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Unusual Redox Chemistry of Ytterbium Carbazole−Bis(oxazoline) Compounds: Oxidative Coupling of Primary Phosphines by an Ytterbium Carbazole−Bis(oxazoline) Dialkyl

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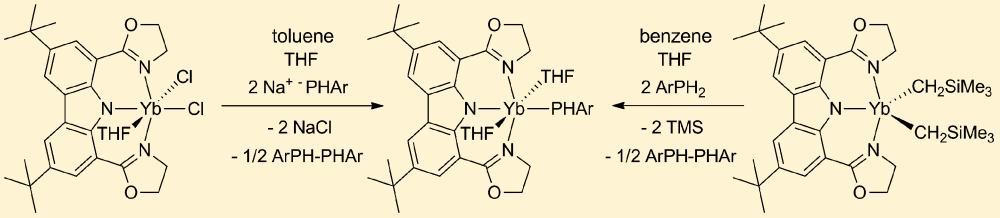
Supporting Information



ABSTRACT: The 1,8-bis(4′,4′-dimethyloxazolin-2′-yl)-3,6-di-*tert*-butylcarbazole anion (Czx) forms monomeric, six-coordinate halide complexes of Yb(II), (Czx)Yb(X)(THF)$_2$ (X = I (**2**), Cl (**3**)), by metathesis of YbX_2 with NaCzx (**1**) or Na/Hg reduction of (Czx)Yb(Cl)$_2$(THF). The crystal structure of **1** reveals a polymeric chain structure in which the oxazoline ring bridges to the Na^+ of an adjacent unit. The iodo complex **2** serves as a precursor to divalent silylamide, alkyl, and phosphide complexes, (Czx)Yb(X)(THF)$_n$ (**4**, X = N(SiMe$_3$)$_2$, n = 1; **5**, X = CH(SiMe$_3$)$_2$, n = 1; **7a**, X = 2,4,6-Me$_3$C$_6$H$_2$PH, n = 2; **7b**, X = 2,4,6-Pr$^i_3$C$_6$H$_2$PH, n = 2). The X-ray structure of **4** reveals a distorted-trigonal-bipyramidal geometry with the Czx ligand occupying two axial sites and one equatorial site in a pseudo-*mer* coordination mode. In contrast to the typical metathesis chemistry observed with LiCH(SiMe$_3$)$_2$, an unusual *oxidation* occurs when **2** or **3** is treated with LiCH$_2$SiMe$_3$ to generate the previously isolated trivalent alkyl (Czx)Yb(CH$_2$SiMe$_3$)$_2$. Trivalent Yb complexes with the Czx ligand also display unusual redox chemistry: rapid *reduction* to the Yb(II) phosphides **7a**,**b** is observed on treatment of *mer*,*cis*-(Czx)Yb(Cl)$_2$(THF) with ArPH$^-$ Na$^+$ (**6a**,**b**) or, equivalently, on treatment of (Czx)Yb(CH$_2$SiMe$_3$)$_2$ with ArPH$_2$. In both cases, oxidative coupling of the phosphide or phosphine was observed to form *meso*- and *rac*-biphosphines, ArPH−PHAr (Ar = 2,4,6-Me$_3$C$_6$H$_2$ (**9a**), 2,4,6-Pr$^i_3$C$_6$H$_2$ (**9b**)).

INTRODUCTION

Oxazolines have an extensive history as ancillary ligands in transition-metal chemistry, particularly as part of the chiral pybox ligand system widely used in asymmetric synthesis.[1] Lanthanide complexes of several different classes of neutral (Chart 1, **A**−**G**) and charged (Chart 2, **H**−**M**) multidentate ligands containing oxazolines have been reported, but only **F** and **K** had been used to support organometallic chemistry prior to our report of trivalent lanthanide alkyls supported by the carbazole−bis(oxazoline) (Chart 2; Czx) ligand.[2−4] A chiral Czx ligand framework was originally introduced by Nakada and Inoue to prepare Cr^{2+} catalysts in situ for the asymmetric allylation and propargylation of aldehydes; this work has been further extended by Connell for the synthesis of butadien-2-ylcarbinols.[5,6]

Oxazolines are attractive ligands in organolanthanide chemistry because they are highly resistant to alkylation and easily modified to vary the steric bulk and introduce chirality, simply by the choice of an appropriate amino alcohol precursor. However, neutral oxazolines are prone to ligand loss even in multidentate arrays; therefore, including the anionic carbazolide unit is designed to provide a better anchor to the lanthanide center. Two other carbazole anion based chelates have been introduced into organolanthanide chemistry recently, including one with phosphine and another with phosphinimine groups in the 1- and 8-positions of the carbazole ring.[7,8]

Previously we reported that the Czx ligand supports monomeric complexes of trivalent lanthanides, including five-coordinate dialkyls, (Czx)Ln(CH$_2$SiMe$_3$)$_2$, and six-coordinate dichlorides, *mer*,*cis*-(Czx)Ln(Cl)$_2$(THF), in which the Czx ligand invariably adopts a rigid *mer* coordination mode.[4] While the complexes were exceptionally stable to ligand redistribution and even to thermal degradation of the dialkyls, the reactivity of the latter with alkenes and other unsaturated molecules was disappointing. This was mainly attributed to the steric crowding caused by the Czx ligand; thus, we felt this ligand might be better suited to divalent lanthanide chemistry. In this

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Chart 1. Neutral Multidentate Ligands Containing Oxazolines

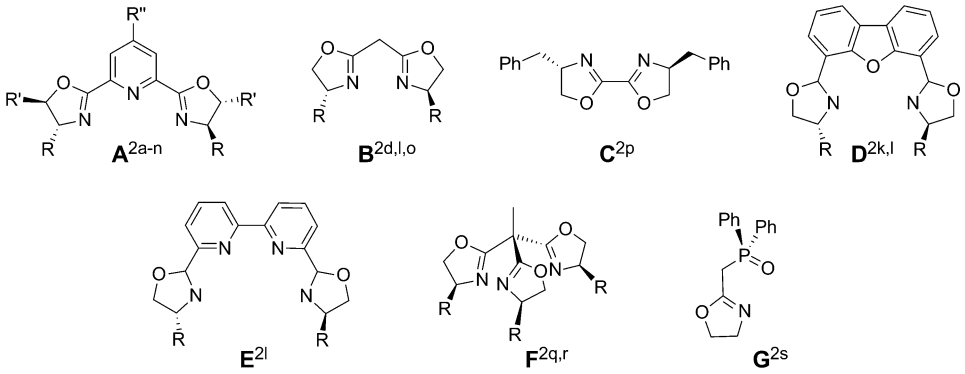
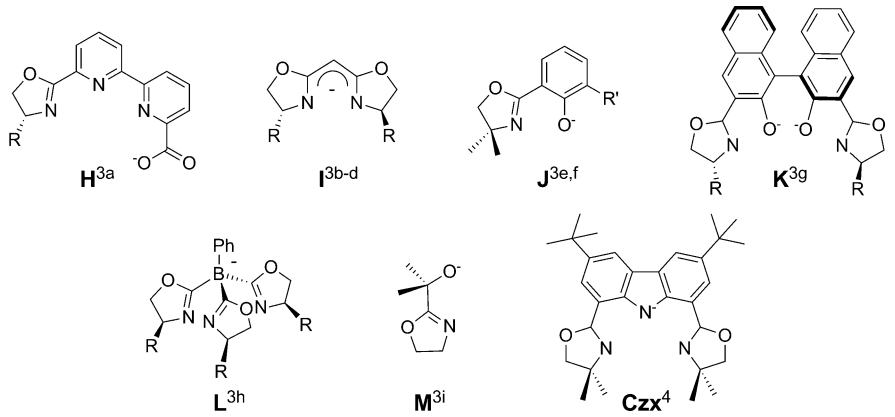


Chart 2. Anionic Multidentate Ligands Containing Oxazolines



contribution, we report some of our results using the Czx ligand to support Yb(II) chemistry. Most notably, we report some unusual redox chemistry involving both *reduction to* and *oxidation from* the divalent oxidation state of ytterbium.

RESULTS AND DISCUSSION

The most convenient access point to divalent ytterbium chemistry is by the metathesis reaction between the sodium salt of the carbazole–bis(oxazoline) ligand, Czx, and YbI_2 (Scheme 1). Deprotonation of the parent ligand HCzx with $NaN(SiMe_3)_2$ proceeds smoothly in toluene to afford the crystalline salt NaCzx (**1**) as a toluene solvate. In the solid state, **1** forms a polymeric chain structure in which one of the oxazoline oxygens bridges to the sodium cation of another unit (Figure 1 and Table 1). The Na is four-coordinate, but the geometry is best described as a square-based pyramid where the three Czx nitrogens occupy the basal plane and the other basal vertex is missing. Oxazoline rings do not usually bridge through oxygen, since this center bears a formal positive charge in one resonance contributor; however, two examples of oxygen bridging to lithium cations have been reported with tris(oxazoline)borate ligands.[9]

Reaction of the crystalline salt **1** with YbI_2 in THF afforded the deep green, six-coordinate iodo complex *mer,trans*-(Czx)YbI$(THF)_2$ (**2**) in excellent yield after recrystallization from toluene. This complex readily loses 1 equiv of THF on standing, as confirmed by the elemental analysis, and as a result, we were unable to obtain crystals of suitable stability for X-ray analysis. However, the observation of a simple seven-line spectrum in the ^{1}H NMR to 194 K indicates a highly symmetrical C_{2v} structure that can only be accommodated by a *mer*-Czx, *trans*-THF octahedral geometry. The analogous chloro complex, *mer,trans*-(Czx)YbCl$(THF)_2$ (**3**) was prepared by sodium amalgam reduction of the previously reported trivalent dichloro complex *mer,cis*-(Czx)Yb$(Cl)_2$(THF) in THF (Scheme 2). The ^{1}H NMR of **3** was broader at room temperature, suggesting THF exchange, but the spectrum sharpened to a simple seven-line pattern below about 250 K, confirming the *mer,trans* geometry. In the case of **3**, THF loss is less facile, as indicated by an elemental analysis consistent with a bis(THF) adduct. Presumably, the smaller chloro ligand decreases steric crowding within the metal coordination sphere, resulting in tighter THF binding.

