Synthesis of 1,3-azaphosphol-2-ones. Crystal and molecular structures of [*SP-4-2*]-dichlorobis(3-phenyl-1,3-dihydrobenzo[1,3]azaphosphol-2-one-P)palladium(II) and its chloro(methyl)platinum(II) analogue†

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Reaction of secondary phosphine (±)-(2-aminophenyl)phenylphosphine, (±)-app, with PCl_5 in toluene gives the hydrochloride salt of the expected chlorophosphine (±)-(2-aminophenyl)chlorophenylphosphine, (±)-acpp.HCl, however, this is not the case with triphosgene. Rather the first example of a 1,3-azaphosphol-2-one is isolated, *viz.* (±)-3-phenyl-1,3-dihydrobenzo[1,3]azaphosphol-2-one, (±)-pbap. The hydrochloride salt (±)-acpp.HCl readily reacts with excess vinyl-, 2-methylphenyl- or 2-methoxyphenyl magnesium bromide to give the corresponding tertiary phosphines (±)-(2-$H_2NC_6H_4$)PPhR (where R = CH=CH_2, 2-C_6H_4Me or 2-C_6H_4OMe). Hydrophosphination of the vinyl substituted tertiary phosphine with (±)-app in the presence of KOBu^t provides a synthetic route to the elusive P_2N_2 quadridentate ligand (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_2)_2$($PPhC_6H_4NH_2$-2)$_2$, albeit in low yield. The azaphospholone (±)-pbap can be readily deprotonated with KOBu^t in thf and subsequently alkylated with methyl iodide or benzyl bromide to give the analogous N-methyl or N-benzyl derivatives. Alkylation with 1,3-dibromopropane gives the bis(azaphospholone) (R_P*,R_P*)- and (R_P*,S_P*)-1,3-bis[1-{3-phenyl-1,3-dihydrobenzo[1,3]azaphosphol-2-one}]propane. The latter and the N-methyl substituted azaphospholone can also be synthesised by the reaction of the corresponding secondary phosphine, *viz.* (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_2)_3$(NHC_6H_4PHPh-2)$_2$ and (±)-(2-methylaminophenyl)phenylphosphine, with triphosgene. All three azaphospholones react with [PtClMe(1,5-cyclooctadiene)] in thf to give complexes of the type *cis*-[PtClMeL_2] in which ligand L is coordinated *via* the P atom of the azaphospholones. The ligand (±)-pbap has also been complexed to palladium(II) *via* the reaction with $Li_2[PdCl_4]$ in methanol to give *cis*-[$PdCl_2${(±)-pbap}$_2$]. The structures of *cis*-[PtClMe{(±)-pbap}$_2$] and *cis*-[$PdCl_2${(±)-pbap}$_2$] have been confirmed by X-ray analysis.

Introduction

Metathesis of chlorophosphines with organometallic reagents has been, and continues to be, an important preparative route to unidentate, bidentate and, to a lesser degree, multidentate tertiary phosphines.[1] A common synthetic route to chlorophosphines involves chlorination of the analogous primary or secondary phosphine with, for example, C_2Cl_6, PCl_5 or more recently triphosgene, $(Cl_3CO)_2CO$.[2,3] The latter is often the reagent of choice particularly for small scale reactions as the side products are CO and HCl.

Tertiary phosphine (2-aminophenyl)diphenylphosphine, adpp, **1**, is a versatile hybrid ligand that can be used to prepare a range of related bidentate PN and multidentate P_2N_2 and very recently P_3N_3 ligands *via* derivatisation of the amino or diphenylphosphino groups.[4] Derivatisation of the latter has typically been achieved *via* reductive cleavage of a phenyl group from adpp using three equivalents of lithium in thf or sodium in liquid ammonia, to give the secondary phosphine (±)-2-$H_2NC_6H_4PHPh$, (±)-app, **2**, upon hydrolysis followed by metallation with sodium in thf and alkylation with, for example, CH_3I, $Br(CH_2)_nBr$ (where n = 3–6) or $CH_3C(CH_2Br)_3$ to give (±)-2-$H_2NC_6H_4PMePh$, (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_2)_n$($PPhC_6H_4NH_2$-2)$_2$ and (R_P*,R_P*,R_P*)- and (R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$, respectively.[4–6] This approach typically, however, does not allow access to substituted (2-aminophenyl)phosphines of the type (±)-2-$H_2NC_6H_4PPhR$ (where R = aryl or vinyl group). A rare exception is the 2-chlorophenyl substituted PN ligand (±)-(2-aminophenyl)(2-chlorophenyl)methylphosphine.[7] In the current work conversion of secondary phosphine (±)-app, **2**, to the corresponding chlorophosphine has been investigated using PCl_5 or triphosgene. The hydrochloride salt of the expected chlorophosphine (±)-(2-aminophenyl)chlorophenylphosphine, (±)-acpp.HCl, **3**, is isolated using PCl_5. Further reaction of **3** with an excess of the appropriate Grignard reagent does provide a route to substituted (2-aminophenyl)phosphines of the type (±)-2-$H_2NC_6H_4PPhR$ (where R = aryl or vinyl group). No formation of a chlorophosphine, however, was observed using triphosgene, rather a stable azaphospholone was isolated, *viz.* (±)-3-phenyl-1,

