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Synthesis and Structural Characterization of the First Lanthanide(II) Cuboidal Cluster. Unexpected C−O Activation by an Unchanged Ytterbium(II) Center

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The two new sterically demanding secondary phosphines (C_6H_4-2-OMe)RPH (**1a**) and (C_6H_3-2-OMe-3-Me)RPH (**1b**) [$R = CH(SiMe_3)_2$] are synthesized by the reaction of $RPCl_2$ with 1 equiv of LiC_6H_4-2-OMe or LiC_6H_3-2-OMe-3-Me, respectively, followed by in situ reduction with $LiAlH_4$. Metalation of **1** with Bu^nLi, followed by metathesis with $KOBu^t$, yields the potassium salts K{PR(C_6H_4-2-OMe)} (**2a**) and K{PR(C_6H_3-2-OMe-3-Me)} (**2b**). The reaction of K{PR(C_6H_3-2-OMe-3-Me)} with YbI_2 yields the diphosphide complex [Yb^{II}{PR(C_6H_3-2-OMe-3-Me)}$_2$(THF)$_2$] (**3**), in which the phosphides act as *P*,*O*-chelating ligands. In contrast, reaction of K{PR(C_6H_4-2-OMe)} with YbI_2 under similar conditions yields the unexpected alkoxophosphide complex [Yb^{II}{PR(C_6H_4-2-O)}(THF)]$_4$·4Et_2O (**4**), via an unusual ligand cleavage reaction involving the transfer of a methyl group from oxygen to phosphorus. Compounds **1**−**4** have been characterized by elemental analyses and multinuclear NMR spectroscopy and compounds **3** and **4** by X-ray crystallography. Compound **3** is monomeric in the solid state, with a distorted all-*trans*-octahedral geometry about the Yb center; compound **4** crystallizes as an unprecedented tetrameric cluster containing a Yb_4O_4 cuboidal core. Multi-element NMR spectroscopy suggests that **4** maintains an oligomeric structure in THF solution. The P-containing side product formed in the synthesis of **4** has been isolated and identified as (Me)PR(C_6H_4-2-OMe) by comparison of its NMR and mass spectra with those of an authentic sample.

Introduction

Although the lanthanide elements are regarded as hard metal centers which tend to favor complexation by hard donor ligands such as alkoxides (RO) and dialkylamides (R_2N),[1] the past few years have seen much progress in the synthesis of lanthanide complexes with soft donor ligands,[2] such as organochalcogenides (RE, E = S, Se, Te)[3,4] and (di)organopnictides (R_2E, E = P, As).[5,6]

Organophosphide complexes, $Ln(PR_2)_2$, of the three lanthanide elements readily accessible in the +2 oxidation state (Eu, Sm, Yb) fall into three main classes: solvated monomers [e.g., $Yb(PPh_2)_2(THF)_4$],[6b] ate complexes [e.g., Eu{(μ-PBu^t_2)$_2$Li(THF)$_2$}$_2$],[6e] and unsymmetrical phosphide-bridged dimers [e.g., {$(Me_3Si)_2P$}-Sm{μ-$P(SiMe_3)_2$}$_3$Sm(THF)$_3$].[6g] The structure adopted in each case is dependent upon the steric requirements of the ligands, the presence of coligands such as THF or *N*-methylimidazole (*N*-MeIm), and the chosen synthetic pathway.

Although a number of Ln(II) phosphide complexes have been isolated in recent years, little is known about their reactions and relative reactivities in comparison to compounds such as SmI_2, a compound that is now in widespread use as a reagent in organic synthesis.[7] In light of the wide range of reactions mediated by lanthanide(II) compounds, and especially by organolanthanide complexes such as Cp^*_2Sm (Cp^* = pentamethylcyclopentadienyl),[1] many of which are without precedent in the rest of the periodic table, it seemed likely to us that other sterically hindered, coordinatively unsaturated complexes of the lanthanides might exhibit

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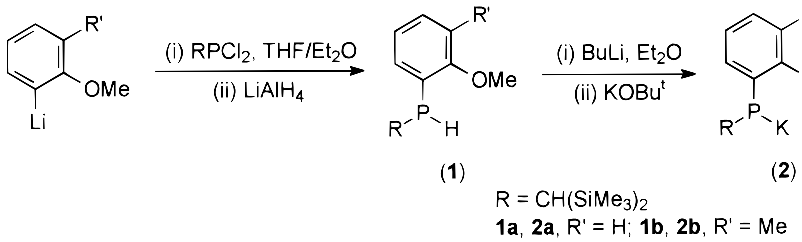
Scheme 1



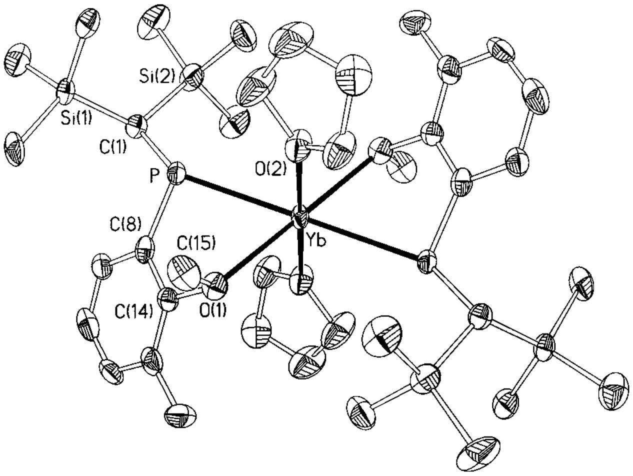


Figure 1. Molecular structure of **3**, with 40% probability ellipsoids. H atoms and minor disorder components omitted for clarity.

interesting reactivity patterns. In this regard, we have recently become interested in the effect of sterically demanding, potentially chelating phosphide ligands on the structures and reactions of their complexes with main group and lanthanide metals and, in particular, in how minor changes at the periphery of such ligands affect their reactivities.[8] We herein report the syntheses of two new secondary phosphines and their potassium salts and the synthesis and structural characterization of a novel complex of ytterbium(II) with a chelating phosphide ligand. We also report that a relatively minor change in the substituents on such chelating phosphide ligands enables the isolation of a remarkable cluster complex containing an unusual alkoxophosphide ligand, obtained via an unexpected ligand cleavage reaction.

