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Contribution from the Materials and Molecular Research Division of Lawrence Berkeley Laboratory
and Department of Chemistry, University of California, Berkeley, California 94720

Tertiary Phosphine Complexes of the f-Block Metals. Preparation of Pentamethylcyclopentadienyl-Tertiary Phosphine Complexes of Ytterbium(II), Ytterbium(III) and Europium(II). Crystal Structure of $Yb(Me_5C_5)_2Cl(Me_2PCH_2PMe_2)$

T. DON TILLEY, RICHARD A. ANDERSEN, and ALLAN ZALKIN*

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The diphosphine, $Me_2PCH_2CH_2PMe_2$, reacts with $M(Me_5C_5)_2(OEt_2)$ to give insoluble $M(Me_5C_5)_2(Me_2PCH_2CH_2PMe_2)$, where M is Eu or Yb. In contrast, $Me_2PCH_2PMe_2$ gives the hydrocarbon-soluble complexes $M(Me_5C_5)_2(Me_2PCH_2PMe_2)$, where M is Eu or Yb. The ytterbium complex reacts with $YbCl_3$ in toluene to give $Yb(Me_5C_5)_2Cl(Me_2PCH_2PMe_2)$, and the crystal structure shows that the phosphine is acting as a monodentate ligand. $Yb(Me_5C_5)_2Cl(Me_2PCH_2PMe_2)$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 16.358$ (6) Å, $b = 8.595$ (4) Å, $c = 20.712$ (7) Å, $\beta = 104.75$ (4)°, $V = 2816$ Å^3, and $d(\text{calcd}) = 1.45$ g cm^{-3} for $Z = 4$ and mol wt = 615.15. Diffraction data were collected with a CAD-4 automated diffractometer, and the structure was refined to $R = 0.054$ for 3309 reflections with $4° < 2\theta < 45°$ (Mo Kα radiation). The Yb is coordinated to the two Me_5C_5 groups, to the chlorine atom, and to one phosphorus atom of the bis(dimethylphosphino)methane ligand. The Yb-P and Yb-Cl distances are 2.94 and 2.53 Å, respectively. The centroids of the C_5Me_5 ligands and the Cl and P atoms are in an approximate tetrahedral arrangement about the Yb atom.

Introduction

The coordination chemistry of lanthanide metals with nitrogen or oxygen ligands is extensive.[1] Since lanthanide ions form their most stable coordination complexes with nitrogen or oxygen rather than with phosphorus or sulfur ligands, these metals are classified as "class a"[2a] or "hard"[2b] acceptors.[3] Until recently the idea that f-block metals could form isolatable complexes with tertiary phosphines was viewed with considerable skepticism. The successful isolation of 1,2-bis(dimethylphosphino)ethane (dmpe) complexes of tetravalent thorium or uranium of the type $MX_4(dmpe)_2$[4a] and of the trivalent uranium species $U(Me_5C_5)_2Cl(dmpe)$[4b] raises an obvious question about the "class a" classification of the f-block metals.

In order to examine the coordinative affinity of f-block metals for phosphine ligands, we have begun a systematic study of their general coordination chemistry. In this paper we describe the phosphine complexes of the di- and trivalent bis(pentamethylcyclopentadienyl)ytterbium and the divalent europium fragments. In a related study we described the preparation and crystal structure of $Yb[N(SiMe_3)_2]_2(dmpe)$ and some related europium(II) derivatives.[5]

Synthetic Studies

Addition of 1 molar equiv of 1,2-bis(dimethylphosphino)ethane to the diethyl ether complex of bis(pentamethylcyclopentadienyl)ytterbium(II) in benzene results in instantaneous precipitation of a green material whose elemental analysis suggests the formulation $Yb(Me_5C_5)_2(dmpe)$. Support for this composition is obtained by aqueous hydrolysis of the complex suspended in benzene-d_6. Examination of the benzene solution by ^1H NMR spectroscopy shows resonances due to Me_5C_5H and $Me_2PCH_2CH_2PMe_2$ in an area ratio of 2:1. In addition, the $^{31}P\{^1H\}$ NMR spectrum of this solution shows the presence of $Me_2PCH_2CH_2PMe_2$ as the only phosphorus-containing species. The compound is insoluble in hot toluene though sparingly soluble in diethyl ether. The complex dissolves in tetrahydrofuran, giving $Yb(Me_5C_5)_2(thf)$.[6] The europium complex $Eu(Me_5C_5)_2(OEt_2)$ behaves similarly, affording red, insoluble $Eu(Me_5C_5)_2(dmpe)$.

