Synthesis, structures and reactivity of 2-phosphorylmethyl-1*H*-pyrrolato complexes of titanium, yttrium and zinc†

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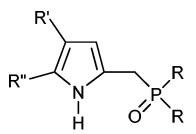
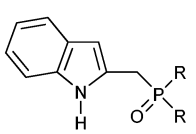
The reaction of secondary phosphines HPR_2 (R = Ph, Cy) with pyrrole-2-aldehydes gives a new family of 2-phosphorylmethyl-1*H*-pyrroles as potentially chelating mono-anionic ligands. The reaction with $Ti(NMe_2)_4$ affords octahedral $Ti(NMe_2)_2\{NC_4H_2(4\text{-}R')CH_2P(O)R_2\}_2$ (R′ = H, Bu^t). While the diphenylphosphoryl complexes adopt a configuration with *trans*-pyrrolato ligands, the dicyclohexyl analogue prefers an all-*cis* conformation, with profound consequences on metal–ligand bonding. The reaction of sterically undemanding $HNC_4H_3CH_2P(O)Ph_2$ with $Y[N(SiHMe_2)_2]_3(THF)_2$ give the homoleptic complex $Y[NC_4H_3CH_2P(O)Ph_2]_3$; mixed-ligand intermediates $Y[N(SiHMe_2)_2]_2(N\text{–}O)$ and $Y[N(SiHMe_2)_2](N\text{–}O)_2$ were identifiable but could not be isolated. The bulky ligand $HNC_4H_2(5\text{-}Bu^t)CH_2P(O)Ph_2$ does not react with $Ti(NMe_2)_4$ but protolyses $Zn[N(SiMe_3)_2]_2$ to give a 1 : 2 complex $Zn(N\text{–}O)_2$ as the only isolable product. On the other hand, its reaction with $Y[N(SiHMe_2)_2]_3(THF)_2$ affords the mono-amido complex $Y\{N(SiHMe_2)_2\}\{NC_4H_3(5\text{-}Bu^t)CH_2P(O)Ph_2\}_2$ which shows good activity for the ring-opening polymerisation of cyclic esters.

Introduction

Amongst the many ligand systems investigated in the context of non-metallocene polymerisation catalysts,[1] salicylaldiminato and pyrrolaldiminato ligand[2] motifs are particularly prominent. The latter have been investigated by a number of research groups including ourselves.[3–8] The combination of an anionic pyrrolate moiety with other donors is, however, less common. In an effort to explore routes to new N–P and N–O chelate ligands based on pyrrolates, we became interested in pyrrole- and indole-based compounds of types **I** and **II**. To the best of our knowledge, such compounds or their metal complexes have not been reported before. Such ligand types provide a very versatile scaffold since the substitution pattern of the pyrrole ring and the phosphorus can easily be varied and reduction of the phosphine oxide can generate an analogous series of pyrrolyl phosphine ligands. We now report the synthesis of derivatives of type **I** with pyrroles containing 2-methylphosphoryl substituents, their coordination chemistry and applications in the ring-opening polymerisation (ROP) of cyclic esters.



I



II

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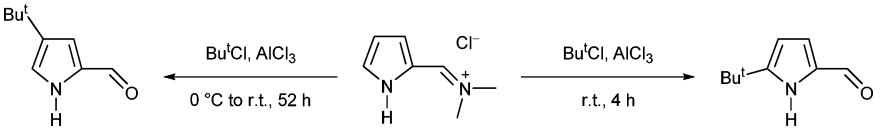
Results and discussion

Ligand synthesis

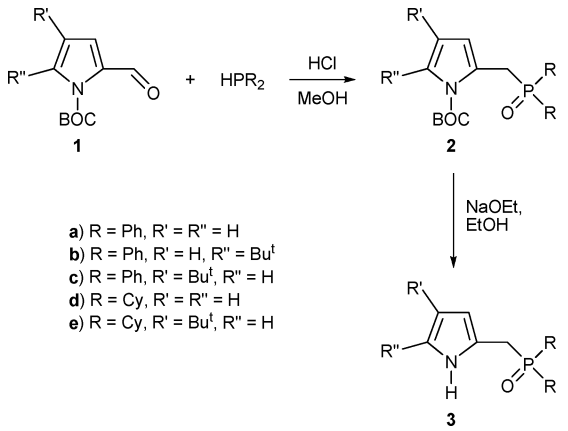
The ligand synthesis starts with the commercially available pyrrole-2-aldehyde. *t*-Butyl substituted pyrrole aldehydes as starting materials for sterically more hindered ligands have been reported by Mueller-Westerhoff and Swiegers from the Friedel–Crafts alkylation of *N*,*N*-dimethylpyrrole-2-forminium chloride.[9] This is itself accessible *via* a Vilsmeier–Haack type reaction from pyrrole, phosgene and dimethyl formate.[10] However, we found the Friedel–Crafts alkylation to be very temperature sensitive: if the reaction is allowed to undergo a controlled exotherm on the slow but frequent addition of solid $AlCl_3$, 5-*t*-butyl-pyrrole-2-aldeyde is formed with high regioselectivity. On the other hand, if the reaction mixture is cooled and kept as close to 0 °C as possible throughout the addition of $AlCl_3$, the kinetic product 4-*t*-butylpyrrole-2-aldeyde is produced (Scheme 1).

The *t*-butoxycarbonyl (BOC) protected aldehydes **1** (**a**, R′ = R″= H; **b**, R′ = H, R″ = Bu^t; **c**, R′ = Bu^t, R″ = H) react with diphenyl or dicyclohexyl phosphine in the presence of 1.1 equivalents of hydrochloric acid in methanol to produce BOC-protected pyrrole-phosphine oxides (**2**). Compounds **2** crystallise readily on cooling the methanol solutions and are isolated in yields of up to 91%. In the case of the dicyclohexyl derivative **2e**, the ionic intermediate, [4-Bu^t-pyr-$CH_2P(Cy)_2OH$]Cl, could be detected by its ^{1}H and ^{31}P NMR spectra. Deprotection by treatment with base in ethanol afforded the ligands **3** (Scheme 2).

In the case of the 5-Bu^t derivative **1b**, BOC protection of the NH function proved difficult due to steric hindrance, and as a consequence an increased amount of side products was formed. However, the direct reaction of the 5-*t*-butyl-pyrrole-2-aldehyde with diphenyl phosphine under acidic conditions yielded **3b** directly. Although the yield was only 39%, this procedure



Scheme 1



Scheme 2

shortens the synthesis by two steps and the overall product yield is comparable to the BOC-protected route.

The crystal structure of **3a** is shown in Fig. 1. The compound exists in the solid state in the form of one-dimensional chains held together by intermolecular hydrogen bonds, with an N···O separation of 2.868 (3) Å and an N–H···O angle of 154.3°.

Metal complexes

The 2-[(diphenylphosphoryl)methyl]-1*H*-pyrrole ligands **3a** and **3c** readily protolyse tetrakis(dimethylamido)titanium in toluene to form the bis-ligand complexes **5a** and **5c** in about 80% yields (Scheme 3).

The mono-ligated titanium complexes **4a** and **4c** can be identified as reaction intermediates. They are formed as the major product if the reaction is carried out with more than 3 molar equivalents of $Ti(NMe_2)_4$ and can be isolated as orange solids by extraction of the crude mixture with light petroleum, followed by immediate removal of volatiles *in vacuo*. However, attempts to purify these complexes by recrystallisation are thwarted by ligand redistribution, and the less soluble 2 : 1 complexes **5** are obtained instead. The crystal structures of **5a** and **5c** are depicted in Fig. 2 and 3, respectively. In both complexes the metal centre

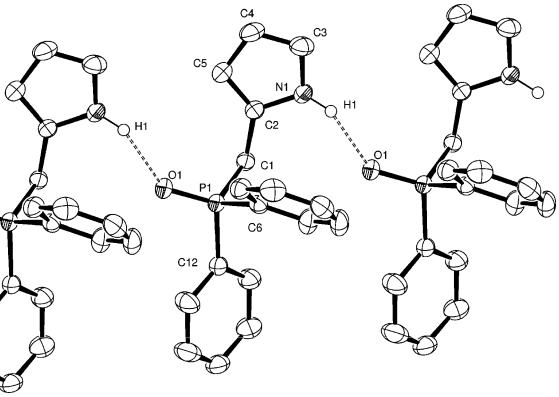
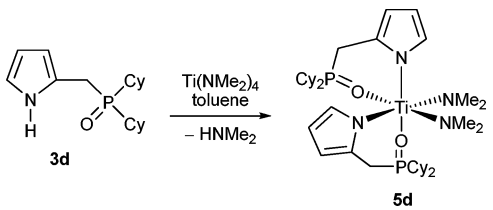


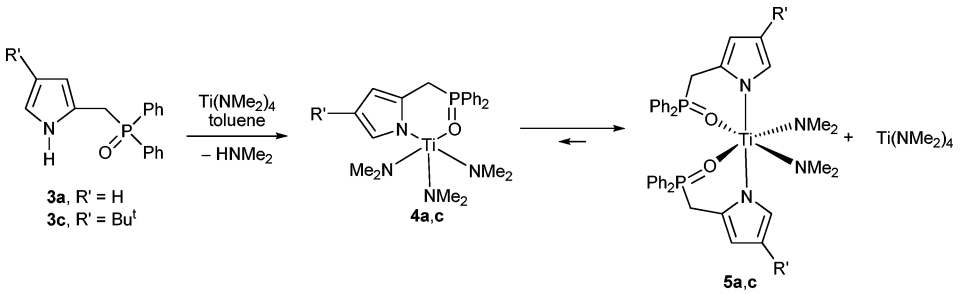
Fig. 1 Molecular structure of **3a** illustrating the intermolecular hydrogen bonding pattern. Ellipsoids are drawn at 50% probability. Hydrogen atoms except H(1) have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–P(1) 1.807(2), C(6)–P(1) 1.802(2), C(12)–P(1) 1.805(2), O(1)–P(1) 1.4900(17); O(1)–P(1)–C(1) 113.93(10), O(1)–P(1)–C(6) 111.85(11), C(6)–P(1)–C(12) 106.08(11), C(1)–P(1)–C(6) 106.03(11).

has a distorted octahedral environment with the pyrrolato ligands in *trans* positions [N(pyr)–Ti–N(pyr) angles: **5a**, 164.0(2); **5c**, 164.40(17)°].