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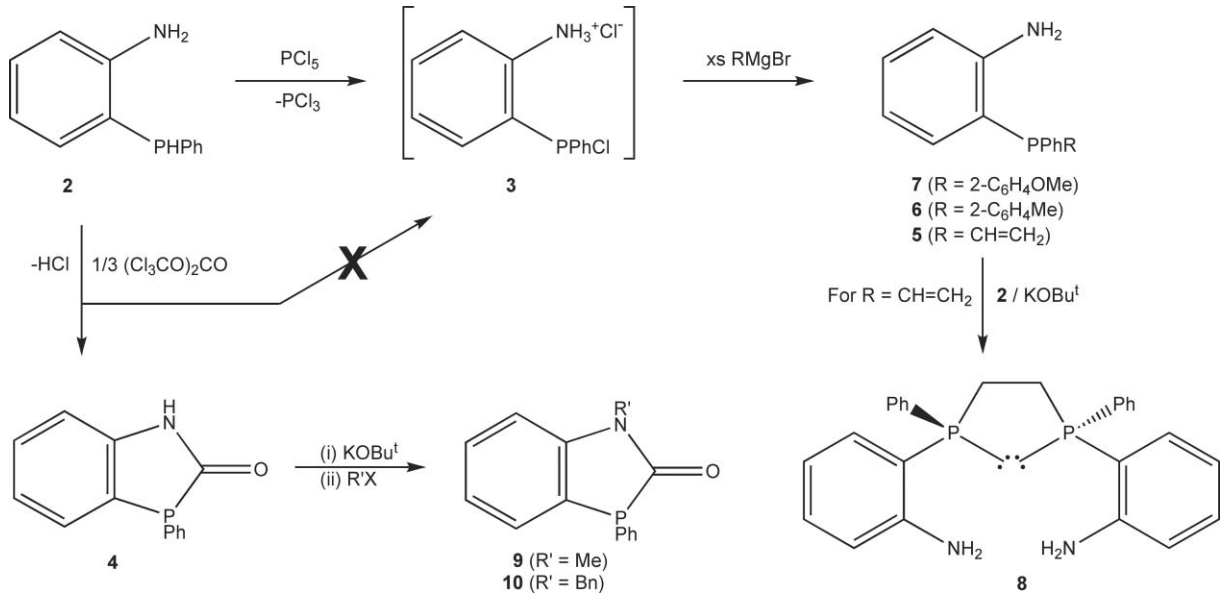


Scheme 1 Synthesis of azaphospholone **4** and its N-substituted derivatives **9** and **10**, tertiary phosphines **5–7** and the quadridentate NP_2N ligand **8**.

3-dihydrobenzo[1,3]azaphosphol-2-one, (±)-pbap, **4**, the first example of a 1,3-azaphosphol-2-one. Several examples of azaphospholes and, in particular, benzazaphospholes have been reported in the literature but there appear to be no examples of the related benzazaphospholones.[8]

Results and discussion

Reaction of (±)-app, 2, with PCl_5: synthesis of (±)-2-$H_2NC_6H_4$-PPhR (where R = CH=CH_2, 2-C_6H_4Me or 2-C_6H_4OMe) and (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_2)_2(PPhC_6H_4NH_2$-2)$_2$

The reaction of the secondary phosphine (±)-app, **2**, with PCl_5 in dry toluene gave a moisture sensitive white solid that is believed to be the hydrochloride salt of (±)-(2-aminophenyl)(chloro)phenylphosphine, (±)-acpp.HCl, **3** (see Scheme 1). The latter was insoluble in most common solvents and hence no useful NMR data could be obtained. The assignment was confirmed by further reaction of **3** with an excess of the appropriate Grignard reagent in thf to give the bidentate PN ligands (±)-(2-aminophenyl)phenylvinylphosphine, (±)-apvp, **5**, (±)-(2-aminophenyl)(2-methylphenyl)phenylphosphine, (±)-aptp, **6**, and (±)-(2-aminophenyl)(2-methoxyphenyl)phenylphosphine, (±)-aapp, **7**. Whereas one singlet ^{31}P resonance was observed for both **6** and **7** in their respective $^{31}P\{^1H\}$ NMR spectra, two singlets were found in the analogous spectrum of **5**. Molecular models suggest the existence of two conformers resulting from restricted rotation of the 2-aminophenyl group with respect to the double bond may account for the observation of two rather than one ^{31}P resonance for (±)-apvp, **5**. Selected NMR data is given in Table 1.

Vinylphosphine **5** was seen as a potential precursor to the elusive quadridentate PN_2P ligand (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_2)_n(PPhC_6H_4NH_2$-2)$_2$ (where n = 2) which cannot be synthesised in the same manner as its analogues (where n = 3–6).[5] The quadridentate ligand (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_2)_2(PPhC_6H_4NH_2$-2)$_2$, C_2-NP_2N, **8**, was isolated in *ca.* 12% yield (based on the quantity of unreacted secondary phosphine recovered from the reaction) by heating a thf solution of **2**, **5** and a catalytic amount of KOBu^t under reflux for 20 days. The yield of the addition reaction could not be improved by using higher boiling point solvents such as benzene or toluene or by attempting a free-radical catalysed reaction using AIBN in toluene at 110 °C.

Reaction of (±)-app, 2, with triphosgene: synthesis of (±)-3-phenyl-1,3-dihydrobenzo[1,3]azaphosphol-2-one, (±)-pbap, 4, and its N-substituted derivatives

No evidence for the formation of chlorophosphine (±)-acpp or its hydrochloride salt (±)-acpp.HCl, **3**, was observed upon reaction of secondary phosphine **2** with one-third equivalent of triphosgene in thf, rather the first example of a 1,3-azaphosphol-2-one, *viz.* (±)-3-phenyl-1,3-dihydrobenzo[1,3]azaphosphol-2-one, (±)-pbap, **4**, was isolated in 80% yield upon crystallisation from toluene. The amido group of **4** can be readily deprotonated by reaction with KOBu^t in thf and subsequently treated with MeI or BnBr to give the N-substituted derivatives (±)-1-methyl-3-phenyl-1,3-dihydrobenzo[1,3]azaphosphol-2-one, (±)-mpbap, **9**, and (±)-1-benzyl-3-phenyl-1,3-dihydrobenzo[1,3]azaphosphol-2-one, (±)-bpbap, **10**, respectively (Scheme 1). The N-methyl substituted 1,3-azaphosphol-2-one **9** has also been prepared by the reaction of the N-methyl substituted analogue of **2**, *viz.* (±)-(2-methylaminophenyl)phenylphosphine, (±)-mapp, **11**, with one-third equivalent of triphosgene in thf (Scheme 2). The N-methyl substituted secondary phosphine **11** was prepared in two steps from adpp, **1**. Reaction of the latter with *n*-butyllithium/tmeda in *n*-hexane followed by the addition of MeI gave (2-methylaminophenyl)diphenylphosphine, madpp, **12**, which was further reacted with three equivalents of lithium in thf to give **11** upon hydrolysis.

