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(Me₅C₅)₂Yb₂(μ-PHPPh)₂(thf)₄, a Compound with a Bridging Phosphide Ligand and an Agostic Yb-H-P Interaction

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Materials & Chemical Sciences Division

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**$(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$, a Compound
with a Bridging Phosphide Ligand and
an *Agostic* Yb-H-P Interaction**

D.J. Berg, R.A. Andersen, and A. Zalkin

November 1989



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$(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$, a Compound with a Bridging Phosphide
Ligand and an Agostic Yb...H-P Interaction

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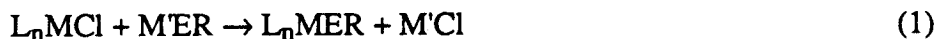
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Abstract

Phenylphosphine reacts with $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ to give $\text{Me}_5\text{C}_5\text{H}$ and $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PhPh})_2(\text{thf})_4$. Crystals of the ytterbium compound are monoclinic, $P2_1/c$ with $a = 8.981(2) \text{ \AA}$, $b = 14.630(2) \text{ \AA}$, $c = 19.081(3) \text{ \AA}$, $\beta = 98.53(2)^\circ$. The structure was refined by full-matrix least squares to a conventional R-factor of 0.048, 3124 data, $F^2 > 2\sigma(F)^2$. The crystal structure shows that the two $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{thf})_2$ centers are asymmetrically bridged by phenylphosphide groups with Yb-P distances of $2.959(2) \text{ \AA}$ and $3.068(2) \text{ \AA}$. The asymmetry in the bridge is the result of a short, $1.86(6) \text{ \AA}$, Yb...H interaction (the hydrogen atom was located in the x-ray study and refined isotropically) which is correlated with the longer Yb-P distance. This type of Yb...H-P interaction has not been observed previously in bridging phosphide compounds. Though PhPH_2 reacts with $(\text{Me}_5\text{C}_5)_2\text{Yb}$ by way of a proton transfer reaction, cyclohexylphosphine, p-toluidine, or ammonia give 1:1 coordination compounds. These results are explained by the pKa's of the protic acids relative to the pKa of $\text{Me}_5\text{C}_5\text{H}$.

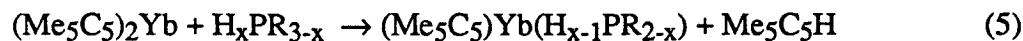
Organometallic alkoxides and amides of the 4f-transition metals (lanthanides) constitute an extensive class of compounds.¹ In contrast, the organometallic derivatives of the second-row non-metals, the thiolates or phosphides, are comparatively rare. The synthetic routes to these second-row compounds are similar to those used to prepare the alcohols and amides, *viz.*, metathetical exchange^{2a-c} (eq. 1), electron transfer^{2d} (eq. 2) and proton transfer^{2c,e-i} (eq. 3) reactions. Each of these



synthetic reactions has difficulties that are often unique for a given lanthanide metal and its associated ligands, L_n in eq. 1-3. The metathetical exchange reaction often incorporates $M'Cl$ into the product, the electron-transfer reactions require that the bivalent compounds are readily available; limiting this reaction to Eu, Sm, and Yb, and the proton-exchange reaction is limited to those reactions in which the pK_a of HL_n is greater than HER. Recently we have shown that pK_a 's determined in water are a useful qualitative guide for the reaction shown in eq. 4, where HER is an alcohol or thiol.²ⁱ It is difficult to extend



this concept to primary and secondary phosphines since only a few pK_a 's have been measured and the values range from 22-36 in tetrahydrofuran,^{3a} or from 23-27 in dimethylsulfoxide.^{3b} Since the pK_a (H_2O) of CpH is 16^{4a} or 18 in $dmso$,^{4b} the reaction shown in eq. 4 where HER is H_xPR_{3-x} and R' is H should be endothermic. However, since the pK_a of Me_5C_5H in $dmso$ is 26,^{4b} those phosphines whose pK_a 's are less than 26 should undergo proton-transfer reactions, shown in eq. 5, exothermically.



In this paper we show that the use of pK_a values determined in $dmso$ are a useful, qualitative guide for preparation of primary phosphides and that the crystal structure of

$(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\text{thf})_4(\mu\text{-PPh})_2$ contains a bridging phosphide with a unique Yb...H-P-Yb interaction.