Results and Discussion

The secondary phosphines $\{(Me_3Si)_2CH\}(C_6H_4\text{-2-OMe})PH$ (**1a**) and $\{(Me_3Si)_2CH\}(C_6H_3\text{-2-OMe-3-Me})PH$ (**1b**) were synthesized by the reaction of $RPCl_2$ [R = CH(SiMe$_3$)$_2$] with either Li(C_6H_4OMe) or Li(C_6H_3-2-OMe-3-Me), respectively, in ether/THF solutions, followed by in situ reduction with $LiAlH_4$ (Scheme 1). A simple aqueous workup gave the phosphines as colorless, viscous oils in good yield. The ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectra of **1a** and **1b** are as expected, although the diastereotopic $SiMe_3$ groups give rise to two signals in the ^1H spectra but only one signal in the $^{13}C\{^1H\}$ spectra in each case.

The potassium salts [RP(C_6H_4-2-OMe)]K (**2a**) and [RP(C_6H_3-2-OMe-3-Me)]K (**2b**) were prepared in a manner similar to the previously reported [RP(C_6H_4-2-CH_2NMe_2)]K,[8] via metalation of the respective secondary phosphine with Bu^{n}Li in ether, followed by metathesis with KOBu^t. The potassium salts precipitate rapidly from diethyl ether solutions and are isolated in moderate to good yield as bright orange, pyrophoric powders, which can be used without further purification. In common with [RP(C_6H_4-2-CH_2NMe_2)]K, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **2a** and **2b** in THF-d_8 solution exhibit singlets for the Me_3Si groups, suggesting that rapid, reversible P−K bond cleavage results in symmetrization of the complex on the NMR time scale.[8]

Metathesis between 2 equiv of K{PR(C_6H_3-2-OMe-3-Me)} and YbI_2 in THF/ether gives the Yb(II) diphosphide [Yb^{II}\{PR(C_6H_3-2-OMe-3-Me)\}$_2$(THF)$_2$] (**3**) in excellent yield, according to eq 1.

$$2[K\{PR(C_6H_3\text{-2-OMe-3-Me})\}] + YbI_2 \xrightarrow{\text{THF/ether}} [Yb^{II}\{PR(C_6H_3\text{-2-OMe-3-Me})\}_2(THF)_2]\ (\mathbf{3}) + 2KI \quad (1)$$

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **3** are consistent with a symmetrical, all-*trans*-octahedral structure in solution. The ^{31}P NMR spectrum consists of a singlet at −56.8 ppm with satellites due to coupling to ^{171}Yb ($I = {}^1/_2$, 14.3% natural abundance; $J_{YbP} = 983$ Hz).

Recrystallization of **3** from toluene at −30 °C gave single crystals suitable for an X-ray crystallographic study. This confirmed that **3** adopts a centrosymmetric, all-*trans*, distorted octahedral geometry in the solid state with the phosphide ligands binding through both their O and P atoms to form five-membered chelate rings with a bite angle of 66.09(15)°. This compares with a bite angle of 60.9(2)° for the related tridentate ligand in the dinuclear phosphide-bridged complex [(Pr$^i{}_2$N)$_2$La\{μ-P(C_6H_4-2-OMe)$_2$\}Li(THF)]·C_6H_5Me.[5f] The larger bite angle in **3** is to be expected due to the slightly smaller ionic radius of Yb(II) compared to that of La(III) (1.02 vs 1.032 Å for a six-coordinate complex).[9] The molecular structure of **3** is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. The Yb−P distance of 2.969(3) Å is similar to Yb−P

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

Yb−P	2.969(3)	Yb−O(1)	2.502(6)	Yb−O(2)	2.535(7)
P−C(1)	1.939(9)	P−C(8)	1.873(10)	C(1)−Si(1)	1.938(9)
C(1)−Si(2)	1.935(10)	C(14)−O(1)	1.479(11)	C(15)−O(1)	1.487(11)
Si−C(Me)[a]	1.932				

P−Yb−O(1)	66.09(15)	P−Yb−O(2)	87.63(16)
O(1)−Yb−O(2)	92.8(2)	Yb−P−C(1)	142.9(3)
Yb−P−C(8)	94.7(3)	C(1)−P−C(8)	104.1(4)
Yb−O(1)−C(14)	115.8(5)	Yb−O(1)−C(15)	117.2(6)

[a] Average value.

distances in a range of ytterbium(II) phosphides, including $[\{(mes)_2P\}_2Yb(THF)_4]$ (Yb−P = 2.925(2) Å),[6a] $[\{(mes^*)HP\}_2Yb(THF)_4]$ (3.025(2) Å),[6c] and $[(Ph_2P)_2Yb(THF)_4]$ (2.991(2) Å)[6b] [mes = 2,4,6-Me_3-C_6H_2; mes* = 2,4,6-Bu^t_3-C_6H_2]. The Yb−O(Ar) distance of 2.502(6) Å is slightly shorter than the Yb−O(THF) distance (2.535(7) Å), but both are quite long in comparison to Yb−O(THF) distances in related complexes, possibly as a consequence of steric congestion in **3**. For example, the Yb−O distances are 2.439(4) Å in $[\{(mes)_2P\}_2Yb(THF)_4]$,[6a] 2.437(4) and 2.430(4) Å in $[(Ph_2P)_2Yb(THF)_4]$,[6b] and 2.480(4) and 2.506(3) Å in $[\{(mes^*)HP\}_2Yb(THF)_4]$,[6c] respectively; the Yb−O(THF) distances in $[Yb(OCBu^t_3)_2(THF)_2]$[10] are 2.38(2) and 2.39(3) Å and in $[Yb(THF)_6][CPh_3]_2$ are 2.390(7) Å.[11] The phosphorus atoms in lanthanide phosphides have been reported to adopt a planar configuration in complexes with sterically hindered ligands, but to adopt a pyramidal geometry at P in less hindered complexes. For example, the sum of angles about phosphorus in the two complexes $[Yb(PPh_2)_2(THF)_4]$ and $[Yb\{P(mes)_2\}_2(THF)_4]$ is 332.7° and 360°, respectively.[6a,b] However, the P atoms in **3** adopt a pyramidal geometry (sum of angles at P = 341.7°), despite the large steric bulk of the ligands.

