Reactions of phosphavinyl Grignard reagents with aldehydes: synthesis, characterisation and further reactivity of β-phosphaallylic alcohols

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The reactions of the phosphavinyl Grignard reagents, *Z*-[RP=C(Bu^t)MgCl(OEt$_2$)], R = cyclohexyl (Cy) or cyclopentyl (Cy^P), with benzaldehyde have afforded the β-phosphaallylic alcohols, *Z*-RP=C(Bu^t)C(H)(OH)Ph, after quenching with methanol. This methodology has been successfully applied to a series of other alkyl, aryl and functionalised aldehydes. The β-phosphaallylic alcohol, *Z*-CyP=C(Bu^t)C(H)(OH)Ph, undergoes unusual reactions with ZnEt$_2$, M{N(SiMe$_3$)$_2$} (M = Na or K) and Sn{N(SiMe$_3$)$_2$}$_2$ to give three isomers (*Z,Z*-, *Z,E*- and *E,E*-) of the bis(alkenyl)diphosphine mono-oxide, PhC(H)=C(Bu^t)P(Cy)P(=O)(Cy)C(Bu^t)=C(H)Ph. By contrast its reaction with Ti(OPr^i)$_4$ led to the formation of the secondary phosphine oxide, *Z*-CyP(H)(=O)C(Bu^t)=C(H)Ph. A facile synthesis of the phosphaalkenes, *E*-RP=C(H)Bu^t, R = Cy or mesityl (Mes), is also reported, as is an unusual tungsten complex of one of these, [{W(CO)$_4$[η^1-P,η^2-P=C–CyP=C(H)Bu^t]}$_2$]. The X-ray crystal structures of seven of the reported complexes are discussed.

Introduction

In recent years we have been investigating the reactivity of phosphavinyl Grignard reagents, *Z*-[RP=C(Bu^t)MgCl(OEt$_2$)] **1**, R = alkyl or aryl, towards main group and transition metal halide complexes.[1–8] This work has shown that phosphavinyl Grignard reagents in some cases behave similarly to vinyl Grignard reagents in that they form terminal phosphavinyl-metal complexes. More often than not, however, they behave differently in that they undergo facile metal mediated phosphavinyl coupling reactions to give a variety of novel heterocyclic and/or metallo-cage compounds. We are also interested in exploring the analogy between phosphavinyl and vinyl Grignard reagents in organic synthesis and see **1** as being potentially very useful synthons in this respect. A brief hint of this potential has come from previous work by Bickelhaupt *et al.* who have examined the cross-coupling of a sterically hindered phosphavinyl Grignard reagent with aryl halides,[9] and the 1,2-addition reactions of the phosphavinyl magnesium carbenoid, [Mes*P=C(Cl)MgBr], Mes* = C$_6$H$_2$Bu$^t_3$-2,4,6, with acetophenone and acetyl chloride which gave the expected β-phosphaallylic alcohol and phosphaenone products.[10] Herein, we report our efforts to extend this work to the reactions of the less hindered Grignard reagents, **1**, with mono- and dialdehydes. The further reactivity of generated β-phosphaallylic alcohols towards metal alkyls, amides and alkoxides has given a variety of unexpected results.

Results and discussion

In the initial stages of this study the reaction of *Z*-[CyP=C(Bu^t)MgCl(OEt$_2$)] **1a**, Cy = cyclohexyl, with benzaldehyde was carried out and the mixture quenched with aqueous HCl. This did not give the expected phosphaallylic alcohol, CyP=C(Bu^t)C(H)(OH)Ph, but instead the saturated (2-hydroxylalkyl)phosphine oxide, **2**, which could only be crystallised in low yield as its *SRR*/*RSS* enantiomeric pair (Scheme 1). Compound **2** presumably forms as a result of addition of water to the P=C bond of the phosphaallylic alcohol during the quenching procedure. The spectroscopic data for **2** are consistent with its proposed structure. Its ^{31}P{^{1}H} NMR spectrum displays a singlet at δ 46.2 ppm which is in the typical region for (2-hydroxylalkyl)phosphines.[11] In addition its infra-red spectrum exhibits an O–H stretching band at 3418 cm^{-1} which is strongly suggestive of the hydroxy functionality participating in hydrogen bonding.

A crystal structure analysis was carried out on **2** and the molecular structure of its *SRR* isomer is depicted in Fig. 1 (see Table 1†). It should be noted that the compound crystallises in the centrosymmetric space group, $P2_1/n$, and therefore its *RSS* enantiomer is present in equal amounts in the same crystal. The compound is monomeric and contains an intramolecular hydrogen bond between O(1) and H(19) [1.78(5) Å, O(1)–H(19)–O(2) 151(1)°]. In addition, the P(1)–O(1) distance [1.499(2) Å] is in the normal range for a double bond and all other interactions are consistent with single bonds.[12]

In order to avoid P=C addition products, the reaction of **1a** with benzaldehyde was repeated and in this case quenching with methanol led to the β-phosphaallylic alcohol, **3a**, in moderate yield. The generality of this reaction was tested by treating a series of alkyl, aryl and functionalised aldehydes with two phosphavinyl Grignard reagents, **1a** and **1b**, Cy^P = cyclopentyl, which in all cases afforded the expected product, **3**–**4**,

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† CCDC reference numbers 212717–212723. See http://www.rsc.org/suppdata/nj/b3/b306607j/ for crystallographic data in .cif or other electronic format.

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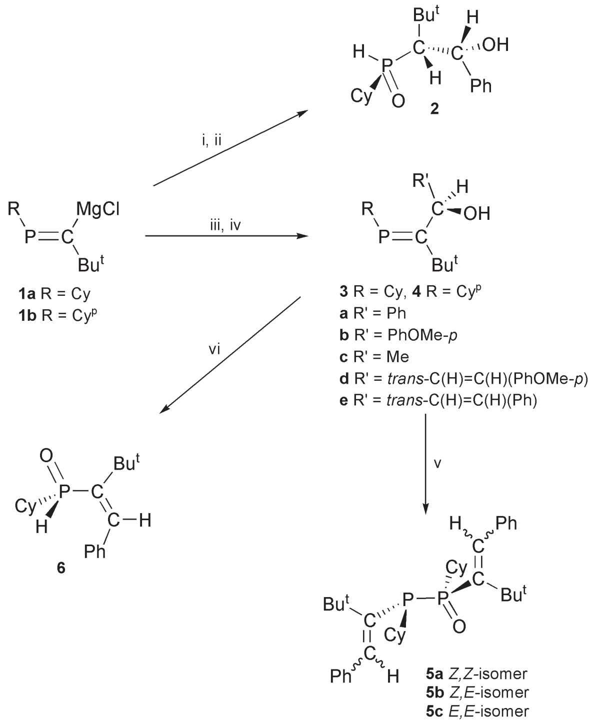


Scheme 1 *Reagents and conditions:* i, R = Cy, PhC(O)H, Et_2O; ii, HCl/H_2O; iii, R′C(O)H, Et_2O; iv, methanol; v, R = Cy, R′ = Ph, $ZnEt_2$, M{N(SiMe$_3$)$_2$} M = Na or K, Et_2O; vi, R = Cy, R′ = Ph, Ti(OPr^i)$_4$, Et_2O.

in high yields (Scheme 1). The ^{31}P {^{1}H} NMR spectra of **3**–**4** each display low field singlet resonances in a narrow chemical shift range (257.7–273.1 ppm) which is compatible with the P=C double bonds in these compounds.[13] The fact that only one resonance is seen in the spectrum of each compound confirms that their syntheses are stereospecific, presumably for the *Z*-isomers. The infra-red spectra of **3**–**4** all exhibit O–H stretching absorptions at frequencies consistent with their alcoholic functionalities participating in hydrogen bonding. A crystal structure analysis was carried out on one compound, **3a**, to confirm its proposed structure and *Z*-stereochemistry (Fig. 2, Table 1). The compound was found to crystallise with two independent molecules in the asymmetric unit which have essentially identical geometries and are held together with a single hydrogen bond [O(2)–H(1) 2.10(4) Å, O(1)–H(1)–O(2) 165(1)°]. Of note are the P(1)–C(1) and P(2)–C(19) bond lengths (1.682 Å avge.) which are normal for fully localised double bonds.[13]

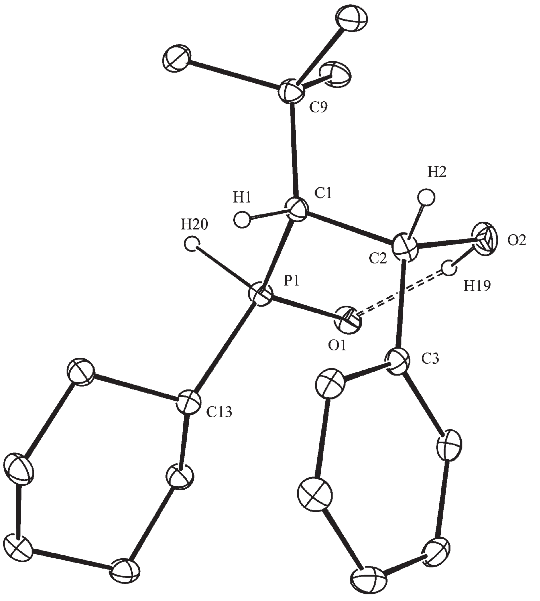


Fig. 1 Molecular structure of compound **2**. Selected bond lengths (Å) and angles (°): P(1)–O(1) 1.4992(19), P(1)–C(13) 1.814(3), P(1)–C(1) 1.832(3), P(1)–H(20) 1.36(3), O(2)–C(2) 1.438(3), C(1)–C(2) 1.559(4), O(1)–P(1)–C(1) 111.63(12), O(1)–P(1)–C(13) 114.49(12), C(2)–C(1)–P(1) 108.77(18).