The infrared spectra and melting points (see Experimental Section for details) of these two phosphine complexes are identical, which suggests that the complexes have a similar structure. The insolubility in noncoordinating solvents indicates that the dmpe complexes are some type of coordination polymer. One such polymer is shown (I). The phosphine ligand is acting as a bridging rather than as a chelating ligand, yielding an eight-coordinate complex (defining the coordination number of the pentamethylcyclopentadienyl ligand as 3). Eight-coordination is not unusual since some $M(Me_5C_5)_2L_2$ complexes, where M = Yb[7a] or Sm[7b] and L is a monodentate ligand, have been described. If it is accepted that I is a reasonable structural formulation, then replacing the ethylene bridge in $Me_2PCH_2CH_2PMe_2$ by a methylene bridge should prevent polymerization, due to increased steric hindrance between the Me_5C_5 groups on adjacent metal atoms. Thus, $Me_2PCH_2PMe_2$ should yield hydrocarbon-soluble, monomeric complexes.

Addition of a slight excess of bis(dimethylphosphino)methane (dmpm) to a toluene solution of $Yb(Me_5C_5)_2(OEt_2)$ yields a green solution from which green, diamagnetic $Yb(Me_5C_5)_2(dmpm)$ may be isolated by crystallization from that solvent. The NMR spectral data (see Experimental Section for details) support this formulation. In particular, the $^{31}P\{^1H\}$ NMR spectrum of the complex contains a single resonance at δ -39.6, significantly deshielded from that of the free phosphine at δ -55.7. The red europium complex, $Eu(Me_5C_5)_2(dmpm)$, was prepared similarly. As europium(II) is paramagnetic (an f^7 ion), no NMR spectral data are ob-

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[1] (a) Sigha, S. P. *Struct. Bonding (Berlin)* **1976**, *25*, 69. (b) Moeller, T. In "Comprehensive Inorganic Chemistry"; Bailar, J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: London, 1973; Vol. 4, p 1. (c) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 981.

[2] (a) Ahrland, S.; Chatt, J.; Davies, N. R. *Q. Rev., Chem. Soc.* **1958**, *12*, 265. (b) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

[3] Classification of acceptors as "class a" or "hard" (those metals whose coordinative affinity for Lewis bases is in the sequence N ≫ P > As) or as "class b" or "soft" (those metals whose coordinate affinity for Lewis bases is in the sequence N ≪ P > As) is generally accepted. However, the reasons for the origin of the phenomenon are not without controversy. (a) Ahrland, S. *Struct. Bonding (Berlin)* **1966**, *1*, 207; **1973**, *15*, 167. (b) Jørgensen, C. K. *Ibid.* **1966**, *1*, 234. (c) Williams, R. J. P.; Hale, J. D. *Ibid.* **1966**, 249. (d) For a general discussion see: Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978; p 276.

[4] (a) Edwards, P. G.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1981**, *103*, 7792. (b) Duttera, M. R.; Fagan, P. J.; Marks, T. J.; Day, V. W. *Ibid.* **1982**, *104*, 365.

[5] Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725 and references therein.

[6] Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999.

[7] (a) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Zalkin, A. *Inorg. Chem.* **1982**, *21*, 2647. (b) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507.

