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C_2-Symmetric ytterbium(II) complexes with a novel, chiral P,N-donor ligand

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Abstract

The diastereomeric secondary phosphanes {$(Me_3Si)_2CH$}{C_6H_4-2-(*R* or *S*)-CH(Me)NMe_2}PH (**3**) may readily be isolated as a 50/50 mixture of epimers at phosphorus via the reaction of enantiomerically pure Li{C_6H_4-2-(*R* or *S*)-CH(Me)NMe_2} with {$(Me_3Si)_2CH$}PCl_2, followed by reduction with $LiAlH_4$. Treatment of either C-stereoisomer of **3** with ^{n}BuLi(tmeda) gives the lithium phosphanides [{$(Me_3Si)_2CH$}{C_6H_4-2-(*R*/*S*)-CH(Me)NMe_2}P]Li(tmeda) [(*R*)-**4**, (*S*)-**4**], which may be isolated as orange, crystalline solids (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). Treatment of **3** with ^{n}BuLi, followed by metathesis with KO^{t}Bu yields the corresponding potassium salts [{$(Me_3Si)_2CH$}{C_6H_4-2-(*R*/*S*)-CH(Me)NMe_2}P]K [(*R*)-**6**, (*S*)-**6**] as pyrophoric orange solids. A simple metathesis reaction between YbI_2 and two equivalents of (*R*)-**6** or (*S*)-**6** gives the C_2-symmetric Yb(II) complexes [{$(Me_3Si)_2CH$}{C_6H_4-2-(*R*/*S*)-CH(Me)NMe_2}P]$_2$Yb·($C_6H_{11}Me$) [(*R*)-**7**, (*S*)-**7**], after recrystallization from methylcyclohexane. Compounds **3**, **4**, **6** and **7** have been characterized by multi-element NMR spectroscopy and (*R*)-**4**, (*R*)-**7** and (*S*)-**7** have additionally been characterized by X-ray crystallography.

Keywords: *P*,*N*-ligands; Alkali metals; Ytterbium; Chirality; C_2-symmetric

1. Introduction

There is currently intense interest in the synthesis of chiral complexes of the lanthanide(III) and group 3 cations [1]. Such complexes are excellent enantioselective catalysts for a range of organic transformations; for example, enantiomerically pure lanthanide(III) and Group 3 metallocene derivatives stereoselectively catalyse the hydroamination/cyclisation of aminoalkenes, and the hydrogenation or hydrosilylation of olefins [2]. Shibasaki and co-workers and Aspinall and co-workers have found that chiral heterometallic binaphtholate complexes catalyse a variety of reactions including asymmetric variants of the aldol and nitroaldol reactions; these bifunctional compounds also mediate the enantioselective alkylation and hydrocyanation of aldehydes [1,3].

Somewhat surprisingly, there has been far less progress in the synthesis of chiral complexes of the lanthanides in the less common +2 oxidation state. This is in spite of the fact that the chemistry of Sm(II) is now well developed and SmI_2 has become the reagent of choice for a variety of organic transformations, many of which are inaccessible with more conventional reagents [4]. Reactions mediated by SmI_2 frequently proceed with a high degree of stereospecificity despite the lack of a stereodefined coordination environment at the Sm(II) centre due to chelation control. However, the sense and magnitude of stereoselection is often difficult to predict and is highly substrate dependent. There have been relatively few attempts to control the stereoselectivity of Sm(II)-mediated reactions through the use of chiral ligands or additives: addition of the chiral phosphane oxide (*R*)-BINAPO to SmI_2 allows the enantioselective synthesis of γ-butyrolactones via the addition of ketones to α,β-unsaturated esters [5]; however, addition of chirally modified polyethers to SmI_2 produces no enantio- and only moderately increased diastereoselectivity in the pinacol coupling of aldehydes [6].

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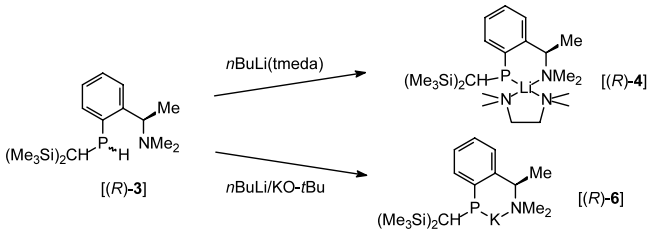
Although chirally modified tertiary phosphane ligands are a mainstay in the synthesis of stereoselective transition metal catalysts, the mismatch between the soft tertiary phosphane centres in these ligands and the hard lanthanide cations makes such phosphanes inappropriate ligands for these latter metals. We recently reported the synthesis of several lanthanide(II) complexes with chelating, donor-functionalized phosphanide ligands bearing a negative charge at the phosphorus atom [7]. The unique steric and electronic properties of these phosphanide ligands make their complexes with lanthanide(II) ions quite stable in the absence of air and allow the isolation of complexes with very low coordination numbers; the five-coordinate complex [{$(Me_3Si)_2CH$}$(C_6H_4$-2-$CH_2NMe_2)$P]$_2$Sm(THF) (**1**) [7a] readily loses coordinated solvent on heating under vacuum to give the coordinatively unsaturated complex [{$(Me_3Si)_2CH$}$(C_6H_4$-2-$CH_2NMe_2)$P]$_2$Sm (**2**) [7b]. The ready isolation of these complexes prompted us to investigate the possibility of synthesising chiral analogues. We herein report the first results from this study and the structural characterisation of both enantiomers of a homochiral ytterbium(II) phosphanide.