The cyclohexyl ligand **3d** reacts with $Ti(NMe_2)_4$ in analogues fashion to give **5d** (Scheme 4). However, unlike **5a** and **5c**, this complex adopts an all-*cis* geometry, with one pyrrolate moiety *trans* to dimethylamide, while the other is *trans* to a P=O donor (Fig. 4). This structural isomerism has a profound influence on the bonding of the O–N ligands. Whereas in **5a** and **5c** the



Scheme 4



Scheme 3

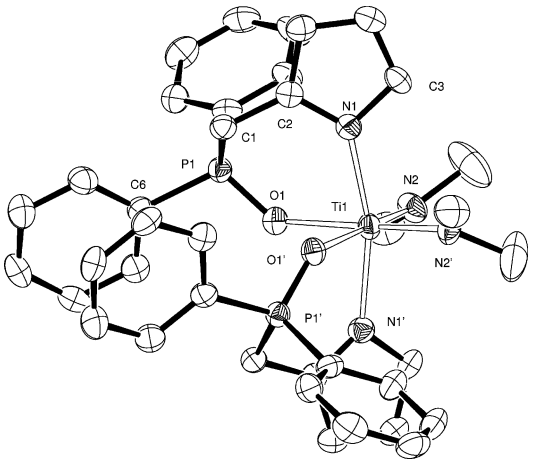


Fig. 2 Molecular structure of **5a** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–N(1) 2.147(4), Ti(1)–N(2) 1.913(3), Ti(1)–O(1) 2.121(4); N(1)–Ti(1)–N(1′) 164.0(2), N(2)–Ti(1)–O(1′) 173.98(18), N(1)–Ti(1)–O(1) 83.44(15). Symmetry operations to generate related atoms: ' $= -x, y, \frac{1}{2} - z$.

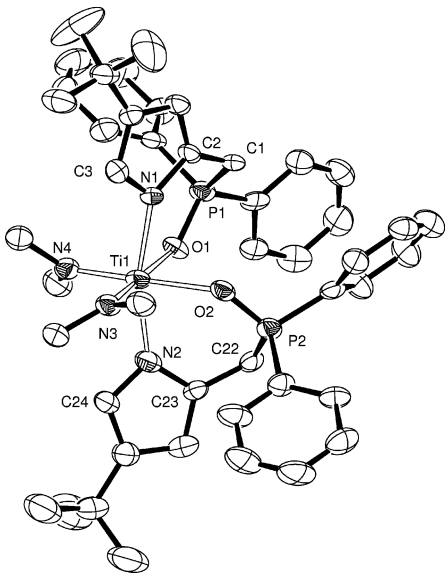


Fig. 3 Molecular structure of **5c**·2.5(C_6D_6) showing 50% probability ellipsoids. Hydrogen atoms and two and a half molecules of benzene have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–N(1) 2.144(4), Ti(1)–N(2) 2.146(5), Ti(1)–N(3) 1.907(4), Ti(1)–N(4) 1.913(4), Ti(1)–O(1) 2.148(3), Ti(1)–O(2) 2.120(3); N(1)–Ti(1)–N(2) 164.40(17), N(3)–Ti(1)–O(1) 176.36(16), N(4)–Ti(1)–O(2) 169.56(17), N(1)–Ti(1)–O(1) 85.53(15), O(2)–Ti(1)–N(2) 83.63(15).

Ti–N(pyr) distances are all about the same, *ca.* 2.14 Å, in **5d** they differ significantly, with the Ti–N(pyr) bond *trans* to NMe_2 being almost 0.1 Å longer than the one *trans* to O(1). The strong *trans* influence of the amido ligand is even more pronounced in the Ti–O bond lengths distribution, *i.e.* the bond *trans* to NMe_2 is 0.118 Å longer than the one *trans* to N(pyr). If one defines the equatorial plane as the one containing both NMe_2 ligands, this leads overall to an axial compression (sum of axial bond lengths in **5d** = 4.127 Å *versus ca.* 4.28 in **5a**,**c**), while all equatorial bonds are elongated

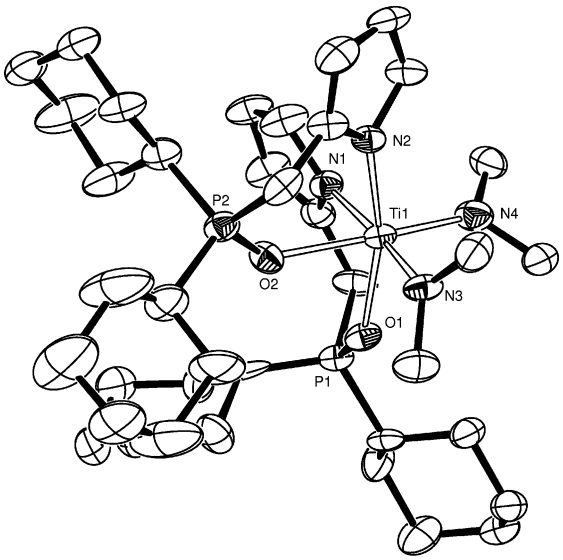


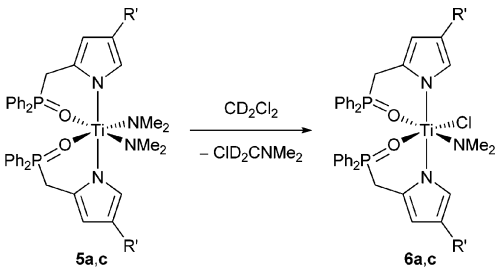
Fig. 4 Molecular structure of one of the two independent molecules of **5d** in the asymmetric cell, showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–N(1) 2.183(9), Ti(1)–N(2) 2.088(8), Ti(1)–N(3) 1.940(9), Ti(1)–N(4) 1.939(10), Ti(1)–O(1) 2.039(7), Ti(1)–O(2) 2.157(8); N(1)–Ti(1)–N(3) 176.0(4), N(4)–Ti(1)–O(2) 168.7(4), N(2)–Ti(1)–O(1) 164.4(3), O(1)–Ti(1)–N(1) 87.7(3), N(2)–Ti(1)–O(2) 85.0(3).

to varying degrees, with the Ti–NMe_2 bond lengths being least affected.

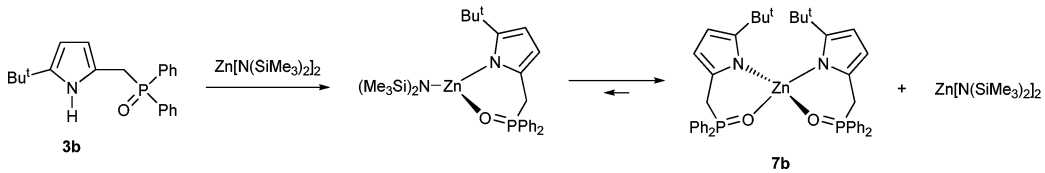
Crystals of **5d** shows evidence for twin components which could only partially be accounted for in the modelling procedure, resulting in high residual values. The structure also contains voids (*ca.* 68 $Å^3$), in which no significant electron density could be located. Despite these points, **5d** could be fully refined using the data set.

Efforts to obtain analogous titanium complexes from the bulkier, 5-Bu^t substituted ligand **3b** by reacting it with tetrakis(dimetylamido)titanium under a variety of conditions failed to give evidence for ligand coordination. Heating the mixture to 100 °C in a teflon-sealed NMR tube did cause a change in the $^{31}P\{^1H\}$ NMR but under such forcing conditions several phosphorus signals appeared which could not be assigned.

Since **5a** and **5c** have limited solubility in toluene, attempts were made to record the NMR spectra in dichlororomethane. Somewhat unexpectedly, the solutions changed colour from orange to dark red and gave much more complex spectra. Evidently, the complexes reacted readily with the solvent under formation of the mono-chloro derivatives **6a**,**c** (Scheme 5). For this



Scheme 5



3b **7b**

Scheme 6

reason the ^{13}C NMR spectra of **5a** and **5c** proved impossible to obtain.

The pattern of the PCH_2 moieties is particularly indicative: the reduction to C_1 symmetry produces two groups of CH_2P signals, a total of four signal sets since each CH_2 group is diastereotopic. In complexes **5** a multiplet and a doublet of doublets are present for the diastereotopic CH_2P groups. The reason for the difference in coupling patterns of these protons is clearer from the spectra of **6**. In **6**, one set of protons do in fact appear as the expected ABX doublet of doublets (at δ 3.88 and 3.43). The other set, however, shows also coupling to the proton in 3-position of the pyrrole ring and should thus appear as a doublet of doublet of doublets; actually, a virtual triplet is observed. The $^1H\{^{31}P\}$ NMR spectrum does indeed show the expected small coupling of one of the protons of the CH_2P group to the 3-proton of the pyrrole ring (see ESI†).

Both **6a** and **6c** proved to be unstable in solution and are poorly crystalline, precluding crystal structure determination. The identity of **6a**,**c** was established unequivocally by reaction of **5a**,**c** with trimethylchlorosilane in hexanes; identical spectra were obtained for the compounds synthesised by this route.

Since many zinc complexes show good activity as initiators for ring-opening polymerisations of cyclic esters, the reaction of **3b** with zinc amides was included in the present study. Thus treatment of $Zn[N(SiMe_3)_2]_2$ with one molar equivalent of **3b** in deuterated benzene, yields (N-O)ZnN$(SiMe_3)_2$ *in situ*. However, on removal of the solvent the product undergoes ligand exchange to give the sterically saturated 2 : 1 complex $Zn[NC_4H_3(5\text{-}Bu^t)\text{-}2\text{-}CH_2P(O)Ph_2]_2$ (**7b**) and free $Zn[N(SiMe_3)_2]_2$ (Scheme 6).

Compound **7b** was purified by extraction in toluene. Cooling this solution to −35 °C for 2 d gave colourless crystals of **7b**·toluene. The molecular structure is shown in Fig. 5. The geometry around the zinc is a distorted tetrahedron. The N(1)–Zn(1)–N(2) angle [136.21(14)°] is significantly wider than the O(1)–Zn(1)–O(2) angle [93.72(11)°]. The two ligands show differences in bond lengths and angles to the metal; this is presumably due to the need to accommodate the phenyl and *t*-butyl groups around the metal centre.