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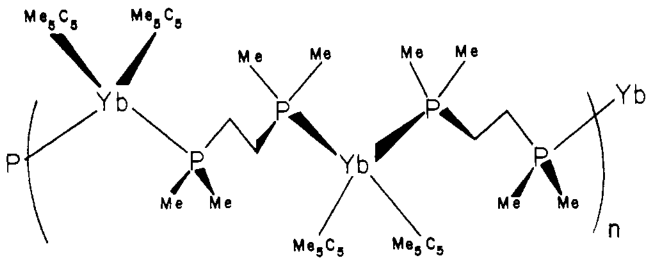

I

tainable. However, hydrolysis of a benzene solution of the complex and examination of this solution by ^{1}H NMR spectroscopy show that Me_5C_5H and $Me_2PCH_2PMe_2$ are present in a 2:1 ratio. Further, the $^{31}P\{^1H\}$ NMR spectrum of the hydrolysate shows only the presence of $Me_2PCH_2PMe_2$. Not surprisingly, the infrared spectra and melting points of the Yb(II) and Eu(II) complexes are identical. It is noteworthy that diethyl ether displaces the coordinated $Me_2PCH_2PMe_2$, giving $M(Me_5C_5)_2(OEt_2)$, M = Yb or Eu. This is to be contrasted with the observation that diethyl ether will not, though tetrahydrofuran will, displace dmpe from I.

It is significant that we have been unable to isolate complexes with the monodentate phosphines PMe_3 or P-*n*-Bu_3 nor with the bidentate phosphine $Ph_2PCH_2CH_2PPh_2$. In the monodentate phosphine case this is presumably due to the inability of two monodentate phosphines to fit comfortably around the sterically congested metal atom and the heat of formation of one metal–phosphorus bond is less than that of one metal–oxygen bond. In the bidentate phosphine case, the reason is less clear since $Ph_2PCH_2CH_2PPh_2$ is a poorer σ donor than its permethyl analogue and it is also sterically larger.

We[8a] and others[8b] have shown that the divalent species $Yb(Me_5C_5)_2(L)$, where L is tetrahydrofuran or 1,2-dimethoxyethane, may be oxidized by ytterbium trichloride or dichloromethane to the trivalent metallocene $Yb(Me_5C_5)_2Cl(L)$. The divalent phosphine complex behaves similarly. Mixing $Yb(Me_5C_5)_2(dmpm)$ and $YbCl_3$ in toluene gives the purple, hydrocarbon-soluble $Yb(Me_5C_5)_2Cl(dmpm)$. The complex is paramagnetic, $\mu_{eff} = 4.4\ \mu_B$ at 30 °C in benzene solution, and accordingly we have been unable to observe a $^{31}P\{^1H\}$ NMR spectrum of this complex.

The coordination geometry of this complex is of considerable interest as numerous possibilities exist. If both phosphorus atoms of the diphosphine are coordinated to the ytterbium atom, a nine-coordinate complex will result. Nine-coordination in bis(pentamethylcyclopentadienyl)lanthanide chemistry is unknown, though eight-coordination is common.[7,9] Two eight-coordinate formulations are possible. In one isomer, $Me_2PCH_2PMe_2$ is acting as a monodentate phosphine, and in the other isomer, an outer-sphere complex, $[Yb(Me_5C_5)_2(dmpm)]Cl$, may be written. For an answer to this question, an X-ray crystal structure determination was undertaken, and the results are described below.

Structural Studies

ORTEP diagrams of $Yb(Me_5C_5)_2Cl(Me_2PCH_2PMe_2)$ are shown in Figures 1 and 2. Positional and thermal parameters are given in Table I, and some selected bond lengths and angles are listed in Tables II and III. The key point to emerge from the X-ray study is that the diphosphine is acting as a monodentate ligand, giving an eight-coordinate complex. The coordination geometry may be described as pseudotetrahedral if the midpoints of the two Me_5C_5 centroids occupy two coordination sites. The other two coordination positions are occupied by a phosphorus atom and a chlorine atom. The angle defined by the intersection of the two planes that contain the centroid–Yb–centroid and P(1)–Yb–Cl atom is 88.1°. In a regular tetrahedron this angle is 90°. The centroid–Yb–centroid angle is 134.9°, and the (C(1,...,5) centroid)–Yb–P(1) and (C(1,...,5) centroid)–Yb–Cl angles are 108.0 and 106.3°, respectively. The (C(6,...,10) centroid)–Yb–P(1) and (C(6,...,10) centroid)–Yb–Cl angles are 105.7 and 108.6°, re-