2. Results and discussion

The reaction of enantiomerically pure (*R*)- or (*S*)-*N*,*N*-dimethylaminomethyl-α-methyl-2-phenyllithium with {$(Me_3Si)_2CH$}PCl_2 in ether at low temperature yields the chlorophosphanes {$(Me_3Si)_2CH$}{C_6H_4-2-(*R* or *S*)-CH(Me)NMe_2}PCl, which may be reduced in situ with $LiAlH_4$ to give the secondary phosphanes {$(Me_3Si)_2CH$}{C_6H_4-2-(*R* or *S*)-CH(Me)NMe_2}PH (**3**), after a simple aqueous work-up, as viscous, colourless oils (Scheme 1). Compounds (*R*)-**3** and (*S*)-**3** are chiral at both the phosphorus and benzylic carbon centres [(*R*) and (*S*) refer to the stereochemistry of the benzylic carbon atom which has fixed chirality] and are isolated as 50/50 mixtures of the two possible epimers at phosphorus.

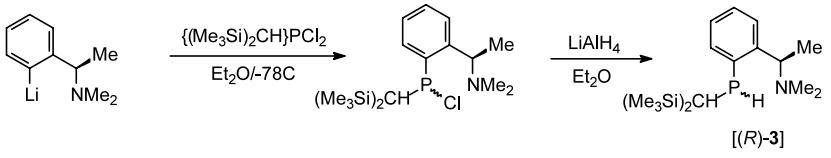
Metalation of either (*R*)- or (*S*)-**3** with ^{n}BuLi(tmeda) in ether gives the corresponding lithium complexes [{$(Me_3Si)_2CH$}{C_6H_4-2-(*R*/*S*)-CH(Me)NMe_2}P]Li(tmeda) [(*R*)-**4**, (*S*)-**4**] as orange crystalline solids in good yield [tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine] (Scheme 2). The ^{1}H-, ^{13}C- and ^{31}P-NMR spectra of **4** indicate the presence of only one ligand environment;



Scheme 2.

the ^{31}P and ^{7}Li-NMR spectra of **4** consist of broad singlets at −74 and −0.1 ppm, respectively, which do not exhibit ^{7}Li–^{31}P coupling. This suggests that the lithium atom effectively 'hops' between the two phosphorus lone pairs, resulting in rapid 'inversion' at the phosphorus centre on the NMR time scale and hence a rapid equilibrium between the two possible epimers of **4** (similar behaviour has been observed for the achiral analogue [{$(Me_3Si)_2CH$}{C_6H_4-2-CH_2NMe_2}P]Li$(THF)_2$ (**5**)) [8]. Whilst the diastereotopic $SiMe_3$ groups appear as distinct peaks in the ^{1}H-NMR spectrum of 4, the NMe_2 groups of both the phosphanide ligand and the tmeda co-ligand exhibit single peaks, the former of which is significantly broadened. This suggests that the Li–N bonds are also labile, allowing rapid inversion at nitrogen on the NMR time scale.

The structure of (*R*)-**4** was determined by X-ray crystallography; details of bond lengths and angles are given in Table 1 and the molecular structure of (*R*)-**4** is shown in Fig. 1. Compound (*R*)-**4** crystallises with two independent molecules in the asymmetric unit, which differ only trivially in their bond lengths and angles. Each lithium is coordinated by the P and N atoms of a chelating aminophosphanide ligand and the two N atoms of a molecule of tmeda, giving a four-coordinate, distorted tetrahedral Li atom. The six-membered chelate ring formed by the aminophosphanide ligand is folded along the P–C_α vector such that the C(108)–P(1)–Li(1) and C(113)–C(114)–N(11) angles are 78.14(7) [79.25(8)] and 110.53(11)° [110.53(12)°] (figures in square brackets refer to the second molecule in the asymmetric unit); the P–Li–N bite angle of the ligand is 89.21(10)° [91.38(11)°]. This compares with a bite angle of 93.8(3)° [94.5(3)°] in the achiral analogue **5** [8]. The phosphorus centre in the crystal of **4** studied adopts an *R* configuration, which minimizes steric interactions between the bulky $(Me_3Si)_2CH$ substituent and the α-methyl group. The Li–P distance of 2.629(3) Å [2.584(3)



Scheme 1.

Table 1
Selected bond lengths (Å) and bond angles (°) for (*R*)-**4**

Molecule 1		Molecule 2	
Bond lengths			
Li(1)–P(1)	2.629(3)	Li(2)–P(2)	2.584(3)
Li(1)–N(11)	2.153(3)	Li(2)–N(21)	2.121(3)
Li(1)–N(12)	2.159(3)	Li(2)–N(22)	2.119(3)
Li(1)–N(13)	2.246(3)	Li(2)–N(23)	2.206(3)
P(1)–C(101)	1.8946(15)	P(2)–C(201)	1.8938(15)
P(1)–C(108)	1.8153(15)	P(2)–C(208)	1.8225(16)
Si(11)–C(101)	1.8823(16)	Si(21)–C(201)	1.879(2)
Si(12)–C(101)	1.8826(16)	Si(22)–C(201)	1.875(2)
Si–C(Me) avg.	1.875	Si–C(Me) avg.	1.876
Bond angles			
P(1)–Li(1)–N(11)	89.21(10)	P(2)–Li(2)–N(21)	91.38(11)
P(1)–Li(1)–N(12)	118.29(11)	P(2)–Li(2)–N(22)	117.07(12)
P(1)–Li(1)–N(13)	134.62(12)	P(2)–Li(2)–N(23)	131.08(13)
N(12)–Li(1)–N(13)	84.08(10)	N(21)–Li(2)–N(22)	122.74(14)
N(11)–Li(1)–N(13)	111.57(12)	N(21)–Li(2)–N(23)	111.30(13)
N(11)–Li(1)–N(12)	123.51(13)	N(22)–Li(2)–N(23)	86.96(12)
Li(1)–P(1)–C(108)	78.14(7)	Li(2)–P(2)–C(201)	129.15(9)
Li(1)–P(1)–C(101)	122.16(8)	Li(2)–P(2)–C(208)	79.25(8)
C(101)–P(1)–C(108)	104.60(7)	C(201)–P(2)–C(208)	104.54(7)