The reaction of **3a** with $Y[N(SiHMe_2)_2]_3(THF)_2$ in toluene also proceeds with complete exchange of the amide ligands to give the homoleptic complex $Y[NC_4H_3CH_2P(O)Ph_2]_3$ (**8a**) (Scheme 7). The intermediates **8-I** and **8-II** were observed whilst monitoring the reaction by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum showed formation of three new signals after 3 min reaction time (see ESI†); the ^{31}P NMR signals appear as doublets due to coupling to yttrium. In the corresponding ^1H NMR spectrum three N(SiHMe$_2$)$_2$ resonances are observed. The difficulties of synthesizing stable mixed-ligand group 3 complexes, such as intermediates **8-I** and **8-II**, are of course well documented and have recently been reviewed.[11]

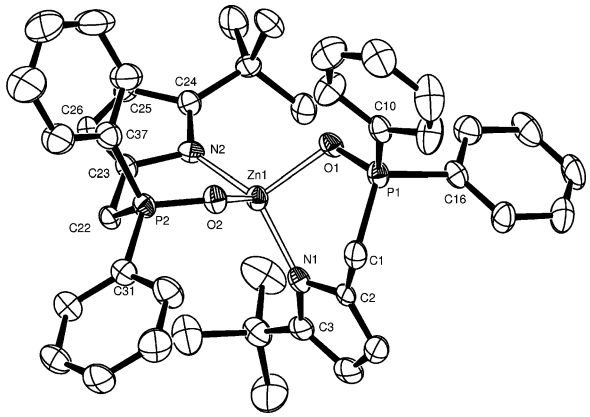


Fig. 5 Molecular structure of **7b**·PhMe. Ellipsoids are drawn at 50% probability. Hydrogen atoms and one molecule of toluene have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 1.953(3), Zn(1)–N(2) 1.918(3), Zn(1)–O(1) 2.017(3), Zn(1)–O(2) 2.062(3); N(1)–Zn(1)–O(1) 99.75(12), N(2)–Zn(1)–O(2) 96.97(12), N(1)–Zn(1)–N(2) 136.21(14), O(1)–Zn(1)–O(2) 93.72(11).

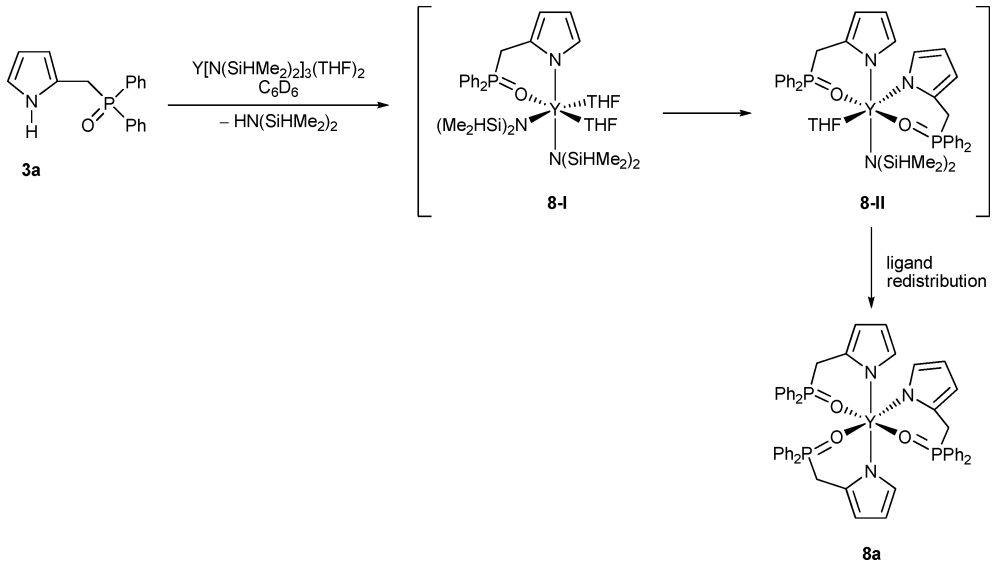
On cooling to 0 °C, **8a** precipitated as a white solid and was collected by filtration. Extraction of the white precipitate in toluene and cooling to −35 °C for 24 h, gave colourless blocks of **8a**·toluene suitable for X-ray diffraction (Fig. 6). Two of the nitrogen atoms are mutually *trans* while the third is *trans* to an O atom. However, unlike the titanium complexes, there are no meaningful differences between the bond lengths, and there is no significant *trans* effect in evidence.

By contrast, the reaction of the 5-*t*-butyl substituted pyrrole **3b** with $Y[N(SiHMe_2)_2]_3(THF)_2$ leads to the desired mixed-ligand yttrium amido complex $Y[N(SiHMe_2)_2][NC_4H_3(5\text{-}Bu^t)\text{-}2\text{-}CH_2P(O)Ph_2]_2$ (**9b**) (Scheme 8).

Cooling the reaction mixture in toluene to −30 °C for two days gave **9b** as very small colourless blocks, which did not prove suitable for X-ray crystallography. The $^{31}P\{^1H\}$ and ^{13}C and ^1H NMR spectra were however consistent with the formulation of **9b**. The ^1H NMR of **9b** demonstrates the formation of a single product, with just one set of signals for the pyrrolato and amido ligands. The hydrogen atoms of the CH_2P groups are again inequivalent and show a coupling pattern that is essentially identical as discussed above for the titanium complex **6a**. The $^{31}P\{^1H\}$ shows a single doublet at δ 43.82 ppm ($^2J_{P\text{-}Y} = 3.0$ Hz).

Ring-opening polymerisations

Complexes **5a**, **5d**, **7b**, **8a** and **9b** were tested as initiators in the ROP of ε-caprolactone (Table 1). **5d**, **7b** and **8a** are ineffective initiators towards the polymerisation of ε-caprolactone under the conditions tested. While this is not surprising for the comparatively stable bis-ligand zinc complex **7b**, yttrium complexes



Scheme 7

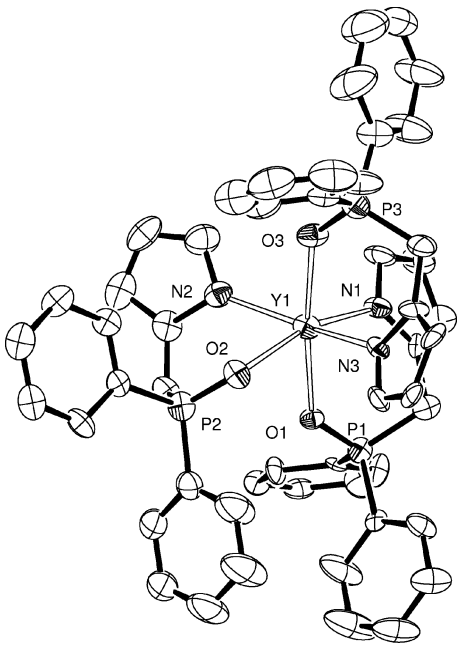
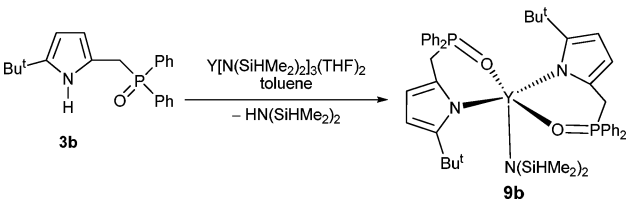


Fig. 6 Molecular structure of **8a**·PhMe. Ellipsoids are drawn at 50% probability. Hydrogen atoms and one molecule of toluene have been omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Y(1)–O(1) 2.268(8), Y(1)–O(2) 2.259(8), Y(1)–O(3) 2.234(9), Y(1)–N(1) 2.334(10), Y(1)–N(2) 2.361(11), Y(1)–N(3) 2.360(10); O(1)–Y(1)–O(3) 173.6(3), O(2)–Y(1)–N(1) 161.0(4), N(2)–Y(1)–N(3) 161.8(4).



Scheme 8

of a variety of structural types have been widely used in ring opening polymerisation reactions of cyclic esters.[12–17] Tris-chelate lanthanide complexes related to **8a** have shown good reactivity in such reactions even though opening of at least one chelate ring is required in the activation step; for example, Arnold *et al.* recently reported the synthesis of $Y[OCH(Bu^t)CH_2P(O)Bu^t_2]_3$ which shows high activity for the ROP of *rac*-lactide.[18] Evidently pyrrolate-based chelate complexes are either too stable or insufficiently nucleophilic to initiate these reactions.

The mono-amido complex **9b** is an effective initiator that rapidly polymerises ε-caprolactone with good molecular weight control and high initiator efficiency. Interestingly, the initiator efficiency rises with monomer concentration, from 22%, at [M] = 0.73 mol dm^{-3} to 75% at 4.0 mol dm^{-3}, giving ~7 turnovers s^{-1} at 20 °C.

In industry, solvent-free ROP processes[19–22] are of course preferred. To overcome viscosity problems, such reactions are best carried out at elevated temperatures (Table 1, runs 4–6). Under such conditions, **9b** demonstrated well-controlled behaviour at [M] : [I] = 200 : 1, with almost quantitative initiator efficiency and a high turnover frequency of >19 s^{-1}. Increasing [M] : [I] = 500 : 1 increases the TOF to ~31 s^{-1} but the polydispersity broadens (M_w/M_n = 2) and agreement between found and calculated number-average molecular weight is poorer.

The results of the polymerisation of *rac*-lactide with **9b** are summarised in Table 2. The reactivity of **9b** towards this monomer mirrors its reactivity with ε-caprolactone. The best control is accessible in the melt at high temperatures, where ≈100% initiator efficiency are obtained with narrow polydispersity (M_w/M_n = 1.3).

Conclusion

The first examples of 2-phosphorylmethyl-1*H*-pyrrolates and their complexes have been prepared. The ligands are readily accessible from the corresponding pyrrole aldehydes and dialkyl or diaryl phosphines in the presence of HCl in good yields. They form a

Table 1 Polymerisation of ε-caprolactone

Run	Init.	Time	Temp./°C	[Monomer]/ mol dm^{-3}	[M]/[I] ratio	Conv.[a] (%)	TOF/s^{-1} [b]	M_n/kg mol^{-1} [c]	M_n(calc)/ kg mol^{-1} [d]	M_w/M_n	Init. Eff. (%)
1	**5a**	15 h	20	0.73	100	17	0.002	5000	1938	1.2	39
2	**9b**	200 s	20	0.73	100	58	0.3	30 000	6612	1.6	22
3	**9b**	15 s	20	4.0	100	100	6.7	15 300	11 400	1.5	75
4	**9b**	10 s	80	9.44[e]	200	97	19.4	25 200	22 116	1.5	98
5	**9b**	15 s	80	9.44[e]	500	95	31.7	86 200	54 150	2.0	63
6	**9b**	1000 s	80	9.44[e]	1000	61	0.6	101 500	69 540	1.8	68

Conditions: 40 μm catalyst, solvent: toluene.[a] Conversion = weight of polymer obtained/weight of monomer used × 100. [b] TOF = turnover frequency. [c] Determined by GPC relative to polystyrene standards. [d] M_n(calc) = (molecular mass of M × conversion/100) × [M]/[I]. [e] Neat monomer.