It was thought of interest to attempt the reactions of the phosphaallylic alcohol, **3a**, with a series of main group and transition metal alkyls, amides and alkoxides in order to generate metal-phosphaallylic alkoxides of the type, [M{OC(Ph)C(Bu^t)=P(Cy)}$_n$], as these could potentially exhibit intramolecular η^1-P and or η^2-P=C coordination to the metal centre. To this end **3a** was reacted with $ZnEt_2$, Sn{N(SiMe$_3$)$_2$}$_2$, Na{N(SiMe$_3$)$_2$} and K{N(SiMe$_3$)$_2$} which, surprisingly, led to the same outcome in all cases, *i.e.* the high yield formation of the bis(alkenyl)diphosphine mono-oxide compound, PhC(H)=C(Bu^t)P(Cy)P(Cy)(=O)C(Bu^t)=C(H)Ph, as a mixture of its *Z,Z*-, **5a**, *Z,E*-, **5b**, and *E,E*-, **5c**, isomers (Scheme 1). All three isomers are separable by fractional crystallisation and have been spectroscopically and crystallographically characterised. Interestingly, their formation rates were found to be greatly dependent on the base used. The reactions involving Na{N(SiMe$_3$)$_2$} and K{N(SiMe$_3$)$_2$} were over within 30 minutes, whilst that involving $ZnEt_2$ was complete after 48 hours. More sluggish still was the reaction of **3a** with Sn{N(SiMe$_3$)$_2$}$_2$ which was only 50% complete after 14 days.

In an attempt to elucidate the mechanism of formation of **5**, the reaction of **3a** with $ZnEt_2$ was carefully monitored by ^{31}P{^{1}H} NMR spectroscopy. After 30 minutes only one singlet at 273.1 ppm corresponding to **3a** was observable. After 2 hours two new singlet resonances at 270.6 and 271.5 ppm began to appear. After 16 hours, the resonance for **3a** had disappeared and after 40 hours the two new resonances had been replaced by those for **5**. It seems likely that the intermediate low field resonances are due to the originally predicted zinc alkoxide, [Zn{OC(Ph)C(Bu^t)=PCy}$_2$], which would exist as two diastereoisomers due to the chiral carbon centre in each alkoxide ligand. The mechanism by which this compound converts, essentially quantitatively, to **5** is unknown but one possibility is that it undergoes a series of rearrangement and coupling reactions which involve the elimination of ZnO. Similarly, the reactions involving the alkali metal amide starting materials could involve elimination of M_2O, but these would have to be intermolecular processes. Insoluble powders were obtained as by-products in all these reactions but attempts to identify them as metal oxides by X-ray powder diffraction failed as they gave no discernable diffraction patterns. We know of no similar coupling reactions that involve metal oxide elimination in organophosphorus chemistry, however rhenium alkoxides are known to decompose to rhenium oxides with concomitant alkyl coupling reactions.[14]

The ^{31}P{^{1}H} NMR spectra of compounds **5** display similar AB patterns with resonances in the region of *ca.* δ 50–60 ppm corresponding to the P(V) centres and δ 0–20 ppm for the P(III) centre. The couplings between the two phosphorus centres are in the normal region for one bond P–P interactions and are close to those in related compounds, *e.g.* Ph$_2$P(=O)PPh$_2$.[15] All other spectroscopic data for **5** are consistent with their structures which were confirmed by X-ray crystal structure analyses. The molecular structures of **5a–c** are depicted in Figs. 3–5 (see Table 1). All compounds are monomeric and display P–P, C=C and P=O bond lengths in the normal regions.[12] It is of note that each compound contains two chiral phosphorus centres and all crystallise as their *SR*/*RS* diastereoisomers.

In a similar reaction to those that formed **5**, the alcohol, **3a**, was treated with 1 equiv. of [Ti(OPr^i)$_4$] in diethyl ether and the reaction monitored by ^{31}P{^{1}H} NMR spectroscopy.

Table 1 Crystal data for compounds **2**, **3a**, **5a-c**, **6** and **9**

	2	3a	5a	5b	5c	6	9
Chemical formula	$C_{18}H_{29}O_2P$	$C_{18}H_{27}OP$	$C_{36}H_{52}OP_2$	$C_{36}H_{52}OP_2$	$C_{36}H_{52}OP_2$	$C_{18}H_{27}OP$	$C_{30}H_{42}O_8P_2W_2$
Fw	308.38	290.37	562.72	562.72	562.72	290.37	960.28
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/c$
a (Å)	6.0830(12)	12.988(3)	14.908(3)	11.235(2)	10.787(2)	6.3490(13)	25.598(5)
b (Å)	19.234(4)	14.268(3)	10.424(2)	14.236(3)	11.073(2)	14.028(3)	9.4670(19)
c (Å)	14.925(3)	18.557(4)	20.972(4)	21.449(4)	15.414(3)	19.120(4)	17.439(4)
α (°)	90	90	90	90	80.23(3)	90	90
β (°)	100.12(3)	97.76(3)	97.64(3)	103.64(3)	69.52(3)	95.05(3)	125.82(3)
γ (°)	90	90	90	90	79.05(3)	90	90
V (Å^3)	1719.1(6)	3407.4(12)	3230.1(11)	3333.8(11)	1682.6(6)	1696.3(6)	3426.8(12)
Z	4	8	4	4	2	4	4
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
μ (Mo-Kα) (mm^{-1})	0.163	0.156	0.161	0.156	0.154	0.157	6.846
Reflections collected	16 590	23 049	26 407	28 003	14 339	29 071	27 823
Unique reflections (R_{int})	2988 (0.1020)	5894 (0.1052)	5668 (0.1011)	5856 (0.0829)	5859 (0.0656)	3294 (0.0975)	3935 (0.1137)
R 1 ($I > 2\sigma(I)$)	0.0556	0.0538	0.0531	0.0751	0.0916	0.0408	0.0393
$wR2$ (all data)	0.1249	0.1134	0.1085	0.19	0.2767	0.1024	0.0882

This showed a sluggish reaction in which the signal corresponding to **3a** was replaced over 8 days by several signals including two prominent singlets at δ 48 and 29 ppm. Upon work-up a moderate yield of the *Z*-isomer of the secondary phosphine oxide, **6**, was obtained as a crystalline solid (Scheme 1). This was subsequently shown by $^{31}P\{^1H\}$ NMR spectroscopy to be the compound that gave rise to the signal at δ 29 ppm in the reaction mixture. The identity of the other product could not be determined despite considerable effort. The mechanism of formation of **6**, which is an isomer of **3a**, is unknown but one possibility is that the reaction of **3a** with $[Ti(OPr^i)_4]$ initially leads to an intermediate titanium phosphaallylic alkoxide, $[Ti(OPr^i)_3\{OC(Ph)C(Bu^t)=P(Cy)\}]$, which was not observed in the spectroscopic monitoring of the reaction. This could then rapidly decompose to give **5**, as in the aforementioned related reactions, and the presence of adventitious water could lead to hydrolysis of the P–P bond of **5** to give **6**, its corresponding *E*-isomer and both isomers of the phosphinous acid, $CyP(OH)C(Bu^t)=C(H)Ph$, one of which could have given rise to the singlet at δ 48 ppm. In line with this speculation is the fact that this signal does not exhibit a one bond PH coupling in the corresponding proton coupled ^{31}P NMR spectrum. Diphosphines are generally considered to be reasonably inert to P–P bond hydrolysis but this can occur under alkaline conditions[16] as in the reaction mixture that afforded **6**. To test this theory an ethereal solution of the isomeric mixture of **5** was treated with 1 equiv. of water in the presence of zinc hydroxide and indeed two major singlet resonances rapidly appeared at δ 48 and 29 ppm in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture. X-ray crystallography confirmed the structure of **6** (Fig. 6, Table 1) which was found to be monomeric with no extraordinary intermolecular interactions.