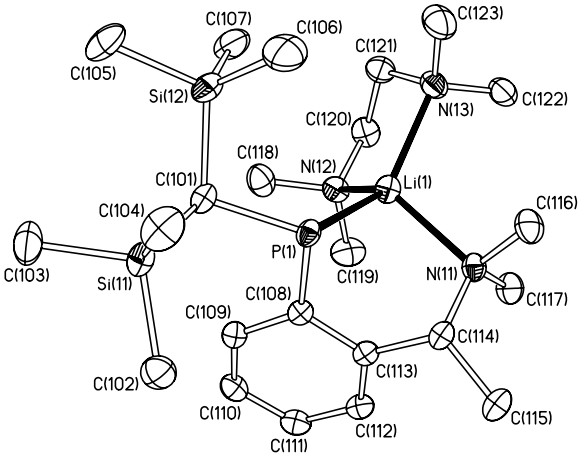


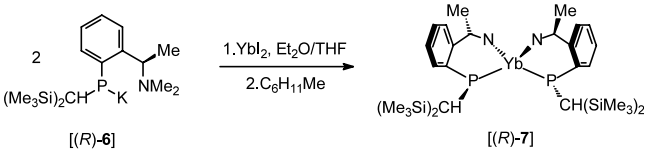
Fig. 1. Molecular structure of one of the two independent molecules of (*R*)-**4**, with 40% probability displacement ellipsoids and with H atoms omitted for clarity.

Å] is at the longer end of the typical range of distances for Li–P bonds in lithium phosphanides [9].

Treatment of either stereoisomer of in situ prepared [{(Me$_3$Si)$_2$CH}{C$_6$H$_4$-2-(*R*/*S*)-CH(Me)NMe$_2$}P]Li with one equivalent of KO^{t}Bu in ether gives the corresponding potassium salts [{(Me$_3$Si)$_2$CH}{C$_6$H$_4$-2-(*R*/*S*)-CH(Me)NMe$_2$}P]K [(*R*)-**6**, (*S*)-**6**], after removal of the LiO^{t}Bu side product by washing with light petroleum, as orange, pyrophoric powders (Scheme 2). Once again, multi-element NMR spectroscopy indicates rapid interconversion of the two possible epimers for each compound on the NMR time scale.

A simple metathesis reaction between two equivalents of either (*R*)-**6** or (*S*)-**6** and YbI$_2$ in ether–THF gives a sticky red solid which may be recrystallized from cold methylcyclohexane as deep red hexagonal plates of the methylcyclohexane solvate [{(Me$_3$Si)$_2$CH}{C$_6$H$_4$-2-(*R*/*S*)-CH(Me)NMe$_2$}P]$_2$Yb·(C$_6$H$_{11}$Me) [(*R*)-**7**, (*S*)-**7**] (Scheme 3). Both (*R*)-**7** and (*S*)-**7** were characterized by multi-element NMR spectroscopy and X-ray crystallography.

Compounds (*R*)-**7** and (*S*)-**7** are enantiomeric and so only the structure of (*R*)-**7** will be discussed here; that of (*S*)-**7** is insignificantly different apart from the change in chirality, and derived geometry standard uncertainties are a factor of two smaller. The molecular structure of (*R*)-**7** is shown in Fig. 2 and selected bond lengths and angles are given in Table 2. Compound (*R*)-**7** crystallises as discrete monomers with exact crystallographic C_2-symmetry in which the Yb centre is coordinated by the P and N atoms of two aminophosphide ligands, generating two folded, six-membered chelate rings and giving the ytterbium centre a distorted tetrahedral geometry. The bite angle of the ligands [85.29(9)°] compares with bite angles of 83.29(4) and 84.27(4)° in the calcium complex of the related achiral ligand, [{(Me$_3$Si)$_2$CH}{C$_6$H$_4$-2-CH$_2$NMe$_2$}P]$_2$Ca (**8**) [10] [according to Shannon the ionic radii of Ca(II) and Yb(II) differ by just 0.02 Å] [11]. The Yb–P distance of 2.8458(11) Å is at the lower end of the range of distances reported for Yb(II)–P bonds; for example, the Yb–P distances in (Ph$_2$P)$_2$Yb(THF)$_4$ and {(2,4,6-Me$_3$C$_6$H$_2$)$_2$P}$_2$Yb(THF)$_4$ are 2.991(2) and 2.925(2) Å, respectively [12,13], whilst the Yb–P distance in the closely related complex [{(Me$_3$Si)$_2$CH}(C$_6$H$_3$–2-OMe–3-Me)P]$_2$Yb(THF)$_2$ is 2.969(3) Å [7c], and the Yb–P distance in the primary phosphanide complex {(2,4,6-^{t}Bu$_3$C$_6$H$_2$)PH}$_2$Yb(THF)$_4$ is 3.025(2) Å [14]. In addition to contacts with the P and N atoms of the ligands the ytterbium atoms also have short contacts with the *ipso* carbon atoms of the aromatic rings adjacent to phosphorus [Yb···C(8) 3.037 Å]. Similar short contacts are observed between Sm and the same *ipso* carbon in **1** [7a], but not in its unsolvated, four-coordinate analogue **2** [7b], which adopts a similar structure to **7** in the solid state; the calcium analogue **8** also exhibits no short Ca···C contacts [10]. The phosphorus centres in (*R*)-**7** are distinctly pyramidal [sum of angles at P = 300.51°] and these centres adopt an *R*-configuration. Once again, this configuration mini-



Scheme 3.