Table 2 Polymerisation of *rac*-lactide using initiator **9b**

Time/s	Temp./°C	[Monomer] mol dm^{-3}	Conv.[a] (%)	TOF[b]/s^{-1}	M_n/kg mol^{-1} [c]	M_n(calc)/kg mol^{-1} [d]	M_w/M_n	Init. Eff.(%)
300	50	1.6	40	0.26	37 002	9280	1.3	25
15	140	5.98[e]	100	13.3	19 500	23 200	1.3	119

Conditions: 40 μm catalyst, solvent: THF, [M] : [I] = 200 : 1.[a] Conversion = weight of polymer obtained/weight of monomer used × 100. [b] TOF = turnover frequency. [c] Determined by GPC relative to polystyrene standards. [d] M_n(calc) = (molecular mass of M × conversion/100) × [M]/[I]. [e] Neat monomer.

new class of N–O chelate ligands, and provide a flexible ligand scaffold since their substitution patterns, and hence their steric and electronic properties, are readily modified. The reactions with Group 3 and 4 metals afford mono-, bis- and tris-ligated complexes, depending on the steric demand. The reaction with $Ti(NMe_2)_4$ octahedral complexes $(N–O)_2Ti(NMe_2)_2$ which show low reactivity towards cyclic esters but react with dichloromethane to give the mono-chloro derivatives. Unsubstituted phosphoryl-methylpyrroles protolyse $Y[N(SiHMe_2)_2]_3(THF)_2$ to give unreactive 3 : 1 products $Y(N–O)_3$, whereas the bulky 5-Bu^t substituted analogues lead to mixed-ligand species $(N–O^{t\text{-}Bu})_2Y\text{-}N(SiHMe_2)_2$ which are highly active for the polymerisation of ε-caprolactone and *rac*-lactide in the presence or absence of solvents. The highest initiator efficiencies, turnover frequencies and molecular weight control is achieved at elevated temperatures in neat monomer.

Experimental section

General procedures

Syntheses were performed under nitrogen using standard Schlenk line techniques. Solvents were distilled from sodium–benzophenone (diethyl ether, THF), sodium (toluene, ethyl acetate), sodium–potassium alloy (light petroleum, b.p. 40–60 °C), or CaH_2 (dichloromethane). NMR solvents (CD_2Cl_2, C_6D_6) were dried over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. ε-Caprolactone was dried for a minimum of 24 h over fresh calcium hydride, then distilled under vacuum and used immediately. *rac*-Lactide (LA) was recrystallised at −25 °C from a saturated dry ethyl acetate solution and then sublimed *in vacuo* at 130 °C before use. $Ti(NMe_2)_4$,[23] $Zn[N(SiMe_3)_2]_2$,[24] and $Y[N(SiHMe_2)_2]_2(THF)_2$,[25] 2-carboxaldehyde-1*H*-pyrrole-1-butoxycarbonyl,[26] 5-*t*-butyl-2-carboxaldehyde-1*H*-pyrrole-1-butoxycarbonyl,[26] 4-*t*-butyl-2-carboxaldehyde-1*H*-pyrrole-1-butoxycarbonyl[26] and *N,N*-dimethylpyrrole-2-formiminium chloride[9,10] were synthesised using literature procedures.

NMR spectra were recorded using Bruker DPX-300 spectrometer with a 5 mm BBO probe. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^1H, ^{13}C), ^{19}F is relative to $CFCl_3$. Nitrogen was purified by passing through columns of supported P_2O_5, with moisture indicator, and activated 4 Å molecular sieves. Elemental analyses were performed by London Metropolitan University. IR data of neat solids were recorded on a Perkin–Elemer Spectrum 1000 FT spectrometer equipped with a SensIR DuraSampl*IR* II diamond ATR attachment.

Polymer molecular weights were determined by gel permeation chromatography (GPC) using a Polymer Laboratories PL-GPC 220 instrument equipped with a PLgel 5 Å MIXED C column and a refractive index detector. The GPC column was eluted with THF at 40 °C at 1 cm^3 min^{-1} and was calibrated using 9 monodisperse polystyrene standards in the range 580–1 000 000 Da.

5-*t*-Butyl-1*H*-pyrrole-2-aldehyde[9,10]. To a suspension of *N,N*-dimethylpyrrole-2-formiminium chloride (6.2 g, 39 mmol) in 1,2-dichloroethane (40 cm^3) was added, *via* syringe, degassed *t*-butyl chloride (4.6 cm^3, 42 mmol). To this was added solid $AlCl_3$ (6.0 g, 45 mmol) in small portions and the reaction was allowed to warm up. The resultant orange solution was left to stir for ~2 h and then quenched by slowly adding ice-cold water. The product was extracted with water (300 cm^3) and the layers separated. To the aqueous layer was added excess aqueous KOH, which was subsequently acidified by adding concentrated HCl. The product was extracted with ethyl acetate (3 × 200 cm^3), the organic fractions were combined, dried over $MgSO_4$ and filtered. Removal of volatiles *in vacuo* gave a black oil of the title product. Recrystallisation in diethyl ether–light petroleum (2 : 3) at −30 °C gave the pure aldehyde as an off-white crystalline solid (3.39 g, 57%). ^1H NMR (300 MHz, 300 K, $CDCl_3$): δ 10.10 (br s, 1H, NH), 9.36 (s, 1H, CHO), 6.91–6.81 (m, 1H, pyrrole), 6.13–6.11 (m, 1H, pyrrole), 1.35 (s, 9H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ 178.43 (CHO), 152.08 (pyrrole), 131.62 (pyrrole), 122.83 (pyrrole), 107.21 (pyrrole), 32.03 (CMe_3), 30.02 (CMe_3) ppm.

4-*t*-Butyl-1*H*-pyrrole-2-aldehyde[9,10]. To a suspension of *N*,*N*-dimethylpyrrole-2-formiminium chloride (6.2 g, 39 mmol) in 1,2-dichloroethane (40 cm^3) at 0 °C was added *via* syringe degassed *t*-butyl chloride (4.6 cm^3, 42 mmol). To the resulting orange solution was added solid $AlCl_3$ (6.0 g, 45 mmol) slowly in small portions, while keeping the temperature as close to 0 °C as possible. After complete addition of $AlCl_3$, the reaction was stirred at 0 °C for 20 min, then allowed to reach room temperature and stirred for 52 h. The reaction was then quenched by the slow addition of ice-cold water. Work-up was as described for 5-*t*-butyl-1H-pyrrole-2-aldehyde. Recrystallisation in diethyl ether–light petroleum (1 : 1) at −30 °C gave the pure aldehyde as a yellow crystalline product (3.79 g, 65%). ^{1}H NMR (300 MHz, 300 K, $CDCl_3$): δ 9.61 (br s, 1H NH), 9.44 (s, 1H, CHO), 7.01–6.99 (m, 1H, pyrrole), 6.91–6.87 (m, 1H, pyrrole), 1.28 (s, 9H, Bu^t) ppm.^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ 179.20 (CHO), 138.58 (pyrrole), 132.48 (pyrrole), 122.52 (pyrrole), 111.37 (pyrrole), 32.03 (CMe$_3$), 30.02 (CMe_3) ppm.

2-Carboxaldehyde-1*H*-pyrrole-*N*-butoxycarbonyl. Pyrrole-2-carboxaldehyde (21.2 g, 223 mmol) and *N*,*N*-dimethyl-aminopyridine (0.86 g, 7.0 mmol) were dissolved in MeCN (250 cm^3), and stirred. Di-*t*-butyl dicarbonate (60.0 cm^3, 57.0 g, 261 mmol) was added slowly, and a large amount of gas was evolved. After stirring overnight, the solvent was removed *in vacuo*, and the product crystallised from EtOH (50 cm^3). Three crops of crystals were obtained, each yielding a yellow solid (combined 37.9 g, 87%). ^{1}H NMR (300 MHz, 300 K, $CDCl_3$): δ 10.32 (s, 1H, CHO), 7.43 (t, 1H, J = 2.1 Hz, pyrrole H^5), 7.18 (dd, 1H, J = 1.6, 3.7 Hz, pyrrole H^4), 6.28 (t, 1H, J = 3.4 Hz, pyrrole H^3), 1.63 (s, 9H, Bu^t) ppm.

2-Diphenylphosphorylmethyl-1*H*-pyrrole-*N*-butoxycarbonyl (2a). To a solution of 2-carboxaldehyde-1*H*-pyrrole-1-butoxycarbonyl (12.1 g, 62 mmol) in methanol (250 cm^3) were added diphenyl phosphine (12.5 cm^3, 62 mmol) and conc. hydrochloric acid (5.5 cm^3, 66 mmol). The reaction mixture was degassed and allowed to stir at room temperature for 16 h. The solvent volume was reduced under vacuum to 100 cm^3 and the solution was kept at 2 °C. A first crop of colourless crystals formed. The mother liquor was reduced to 40 cm^3 and kept at 2 °C to give another batch of crystals (combined yield 20.8 g, 91%). Anal. calcd for $C_{22}H_{24}NO_3P$: C, 69.28; H, 6.34; N, 3.67%. Found: C, 69.18; H, 6.33; N, 3.61%. IR (solid)/cm^{-1}: 3056, 2981, 2918, 1739 (C=O), 1333, 1313, 1186 (P=O). ^{1}H NMR (300 MHz, 300 K, $CDCl_3$): δ 7.69–7.65 (m, 4H, Ph), 7.43–7.26 (m, 6H, Ph), 7.08 (m, 1H, pyrrole H^4), 6.23–6.21 (m, 1H, pyrrole H^3), 6.06 (t, 1H, ^3J = 3.3 Hz, pyrrole H^5), 4.23 (d, 2H, ^2J = 14.0 Hz, PCH_2), 1.44 (s, 9H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ 148.23 (C=O), 131.93 (d, J_{C-P} = 99.3 Hz, aromatic C–P), 131.22 (d, $^3J_{C-P}$ = 9.3 Hz, *m*-Ph), 131.01 (d, $^4J_{C-P}$ = 2.5 Hz, *p*-Ph), 128.38 (d, $^2J_{C-P}$ = 11.7 Hz, *o*-Ph), 124.18 (d, $^2J_{C-P}$ = 8.2 Hz, pyrrole C^2), 121.60 (d, $^4J_{C-P}$ = 3.0 Hz, pyrrole C^4), 115.10 (d, $^3J_{C-P}$ = 6.6 Hz, pyrrole C^3), 110.42 (d, $^5J_{C-P}$ = 3.0 Hz, pyrrole C^5), 83.90 (OCMe$_3$), 30.42 (d, J_{C-P} = 69.0 Hz, CH$_2$P), 27.85 (CMe_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 300 K, 121 MHz): δ 33.47 ppm.