In contrast to the facile preparation of **3**, a similar metathetical reaction between the closely related potassium phosphide K{PR(C_6H_4-2-OMe)} (**2b**) and YbI_2 in THF/ether yields an orange solid, which after recrystallization from toluene over 2 days is isolated as deep orange-red crystals of composition $[Yb^{II}\{PR(C_6H_4\text{-}2\text{-}O)\}(THF)]_4 \cdot 4Et_2O$ (**4**). The structure of **4** was determined by X-ray crystallography and consists of a tetrameric alkoxophosphide cluster with a cuboidal Yb_4O_4 core. The molecular structure of **4** is shown in Figure 2, and selected bond lengths and angles are listed in Table 2.

The Yb atoms sit at alternate corners of a Yb_4O_4 "cube", and each is coordinated by three μ_3-alkoxide groups, two μ_2-phosphide groups, and a molecule of THF. Thus each alkoxophosphide ligand bridges three Yb atoms via its alkoxo oxygen and also bridges two of these same Yb atoms via its phosphido P atom. Although the Yb_4O_4 core in **4** is highly distorted from a regular cube, both it and the cluster as a whole possess exact crystallographic S_4 symmetry. The top and bottom faces of the cuboidal core [Yb−O(1)−Yb(A)−O(1A) and Yb(B)−O(1B)−Yb(C)−O(1C)] are essentially planar, parallel rhombuses that are twisted through an angle of 90° with respect to each other; the folding angle between the O(1)−Yb−O(1A) and O(1)−Yb(A)−O(1A) planes is 174.6°. The internal angles within this rhombus are 69.75(10) [O(1)−Yb−O(1A)] and 110.07(10)° [Yb−O(1)−Yb(A)].

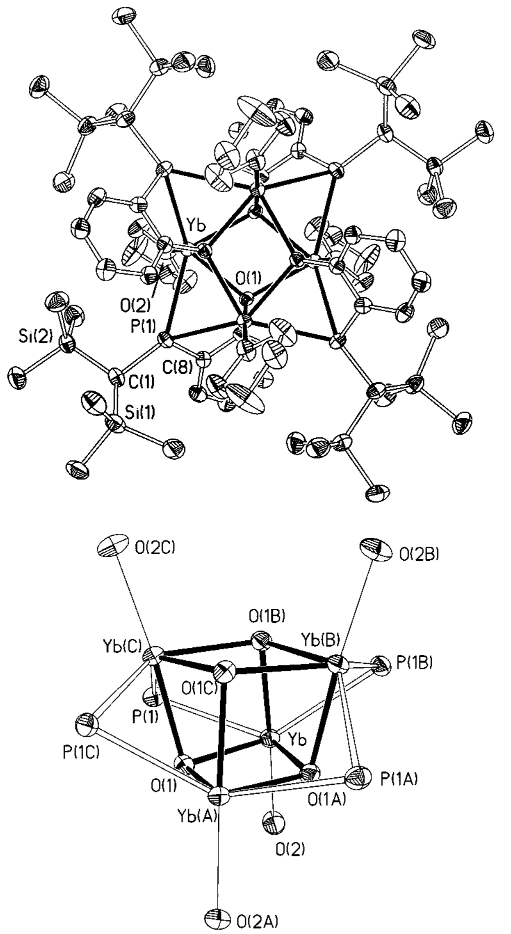

Figure 2. (a) Molecular structure of **4**, with 40% probability ellipsoids; H atoms omitted for clarity. (b) Structure of the cuboidal core of **4**, together with completion of the Yb coordination.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4[a]

Yb−P(1)	2.9604(13)	Yb−P(1B)	2.9601(12)	Yb−O(1)	2.400(3)
Yb−O(1A)	2.404(3)	Yb−O(1B)	2.459(3)	Yb−O(2)	2.445(3)
P(1)−C(1)	1.895(5)	P(1)−C(8)	1.840(5)	C(1)−Si(1)	1.881(5)
C(1)−Si(2)	1.865(5)	Si−C(Me)[b]	1.875		

P(1)−Yb−O(1)	64.03(7)	P(1)−Yb−P(1B)	126.532(13)
O(1)−Yb−O(1A)	69.75(10)	O(1A)−Yb−O(2)	103.92(11)
P(1B)−Yb−O(1A)	79.17(7)	O(2)−Yb−O(1B)	173.35(10)
Yb−O(1)−Yb(A)	110.07(10)	Yb−O(1)−Yb(C)	95.85(10)
Yb(A)−O(1)−Yb(C)	95.76(11)	Yb−P(1)−YbC	75.08(3)

[a] Symmetry operations for **4**: A 2−*x*, 1−*y*, *z*; B 1/2+*y*, 3/2−*x*, 1/2−*z*; C 3/2−*y*, −1/2+*x*, 1/2−*z*. [b] Average value.