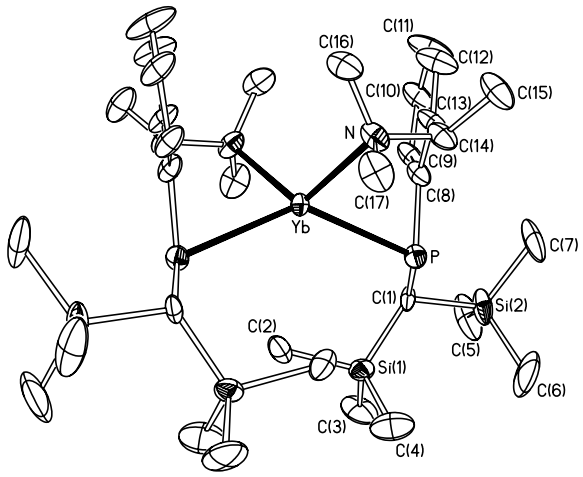


Fig. 2. Molecular structure of (*R*)-**7**, with 40% probability displacement ellipsoids and with H atoms omitted for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) for (*R*)-**7**

Bond lengths			
Yb–P	2.8458(11)	Si(1)–C(1)	1.867(5)
Yb–N	2.478(4)	Si(2)–C(1)	1.887(4)
P–C(1)	1.886(4)	Si–C(Me) avg.	1.872
P–C(8)	1.825(5)		
Bond angles			
P–Yb–N	85.29(9)	Yb–P–C(1)	118.56(11)
P–Yb–P′	135.78(5)	Yb–P–C(8)	77.75(14)
P–Yb–N′	118.35(8)	C(1)–P–C(8)	104.2(2)
N–Yb–N′	117.1(2)		

Primes indicate symmetry-generated atoms (C_2-axis through Yb)

mizes steric interactions between the $CH(SiMe_3)_2$ substituents and the benzylic methyl groups.

In our recent reports on the Yb(II) and heavier Group 2 derivatives of the achiral ligand $\{(Me_3Si)_2CH\}\{C_6H_4$-2-$CH_2NMe_2\}P^-$, i.e. $[\{(Me_3Si)_2CH\}\{C_6H_4$-2-$CH_2NMe_2\}P]_2M(L)$ [ML = Yb (**5**), Ca (**8**), Sr(THF), Ba(THF)] [7,10], we noted that these compounds were subject to highly unusual dynamic processes in solution which we attributed to a novel monomer-dimer equilibrium in which the dimer was favoured at low temperature. This equilibrium manifested itself in the extremely broad, temperature dependent ^{1}H-, ^{13}C- and ^{31}P-NMR spectra of these complexes (and for **5** its ^{171}Yb spectrum).

In contrast, the r.t. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra of **7** are consistent with the structure obtained in the solid state and remain sharp over a wide temperature range; a single resonance is seen in both the ^{31}P and ^{171}Yb spectra of (*R*)-**7** and the ^{1}H and ^{13}C spectra are consistent with the presence of only a single ligand environment (Fig. 3); the ^{31}P signal exhibits satellites due to coupling to ^{171}Yb ($I = 1/2$, 14% natural abundance). The sharpness of these spectra indicate either that any dynamic processes operating on this compound are slow on the NMR time scale, in which case the single peaks observed in the ^{31}P and ^{171}Yb spectra suggest that just a single diastereomer is present in solution, or that the two diastereomers are in rapid equilibrium on the NMR time scale. Although it is not possible to distinguish conclusively between these two extremes, given the wide temperature range over which the spectra remain sharp and bearing in mind the behaviour of the achiral analogue (**5**), the data possibly favour the former.

3. Experimental

3.1. General comments

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Ether, THF, methylcyclohexane and light petroleum (b.p. 40–60 °C) were distilled under nitrogen from sodium, potassium or sodium–potassium alloy. With the exception of THF, which was stored over activated 4 Å molecular sieves, all solvents were stored over a potassium film. Deuterated THF, benzene and toluene were distilled from potassium, deoxygenated by three freeze–pump–thaw cycles and were stored over activated 4 Å molecular sieves. Deuterated chloroform was distilled from CaH_2 and was deoxygenated and stored in a similar way. Tmeda was distilled under nitrogen from CaH_2 and was stored over activated 4 Å molecular sieves. BuLi was obtained from Aldrich as a 2.5 M solution in hexanes. The compounds $(Me_3Si)_2CHPCl_2$ [15], (*R*)- and (*S*)-$C_6H_5CHMeNMe_2$ [16] and YbI_2 [17] were prepared by previously published procedures. All other compounds were used as supplied by the manufacturer.