Reaction of **2** (or **3**) with 1 equiv of $NaN(SiMe_3)_2$ proceeds smoothly in toluene to afford the silylamido complex (Czx)Yb$[N(SiMe_3)_2][THF]$ (**4**) in high yield (Scheme 1). The same complex can also be made by carrying out the acid–base reaction between $Yb[N(SiMe_3)_2]_2[THF]_2$ and HCzx in toluene at 80 °C.[10] Complex **4** can be heated at 100 °C for a prolonged period of time without ligand redistribution, and similarly, reaction of 2 equiv of HCzx with $Yb[N(SiMe_3)_2]_2[THF]_2$ at high temperature produces exclusively **4**, strongly indicating that formation of the bis(Czx) complex, $(Czx)_2Yb$, is precluded on steric grounds. Our previous study showed that having two methyl groups at the 4′-position of the oxazoline ring substantially increases the steric profile of the ligand, while we have also found that having just one larger substituent such as isobutyl allows formation of bis(Czx) complexes of Yb(II) but not the smaller Yb(III).[4,10]

The crystal structure of **4** (Table 1, Figure 2) shows a distorted-trigonal-bipyramidal geometry at the Yb(II) center with the Czx ligand occupying one equatorial and two axial

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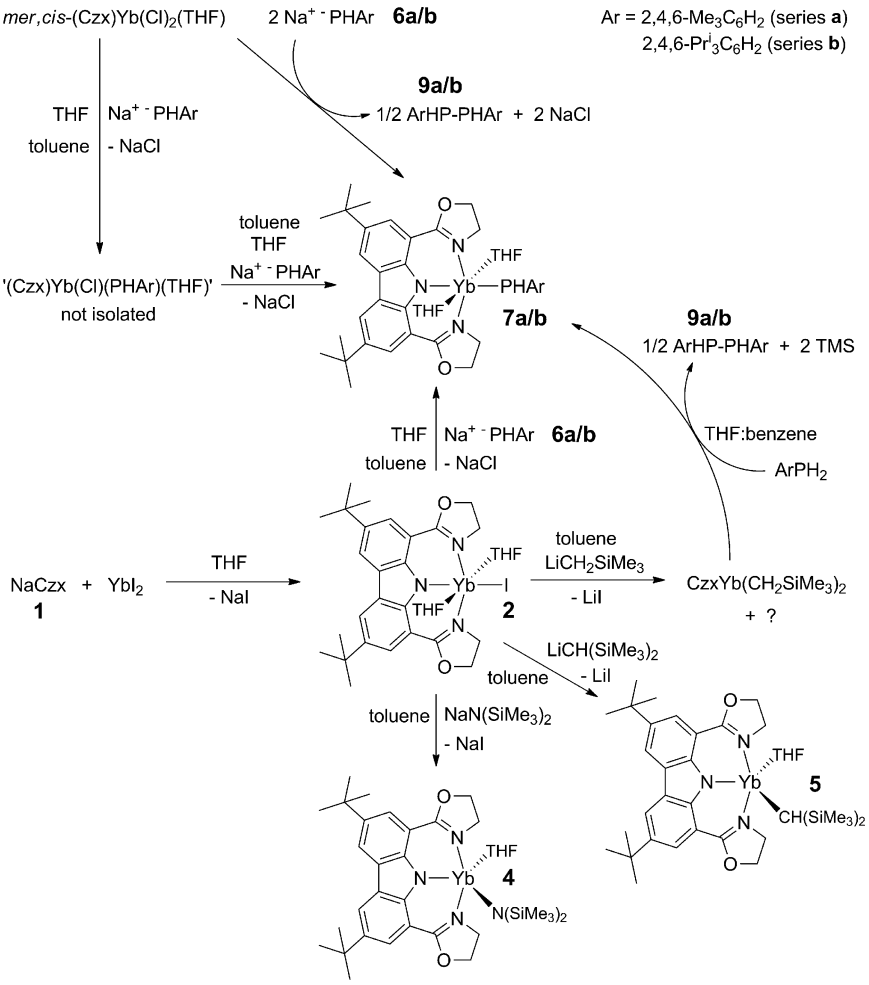
Scheme 1. Interconversion of Ytterbium Carbazole−Bis(oxazoline) (Czx) Complexes



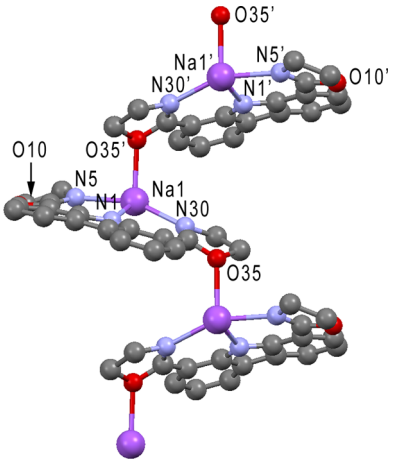


Figure 1. Ball and stick representation of the polymeric structure of NaCzx (**1**). Hydrogens, *tert*-butyl groups, oxazoline methyl groups, and toluenes of solvation have been omitted for clarity.

sites. This is very similar to the coordination environment observed in the trivalent dialkyls $(Czx)Ln(CH_2SiMe_3)_2$ (Ln = Y, Er).[4] The Yb−N distances for the carbazole and oxazoline nitrogens are considerably longer in divalent **4** ($Yb-N_{carb}$ = 2.4233(11) Å; $Yb-N_{ox}$ = 2.4891(10), 2.5050(11) Å) than in the trivalent complexes $(Czx)Yb(CH_2SiMe_3)_2$ ($Yb-N_{carb}$ = 2.278(2), 2.308(2) Å; N_{ox} = 2.404(3)−2.416(3) Å) and *mer,cis*-

Table 1. Selected Bond Distances (Å) and Angles (deg) for $NaCzx{\cdot}2C_7H_8$ (1) and $(Czx)Yb[N(SiMe_3)_2][THF]$ (4)[a]

Complex **1**			
Na1−N5	2.279(2)	C4−N5	1.277(3)
Na1−N5	2.406(2)	C4−O10	1.372(3)
Na1−N30	2.414(2)	C29−N30	1.278(3)
Na1−O35	2.432(2)	C29−O35	1.386(2)
O35−Na1−N1	111.35(7)	N1−Na1−N5	81.21(7)
O35−Na1−N5	88.25(6)	N1−Na1−N30	81.80(7)
O35−Na1−N30	112.73(6)	N5−Na1−N30	156.77(7)
Complex **4**			
Yb1−N1	2.5050(11)	C3−O1	1.363(2)
Yb1−N2	2.4233(11)	C16−N3	1.287(2)
Yb1−N3	2.4891(11)	C16−O2	1.369(2)
Yb1−N4	2.3707(12)	N4−Si1	1.6981(12)
Yb1−O3	2.4267(10)	N4−Si2	1.6991(13)
C3−N1	1.286(2)		
N1−Yb1−N2	77.99(4)	N3−Yb1−N4	100.36(4)
N1−Yb1−N3	153.67(4)	N3−Yb1−O3	85.75(4)
N1−Yb1−N4	103.64(4)	N4−Yb1−O3	129.96(4)
N1−Yb1−O3	87.07(4)	Yb1−N4−Si1	128.73(6)
N2−Yb1−N3	78.20(4)	Yb1−N4−Si2	108.90(6)
N2−Yb1−N4	130.85(4)	Si1−N4−Si2	122.34(7)
N2−Yb1−O3	99.13(4)		

[a]Estimated standard deviations are given in parentheses.

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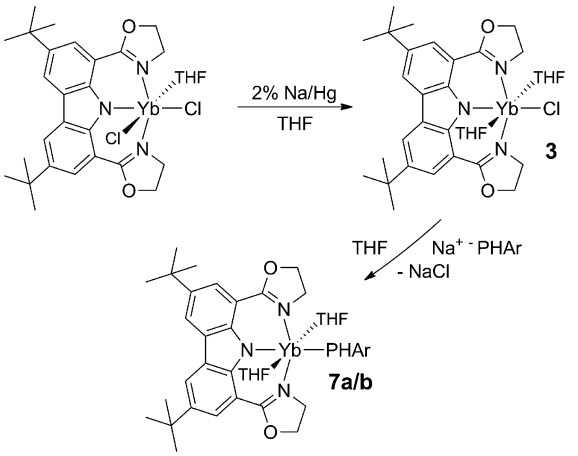
Scheme 2. Formation of *mer,trans*-(Czx)Yb(PHAr)(THF)$_2$ (7a,b) by Reduction and Metathesis



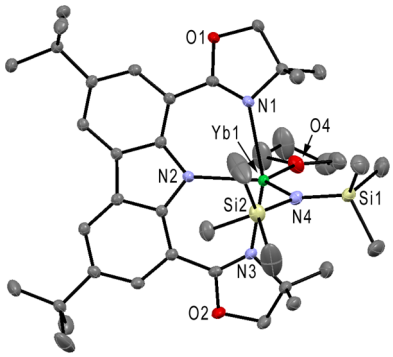


Figure 2. ORTEP plot for (Czx)Yb[N(SiMe$_3$)$_2$][THF] (**4**). Hydrogens are omitted for clarity; ellipsoids are given at the 65% probability level.