In an attempt to generate bifunctional β-phosphaallylic alcohols, the dialdehydes benzene-1,2-; -1,3- and -1,4-dicarboxaldehyde were reacted with 2 equiv. of **1a**. No reactivity was observed for the 1,2-dicarboxaldehyde whilst the reactions involving the 1,3- and 1,4-dicarboxaldehydes afforded oily, inseparable mixtures after quenching with methanol and extraction of the products into hexane. In order to circumvent this problem, **1b** was reacted with the 1,3- and 1,4-dicarboxaldehydes which in the former gave the expected bis-phosphaallylic alcohol, **7** (Scheme 2), whilst the latter reaction

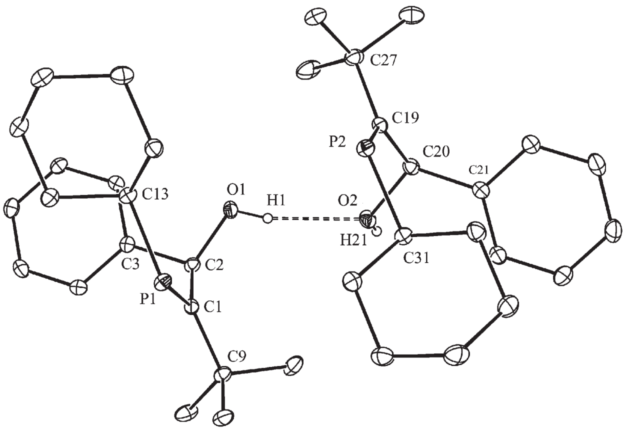


Fig. 2 Molecular structure of compound **3a**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.681(2), P(2)–C(19) 1.682(3), O(1)–C(2) 1.424(3), O(2)–C(20) 1.444(3), C(1)–C(2) 1.540(3), C(19)–C(20) 1.528(3), C(1)–P(1)–C(13) 108.65(11), C(19)–P(2)–C(31) 108.78(12), C(9)–C(1)–P(1) 118.80(17), C(2)–C(1)–P(1) 125.30(18), O(1)–C(2)–C(3) 107.74(19), O(1)–C(2)–C(1) 112.11(19), O(2)–C(20–C(19) 106.88(19), O(2)–C(20)–C(21) 112.1(2).

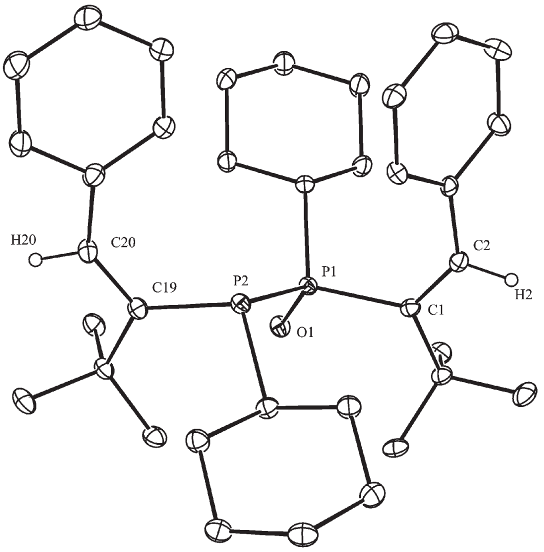


Fig. 3 Molecular structure of compound **5a**. Selected bond lengths (Å) and angles (°): P(2)–P(1) 2.2489(10), C(1)–C(2) 1.343(3), C(19)–(20) 1.347(3), P(1)–O(1) 1.4923(18), C(1)–P(1) 1.857(2), C(19)–P(2) 1.847(2), C(2)–C(1)–C(9) 120.4(2), C(2)–C(1)–P(1) 123.24(18), C(9)–C(1)–P(1) 115.80(17), C(20)–C(19)–C(27) 116.6(2), C(20)–C(19)–P(2) 116.2(2), C(27)–C(19)–P(2) 127.25(17), P(2)–P(1)–O(1) 116.32(7).

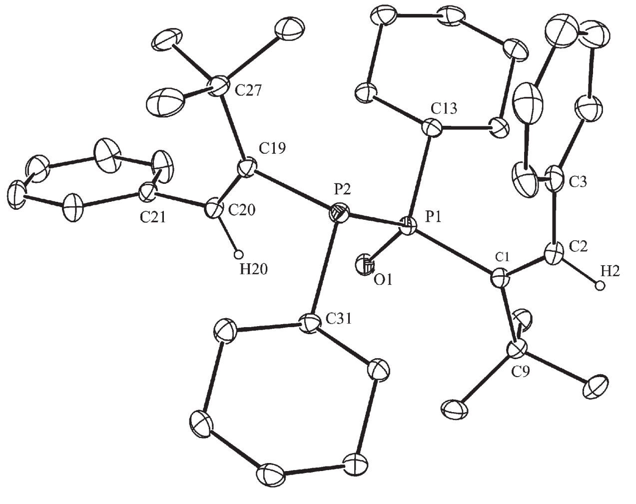


Fig. 4 Molecular structure of compound **5b**. Selected bond lengths (Å) and angles (°): P(2)–P(1) 2.2493(13), C(1)–C(2) 1.334(5), C(19)–(20) 1.329(5), P(1)–O(1) 1.489(2), C(1)–P(1) 1.856(3), C(19)–P(2) 1.870(3), C(2)–C(1)–C(9) 120.8(3), C(2)–C(1)–P(1) 122.3(3), C(9)–C(1)–P(1) 116.9(3), C(20)–C(19)–C(27) 128.0(3), C(20)–C(19)–P(2) 117.0(3), C(27)–C(19)–P(2) 115.0(3), P(2)–P(1)–O(1) 114.18(10).

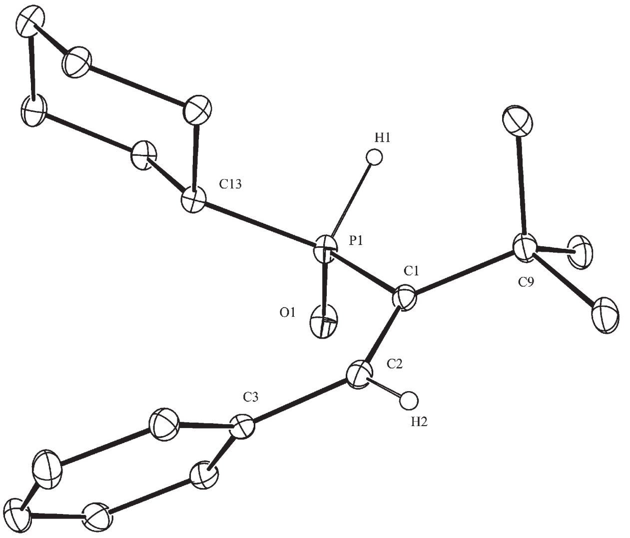


Fig. 6 Molecular structure of compound **6**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.8197(17), P(1)–O(1) 1.4865(13), C(1)–C(2) 1.339(2), C(2)–C(3) 1.481(2), C(1)–C(9) 1.541(2), C(2)–C(1)–P(1) 120.61(12), C(9)–C(1)–P(1) 116.89(12), C(2)–C(1)–C(9) 122.44(15), O(1)–P(1)–C(1) 114.94(8).

gave an intractable mixture of products. Compound **7** was isolated as colourless crystals which, unfortunately, were not of suitable quality for X-ray analysis. Its $^{31}P\{^{1}H\}$ NMR spectrum displays two singlet resonances at δ 272.2 and δ 272.1 ppm which were assigned to its two diastereoisomers. These could not be completely separated by standard methods though the ratio of the two isomers was approximately 80 : 20 in the recrystallised material. Attempts to react **7** with either $ZnEt_2$ or $M\{N(SiMe_3)_2\}$ (M = Na or K) resulted in complex mixtures of inseparable products.

Efforts were made to extend this study by examining the reactions of phosphavinyl Grignard reagents with a series of other unsaturated organic substrates such as imines, esters, carboxylic acids, isocyanides and cyanides. In all cases, however, no reactivity was observed. By contrast, the reactions of **1a** with ketones such as acetophenone or 4-*tert*-butylcyclohexanone yielded the phosphaalkene, *E*-CyP=C(H)Bu^t, **8a**. This suggests that the basicity of **1a** is too high to undergo nucleophilic addition to the enolizable ketones. An intentional, high yielding synthesis of compound **8a** was achieved by the direct addition of methanol to **1a** (Scheme 2). Its $^{31}P\{^{1}H\}$ NMR spectrum exhibits a low field singlet at 257.8 ppm, whilst a characteristic vinylic proton signal at δ 8.64 ppm was observed in its ^{1}H NMR spectrum ($^{2}J_{PH}$ = 24.8 Hz). Considering the stereochemistry of **1a**, it was not unexpected for **8a** to acquire *E*- stereochemistry upon its formation. The assignment of this stereochemistry is supported by the size of the $^{2}J_{PH}$ coupling which is in the characteristic range for *E*-phosphaalkenes, according to the "*cis*-rule".[17] The generality of the reaction that yielded **8a** was tested by treating the mesityl substituted phosphavinyl Grignard reagent, **1c**, Mes = 2,4,6-trimethylphenyl, with methanol which led to a high yield of the *E*-phosphaalkene, **8b**. This compound has been fully spectroscopically characterised.