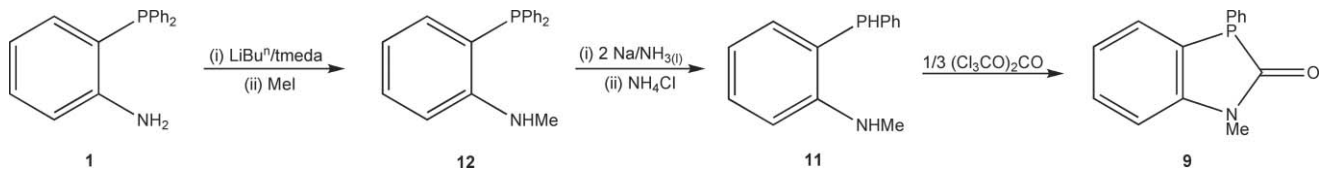
Reaction of (±)-pbap, **4**, with KOBu^t in thf followed by the addition of half an equivalent of 1,3-dibromopropane

Table 1 Selected $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR data[a]

	$^{31}P\{^{1}H\}$	^{1}H	
Compound	δP	δNH	δ(Other)
4	–30.9 s	9.73 bs	—
5	– 10.9 s, –11.0 s	4.20 bs	5.59 m, 5.93 m (C=CH_2)
6	–27.1 s	4.16 bs	2.40 s (C*Me*)
7	–31.1 s	4.12 bs	3.74 s (O*Me*)
8	–31.0 s	3.94 bs	2.12 m (NCH_2)
9	–35.7 s	—	3.07 s (N*Me*)
10	–36.3 s	—	4.89, 4.96 ABq (NCH_2Ph)
11	–60.7 s	4.25 bs	2.80 s (N*Me*), 5.09 d (P*H*)
13	–36.7 s	—	1.90 m (CCH_2), 3.72 m (NCH_2)
14	–60.3 s, –60.5 s	4.06 bs	1.52 m (CCH_2), 2.82 m (NCH_2) 5.07 d (P*H*)

	$^{31}P\{^{1}H\}^{b}$		$^{1}H^{b}$
Compound	δP[c]	δPt*Me*	δ(Other)
cis-[PtClMe(**4**)$_2$]	–5.0 d (4310), 1.3 (1625)	1.16 bs	11.16 d, 11.61 d (N*H*)
cis-[PtClMe(**9**)$_2$]	–5.2 d (4357), 0.6 (1621)	0.66 bs	2.62 s, 2.91 s (N*Me*)
cis-[PtClMe(**10**)$_2$]	–4.7 d (4362), 1.7 (1621)	0.33 bs	3.91, 4.03 ABq (NCH_2)
cis-[PdCl$_2$(**4**)$_2$]	28.9 s	—	11.16 d (N*H*)

[a] In $CDCl_3$ unless otherwise stated. [b] In $(CD_3)_2SO$. [c] $^{1}J_{PtP}$ given in Hz in parentheses.



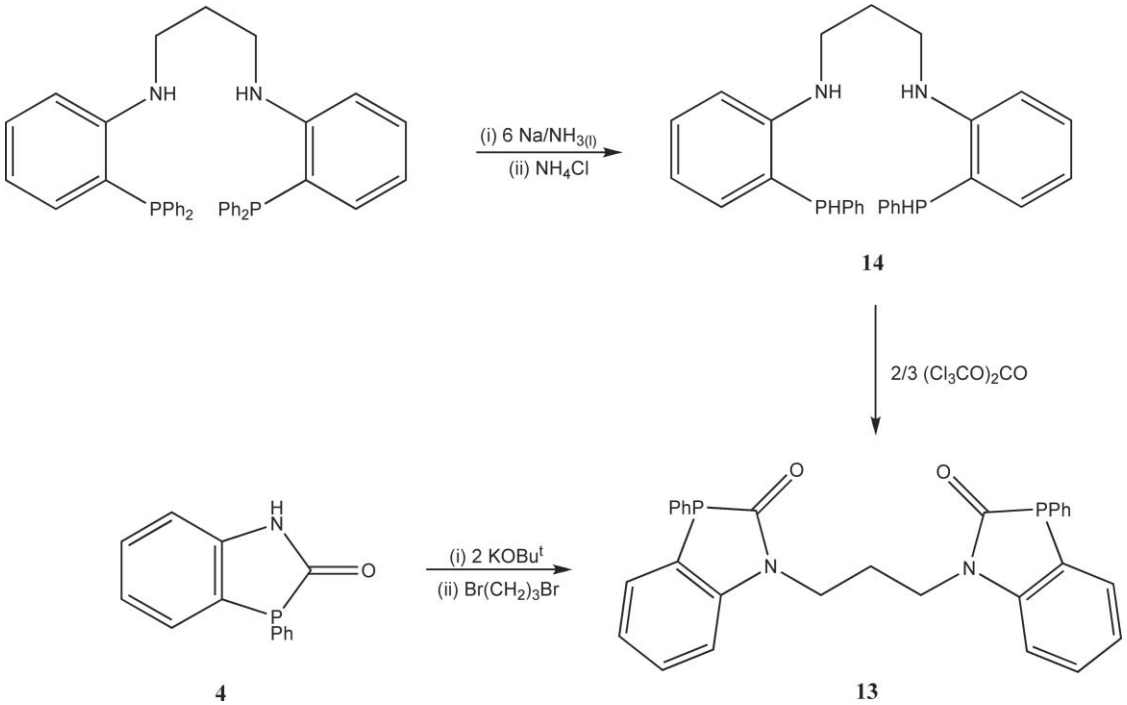
Scheme 2 Alternative synthesis of N-methyl substituted azaphospholone **9**.

gave the first example of a bis(1,3-azaphosphol-2-one), *viz.* (R_P*,R_P*)- and (R_P*,S_P*)-1,3-bis[1-{3-phenyl-1,3-dihydrobenzo-[1,3]azaphosphol-2-one}]propane, (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_2)_3$(pbap)$_2$, **13** (Scheme 3). The latter has also been prepared by the reaction of bis(secondary phosphine) (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_2)_3(NHC_6H_4PHPh\text{-}2)_2$, C_3-PN_2PH, **14**, with two-third equivalent of triphosgene in thf. The bis(secondary phosphine) (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_2)_3(NHC_6H_4PHPh\text{-}2)_2$, **14**, was synthesised from the linear quadridentate PN_2P ligand $(CH_2)_3(NHC_6H_4PPh_2\text{-}2)_2$ by reaction with six equivalents of lithium in thf followed by hydrolysis with NH_4Cl.