(Czx)Yb(Cl)$_2$(THF) (Yb−N$_{carb}$ = 2.289(3) Å; Yb−N$_{ox}$ = 2.391(3), 2.405(3) Å), consistent with the ca. 0.15 Å larger radius of Yb(II).[11] Four Yb(II) complexes with a simple carbazole anion have been structurally reported with a median Yb−N$_{carb}$ distance of 2.37 Å (range 2.356−2.397 Å).[12] The longer Yb−N distances result in a smaller effective bite angle for the Czx ligand, as reflected in the N$_{ox}$−Yb−N$_{ox}$ angle of ca. 154° in **4** vs 161−162° for the aforementioned Yb(III) complexes. The Yb−N bond distance to the silylamido group of 2.3707(12) Å is typical of other Yb(II) silylamido complexes reported in the literature (Yb−N range 2.304−2.469 Å; median 2.35 Å).[13]

Complex **2** reacts rapidly with LiCH(SiMe$_3$)$_2$ in toluene to afford the expected metathesis product (Czx)Yb[CH(SiMe$_3$)$_2$]-[THF] (**5**) in excellent yield as a dark green microcrystalline powder (Scheme 1). The identity of this complex was confirmed by ^{1}H and ^{13}C NMR, but we were unable to obtain an acceptable elemental analysis on this complex, possibly due to loss of solvent. The thermal stability of **5** is remarkable for a divalent alkyl: no decomposition was observed during VT NMR studies at 110 °C, and the complex was recovered unchanged after heating at 80 °C for several hours. An identical reaction procedure using LiCH$_2$SiMe$_3$ resulted in an immediate color change from deep green to red-orange, and after the usual workup to remove LiI, the previously reported, paramagnetic, *trivalent* dialkyl (Czx)Yb(CH$_2$SiMe$_3$)$_2$ was obtained in 30−45% yield based on Yb (Scheme 1). The identity of this complex was confirmed by variable-temperature ^{1}H NMR ,with the most diagnostic resonances being those of the strongly shielded CH$_2$SiMe$_3$ group (δ −39.9, $\upsilon_{1/2}$ = 30 Hz, Si*Me*$_3$; δ −174.7, $\upsilon_{1/2}$ = 54 Hz, *C*H$_2$).[4] The unexpected oxidation of Yb(II) under reducing conditions is very surprising. The yield of trivalent dialkyl, while not high, accounts for nearly half of the Yb present. One possible explanation is that a redox disproportionation of (Czx)Yb(CH$_2$SiMe$_3$)(THF)$_x$ occurs to produce the observed trivalent product and metallic Yb(0) or a reduced Czx ligand. As far as we know, a disproportionation to form Yb(0) is unprecedented and calculated redox potentials suggest that such a redox reaction is unlikely.[14] In addition, we do not have any evidence that metallic Yb forms.[15a] A similar oxidation of a U(IV) complex to U(V) on treatment with *n*-BuLi involving ligand metalation and degradation has been reported by Gambarotta, although the exact mechanism also remains unknown in that case.[15b] Presumably, the redox stability of the closely related CH(SiMe$_3$)$_2$ complex **5** is attributable to the greater steric bulk of this alkyl, which stabilizes its complex with the larger Yb(II) and disfavors oxidation to the smaller Yb(III) center. We plan to explore this interesting result further with other types of ligands in future work.

We also explored the reaction of **2** with the sodium arylphosphide salts of mesitylphosphine and 2,4,6-triisopropylphenylphosphine (Scheme 1; 2,4,6-Me$_3$C$_6$H$_2$PH$^-$Na$^+$ (**6a**), 2,4,6-Pr$^i_3$C$_6$H$_2$PH$^-$Na$^+$ (**6b**)). In this case, the reaction proceeded rapidly to produce the divalent phosphides **7a**,**b**, respectively, as dark green microcrystalline powders in excellent yield. Despite the rather large size of the phosphides used, both complexes were isolated as bis(THF) solvates, although again, THF loss occurred readily over time in the solid state so that the elemental analyses were more consistent with mono(THF) adducts. The PH resonances at δ 2.69 (**7a**) and 2.89 (**7b**) with $^1J_{PH}$ coupling constants of 175 and 177 Hz, respectively, confirmed that these were primary phosphide complexes.[16] The ^{31}P{^{1}H} resonances of **7a**,**b** were shifted downfield by ca. 45 ppm relative to their Na$^+$ salts (Δ = +44.84 (**7a**), +46.93 (**7b**) ppm), and both showed distinct ^{171}Yb satellites (^{171}Yb, I = $^1/_2$, 14% natural abundance: $^1J_{PYb}$ = 600 (**7a**), 631 (**7b**) Hz). The $^1J_{PYb}$ coupling constant observed here is comparable to those for other known Yb(II) phosphides ($^1J_{PYb}$ range 580−992 Hz).[17]

Interestingly, in the course of exploring similar chemistry of the trivalent halide *mer,cis*-(Czx)Yb(Cl)$_2$(THF), with 2 equiv of **6a**,**b** in a mixture of toluene and THF (4/1), we observed a rapid color change from pale yellow to deep red and finally to dark green within 2 h (Scheme 1). Workup of the green solution produced the *divalent* phosphides **7a**,**b** in moderate yield. Examination of the reaction mixture by ^{31}P{^{1}H} NMR showed, in addition to **7a** or **7b**, the formation of the biphosphines ArHP−PHAr (Scheme 1; Ar = 2,4,6-Me$_3$C$_6$H$_2$ (**9a**), 2,4,6-Pr$^i_3$C$_6$H$_2$ (**9b**)) as their meso and racemic isomers (δ_{meso} −109 (**9a**), −112 (**9b**); δ_{rac} −118 (**9a**), −117 (**9b**)). The meso and racemic isomers of **9a** have been reported in the literature, and they show a distinctive AA′XX′ pattern in the ^{1}H-coupled ^{31}P NMR spectrum; a similar pattern was observed for **9b** (Figure 3).[18] Attempts to stop the reaction at the "red" stage by using only 1 equiv of **6a** or **6b** or by carrying the reaction out at low temperature always resulted in formation of **7a** or **7b** during workup.

In order to explore this further, we reacted the analogous yttrium complex *mer,cis*-(Czx)Y(Cl)$_2$(THF), with 1 or 2 equiv

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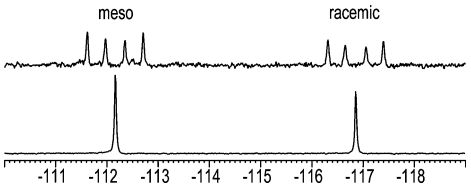

Figure 3. $^{31}P\{^{1}H\}$ (bottom) and ^{31}P (top) AA′XX′ spectrum of (2,4,6-$Pr^{i}_{3}C_{6}H_{2}PH)_{2}$ (**9b**) in benzene-d_6/THF-d_8 at 202 MHz.

of **6a** or **6b**. In this case, the reaction mixture rapidly turned deep red and we were able to isolate the red-orange trivalent mono(phosphide) complexes (Czx)Y(Cl)(PHAr)(THF) (**8a,b**; eq 1), regardless of the number of equivalents of sodium

$$\textit{mer, cis}\text{-CzxY(Cl)}_2\text{(THF)} \xrightarrow[-\text{NaCl}]{\text{Na}^{+-}\text{PHAr, toluene, THF}} \underset{\textbf{8a,b}}{\text{CzxY(Cl)(PHAr)(THF)}} \quad (1)$$

phosphide **6** used. As expected for a metal without a stable divalent state, no biphosphine was observed in the yttrium case. It is reasonable to assume that since Y(III) cannot form a bis(phosphide) complex, the slightly smaller Yb(III) ion is even less likely to do so.[19] We therefore believe that the red intermediate (Czx)Yb(Cl)(PHAr)(THF) forms first in a rapid salt metathesis reaction and this species undergoes a reaction similar to sterically induced reduction (SIR) with loss of a $ArPH^{\bullet}$ radical to form $(Czx)Yb(Cl)(THF)_2$ (**3**) ,which then undergoes a salt metathesis step with another 1 equiv of **6a,b** to form **7a,b** (Scheme 1). Evans has shown many examples of SIR reactivity in sterically oversaturated $Ln(C_5Me_5)_3$, but similar reaction chemistry with other ligand types is, to our knowledge, extremely rare.[20] In fact, the only non-Cp example of this type of chemistry appears to be the Ln−N bond homolysis (Ln = Eu, Yb) observed along with protonolysis during reactions of chelating indenes bearing pendant amine or furan arms with $Ln[N(SiMe_3)_2]_3$ or $Ln[N(SiMe_3)_2]_3(\mu\text{-Cl})Li(THF)_3$ reported by Wang.[21] In that chemistry, reaction occurred at toluene reflux to form divalent Ln bis(indenyl) complexes and evidence was presented for loss of $^{\bullet}N(SiMe_3)_2$ radical and formation of the hydrazine $(Me_3Si)_2N-N(SiMe_3)_2$. In principle, the yttrium complexes **8a,b** could behave as if they contained "Y^{2+}" centers by loss of a $ArPH^{\bullet}$ radical, but we have yet to see evidence for that type of chemistry; further work is underway to explore the reaction chemistry of **7** and **8**.