^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL Lambda 500 spectrometer operating at 500 and 125.65 MHz, respectively, or a Bruker Avance 300 spectrometer operating at 300 and 75.47 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. ^{31}P-NMR spectra were recorded on a Bruker WM300 spectrometer operating at 121.5 MHz and chemical shifts are quoted relative to external 85% H_3PO_4. ^{171}Yb spectra were recorded on a Bruker WM300 spectrometer operating at 123.83 MHz and are quoted relative to external $(\eta^5$-$C_5Me_5)_2Yb(THF)_2$ [18]; ^{7}Li-NMR spectra were recorded on a Bruker WM300 spectrometer, operating at 116.65 MHz and are quoted relative to external 0.1 M LiCl. Where possible, elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University; due to the air sensitive nature of (*R*)- and (*S*)-**6** satisfactory elemental analyses of these compounds could not be obtained.

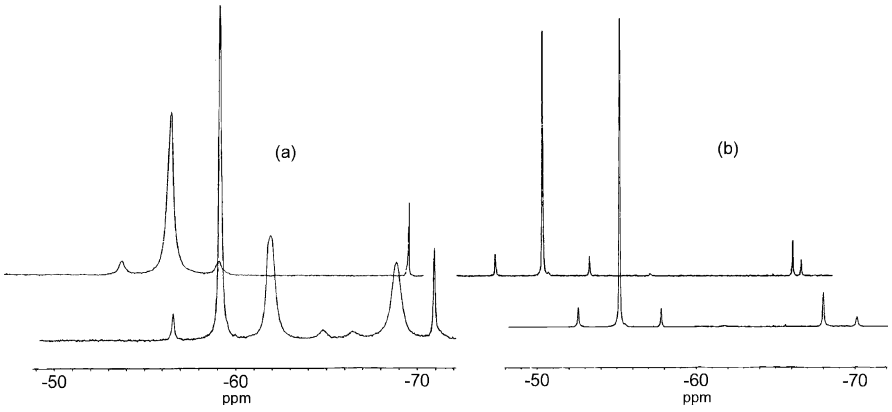


Fig. 3. $^{31}P\{^{1}H\}$-NMR spectra of (a) **5** at 294 K (upper) and 203 K (lower) and (b) (*R*)-**7** at 294 K (upper) and 193K (lower) in d_8-toluene.

3.2. Preparation of {$(Me_3Si)_2CH$}(C_6H_4-2-(*R*)-$CHMeNMe_2$)PH [(*R*)-**3**]

^{t}BuLi (15.0 ml, 22.50 mmol) was added to a solution of (*R*)-*N*,*N*-dimethyl-1-phenethylamine (3.12 g, 20.91 mmol) in light petroleum (5 ml). This mixture was stirred for 16 h and then the solid was isolated by filtration and washed with light petroleum (5 × 15 ml). Residual solvent was removed in vacuo to leave LiC_6H_4-2-(*R*)-$CHMeNMe_2$ as a pyrophoric colourless powder.

A solution of LiC_6H_4-2-(*R*)-$CHMeNMe_2$ (2.36 g, 15.21 mmol) in THF (20 ml) was added dropwise to a solution of $\{(Me_3Si)_2CH\}PCl_2$ (3.97 g, 15.20 mmol) in cold (−78 °C) ether (15 ml). This mixture was allowed to warm slowly to room temperature (r.t.) and was stirred for 16 h. Solids were removed by filtration and $LiAlH_4$ (1.14 g, 30.40 mmol) was added to the filtrate, which was then heated under reflux for 3 h. Excess $LiAlH_4$ was destroyed by the addition of deoxygenated water (20 ml) and the organic phase was extracted into light petroleum (3 × 15 ml) and dried over activated 4 Å molecular sieves. Solvent was removed in vacuo to give (*R*)-**3** as a colourless, viscous oil containing a 50/50 mixture of the two possible phosphorus epimers. Yield 3.99 g, 77%. Anal. Calc. for $C_{17}H_{34}NPSi_2$: C, 60.12; H, 10.09; N, 4.12. Found: C, 60.15; H, 9.95; N, 4.15%. ^{1}H-NMR ($CDCl_3$, 297 K): δ 0.01 (s, 9H, $SiMe_3$), 0.03 (s, 9H, $SiMe_3$), 0.06 (s, 9H, $SiMe_3$), 0.08 (s, 9H, $SiMe_3$), 0.48 (d, $^{3}J_{HH} = 5.0$ Hz, 1H, CHP), 0.50 (d, $^{3}J_{HH} = 5.0$ Hz, 1H, CHP), 1.13 (d, $J_{HH} = 6.5$ Hz, 3H, Me), 1.17 (d, $J_{HH} = 6.5$ Hz, 3H, Me), 2.02 (s, 6H, NMe_2), 2.03 (s, 6H, NMe_2), 3.84 (m, 1H, CHMe), 3.91 (m, 1H, CHMe), 4.31 (dd, $J_{PH} = 211.7$ Hz, $J_{HH} = 5.0$ Hz, 1H, PH), 4.49 (dd, $J_{PH} = 211.8$ Hz, $J_{HH} = 5.0$ Hz, 1H, PH), 6.94–7.55 (m, 8H, ArH). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 297 K): δ 0.99 ($SiMe_3$), 1.05 ($SiMe_3$), 5.62 (d, $J_{PC} = 43.1$ Hz, CHP), 5.68 (d, $J_{PC} = 42.0$ Hz, CHP), 18.59 (Me), 18.86 (Me), 42.77 (NMe_2), 62.40 (CHMe), 62.53 (CHMe), 126.06, 126.53, 128.43, 132.26, 136.11 (Ar), 149.30 (d, $J_{PC} =$ 30.0 Hz, Ar). ^{31}P-NMR ($CDCl_3$, 297 K): δ −71.9 (d, $J_{PH} = 211.8$ Hz), −72.5 (d, $J_{PH} = 211.7$ Hz).