The proposed mechanism for the reaction of triphosgene with (±)-app, **2**, is shown in Fig. 1. Nucleophilic attack of the phosphino group of **2** on C(2) of triphosgene followed by loss of HCl and phosgene presumably gives an acyl intermediate $Cl_3COC(O)P(Ph)C_6H_4NH_2\text{-}2$ which undergoes further nucleophilic attack by the amino group at the acyl C atom with further loss of HCl and phosgene to give azaphospholone (±)-pbap, **4**. The two equivalents of phosgene generated in the reaction further react with **2** in a similar manner, *i.e. via* sequential nucleophilic attack by the phosphino and amino groups on the acyl C atom, to give more HCl and **4**. Thus one equivalent of triphosgene reacts with three equivalents of **2** to produce three equivalents of **4** and six equivalents of HCl.

Complexes of the 1,3-azaphosphol-2-ones 4, 9, and 10

The three 1,3-azaphosphol-2-ones have been coordinated to platinum(II) *via* the reaction with [PtClMe(1,5-cyclooctadiene)] in thf to give complexes of the type *cis*-[PtClMeL$_2$] [where L = (±)-pbap, **4**, (±)-mpbap, **9**, or (±)-bpbap, **10**]. The $^{31}P\{^{1}H\}$ NMR spectra of the three complexes in $(CD_3)_2SO$ each showed a pair of doublet ^{31}P resonances ($^{2}J_{PP}$ ~ 14 Hz) with associated satellites due to ^{195}Pt-^{31}P coupling ($^{1}J_{PtP}$ ~ 4350 and 1625 Hz) consistent with a *cis* stereochemistry for each of the complexes. A palladium(II) complex of **4**, *viz. cis*-[PdCl$_2$(**4**)$_2$], was also prepared *via* the reaction of two equivalents of the ligand with a solution of $Li_2[PdCl_4]$ in methanol. The structures of the complexes *cis*-[PtClMe(**4**)$_2$] and *cis*-[PdCl$_2$(4)$_2$] have been confirmed by X-ray analysis. The molecular structures of the two complexes are depicted in Fig. 2 and 3, and selected bond lengths and angles are given in Table 2. The structural data clearly shows the presence of two *cis* disposed 1,3-azaphosphol-2-ones bound to the metal centre as unidentate ligands through the stereogenic phosphorus donor atoms. The latter have opposite relative configurations in the two structures and hence they are both correctly *meso* complexes. The metal centres in these two complexes have distorted square-planar coordination geometries. Each of the 1,3-azaphosphol-2-one ligands has a planar structure with the carbonyl moiety lying in the same plane as the six carbon atoms of the 1,2-substituted benzene



Scheme 3 Synthesis of bis(azaphospholone) **13**.

Table 2 Selected non-hydrogen interatomic distances (Å) and interatomic angles (°) for *cis*-[PtClMe(**4**)$_2$] and *cis*-[PdCl$_2$(**4**)$_2$]

cis-[PtClMe(4)$_2$]		*cis*-[PdCl$_2$(4)$_2$]	
Pt–Cl(1)[a]	2.2873(13)	Pd–Cl(1)	2.3516(7)
Pt–Cl(2)[a]	2.3032(15)	Pd–Cl(2)	2.3404(7)
Pt–P(1)	2.2435(9)	Pd–P(1)	2.2420(7)
Pt–P(2)	2.2345(9)	Pd–P(2)	2.2282(7)
Pt–C(1)[a]	2.2873(13)		
Pt–C(2)[a]	2.3032(15)		
P(1)–C(10)	1.880(4)	P(1)–C(10)	1.888(3)
P(2)–C(30)	1.915(4)	P(2)–C(30)	1.874(3)
P(1)–C(11)	1.798(4)	P(1)–C(11)	1.783(3)
P(2)–C(31)	1.794(4)	P(2)–C(31)	1.794(3)
P(1)–C(20)	1.811(4)	P(1)–C(21)	1.811(3)
P(2)–C(41)	1.816(4)	P(2)–C(41)	1.810(3)
N(1)–C(10)	1.351(4)	N(1)–C(10)	1.355(3)
N(1)–C(12)	1.413(5)	N(1)–C(12)	1.408(3)
N(2)–C(30)	1.337(5)	N(2)–C(30)	1.358(4)
N(2)–C(32)	1.398(6)	N(2)–C(32)	1.398(5)
O(1)–C(10)	1.219(5)	O(1)–C(10)	1.211(3)
O(2)–C(30)	1.196(5)	O(2)–C(30)	1.216(4)
Cl(1)–Pt–P(1)[a]	90.41(5)	Cl(1)–Pd–P(1)	88.17(2)
C(1)–Pt–P(1)[a]	90.41(5)		
Cl(2)–Pt–P(2)[a]	87.21(5)	Cl(2)–Pd–P(2)	84.56(5)
C(2)–Pt–P(2)[a]	87.21(5)		
Cl(2)–Pt–P(1)[a]	174.08(5)	Cl(2)–Pd–P(1)	176.91(3)
C(2)–Pt–P(1)[a]	174.08(5)		
Cl(1)–Pt–P(2)[a]	170.99(5)	Cl(1)–Pd–P(2)	173.46(3)
C(1)–Pt–P(2)[a]	170.99(5)		
P(1)–Pt–P(2)	98.30(3)	P(1)–Pd–P(2)	96.30(3)
Cl(1)–Pt–C(2)	84.18(6)	Cl(1)–Pd–Cl(2)	91.22(3)
Cl(2)–Pt–C(1)	84.18(6)		

[a] There is disorder of the methyl and chloro ligands and hence distances and angles listed here involving these atoms are presumably for the weighted average positions.

ring and the nitrogen and phosphorus atoms of the heterocycle. This arrangement maximises the π interaction between the sp^2 hybridised nitrogen atom and the carbonyl moiety, presumably a key feature in terms of stabilising the 1,3-azaphosphol-2-one structure.