The observation of reduction chemistry during metathesis reactions of $(Czx)Yb(Cl)_2(THF)$ with sodium phosphides **6a,b** prompted us to see whether reduction would also occur during an acid−base (protonolysis) reaction between (Czx)Yb-$(CH_2SiMe_3)_2$ and the primary arylphosphines $ArPH_2$ (Scheme 1; Ar = 2,4,6-$Me_3C_6H_2$, 2,4,6-$Pr^{i}_{3}C_6H_2$). Initially, we had hoped to form a rare example of a lanthanide phosphinidene by double deprotonation of $ArPH_2$, but once again reduction was observed to produce **7a,b** and the corresponding biphosphines ArPH−PHAr.[22] The $^{31}P\{^{1}H\}$ NMR spectra shown in Figure 4 for the reaction of 2,4,6-*i*-$Pr_3C_6H_2PH_2$ with (Czx)Yb-$(CH_2SiMe_3)_2$ shows steady loss of the phosphine with production of **7b** and a roughly equal ratio of the meso and racemic biphosphines. At NMR concentrations (0.1 M in Yb complex) at 65 °C, this reaction takes about 5 h to reach completion; full kinetic studies have not been carried out. Not surprisingly, the smaller mesitylphosphine requires only 1 h to

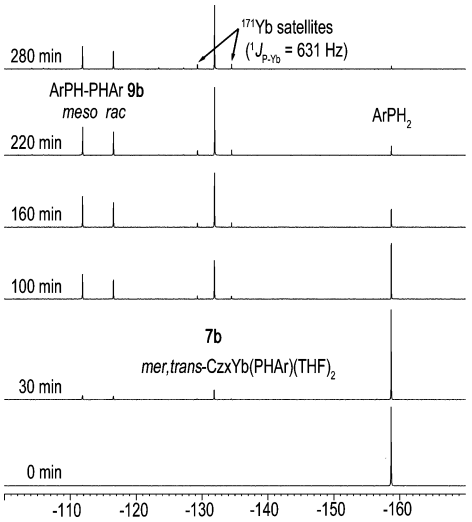

Figure 4. $^{31}P\{^{1}H\}$ NMR spectra (202 MHz, 65 °C, benzene-d_6/THF-d_8) over time for the reaction mixture containing 2 equiv of 2,4,6-$Pr^{i}_{3}C_6H_2PH_2$ and $(Czx)Yb(CH_2SiMe_3)_2$.

reach completion under the same conditions. We also briefly explored the reaction of phenylphosphine with (Czx)Yb-$(CH_2SiMe_3)_2$, and although reduction occurred as indicated by the formation of a green solution, the product appeared to be a more complex mixture, probably involving bridging phosphides. In this case, the predominant phenylphosphine oxidation product was identified as Ph_5P_5 by high-resolution MS and the characteristic $^{31}P\{^{1}H\}$ NMR pattern.[23]

SUMMARY

The Czx ligand allows isolation of monomeric Yb(II) complexes containing halides, as well as bulky silylamide, phosphide, and alkyl ligands. However, an unusual *oxidation* to the previously isolated trivalent alkyl $(Czx)Yb(CH_2SiMe_3)_2$ was observed on alkylation of the divalent halides **2** and **3** with the smaller alkyl $LiCH_2SiMe_3$. Additionally, metal *reduction* was observed on treatment of trivalent $(Czx)Yb(Cl)_2(THF)$ with $ArPH^{-}Na^{+}$ or, equivalently, on treatment of trivalent (Czx)-$Yb(CH_2SiMe_3)_2$ with $ArPH_2$. In both cases, oxidative coupling of the phosphide or phosphine was observed to form the biphosphine ArPH−PHAr. These results clearly establish the Czx ligand system as a versatile platform from which to explore monomeric lanthanide chemistry in a range of oxidation states. Further work to map out the unusual redox chemistry in the Yb−Czx system is underway.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed under an argon atmosphere in a double-station glovebox (Braun MB150-GII). Diethyl ether and tetrahydrofuran (THF) were predried by distillation from sodium benzophenone ketyl under argon and stored over activated 4 Å molecular sieves. Hexane and toluene from a MBraun solvent purification system were likewise stored over 4 Å sieves for several days prior to use. Anhydrous $LnCl_3$ salts (Ln = Y, Yb) were purchased from Aldrich and converted to their THF solvates, $LnCl_3(THF)_x$, by extraction with anhydrous THF. Base-free YbI_2 was prepared from Yb and NH_4I in liquid ammonia followed by desolvation under vacuum at 135 °C.[24] The parent ligand 1,8-bis(4′,4′-dimethyloxazolin-2′-yl)-3,6-di-*tert*-butylcarbazole (HCzx), as well as its dialkyl and dichloro lanthanoid (Ln = Yb, Y) complexes (Czx)Ln-$(CH_2SiMe_3)_2$ and *mer,cis*-(Czx)Ln$(Cl)_2(THF)$, respectively, were prepared as previously reported.[4] $NaN(SiMe_3)_2$ was prepared by

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deprotonation of hexamethyldisilazane (Aldrich) with NaH in THF, followed by repeated recrystallization from warm hexane. The primary phosphines (2,4,6-trimethylphenyl)phosphine (2,4,6-$Me_3C_6H_2PH_2$) and (2,4,6-triisopropylphenyl)phosphine (2,4,6-$Pr^i_3C_6H_2PH_2$) were prepared according to literature procedures.[22a,25]

NMR spectra were recorded on Bruker AMX-500 (^{1}H, ^{13}C, and ^{31}P at 500, 125, and 202 MHz, respectively) and Bruker AMX-360 (^{1}H at 360 MHz) spectrometers. The NMR spectra of air-sensitive compounds were recorded using 5 mm NMR tubes fitted with a Teflon valve (Brunfeldt). NMR assignments (Figure 5), where

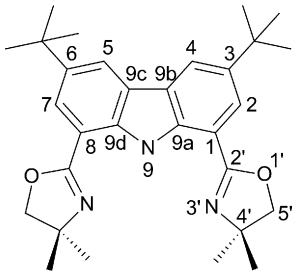

Figure 5. Atom-numbering scheme for the Czx ligand framework.

specified, were confirmed using 2D ^{1}H−^{13}C COSY (HMQC, HMBC) or NOESY experiments. Elemental analyses were conducted at the Department of Chemistry, University of British Columbia. Uncorrected melting points were taken on samples sealed in capillary tubes under argon using either hot stage (Reichert 7905) or oil bath (Büchi) melting point instruments.

NaCzx·2C$_7$H$_8$ (1). A solution of Na[N(SiMe$_3$)$_2$] (0.19 g, 1.0 mmol) dissolved in 5 mL of toluene was added to a solution of HCzx (0.48 g, 1.0 mmol) in 10 mL of toluene in the glovebox. The bright yellow precipitate that formed was isolated using a glass frit and washed repeatedly with hexane and toluene, affording the salt **1** as a powder after drying under reduced pressure. Recrystallization of the crude powder from toluene afforded bright yellow crystals of pure **1** as the toluene solvate. Yield: 0.46 g (68%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.73 (d, J = 1.8 Hz, 2H, 4,5-aryl H), 8.67 (d, J = 2.4 Hz, 2H, 2,7-aryl H), 6.97−7.10 (m, 10H, $C_6H_5CH_3$), 3.77 (s, 4H, CH_2O), 2.10 (s, 6H, $C_6H_5CH_3$), 1.60 (s, 18H, $C(CH_3)_3$), 1.08 (s, 12H, 4′-$(CH_3)_2$); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 166.20 (C═N), 152.14 (9a,9d-aryl C), 135.71 (3,6-aryl C), 126.02 (2,7-aryl CH), 121.11 (4,5-aryl CH), 110.99 (1,8-aryl C), 77.18 (CH_2O), 67.62 (4′-$C(CH_3)_2$)), 35.15 ($C(CH_3)_3$), 33.03 ($C(CH_3)_3$), 29.03 (4′-CH_3); toluene peaks omitted. The 9b,9c-aryl C resonance falls underneath the C_6D_6 solvent resonance.

***mer,trans*-(Czx)Yb(I)(THF)$_2$ (2).** YbI$_2$ (0.43 g, 1.0 mmol) was partially dissolved in 10 mL of THF in a 50 mL Erlenmeyer flask and a solution of NaCzx (**1**; 0.68 g, 1.0 mmol) in 5 mL of THF was added dropwise by Pasteur pipet. The remaining solid YbI$_2$ dissolved, and the solution rapidly changed color to dark green. After it was stirred for 1 h, the reaction mixture was filtered through Celite to remove NaI and the solvent was removed from the filtrate under reduced pressure. The resulting green powder was recrystallized from toluene to afford pure **2** as a dark green microcrystalline powder. Yield: 0.83 g (91%). Mp: 214 °C dec. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.76 (s, 2H, 2,7-aryl H), 8.72 (s, 2H, 4,5-aryl H), 3.70 (s, 4H, CH_2O), 3.00 (t, 8H, α-CH_2 THF), 1.87 (s, 12H, 4′-$(CH_3)_2$), 1.54 (s, 18H, $C(CH_3)_3$), 0.68 (t, 8H, β-CH_2 THF). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 166.37 (C═N), 149.24 (9a,9d-aryl C), 138.44 (3,6-aryl C), 126.75 (2,7-aryl CH), 121.52 (4,5-aryl CH), 110.82 (1,8-aryl C), 79.81 (CH_2O), 69.92 (α-CH_2 THF), 69.16 (4′-$C(CH_3)_2$)), 35.02 ($C(CH_3)_3$), 32.65 ($C(CH_3)_3$), 29.25 (4′-CH_3), 25.20 (β-CH_2 THF). The 9b,9c-aryl C resonance is overlapped by the C_6D_6 resonance. Crystals of this complex lose 1 equiv of THF readily on standing, preventing a crystal structure determination and giving an elemental analysis more consistent with the mono(THF) solvate. Anal. Calcd for $C_{34}H_{46}IN_3O_3Yb$ (mono(THF) solvate): C, 48.34; H, 5.49; N, 4.97. Found: C, 48.10; H, 5.54; N, 4.43.