Table I. Positional and Isotropic Thermal Parameters in $(C_5Me_5)_2YbCl(Me_2PCH_2CH_2PMe_2)$

atom	*x*	*y*	*z*	*B*, Å^2
Yb	0.23280 (2)	0.08305 (4)	0.17649 (2)	2.78[a]
Cl	0.31442 (19)	0.3313 (3)	0.17174 (15)	5.37[a]
P(1)	0.35006 (15)	−0.0247 (3)	0.09936 (13)	3.50[a]
P(2)	0.40632 (21)	−0.2765 (4)	0.00839 (17)	5.59[a]
C(1)	0.3512 (6)	0.0223 (12)	0.2862 (5)	3.64 (18)
C(2)	0.2933 (6)	0.1204 (12)	0.3052 (5)	4.08 (20)
C(3)	0.2179 (6)	0.0323 (13)	0.2983 (5)	4.28 (20)
C(4)	0.2296 (6)	−0.1139 (12)	0.2733 (5)	4.07 (20)
C(5)	0.3129 (6)	−0.1219 (11)	0.2653 (5)	3.37 (17)
C(6)	0.0904 (7)	−0.0369 (13)	0.0976 (5)	4.46 (21)
C(7)	0.0676 (7)	0.0651 (12)	0.1431 (5)	4.42 (21)
C(8)	0.0876 (6)	0.2202 (12)	0.1281 (5)	4.37 (20)
C(9)	0.1239 (6)	0.2121 (12)	0.0711 (5)	4.39 (21)
C(10)	0.1250 (7)	0.0528 (13)	0.0533 (5)	4.48 (21)
C(11)	0.4448 (8)	0.0695 (14)	0.2951 (6)	5.56 (26)
C(12)	0.3112 (9)	0.2808 (17)	0.3373 (7)	7.0 (3)
C(13)	0.1447 (10)	0.0904 (16)	0.3276 (8)	7.0 (3)
C(14)	0.1719 (9)	−0.2524 (17)	0.2687 (7)	8.49 (28)
C(15)	0.3529 (7)	−0.2691 (14)	0.2473 (6)	5.46 (24)
C(16)	0.0732 (9)	−0.2080 (17)	0.0918 (7)	7.1 (3)
C(17)	0.0094 (9)	0.0231 (19)	0.1852 (7)	7.1 (3)
C(18)	0.0735 (9)	0.3720 (18)	0.1620 (7)	7.2 (3)
C(19)	0.1451 (8)	0.3504 (17)	0.0356 (7)	6.40 (28)
C(20)	0.1389 (8)	−0.0038 (18)	−0.0117 (7)	6.62 (29)
C(21)	0.3477 (8)	0.1055 (15)	0.0273 (7)	5.72 (27)
C(22)	0.4642 (7)	−0.0109 (15)	0.1403 (6)	5.53 (25)
C(23)	0.3407 (6)	−0.2236 (12)	0.0653 (5)	4.03 (19)
C(24)	0.3318 (10)	−0.2246 (20)	−0.0724 (8)	8.6 (4)
C(25)	0.3886 (10)	−0.4896 (22)	0.0076 (8)	8.3 (4)

[a] Values derived from anisotropic thermal parameters.

Table II. Selected Interatomic Distances (Å)

Yb-Cl	2.532 (3)	Yb-C(5)	2.642 (9)
Yb-P(1)	2.941 (3)	Yb-C(6)	2.688 (11)
Yb-C(1)	2.635 (9)	Yb-C(7)	2.617 (11)
Yb-C(2)	2.617 (10)	Yb-C(8)	2.612 (10)
Yb-C(3)	2.633 (10)	Yb-C(9)	2.680 (10)
Yb-C(4)	2.634 (10)	Yb-C(10)	2.718 (11)
P(1)-C(21)	1.858 (13)	P(2)-C(23)	1.842 (10)
P(1)-C(22)	1.847 (12)	P(2)-C(24)	1.855 (17)
P(1)-C(23)	1.841 (10)	P(2)-C(25)	1.854 (19)

Table III. Selected Angles (deg)[a]