The Yb−O(alkoxo) distances [2.400(3), 2.404(3), 2.459(3) Å] are similar to the Yb−O(THF) distance of 2.445(3) Å and are somewhat longer than previously reported terminal and μ_2-bridging Yb(II)−O(alkoxide) distances, consistent with the μ_3-bridging mode observed in **4**. For example, the Yb−O(μ_2-OR) distances in $[Yb(\mu_2\text{-}OCBu^t_3)\{N(SiMe_3)_2\}]_2$ range from 2.294(5) to 2.320(5) Å,[10] the bridging and terminal Yb−O(Ar) distances in $[Yb(\mu_2\text{-}OC_6H_2\text{-}2,6\text{-}Bu^t_2\text{-}4\text{-}Me)(OC_6H_2\text{-}2,6\text{-}Bu^t_2\text{-}4\text{-}Me)]_2$ range from 2.08(2) to 2.37(2) Å,[12] and the terminal Yb−O(Ar)

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distances in [Yb(OC_6H_2-2,6-Bu^t_2-4-Me)$_2$(OEt_2)$_2$] are 2.126(9) and 2.182(8) Å, respectively.[12] The phosphido P atoms bridge Yb atoms in four of the faces of the cube in an essentially symmetrical μ_2-fashion; the Yb−P distances of 2.9604(13) and 2.9601(12) Å lie within the range of distances found for other Yb(II)−P bonds (see above).[6]

Although the Yb atoms in **4** are six-coordinate, their geometry is perhaps best described as pentagonal bipyramidal, with O(1B) and O(2) in the axial positions [O(1B)−Yb−O(2) = 173.35(10)°] and with one equatorial coordination site vacant. This vacant coordination site is sterically occluded by the Me_3Si groups of two adjacent ligands, preventing further oligomerization or coordination by THF. The clusters pack in the crystal in such a way that large columnar cavities, aligned along the *c* axis, are completely surrounded by $SiMe_3$ groups. These cavities contain the solvent of crystallization, four molecules of diethyl ether per molecule of cluster.

While a number of Ln(III) clusters are known, very few clusters containing low oxidation state lanthanide centers have been reported to date. A recent review lists only two organolanthanide(II) clusters,[13] the Yb(II) complex [Li(THF)$_4$]$_2$[($C_5Me_4SiMe_2Bu^t$)$_6$Yb$_6$(μ_3-I)$_8$][14] and the mixed valence Yb(II)/Yb(III) cluster [Cp*$_6$Yb$_4$(μ-F)$_4$],[15] and in no case has such a polynuclear complex been reported to adopt a cuboidal structure. In contrast, lanthanide(III) clusters are known for a range of ligand environments, including hexanuclear and octanuclear sulfide and selenide clusters,[4] tetra-, penta-, and hexanuclear oxo- or non-oxo-centered alkoxide clusters,[16,17] a tetrameric amide cluster,[18] and related N- and O-donor ligand clusters.[19] However, lanthanide(III) clusters containing cuboidal cores are themselves limited to a very few recently reported examples. These are (i) an ytterbium(III) selenide, [(py)$_8$Yb$_4$Se$_4$(SePh)$_4$],[20] (ii) a stacked Yb(III) double cuboidal sulfide complex, [(Py)$_{10}$Yb$_6$S$_6$(SPh)$_6$],[20] (iii) a Gd(III) β-diketonate complex, [Gd$_4$(μ_3-OH)$_4$(μ_2-OH$_2$)$_2$(OH$_2$)$_4$($CF_3COCHCOCF_3$)]·2(C_6H_6)·H_2O,[21] (iv) a Eu(III) complex of tyrosine, [Eu$_{15}$(Cl)(μ_3-Tyr)$_{10}$(μ_3-OH)(μ_2-H$_2$O)$_5$(OH)$_{12}$(H$_2$O)$_8$]-[ClO$_4$]$_2$·56H$_2$O,[22] and (v) a Sm(III) Schiff base complex [(3,5-Bu^t_4-salophen)Sm(OH)]$_4$·(C_6H_5Me)$_4$.[23] The formation of the Yb(II) cuboidal cluster **4** would therefore appear to be without precedent.

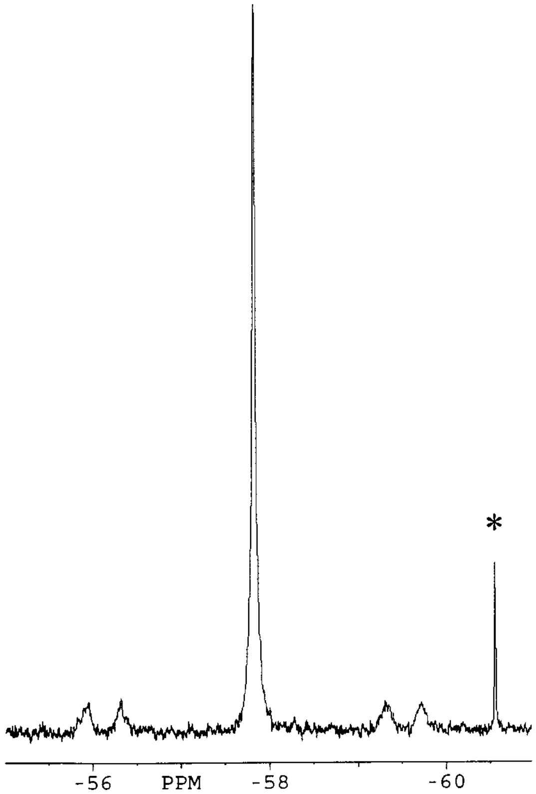

Figure 3. $^{31}P\{^1H\}$ NMR spectrum of **4** in THF-d_8 [* minor impurity].