Addition of phenylphosphine [$\text{pK}_a(\text{dmsO}) = 22$,^{3b} $\text{pK}_a(\text{thf}) = 25$ ^{3a}] to $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt})_2$ in toluene slowly gave a red precipitate that was insoluble in hydrocarbons and diethyl ether though soluble in tetrahydrofuran; cooling a thf solution gave orange-red $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$, Figure I. The red precipitate is also soluble in pyridine or acetonitrile, but the only compounds isolated from these solutions are $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{py})_2$ ⁵ or $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{NCMe})_2$. The infrared spectrum of the phosphide complex shows an absorption at 2259 cm^{-1} due to the P-H stretching frequency, 34 cm^{-1} lower than that found in free PhPH_2 (liquid) of 2293 cm^{-1} .⁶ The compound is diamagnetic as the Me_5C_5 resonance in the ^1H NMR spectrum at $\delta 1.97$ is typical of $\text{Me}_5\text{C}_5\text{Yb}$ resonances in diamagnetic, bivalent Yb(II) compounds.^{5,7} The phenyl ring resonances have normal chemical shifts and the H-H coupling constants are resolved though the P-H resonance is not observed. The ^{31}P NMR spectrum consists of a doublet centered at $\delta\text{-}89.9$ with $^1J_{\text{HP}} = 185\text{ Hz}$ confirming the identity of the bridging phenyl phosphide group. The ^{31}P NMR resonance is deshielded by 33 ppm and $^1J_{\text{HP}}$ is decreased by 12 Hz on forming the ytterbium compound relative to free PhPH_2 in C_6D_6 which is a triplet centered at $\delta\text{-}122.7$ and $^1J_{\text{HP}} = 197\text{ Hz}$.⁸ It is difficult to interpret these spectroscopic differences in terms of structure since chemical shifts and coupling constants depend upon the identity and number of groups bonded to phosphorus, i.e., on the amount of s-character in the P-H bond.⁹ Further, few transition metal compounds with bridging PRH groups are known, though many with bridging PR_2 groups are known, and the chemical shifts in the latter group of compounds are largely dependent upon the degree of metal-metal bonding.^{9d} However, the data that are available show that on going from a neutral primary phosphine to a non-bridging phosphide, i.e., the coordination number at phosphorus does not change, the chemical shift changes slightly, ca., 2-5 ppm, the HP-coupling constant decreases slightly, ca. 20 Hz in the ^{31}P NMR spectrum, and the HP-stretching frequency in the infrared spectrum decreases by a few wave numbers. However, on going from a non-bridging to a bridging phosphide, i.e., the coordination number of phosphorus increases from three to four, the

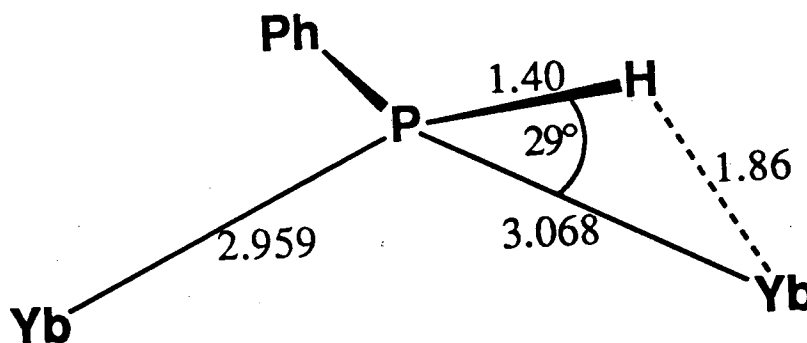
chemical shift in the ^{31}P NMR spectrum is strongly deshielded, shifts as large as 100 ppm have been observed, and $^1J_{\text{HP}}$ increases, often by a factor of two.^{8,10} In recently reported $(\text{Me}_5\text{C}_5)_2\text{Hf}(\text{X})(\text{PPh})_2$, where X is I or H, where the coordination number of phosphorus is three, the ^{31}P NMR chemical shift is deshielded by 150 ppm and J_{HP} increases by 30 Hz; clearly structural assignments using these chemical shift and coupling constant arguments are not very trustworthy.^{10j} Therefore, going from PhPH_2 to $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$, the PH-stretching frequency should decrease, the ^{31}P NMR chemical shift should be strongly deshielded and the PH-coupling constant should increase substantially. Though the PH-stretching frequency decreases and ^{31}P NMR chemical shift is deshielded, the decrease in $^1J_{\text{HP}}$ is unexpected. Either the hybridization at phosphorus has changed so that the amount of s-character in the H-P bond is similar to that found in three coordinate phosphorus compounds or the H-P bond is weakened so that there is less s-character in the bond. The observation that there is an agostic $\text{Yb}\cdots\text{H-P}$ interaction in $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$ in the solid state, Figure I, is compatible with the above inference. We do not wish to put too much meaning on a single coupling constant since the ^{31}P NMR spectrum is measured in the potentially coordinating solvent tetrahydrofuran, and cleavage of the dimer into monomeric units in solution would also lead to a decrease in $^1J_{\text{HP}}$, since the coordination number of phosphorus in the monomer is three. Further, the phosphide slowly (hours) decomposes in tetrahydrofuran at 25°C but faster at 65°C, $t_{1/2}$ is ca. 2h, to give phenylphosphine as the only identifiable product.