Cl-Yb-P(1)	79.7 (1)	Yb-P(1)-C(22)	116.9 (4)
Cl-Yb-Cp(1)[a]	106.3	Yb-P(1)-C(23)	119.9 (3)
Cl-Yb-Cp(2)[a]	108.6	C(21)-P(1)-C(22)	98.2 (6)
P(1)-Yb-Cp(1)[a]	108.0	P(1)-C(23)-P(2)	118.0 (5)
P(1)-Yb-Cp(2)[a]	105.7	C(23)-P(2)-C(24)	99.2 (6)
Cp(1)[a]-Yb-Cp(2)[a]	134.9	C(23)-P(2)-C(25)	97.7 (6)
Yb-P(1)-C(21)	111.3 (4)	C(24)-P(2)-C(25)	99.5 (7)

[a] Cp(1) is the centroid of the cyclopentadienyl ring represented by atoms C(1)–C(5). Cp(2) is the centroid of atoms C(6)–C(10).

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(8) (a) Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267. (b) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652.

(9) (a) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271. (b) No nine-coordinate complexes are known even with the sterically smaller cyclopentadienyl or substituted-cyclopentadienyl complexes of the type $Cp_2MCl(L)$: Raymond, K. N.; Eigenbrot, C. E. *Acc. Chem. Res.* **1980**, *13*, 273. (c) Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 1190, 1191. (d) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *Ibid.* **1981**, 292, 706. (e) Schumann, H.; Genthe, W.; Bruncks, N. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 119. (f) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115.

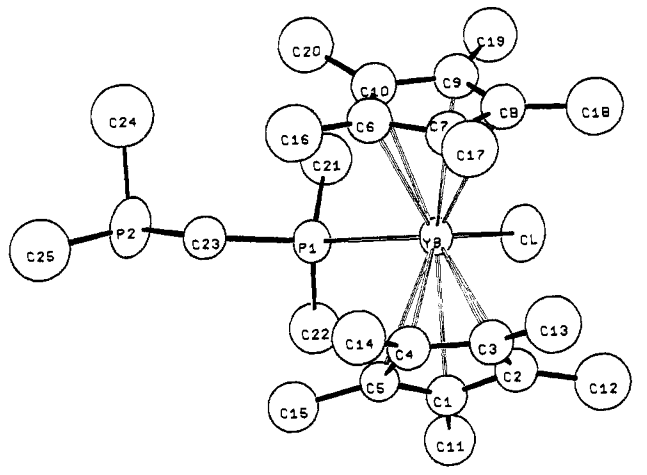

Figure 1. ORTEP drawing of the molecule showing the atom-numbering scheme.

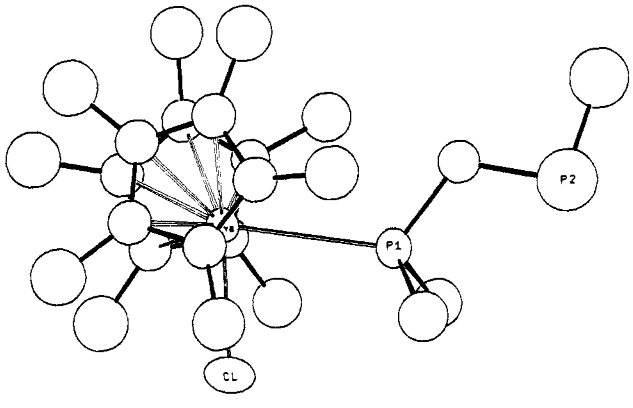

Figure 2. ORTEP view down a line through the centroids of the cyclopentadienyl rings. The second methyl carbon of the P(2) atom is eclipsed by the adjacent methyl group.

spectively. The P(1)–Yb–Cl angle is 79.69 (9)°.