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **4** in THF-d_8 exhibit only one set of ligand resonances, consistent with a highly symmetrical species; the $^{31}P\{^1H\}$ NMR spectrum (Figure 3) consists of a singlet at −57.8 ppm with two pairs of satellites due to coupling to two inequivalent ^{171}Yb centers (J_{YbP} = 603.8 and 764.9 Hz). The ^{171}Yb NMR spectrum of **4** consists of a doublet of doublets centered on 663.6 ppm (J_{YbP} = approximately 603 and 767 Hz), indicating the presence of only one Yb environment in solution with the Yb nucleus coupled to two inequivalent ^{31}P nuclei. While this is consistent with complex **4** retaining in solution a tetrameric structure similar to that observed in the solid state, in which each alkoxophosphide ligand essentially chelates one Yb atom while bridging via phosphorus to a second Yb atom, a dimeric or hexameric structure may account equally well for the observed spectra. However, given the oxophilic nature of the lanthanides and the sterically hindered nature of the P center of the ligand, it is unlikely that a dimeric species would be bridged by μ_2-P atoms in preference to μ_2-O atoms, and thus we propose that complex **4** exists as a tetramer or higher oligomer in THF solution. Unfortunately the extremely limited

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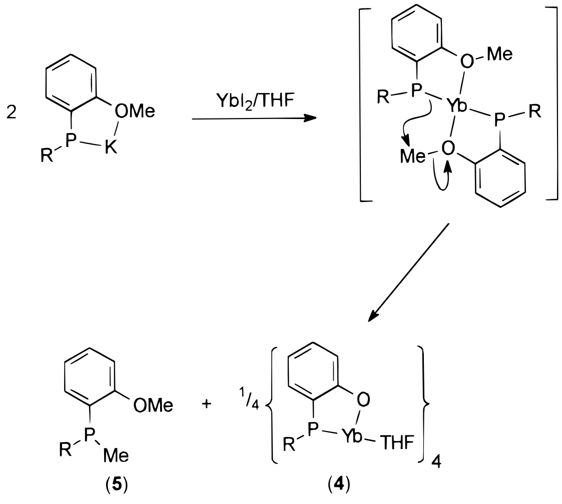
Scheme 2



solubility of this complex, even in strong donor solvents such as THF, prevented confirmation of the aggregation state in solution by a cryoscopic molecular weight determination.

In repeated reactions compound **4** is reproducibly isolated in crystalline form in 50% yield or better. The sole organic side product in this reaction was isolated and identified as the tertiary phosphine MePR(C_6H_4-2-OMe) (**5**) by comparison of its NMR and mass spectra with those of an authentic sample, synthesized by the reaction of {$(Me_3Si)_2CH$}(C_6H_4-2-OMe)PCl with MeLi. We therefore postulate that the formation of **4** proceeds according to Scheme 2: The initial formation of a Yb(II) diphosphide intermediate similar to **3** is followed by transfer of a methyl group from the O atom of one phosphide ligand to the adjacent P atom of the other phosphide ligand in the intermediate complex. This is rapidly followed by elimination of the neutral tertiary phosphine (**5**) and the aggregation and precipitation of the Yb(II) alkoxophosphide (**4**).

It therefore appears that cluster formation involves a remarkable shift of a methyl group from oxygen to phosphorus, requiring both C−O cleavage and P−C bond formation, without affecting the oxidation state of the ytterbium(II) center. Nevertheless, the Yb(II) center appears to be essential for this reaction: the precursor secondary phosphine RPH(C_6H_4-2-OMe) and its potassium derivative are stable for long periods in the absence of air, even in THF solutions at elevated temperatures, and the reaction between **2a** and $SmI_2(THF)_2$ yields the expected Sm(II) diphosphide, with no evidence of C−O cleavage in this case.[24]

To our knowledge this represents only the second example of C−O cleavage mediated by an unchanged Yb(II) center.[25] The only previous report of such a reaction is the selective cleavage of ethyl ethers by Yb{$C(SiMe_3)_3$}$_2$, which proceeds according to eq 2, i.e., via *proton transfer* from a methyl group of diethyl ether to the central carbon of one of the alkyl ligands.[26] The reaction leading to **4** thus appears to be the first in which C−O cleavage by an unchanged Ln(II) center involves *alkyl group transfer*.

$$\mathrm{Yb\{C(SiMe_3)_3\}_2 + 2Et_2O \xrightarrow{ether} 1/2[Yb\{C(SiMe_3)_3\}(OEt)(OEt_2)]_2 + HC(SiMe_3)_3 + CH_2{=}CH_2} \quad (2)$$

The facile synthesis of **4** is quite unexpected, and the reasons behind its formation are, as yet, unknown. However, it is clear that, by means of the ligand cleavage reaction, the Yb(II) centers are able to maximize their contacts with hard anionic O-donors. The preferential isolation of **3**, rather than an analogue of **4**, is also not easily explained, but may be due in part to steric effects: formation of a cluster similar to **4** with the ligand PR(C_6H_3-2-OMe-3-Me) may lead to unfavorable steric interactions between the 3-Me groups and the cuboidal core.

Conclusions

The novel, potentially chelating phosphide ligands {$(Me_3Si)_2CH$}(C_6H_3-2-OMe-3-Me)P and {$(Me_3Si)_2CH$}(C_6H_4-2-OMe)P may readily be isolated as their potassium salts. The small difference in substituents at the periphery of these two ligands has a dramatic effect on their reactions with ytterbium diiodide. The potassium salt of the former ligand acts as an effective transfer reagent for the synthesis of a low oxidation state ytterbium phosphide complex. However, the latter ligand undergoes an unusual cleavage reaction upon reaction with YbI_2, yielding an unprecedented alkoxophosphide complex of ytterbium(II), which contains a cuboidal core in the solid state. The difference in reactivity between the two phosphide ligands appears to be a purely steric phenomenon, the 3-Me group adding just enough steric bulk to prevent the assembly of a cuboidal structure and thus to hinder the ligand cleavage reaction. Further investigations of these and related complexes are currently underway.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Ether, THF, light petroleum (bp 40−60 °C), and toluene were distilled from sodium, potassium, or sodium/potassium alloy under an atmosphere of dry nitrogen and stored over a potassium film (with the exception of THF, which was stored over activated 4Å molecular sieves). Deuterated THF and C_6D_6 were distilled from potassium, deoxygenated by three freeze−pump−thaw cycles, and stored over activated 4Å molecular sieves. Tmeda (*N*′,*N*′,*N*″,*N*″-tetramethylethylenediamine) was distilled from CaH_2 and stored over activated 4Å molecular sieves. $KOBu^t$, $LiAlH_4$, anisole, and 2-methylanisole were purchased from Aldrich and used without further purification. Butyllithium was obtained from Aldrich as a 2.5 M solution in hexanes. Methyllithium was obtained from Acros Organics as a 1.8 M solution in ether. YbI_2,[27] *o*-Li(C_6H_4OMe),[28] and {$(Me_3Si)CH$}PCl_2[29] were prepared according to published