2-Diphenylphosphorylmethyl-5-*t*-butyl-1H-pyrrole-*N*-*t*-butoxycarbonyl (2b). This compound was made as described for **2a** using 5-*t*-butyl-2-carboxaldehyde-1*H*-pyrrole-1-butoxycarbonyl, as a cream microcrystalline solid in 61% yield. ^{1}H NMR (300 MHz, 300 K, $CDCl_3$): δ 7.67–7.42 (m, 10H, Ph), 5.87 (d, 1H, ^3J = 3.6 Hz, pyrrole H^3), 5.81 (d, 1H, ^3J = 3.6 Hz, pyrrole H^4), 3.94 (d, 2H, J_{H-P} = 14.7 Hz, PCH_2), 1.51 (s, 9H, Bu^t), 1.34 (s, 9H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ 151.33 (C=O), 144.73 (d, $^5J_{C-P}$ = 3.3 Hz, pyrrole C^5), 132.01 (d, J_{C-P} = 98.8 Hz, aromatic C–P), 131.75 (d $^4J_{C-P}$ = 2.7 Hz, *p*-Ph), 131.33 (d, $^3J_{C-P}$ = 9.3 Hz, *m*-Ph), 128.50 (d, $^2J_{C-P}$ = 11.5 Hz, *o*-Ph), 123.60 (d, $^2J_{C-P}$ = 7.1 Hz, pyrrole C^2), 111.40 (d, $^3J_{C-P}$ = 6.6 Hz, pyrrole C^3), 107.79 (d, $^4J_{C-P}$ = 2.7 Hz, pyrrole C^4), 83.69 (OCMe$_3$), 33.06 (CMe$_3$), 31.75 (d, J_{C-P} = 69.7 Hz, CH$_2$P), 30.62 (CMe_3), 27.77 (CMe_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 300 K, 121 MHz): δ 28.43 ppm.

2-Diphenylphosphorylmethyl-4-*t*-butyl-1*H*-pyrrole-*N*-*t*-butoxycarbonyl (2c). The compound was made as described for **2a** as a cream microcrystalline solid in 88% yield. ^{1}H NMR (300 MHz, 300 K, $CDCl_3$): δ 7.71–7.40 (m, 10H, Ph), 6.79 (m, 1H, pyrrole H^5), 6.17 (d, 1H, ^4J = 3.6 Hz, pyrrole H^3), 4.24 (d, 2H, $^2J_{H-P}$ = 14.1 Hz, PCH_2), 1.44 (s, 9H, Bu^t) 1.14 (s, 9H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ 149.45 (C=O), 136.80 (d, $^4J_{C-P}$ = 3.3, pyrrole C^4), 132.38 (d, J_{C-P} = 99.0 Hz, aromatic C–P), 131.88 (d, $^4J_{C-P}$ = 2.7 Hz, *p*-Ph), 131.38 (d, $^3J_{C-P}$ = 9.3 Hz, *m*-Ph), 128.40 (d, $^2J_{C-P}$ = 11.5 Hz, *o*-Ph), 123.86 (d, $^2J_{C-P}$ = 8.2 Hz, pyrrole C^2), 115.81 (d, $^5J_{C-P}$ = 3.3 Hz, pyrrole C^5), 114.54 (d, $^3J_{C-P}$ = 6.6 Hz, pyrrole C^3), 83.35 (OCMe$_3$), 30.96 (CMe$_3$), 30.77 (CMe_3), 30.72 (d, J_{C-P} = 68.6 Hz, CH$_2$P), 27.93 (CMe_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 300 K, 121 MHz): δ 31.33 ppm.

2-Dicyclohexylphosphorylmethyl-1*H*-pyrrole-*N*-*t*-butoxycarbonyl (2d). The compound was made as described for **2a**, using dicyclohexylphosphine. The crude product was washed with aqueous sodium bicarbonate, extracted with ethyl acetate and the organic fraction dried over $MgSO_4$. All volatiles were then evaporated and the resulting off-white solid was recrystallised in diethyl ether to give the title product as cream coloured needles, yield 58%. ^{1}H NMR (300 MHz, 300 K, $CDCl_3$): δ 7.17 (m, 1H, pyrrole H^4), 6.36 (m, 1H, pyrrole H^3), 6.08 (m, 1H, pyrrole H^5), 3.59 (d, 2H, ^2J = 12.3 Hz, PCH_2), 1.88–1.19 (m, 22H, Cy), 1.59 (s, 9H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ 149.87 (C=O), 125.78 (d, $^2J_{C-P}$ = 7.1 Hz, pyrrole C^2), 121.32 (d, $^4J_{C-P}$ = 2.7 Hz, pyrrole C^4), 114.70 (d, $^3J_{C-P}$ = 5.5 Hz, pyrrole C^3), 110.71 (d, $^5J_{C-P}$ = 2.2 Hz, pyrrole C^5), 83.70 (OCMe$_3$), 36.24 (d, J_{C-P} = 64.2 Hz, CH$_2$P), 28.03 (CMe_3), 26.81 (d, $^2J_{C-P}$ = 2.7 Hz, *o*-Cy), 26.65 (d, $^2J_{C-P}$ = 2.7 Hz, *o*-Cy), 26.03 (*p*-Cy), 25.76 (d, $^3J_{C-P}$ = 2.8 Hz, *m*-Cy), 25.52 (d, $^3J_{C-P}$ = 3.0 Hz, *m*-Cy), 23.58 (d, J_{C-P} = 57.1 Hz, Cy C–P) ppm. ^{31}P{^{1}H} NMR (121 MHz, 300 K, $CDCl_3$,): δ 48.67 ppm.

2-Dicyclohexylphosphorylmethyl-4-*t*-butyl-1H-pyrrole-*N*-*t*-butylcarbonyl (2e). The compound was made as described for **2a**, using dicyclohexylphosphine. In addition to that procedure; after removal of all volatiles *in vacuo*, the resulting off-white solid was washed with aqueous sodium bicarbonate, extracted with diethyl ether, dried over $MgSO_4$, filtered and recrystallised from diethyl ether to give the title product as colourless blocks in 55% yield. ^{1}H NMR (300 MHz, 300 K, $CDCl_3$): δ 6.88–6.87 (m, 1H, pyrrole H^5), 6.40–6.35 (m, 1H, pyrrole H^3), 3.56 (d, 2H, ^2J = 12.3 Hz, PCH_2), 1.92–1.20 (m, 22H, Cy), 1.58 (s, 9H, Bu^t), 1.21 (s, 9H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ 150.00 (C=O), 137.02 (d, $^4J_{C-P}$ = 2.7 Hz, pyrrole C^4), 125.70 (d, $^2J_{C-P}$ = 7.2 Hz,

pyrrole C^2), 115.31 (d, $^5J_{C-P}$ = 2.7 Hz, pyrrole C^5), 114.70 (d, $^3J_{C-P}$ = 5.5 Hz, pyrrole C^3), 83.70 (O*C*Me$_3$), 36.28 (d, $^2J_{C-P}$ = 64.2 Hz, CH$_2$P), 30.79 (C*Me*$_3$), 28.03 (C*Me*$_3$), 28.01 (*C*Me$_3$), 26.85 (d, $^2J_{C-P}$ = 3.0 Hz, *o*-Cy), 26.70 (d, $^2J_{C-P}$ = 3.0 Hz, *o*-Cy), 26.04 (*p*-Cy), 25.75 (d, $^3J_{C-P}$ = 2.3 Hz, *m*-Cy), 25.46 (d, $^3J_{C-P}$ = 3.0 Hz, *m*-Cy), 23.80 (d, J_{C-P} = 57.6 Hz, Cy C–P) ppm. ^{31}P{^{1}H} NMR (121 MHz, 300 K, CDCl$_3$,): δ 48.44 ppm.

2-Diphenylphosphorylmethyl-1*H*-pyrrole (3a). Sodium chunks (3.5 g, 152 mmol) were dissolved in ethanol (150 cm^3), cooling with ice as necessary. **2a** (10.31 g, 27 mmol) was suspended in ethanol (150 cm^3) and the ethoxide solution was added slowly. The reaction mixture was stirred at room temperature for 1 h before the solvent was removed *in vacuo*. The resulting solid was hydrolysed with aqueous ammonium chloride (200 cm^3). The water phase was extracted with dichloromethane (3 × 100 cm^3) and the combined organic phases washed with water (2 × 100 cm^3) and aqueous NaCl (2 × 100 cm^3). After drying over MgSO$_4$ the solvent was removed under vacuum. Recrystallisation of the crude product from ethanol gave the product as creamy-white needles (5.63 g, 74%). Anal. calcd for C$_{17}$H$_{16}$NOP: C, 72.59; H, 5.73; N, 4.98%. Found: C, 72.64; H, 5.67; N, 4.85%. IR (solid)/cm^{-1}: 3235 (N–H), 3140, 1573, 1438, 1173 (P=O). ^{1}H NMR (300 MHz, 300 K, CDCl$_3$): δ 9.39 (br s, 1H NH), 7.68–7.42 (m, 10H, Ph), 6.72–6.71 (m, 1H, pyrrole H^4), 6.07–6.04 (m, 1H, pyrrole H^3), 5.87 (m, 1H, pyrrole H^5), 3.66 (d, 2H, $^2J_{H-P}$ = 12.8 Hz, PC*H*$_2$) ppm. ^{13}C NMR (75 MHz, 300 K, CDCl$_3$): δ 131.97 (d, J_{C-P} = 99.3 Hz, aromatic C-P), 131.96 (d, $^4J_{C-P}$ = 2.6 Hz, *p*-Ph), 130.83 (d, $^3J_{C-P}$ = 9.4 Hz, *m*-Ph), 128.58 (d, $^2J_{C-P}$ = 11.8 Hz, *o*-Ph), 121.03 (d, $^2J_{C-P}$ = 9.4 Hz, pyrrole C^2), 118.23 (pyrrole C^4), 108.20 (d, $^3J_{C-P}$ = 7.5 Hz, pyrrole C^3), 107.86 (pyrrole C^5), 29.73 (d, J_{C-P} = 69.3 Hz, CH$_2$P) ppm. ^{31}P{^{1}H} NMR (121 MHz, 300 K, CDCl$_3$): δ 34.69 ppm.

2-Diphenylphosphorylmethyl-5-*t*-butyl-1*H*-pyrrole (3b).

Method A. The compound was made from **2b** as described for **3a**. In addition to the procedure for **3a** the reaction required refluxing for 20 h. The title product was isolated in 69% yield as a cream solid after standard organic work up.