Because compound **8a** is an oil, attempts were made to form a crystalline complex of it *via* its treatment with $[W(CO)_5(THF)]$, though this led to a complex mixture of phosphorus containing products. One complex, **9** (Scheme 2), was, however, obtained as a crystalline solid in very low yield (< 1%). Because of this it could not be spectroscopically characterised but its X-ray crystal structure was obtained, the details of which are included here due to its novelty. The molecular structure of the compound (Fig. 7, Table 1) shows it to be dimeric with each phosphaalkene ligand coordinated to two $W(CO)_4$ fragments through both an η^1-P interaction, [P(1)–W(1′), 2.546 (2) Å] and a longer η^2-P=C interaction [P(1)–W(1), 2.5689(16) Å; C(1)–W(1), 2.457 (6) Å]. As is

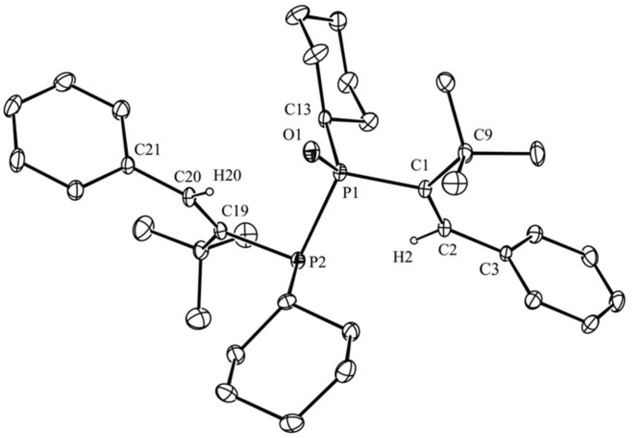
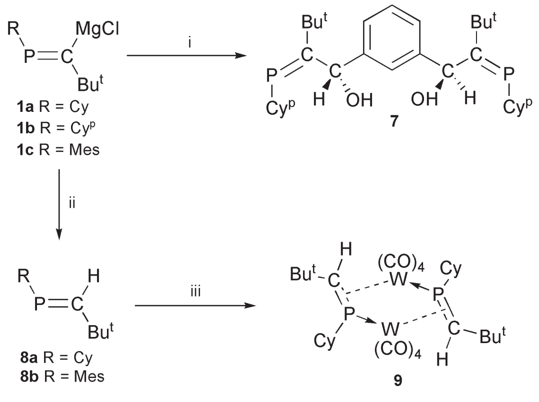


Fig. 5 Molecular structure of compound **5c**. Selected bond lengths (Å) and angles (°): P(2)–P(1) 2.2459(18), C(1)–C(2) 1.332(6), C(19)–(20) 1.334(6), P(1)–O(1) 1.499(3), C(1)–P(1) 1.853(4), C(19)–P(2) 1.878(4), C(2)–C(1)–C(9) 128.0(4), C(2)–C(1)–P(1) 115.1(3), C(9)–C(1)–P(1) 116.9(3), C(20)–C(19)–C(27) 128.2(4), C(20)–C(19)–P(2) 117.4(3), C(27)–C(19)–P(2) 114.3(3), P(2)–P(1)-O(1) 111.00(15).



Scheme 2 *Reagents and conditions:* i, R = Cy^P, $C_6H_4\{C(O)H\}_2$-1,3, Et_2O; ii, methanol, Et_2O; iii, R = Cy, $W(CO)_5(THF)$, THF.

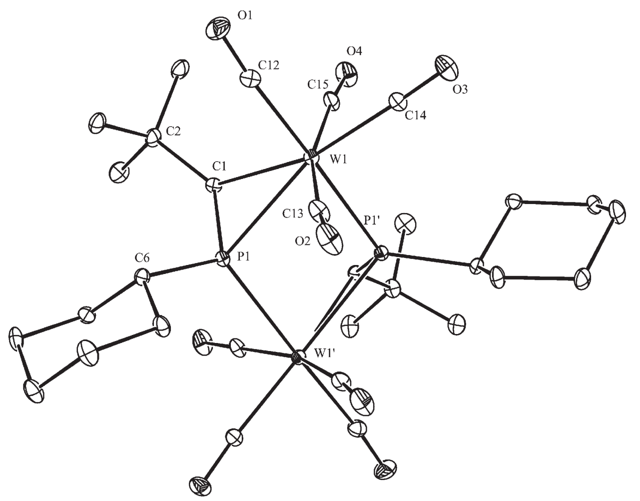


Fig. 7 Molecular structure of compound **9**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.749(6), P(1)–W(1) 2.5689(16), C(1)–W(1) 2.457(6), P(1)–W(1′) 2.546(2), C(2)–C(1)–P(1) 133.5(4), C(2)–C(1)–W(1) 125.9(4), P(1)–C(1)–W(1) 73.1(2) W(1′)–P(1)–W(1) 104.59(6).

normally the case with η^2-phosphaalkene ligation[2] the P=C bond has undergone an elongation from the normal uncoordinated bond length range to 1.749(6) Å, *cf.* the P=C bond in **3a** [1.682 Å avge.]. It is also noteworthy that the coordinated phosphaalkene possesses *Z*-stereochemistry as opposed to the *E*-stereochemistry of the free ligand. Such phosphaalkene isomerisations upon coordination to a metal fragment are not without precedent[2] and arise from the relatively weak nature of the π-component of the P=C bond.

Conclusion

The reactions of phosphavinyl Grignard reagents toward a variety of aldehydes have been investigated and found to lead to the formation of a series of β- phosphaallylic alcohols. One of these, **3a**, undergoes a novel coupling and rearrangement reaction with several metal alkyls and amides to give the bis(alkenyl)diphosphine mono-oxide, **5**, in three isomeric forms. A facile, stereospecific synthetic route to *E*-phosphaalkenes has also been described. This work has demonstrated the potential for the use of phosphavinyl Grignard reagents in organophosphorus synthesis, an area we continue to explore.

Experimental details

General remarks

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. The solvents diethyl ether and hexane were distilled over either potassium or Na/K alloy then freeze/thaw degassed prior to use. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on either Bruker DPX400 or Jeol Eclipse 300 spectrometers in deuterated solvents and were referenced to the residual ^{1}H resonances of the solvent used (^{1}H and ^{13}C NMR) or to external 85% H_3PO_4, 0.0 ppm (^{31}P NMR). Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Microanalyses were obtained from the Warwick Microanalysis Service. The starting materials *Z*-[(Cy)P=C(Bu^t)MgCl(OEt$_2$)] (**1a**), *Z*-[(Cy^P)P=C(Bu^t)MgCl(OEt$_2$)] (**1b**) and *Z*-[(Mes)P=C(Bu^t)MgBr(OEt$_2$)] (**1c**) were prepared by a literature procedure.[1] All other reagents were used as received.

SRR/*RSS*-CyP(H)(=O)C(H)(Bu^t)C(H)(OH)Ph 2

A solution of benzaldehyde (0.16 ml, 1.58 mmol) in diethyl ether (20 ml) was cooled to −78 °C and a solution of **1a** (0.50 g, 1.58 mmol) in diethyl ether (5 ml) added to it over 5 mins. The resultant solution was warmed to room temperature and stirred for 30 minutes. To this was added 1 M HCl (10 ml) drop wise with rapid stirring. The organic layer was removed by cannula, dried over $MgSO_4$, filtered and the filtrate placed at −35 °C overnight to give colourless crystals of **2** (0.05 g, 10%) m.p. 190–192 °C; ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 7.45 (d, $^3J_{HH} = 7.2$ Hz, 2H, Ph), 7.14 (v. tr., $^3J_{HH} = 6.6$ Hz, 2H, Ph), 7.05 (d, $^3J_{HH} = 7$ Hz, 1H, Ph), 6.60 (br d, $^1J_{PH} = 435.7$ Hz, 1H, PH), 5.46 (br d, $^3J_{PH} = 7$ Hz, 1H, C*H*(OH)), 2.08 (br m, 1H, C*H*(Bu^t)PO), 1.60–0.81 (m, 11H, Cy), 1.23 (s, 9H, CMe$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 46.2 (s, P=O); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 145.5 (s, Ph), 128.5 (s, Ph), 126.6 (s, Ph), 126.4 (s, Ph), 73.5 (d, $^2J_{PC} = 3.5$ Hz, Ph*C*(OH)), 52.3 (br d, $^1J_{PC} = 11.5$ Hz, *C*(Bu^t)P=O), 36.4 (d, $^1J_{PC} = 64.6$ Hz, Cy), 33.2 (s, *C*Me$_3$), 29.8 (s, C*Me*$_3$), 26.0 (d, $^2J_{PC} = 8.1$ Hz, Cy), 25.7 (s, Cy), 25.0 (s, Cy); MS APCI *m*/*z* 309 ([M$^+$], 100%), 291 ([M$^+ -$ H$_2$O], 13%); IR (Nujol) ν/cm^{-1}: 3418 (br s), 1644 (m), 1277 (w), 1222 (m), 1157 (m), 1112 (m), 1061 (m), 976 (w), 936 (w), 846 (w), 760 (m), 700 (m); Microanalysis found: C 69.72, H 9.44%; calc. for $C_{18}H_{29}O_2P$: C 70.10, H 9.48%.

General procedure for the preparation of 3–4

A solution of the appropriate aldehyde (1.58 mmol) in diethyl ether (20 ml) was cooled to −78 °C and **1a** or **1b** (1.58 mmol) in diethyl ether (10 ml) added to it over 5 mins with stirring. The resultant solution was warmed to room temperature and stirred for 30 minutes after which methanol (0.20 ml, 4.74 mmol) was added to give an immediate formation of a white precipitate. The resultant suspension was filtered and volatiles removed *in vacuo* from the filtrate. The oily residue was extracted into hexane (10 ml). This was then filtered and the solvent removed *in vacuo* to give an oil. In the case of **3a** and **3d** the oily product was extracted into hexane (10 ml), filtered and the volume lowered to *ca.* 3 ml *in vacuo*. Placement at −35 °C overnight afforded crystals of the compound.