***mer,trans*-(Czx)Yb(Cl)(THF)$_2$ (3).** (Czx)YbCl$_2$(THF) (0.79 g, 1 mmol) was dissolved in 5 mL of THF and transferred onto Na/Hg (2% Na, 0.23 g, 10 mmol) in 10 mL of THF. The reaction mixture rapidly turned dark green. After 1 h the solution was filtered through Celite to remove NaCl and taken to dryness under reduced pressure. The resulting dark green powder was recrystallized from a mixture of toluene and hexanes to afford pure **3** as dark green microcrystals. Yield: 0.67 g (81%). ^{1}H NMR (360 MHz, C_6D_6): δ 8.74 (s, 2H, 2,7-aryl H), 8.72 (s, 2H, 4,5-aryl H), 3.77 (s, 4H, CH_2O), 3.48 (s, 8H, α-CH_2 THF), 1.71 (s, 12H, 4′-$(CH_3)_2$), 1.52 (s, 18H, $C(CH_3)_3$), 1.18 (s, 8H, β-CH_2 THF). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 165.71 (C═N), 149.52 (9a,9d-aryl C), 138.03 (3,6-aryl C), 126.27 (2,7-aryl CH), 121.24 (4,5-aryl CH), 110.01 (1,8-aryl C), 79.10 (CH_2O), 68.83 (α-CH_2 THF), 67.83 (4′-$C(CH_3)_2$), 34.99 ($C(CH_3)_3$), 32.68 ($C(CH_3)_3$), 28.64 (4′-CH_3), 25.54 (β-CH_2 THF). The 9b,9c-aryl C resonance is obscured by the C_6D_6 resonance. Anal. Calcd for $C_{38}H_{54}ClN_3O_4Yb$ (bis(THF) solvate): C, 55.30; H, 6.59; N, 5.09. Found: C, 54.88; H, 6.39; N, 5.31.

(Czx)Yb[N(SiMe$_3$)$_2$][THF] (4). The silylamide complex **4** was prepared by the reaction of (Czx)Yb(I)(THF)$_2$ (**2**; 0.46 g, 0.5 mmol) with Na[N(SiMe$_3$)$_2$] (0.09 g, 0.5 mmol) in 10 mL of toluene. After it was stirred for 1 h, the reaction mixture was filtered through Celite to remove NaI and the filtrate was taken to dryness under reduced pressure. Recrystallization from toluene afforded **4** as dark green crystals suitable for X-ray crystallography. Yield: 0.40 g (92%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.77 (d, J = 2.0 Hz, 2H, 2,7-aryl H), 8.68 (d, J = 2.1 Hz, 2H, 4,5-aryl H), 3.69 (s, 4H, CH_2O), 3.42 (m, 4H, α-CH_2 THF), 1.50 (s, 18H, $C(CH_3)_3$), 1.49 (s, 12H, 4′-$(CH_3)_2$), 1.05 (m, 4H, β-CH_2 THF), 0.36 (s, 18H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 166.95 (C═N), 149.61 (9a,9d-aryl C), 138.37 (3,6-aryl C), 126.28 (2,7-aryl CH), 121.78 (4,5-aryl CH), 110.37 (1,8-aryl C), 78.42 (CH_2O), 69.18 (α-CH_2 THF), 68.39 (4′-$C(CH_3)_2$)), 34.99 ($C(CH_3)_3$), 32.64 ($C(CH_3)_3$), 29.11 (4′-CH_3), 25.56 (β-CH_2 THF), 6.52 ($Si(CH_3)_3$). The 9b,9c-aryl C resonance is obscured by the C_6D_6 resonance. Anal. Calcd for $C_{40}H_{64}N_4O_3Si_2Yb$: C, 54.71; H, 7.35; N, 6.38. Found: C, 54.38; H, 7.16; N, 6.44.

(Czx)Yb[CH(SiMe$_3$)$_2$][THF] (5). (Czx)Yb(I)(THF)$_2$ (**2**; 0.46 g, 0.5 mmol) was dissolved in 10 mL of toluene, and a solution of Li[CH(SiMe$_3$)$_2$] (0.08 g, 0.5 mmol) in 5 mL of toluene was added by Pasteur pipet. After 1 h, the reaction mixture was filtered through Celite to remove LiI and the filtrate was taken to dryness under reduced pressure. Recrystallization of the crude powder from a mixture of toluene, hexane, and a few drops of THF afforded **5** as a dark green microcrystalline powder. Yield: 0.39 g (89%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.64 (d, J = 2.0 Hz, 2H, 2,7-aryl H), 8.62 (d, J = 2.4 Hz, 2H, 4,5-aryl H), 3.78 (s, 4H, CH_2O), 3.55 (m, 4H, α-CH_2 THF), 1.84 (s, 12H, 4′-$(CH_3)_2$), 1.47 (s, 18H, $C(CH_3)_3$), 1.45 (m, 4H, β-CH_2 THF), 0.33 (s, 18H, $Si(CH_3)_3$), −1.84 (s, 1H, CH). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 166.36 (C═N), 149.20 (9a,9d-aryl C), 138.25 (3,6-aryl C), 128.45 (9b,9c-aryl C), 126.63 (2,7-aryl CH), 121.44 (4,5-aryl CH), 110.73 (1,8-aryl C), 79.87 (CH_2O), 69.18 (α-CH_2 THF), 68.39 (4′-$C(CH_3)_2$)), 35.01 ($C(CH_3)_3$), 32.61 ($C(CH_3)_3$), 29.22 (4′-CH_3), 26.16 (β-CH_2 THF), 6.96 ($Si(CH_3)_3$), 1.44 (CH). A satisfactory analysis of **5** was not obtained despite repeated attempts. Solvent loss during shipping is the most likely reasons for the poor analyses.

2,4,6-Me$_3$C$_6$H$_2$PH$^-$Na$^+$ (6a). Solid Na[N(SiMe$_3$)$_2$] (0.18 g, 1.0 mmol) was added to a solution of (2,4,6-trimethylphenyl)phosphine (2,4,6-$Me_3C_6H_2PH_2$; 0.15 g, 1.0 mmol) in 5 mL of hexanes. The white salt of **6a** that precipitated after a few minutes was filtered off on a glass frit, washed repeatedly with hexanes, and dried under reduced pressure. Yield: 0.14 g (80%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 6.82 (s, 2H, 2,4,6-$Me_3C_6H_2$), 2.60 (s, 6H, 2,6-Me), 2.54 (d, $^1J_{P-H}$ = 176 Hz, 1H, P−H), 2.26 (s, 3H, 4-Me). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 150.12 (d, $^1J_{P-C}$ = 44.6 Hz, aryl C-PH), 136.13 (d, $^2J_{P-C}$ = 9.2 Hz, 2,6-aryl CMe), 127.74 (d, $^3J_{P-C}$ = 2.1 Hz, 3,5-aryl CH), 125.99 (4-aryl CMe), 25.59 (d, $^3J_{P-C}$ = 13.8 Hz, 2,6-aryl-CH_3), 21.40 (4-aryl-CH_3). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ −167.65.

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2,4,6-$Pr^i_3C_6H_2PH^-Na^+$ (6b). The sodium phosphide **6b** was prepared using the same procedure as for **6a** above, starting from (2,4,6-triisopropylphenyl)phosphine (2,4,6-$Pr^i_3C_6H_2PH_2$; 0.24 g, 1.0 mmol). Yield: 0.22 g (85%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.16 (s, 2H, 2,4,6-*i*-$Pr_3C_6H_2$), 4.00 (m, 2H, 2,6-C*H*$(CH_3)_2$), 3.02 (m, 1H, 4-C*H*$(CH_3)_2$), 2.89 (d, $^1J_{P-H}$ = 177 Hz, 1H, P-*H*), 1.55 (d, *J* = 6.4 Hz, 12H, 2,6-CH(*CH*$_3)_2$), 1.44 (d, *J* = 7.3 Hz, 6H, 4-CH(*CH*$_3)_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 148.25 (d, $^1J_{P-C}$ = 44.2 Hz, aryl *C*-PH), 147.62 (d, $^2J_{P-C}$ = 7.6 Hz, 2,6-aryl *C*-Pr^i), 140.24 (4-aryl *C*-Pr^i), 119.51 (3,5-aryl *C*H), 35.10 (4-*C*H$(CH_3)_2$), 33.82 (d, $^3J_{P-C}$ = 12.7 Hz, 2,6-*C*H$(CH_3)_2$), 25.46 (4-CH(*CH*$_3)_2$), 24.40 (2,6-CH(*CH*$_3)_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ −178.96.