Method B. To a solution of 5-*t*-butyl-1*H*-pyrrole-2-aldehyde (7.00 g, 46 mmol) in degassed methanol (150 cm^3) were added diphenylphosphine (9.25 cm^3, 46 mmol) and conc. hydrochloric acid (3.9 cm^3, 46 mmol). The resulting orange solution was stirred at room temperature for 16 h. The solvent volume was reduced under vacuum to ~50 cm^3 and the solution was kept at –30 °C for 36 h to give the title compound as an off-white microcrystalline solid (6.1 g, 39%). Anal. calcd for C$_{21}$H$_{24}$NOP: C, 74.76; H, 7.17; N, 4.15%. Found: C, 74.25; H, 6.77; N, 4.28%. ^{1}H NMR (300 MHz, 300 K, CDCl$_3$): δ 9.13 (br s, 1H, NH), 7.67–7.60 (m, 4H, Ph), 7.56–7.51 (m, 6H, Ph), 5.73–5.72 (m, 2H, pyrrole H^3 + H^4), 3.64 (d, 2H, $^2J_{H-P}$ = 13.2 Hz, PC*H*$_2$), 1.24 (s, 9H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, CDCl$_3$): δ 142.65 (d, $^5J_{C-P}$ = 3.3 Hz, pyrrole C^5), 132.15 (d, J_{C-P} = 98.8 Hz, aromatic C-P), 131.99 (d, $^4J_{C-P}$ = 2.7 Hz, *p*-Ph), 131.24 (d, $^3J_{C-P}$ = 9.3 Hz, *m*-Ph), 130.93 (d, $^2J_{C-P}$ = 12.1 Hz, *o*-Ph), 119.21 (d, $^2J_{C-P}$ = 9.3 Hz, pyrrole C^2), 107.58 (d, $^3J_{C-P}$ = 7.7 Hz, pyrrole C^3), 102.03 (d, $^4J_{C-P}$ = 1.1 Hz, pyrrole C^4), 31.34 (*C*Me$_3$), 30.46 (C*Me*$_3$), 30.08 (d, J_{C-P} = 69.2 Hz, CH$_2$P) ppm. ^{31}P{^{1}H} NMR (121 MHz, 300 K, CDCl$_3$,): δ 30.97 ppm.

2-Diphenylphosphorylmethyl-4-*t*-butyl-1*H*-pyrrole (3c). The compound was made as described for **3a** as cream needles after recrystallisation in ethanol at –20 °C in 81% yield. Anal. calcd for C$_{21}$H$_{24}$NOP: C, 74.76; H, 7.17; N, 4.15%. Found: C, 74.30; H, 7.01; N, 4.25%. ^{1}H NMR (300 MHz, 300 K, CDCl$_3$): δ 8.86 (br s, 1H, NH), 7.64–7.57 (m, 4H, Ph), 7.52–7.40 (m, 6H, Ph), 6.49–6.47 (m, 1H, pyrrole H^3), 5.76–5.73 (m, 1H, pyrrole H^5), 3.60 (d, 2H, $^2J_{H-P}$ = 12.7 Hz, PC*H*$_2$), 1.16 (s, 9H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, CDCl$_3$): δ 135.54 (d, $^4J_{C-P}$ = 3.3 Hz, pyrrole C^4), 132.11 (d, J_{C-P} = 99.4 Hz, aromatic C-P), 131.70 (d, $^4J_{C-P}$ = 2.7 Hz, *p*-Ph), 130.51 (d, $^3J_{C-P}$ = 9.3 Hz, *m*-Ph), 128.54 (d, $^2J_{C-P}$ = 11.5 Hz, *o*-Ph), 120.80 (d, $^2J_{C-P}$ = 9.3 Hz, pyrrole C^2), 113.02 (d, $^3J_{C-P}$ = 7.7 Hz, pyrrole C^3), 106.93 (d, $^5J_{C-P}$ = 1.1 Hz, pyrrole C^5), 31.67 (*C*Me$_3$), 30.45 (d, J_{C-P} = 69.2 Hz, CH$_2$P), 30.42 (C*Me*$_3$) ppm. ^{31}P{^{1}H}-NMR (121 MHz, 300 K, CDCl$_3$): δ 31.67 ppm.

2-Dicyclohexylphosphorylmethyl-1*H*-pyrrole (3d). The compound was made as described for **3a** as a sticky cream solid in 78% yield. Anal. calcd for C$_{17}$H$_{28}$NOP: C, 69.60; H, 9.62; N, 4.77%. Found: C, 69.09; H, 9.35; N, 4.85%. ^{1}H NMR (300 MHz, 300 K, CDCl$_3$): δ 9.52 (br s, 1H, NH), 6.72–6.71 (m, 1H, pyrrole H^4), 6.10–6.08 (m, 1H, pyrrole H^3), 5.91 (m, 1H, pyrrole H^5), 3.03 (d, 2H, $^2J_{H-P}$ 11.0 Hz, PC*H*$_2$), 1.93 - 1.16 (m, 22H, Cy) ppm. ^{13}C NMR (75 MHz, 300 K, CDCl$_3$): δ 122.87 (d, J_{C-P} = 8.8 Hz, pyrrole C^2), 117.72 (pyrrole C^4), 107.80 (pyrrole C^5), 107.08 (d, $^3J_{C-P}$ = 7.1 Hz, pyrrole C^3), 36.56 (d, J_{C-P} = 63.7 Hz, CH$_2$P), 26.66 (d, $^2J_{C-P}$ = 2.0 Hz, *o*-Cy), 26.50 (d, $^2J_{C-P}$ = 2.4 Hz, *o*-Cy), 25.87 (*p*-Cy), 25.66 (d, $^3J_{C-P}$ = 2.6 Hz, *m*-Cy), 25.07 (d, $^3J_{C-P}$ = 3.4 Hz, *m*-Cy), 22.45 (d, J_{C-P} = 57.8 Hz, Cy C–P) ppm. ^{31}P{^{1}H} NMR (121 MHz, 300 K, CDCl$_3$,): δ 51.65 ppm.

2-Dicyclohexylphosphorylmethyl-4-*t*-butyl-1H-pyrrole (3e). The compound was made as described for **3a** as a sticky cream solid in 84% yield. Anal. calcd for C$_{21}$H$_{36}$NOP: C, 72.17; H, 10.38; N, 4.01%. Found: C, 71.78; H, 9.89; N, 4.43%. ^{1}H NMR (300 MHz, 300 K, CDCl$_3$): δ 9.00 (br s, 1H, NH), 6.50–6.48 (m, 1H, pyrrole H^5), 5.87–5.84 (m, 1H, pyrrole H^3), 3.01 (d, 2H, $^2J_{H-P}$ = 10.8 Hz, PC*H*$_2$), 1.90–1.16 (m, 22H, Cy), 1.22 (s, 9H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, CDCl$_3$): δ 135.61 (pyrrole C^4), 122.90 (d, $^2J_{C-P}$ = 7.7 Hz, pyrrole C^2), 112.64 (pyrrole C^5), 105.75 (d, $^3J_{C-P}$ = 6.8 Hz, pyrrole C^3), 35.72 (d, $^2J_{C-P}$ = 62.9 Hz, CH$_2$P), 31.79 (C*Me*$_3$), 30.48 (*C*Me$_3$), 27.22 (d, $^2J_{C-P}$ = 4.0 Hz, *o*-Cy), 26.55 (d, $^2J_{C-P}$ = 4.6 Hz, *o*-Cy), 25.89 (*p*-Cy), 25.60 (d, $^3J_{C-P}$ = 2.6 Hz, *m*-Cy), 24.97 (d, $^3J_{C-P}$ = 3.3 Hz, *m*-Cy), 23.29 (d, J_{C-P} = 57.3 Hz, Cy C–P) ppm. ^{31}P{^{1}H} NMR (121 MHz, 300 K, CDCl$_3$,): δ 51.54 ppm.

Ti(NMe$_2$)$_3${NC$_4$H$_3$-2-CH$_2$P(O)Ph$_2$} (4a). To a suspension of **3a** (0.2 g, 0.7 mmol) in toluene (20 cm^3) at –78 °C was added slowly Ti(NMe$_2$)$_4$ (0.47 cm^3, 2.1 mmol) in toluene (75 cm^3), resulting in an orange solution. The mixture was stirred for 1 h. The solvent and excess Ti(NMe$_2$)$_4$ were then removed under reduced pressure and the orange solid residue was extracted with light petroleum (20 cm^3). On removal of all volatiles *in vacuo*, **4a** was obtained as a yellow-orange solid (0.17 g, 55%). Anal Calc for TiC$_{23}$H$_{33}$N$_4$OP: C, 60.00; H, 7.22; N, 12.17%. Found: C, 59.80; H, 6.99; N, 12.51%. ^{1}H NMR (300 MHz, 300 K, C$_6$D$_6$): δ 7.37–7.18 (m, 4H, Ph), 7.08 (m, 1H, pyrrole H^4), 7.05–6.99 (m, 6H, Ph), 6.72 (m, 1H, pyrrole H^3), 6.33 (m, 1H, pyrrole H^5), 3.64 (d, 2H, $^2J_{H-P}$ = 11.9 Hz, PC*H*$_2$), 3.52, (s, 18H, NMe$_2$) ppm. ^{13}C NMR (75 MHz, 300 K, C$_6$D$_6$): δ 132.21 (d, $^4J_{C-P}$ = 3.9 Hz, *p*-Ph), 131.81 (pyrrole C^4), 131.45 (d, $^3J_{C-P}$ = 11.2 Hz, *m*-Ph), 129.82 (d, J_{C-P} = 102.4 Hz, aromatic

C–P), 128.41 (d, $^2J_{C\text{-}P} = 12.5$ Hz, *o*-Ph), 122.74 (d, $^2J_{C\text{-}P} = 7.9$ Hz, pyrrole C^2), 109.18 (d, $^3J_{C\text{-}P} = 7.7$ Hz, pyrrole C^3), 107.65 (pyrrole C^5), 47.52 (NMe_2), 30.39 (d, $J_{C\text{-}P}$= 64.8 Hz, CH_2P) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, C_6D_6,): δ 40.05 ppm.

Ti(NMe$_2$)$_3${NC$_4$H$_3$(4-Bu^t)CH$_2$P(O)Ph$_2$} **(4c).** This compound was synthesised as described for complex **4a** and obtained as a yellow-orange solid in 65% yield. Anal Calc for $TiC_{27}H_{41}N_4OP$: C, 62.79; H, 8.00; N, 10.85. Found: C, 62.80; H, 7.89; N, 10.51. ^1H NMR (300 MHz, 300 K, C_6D_6): δ 7.32–7.26 (m, 4H, Ph), 7.12–7.08 (m, 7H, Ph + pyrrole H^5), 6.11 (s, 1H, pyrrole H^3), 3.59 (d, 2H, $^2J_{H\text{-}P} = 12.00$ Hz, PC*H*$_2$), 3.53, (s, 18H, NMe_2), 1.68 (s, 9H, Bu^t) ppm. $^{31}P\{^1H\}$-NMR (121 MHz, 300 K, C_6D_6,): δ 40.22 ppm.