An ORTEP diagram of $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$ is shown in Figure I, bond distances and angles are shown in Table I, positional parameters are in Table II, and crystal data are in Table III. The Yb_2P_2 ring is planar with $\text{Yb-P-Yb}'$ and $\text{P-Yb-P}'$ angles of $113.46(6)^\circ$ and $66.54(6)^\circ$, respectively, and unequal Yb-P distances of $2.959(2) \text{ \AA}$ and $3.068(2) \text{ \AA}$ which average to $3.014 \pm 0.027 \text{ \AA}$. The longer Yb-P distance is bridged by the hydrogen atom which was located and refined isotropically in the X-ray study.

The geometry at ytterbium is similar to that found in $(\text{Me}_5\text{C}_5)_2\text{Eu}_2(\mu\text{-C}\equiv\text{CPh})_2(\text{thf})_4$ ¹¹ and is best described as a highly distorted trigonal bipyramid with the centroid of the Me_5C_5 group

occupying one coordination site with a Yb-centroid distance of 2.43 Å. The other two equatorial sites are occupied by O(2), Yb-O(2) = 2.442(7) Å, and P', Yb-P' = 3.068(2) Å, and the axial positions are occupied by O(1), Yb-O(1) = 2.496(6) Å, and P, Yb-P = 2.959(2) Å. The geometry at phosphorus is remarkably like that of free PhPH₂ in gas phase,¹² with one hydrogen atom being replaced by Yb' and the lone pair being replaced by Yb. The H-P-C(11) angle in the phosphide is 96(2)°, the P-H distance is 1.40(6) Å and the P-C(11) distance is 1.825(8) Å; in PhPH₂ the corresponding values are 94(5)°, 1.42 Å and 1.839(5) Å, respectively.¹² The small geometrical change on going from PhPH₂ to the bridging phosphide is consistent with the small difference in ¹J_{HP} in these two compounds. The P-H distance is close to that found in the X-ray crystallographic study of mesitylPHLi(thf)₃ of 1.42(6) Å^{10a} and mesitylPHLi(thf)₂ of 1.39(3) Å.^{10b}

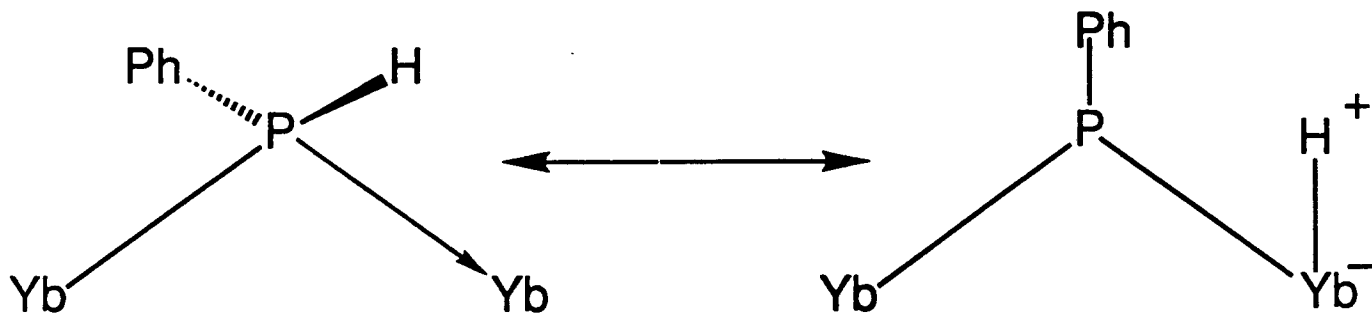
The most striking, indeed unique, feature of the phosphide molecule shown in Figure I is the presence of a non-linear Yb...H-P interaction shown symbolically below. The short Yb...H-P interaction