Conclusion

This work describes a high yielding synthetic route to 1,3-benzazaphosphol-2-ones under mild conditions *via* the reaction of a (2-aminophenyl) substituted secondary phosphine with one-third equivalent of triphosgene. Derivatisation at the N atom, by deprotonation and subsequent alkylation, and coordination as a unidentate ligand *via* the P centre [to palladium(II) and platinum(II)] has also been demonstrated for azaphospholone (±)-pbap, **4**, in this work. Conversion of (2-aminophenyl) substituted secondary phosphines to the corresponding chlorophosphine can be achieved *via* reaction with PCl_5 and the latter readily alkylated by metathesis with an appropriate Grignard reagent. Further work is focusing on the reactivity of the carbonyl moiety of azaphospholone **4** and the resolution of the latter.

Experimental

Procedures and materials

Reactions involving air-sensitive reagents were performed under argon using Schlenk techniques. Solvents were dried and purified by distillation under argon. NMR spectra were obtained using a Varian Gemini 300 spectrometer operating at 300 MHz (^{1}H), 121.5 MHz (^{31}P{^{1}H}) or 75 MHz (^{13}C{^{1}H}). Chemical shift values (δ) are reported in ppm referenced relative to tetramethylsilane for ^{1}H, $CDCl_3$ (77.0 ppm) or CD_2Cl_2 (53.8 ppm) as appropriate for ^{13}C{^{1}H} and external 85% aqueous H_3PO_4 for ^{31}P{^{1}H}. Melting

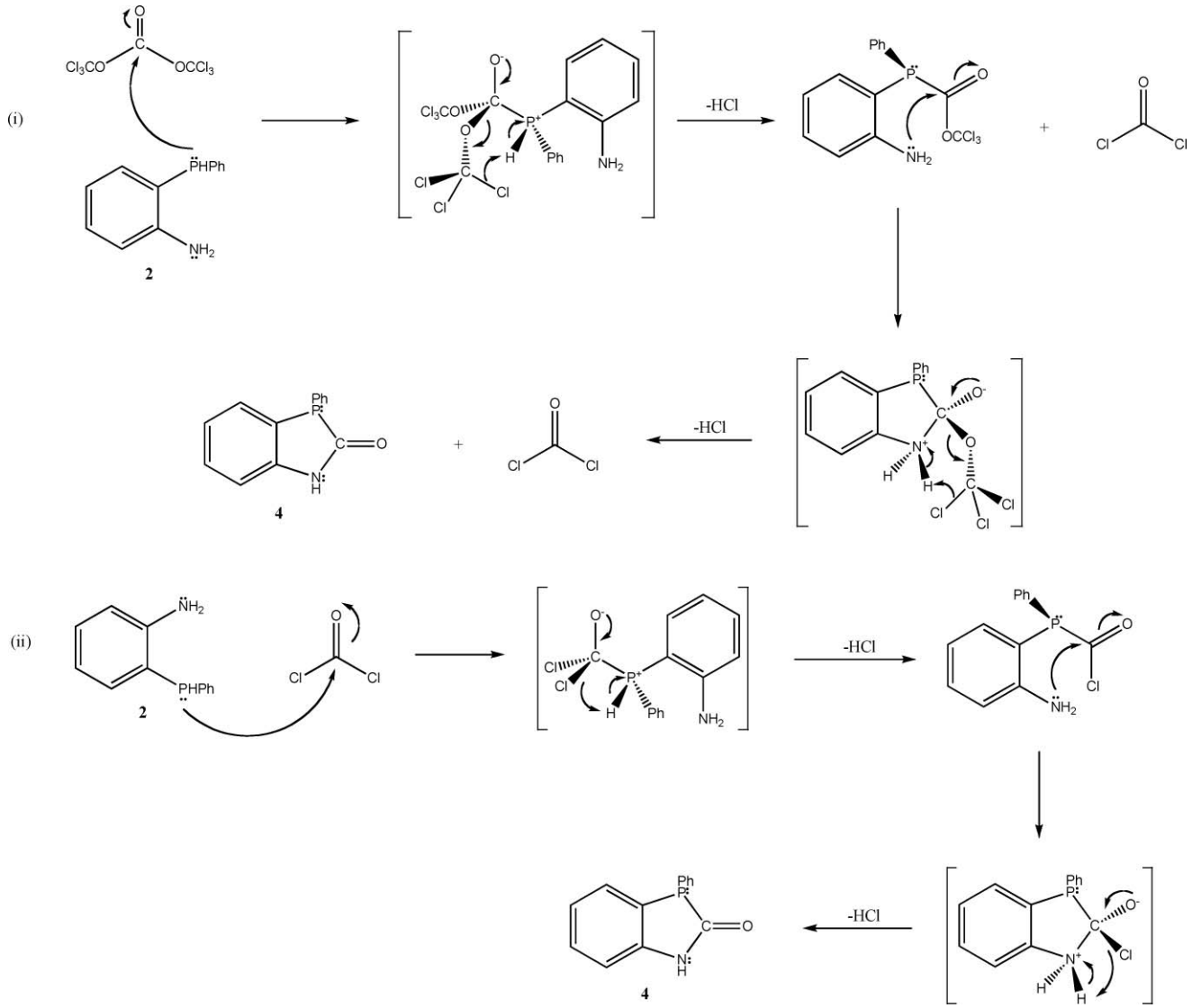


Fig. 1 Proposed mechanism for the formation of **4**

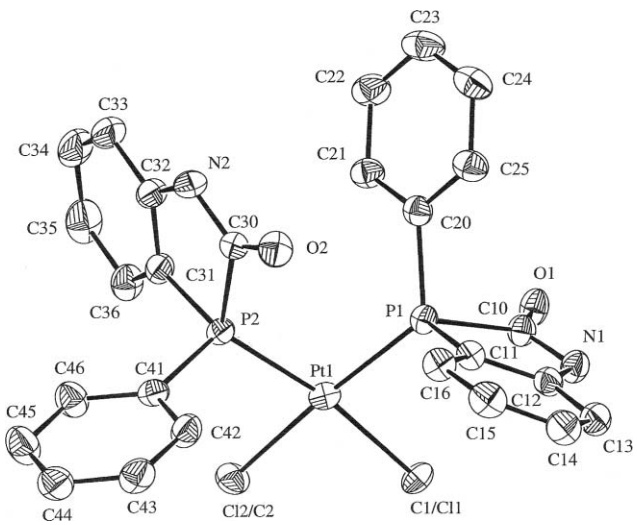


Fig. 2 Molecular structure of the complex *cis*-[PtClMe(**4**)$_2$] (ellipsoids show 30% probability levels).