***mer,trans*-(Czx)Yb(2,4,6-$Me_3C_6H_2PH)(THF)_2$ (7a).** A solution of 2,4,6-$Me_3C_6H_2PH^-Na^+$ (**6a**; 0.093 g, 0.53 mmol) in toluene/THF (4/1) was added by pipet to a solution of (Czx)Yb(I)$(THF)_2$ (**2**; 0.46 g, 0.53 mmol) in toluene. After it was stirred for 3 h, the reaction mixture was filtered through Celite to remove NaI and the filtrate was taken to dryness under reduced pressure. The crude product was recrystallized from a mixture of toluene and hexane to afford **7a** as dark green microcrystals. Yield: 0.45 g (96%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.63 (s, 4H, overlapping 2,7- and 4,5-Czx aryl *H*), 6.90 (s, 2H, 3,5-arylC*H*), 3.73 (s, 4H, 5′-CH_2O), 3.55 (s, 8H, α-CH_2 THF), 2.69 (d, $^1J_{P-H}$ = 175 Hz, 1H, P-*H*), 2.57 (s, 6H, 2,6-aryl-CH_3), 2.34 (s, 3H, 4-aryl-CH_3), 1.47 (s, 30H, C$(CH_3)_3$ and 4′,4′-$(CH_3)_2$), 1.44 (s, 8H, β-CH_2 THF). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 166.45 (*C*═N), 150.61 (d, $^1J_{P-C}$ = 42 Hz, aryl *C*-PH), 149.31 (9a,9d-Czx aryl *C*), 138.14 (3,6-Czx aryl *C*), 136.26 (d, $^2J_{P-C}$ = 9.2 Hz, 2,6-aryl *C*-CH_3), 127.85 (3,5-aryl *C*H and 9b,9c-Czx aryl *C*), 126.45 (2,7-Czx aryl *C*H and 4-aryl *C*-CH_3), 121.48 (4,5-Czx aryl *C*H), 110.65 (1,8-Czx aryl *C*), 79.32 (CH_2O), 69.13 (4′-C$(CH_3)_2$), 68.13 (α-CH_2 THF), 35.00 (*C*$(CH_3)_3$), 32.68 (C(*C*$H_3)_3$), 28.78(4′,4′-CH_3), 26.16 (β-CH_2 THF), 25.56 (d, $^3J_{P-C}$ = 12.6 Hz, 2,6-aryl-CH_3), 21.49 (4-aryl-CH_3). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ −122.81 ($^1J_{Yb-P}$ = 600 Hz). Anal. Calcd for $C_{43}H_{58}N_3O_3PYb$ (mono(THF) solvate): C, 59.43; H, 6.73; N, 4.84. Found: C, 59.56; H, 6.82; N, 4.72.

***mer,trans*-(Czx)Yb(2,4,6-$Pr^i_3C_6H_2PH)(THF)_2$ (7b).** Complex **7b** was prepared using the same procedure as **7a** using (Czx)Yb(I)$(THF)_2$ (**2**; 0.46 g, 0.53 mmol) and 2,4,6-$Pr^i_3C_6H_2PH^-Na^+$ (**6b**; 0.14 g, 0.54 mmol). The crude product was recrystallized from a mixture of toluene and hexane to afford **7b** as a dark green powder. Yield: 0.41 g (80%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.73 (s, 2H, 2,7-aryl *H*), 8.71 (s, 2H, 4,5-aryl *H*), 7.16 (s, 2H, 2,4,6-$Pr^i_3C_6H_2$), 4.00 (m, 2H, 2″,6″-C*H*$(CH_3)_2$), 3.68 (s, 4H, CH_2O), 3.56 (m, 8H, α-CH_2 THF), 3.02 (m, 1H, 4″-C*H*$(CH_3)_2$), 2.89 (d, $^1J_{P-H}$ = 177 Hz, 1H, P−H), 1.55 (d, *J* = 6.4 Hz, 12H, 2″,6″-CH(*CH*$_3)_2$), 1.54 (s, 12H, 4′-$(CH_3)_2$), 1.50 (s, 18H, C(*CH*$_3)_3$), 1.44 (d, *J* = 7.3 Hz, 6H, 4″-CH(*CH*$_3)_2$), 1.38 (m, 8H, β-CH_2 THF). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 166.22 (*C*═N), 149.40 (9a,9d-Czx aryl *C*), 148.25 (d, $^1J_{P-C}$ = 44.2 Hz, aryl *C*-PH), 147.62 (d, $^2J_{P-C}$ = 7.6 Hz, 2,6-aryl *C*-Pr^i), 140.24 (4-aryl *C*-Pr^i), 138.25 (3,6-Czx aryl *C*), 128.40 (9b,9c-Czx aryl *C*), 126.49 (2,7-Czx aryl *C*H), 121.57 (4,5-Czx aryl *C*H), 119.51 (d, $^3J_{P-C}$ = 2.4 Hz, 3,5-aryl *C*H), 110.64 (1,8-Czx aryl *C*), 79.13 (CH_2O), 69.09 (4′,4′-*C*$(CH_3)_2$), 68.28 (α-CH_2 THF), 35.10 (4-*C*H$(CH_3)_2$), 35.02 (Czx *C*$(CH_3)_3$), 33.82 (d, $^3J_{P-C}$ = 12.7 Hz, 2,6-*C*H$(CH_3)_2$), 32.65 (Czx C(*C*$H_3)_3$), 28.79 (4′,4′-*C*H_3), 26.08 (β-CH_2 THF), 25.46 (4-CH$(CH_3)_2$), 24.40 (2,6-CH$(CH_3)_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ −132.03 ($^1J_{Yb-P}$ = 631 Hz). Anal. Calcd for $C_{49}H_{70}N_3O_3PYb$ (mono(THF) solvate): C, 61.75; H, 7.40; N, 4.41. Found: C, 61.90; H, 7.49; N, 4.31.

(Czx)Y(Cl)(2,4,6-$Me_3C_6H_2PH)(THF)$ (8a). Addition of a toluene solution of (Czx)$Y(Cl)_2(THF)$ (0.35 g, 0.5 mmol in 10 mL) to a solution of 2,4,6-$Me_3C_6H_2PH^-Na^+$ (**6a**; 0.17 g, 1 mmol) in a mixture of toluene and THF (10 mL) resulted in a rapid color change from pale yellow to dark red with deposition of a white solid. The solvent was removed under reduced pressure after 6 h, and the residue was extracted with toluene and filtered through Celite to remove NaCl and the filtrate taken to dryness. The resulting deep orange powder was recrystallized from a mixture of toluene and hexane to afford **8a** as fine red-orange crystals. Yield: 0.34 g (82%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.53 (s, 4H, overlapping Czx 2,7- and 4,5-aryl *H*), 6.56 (s, 2H, 2,4,6-$Me_3C_6H_2$), 3.70 (d, $^1J_{H-H}$ = 8.0 Hz, 2H, *Ha*/Hb CH_2O), 3.59 (d, $^1J_{H-H}$ = 8.0 Hz, 2H, Ha/*Hb* CH_2O), 3.56 (m, 4H, α-CH_2 THF), 3.32 (dd, $^2J_{Y-H}$ = 9.2 Hz, $^1J_{P-H}$ = 180 Hz, 1H, P-*H*), 2.33 (d, $^4J_{P-H}$ = 5.6 Hz, 6H, 2,6-aryl-CH_3), 2.16 (d, $^4J_{H-H}$ = 1.8 Hz, 3H, 4-aryl-CH_3), 1.81 (s, 6H, Czx 4′-CH_3(*a*)), 1.45 (s, 18H, C$(CH_3)_3$ and overlapping 6H, 4′-CH_3(*b*)), 1.43 (m, 4H, β-CH_2 THF). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 169.34 (*C*═*N*), 147.45 (9a,9d-Czx aryl *C*), 144.20 (d, $^1J_{C-P}$ = 36.8 Hz, aryl*C*-PH), 140.68 (3,6-Czx aryl *C*), 137.45 (d, $^2J_{P-C}$ = 10.2 Hz, 2,6-aryl *C*-Me), 129.12 (4-aryl *C*-Me), 127.82 (3,5-aryl *C*H), 127.73 (9b,9c-Czx aryl *C*), 126.93 (2,7- or 4,5-Czx aryl *C*H) 122.93 (4,5- or 2,7-Czx aryl *C*H), 110.07 (1,8-Czx aryl *C*), 79.88 (CH_2O), 69.44 (4′-*C*$(CH_3)_2$), 68.21 (α-CH_2 THF), 35.07 (Czx *C*$(CH_3)_3$), 32.40 (Czx C(*C*$H_3)_3$), 28.98 (*C*H_3(a) of 4′-C$(CH_3)_2$), 27.30 (d, $^3J_{P-C}$ = 4.6 Hz, *C*H_3(b) of 4′-C$(CH_3)_2$), 26.15 (β-CH_2 THF), 25.00 (d, $^3J_{P-C}$ = 12.3 Hz, 2,6-aryl-CH_3), 21.35 (4-aryl *C*H_3). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ −108.46 (d, $^1J_{PY}$ = 64 Hz). Anal. Calcd for $C_{43}H_{58}ClN_3O_3PY$: C, 62.96; H, 7.13; N, 5.12. Found: C, 62.61; H, 7.02; N, 5.22.