results in unequal Yb-P distances; the longer distance being associated with the bridging hydrogen atom. This "agostic"¹³ interaction has not been observed in bridging primary-phosphide compounds though few have been crystallographically characterized and in the X-ray structures, the hydrogen atom on phosphorus is seldom located and refined but is usually placed in an idealized position.¹⁰ The Yb...H distance of 1.86(6) Å is short, indeed, it is the shortest Yb...H

distance measured to date in a X-ray study. In $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-CH}_2=\text{CH}_2)\text{Pt}(\text{PPh}_3)_2$,^{14a} $(\text{Me}_5\text{C}_5)_2\text{Yb}((\mu\text{-Me})\text{Be}(\text{Me}_5\text{C}_5))$,^{14b} $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{Me}_3\text{Al})_2$,^{14c} and $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{dmpe})$ ^{14d} the Yb...H distance ranges from 2.58 Å to 3.15 Å. More surprisingly, the Yb...H distance is as short or shorter than expected for a direct Yb-H-Yb bridging distance based upon the Lu-H distances of 2.13(2) Å and 1.98(2) Å in $\text{Cp}_4\text{Lu}_2(\text{thf})_2(\mu\text{-H})_2$ ^{15a} and upon the Y-H distances which range from 2.17(8) Å to 2.27(6) Å in $\text{Cp}_4\text{Y}_2(\text{thf})_2(\mu\text{-H})_2$ ^{15b} and $(\text{Me}_2\text{C}_5\text{H}_3)_4\text{Y}_2(\text{thf})(\mu\text{-H})_2$,^{15c} since the radius of Yb(II) in seven coordination is approximately equal to that of Lu(III) and Y(III) in nine coordination.¹⁶ The short Yb...H contact distance does not lengthen the P-H distance, relative to that found in PhPH_2 or in the mesitylphosphides mentioned above, though the H-P-Yb angle is necessarily small.

The closest analogues to the bridging phosphide interaction which is supplemented by a bridging (agostic) Yb...H-P interaction are found in bridging alkyls such as $(\text{Me}_3\text{SiCH}_2)_2\text{Cr}_2(\text{PMe}_3)_2(\mu\text{-CH}_2\text{SiMe}_3)_2$,¹⁷ in which the bridging Me_3SiCH_2 group with the longer Cr-C distance is bridged by a short Cr...H contact distance of 2.26(3) Å, and in related alkyls¹⁸ and silyls.¹⁹ The crystal structure of hexameric cyclohexyllithium also shows α - and β -agostic interactions for the cyclohexyl groups on the trigonal faces.²⁰ A molecular orbital treatment of the bridging alkyl interaction which is supplemented by a M...H-C bridging (agostic) interaction has been given,²¹ a derivative of which could doubtless be given to rationalize the Yb...H-P interaction described in this paper. A simple valence bond description, shown below, however,



provides a convenient structural model that is consistent with the information that is known currently.

Using an equilibrium acidity scale as a guide, neither cyclohexylphosphine [$\text{pK}_a(\text{thf}) = 32$]^{3a}, aniline [$\text{pK}_a(\text{dmsO}) = 31$]^{4c} nor ammonia [$\text{pK}_a(\text{dmsO}) = 41$]^{4c} should react with $(\text{Me}_5\text{C}_5)_2\text{Yb}$ by proton transfer reactions and they do not. In each case, 1:1 coordination compounds of the type $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{L})$, where L = cyclohexylphosphine, p-toluidine (used for convenience, rather than aniline), or ammonia, were isolated. In solution, all of the coordination complexes are undergoing chemical exchange and only averaged chemical shifts, which are close to those of the individual components, are observed. In contrast, neither diphenylphosphine [$\text{pK}_a(\text{dmsO}) = 23$]^{3b} nor fluorene [$\text{pK}_a(\text{dmsO}) = 23$]^{4c} react with $(\text{Me}_5\text{C}_5)_2\text{Yb}$ though they should do so on the basis of their equilibrium acidities. Further, phenylacetylene [$\text{pK}_a(\text{dmsO}) = 29$]^{4c} should not react by proton transfer though it does so.¹¹ It seems reasonable to postulate that the thermodynamic extent of a reaction, as measured by the equilibrium acidity, is a reasonable guide for the synthetic chemist, though it does not address the kinetic feasibility of a given reaction nor the effect of coordination upon acidity. In absence of quantitative knowledge about the latter two effects, we offer the following rule as a guide: equilibrium acidities are most reliable when the acids have a lone-pair or pairs of electrons that are not sterically prevented from coordinating to the metal center. It follows that, if an entering protic acid has a pK_a less than that of the leaving protic acid, then the rate of proton transfer will be rapid leading to a productive event.