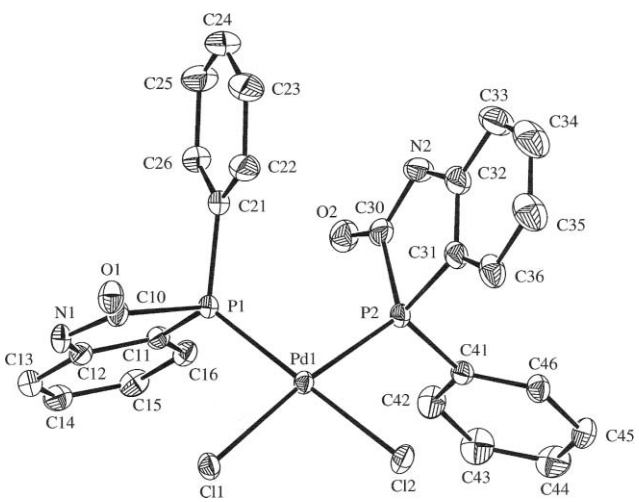


Fig. 3 Molecular structure of the complex *cis*-[PdCl$_2$(**4**)$_2$] (ellipsoids show 30% probability levels).

points were determined using a Leica Galen III melting point apparatus and microscope fitted with a digital meter.

Elemental analyses were carried out by staff in the micro-analytical laboratory at the Research School of Chemistry and mass spectra for compounds with molecular weights over 400 obtained by staff at the Research School of Chemistry. ESI-MS spectra were recorded on a FISONS VG QUATTRO II mass spectrometer, operating at a cone voltage between 40 and 70 V, with positive ion detection. EI MS and HR-EI MS were recorded on a VG autospec mass spectrometer, operating at 70 eV using positive ion detection. Mass spectra are recorded in mass/charge ratios (m/z).

The compounds (2-aminophenyl)diphenylphosphine, adpp, **1**,[15] (±)-(2-aminophenyl)phenylphosphine, (±)-app, **2**,[4] 1,3-bis[2-(diphenylphosphinophenyl)amino]propane, $(CH_2)_3(NHC_6H_4\text{-}PPh_2\text{-}2)_2$,[16] and [*SP-4-2*]-chloro(cycloocta-1,5-diene)methyl-platinum(II), [PtClMe(cod)],[17] were prepared by literature procedures.

Preparations

(±)-(2-Aminophenyl)chlorophenylphosphine hydrochloride, (±)-acpp.HCl, 3. Secondary phosphine **2** (6.06 g, 0.0301 mol) was dissolved in toluene (50 mL) and added dropwise to a stirred suspension of PCl_5 (6.27 g, 0.0301 mol) in toluene (50 mL) at 0 °C. The reaction mixture was stirred at this temperature for 2 h and then allowed to warm to room temperature overnight. The resulting white precipitate was filtered off under argon, washed with toluene (3 × 20 mL) and dried *in vacuo* (7.69 g, 94% assuming the product is the mono-hydrochloride).

(±)-(2-Aminophenyl)(2-methoxyphenyl)phenylphosphine, (±)-aapp, 7. The Grignard reagent (2-methoxyphenyl)magnesium bromide was prepared by suspending magnesium turnings (2.26 g, 0.0930 mol) in thf (100 mL) followed by the slow addition of 2-bromoanisole (17.2 g, 0.0920 mol). The solution was cooled to 0 °C and solid **3** (6.03 g, 0.0222 mol) added in portions. The reaction mixture was stirred overnight at ambient temperature and subsequently heated under reflux for 2 h. The reaction mixture was cooled to 0 °C and a saturated aqueous ammonium chloride solution (50 mL) followed by water (50 mL) were added and the resulting two phases separated. The aqueous phase was extracted with dichloromethane (3 × 60 mL) and the combined organic extracts dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The residue was dissolved in hot methanol (20 mL) to yield a white solid upon cooling. The crystallisation was completed at −4 °C overnight. The crystals were filtered off and washed with cold methanol (3 × 5 mL). The volume of the filtrate was reduced by *ca.* 80%, twice, and cooled at −4 °C to give a further two crops of crystals (4.28 g, 68%), mp 164–165 °C. (Found: C, 74.13; H, 6.18; N, 4.67. Calc. for $C_{19}H_{18}OPN$: C, 74.26; H, 5.90; N, 4.56%.) ^{1}H NMR (CD_2Cl_2): δ 3.74 (s, 3 H, O*Me*); 4.12 (bs, 2 H, NH_2); 6.35–7.34 (m, 13 H, aromatics). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −31.1 (s, 1 P). LR-EI MS: m/z 307 $(M)^+$, 276 $(M - OMe)^+$, 230 $(M - Ph)^+$.

(±)-(2-Aminophenyl)(2-methylphenyl)phenylphosphine, (±)-aptp, 6. The Grignard reagent (2-methylphenyl)magnesium bromide was prepared by suspending magnesium turnings (0.76 g, 0.0314 mol) in thf (40 mL) followed by the slow addition of 2-bromotoluene (5.38 g, 0.0314 mol). The solution was cooled to 0 °C and solid **3** (1.92 g, 0.0081 mol) added in portions. The reaction mixture was stirred overnight at ambient temperature and subsequently heated under reflux for 2 h. The reaction mixture was cooled to 0 °C and a saturated aqueous ammonium chloride solution (30 mL) followed by water (30 mL) were added and the resulting two phases separated. The aqueous phase was extracted with dichloromethane (3 × 20 mL) and the combined organic extracts dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The residue was dissolved in hot methanol (10 mL) to yield a white solid upon cooling. The crystallisation was completed at −4 °C overnight. The crystals were filtered off, washed with cold methanol (2 mL) and dried *in vacuo* (1.40 g, 60%). (Found: C, 76.35; H, 6.31; N, 4.70. Calc. for $C_{19}H_{18}PN.0.5H_2O$: C, 75.98; H, 6.38; N, 4.66%.) ^{1}H NMR ($CDCl_3$): δ 2.40 (s, 3 H, C*Me*); 4.16 (bs, 2 H, NH_2); 6.68–7.37 (m, 13 H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −27.1 (s, 1 P). LR-EI MS: m/z 291 $(M)^+$, 275 $(M - CH_4)^+$, 198 $(M–C_6H_5NH_2)^+$. HR-EI MS: Found for $(M)^+$ 291.1168 (calc. for $C_{19}H_{18}NP$: 291.1177).