3.3. Preparation of {$(Me_3Si)_2CH$}(C_6H_4-2-(*S*)-$CHMeNMe_2$)PH [(*S*)-**3**]

Compound (*S*)-**3** was prepared by a similar procedure to (*R*)-**3** from LiC_6H_4-2-(*S*)-$CHMeNMe_2$ (2.10 g, 13.53 mmol) and $\{(Me_3Si)_2CH\}PCl_2$ (3.53 g, 13.51 mmol). Compound (*S*)-**3** was isolated as a colourless oil containing a 50/50 mixture of the two possible phosphorus epimers. Yield 3.58 g, 78%. Anal. Calc. for $C_{17}H_{34}NPSi_2$: C, 60.12; H, 10.09; N, 4.12. Found: C, 60.01; H, 9.97; N, 4.10%. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$-NMR data were identical to those of (*R*)-**3**.

3.4. Preparation of [{$(Me_3Si)_2CH$}(C_6H_4-2-(*R*)-$CHMeNMe_2$)P]Li(tmeda) [(*R*)-**4**]

^{n}BuLi (0.59 ml, 1.47 mmol) was added to a solution of (*R*)-**3** (0.50 g, 1.47 mmol) and tmeda (0.22 ml, 1.47 mmol) in ether (15 ml). This mixture was stirred at r.t. for 2 h, concentrated to ~5 ml and cooled to 5 °C for 60 h. Yellow crystals of (*R*)-**4** were isolated and washed with a little light petroleum. Yield 0.54 g, 79%. Anal. Calc. for $C_{23}H_{49}LiN_3PSi_2$: C, 59.83; H, 10.70; N, 9.10. Found: C, 58.56; H, 10.58; N, 8.32%. ^{1}H-NMR (d_8-THF, 297 K): δ 0.01 (s, 9H, $SiMe_3$), 0.12 (s, 9H, $SiMe_3$), 0.36 (s, 1H, CHP), 1.22 (d, $J_{HH} = 7.1$ Hz, 3H, Me), 2.14 (s, 12H, tmeda), 2.22 (s, 6H, NMe_2), 2.30 (s, 4H, tmeda), 4.37 (m, 1H, CHMe), 6.25–7.01 (m, 4H, ArH). $^{13}C\{^{1}H\}$-NMR (d_8-THF, 297 K): δ 1.68 ($SiMe_3$), 2.01 ($SiMe_3$), 4.35 (d, $J_{PC} = 68.1$ Hz, CHP), 6.94 (Me), 40.27 (NMe_2), 46.01 (tmeda), 58.67 (tmeda), 58.87 (CHMe), 113.66, 124.62, 125.56, 127.52 (Ar), 136.78 (d, $J_{PC} =$ 23.7 Hz, Ar), 163.76 (d, $J_{PC} = 69.2$ Hz, Ar). $^{31}P\{^{1}H\}$-NMR (d_8-THF, 297 K): δ −74.0. ^{7}Li-NMR (d_8-THF, 297K): δ −0.1.

3.5. Preparation of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-(S)-CHMeNMe$_2$)P]Li(tmeda) [(S)-4]

Compound (*S*)-**4** was synthesised using a similar procedure to that used for (*R*)-**4** from (*S*)-**3** 0.60 g, 1.76 mmol), tmeda (0.26 ml, 1.76 mmol) and ^{n}BuLi (0.71 ml, 1.76 mmol). Yield 0.63 g, 77%. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}-NMR data were identical to those of (*R*)-**4**.

3.6. Preparation of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-(R)-CHMeNMe$_2$)P]K [(R)-6]

^{n}BuLi (1.96 ml, 4.90 mmol) was added to a solution of (*R*)-**3** (1.66 g, 4.89 mmol) in ether (15 ml). This mixture was stirred for 2 h and was then added dropwise to a solution of KO^{t}Bu (0.55 g, 4.90 mmol) in ether (5 ml). Stirring was continued for 3 h and then solvent was removed in vacuo. The solid was washed with light petroleum (5 × 15 ml) and residual solvent was removed in vacuo to give (*R*)-**6** as a pyrophoric orange/red powder. Yield 1.27 g, 69%. ^{1}H-NMR (C$_6$D$_6$, 296 K): δ 0.31 (s, 9H, SiMe$_3$), 0.33 (s, 9H, SiMe$_3$), 0.44 (s, 1H, CHP), 1.01 (d, $J_{HH} = 6.7$ Hz, 3H, Me), 1.98 (s, 6H, NMe$_2$), 4.37 (m, 1H, CHMe), 6.31–7.09 (m, 4H, ArH). ^{13}C{^{1}H}-NMR (C$_6$D$_6$, 296 K): δ 1.95 (SiMe$_3$), 2.45 (SiMe$_3$), 6.91 (d, $J_{PC} = 71.4$ Hz, CHP), 15.61 (Me), 45.49 (NMe$_2$), 57.51 (CHMe), 113.05, 125.68, 127.10, 128.39, 136.46 (Ar), 165.90 (d, $J_{PC} = 77.0$ Hz). ^{31}P{^{1}H}-NMR (C$_6$D$_6$, 296 K): δ −58.6.

3.7. Preparation of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-(S)-CHMeNMe$_2$)P]K [(S)-6]

Compound (*S*)-**6** was synthesised using a similar procedure to that used for the preparation of (*R*)-**6** from (*R*)-**3** (3.08 g, 9.07 mmol), ^{n}BuLi (3.63 ml, 9,08 mmol) and KO^{t}Bu (1.02 g, 9.09 mmol) and was isolated as a pyrophoric orange/red powder. Yield 2.40 g, 70%. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}-NMR data were identical to those of (*R*)-**6**.