Experimental Section. All experimental work was done as previously described.^{2d}

$(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$. To $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (1.02 g, 1.97 mmol) dissolved in 50 mL of toluene was added phenylphosphine (0.40 mL) by syringe with rapid stirring. The solution slowly changed color (3-4 h) to brown and deposited a dark red precipitate. After stirring overnight, the suspension was allowed to settle and the colorless supernatant was filtered and discarded. The red residue was washed with 100 mL of hexane and dried under reduced pressure. Tetrahydrofuran (100 mL) was added to the red solid to produce a deep red solution which was filtered and the filtrate was concentrated to 50 mL. Slow cooling to -78°C produced red-orange crystals, 0.35 g (32 % yield). M.p. 193-195°C dec. IR: 3060 (w), 2718 (w), 2259 (m), 1575

(m), 1180 (w), 1095 (w), 1069 (w), 1033 (s), 919 (w), 880 (s), 848 (sh w), 732 (s), 697 (m-s), 480 (w-m), 308 (w), 256 (br s) cm^{-1} . $^1\text{H NMR}$ ($\text{C}_4\text{D}_8\text{O}$, 21°C): δ 7.21 ppm (2H, dd), 6.85 (2H, t), 6.62 (1H, t), 1.97 (30H, s). The PH proton was not observed and it may be obscured by the α -H of the protonic impurities on thf-dg. $^{31}\text{P NMR}$: δ -89.9 relative to external H_3PO_4 (d, $^1J_{\text{P-H}} = 185$ Hz). A satisfactory combustion analysis could not be obtained for this compound, presumably due to loss of coordinated thf. $^1\text{H NMR}$ of PhPH_2 (C_6D_6 , 20°C): δ 7.40 (2H, m), 7.14 (3H, m), 3.98 (2H, d, $^1J_{\text{P-H}} = 197$ Hz). $^{31}\text{P NMR}$: δ -122.7 relative to external 85% H_3PO_4 (t, $^1J_{\text{P-H}} = 197$ Hz). Neat PhPH_2 has $\nu_{\text{PH}} = 2293$ cm^{-1} .

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{H}_2\text{N-p-tolyl})$. To $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (1.18 g, 2.28 mmol) and p-toluidine (0.25 g, 2.3 mmol) in a Schlenk flask was added 100 mL of toluene. The dark brown solution was stirred for 1 h, filtered, and the filtrate was concentrated to 20 mL. Cooling at -10°C for several days produced large brown crystals, 0.65 g (52% yield). M.p. 115 - 118°C . IR: 3339 (s), 3273 (s), 2726 (w-m), 1603 (m), 1573 (m-s), 1515 (vs), 1234 (m), 1151 (vw), 1103 (vw), 1089 (vw), 1020 (w), 966 (vs), 957 (vs), 930 (m), 836 (w), 821 (sh w), 812 (s), 799 (sh w), 732 (m-s), 705 (w), 509 (vs), 447 (m), 407 (m), 373 (vw), 353 (vw), 313 (vw), 302 (w), 276 (br vs) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 32°C): diamagnetic δ 6.95 (2H, m), 6.57 (2H, m), 3.70 (2H, br s), 2.18 (3H, s), 1.90 (30H, s). Anal. Calcd for $\text{C}_{27}\text{H}_{39}\text{NYb}$: C, 58.9; H, 7.14; N, 2.54%. Found: C, 58.7; H, 7.17; N, 2.59%.

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{NH}_3)$. The ammonia complex $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$,²² (2.72 g, 5.70 mmol) was heated at 250°C under vacuum (10^{-1} Torr) and brick red crystals were collected on a water-cooled probe in 50% yield (1.3 g). M.p. 219 - 221°C . IR: 3344 (m), 3263 (m), 2724 (m), 1657 (vw), 1578 (w), 1224 (sh vw), 1186 (br vs), 1093 (vw), 1019 (w), 801 (vw), 722 (vw), 698 (vw), 432 (br s), 309 (w), 301 (vw), 278 (vs), 268 (sh w) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 21°C): δ 1.91 (s), the ammonia protons were not observed. M.S. (E.I.) $m/e = 461$ amu (M^+), 444 ($\text{M}^+ - \text{NH}_3$). Anal. Calcd for $\text{C}_{20}\text{H}_{33}\text{NYb}$: C, 52.2; H, 7.22; N, 3.04 %. Found: C, 51.4; H, 7.30; N, 2.94%. The

ammonia complex can be made less conveniently by adding one molar equivalent of ammonia to $(\text{Me}_5\text{C}_5)_2\text{Yb}$. The best synthesis is mixing equimolar amounts of $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\text{NH}_3)_2$ and $(\text{Me}_5\text{C}_5)_2\text{Yb}$ in hexane followed by crystallization from that solvent.