(±)-(2-Aminophenyl)phenylvinylphosphine, (±)-apvp, 5. Vinyl bromide (5.02 g, 0.0470 mol) was condensed into a 10 mL measuring cylinder at −20 °C before being poured carefully into thf (10 mL) in a dropping funnel pre-cooled with dry ice. The solution of vinyl bromide was added dropwise to a suspension of magnesium turnings (1.14 g, 0.0470 mol) in thf (120 mL) containing a few drops of 1,2-dibromoethane in a 500 mL Schlenk flask fitted with a dry ice condenser. The reaction was carefully initiated and the vinyl bromide solution added at such a rate that the reaction mixture gently refluxed. The reaction mixture was heated under reflux for 1 h and allowed to cool to room temperature.

The brown Grignard solution was added dropwise to a solution of **3** (4.26 g, 0.0157 mol) in thf (150 mL) over a period of 1 h at 0 °C. The resulting brown solution was refluxed for 2 h, allowed to cool to ambient temperature and stirred overnight. The reaction mixture was cooled to 0 °C and a saturated aqueous ammonium chloride solution (30 mL) followed by water (30 mL) were added and the solvent removed under reduced pressure. The residue was dissolved in water (70 mL) and dichloromethane (50 mL), the resulting phases separated and the aqueous phase extracted further with dichloromethane (2 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give a yellow oil (3.2 g, 90%). ^{1}H NMR (CD_2Cl_2): δ 4.20 (bs, 2 H, NH_2); 5.59 (m, ABM portion of ABMX, 1 H, $^3J_{PH} = 18.1$ Hz, $^3J_{HH} = 16.0$ Hz, $^2J_{HH} = 2.1$ Hz, CH=CH*H*), 5.93 (m, ABM portion of ABMX, 1 H, $^3J_{PH} = 30.8$ Hz, $^3J_{HH} = 11.8$ Hz, $^2J_{HH} = 2.1$ Hz, CH=C*H*H), 6.36–7.82 (m, 10 H, aromatics and C*H*=CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −10.9 (s, 1 P); δ −11.0 (s, 1 P). LR-EI MS: m/z 227 $(M)^+$, 212 $(M - Me)^+$.

(R_P*,R_P*)- and (R_P*,S_P*)-1,2-bis[(2-aminophenyl)phenylphosphino]ethane, (R_P*,R_P*)- and (R_P*,S_P*)-C_2-NP_2N, 8. Vinylphosphine **5** (1.83 g, 8.07 mmol) was dissolved in thf (35 mL) and a solution of (±)-app, **2** (1.62 g, 8.07 mmol) in thf (35 mL) was added dropwise to the stirred solution. The reaction mixture was treated with potassium *tert*-butoxide (*ca.* 0.15 g) and heated under reflux for 19 d. Further potassium *tert*-butoxide (total 0.2 g) was added periodically to the solution. The reaction mixture was

cooled to room temperature and treated with saturated aqueous ammonium chloride solution (20 mL). The solvent was removed under reduced pressure and the off-white oily residue dissolved in water (50 mL) and dichloromethane (50 mL). The resulting phases were separated and the aqueous phase was extracted further with dichloromethane (3 × 30 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give a pale yellow oil. Hot methanol (10 mL) was added to the residual oil (1.98 g) and the solution cooled slowly to room temperature. The solution was stored at −4 °C overnight. The white solid that formed, unreacted **5**, was filtered off under argon, washed with cold methanol (2 × 2 mL) and dried *in vacuo* (0.50 g). The filtrate was taken to dryness to give a yellow oil containing the secondary phosphine **2** and the NP_2N quadridentate ligand **8**. These were separated on a silica column [15 × 1.5 cm, silica gel 70–230 mesh, eluant petroleum spirit bp 40–60 °C/dichloromethane, gradient 100 : 0 → 0 : 100] under nitrogen. Fraction 1, **2** (0.52 g, 32%). ^{1}H NMR and ^{31}P{^{1}H} NMR spectra identical to that of an authentic sample. Fraction 2, **8** (0.276 g, 12% based on amount of (±)-app recovered). ^{1}H NMR (CD_2Cl_2): δ 2.12 (m, 4 H, PCH_2); 3.94 (bs, 4 H, NH_2); 6.62–7.32 (m, 18 H, aromatics). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −31.0 (s, 2 P). LR-EI MS: m/z 428 $(M)^+$, 351 $(M - Ph)^+$, 228 $(M - PhPC_6H_4NH_2)^+$ and 200 $(228 - H_2C{=}CH_2)^+$. HR-EI MS: Found for $(M)^+$ 428.1579 (calc. for $C_{26}H_{26}N_2P_2$: 428.1571).

(±)-3-Phenyl-1,3-dihydrobenzo[1,3]azaphosphol-2-one, (±)-pbap, 4. Triphosgene (2.86 g, 9.64 mmol) was dissolved in thf (40 mL) and a solution of **2** (5.77 g, 0.0287 mol) in thf (60 mL) was added dropwise to the stirred solution at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred overnight. The solvent was removed under reduced pressure to leave a pale yellow solid. The latter was recrystallised from hot toluene (100 mL) to give pale yellow crystals. These were filtered off, washed with toluene (2 × 5 mL) and dried *in vacuo* (5.23 g, 80%), mp 161–162 °C. (Found: C, 66.91; H, 4.50; N, 6.02. Calc. for $C_{13}H_{10}NP.0.5H_2O$: C, 66.10; H, 4.69; N, 5.93%.) ^{1}H NMR ($CDCl_3$): δ 7.00–7.46 (m, 9 H, aromatics); 9.73 (bs, 1 H, NH). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −30.9 (s, 1 P). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 112.5–144.0 (m, 12 C, aromatics), 187.3 (d, 1 C, $^1J_{PC}$ = 7.9 Hz, C=O). LR-EI MS: m/z 227 $(M)^+$, 198 $(M - HCO)^+$, 183 $(M - H_2NCO)^+$. HR-EI MS: Found for $(M)^+$ 227.0498 (calc. for $C_{13}H_{10}NOP$: 227.0500). IR (thin film) cm^{-1}: ν(N–H) 3160 (bs); ν(C–H) 2878–3055 (m); ν(C=O) 1654 (s); δ(N–H) 1599 (m); $\nu(P–C)_{asym}$ 1460 (s); $\nu(P–C)_{sym}$ 1060 (m).