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procedures. ^{31}P NMR spectra were recorded on a Bruker WM300 spectrometer operating at 121.5 MHz, ^{171}Yb NMR spectra on a JEOL Lambda 500 spectrometer operating at 87.5 MHz, and ^{1}H and ^{13}C spectra on a Bruker AC200 spectrometer, operating at 200.1 and 50.3 MHz respectively; signals due to *ipso*-carbon atoms were not always resolved in the ^{13}C{^{1}H} spectra. ^{1}H and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane; ^{31}P chemical shifts are quoted relative to external 85% H_3PO_4, and ^{171}Yb chemical shifts are quoted relative to external (η^5-C_5Me_5)$_2$Yb(THF)$_2$.[30] Elemental analyses were obtained by Elemental Microanalysis Ltd., Okehampton, UK. Mass spectra were recorded on a Micromass Autospec M spectrometer operating in EI mode at 70 eV.

Preparation of {(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-OMe) (1a). To a solution of {(Me$_3$Si)$_2$CH}PCl$_2$ (1.86 g, 7.12 mmol) in cold (−78 °C) ether (5 mL) was added, dropwise, a solution of *o*-Li(C$_6$H$_4$-OMe) (0.82 g, 7.12 mmol) in ether/THF (5/10 mL). This solution was allowed to attain room temperature and was stirred for a further 3 h. Solids were removed by filtration, and the solution was heated under reflux over $LiAlH_4$ (0.54 g, 14.24 mmol) for 2 h. Excess $LiAlH_4$ was destroyed by the addition of degassed water (30 mL), and the organic phase was extracted into light petroleum (2 × 30 mL). The organic phase was dried over activated 4Å molecular sieves, and the solvent was removed in vacuo to give **1a** as a colorless oil. Yield: 1.53 g, 72%. Anal. Calcd for $C_{14}H_{27}OPSi_2$: C, 56.33; H, 9.12. Found: C, 55.18; H, 9.60. ^{1}H NMR (CDCl$_3$): δ 0.04 (9H, s, SiMe$_3$), 0.05 (9H, s, SiMe$_3$), 0.58 (1H, dd, $^3J_{HH} = 5.2$ Hz, $J_{PH} = 2.4$ Hz, CHP), 3.83 (3H, s, OMe), 4.34 (1H, dd, $^3J_{HH} = 5.2$ Hz, $J_{PH} = 220$ Hz, PH), 6.78−7.40 (4H, m, ArH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 0.7 (SiMe$_3$), 4.2 (d, $J_{PC} = 41.6$ Hz, CHP), 55.3 (OMe), 109.8, 120.5, 129.5, 134.6, 160.9 (Ar). ^{31}P NMR (CDCl$_3$): δ −73.6 (d, $J_{PH} = 220$ Hz).

Preparation of {(Me$_3$Si)$_2$CH}PH(C$_6$H$_3$-2-OMe-3-Me) (1b). To a solution of 2-methylanisole (1.48 mL, 1.46 g, 11.93 mmol) and tmeda (1.80 mL, 1.39 g, 11.93 mmol) in ether (5 mL) was added BuLi (6.00 mL, 15.00 mmol). This mixture was allowed to stir at room temperature for 16 h, and then the solid was isolated by filtration. The solid was washed with ether (2 × 10 mL) and dried in vacuo to give essentially pure Li(C$_6$H$_3$-2-OMe-3-Me) (1.07 g, 70%).

To a solution of {(Me$_3$Si)$_2$CH}PCl$_2$ (0.97 g, 3.72 mmol) in cold (−78 °C) ether (20 mL) was added, dropwise, a solution of Li(C$_6$H$_3$-2-OMe-3Me) (0.48 g, 3.75 mmol) in THF (20 mL). This solution was allowed to attain room temperature and was stirred for a further 2 h. Solids were removed by filtration, and the solution was heated under reflux over $LiAlH_4$ (0.28 g, 7.44 mmol) for 2 h. Excess $LiAlH_4$ was destroyed by the addition of degassed water (30 mL), and the organic phase was extracted into light petroleum (2 × 30 mL). The organic phase was dried over activated 4Å molecular sieves, and then the solvent was removed in vacuo to give **1b** as a colorless oil. Yield: 0.93 g, 66%. Anal. Calcd for $C_{15}H_{29}OPSi_2$: C, 57.64; H, 9.35. Found: C, 56.65; H, 9.46. ^{1}H NMR (CDCl$_3$): δ 0.35 (9H, s, SiMe$_3$), 0.11 (9H, s, SiMe$_3$) 0.53 (1H, dd, $J_{HH} = 6.0$ Hz, $J_{PH} = 2.6$ Hz, CHP), 2.29 (3H, s, ArMe) 3.80 (3H, s, OMe), 4.87 (1H, dd, $J_{HH} = 6.0$ Hz, $J_{PH} = 215$ Hz, PH) 6.93−7.27 (3H, m, ArH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 0.7 (SiMe$_3$), 4.7 (d, $J_{PC} = 40.7$ Hz, CHP), 16.1 (ArMe), 60.1 (OMe), 123.9, 130.6, 131.4, 131.5, 160.1 (Ar). ^{31}P NMR (CDCl$_3$): δ −69.6 (d, $J_{PH} = 215$ Hz).