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{H}_2\text{Pcyclohexyl})$. Base-free $\text{Yb}(\text{C}_5\text{Me}_5)_2$ (0.55 g, 1.2 mmol) was dissolved in 100 mL of hexane and cyclohexylphosphine (0.55 mL) was added. The dark green solution was stirred 4 h and the solvent was removed under reduced pressure. The tacky yellow-green residue slowly solidified under vacuum (3 h). The solid was redissolved in 40 mL of pentane and the mint green solution was filtered. Concentration of the filtrate to 10 mL, followed by prolonged cooling at -78°C , produced lime green flakes in 31% yield (0.21 g). M.p. $86-88^\circ\text{C}$. IR: 2720 (m), 2304 (m), 2289 (m), 1296 (vw), 1261 (m), 1080 (br m-s), 1018 (br m-s), 828 (sh w), 808 (br s), 724 (m), 674 (m), 385 (br w), 268 (s) cm^{-1} . The ^1H NMR spectrum in C_6D_6 was identical to that of uncomplexed $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and cyclohexylphosphine. Satisfactory elemental analysis could not be obtained for this complex presumably due to the ready loss of phosphine. The infrared of free phosphine contains a P-H stretching frequency at 2280 cm^{-1} . Heating the complex to 80°C under dynamic vacuum gives $(\text{Me}_5\text{C}_5)_2\text{Yb}$.

X-Ray Crystallography of $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$. The air-sensitive red crystals were sealed inside quartz capillaries to protect them from the atmosphere and the crystals were examined with a modified Picker FACS-I automated diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda_{\text{K}\alpha} = 0.7103\text{ \AA}$). Cell dimensions and other crystal data are given in Table III. Intensity data were collected by using a θ - 2θ scan technique. Three standard reflections were measured at every 250th scan, and the intensities were adjusted for the variations in the standards. Lorentz-polarization and absorption corrections (analytical integration method)²³ were made. The structure was refined by a full-matrix least-squares procedure in which the function $\sum w(|kF_o| - |F_c|)^2 / \sum w(|kF_o|^2)$ was minimized. Atomic scattering factors and their anomalous terms were taken from ref. 24. Three dimensional Patterson maps were used to find the Yb atom, and

subsequent least squares refinements and electron density maps were used to find the remaining non-hydrogen atoms. The hydrogen atom positional parameters were estimated and were included in the least-squares, however, only the parameters of the H atom on the phosphorus atom were allowed to vary; the remaining hydrogen atom parameters were fixed and the hydrogen atoms were assigned isotropic thermal parameters. Local unpublished crystallographic computer programs were used.

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Supplementary Material Available: Tables listing thermal parameters, calculated hydrogen positions, additional distances and angles, least-squares planes (5 pages) and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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Figure Caption

Figure 1. An ORTEP drawing of $(\text{Me}_5\text{C}_5)_2\text{Yb}_2(\mu\text{-PPh})_2(\text{thf})_4$, 50% ellipsoids. The hydrogen atom on phosphorus is refined isotropically and all other non-hydrogen atoms were refined anisotropically. The molecule contains a crystallographic center of inversion located in the center of the Yb_2P_2 rhombus so that the labelled atoms are related to the unlabelled or primed atoms by the center of inversion.