3.8. Preparation of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-(R)-CHMeNMe$_2$)P]$_2$Yb·C$_6$H$_{11}$Me [(R)-7]

A solution of (*R*)-**6** (0.78 g, 2.07 mmol) in THF (20 ml) was added to a suspension of YbI$_2$ (0.44 g, 1.03 mmol) in ether (10 ml). This mixture was stirred for 16 h and then solvent was removed in vacuo. The solid was extracted into toluene (20 ml), filtered and solvent was removed in vacuo to give a sticky red solid. Compound (*R*)-**7** was obtained as deep red hexagonal shaped crystals from cold (5 °C) methylcyclohexane. Yield 0.69 g, 71%. Anal. Calc. for C$_{41}$H$_{80}$N$_2$P$_2$Si$_4$Yb: C, 51.92; H, 8.50; N. 2.95. Found: C, 51.05; H, 8.45; N, 3.01%. ^{1}H-NMR (C$_6$D$_6$, 295 K): δ 0.30 (s, 18H, SiMe$_3$), 0.52 (s, 18H, SiMe$_3$), 0.61 (d, $J_{PH} = 4.9$ Hz, 1H, CHP), 0.70 (d, $J_{HH} = 7.1$ Hz, 6H, CHMe), 1.90 (s, 6H, NMe$_2$), 2.14 (s, 6H, NMe$_2$), 4.64 (m, 2H, CHMe), 6.55–7.40 (m, 8H, ArH). ^{13}C{^{1}H}-NMR: δ 1.92 (SiMe$_3$), 3.34 (SiMe$_3$), 5.69 (d, $J_{PC} = 43.3$ Hz, CHP), 18.75 (Me), 32.47 (NMe$_2$), 42.13 (NMe$_2$), 60.13 (d, $J_{PC} = 34.1$ Hz, CHMe), 118.69, 126.02, 129.65, 130.39 (Ar), 136.15 (d, $J_{PC} = 22.7$ Hz, Ar), 170.23 (d, $J_{PC} = 49.3$ Hz, Ar). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ −57.1 ($J_{YbP} = 655.1$ Hz). ^{171}Yb-NMR (C$_6$D$_6$, 296 K): δ 32.5 ($J_{YbP} = 655$ Hz).

3.9. Preparation of [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-(S)-CHMeNMe$_2$)P]$_2$Yb.C$_6$H$_{11}$Me [(S)-7]

Compound (*S*)-**7** was synthesised using a similar procedure to that used for (*R*)-**7** from (*S*)-**6** (0.87 g, 2.30 mmol) and YbI$_2$ (0.49 g, 1.15 mmol). Yield 0.80 g, 73%. Anal. Calc. for C$_{41}$H$_{80}$N$_2$P$_2$Si$_4$Yb: C, 51.92; H, 8.50; N. 2.95. Found: C, 50.98; H, 8.57; N, 3.56%. ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR data were identical to those of (*R*)-**7**.

3.10. Crystal structure determinations of (R)-4, and (R)- and (S)-7

Measurements were made at 160 K on a Bruker AXS SMART CCD diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) and narrow (0.3° in ω) frame exposures. For all compounds cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semi-empirically 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 3 gives 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. The methylcyclohexane solvent molecules in (*R*)-**7** and (*S*)-**7** were found to be highly disordered and could not be modelled with individual atoms; they were treated instead by the SQUEEZE process of PLATON [19]. Unambiguous determination of absolute configuration was achieved in each case, including confirmation of the enantiomeric relationship of (*R*)-**7** and (*S*)-**7**, by refinement of the Flack parameter [20] to a value insignificantly different from zero with a low standard uncertainty. Other programs were Bruker AXS SMART (control) and SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics [21].