Preparation of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-OMe)P]K (2a). To a solution of **1a** (0.48 g, 1.61 mmol) in ether (10 mL) was added BuLi (0.64 mL, 1.61 mmol). This mixture was stirred for 1 h. To the resulting orange solution was added a solution of KOBu^t (0.24 g, 2.14 mmol) in ether (10 mL), and stirring was continued for 3 h. The deep orange precipitate was isolated by filtration and washed with ether (3 × 15 mL). Residual solvent was removed in vacuo to give essentially pure **2a** as a pyrophoric orange powder. Yield: 0.31 g, 59%. Anal. Calcd for $C_{14}H_{26}KOPSi_2$: C, 49.96; H, 7.79. Found: C, 50.23; H, 8.15. ^{1}H NMR (THF-d_8): δ 0.09 (18H, s, SiMe$_3$), 0.13 (1H, d, $J_{PH} = 2.9$ Hz, CHP), 3.81 (3H, s, OMe), 6.05−6.72 (4H, m, ArH). ^{13}C-{^{1}H} NMR (THF-d_8): δ 3.2 (SiMe$_3$), 9.6 (d, $J_{PC} = 67$ Hz, CHP), 57.9 (OMe), 112.4, 113.6, 124.1, 127.5 (Ar). ^{31}P NMR (THF-d_8): δ −70.7.

Preparation of [{(Me$_3$Si)$_2$CH}P(C$_6$H$_3$-2-OMe-3-Me)]K (2b). To a solution of **1b** (1.59 g, 5.08 mmol) in ether (20 mL) was added BuLi (2.04 mL, 5.10 mmol). This mixture was stirred for 1 h and then added dropwise to a solution of KOBu^t (0.57 g, 5.10 mmol) in ether (10 mL). The bright orange precipitate was isolated by filtration after 3 h and was washed with ether (3 × 15 mL). Removal of residual solvent in vacuo gave essentially pure **2b** as a pyrophoric orange powder. Yield: 0.89 g, 50%. Anal. Calcd for $C_{15}H_{28}KOPSi_2$: C, 51.38; H, 8.06. Found: C, 50.80; H, 8.22. ^{1}H NMR (THF-d_8): δ 0.03 (18H, s, SiMe$_3$), 0.91 (1H, d, $J_{PH} = 2.1$ Hz, CHP), 1.98 (3H, s, ArMe) 3.80 (3H, s, OMe), 5.83−6.55 (3H, m, ArH). ^{13}C{^{1}H} NMR (THF-d_8): δ 3.1 (SiMe$_3$), 5.6 (d, $J_{PC} = 67$ Hz, CHP), 17.6 (ArMe), 57.9 (OMe), 116.1, 125.4, 126.2, 127.5 (Ar), 155.1 (d, $J_{PC} = 25$ Hz, Ar), 160.0 (d, $J_{PC} = 72$ Hz, Ar). ^{31}P NMR (THF-d_8): δ −68.4.

Preparation of [Yb^{II}{P(CH[SiMe$_3$]$_2$)(C$_6$H$_3$-2-OMe-3-Me)}$_2$(THF)$_2$] (3). A solution of **2b** (0.47 g, 1.340 mmol) in THF (10 mL) was added to a suspension of YbI$_2$ (0.286 g, 0.67 mmol) in ether (10 mL). The mixture was allowed to stir for 36 h, and then solvent was removed in vacuo. The resulting solid was extracted into toluene (25 mL) and filtered. The filtrate was concentrated to ca. 5 mL and cooled to −30 °C for 12 h, after which time orange crystals of **3** were isolated. Yield: 0.42 g, 67%. This complex rapidly desolvates under vacuum to give the solvent-free complex [Yb{PR(C$_6$H$_3$-2-OMe-3-Me)}$_2$]. Anal. Calcd for $C_{30}H_{56}O_2P_2Si_4Yb$ (formula for solvent-free complex): C, 45.26; H, 7.09. Found: C, 45.19; H, 7.27. ^{1}H NMR (THF-d_8, 298 K): δ 0.13 (s, 36H, SiMe$_3$), 0.57 (m, 2H, CHP), 1.74 (m, 8H, THF), 2.14 (s, 6H, ArMe), 3.59 (m, 8H, THF), 4.22 (s, 6H, OMe), 6.23−7.22 (m, 6H, ArH). ^{13}C{^{1}H} (THF-d_8, 298 K): δ 1.95 (SiMe$_3$), 5.83 (d, $J_{PC} = 42.3$ Hz, CHP), 26.63 (THF), 16.50 (ArMe), 60.81 (OMe), 68.47 (THF), 119.77, 126.10, 132.47 (Ar); ^{31}P{^{1}H} NMR (THF-d_8, 298 K): δ −56.8 ($J_{YbP} = 983$ Hz).

Preparation of [Yb^{II}{P(CH[SiMe$_3$]$_2$)(C$_6$H$_4$-2-O)}(THF)]$_4$-(Et$_2$O)$_4$ (4). A solution of **2a** (0.80 g, 2.376 mmol) in THF (20 mL) was added to a suspension of YbI$_2$ (0.53 g, 1.242 mmol) in diethyl ether (10 mL). The reaction mixture was stirred for 36 h, and then solvent was removed in vacuo. The sticky orange solid was extracted into toluene (30 mL) and filtered. The orange solution was concentrated to ca. 5 mL and cooled to −30 °C for 48 h, after which time deep orange-red crystals of **4** were isolated and dried in vacuo. Prolonged exposure to vacuum leads to desolvation of the complex to [Yb^{II}{P(CH-[SiMe$_3$]$_2$)(C$_6$H$_4$-2-O)}]$_4$. Yield: 0.61 g, 62%, Anal. Calcd for $C_{52}H_{92}O_4P_4Si_8Yb_4$ (solvent-free formula): C, 34.28; H, 5.09. Found: C, 34.20; H, 4.90. ^{1}H NMR (THF-d_8, 298 K): δ −0.10 (s, 9H, SiMe$_3$), 0.13 (s, 9H, SiMe$_3$), 0.93 (d, $J_{PH} = 6.4$ Hz, 1H, CHP), 1.19 (t, 6H, Et$_2$O), 1.85 (s, 8H, THF), 3.45 (q, 4H, Et$_2$O) 3.69 (s, 8H, THF), 6.43 (d, 1H, ArH), 6.52 (t, 1H, ArH), 6.66 (t, 1H, ArH), 6.87 (d, 1H, ArH). ^{13}C{^{1}H} NMR (THF-d_8, 323 K): δ 1.65, 1.97 (SiMe$_3$), 5.12 (CHP), 15.81 (Et$_2$O), 26.58 (THF), 36.53 (Et$_2$O), 66.46 (THF), 114.14, 120.26, 120.57, 127.32 (Ar). ^{31}P{^{1}H} NMR (THF-d_8, 298 K): δ −57.8 ($J_{YbP} = 603.8$ and 764.9 Hz). ^{171}Yb{^{1}H} NMR (THF-d_8, 298 K): δ 663.6 (dd, J_{YbP} = ca. 603 and 767 Hz).