Z-CyP=C(Bu^t)C(H)(OH)Ph 3a

Colourless crystals (yield 50%) m.p. 66–67 °C; ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 7.60 (d, $^3J_{HH} = 8.3$ Hz, 2H, Ph), 7.19 (dd, $^3J_{HH} = 7.2$ Hz, $^3J_{HH} = 8.3$ Hz, 2H, Ph), 7.07 (t, $^3J_{HH} = 7.2$ Hz, 1H, Ph), 5.63 (d, $^3J_{PH} = 5.5$ Hz, 1H, C*H*(OH)), 2.76–0.76 (m, 11H, Cy), 1.26 (d, $^4J_{PH} = 2.2$ Hz, 9H, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 273.1 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 209.1 (d, $^1J_{PC} = 55.4$ Hz, P=*C*), 145.0 (d, $^3J_{PC} = 3.5$ Hz, Ph), 127.9 (s, Ph), 126.5 (s, Ph), 126.3 (s, Ph), 73.1 (d, $^2J_{PC} = 11.5$ Hz, Ph*C*(H)(OH)), 41.8 (d, $^2J_{PC} = 19.6$ Hz, *C*Me$_3$), 37.3 (d, $^1J_{PC} = 35.8$ Hz, Cy), 31.2 (d, $^3J_{PC} = 17.3$, C*Me*$_3$), 30.3 (d, $^2J_{PC} = 15.0$ Hz, Cy), 26.5 (d, $^3J_{PC} = 9.2$ Hz, Cy), 26.0 (s, Cy); MS APCI *m*/*z* 291 ([M$^+$], 25%), 273 ([M$^+ -$ H$_2$O], 58%); IR (Nujol) ν/cm^{-1}: 3437 (br s), 1644 (m), 1263 (m), 1217 (m), 1152 (m), 1102 (m), 1057 (m), 976 (w), 921 (w), 876 (w), 785 (w), 700 (m); Microanalysis found: C 73.50, H 9.32%; calc. for $C_{18}H_{27}OP$: C 74.45, H 9.37%.

Z-CyP=C(Bu^t)C(H)(OH)(*p*-PhOMe) 3b

Colourless oil (yield 79%); ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 7.48 (d, $^3J_{HH} = 8.8$ Hz, 2H, Ph), 6.78 (d, $^3J_{HH} = 8.8$ Hz, 2H, Ph), 5.67 (dd, $^3J_{HH} = {}^3J_{PH} = 5.0$ Hz 1H, C*H*(OH)), 3.32 (s, 3H, OC*H*$_3$), 2.01–0.72 (m, 9H, Cy), 1.26 (s, 9H, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 272.7 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 209.1 (d,

$^{1}J_{PC}$ = 56.5 Hz, P=*C*), 158.8 (s, *C*OMe), 136.4 (d, $^{3}J_{PC}$ = 4.6 Hz, Ph), 127.6 (s, Ph), 113.4 (s, Ph), 73.3 (d, $^{2}J_{PC}$ = 11.5 Hz, Ph*C*H), 54.6 (s, PhO*C*H$_3$), 41.7 (d, $^{2}J_{PC}$ = 19.6 Hz, *C*Me$_3$), 37.4 (d, $^{1}J_{PC}$ = 35.8 Hz, Cy), 30.6 (d, $^{3}J_{PC}$ = 16.1 Hz, Cy), 31.1 (d, $^{3}J_{PC}$ = 17.3 Hz, C*Me*$_3$), 26.5 (d, $^{2}J_{PC}$ = 10.4 Hz, Cy), 26.5 (s, Cy); MS APCI m/z 321 ([M^{+}], 72%), 303 ([M^{+} – H$_2$O], 100%); IR (Nujol) v/cm^{-1}: 3478 (br s), 1609 (s), 1579 (w), 1508 (m), 1463 (s), 1358 (m), 1247 (m), 1167 (s), 1106 (w), 1037 (s), 825 (m); Accurate mass MS (EI) calc. mass for $C_{19}H_{29}O_2P$: 321.1983, measured mass: 321.1982.

Z-CyP=C(Bu^{t})C(H)(OH)Me 3c

Colourless oil (yield 86%); ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 4.60 (dd, $^{3}J_{HH}$ = $^{3}J_{PH}$ = 6.6 Hz, 1H, C*H*(OH)), 2.01–0.73 (m, 9H, Cy), 1.42 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, C(OH)C*H*$_3$), 1.17 (d, $^{4}J_{PH}$ = 2.2 Hz, 9H, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 260.9 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 210.9 (d, $^{1}J_{PC}$ = 56.5 Hz, P=*C*), 70.5 (d, $^{2}J_{PC}$ = 12.7 Hz, Me*C*(H)(OH)), 41.2 (d, $^{2}J_{PC}$ = 19.6 Hz, *C*Me$_3$), 36.6 (d, $^{1}J_{PC}$ = 35.8 Hz, Cy), 31.6 (d, $^{2}J_{PC}$ = 10.4 Hz, Cy), 30.7 (d, $^{3}J_{PC}$ = 17.3 Hz, C*Me*$_3$), 26.8 (d, $^{3}J_{PC}$ = 10.4 Hz, Cy), 26.1 (s, Cy), 26.0 (s, *Me*C(H)(OH)); MS APCI m/z 229 ([M^{+}], 59%); IR (Nujol) v/cm^{-1}: 3307 (br s), 2322 (m), 1714 (m), 1604 (w), 1448 (s), 1363 (m), 1212 (s), 1117 (s), 951 (m), 795 (w); Accurate mass MS (EI) calc. mass for $C_{13}H_{25}OP$: 229.1721, measured mass: 229.1720.

Z-CyP=C(Bu^{t})C(H)(OH)-*trans*-C(H)=C(H)(*p*-PhOMe) 3d

Yellow microcrystalline solid (yield 40%) m.p. 63–64 °C; ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 7.20 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, Ph), 6.70 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, Ph), 6.68 (dd, $^{3}J_{HH}$ = 16.0 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, C*H*=CH), 6.35 (dd, $^{3}J_{HH}$ = 16.0 Hz, $^{3}J_{HH}$ = 5.0 Hz, 1H, CH=C*H*), 5.20 (m, 1H, C*H*(OH)), 3.20 (s, 3H, PhOC*H*$_3$), 2.03–0.73 (m, 9H, Cy), 1.28 (d, $^{4}J_{PH}$ = 1.7 Hz, 9H, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 269.1 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 207.1 (d, $^{1}J_{PC}$ = 56.5 Hz, P=*C*), 159.5 (s, *C*OMe), 130.7 (d, $^{3}J_{PC}$ = 5.8 Hz, PhCH=*C*H), 129.9 (s, Ph), 129.0 (s, Ph*C*H=CH), 127.6 (s, Ph), 114.2 (s, Ph), 73.9 (d, $^{2}J_{PC}$ = 12.7 Hz, *C*(H)(OH)), 54.5 (s, PhO*C*H$_3$), 41.7 (d, $^{2}J_{PC}$ = 19.6 Hz, *C*Me$_3$), 37.2 (d, $^{1}J_{PC}$ = 35.8 Hz, Cy), 31.3 (d, $^{2}J_{PC}$ = 15.0 Hz, Cy), 30.7 (d, $^{3}J_{PC}$ = 17.3, C*Me*$_3$), 26.7 (d, $^{3}J_{PC}$ = 10.4 Hz, Cy), 26.0 (s, Cy); MS APCI m/z 347 ([M^{+}], 50%), 329 ([M^{+} – H$_2$O], 22%); IR (Nujol) v/cm^{-1}: 3407 (br s), 1604 (m), 1508 (m), 1468 (m), 1257 (s), 1172 (w), 1096 (s), 1031 (s), 795 (s); Accurate mass MS (EI) calc. mass for $C_{21}H_{31}O_2P_2$: 347.2140, measured mass: 347.2138.