Table 3
Crystallographic data for (*R*)-**4**, (*R*)-**7** and (*S*)-**7**

	(*R*)-**4**	(*R*)-**7**	(*S*)-**7**
Empirical formula	$C_{23}H_{49}LiN_3PSi_2$	$C_{34}H_{66}N_2P_2Si_4Yb.C_7H_{14}$	$C_{34}H_{66}N_2P_2Si_4Yb.C_7H_{14}$
Formula weight	461.7	948.4	948.4
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$C222_1$	$C222_1$
Unit cell dimensions			
a (Å)	11.4663(5)	11.8219(4)	11.8258(4)
b (Å)	18.5522(8)	19.6677(7)	19.6838(7)
c (Å)	15.1507(6)	21.2859(8)	21.2882(8)
β (°)	110.406(2)		
V (Å^3)	3020.7(2)	4949.2(3)	4955.4(3)
Z	4	4	4
D_{calc} (g cm^{-3})	1.015	1.273	1.271
μ (mm^{-1})	0.18	2.08	2.08
Crystal size (mm^3)	0.50 × 0.35 × 0.30	0.23 × 0.23 × 0.15	0.45 × 0.40 × 0.36
Reflections collected	25813	20500	21315
Independent reflections, R_{int}	13537, 0.0229	5953, 0.0318	5781, 0.0263
Reflections with $F^2 > 2\sigma$	12336	5829	5544
Refined parameters	567	204	204
R (F, $F^2 > 2\sigma$) [a]	0.0318	0.0369	0.0184
R_w (F^2, all data) [a]	0.0806	0.0747	0.0440
Goodness-of-fit on F^2 [a]	1.032	1.288	1.043
Largest difference peak and hole (e^{-3})	0.21, −0.18	1.49, −4.18	0.28, −1.00
Absolute structure parameter	0.01(4)	0.011(9)	−0.006(5)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$; goodness-of-fit = $[\Sigma\, w(F_o^2 - F_c^2)^2/(\text{no. data} - \text{no. params})]^{1/2}$ for all data.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 212379, 212380 and 212381 for compounds (*R*)-**4**, (*R*)-**7** and (*S*)-**7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) For recent reviews see: H.C. Aspinall, Chem. Rev. 102 (2002) 1807;
(b) M. Shibasaki, N. Yoshikawa, Chem. Rev. 102 (2002) 2187;
(c) J. Inanaga, H. Furuno, T. Hayano, Chem. Rev. 102 (2002) 2211;
(d) M. Shibasaki, H. Sasai, T. Arai, Angew. Chem. Int. Ed. Engl. 36 (1997) 1237.
[2] (a) M.A. Giardello, V.P. Conticello, L. Brard, M. Sabat, A.L. Rheingold, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10212;
(b) P.W. Roesky, U. Denninger, C.L. Stern, T.J. Marks, Organometallics 16 (1997) 4486;
(c) C.M. Haar, C.L. Stern, T.J. Marks, Organometallics 15 (1996) 1765;
(d) P.-F. Fu, L. Brard, Y. Li, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 7157.
[3] (a) J. Tian, N. Yamagiwa, S. Matsunaga, M. Shibasaki, Angew. Chem. Int. Ed. Engl. 41 (2002) 3636;
(b) H.C. Aspinall, N. Greeves, E.G. McIver, J. Alloys. Comp. 275–277 (1998) 773;
(c) H.C. Aspinall, J.L.M. Dwyer, N. Greeves, A. Steiner, Organometallics 18 (1999) 1366;
(d) H.C. Aspinall, N. Greeves, P.M. Smith, Tetrahedron Lett. 40 (1999) 1763;
(e) Y.M.A. Yamada, N. Yoshikawa, H. Sasai, M. Shibasaki, Angew. Chem. Int. Ed. Engl. 36 (1997) 1871;
(f) H. Sasai, T. Arai, Y. Satow, K.N. Houk, M. Shibasaki, J. Am. Chem. Soc. 117 (1995) 6194.
[4] (a) T. Imamoto, Lanthanides in Organic Synthesis, Academic Press, London, 1994;
(b) G.A. Molander, C.R. Harris, Chem. Rev. 96 (1996) 307;
(c) G.A. Molander, Chem. Rev. 92 (1992) 29;
(d) T. Skrydstrup, Angew. Chem. Int. Ed. Engl. 36 (1997) 345;
(e) G.A. Molander, C.R. Harris, Tetrahedron 54 (1998) 3321.
[5] K. Mikama, M. Yamaoka, Tetrahedron Lett. 39 (1998) 4501.
[6] H.L. Pederson, T.B. Christensen, R.J. Enemaerke, K. Daasbjerg, T. Skrydstrup, Eur. J. Org. Chem. (1999) 565.
[7] (a) K. Izod, P. O'Shaughnessy, J.M. Sheffield, W. Clegg, S.T. Liddle, Inorg. Chem. 39 (2000) 4741;
(b) W. Clegg, K. Izod, S.T. Liddle, J. Organomet. Chem. 613 (2000) 128;
(c) W. Clegg, K. Izod, S.T. Liddle, P. O'Shaughnessy, J.M. Sheffield, Organometallics 19 (2000) 2090.
[8] W. Clegg, S. Doherty, K. Izod, H. Kagerer, P. O'Shaughnessy, J.M. Sheffield, J. Chem. Soc. Dalton Trans. (1999) 1825.
[9] K. Izod, Adv. Inorg. Chem. 50 (2000) 33 (and references therein).
[10] S. Blair, K. Izod, W. Clegg, Inorg. Chem. 41 (2002) 3886.

[11] R.D. Shannon, Acta. Crystallogr. Sect. A 32 (1976) 751.
[12] G.W. Rabe, G.P.A. Yap, A.L. Rheingold, Inorg. Chem. 34 (1995) 4521.
[13] S. Atlan, F. Nief, L. Ricard, Bull. Chim. Soc. Fr. 132 (1995) 649.
[14] G.W. Rabe, I.A. Guzei, A.L. Rheingold, Inorg. Chem. 36 (1997) 4914.
[15] M.J.S. Gynane, A. Hudson, M.F. Lappert, P.P. Power, H. Goldwhite, J. Chem. Soc. Dalton Trans. (1980) 2428.
[16] J. Blagg, S.G. Davis, C.L. Goodfellow, K.H. Sutton, J. Chem. Soc. Perkin Trans. 1 (1987) 1805.
[17] T.D. Tilley, J.M. Boncella, D.J. Berg, C.J. Burns, R.A. Andersen, Inorg. Synth. 27 (1990) 147.
[18] A.G. Avent, M.A. Edelman, M.F. Lappert, G.A. Lawless, J. Am. Chem. Soc. 111 (1989) 3423.
[19] A.L. Spek, PLATON, A General Purpose Crystallographic Program, University of Utrecht, The Netherlands, 2000.
[20] H.D. Flack, Acta Crystallogr. Sect. A 39 (1983) 876.
[21] (a) SMART and SAINT software for CCD diffractometers; Bruker AXS Inc., Madison, WI, 1997;
(b) G.M. Sheldrick, SHELXTL user manual, version 6; Bruker AXS Inc., Madison, WI, 2001.