The mother liquor was treated with degassed water (5 mL), dried over activated 4Å molecular sieves, and evaporated to give a colorless oil, whose identity was confirmed as {(Me$_3$Si)$_2$CH}(Me)P(C$_6$H$_4$-2-OMe) (**5**) by comparison with an authentic sample (see below).

Preparation of {(Me$_3$Si)$_2$CH}(Me)P(C$_6$H$_4$-2-OMe) (5). To a solution of {(Me$_3$Si)$_2$CH}PCl$_2$ (0.54 g, 2.07 mmol) in cold (−78

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Table 3. Crystallographic Data for 3 and 4

molecular formula	$C_{38}H_{72}O_4P_2Si_4Yb$	$C_{68}H_{164}O_8P_4Si_8Yb_4{\cdot}4C_4H_{10}O$
fw	940.30	2406.91
cryst size, mm	0.28 × 0.18 × 0.14	0.62 × 0.24 × 0.24
temp, K	160	160
cryst syst	monoclinic	tetragonal
space group	$P2_1/n$	$I\bar{4}$
a, Å	12.546(5)	20.323(4)
b, Å	18.212(4)	
c, Å	12.838(8)	12.743(3)
β, deg	118.11(5)	
V, Å^3	2587(2)	5263.2(18)
Z	2	2
D_{calcd}, g cm^{-3}	1.207	1.519
μ, mm^{-1}	1.992	3.723
F(000)	976	2432
θ range, deg.	1.87−25.00	1.89−28.30
max indices, h, k, l	14, 21, 14	25, 24, 16
no. reflns measd	12 527	14 958
no. unique reflns	4295	5129
no. reflns with $F^2 > 2\sigma(F^2)$	2895	4806
transmn coeff range	0.435−0.813	0.266−0.389
R_{int} (on F^2)	0.0595	0.0269
weighting param a^a	0.1306	0.0322
R^b	0.0693	0.0233
$R_w{}^c$	0.1892	0.0544
no. of params	259	216
GoF^d on F^2	1.001	1.022
max, min diff map, e Å^{-3}	5.08, −3.36	1.10, −0.60

[a] $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2$, where $P = (F_o{}^2 + 2F_c{}^2)/3$. [b] Conventional $R = \sum||F_o| - |F_c|/\sum|F_o|$ for "observed" reflections having $F_o{}^2 > 2\sigma(F_o{}^2)$. [c] $R_w = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$ for all data. [d] GoF $= [\sum w(F_o{}^2 - F_c{}^2)^2/(\text{no. unique reflns} - \text{no. of params})]^{1/2}$.

°C) ether (20 mL) was added a solution of *o*-LiC$_6$H$_4$OMe (0.24 g, 2.07 mmol) in THF (10 mL). This mixture was allowed to attain room temperature and was stirred for 2 h. MeLi (1.15 mL, 2.07 mmol) was then added via syringe. The reaction mixture was stirred at room temperature for 1 h, and then solids were removed by filtration. Removal of solvent in vacuo gave essentially pure **5** as a colorless oil. Yield: 0.56 g, 87%. ^{1}H NMR (C$_6$D$_6$, 298 K): δ 0.02 (s, 9H, SiMe$_3$), 0.22 (s, 9H, SiMe$_3$), 0.94 (d, $J_{PH} = 3.2$ Hz, 1H, CHP) 1.41 (d, $J_{PH} = 6.1$ Hz, 3H, PMe), 3.24 (s, 3H, OMe), 6.36−7.31 (m, 4H, ArH). ^{31}P NMR (C$_6$D$_6$, 298 K): δ −31.8. EIMS (70 eV): *m*/*z* (%) 312 (15) [M$^+$], 297 (20) [M$^+$ − Me], 281 (65) [M$^+$ − 2Me], 267 (10) [M$^+$ − Me − MeO], 191 (10) [(Me$_3$Si)$_2$CHP], 179 (45) [Me$_2$SiCHPC$_6$H$_4$], 135 (35) [CHPC$_6$H$_4$O], 73 (100) [SiMe$_3$].

Crystal Structure Determination of 3 and 4. All measurements were made on a Bruker AXS SMART CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and narrow (0.3° in ω) frame exposures. Cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on F^2 values for all unique data. Table 3gives further details. All non-hydrogen atoms were refined anisotropically, and H atoms were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Two-fold disorder was resolved for the THF ligands in **3** and refined with the aid of restraints on geometry and displacement parameters; data for this compound were generally weak, especially at higher angles. The structure of **4** is probably racemically twinned with essentially equal contributions of the two components. Programs were Bruker AXS SMART (control) and SAINT (integration),[31] and SHELXTL for structure solution, refinement, and molecular graphics.[32]

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Supporting Information Available: For **3** and **4** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

OM000057U

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