(Czx)Y(Cl)(2,4,6-$Pr^i_3C_6H_2PH)(THF)$ (8b). Complex **8b** was prepared by the same procedure as **8a** above using (Czx)$Y(Cl)_2$(THF) (0.35 g, 0.5 mmol) and 2,4,6-$Pr^i_3C_6H_2PH^-Na^+$ (**6b**; 0.25 g, 0.5 mmol). Yield: 0.38 g (84%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.56 (4H, overlapping 2,7- and 4,5-Czx aryl *H*), 6.99 (s, 2H, 3,5-arylC*H*), 3.76 (m, 2H, 2,6-aryl-C*H*$(CH_3)_2$), 3.69 (d, $^1J_{H-H}$ = 8.0 Hz, 2H, *Ha* of CH_2O), 3.59 (d, $^1J_{H-H}$ = 8.0 Hz, 2H, *Hb* of CH_2O), 3.57 (m, 4H, α-CH_2 THF), 3.43 (d, $^1J_{H-P}$ = 182 Hz, 1H, P-*H*), 2.85 (m, 1H, 4-arylC*H*$(CH_3)_2$), 1.78 (s, 6H, *C*H_3(a) of 4′-$(CH_3)_2$), 1.46 (s, 6H, *C*H_3(b) of 4′-$(CH_3)_2$), 1.45 (s, 18H, C(*CH*$_3)_3$), 1.43 (m, 4H, β-CH_2 THF), 1.31 (d, *J* = 6.8 Hz, 6H, 4-aryl-CH(*CH*$_3)_2$), 1.27 (d, *J* = 6.8 Hz, 12H, 2,6-aryl-CH(*CH*$_3)_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 169.21 (*C*═N), 148.34 (d, $^2J_{P-C}$ = 7.4 Hz, 2,6-arylC-Pr^i), 147.45 (9a,9d-Czx aryl *C*), 143.17 (d, $^1J_{C-P}$ = 37.8 Hz, aryl *C*-PH), 142.06 (4-aryl *C*-Pr^i), 140.62 (3,6-Czx aryl *C*), 127.63 (9b,9c-Czx aryl *C*), 127.34 (2,7-Czx aryl *C*H), 122.98 (4,5-Czx aryl *C*H), 119.80 (3,5-aryl *C*H), 110.09 (1,8-Czx aryl *C*), 79.89 (CH_2O), 69.44 (4′-*C*$(CH_3)_2$), 68.21 (α-CH_2 THF), 35.07 (4-aryl-CH$(CH_3)_2$ overlapping with Czx-*C*$(CH_3)_3$), 33.73 (d, $^3J_{P-C}$ = 12.6 Hz, 2,6-aryl *C*H$(CH_3)_2$), 32.38 (Czx C(*C*$H_3)_3$), 29.00 (*C*H_3(b) of 4′-CH_3), 27.47 (d, J_{P-C} = 5.4 Hz, *C*H_3(a) of 4′-CH_3), 26.15 (β-CH_2 THF), 25.22 (4-CH$(CH_3)_2$), 24.27 (2,6-CH$(CH_3)_2$); ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ −112.61 (d, $^1J_{P-Y}$ = 67 Hz). Anal. Calcd for $C_{49}H_{70}ClN_3O_3PY$: C, 65.07; H, 7.80; N, 4.65. Found: C, 64.65; H, 7.59; ;N, 4.81.

X-ray Studies. Crystals of NaCzx·$2C_7H_8$ (**1**) were coated in Paratone oil and attached to a glass fiber. Data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using ω scans at 0.3° per frame for 30 s, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART software and refined using SAINTPlus on all observed reflections.[26,27] Data reduction and correction for Lp and decay were performed using the SAINTPlus software, and absorption corrections were applied using SADABS.[28] The structure was solved by direct methods and refined by the least-squares method on F^2 using the SHELXTL program package.[29] One toluene solvent molecule was disordered in three positions with occupancies of 59%, 26%, and 15%. These atoms were held isotropic and modeled as a rigid group. No decomposition was observed during data collection.

Dark green crystals of (Czx)Yb[N$(SiMe_3)_2$][THF] (**4**) were selected from the toluene/THF mother liquor and mounted on a glass fiber under Paratone oil. An arbitrary sphere of data was collected on a Bruker APEX-II diffractometer using a combination of ω and φ scans of 0.5°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and refined by full-matrix least squares on F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. The coordinating THF molecule was found to have a small amount of positional disorder in one carbon atom position. This was subsequently modeled as two partial occupancy carbon atoms (0.80:0.20 ratio). The major component was refined with anisotropic thermal displacement

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parameters, and the minor component was held to be isotropic. Details of the data collection and refinement for **1** and **4** are provided in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

CIF files, figures, and tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **1** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Some recent reviews have been published covering this area: (a) Kobayashi, S.; Yamashita, Y. *Acc. Chem. Res.* **2011**, *44*, 58. (b) Xie, J.-H.; Zhu, S.-F.; Zhou, Q.-L. *Chem. Rev.* **2011**, *111*, 1713. (c) Singh, P. K.; Singh, V. K. *Pure Appl. Chem.* **2010**, *82*, 1845. (d) Framery, E.; Andrioletti, B.; Lemaire, M. *Tetrahedron: Asymmetry* **2010**, *21*, 1110. (e) Hargaden, G. C.; Guiry, P. J. *Chem. Rev.* **2009**, *109*, 2505. (f) Pfaltz, A. Bisoxazolines-a privileged ligand class for asymmetric catalysis. In *Asymmetric Synthesis*, 2nd ed.; Christmann, M., Braese, S., Eds.; Wiley: New York, 2008, pp 139−143. (g) Rasapan, R.; Laventine, D.; Reiser, O. *Coord. Chem. Rev.* **2008**, *252*, 702. (h) Nishiyama, H.; Ito, J.; Shiomi, T.; Hashimoto, T.; Miyakawa, T.; Kitase, M. *Pure Appl. Chem.* **2008**, *80*, 743. (i) Desmoni, G.; Faita, G.; Jörgensen, K. A. *Chem. Rev.* **2006**, *106*, 3561. (j) Johnson, J. S.; Evans, D. A. *Acc. Chem. Res.* **2000**, *33*, 325.

(2) Neutral oxazoline-containing ligands in lanthanide chemistry (see Chart 1): (a) Sato, H.; Suzuki, Y.; Takai, Y.; Kawasaki, H.; Arakawa, R.; Shizuma, M. *Chem. Lett.* **2010**, *39*, 564. (b) Suga, H.; Higuschi, S.; Ohtsuka, M.; Ishimoto, D.; Arikawa, T.; Hashimoto, Y.; Misawa, S.; Tsuchida, T.; Kakehi, A.; Baba, T. *Tetrahedron* **2010**, *66*, 3070. (c) Matsumoto, K.; Suzuki, K.; Tsukuda, T.; Tsubomura, T. *Inorg. Chem.* **2010**, *49*, 4717. (d) Barros, M. T.; Phillips, A. M. F. *Tetrahedron: Asymmetry* **2010**, *21*, 2746. (e) de Bettancourt-Dias, A.; Viswanathan, S.; Rollett, A. *J. Am. Chem. Soc.* **2007**, *129*, 15436. (f) Lu, G.; Morimoto, H.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 6847. (g) Morimoto, H.; Lu, G.; Aoyama, N.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2007**, *129*, 9588. (h) Comelles, J.; Pericas, A.; Moreno-Moreno-Manas, M.; Vallribera, A.; Drudis-Solé, G.; Lledos, A.; Parella, T.; Roglans, A.; Garcia-Granda, S.; Roces-Fernández, L. *J. Org. Chem.* **2007**, *72*, 2077. (i) Aspinall, H. C.; Bickley, J. F.; Greeves, N.; Kelly, R. V.; Smith, P. M. *Organometallics* **2005**, *24*, 3458. (j) Evans, D. A.; Sweeney, Z. K.; Rovis, T.; Tedrow, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 12095. (k) Qian, C.; Wang, L. *Tetrahedron: Asymmetry* **2000**, *11*, 2347. (l) Qian, C.; Wang, L. *Tetrahedron Lett.* **2000**, *41*, 2203. (m) Yuasa, J.; Ohno, T.; Miyata, K.; Tsumatori, H.; Hasegawa, Y.; Kawai, T. *J. Am. Chem. Soc.* **2011**, *133*, 9892. (n) de Bettencourt-Dias, A.; Barber, P. S.; Viswanathan, S.; de Lill, D. T.; Rollett, A.; Ling, G.; Altun, S. *Inorg. Chem.* **2010**, *49*, 8848. (o) Desimoni, G.; Faita, G.; Filippone, M.; Mella, M.; Zampori, M. G.; Zema, M. *Tetrahedron* **2001**, *57*, 10203. (p) Li, D.-P.; Wang, T.-W.; Li, C.-H.; Liu, D.-S.; Li, Y.-Z.; You, X.-Z. *Chem. Commun.* **2010**, *46*, 2929. (q) Lukesova, L.; Ward, B. D.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. *Dalton Trans.* **2007**, 920. (r) Lukesova, L.; Ward, B. D.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. *Organometallics* **2007**, *26*, 4652. (s) Pailloux, S.; Shirima, C. E.; Duesler, E. N.; Smith, K. A.; Paine, R. T. *Polyhedron* **2011**, *30*, 2746.