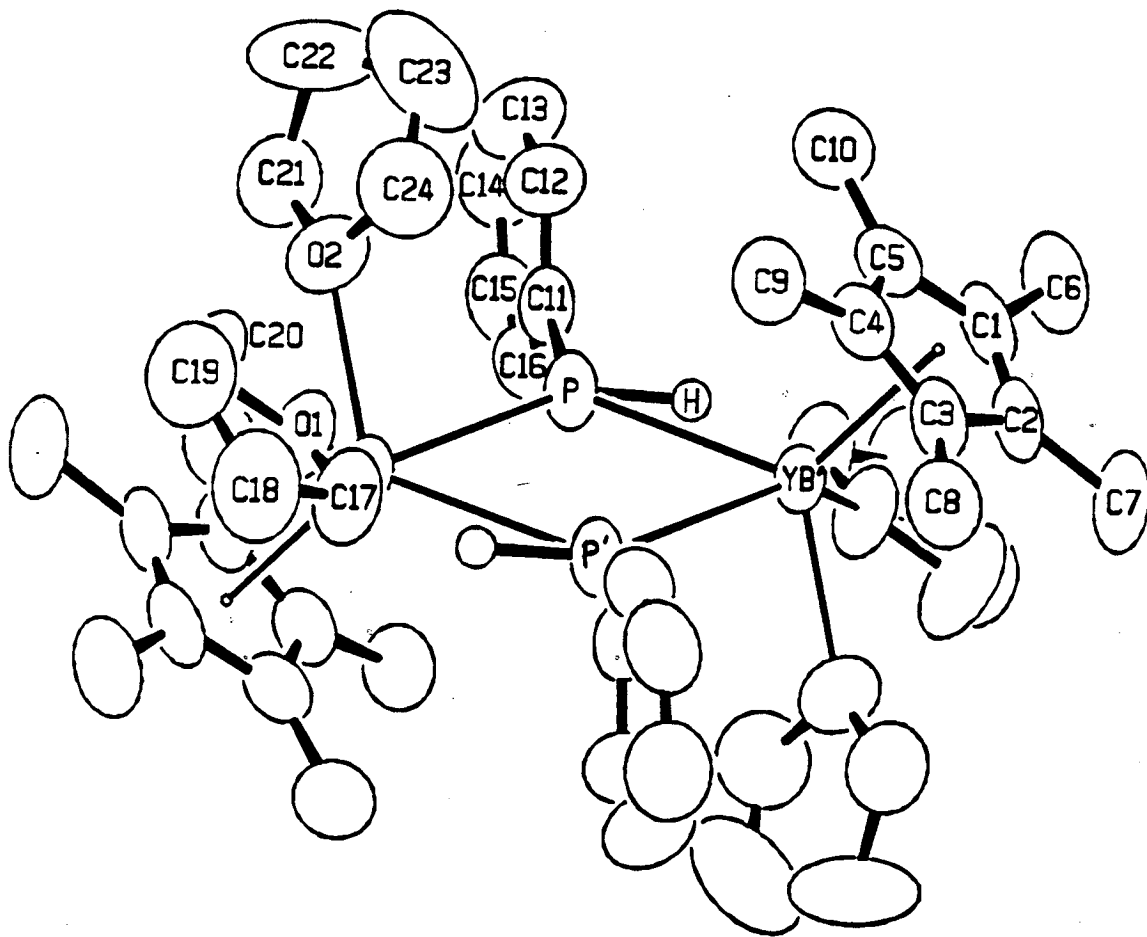


Figure I.

Table I. Selected Distances (Å) and Angles (°)

H-Yb	1.86(6)	C4-Yb	2.683(8)
Ct -Yb	2.430	C5-Yb	2.722(9)
O1-Yb	2.496(6)	P-Yb	2.959(2)
O2-Yb	2.442(7)	P-Yb'	3.068(2)
C1-Yb	2.732(8)	H-P	1.40(6)
C2-Yb	2.726(8)	C11-P	1.825(8)
C3-Yb	2.693(8)		
P-Yb-Ct	112.5	Yb-P-H	142(2)
P-Yb-Ct ^a	121.9	Yb-P-H'	29(2)
O1-Yb-Ct	109.9	C11-P-H	96(2)
O2-Yb-Ct	118.1	Yb-O1-C17	125.0(6)
P-Yb-P'	66.54(6)	Yb-O1-C20	126.9(7)
P-Yb-O1	137.6(2)	C17-O1-C20	107.7(9)
P-Yb-O2	83.1(2)	Yb-O2-C21	128.9(7)
P-Yb-O1'	91.2(2)	Yb-O2-C24	113.9(8)
P-Yb-O2'	119.2(2)	C21-O2-C24	111(1)
Yb-P-Yb'	113.46(6)	P-C11-C12	122.3(7)
Yb-P-C11	121.6(3)	P-C11-C16	121.7(7)
Yb-P-C11'	124.9(3)	P-H-Yb'	129(4)

^aPrime indicates a position at -x, -y, -z.