The ytterbium–chloride bond length of 2.532 (3) Å is longer than that found in $Li(thf)_4[(Me_3Si)_2CH]_3YbCl$, 2.486 (6) Å,[10] as expected since the latter is a four-coordinate Yb(III) ion whereas the former is eight-coordinate. The latter distance is close to the value of 2.43 Å suggested for three-coordinate, monomeric $YbCl_3$ in the gas phase.[11] These are the only terminal Yb–Cl distances that are available, though several Yb–(μ-Cl) distances are known. These distances are 2.58 Å in $Yb_2[(Me_3Si)_2C_5H_3]_4(\mu\text{-}Cl)_2$,[9c] 2.756 ± 0.004 Å in $Yb(Me_5C_5)_2(\mu\text{-}Cl)_2AlCl_2$,[9a] and 2.637 ± 0.010 Å in $Yb_2(MeC_5H_4)_4(\mu\text{-}Cl)_2$.[12]

The ytterbium–phosphorus 1 distance of 2.941 (3) Å is unique, and no comparisons are possible. The other ytterbium–phosphorus distance, Yb···P(2), is greater than 3.5 Å and is obviously nonbonding.

It is instructive to compare the bond lengths and angles of monodentate $Me_2PCH_2PMe_2$ in $Yb(Me_5C_5)_2Cl(Me_2PCH_2PMe_2)$ with those of free $Me_2PCH_2PMe_2$ in the gas phase. The averaged P–C distance in the ytterbium complex is 1.849 ± 0.006 Å. This is identical with that found in the free phosphine, 1.849 (2) Å.[13] The averaged C–P–C and P–C–P angles in the complexed phosphine of 100.4 ± 2.2 and 118.0 (5)° also are identical with those found in the free phosphine, 100 and 118°, respectively. Further, the P···P distance in the coordination complex of 3.157 (4) Å is very close to that found [3.139 (9) Å] in the free phosphine. Thus, $Me_2PCH_2PMe_2$ is not perturbed very much upon coordination to $Yb(Me_5C_5)_2Cl$.

The averaged ytterbium–carbon bond length in the phosphine complex of 2.65 ± 0.03 Å is equal to that (2.63 ± 0.03 Å) found in $Yb(Me_5C_5)_2S_2NEt_2$.[14] This is expected since the coordination environment of ytterbium is similar in both complexes. The averaged ytterbium to carbon bond length is in the range found for related complexes (2.56–2.65 Å).[9]

Experimental Section

All reactions were performed under nitrogen. Analyses were carried out by the microanalytical laboratory of this department. Proton, carbon, and phosphorus NMR spectra were obtained on a JEOL-FX90Q instrument operating at 89.56, 22.50, and 36.25 MHz, respectively.

$Eu(Me_5C_5)_2(Me_2PCH_2CH_2PMe_2)$. 1,2-Bis(dimethylphosphino)ethane (0.17 mL, 0.0010 mol) was added to the diethyl ether complex of bis(pentamethylcyclopentadienyl)europium (0.51 g, 0.0010 mol) in toluene (20 mL). The red suspension was stirred for 1 h, and the solid was collected by filtration, washed with toluene (75 mL), and dried under reduced pressure. A small quantity (ca. 0.15 g) of the precipitate was crystallized from diethyl ether (ca. 20 mL, −10 °C); mp 288–292 C. Anal. Calcd for $C_{26}H_{46}EuP_2$: C, 54.5; H, 8.10; P, 10.8. Found: C, 53.7; H, 7.83; P, 10.5. IR (Nujol): 2721 w, 1421 m, 1302 m, 1284 w, 1150 w, 1091 w, 1015 w, 945 s, 926 m, 889 w, 829 w, 796 w, 720 s, 672 w, 624 m, 637 w, 589 w, 360 m, 349 m, and 253 s cm^{-1}. A portion of the complex was hydrolyzed (H_2O) in benzene-d_6, and the benzene solution was shown to contain Me_5C_5H and $Me_2PCH_2CH_2PMe_3$ in a 2:1 area ratio by ^1H NMR spectroscopy. The phosphine was identified by its $^{31}\{^1H\}$ NMR spectrum.

$Yb(Me_5C_5)_2(Me_2PCH_2CH_2PMe_2)$. 1,2-Bis(dimethylphosphino)ethane (0.17 mL, 0.0010 mol) was added to the diethyl ether complex of bis(pentamethylcyclopentadienyl)ytterbium (0.48 g, 0.00093 mol) in benzene (25 mL). After the mixture was stirred for 1 h, the green suspension was collected by filtration, washed with toluene (75 mL), and dried under reduced pressure. A small portion (ca. 0.2 g) was crystallized from diethyl ether (ca. 20 mL, −10 °C); mp 283–285 °C. Anal. Calcd for $C_{26}H_{46}P_2Yb$: C, 52.6; H, 7.81; P, 10.4. Found: C, 51.8; H, 7.69; P, 10.0. The infrared spectrum was identical with that of its europium analogue.