(3) Anionic oxazoline-containing ligands in lanthanide chemistry (see Chart 2): (a) Bozoklu, G.; Marchal, C.; Gateau, C.; Pacaut, J.; Imbert, D.; Mazzanti, M. *Chem. Eur. J.* **2010**, *16*, 6159. (b) Hong, S.; Tian, S.; Metz, M. V.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14768. (c) Alaaeddine, A.; Amgoune, A.; Thomas, C. M.; Dagorne, S.; Bellemin-Laponnaz, S.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2006**, 3652. (d) Gorlitzer, H. W.; Spiegler, M.; Anwander, R. *J. Chem. Soc., Dalton Trans.* **1999**, 4287. (e) Berg, D. J.; et al. *Can. J. Chem.* **2005**, *83*, 449. (f) Guillon, H.; Daniele, S.; Hubert-Pfalzgraf, L. G.; Letoffe, J. M. *Polyhedron* **2004**, *23*, 1467. (g) Kodama, H.; Ito, J.; Hori, K.; Ohta, T.; Furakawa, I. *J. Organomet. Chem.* **2000**, *603*, 6. (h) Pawlikowski, A.; Ellern, A.; Sadow, A. D. *Inorg. Chem.* **2009**, *48*, 8020. (i) Aspinall, H. C.; et al. *Inorg. Chem.* **2011**, *50*, 11644.

(4) Zou, J.; Berg, D. J.; Stuart, D.; McDonald, R.; Twamley, B. *Organometallics* **2011**, *30*, 4958.

(5) (a) Inoue, M.; Nakada, M. *Heterocycles* **2007**, *72*, 133. (b) Inoue, M.; Nakada, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 252. (c) Inoue, M.; Nakada, M. *Org. Lett.* **2004**, *6*, 2977. (d) Inoue, M.; Suzuki, T.; Nakada, M. *J. Am. Chem. Soc.* **2003**, *125*, 1140. (e) Suzuki, T.; Kinoshita, A.; Kawada, H.; Nakada, M. *Synth. Lett.* **2003**, 570.

(6) (a) Durán-Galván, M.; Worlikar, S. A.; Connell, B. T. *Tetrahedron* **2010**, *66*, 7707. (b) Durán-Galván, M.; Hemmer, J. R.; Connell, B. T. *Tetrahedron Lett.* **2010**, *51*, 5080. (c) Durán-Galván, M.; Connell, B. T. *Eur. J. Org. Chem.* **2010**, 2445.

(7) Wang, L.; Cui, D.; Hou, Z.; Li, W.; Li, Y. *Organometallics* **2011**, *30*, 760.

(8) (a) Johnson, K. R. D.; Hayes, P. G. *Organometallics* **2009**, *28*, 6352. (b) Johnson, K. R. D.; Hayes, P. G. *Organometallics* **2011**, *30*, 58.

(9) (a) Mukherjee, M.; Allern, A.; Sadow, A. D. *J. Am. Chem. Soc.* **2010**, *132*, 7582. (b) Pawlikowski, A. V.; Gray, T. S.; Schoendorff, G.; Baird, B.; Allern, A.; Windus, T. L.; Sadow, A. D. *Inorg. Chim. Acta* **2009**, *362*, 4517.

(10) Zou, J. Ph.D. Thesis, University of Victoria, 2012.

(11) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32A*, 751.

(12) (a) Zurawski, A.; Muller-Buschbaum, K. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1427. (b) Muller-Buschbaum, K.; Zurawski, A. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2300. (c) Quitmann, C. C.; Muller-Buschbaum, K. *Z. Anorg. Allg. Chem.* **2005**, *631*, 350. (d) Abrahams, C. T.; Deacon, G. B.; Gatehouse, B. M.; Ward, G. N. *Acta Crystallogr., Sect. C* **1994**, *50*, 504.

(13) (a) Dietel, A.-M.; Doring, C.; Kempe, R. *Z. Kristallogr. - New Cryst. Struct.* **2008**, *223*, 395. (b) Dietel, A.-M.; Doring, C.; Glatz, G.; Butivskii, M. V.; Tok, O.; Schappacher, F. M.; Pottgen, R.; Kempe, R. *Eur. J. Inorg. Chem.* **2009**, 1051. (c) Datta, S.; Garner, M. T.; Roesky, P. W. *Organometallics* **2008**, *27*, 1207. (d) Hitchcock, P. B.; Khvostov, A. V.; Lappert, M. F.; Protchenko, A. V. *Dalton Trans.* **2009**, 2383. (e) Hasinoff, L.; Takats, J.; Zhang, X. W.; Bond, A. H.; Rogers, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 8833. (f) Chai, Z.-Y.; Wang, Z.-X. *Dalton Trans.* **2009**, 8005. (g) Rabe, G. W.; Rheingold, A. L.; Incarvito, C. D. *Z. Kristallogr. - New Cryst. Struct.* **2000**, *215*, 560. (h) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23*, 2271. (i) O'Connor, P. E.; Twamley, B.; Berg, D. J. *Inorg. Chim. Acta* **2006**, *359*, 2870. (j) van den Hende, J. R.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1994**, 1413. (k) van den Hende, J. R.; Hitchcock, P. B.; Lappert, M. F. *Dalton Trans.* **1995**, 2251. (l) Niemeyer, M. *Inorg. Chem.* **2006**, *45*, 9085.

(14) Reduction potentials have been calculated for the reduction of $Yb^{3+} \rightarrow Yb^{2+}$ (−1.1 V) and $Yb^{2+} \rightarrow Yb^{0}$ (−2.7 V) in aqueous solution: (a) Bratsch, S. G.; Lagowski, J. J. *J. Phys. Chem.* **1985**, *89*, 3317. For related studies, see also: (b) Morss, L. R. *Chem. Rev.* **1976**, *76*, 827. (c) Johnson, D. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1671.

(15) (a) One reviewer suggested a further possibility involving ring opening of THF by the Yb(II) alkyl complex with oxidation of the metal. (b) Korobkov, I.; Gambarotta, S. *Inorg. Chem.* **2010**, *49*, 3409.

(16) Han, L.-B.; Tilley, T. D. *J. Am. Chem. Soc.* **2006**, *128*, 13698.

(17) (a) Schwartz, D. J.; Andersen, R. A. *Organometallics* **1995**, *14*, 4308. (b) Blair, S.; Izod, K.; Clegg, W. *J. Organomet. Chem.* **2003**, *688*, 92. (c) Tardif, O.; Hou, Z.; Nishiura, M.; Koizumi, T.; Wakatsuki, Y. *Organometallics* **2001**, *20*, 4565. (d) Rabe, G. W.; Guzei, I. A.; Rheingold, A. L. *Inorg. Chem.* **1997**, *36*, 4914. (e) Clegg, W.; Izod, K.; Liddle, S. T.; O'Shaughnessy, P.; Sheffield, J. M. *Organometallics* **2000**, *19*, 2090. (f) Izod, K.; O'Shaughnessy, P.; Sheffield, J. M.; Clegg, W.; Liddle, S. T. *Inorg. Chem.* **2000**, *39*, 4741. (g) Rabe, G. W.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1995**, *34*, 4521. (h) Atlan, S.; Nief, F.; Ricard, L. *Bull. Soc. Chim. Fr.* **1995**, *132*, 649.

(18) Baudler, M.; Carlsohn, B.; Koch, D.; Medda, P. K. *Chem. Ber. Recl.* **1978**, *111*, 1210.

(19) The radii of Y^{3+} and Yb^{3+} in six-coordination are estimated to be 0.900 and 0.868 Å, respectively.[11]

(20) (a) Evans, W. J. *Chem. Rev.* **2000**, *200*, 263. (b) Evans, W. J.; Davis, B. L.; Ziller, J. W. *Inorg. Chem.* **2001**, *40*, 6341. (c) Evans, W. J.; Miller, K. A.; Lee, D. S.; Ziller, J. W. *Inorg. Chem.* **2005**, *44*, 4326.

(21) (a) Sheng, E.; Wang, S.; Yang, G.; Zhou, S.; Cheng, L.; Zhang, K.; Huang, Z. *Organometallics* **2003**, *22*, 684. (b) Sheng, E.; Zhou, S.; Wang, S.; Yang, G.; Wu, Y.; Feng, Y.; Mao, L.; Huang, Z. *Eur. J. Inorg. Chem.* **2004**, 2923. (c) Wu, Y.; Wang, S.; Qian, C.; Sheng, E.; Xie, M.; Yang, G.; Feng, Q.; Zhang, L.; Tang, X. *J. Organomet. Chem.* **2005**, *690*, 4139.

(22) Examples of bridging lanthanide phosphinidenes: (a) Masuda, J. D.; Jantunen, K. C.; Ozerov, O. V.; Noonan, K. J. T.; Gates, D. P.; Scott, B. L.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 2408. (b) Cui, P.; Chen, Y.; Xu, X.; Sun, J. *Chem. Commun.* **2008**, 5547. (c) Cui, P.; Chen, Y.; Borzov, M. V. *Dalton Trans.* **2010**, *39*, 6886. (d) Summerscales, O. T.; Gordon, J. C. *RSC Adv.* **2013**, *3*, 6682.

(23) Smith, L. R.; Mills, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3852.

(24) Tilley, T. D.; Boncella, J. M.; Berg, D. J.; Burns, C. J.; Andersen, R. A. *Inorg. Synth.* **1990**, *27*, 146.

(25) (a) Becker, G.; Mundt, O.; Rössler, M.; Schneider, E. Z. *Anorg. Allg. Chem.* **1978**, *443*, 42. (b) Liddle, S.; Izod, K. *Organometallics* **2004**, *23*, 5550.

(26) *SMART, v5.632*; Bruker AXS, Madison, WI, 2005.

(27) *SAINTPlus, v6.22, Data Reduction and Correction Program*; Bruker AXS, Madison, WI, 2001.

(28) Sheldrick, G. M. *SADABS: v2.01, Empirical Absorption Correction Program*; Bruker AXS, Madison, WI, 2001.

(29) Sheldrick, G. M. *SHELXTL: v6.10, Structure Determination Software Suite*; Bruker AXS, Madison, WI, 2001.