Ct is centroid of Me₅C₅ group

Table II. Positional Parameters with Estimated Standard Deviations

Atom	x	y	z
Yb	0.02010(4)	0.16932(2)	0.02359(2)
P	0.08991(28)	-0.02483(14)	0.07973(11)
O1	-0.2075(8)	0.2647(4)	-0.0157(4)
O2	-0.0934(8)	0.1846(5)	0.1317(4)
C1	0.1741(11)	0.3157(6)	-0.0184(6)
C2	0.2127(10)	0.3125(5)	0.0552(6)
C3	0.2969(9)	0.2326(6)	0.0739(5)
C4	0.3118(9)	0.1870(6)	0.0099(5)
C5	0.2372(11)	0.2361(7)	-0.0480(5)
C6	0.0967(15)	0.3935(7)	-0.0630(7)
C7	0.1797(13)	0.3860(7)	0.1057(7)
C8	0.3642(12)	0.2054(8)	0.1471(6)
C9	0.4018(12)	0.1001(8)	0.0033(6)
C10	0.2293(16)	0.2147(10)	-0.1256(6)
C11	0.1989(11)	-0.0452(6)	0.1669(4)
C12	0.1319(12)	-0.0529(8)	0.2278(5)
C13	0.2187(19)	-0.0628(10)	0.2938(6)
C14	0.3702(19)	-0.0685(10)	0.3008(6)
C15	0.4404(13)	-0.0644(8)	0.2417(6)
C16	0.3549(11)	-0.0528(7)	0.1764(5)
C17	-0.2967(15)	0.2596(8)	-0.0828(6)
C18	-0.3799(17)	0.3467(10)	-0.0931(9)
C19	-0.3929(16)	0.3784(10)	-0.0211(9)
C20	-0.2590(20)	0.3395(9)	0.0206(8)

C21	-0.0226(15)	0.1933(9)	0.2018(7)
C22	-0.1433(25)	0.1683(16)	0.2448(9)
C23	-0.2427(17)	0.1065(13)	0.1992(14)
C24	-0.2330(15)	0.1404(13)	0.1286(10)
H	0.073(6)	-0.117(4)	0.0604(29)

Table III. Crystallographic Summary and Data Processing

a, Å ^a	8.981(2)
b, Å	14.630(2)
c, Å	19.081(3)
β, °	98.53(2)
cryst syst	monoclinic
space group	P2 ₁ /c
volume, Å ³	2479.5
d(calcd), g/cm ³	1.483
Z	4
temp (°C)	22.0
empirical formula	C ₂₄ H ₃₇ O ₂ PYb
f(000)	1096
fw	553.51
reflection rules	h0l: l = 2n, Ok0: k = 2n
crystal size (mm)	0.18 x 0.21 x 0.55
abs coeff, cm ⁻¹	38.38
abs corr range	1.70-2.46
cryst decay corr range	0.98-1.02
2θ limits, °	4.3-50.1
sinθ/λ, min,max	0.053, 0.596
hkl limits	h -10,10; k 0,17; l -22,22
scan width, °2θ	1.25 + 0.693xtanθ
variation of standards (%)	1.0,1.4,1.3
no. scan data	8814
no. unique reflections	4414
Rint ^b	0.032

no. non-zero weighted data	3124 ($F^2 > 2\sigma$)
p^c	0.100
extinction k^d	1.1×10^{-8}
max % extinction corr	1.7 %
no. parameters	257
R (non-zero wtd dat) e	0.048
R_w^f	0.058
R (all data)	0.071
Goodness of fit g	1.0
max shift/esd in least square	0.002
max/min in diff map ($e/\text{\AA}^3$)	1.47, -2.45

- a Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved $\text{MoK}\alpha$ components of 35 reflections ($20 < 2\theta < 30$).
- b R_{int} = agreement factor between equivalent or multiply measured reflections = $\frac{\sum [I(\text{hkl}) - \langle I(\text{hkl}) \rangle]}{\sum \langle I(\text{hkl}) \rangle}$
- c In the least squares, the assigned weights to a datum is $= 4F^2 / [\sigma^2(F^2) + (pF^2)^2]$, where F is the observed structure factor and p is assigned a value that adjusts the weighted residuals of the strong reflections to be comparable to the weak ones.
- d Simple extinction correction has the form $(F_{\text{obs}})_{\text{corr}} = (1 + kI)F_{\text{obs}}$, where I is the uncorrected intensity and F_{obs} is the observed scattering amplitude.
- e $R = \frac{\sum [|F_{\text{obs}}| - |F_{\text{calc}}|]}{\sum [|F_{\text{obs}}|]}$
- f $R_w = \sqrt{\frac{\sum [w(|F_{\text{obs}}| - |F_{\text{calc}}|)]^2}{\sum (wF_{\text{obs}}^2)}}$
- g σ_1 = error in observation of unit weight = $\sqrt{\frac{\sum (w(|F_{\text{obs}}| - |F_{\text{calc}}|)]^2}{(\text{no} - \text{nv})}}$, where no is the number of observations and nv is the number of variables.

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