Z-CyP=C(Bu^{t})C(H)(OH)-*trans*-C(H)=C(H)Ph 3e

Yellow oil (yield 76%); ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 7.28 (d, $^{3}J_{HH}$ = 7.2 Hz, 2H, Ph), 7.09 (dd, $^{3}J_{HH}$ = 7.7 Hz, $^{3}J_{HH}$ = 7.2 Hz, 2H, Ph), 7.03 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ph), 6.70 (dd, $^{3}J_{HH}$ = 16.0 Hz, $^{4}J_{HH}$ = 1.7 Hz, 1H, PhC*H*=CH), 6.44 (d, $^{3}J_{HH}$ = 16.0 Hz, $^{3}J_{HH}$ = 5.0 Hz, 1H, CH=C*H*), 5.20 (m, 1H, C*H*(OH)), 1.98–0.86 (m, 11H, Cy), 1.24 (d, $^{4}J_{PH}$ = 2.2 Hz, 9H, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 270.1 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 206.7 (d, $^{1}J_{PC}$ = 56.5 Hz, P=*C*), 137.2 (s, Ph), 132.9 (d, $^{3}J_{PC}$ = 6.9 Hz, PhCH=*C*H), 129.2 (s, Ph*C*H=CH), 128.7 (s, Ph), 127.5 (s, Ph), 126.4 (s, Ph), 73.7 (d, $^{2}J_{PC}$ = 11.5 Hz, *C*H(OH)C), 41.7 (d, $^{2}J_{PC}$ = 19.6 Hz, *C*Me$_3$), 37.1 (d, $^{1}J_{PC}$ = 35.8 Hz, Cy), 31.3 (d, $^{2}J_{PC}$ = 15.0 Hz, Cy), 30.7 (d, $^{3}J_{PC}$ = 17.3, C*Me*$_3$), 26.6 (d, $^{3}J_{PC}$ = 9.2 Hz, Cy), 26.0 (s, Cy); MS APCI m/z 317 ([M^{+}], 100%), 299 ([M^{+} – H$_2$O], 21%); IR (Nujol) v/cm^{-1} 3397 (br s), 1714 (m), 1699 (m), 1599 (m), 1494 (s), 1448 (s), 1388 (m), 1358 (s), 1257 (s), 1232 (m), 1092 (s), 1027 (s), 966 (m), 881 (w), 845 (w), 801 (m), 755 (m), 695 (s); Accurate mass MS (EI) calc. mass for $C_{20}H_{29}OP$: 316.1956, measured mass: 316.1953.

Z-Cy^{p}P=C(Bu^{t})C(H)(OH)Ph 4a

Colourless oil (yield 76%); ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 7.60 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ph), 7.19 (dd, $^{3}J_{HH}$ = 7.2 Hz, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ph), 7.07 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H, Ph), 5.63 (dd, $^{3}J_{PH}$ = $^{3}J_{HH}$ = 5.0 Hz, 1H, C*H*(OH)), 2.76–0.76 (m, 11H, Cy^{p}), 1.26 (d, $^{4}J_{PH}$ = 2.2 Hz, 9H, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 273.1 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 208.7 (d, $^{1}J_{PC}$ = 54.2 Hz, P=*C*), 144.5 (d, $^{3}J_{PC}$ = 4.6 Hz, Ph), 127.8 (s, Ph), 127.5 (s, Ph), 126.5 (s, Ph), 73.5 (d, $^{2}J_{PC}$ = 11.5 Hz, Ph*C*H), 41.7 (d, $^{2}J_{PC}$ = 19.6 Hz, *C*Me$_3$), 37.7 (d, $^{1}J_{PC}$ = 38.1 Hz, Cy^{p}), 32.5 (d, $^{2}J_{PC}$ = 9.2 Hz, Cy^{p}), 31.1 (d, $^{3}J_{PC}$ = 16.2, C*Me*$_3$), 26.4 (d, $^{3}J_{PC}$ = 6.9 Hz, Cy^{p}); MS APCI m/z 277 ([M^{+}], 48%), 259 ([M^{+} – H$_2$O], 100%); IR (Nujol) v/cm^{-1}:3437 (br s), 1644 (m), 1263 (m), 1217 (m), 1152 (m), 1102 (m), 1057 (m), 976 (w), 921 (w), 876 (w), 785 (w), 700 (m).

Z-Cy^{p}P=C(Bu^{t})C(H)(OH)(*p*-PhOMe) 4b

Colourless oil (yield 74%); ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 7.48 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, Ph), 6.78 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, Ph), 5.67 (m, 1H, C*H*(OH)), 3.32 (s, 3H, OC*H*$_3$), 2.01–0.72 (m, 9H, Cy^{p}), 1.26 (s, 9H, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 270.6 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 208.7 (d, $^{1}J_{PC}$ = 54.2 Hz, P=*C*), 158.7 (s, *C*OMe), 136.2 (d, $^{3}J_{PC}$ = 4.6 Hz, Ph), 127.8 (s, Ph), 113.3 (s, Ph), 73.4 (d, $^{2}J_{PC}$ = 11.5 Hz, Ph*CH*), 54.6 (s, PhO*C*H$_3$), 41.7 (d, $^{2}J_{PC}$ = 19.6 Hz, *C*Me$_3$), 37.6 (d, $^{1}J_{PC}$ = 36.9 Hz, Cy^{p}), 32.5 (d, $^{2}J_{PC}$ = 17.3 Hz, Cy^{p}), 31.2 (d, $^{3}J_{PC}$ = 17.3, C*Me*$_3$), 26.4 (d, $^{3}J_{PC}$ = 6.9 Hz, Cy^{p}); MS APCI m/z 307 ([M^{+}], 28%), 289 ([M^{+} – H$_2$O], 100%); IR (Nujol) v/cm^{-1}: 3487 (br s), 1674 (m), 1604 (m), 1508 (m), 1463 (s), 1363 (m), 1252 (m), 1172 (m), 1112 (w), 1036 (w), 825 (s); Accurate mass MS (EI) calc. mass for $C_{18}H_{27}O_2P$: 307.1827, measured mass: 307.1827.

Z-Cy^{p}P=C(Bu^{t})C(H)(OH)Me 4c

Colourless oil (yield 85%); ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 4.60 (m, 1H, C*H*(OH)), 2.01–0.73 (m, 9H, Cy^{p}), 1.42 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, C(OH)C*H*$_3$), 1.20 (s, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 257.7 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 211.1 (d, $^{1}J_{PC}$ = 55.4 Hz, P=*C*), 70.3 (d, $^{2}J_{PC}$ = 12.7 Hz, Me*C*H), 41.2 (d, $^{2}J_{PC}$ = 20.7 Hz, *C*Me$_3$), 36.7 (d, $^{1}J_{PC}$ = 36.9 Hz, Cy^{p}), 33.0 (d, $^{2}J_{PC}$ = 16.2 Hz, Cy^{p}), 30.7 (d, $^{3}J_{PC}$ = 17.3, C*Me*$_3$), 26.5 (d, $^{3}J_{PC}$ = 6.9 Hz, Cy^{p}), 26.2 (d, $^{3}J_{PC}$ = 8.0 Hz, *C*H$_3$CH); MS APCI m/z 215 ([M^{+}], 100%), 197 ([M^{+} – H$_2$O], 18%); IR (Nujol) v/cm^{-1}: 3337 (br s), 2353 (s), 1709 (m), 1609 (m), 1448 (m), 1363 (m), 1257 (w), 1112 (m), 800 (w).

Z-Cy^{p}P=C(Bu^{t})C(H)(OH)- *trans*-C(H)=C(H)(*p*-PhOMe) 4d

Yellow oil (yield 93%); ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 7.20 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, Ph), 6.70 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, Ph), 6.62 (d, $^{3}J_{HH}$ = 16.0 Hz, 1H, PhC*H*=CH), 6.38 (dd, $^{3}J_{HH}$ = 16.0 Hz, $^{3}J_{HH}$ = 5.4 Hz, 1H, PhCH=C*H*), 5.20 (dd, $^{3}J_{HH}$ = $^{3}J_{PH}$ = 5.0 Hz, 1H, C*H*(OH)), 3.20 (s, 3H, PhOC*H*$_3$), 2.03–0.73 (m, 9H, Cy^{p}), 1.28 (d, $^{4}J_{PH}$ = 1.7 Hz, 9H, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 266.1 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 207.2 (d, $^{1}J_{PC}$ = 54.2 Hz, P=*C*), 159.5 (s, *C*OMe), 131.5 (d, $^{3}J_{PC}$ = 5.8 Hz, PhCH=*C*H), 130.0 (s, Ph), 129.2 (s, Ph*C*H=CH), 127.6 (s, Ph), 114.2 (s, Ph), 74.0 (d, $^{2}J_{PC}$ = 11.5 Hz, *C*H(OH)), 54.5 (s, PhO*C*H$_3$), 41.6 (d, $^{2}J_{PC}$ = 19.6 Hz, *C*Me$_3$), 37.4 (d, $^{1}J_{PC}$ = 36.9 Hz, Cy^{p}), 32.8 (d, $^{2}J_{PC}$ = 18.4 Hz, Cy^{p}), 30.8 (d, $^{3}J_{PC}$ = 16.2, C*Me*$_3$), 26.6

(d, $^3J_{PC} = 6.9$ Hz, Cy^p); MS APCI m/z 333 ([M$^+$], 100%), 315 ([M$^+$ – H$_2$O], 38%); IR (Nujol) ν/cm^{-1}: 3407 (br s), 1604 (m), 1508 (m), 1468 (m), 1257 (s), 1172 (w), 1096 (s), 1031 (s), 795 (s); Accurate mass MS (EI) calc. mass for $C_{20}H_{29}O_2P$: 332.1902, measured mass: 332.1902.