$Eu(Me_5C_5)_2(Me_2PCH_2PMe_2)$. Bis(dimethylphosphino)methane (0.30 mL, 0.0018 mol) was added to the diethyl ether complex of bis(pentamethylcyclopentadienyl)europium (0.87 g, 0.0018 mol) in toluene (40 mL), and the red solution was stirred for 30 min. The solution was cooled (−10 °C) and the red needles, mp 251–253 °C, were isolated in quantitative yield. Anal. Calcd for $C_{25}H_{44}EuP_2$: C, 53.8; H, 7.94; P, 11.1. Found: C, 53.4; H, 7.85; P, 10.8. IR (Nujol): 2720 w, 1420 m, 1380 m, 1285 m, 1161 w, 1109 m, 1055 w, 1015 m, 942 s, 925 m, 888 s, 830 m, 795 w, 749 s, 725 s, 705 w, 693 w, 647 w, 623 w, 589 w, 352 s, and 253 s cm^{-1}. A portion of the complex was hydrolyzed (H_2O) in benzene-d_6, and the benzene solution was shown to contain Me_5C_5H and $Me_2PCH_2PMe_2$ in an area ratio of 2:1. The $^{31}P\{^1H\}$ NMR spectrum of the solution contained only $Me_2PCH_2PMe_2$.

$Yb(Me_5C_5)_2(Me_2PCH_2PMe_2)$. Bis(dimethylphosphino)methane (0.16 mL, 0.0011 mol) was added to bis(pentamethylcyclopentadienyl)(diethyl ether)ytterbium (0.57 g, 0.0011 mol) in toluene (25 mL). After the mixture was stirred for 8 h, the green solution was filtered and the filtrate was cooled (−10 °C). The green needles, mp 250–253 °C, were isolated in quantitative yield. Anal. Calcd for $C_{25}H_{44}P_2Yb$: C, 51.8; H, 7.65; P, 10.7 Found: C, 50.6; H, 7.41; P, 10.2. The infrared spectrum was identical with that of its europium analogue. ^1H NMR (PhH-d_6, 26 °C): δ 2.17 s (30 H), Me_5C_5; 1.78 d, J = 4.1 Hz (2 H), CH_2P; 0.95 s (12 H), Me_2P. $^{13}C\{^1H\}$ NMR

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[10] Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 140.

[11] Krasnov, K. S.; Giricheva, N. I.; Girichev, G. V. *J. Struct. Chem. (Engl. Transl.)* **1976**, *17*, 575.

[12] Baker, E. C.; Brown, L. D.; Raymond, K. N. *Inorg. Chem.* **1975**, *14*, 1376.

[13] Rankin, D. W. H.; Robertson, H. E.; Karsch, H. H. *J. Mol. Struct.* **1981**, *77*, 121.

[14] Tilley, T. D.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1982**, *21*, 2644.

Table IV. Data Collection Details for $(C_5Me_5)_2YbCl(Me_2PCH_2PMe_2)$

Crystal Parameters (25 °C)[a]

space group $P2_1/c$	$V = 2816$ Å^3
$a = 16.358$ (4) Å	$Z = 4$
$b = 8.595$ (2) Å	mol wt = 615.1
$c = 20.712$ (6) Å	d(calcd) = 1.45 g cm^{-3}
$\beta = 104.75$ (3)°	μ(calcd, Mo Kα) = 35.3 cm^{-1}

Intensity Data Measurement

radiation: Mo Kα ($\lambda = 0.71073$ Å)
monochromator: highly oriented graphite, $2\theta_m = 12.2°$
scan type: θ(cryst)–2θ(counter)
reflcns measd: $+h,+k,\pm l$ from $3° < 2\theta < 45°$
scan speed: variable from 0.77 to 0.67° (θ) min
scan width: $\Delta\theta = (0.5 + 0.347 \tan\theta)$
bkgd: additional $\Delta 2\theta/4$ at each end of the scan
scan collected: 4205 (incl stds) yielding 3309 unique reflcns
std reflcns: 3 measd every 2 h; 10% decay in intensity obsd

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 27 and 30.2°.

