254/-1.318.

X-ray Crystal Structure of (NP^{fc})Y(CH_2SiMe_3). Crystal data for $C_{73}H_{87}FeN_2O_2P_2SiY$; M_r = 1259.24; triclinic; space group P-1; *a* = 13.461(5) Å; *b* = 14.486(6) Å; *c* = 20.937(8) Å; α = 92.576(5)°; β = 102.380(5)°; γ = 110.943(4)°; V = 3691(3) $Å^3$; Z = 2; T = 100(2) K; λ = 0.71073 Å; μ = 1.079 mm^{-1}; d_{calc} = 1.133 $g.cm^{-3}$; 36477 reflections collected; 12893 unique (R_{int} = 0.0457); R_1 = 0.0405, wR_2 = 0.1030 for 9809 data with [I>2σ(I)] and R_1 = 0.0605, wR_2 = 0.1090 for all 12893 data. Residual electron density ($e^{-}.Å^{-3}$) max/min: 0.377/-0.289.

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.

AUTHOR INFORMATION

The authors declare no competing financial interests.

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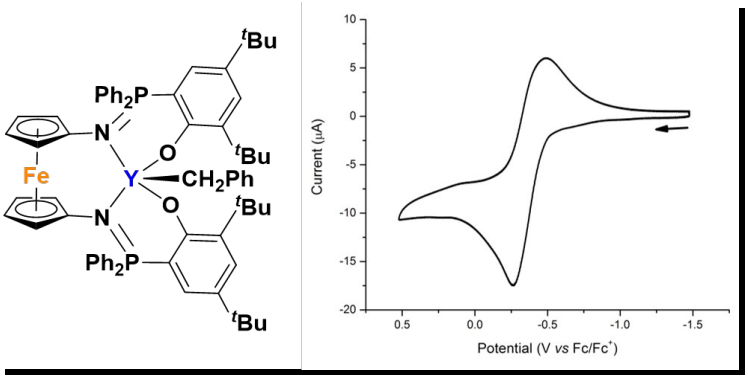
TOC graphic



The synthesis and characterization of two yttrium alkyl complexes supported by a19 bisphosphinimine ferrocene ligand, **NP**^{fc} (1,1'-di(2,4-di-*tert*-butyl-6-di-phenylphosphiniminophenoxy)ferrocene), were accomplished.