Z-Cy^{p}P=C(Bu^t)C(H)(OH)-*trans*-C(H)=C(H)Ph 4e

Yellow oil (yield 79%); ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 7.70 (d, $^3J_{HH} = 7.2$ Hz, 2H, Ph), 7.10 (dd, $^3J_{HH} = {}^3J_{HH} = 7.2$ Hz, 2H, Ph), 7.03 (t, $^3J_{HH} = 7.2$ Hz, 1H, Ph), 6.63 (dd, $^3J_{HH} = 16.0$ Hz, $^4J_{HH} = 1.1$ Hz, 1H, PhC*H*=CH), 6.34 (dd, $^3J_{HH} = 16.0$ Hz, $^3J_{HH} = 4.4$ Hz, 1H, PhCH=C*H*), 5.20 (m, 1H, C*H*(OH)), 2.03–0.83 (m, 9H, Cy^p), 1.25 (d, $^4J_{PH} = 2.2$ Hz, 9H, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 267.6 (s, P=C) ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 206.6 (d, $^1J_{PC} = 54.2$ Hz, P=*C*), 137.2 (s, Ph), 132.9 (d, $^3J_{PC} = 5.8$ Hz, PhCH=*C*H), 129.8 (s, Ph*C*H=CH), 128.7 (s, Ph), 127.5 (s, Ph), 126.5 (s, Ph), 73.9 (d, $^2J_{PC} = 11.5$ Hz, *C*H(OH)), 41.6 (d, $^2J_{PC} = 19.6$ Hz, *C*Me$_3$), 37.4 (d, $^1J_{PC} = 36.9$ Hz, Cy^p), 32.4 (d, $^2J_{PC} = 18.5$ Hz, Cy^p), 30.7 (d, $^3J_{PC} = 17.3$, C*Me*$_3$), 26.6 (d, $^3J_{PC} = 11.5$ Hz, Cy^p); MS APCI m/z 303 ([M$^+$], 100%); IR (Nujol) ν/cm^{-1}: 3398 (br s), 1720 (m), 1674 (m), 1594 (m), 1573 (m), 1489 (s), 1388 (m), 1363 (s), 1262 (m), 1232 (w), 1157 (w), 1097 (s), 1032 (s), 966 (m), 896 (w), 801 (m), 750 (m), 690 (s); Accurate mass MS (ES+) calc. mass for $C_{19}H_{27}OP$: 303.1872 [M + H], measured mass: 303.1870

Z,Z-PhC(H)=C(Bu^t)P(Cy)P(Cy)(=O)C(Bu^t)=C(H)Ph 5a

To a suspension of Na{N(SiMe$_3$)$_2$} (0.24 g, 1.31 mmol) in diethyl ether (20 ml) at –78 °C was added **3a** (0.38 g, 1.31 mmol) in diethyl ether (20 ml). The resultant solution was warmed to room temperature and stirred for 16 hours. It was then filtered and the volatiles removed from the filtrate *in vacuo* to leave an oily residue which was extracted into hexane (10 ml). The extract was concentrated *in vacuo* to *ca.* 3 ml and placed at –35 °C overnight to give colourless crystals of **5a**. (0.09 g, 25%) m.p. 218–220 °C; ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 8.28–7.00 (m, 12H, Ph and C=C*H*), 2.50–0.85 (m, 22H, Cy), 1.47 (s, 9H, CMe$_3$), 1.21 (s, 9H, CMe$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 62.2 (d, $^1J_{PP} = 251.3$ Hz, P*P*=O), –20.6 (d, $^1J_{PP} = 251.3$ Hz, *P*P=O); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 148.9 (dd, $^1J_{PC} = 46.7$ Hz, $^2J_{PC} = 6.9$ Hz, P(O)*C*=CH), 147.8 (dd, $^2J_{PC} = 38.1$ Hz, $^3J_{PC} = 12.2$ Hz, P(O)C=*C*H), 146.3 (dd, $^1J_{PC} = 45.0$ Hz, $^2J_{PC} = 3.5$ Hz, P(O)P*C*=CH), 139.4 (d, $^3J_{PC} = 13.8$ Hz, Ph), 138.0 (d, $^3J_{PC} = 4.6$ Hz, Ph), 136.6 (d, $^4J_{PC} = 8.1$ Hz, P(O)PC=*C*H), 130.3 (s, Ph), 128.7 (s, Ph), 128.6 (s, Ph), 127.2 (s, Ph), 127.1 (s, Ph), 126.6 (s, Ph), 42.1 (dd, $^1J_{PC} = 61.2$ Hz, $^2J_{PC} = 19.6$ Hz, Cy), 41.0 (d, $^2J_{PC} = 6.9$ Hz, *C*Me$_3$), 40.1 (d, $^2J_{PC} = 8.1$, *C*Me$_3$), 34.5 (dd, $^1J_{PC} = 26.5$ Hz, $^2J_{PC} = 4.6$ Hz, Cy), 33.6 (s, Cy), 32.5 (s, C*Me*$_3$), 31.1 (s, C*Me*$_3$), 27.0 (s, Cy), 26.5 (s, Cy), 26.1 (s, Cy), 25.9 (s, Cy), 25.3 (s, Cy); MS APCI m/z 563 ([M$^+$], 12%); IR (Nujol) ν/cm^{-1}: 1298 (m), 1263 (m), 1228 (w), 1177 (m), 1142 (s), 1077 (m), 1042 (m), 997 (m), 921 (w), 886 (w), 856 (w), 745 (s); Accurate mass MS (EI) calc. mass for $C_{36}H_{52}OP_2$: 562.3493, measured mass: 562.3493.

Z,E-PhC(H)=C(Bu^t)P(Cy)P(Cy)(=O)C(Bu^t)=C(H)Ph 5b

To a THF (20 ml) solution of 1 M ZnEt$_2$ (0.66 ml, 0.66 mmol) at –78 °C was added **3a** (0.38 g, 1.31 mmol) dissolved in THF (20 ml). The resultant solution was warmed to room temperature and stirred for 2 days. It was then filtered and the volatiles removed from the filtrate *in vacuo* to leave an oily residue which was extracted into hexane (10 ml). The extract was concentrated *in vacuo* to *ca.* 3 ml and placed at –35 °C overnight to give colourless crystals of **5b**. (0.11 g, 31%) m.p. 188–190 °C, ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 7.97–6.96 (m, 12H, Ph and C=C*H*), 2.53–0.87 (m, 22H, Cy), 1.63 (s, 9H, CMe$_3$), 1.33 (s, 9H, CMe$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 55.4 (d, $^1J_{PP} = 287.2$ Hz, P*P*=O), –12.7 (d, $^1J_{PP} = 287.2$ Hz, *P*P=O); MS APCI m/z 563 ([M$^+$], 100%); IR (Nujol) ν/cm^{-1}: 1298 (m), 1263 (m), 1228 (m), 1177 (m), 1142 (s), 1077 (m), 1042 (m), 997 (m), 921 (w), 886 (w), 856 (w), 745 (s); Accurate mass MS (CI) calc. mass for $C_{36}H_{52}OP_2$: 563.3566, [M + H], measured mass: 563.3581.

E,E-PhC(H)=C(Bu^t)P(Cy)P(Cy)(=O)C(Bu^t)=C(H)Ph 5c

To a suspension of K{N(SiMe$_3$)$_2$} (0.26 g, 1.31 mmol) in diethyl ether (20 ml) at –78 °C was added **3a** (0.38 g, 1.31 mmol) in diethyl ether (20 ml). The resultant solution was warmed to room temperature and stirred for 16 hours. It was then filtered and the volatiles removed from the filtrate *in vacuo* to leave an oily residue which was extracted into hexane (10 ml). The extract was concentrated *in vacuo* to *ca.* 3 ml and placed at –35 °C overnight to give colourless crystals of **5c**. (0.11 g, 31%) m.p. 190–192 °C; ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 8.20–7.01 (m, 12H, Ph and C=C*H*), 2.43–0.63 (m, 22H, Cy), 1.65 (s, 9H, CMe$_3$), 1.63 (s, 9H, CMe$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 50.1 (d, $^1J_{PP} = 332.1$ Hz, P*P*=O), 0.0 (d, $^1J_{PP} = 332.1$ Hz, *P*P=O); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 148.9 (dd, $^1J_{PC} = 41.5$ Hz, $^2J_{PC} = 6.9$ Hz, P(O)*C*=C), 147.8 (dd, $^2J_{PC} = 38.1$ Hz, $^3J_{PC} = 11.5$ Hz, P(O)C=*C*), 146.4 (dd, $^1J_{PC} = 45.0$ Hz, $^2J_{PC} = 3.5$ Hz, P(O)P*C*=C), 139.4 (d, $^3J_{PC} = 13.9$ Hz, Ph), 138.0 (d, $^3J_{PC} = 5.8$ Hz, Ph), 136.6 (d, $^3J_{PC} = 6.9$ Hz, P(O)PC=*C*), 130.5 (s, Ph), 129.0 (s, Ph), 128.7 (s, Ph), 128.6 (s, Ph), 127.1 (s, Ph), 126.6 (s, Ph), 42.2 (dd, $^1J_{PC} = 51.2$ Hz, $^2J_{PC} = 19.6$ Hz, Cy), 41.1 (d, $^2J_{PC} = 6.9$ Hz, *C*Me$_3$), 40.1 (d, $^2J_{PC} = 8.1$, *C*Me$_3$), 34.5 (dd, $^1J_{PC} = 43.1$ Hz, $^2J_{PC} = 4.6$ Hz, Cy), 33.6 (d, $^2J_{PC} = 13.1$ Hz, Cy), 32.5 (s, C*Me*$_3$), 31.1 (s, C*Me*$_3$), 27.0 (s, Cy), 26.7 (s, Cy), 26.1 (s, Cy), 25.9 (s, Cy), 25.3 (s, Cy); MS APCI m/z 563 ([M$^+$], 100%); IR (Nujol) ν/cm^{-1}: 1298 (m), 1263 (m), 1228 (m), 1177 (m), 1142 (s), 1077 (m), 1042 (m), 997 (m), 921 (w), 886 (w), 856 (w), 745 (s); Accurate mass MS (CI) calc. mass for $C_{36}H_{52}OP_2$: 563.3566, [M + H], measured mass: 563.3576.