Ti(NMe$_2$)$_2${NC$_4$H$_3$CH$_2$P(O)Ph$_2$}$_2$ (5a). To a suspension of **3a** (0.2 g, 0.7 mmol) in toluene (40 cm^3) at −78 °C was slowly added $Ti(NMe_2)_4$ (0.08 cm^3, 0.35 mmol) in toluene (25 cm^3), resulting in an orange solution. The solvent and excess $Ti(NMe_2)_4$ were removed under reduced pressure and the orange solid residue was washed with light petroleum (100 cm^3) and extracted in toluene (3 × 75 cm^3). Cooling of the toluene solution to 5 °C overnight yielded orange crystals of **5a** (0.41 g, 85%). Anal Calc for $TiC_{38}H_{42}N_4O_2P_2$: C, 65.52; H, 6.08; N, 8.04%. Found: C, 65.10; H, 6.16; N 7.95%. ^1H NMR (300 MHz, 300 K, CD_2Cl_2): δ 7.70–7.32 (m, 20H, Ph), 6.87 (br s, 2H, pyrrole), 6.33 (br s, 2H, pyrrole), 5.94 (br s, 2H, pyrrole), 4.12 (br m, 1H, PC*H*H), 3.59 (s, 12H, NMe_2), 3.22 (br m, 1H, PCH*H*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, C_6D_6): δ 40.49 ppm.

Ti(NMe$_2$)$_2${NC$_4$H$_3$(4-Bu^t)CH$_2$P(O)Ph$_2$}$_2$ (5c). The compound was made as described for **5a** in 78% yield as orange crystals suitable for X-ray crystallography. Anal Calc for $TiC_{46}H_{58}N_4O_2P_2$: C, 68.31; H, 7.23; N, 6.93%. Found: C, 68.83; H, 7.81; N, 7.12%. ^1H NMR (300 MHz, 300 K, CD_2Cl_2): δ 7.76 (br s, 2H, pyrrole H^5), 7.24–6.80 (m, 20H, Ph), 6.08 (br s, 2H, pyrrole H^3), 4.08–3.96 (m, 1H, PC*H*H), 3.74 (s, 12H, NMe_2), 3.22 (dd, $^2J_{H\text{-}P} = 8.9$ Hz, $^2J_{H\text{-}H} = 5.1$ Hz, 1H, PCH*H*), 1.74 (s, 9H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, C_6D_6): 132.51 (pyrrole C^4), 132.16–131.41 (m. Ph), 125.79 (pyrrole C^5), 121.49 (d, $^2J_{C\text{-}P}$ = 9.2 Hz, pyrrole C^2), 106.44 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, pyrrole C^3), 50.30 (NMe_2), 33.00 (C*Me$_3$*), 31.61 (d, $J_{C\text{-}P}$ = 65.8 Hz, CH_2P), 31.05 (*C*Me$_3$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, C_6D_6): δ 40.32 ppm.

Ti(NMe$_2$)$_2${NC$_4$H$_3$CH$_2$P(O)Cy$_2$}$_2$ (5d). The compound was prepared from **3d** as described for **5a** in 61% yield as orange crystals suitable for X-ray crystallography. Anal Calc for $TiC_{38}H_{66}N_4O_2P_2$: C, 63.32; H, 9.23; N, 7.77; Found; C, 62.93; H, 8.91; N, 7.32. ^1H NMR (300 MHz, 300 K, C_6D_6): δ 8.12 (m, 1H, pyrrole H^4), 7.05 (s, 1H, pyrrole H^4), 6.90 (m, 1H, pyrrole H^5), 6.61 (m, 1H, pyrrole H^5), 6.41 (m, 1H, pyrrole H^3), 6.35 (s, 1H, pyrrole H^3), 3.84–2.89 (m, 2H, PC*H*H), 3.63 (s, 6H, NMe_2), 3.61 (s, 6H, NMe_2), 3.32–3.23 (m, 1H, PC*H*H), 3.06–2.97 (m, 1H, PC*H*H), 1.86–1.03 (m, 44H, Cy) ppm. ^{13}C NMR (75 MHz, 300 K, C_6D_6): δ 131.94 (d, $^4J_{C\text{-}P}$ = 1.0 Hz, pyrrole C^4), 131.46 (d, $^4J_{C\text{-}P}$ = 1.0, pyrrole C^4), 124.55 (d, $^2J_{C\text{-}P} = 9.2$ Hz, pyrrole C^2), 123.19 (d, $^2J_{C\text{-}P} = 10.2$ Hz, pyrrole C^2), 106.69–106.00 (m, pyrrole C^3 + C^5), 51.58 (NMe_2), 48.76 (NMe_2), 35.37 (d, $J_{C\text{-}P} = 56.5$ Hz, CH_2P), 34.59 (d, $J_{C\text{-}P}$ = 64.09 Hz, CH_2P), 27.07–25.08 (m, 24C, Cy) ppm. $^{31}P\{^1H\}$-NMR (121 MHz, 300 K, C_6D_6): δ 62.29, 58.54 ppm.

TiCl(NMe$_2$){NC$_4$H$_3$CH$_2$POPh$_2$}$_2$ (6a). On dissolving **5a** (0.07 g, 0.10 mmol) in dichloromethane in an NMR tube an orange solution was obtained. Over a period of 2 h the solution turned dark red. After removal of all volatiles under *vacuo* the title complex was observed as a dark-red solid (0.07 g, 0.10 mmol, 100%). Anal Calc for $TiC_{36}H_{36}ClN_3O_2P_2$: C, 62.85; H, 5.27; N, 6.11, Found; C, 62.43; H, 5.15; N, 6.26 ^1H NMR (300 MHz, 300 K, CD_2Cl_2): δ 7.59–7.31 (m, 20H, Ph), 7.10 (s, 1H, pyrrole), 7.05–7.00 (m, 1H, pyrrole), 6.60–6.55 (s, 1H, pyrrole), 5.99–5.97 (s, 2H, pyrrole), 5.59 (s, 1H, pyrrole), 4.70 (ddd, 1H, $^2J_{H\text{-}P} = 16.6$ Hz, $^2J = 7.4$ Hz, $^4J = 3.9$ Hz, PC*H*H), 4.22 (ddd, 1H, $^2J_{H\text{-}P} = 16.0$ Hz, $^2J = 6.3$ Hz, $^4J = 4.1$ Hz, PCH*H*), 3.88 (dd, 1H, $^2J_{H\text{-}P} = 9.2$ Hz, $^2J = 6.3$ Hz, PC*H*H), 3.77 (s, 6H, NMe_2) 3.43 (dd, 1H, $^2J_{H\text{-}P}$ = 7.4 Hz, ^2J = 7.4 Hz, PCH*H*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, CD_2Cl_2): 44.65, 44.33 ppm.

TiCl(NMe$_2$){NC$_4$H$_3$(4-Bu^t)CH$_2$P(O)Ph$_2$)$_2$ (6c). On dissolving **5c** (0.08 g, 0.10 mmol) in CD_2Cl_2 in an NMR tube an orange solution was obtained which darkened to red over 2 h at 20 °C. After removal of all volatiles under vacuum, **6c** was observed as a dark-red solid as a mixture of two isomers (70:30) (0.08 g, 0.10 mmol, 100%). Anal Calc for $TiC_{36}H_{36}ClN_3O_2P_2$: C, 66.04; H, 6.55; N, 5.25, Found; C, 65.56; H, 6.38; N, 5.31. The same products was produced by reaction of **5c** with 1.4 equivalents of trimethylchlorosilane in hexanes. ^1H NMR (300 MHz, 300 K, CD_2Cl_2) (most abundant isomer only): δ 7.95–6.92 (m, 20H, Ph), 6.98–6.92 (m, 1H, pyrrole H^5), 6.44–6.37 (s, 1H, pyrrole H^5), 5.81 (s, 1H, pyrrole H^3), 5.41 (s, 1H, pyrrole H^3), 4.86–4.75 (m, 1H, PC*H*H), 4.29–4.18 (m, 1H, PCH*H*), 3.69 (br s, 7H, NMe_2 + PC*H*H), 3.34 (dd, 1H, $^2J_{H\text{-}P} = 8.7$, $^2J = 5.3$ Hz, PCH*H*), 1.26 (s, 9H, Bu^t), 1.19 (s, 9H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, CD_2Cl_2) (most abundant isomer only): δ 132.84–127.63 (m, pyrrole C^4 + Ph), 127.23 (d, $^5J_{C\text{-}P} = 1.6$ Hz pyrrole C^5), 125.69 (d, $^5J_{C\text{-}P} = 1.3$ Hz pyrrole C^5), 123.90 (d, $^2J_{C\text{-}P} = 7.3$ Hz pyrrole C^2), 123.73 (d, $^2J_{C\text{-}P}$ = 7.3 Hz pyrrole C^2), 105.30 (d, $^3J_{C\text{-}P} = 7.7$ Hz pyrrole C^3), 104.21 (d, $^3J_{C\text{-}P} = 8.2$ Hz pyrrole C^3), 51.61 (NMe_2), 32.37 (C*Me$_3$*), 31.90 (C*Me$_3$*), 31.81 (*C*Me$_3$), 31.12 (d, $J_{C\text{-}P}$ = 84.3 Hz, CH_2P), 30.36 (*C*Me$_3$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, CD_2Cl_2): 50.25, 48.04 (minor isomer) 43.96, 43.00 (major isomer).