(PhH-d_6, 26 °C): δ 112 s, Me_5C_5; 44.6 s, CH_2P; 15.8 s, Me_2P; 12.0 s, Me_5C_5. $^{31}P\{^1H\}$ NMR (PhH-d_6, 26 °C): δ −39.6.

$Yb(Me_5C_5)_2Cl(Me_2PCH_2PMe_2)$. Bis(pentamethylcyclopentadienyl)(bis(dimethylphosphino)methane)ytterbium (0.74 g, 0.0013 mol) in toluene (75 mL) was added to a suspension of ytterbium trichloride (0.36 g, 0.0013 mol) in toluene (10 mL). The suspension was stirred for 24 h, the solution was filtered, and the filtrate was concentrated to ca. 10 mL and cooled (−10 °C). The prisims (0.52 g, 66%) were collected and dried under reduced pressure; mp 208 °C dec. Anal. Calcd for $C_{25}H_{44}ClP_2Yb$: C, 48.8; H, 7.21; Cl, 5.77; P, 10.1. Found: C, 48.6; H, 7.06; Cl, 5.77; P, 9.88. IR (Nujol): 2718 w, 1292 m, 1276 w, 1149 m, 1087 w, 1014 m, 943 s, 908 s, 880 w, 830 w, 799 w, 759 m, 723 m, 709 w, 699 w, 683 w, 615 w, 590 w, 372 m, 298 s, and 248 s cm^{-1}. The effective magnetic moment (PhH, 30 °C) was 4.4 μ_B.

X-ray Crystallography

A crystal, approximately 0.4 × 0.4 × 0.25 mm, was sealed inside a quartz capillary and mounted on a CAD4 automatic diffractometer, and a set of θ–2θ scan data were collected. Details are given in Table IV. Data were corrected for crystal decay, absorption,[15] and Lorentz and polarization effects.

The ytterbium atom position was located with the use of a three-dimensional Patterson map, and subsequent least-squares and electron density maps resolved the location of all of the non-hydrogen atoms. The structure was refined to convergence by using anisotropic thermal parameters for the Yb, Cl, and P atoms and isotropic thermal parameters for the carbon atoms. Atomic scattering factors of Doyle and Turner[16] were used, and anomalous scattering corrections[17] were applied. The final R factors for 3202 unique data ($F^2 > 3\sigma(F^2)$) are $R_F = 0.053$ and $R_{wF} = 0.073$.[18] An extinction correction was applied to the observed structure factors.[19]

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Registry No. $Eu(Me_5C_5)_2(Me_2PCH_2CH_2PMe_2)$, 84254-50-2; $Yb(Me_5C_5)_2(Me_2PCH_2CH_2PMe_2)$, 84254-51-3; $Eu(Me_5C_5)_2(Me_2PCH_2PMe_2)$, 84254-52-4; $Yb(Me_5C_5)_2(Me_2PCH_2PMe_2)$, 84254-53-5; $Yb(Me_5C_5)_2Cl(Me_2PCH_2PMe_2)$, 84254-54-6; $Eu(Me_5C_5)_2(OEt_2)$, 84254-55-7; $Yb(Me_5C_5)_2(OEt_2)$, 74282-47-6; ytterbium trichloride, 10361-91-8.

Supplementary Material Available: Listings of anisotropic thermal parameters and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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(15) Templeton, L. K.; Templeton, D. H. "Abstracts, American Crystallographic Association Proceedings, 1973"; American Crystallographic Association: Storrs, CT, 1973; Series 2, Vol. 1, p 143.

(16) Doyle, P. A.; Turner, P. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 390.

(17) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(18) $R_F = \sum||F_o| - |F_c||/\sum|F_o|$; $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

(19) $(F_o)_{cor} = (1 + kI)F_o$, where $k = 2.6 \times 10^{-7}$ and I is the uncorrected intensity.