Z-PhC(H)=C(Bu^t)P(O)(H)Cy 6

To a solution of Ti(OPr^i)$_4$ (0.09 ml, 1.27 mmol) in diethyl ether (20 ml) at –78 °C was added **3a** (0.37 g, 1.27 mmol) in diethyl ether (20 ml). The resultant solution was warmed to room temperature and stirred for eight days. It was then filtered and the volatiles removed from the filtrate *in vacuo* to leave an oily residue which was extracted into hexane (15 ml). The extract was concentrated *in vacuo* to *ca.* 5 ml and placed at –35 °C overnight to give colourless crystals of **6**. (0.11 g, 31%) m.p. 91–93 °C, ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 7.52 (d, $^3J_{HH} = 7.7$ Hz, 2H, Ph), 7.11 (br, s, 1H, PhC*H*=C), 7.08 (dd, $^3J_{HH} = 7.7$ Hz, 2H, Ph), 7.02 (t, $^3J_{HH} = 7.2$ Hz, 1H, Ph), 6.93 (ddd, $^1J_{PH} = 441.7$ Hz, $^3J_{PH} = 7.2$ Hz, $^4J_{PH} = 2.2$ Hz, 1H, P*H*), 2.30–0.66 (m, 11H, Cy), 1.26 (s, 9H, CMe$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 28.6 (s, P=O); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 145.0 (d, $^1J_{PC} = 76.2$ Hz, P*C*=CPh), 138.9 (d, $^2J_{PC} = 8.1$ Hz, PC=*C*Ph), 137.3 (d, $^3J_{PC} = 8.1$ Hz, Ph), 129.2 (s, Ph), 128.0 (s, Ph), 127.7 (s, Ph), 37.0 (d, $^2J_{PC} = 9.2$ Hz, *C*Me$_3$), 36.4 (d, $^1J_{PC} = 68.1$ Hz, Cy), 30.1 (d, $^3J_{PC} = 3.5$, CMe$_3$), 26.7 (s, Cy), 26.1 (s, Cy), 25.6 (s, Cy); MS APCI m/z 291 ([M$^+$], 29%); IR (Nujol) ν/cm^{-1}: 2332 (m), 1599 (m), 1268 (m), 1212 (m), 1157 (s), 1117 (s), 1012 (s), 941 (w), 921 (w), 876 (w), 750 (m), 705 (w); Accurate mass MS (ES+) calc. mass for $C_{18}H_{27}OP$: 291.1872 [M + H], measured mass: 291.1873.

$C_6H_4\{C(H)(OH)C(Bu^t){=}PCy^P\}_2$-1,3 7

To a solution of benzene-1,3-dicarboxaldehyde (0.11 g, 0.83 mmol) in diethyl ether (20 ml) at −78 °C was added **1b** (0.50 g, 1.65 mmol) in diethyl ether (20 ml). The resultant solution was warmed to room temperature and stirred for 30 minutes. Methanol (0.20 ml, 4.74 mmol) was then added with the immediate formation of a white precipitate. The suspension was filtered and volatiles were removed *in vacuo*. The oily residue was extracted into hexane (10 ml), filtered and the solvent removed *in vacuo* from the filtrate to give a colourless oil. This was extracted into hexane (10 ml) and concentrated to *ca.* 3 ml *in vacuo*. Placement at −35 °C overnight gave colourless crystals of **7** (0.06 g, 15%) m.p. 122–124 °C; Data for major isomer only: ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 7.74 (s, 1H, Ph), 7.56 (d, $^3J_{HH} = 7.7$ Hz, 2H, Ph), 7.23 (t, $^3J_{HH} = 7.7$ Hz, 1H, ArH), 5.64 (dd, $^3J_{PH} = {^3J_{HH}} = 5.0$ Hz, 2H, C(OH)*H*), 3.03–0.85 (m, 22H, Cy), 1.27 (s, 18H, CMe$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 272.1 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 208.9 (d, $^1J_{PC} = 54.2$ Hz, P=*C*), 144.2 (d, $^3J_{PC} = 4.6$ Hz, Ar), 128.5 (s, Ar), 125.1 (s, Ar), 124.6 (s, Ar), 73.6 (d, $^2J_{PC} = 11.5$ Hz, *C*H(OH)), 41.8 (d, $^2J_{PC} = 19.6$ Hz, *C*Me$_3$), 37.7 (d, $^1J_{PC} = 38.1$ Hz, Cy), 31.5 (d, $^2J_{PC} = 18.5$ Hz, Cy), 31.1 (s, C*Me*$_3$), 26.4 (s, Cy); MS APCI m/z 473 ([M$^+$ − H], 95%); IR (Nujol) v/cm^{-1}: 3447 (br s), 1700 (m), 1594 (m), 1282 (m), 1216 (m), 1155 (m), 1115 (m), 1048 (s), 961 (w), 900 (w), 802 (m), 720 (m).

E-CyP=C(H)Bu^t 8a

To a solution of **1a** (0.50 g, 1.58 mmol) in diethyl ether (20 ml) at 25 °C was added methanol (0.20 ml, 4.74 mmol) to give the immediate formation of a white precipitate. The suspension was filtered and volatiles were removed *in vacuo* from the filtrate to yield an oily residue which was extracted into hexane (10 ml). The resultant suspension was then filtered and volatiles removed from the filtrate *in vacuo*. This gave **8a** as a colourless oil (0.28 g, 96%), ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 8.64 (d, $^2J_{PH} = 24.8$ Hz, 1H, P=C*H*), 2.10–1.10 (m, 11H, Cy), 1.15 (d, $^4J_{PH} = 1.7$ Hz, 9H, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 257.8 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 198.2 (d, $^1J_{PC} = 44.8$ Hz, P=*C*), 41.1 (d, $^1J_{PC} = 33.2$ Hz, Cy), 36.1 (d, $^2J_{PC} = 11.9$ Hz, *C*Me$_3$), 32.3 (d, $^2J_{PC} = 9.1$ Hz, Cy), 30.8 (s, C*Me*$_3$), 30.5 (d, $^3J_{PC} = 12.2$ Hz, Cy), 26.0 (s, Cy); MS APCI m/z 185 ([M$^+$], 25%); IR (Nujol) v/cm^{-1}: 1448 (s), 1358 (m), 1258 (m), 1167 (m), 1117 (m), 1017 (m), 936 (w), 886 (w), 846 (w), 801 (w).

E-MesP=C(H)Bu^t 8b

A similar procedure to the preparation of **8a** was employed. Colourless oil (yield 88%), ^{1}H NMR (300.5 MHz, C_6D_6, 298 K) δ 8.43 (d, $^2J_{PH} = 25.3$ Hz, 1H, P=C*H*), 7.15 (s, 2H, ArH), 2.31 (s, 6H, Me), 2.13 (s, 3H, Me), 1.15 (d, $^4J_{PH} = 2.2$ Hz, 9H, C*Me*$_3$); ^{31}P NMR (121.7 MHz, C_6D_6, 298 K) δ 228.4 (s, P=C); ^{13}C NMR (75.6 MHz, C_6D_6, 298 K) δ 203.3 (d, $^1J_{PC} = 43.8$ Hz, P=*C*), 186.7 (d, $^1J_{PC} = 51.9$ Hz, Ar), 140.0 (d, $^2J_{PC} = 5.8$ Hz, Ar), 137.6 (s, Ar), 128.7 (s, Ar), 38.9 (d, $^2J_{PC} = 13.8$ Hz, *C*Me$_3$), 30.1 (d, $^3J_{PC} = 10.8$ Hz, C*Me*$_3$), 23.0 (d, $^3J_{PC} = 9.2$ Hz, Me), 20.9 (s, Me); MS APCI m/z 221 ([M$^+$], 17%), 151 ([M$^+$ − CHBu^t], 100%); IR (Nujol) v/cm^{-1}: 1604 (m), 1458 (s), 1358 (m), 1258 (m), 1102 (m), 1031 (m), 871 (w), 845 (w), 806 (w).

Structure determinations

Crystals of **2**, **3a**, **5a–c**, **6** and **9** suitable for X-ray structure determination were mounted in silicone oil or epoxy resin. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[18] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms either included in calculated positions (riding model) or their positions and thermal parameters refined isotropically. The relatively high *r*-factor for the structure of **5c** was due to the poor quality of the sample used in the experiment. Despite this, the molecular connectivity shown for this compound in Fig. 5 is unambiguous. Crystal data, details of data collections and refinements are given in Table 1. The molecular structures of the complexes are depicted in Figs. 1–7 and show ellipsoids at the 30% probability level.

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