Zn{NC$_4$H$_3$(5-Bu^t)CH$_2$P(O)Ph$_2$}$_2$ (7b). To a solution of **3b** (0.88 g, 2.6 mmol) in toluene (40 cm^3) was added $Zn[N(SiMe_3)_2]_2$ (0.5 g, 1.3 mmol). The resultant orange solution was left to stir overnight. After removal of volatiles *in vacuo* the product was washed with light petroleum, extracted into toluene, filtered and cooled to −30 °C for 24 h to give **7b** as colourless blocks (0.49 g, 77%). Anal. Calcd. for $C_{42}H_{46}N_2O_2P_2Zn$: C, 68.34; H, 6.28; N, 3.80%. Found: C, 68.2; H, 6.34; N, 3.75%. ^1H NMR (300 MHz, 300 K, C_6D_6): δ 7.63–7.53 (m, 8H, Ph), 7.24–6.99 (m, 12H, Ph), 6.64 (d, 2H, ^3J = 3.02, pyrrole H^3), 6.46–6.45 (m, 2H, pyrrole H^4), 4.15 (dd, 2H, $^2J_{C\text{-}P} = 12.3$ Hz, $^2J = 3.6$ Hz, C*H*HP) 3.95 (dd, 2H, $^2J_{C\text{-}P} = 12.1$ Hz, $^2J = 4.0$ Hz, CH*H*P), 1.79 (s, 18H, Bu^t) ppm. ^{13}C NMR (75 MHz, 300 K, C_6D_6): δ 151.58 (d, $^5J_{C\text{-}P} = 2.5$ Hz, pyrrole C^5), 132.83 (d, $^4J_{C\text{-}P} = 2.4$ Hz, *p*-Ph), 132.08 (d, $^4J_{C\text{-}P} = 2.4$ Hz, *p*-Ph), 131.71 (d, $^3J_{C\text{-}P} = 10.3$ Hz, *m*-Ph), 131.45 (d, $^3J_{C\text{-}P} = 10.3$ Hz, *m*-Ph), 130.42 (d, $J_{C\text{-}P} = 60.6$ Hz, aromatic C–P), 129.29 (d, $J_{C\text{-}P}$ = 54.5 Hz, aromatic C–P), 128.52 (d, $^2J_{C\text{-}P} = 12.1$ Hz, *o*-Ph), 124.12 (d, $^2J_{C\text{-}P} = 11.3$ Hz, pyrrole C^2), 109.94 (d, $^3J_{C\text{-}P} = 8.0$ Hz, pyrrole C^3), 104.32 (pyrrole C^4), 32.93 (*C*Me$_3$), 32.65 (d, $J_{C\text{-}P} = 86.0$ Hz,

Table 3 Crystal and refinement data

Compound	**3a**	**5a**	**5c**·2.5(C_6H_6)	**5d**	**7b**·(C_7H_7)	**8a**·(C_7H_8)
Empirical formula	$C_{17}H_{16}NOP$	$C_{38}H_{42}N_4O_2P_2Ti$	$C_{46}H_{58}N_4O_2P_2Ti$·2.5(C_6H_6)	$C_{38}H_{66}N_4O_2P_2Ti$	$C_{42}H_{46}N_2O_2P_2Zn$·C_7H_8	$C_{51}H_{45}N_3O_3P_3Y$·C_7H_8
Formula weight	281.28	696.60	1004.07	720.79	830.25	1021.85
Temperature/K	120(2)	120(2)	140(2)	120(2)	140(2)	140(2)
Crystal size/mm	0.04 × 0.08 × 0.10	0.01 × 0.09 × 0.09	0.01 × 0.09 × 0.09	0.05 × 0.08 × 0.12	0.06 × 0.20 × 0.40	0.04 × 0.08 × 0.12
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$Pbcn$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	11.3992(3)	15.392(5)	12.1366(13)	10.7254(5)	11.2743(8)	14.899(3)
b/Å	5.7594(1)	12.636(5)	16.2331(17)	19.2509(7)	11.3563(8)	18.890(3)
c/Å	22.1848(5)	18.352(5)	16.3753(17)	19.6142(8)	18.7268(13)	22.165(3)
α/°	90	90	108.236(9)	81.173(3)	81.072(6)	90
β/°	95.068(1)	90	95.852(9)	88.666(2)	75.302(6)	127.768(10)
γ/°	90	90	107.144(9)	89.788(3)	74.362(6)	90
V/Å^3	1450.79(6)	3569(2)	2860.2(6)	4000.8(3)	2223.6(3)	4931.2(16)
Z	4	4	2	4	2	4
μ/mm^{-1}	0.184	0.368	0.250	0.330	0.664	1.329
D_{calcd}/g cm^{-3}	1.288	1.296	1.166	1.197	1.240	1.376
No. of reflections collected	18 282	32 736	29 354	44 782	30 544	40 276
No. of unique reflections	3329	4102	9990	10 375	10 334	6410
R_{int}	0.065	0.172	0.1019	0.0865	0.0927	0.380
R_1 [$I > 2\sigma(I)$]	0.055	0.096	0.081	0.124	0.060	0.089
wR_2 (all data)	0.117	0.182	0.227	0.334	0.165	0.182

CH_2P), 32.55 (CMe_3) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, C_6D_6,): δ 40.39 ppm.

Y{NC$_4$H$_3$CH$_2$P(O)Ph$_2$}$_3$ (8a). To a stirred solution of Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (0.2 g, 0.28 mmol) in toluene (40 cm^3) at −78 °C was slowly added *via* cannula a suspension of **3a** (0.24 g, 0.84 mmol) in toluene (45 cm^3). The resultant yellow-orange solution was allowed to warm to room temperature and stirred for 12 h. The volatiles were removed and the off-white solid residue extracted with dichloromethane (3 × 25 cm^3). Recrystallisation from toluene at −30 °C gave colourless blocks of **8a**·toluene suitable for X-ray diffraction. (0.17 g, 64%). Anal. Calcd. for $C_{51}H_{45}N_3O_3P_3Y$: C, 65.88; H, 4.88; N, 4.52%. Found: C, 65.48; H, 4.43; N, 3.99%. ^{1}H NMR (300 MHz, 300 K, CD_2Cl_2): δ 7.46–7.58 (m, 12H, Ph), 7.36–7.19 (m, 18H, Ph), 6.94 (m, 3H, pyrrole H^4), 5.98 (m, 3H pyrrole H^3), 5.89 (m, 3H, pyrrole H^5), 3.76 (d, $^2J_{H-P}$ = 11.2 Hz, 6H, CH_2P) ppm. ^{13}C NMR (75 MHz, 300 K, CD_2Cl_2): δ 135.55 (pyrrole C^4), 132.08–129.07 (m, Ph), 128.92 (d, $^2J_{C-P}$ = 11.8 Hz, *o*-Ph), 119.47 (d, $^2J_{C-P}$ = 5.1 Hz, pyrrole C^2), 109.72 (d, $^3J_{C-P}$ = 7.5 Hz, pyrrole C^3), 108.32 (pyrrole C^5), 29.64 (d, J_{C-P} = 67.1 Hz, CH_2P) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, CD_2Cl_2,): δ 45.61 (d, $^2J_{P-Y}$ = 4.5 Hz) ppm.

Y{N(SiHMe$_2$)$_2$}{NC$_4$H$_3$(5-Bu^t)CH$_2$P(O)Ph$_2$}$_2$ (9b). To a stirred solution of Y[N(SiMe$_2$H)$_2$]$_3$(THF)$_2$ (0.4 g, 0.56 mmol) in toluene (40 cm^3) was added a stirred suspension of **3b** (0.4 g, 1.2 mmol) in toluene. The resultant orange solution was left to stir overnight. The solvent was concentrated *in vacuo* and cooled to −30 °C for 48 h to give **9b** as small colourless blocks (0.23 g, 50%). Anal. Calcd. for $C_{46}H_{60}N_3O_2P_2Si_2Y$: C, 61.80; H, 6.76; N, 4.70. Found: C, 61.71, H, 6.68, N, 5.12%. ^{1}H NMR (300 MHz, 300 K, C_6D_6): δ 7.55–7.49 (m, 8H, Ph), 7.13–7.02 (m, 12H, Ph), 6.32 (m, 2H, pyrrole H^3), 6.20 (m, 2H pyrrole H^4), 5.79 (m, 1H, *H*SiMe$_2$), 4.17 (m, 2H, C*H*HP), 3.31 (dd, 2H, $^2J_{H-P}$ = 8.1 Hz, ^2J = 7.7 Hz, CH*H*P), 1.64 (s, 18H, Bu^t), 0.65 (br s, 12H, SiMe$_2$) ppm. ^{13}C NMR (75 MHz, 300 K, C_6D_6): δ 153.24 (pyrrole C^5), 132.43–131.89 (m, Ph), 128.55 (d, $^2J_{C-P}$ = 12.1 Hz, *o*-Ph), 122.52 (d, $^2J_{C-P}$ = 9.9 Hz, pyrrole C^2), 110.41 (d, $^3J_{C-P}$ = 8.8 Hz, pyrrole C^3), 104.36 (pyrrole C^4), 33.56 (CMe_3), 33.04 (CMe_3), 29.97 (d, $^1J_{C-P}$ = 66.9 Hz, CH_2P), 3.16 (SiMe$_2$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, 300 K, CD_2Cl_2,): δ 43.82 (d, $^2J_{P-Y}$ = 3.0 Hz) ppm.

Polymerisations.

ε-*Caprolactone.* A solution of the catalyst (40 μmol) in toluene (0.5 cm^3), either at room temperature or pre-heated in an oil bath was added to the required quantity of ε-caprolactone, neat or in a solution of toluene. After the required time the reaction was quenched with acetic acid (5% in methanol) and the mixture poured into 50 cm^3 methanol. The polymer precipitated over 5 h. The solid was the filtered, dissolved in THF and reprecipitated from methanol. The polymer was then dried under reduced pressure until a constant mass was obtained.

rac-*Lactide.* A pre-heated solution of catalyst (40 μmol) at 50 °C in toluene (0.5 cm^3) was added to either a solution of *rac*-LA (1.15 g, 8.0 mmol) in toluene (4.5 cm^3) at 50 °C or neat *rac*-LA (1.15 g, 8.0 mmol) at 140 °C. The reaction was quenched with acetic acid (5% in methanol) and the mixture was poured into 100 cm^3 methanol. The polymer precipitated over 5 h. The solid was the filtered, dissolved in THF and reprecipitated from methanol. The polymer was then dried under reduced pressure to constant mass.

X-ray crystallography. In all cases, crystals were suspended in perfluoronated polyether oil, mounted on glass fibres and transferred directly to the cold N_2 stream of the diffractometer. Data for compounds 3**a**, **5a** and **5d** were collected on a Bruker–Nonius KappaCCD diffractometer, and for compounds **5c**, **7b** and **8a** were collected on an Oxford Diffraction Xcalibur diffractometer with Sapphire-3 CCD detector. Both diffractometers were equipped with molybdenum targets [λ(Mo Kα) = 0.71069 Å].

Data collection and processing were carried out using APEX2 and SAINT,[27] DENZO and SCALEPACK (**3a**, **5a** and **5d**),[28] or CrysAlis CCD and RED (**5c**, **7b** and **8a**).[29]

Structures were determined by direct methods using SHELXS (**3a**, **5a** and **5d**)[30] or SIR-92 (**5c**, **7b** and **8a**).[31] In all cases refinement was carried out by full-matrix least-squares methods using SHELXL-97[30] within the WinGX suite.[32] Non-hydrogen atoms (except those for solvent molecules in **5c** and **8a**) were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model. Crystals of **8a** were weakly diffracting and data were collected only to $2\theta = 45°$. Crystals of **5d** were found to be twinned, and this could only partially be accounted for in the refinement process. As a result, the residual electron density in this structure was high.

Crystal and refinement data are collected in Table 3.†

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