(2-Methylaminophenyl)diphenylphosphine, madpp, 12. The salt [Li(tmeda)][2-$NHC_6H_4PPh_2$ (12.5 g, 0.0312 mol)[5] was suspended in thf (400 mL) and the mixture cooled to −78 °C. Methyl iodide (5.12 g, 0.0312 mol) in thf (100 mL) was added dropwise to the stirred suspension. The solution was allowed to warm slowly to ambient temperature and stirred overnight. The reaction mixture was stirred overnight at room temperature. An aqueous solution of ammonium chloride (50 mL, 20% w/v) was added to the reaction mixture and the solvent distilled off under argon at 1 atm. Water (200 mL) was added to the residue and the mixture extracted with dichloromethane (3 × 100 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give a pale yellow solid residue. The latter was crystallised from hot aqueous ethanol (100 mL, 90% w/v) to give an off-white microcrystalline solid. The solid was filtered off, washed with cold aqueous ethanol (2 × 5 mL, 90% w/v) and dried *in vacuo* (6.54 g, 72%), mp 114.5–115 °C. ^{1}H NMR ($CDCl_3$): δ 2.82 (s, 3 H, NCH_3); 4.85 (bs, 1 H, NH); 6.63–7.35 (m, 14 H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −21.9 (s, 1 P) [lit.[15] ^{31}P{^{1}H} NMR: δ −23.0].

(±)-(2-Methylaminophenyl)phenylphosphine, (±)-mapp, 11. Compound **12** (6.5 g, 0.0223 mol) was dissolved in thf (200 mL). Lithium wire (0.50 g, 0.0721 mol) was added piece wise to the stirred solution and the reaction mixture stirred at ambient temperature for one week. Solid ammonium chloride (5 g) was added to the reaction mixture followed by water (200 mL). The resulting two phases were separated and the aqueous layer extracted with dichloromethane (3 × 80 mL). The organic extracts dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give a residual oil. The product was obtained as a clear colourless oil by distillation under reduced pressure (3.80 g, 79%), bp 135 °C, 0.05 mm Hg. ^{1}H NMR ($CDCl_3$): δ 2.80 (s, 3 H, NCH_3); 4.25 (bs, 1 H, NH); 5.09 (d, 1 H, $^1J_{PH}$ = 222 Hz, PH); 6.30–7.75 (m, 9 H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −60.7 (s, 1 P). LR-EI MS: m/z 216 $(M)^+$, 215 $(M - H)^+$, 200 $(215 - Me)^+$.

(±)-N-methyl-3-phenyl-1,3-dihydrobenzo[1,3]azaphosphol-2-one, (±)-mpbap, 9.

Method 1. Triphosgene (1.76 g, 5.92 mmol) was dissolved in thf (20 mL) and a solution of secondary phosphine **11** (3.82 g, 17.7 mmol) in thf (20 mL) was added dropwise to the stirred solution at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred overnight. The solvent was removed under reduced pressure to leave a pale yellow solid (3.07 g, 72%). ^{1}H NMR ($CDCl_3$): δ 3.07 (s, 3 H, NMe), 6.91–7.51 (m, 9 H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −35.7 (s, 1 P). LR-EI MS: m/z 241 $(M)^+$, 212 $(M - HCO)^+$, 183 $(M - HMeNCO)^+$. HR-EI MS: Found for $(M)^+$ 241.0657 (calc. for $C_{14}H_{12}NOP$: 241.0657).

Method 2. Azaphospholone **4** (0.25 g, 1.10 mmol) was dissolved in thf (2 mL) and excess KOBu^t (0.25 g, 2.20 mmol) was added to the stirred solution. The colour of the reaction mixture changed from pale yellow to green. The reaction mixture was stirred for 0.5 h. Iodomethane (0.16 g, 1.10 mmol) was added and the reaction mixture stirred overnight. The resultant white precipitate was filtered off and the solvent removed under reduced pressure. Dichloromethane (20 mL) and water (30 mL) were added, the organic layer separated and the aqueous phase extracted twice with dichloromethane (2 × 5 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give a light yellow solid (0.15 g, 56%). NMR spectra were identical to that described above.

(±)-N-benzyl-3-phenyl-1,3-dihydrobenzo[1,3]azaphosphol-2-one, (±)-bpbap, 10. Azaphospholone **4** (0.25 g, 1.10 mmol) was dissolved in thf (2 mL) and excess KOBu^t (0.25 g, 2.20 mmol) was added to the stirred solution. The reaction mixture was stirred for 0.5 h. Benzyl bromide (0.19 g, 1.10 mmol) was added and the reaction mixture stirred overnight. The resultant white precipitate was filtered off and the solvent removed under reduced pressure. Dichloromethane (20 mL) and water (30 mL) were added, the organic layer separated and the aqueous phase extracted twice with dichloromethane (2 × 5 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give a light yellow solid (0.22 g, 63%). ^{1}H

NMR ($CDCl_3$): δ 4.89, 4.96 (ABq, 2 H, $^2J_{HH}$ = 15 Hz, NCH_2Ph), 6.83–7.51 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ –36.3 (s, 1 P). LR-EI MS: *m/z* 317 $(M)^+$, 288 $(M - HCO)^+$, 183 $(M - HBnNCO)^+$. HR-EI MS: Found for $(M)^+$ 317.0971 (calc. for $C_{14}H_{12}NOP$: 317.0970).

(R_P*,R_P*)- and (R_P*,S_P*)-1,3-Bis[2-(phenylphosphinophenyl)-amino]propane, (R_P*,R_P*)- and (R_P*,S_P*)-CH_2[$CH_2NHC_6H_4$-PHPh]$_2$, C_3-PN_2PH, 14. The quadridentate PN_2P ligand 1,3-bis[2-(diphenylphosphinophenyl)amino]propane (4.85 g, 8.16 mmol) was dissolved in thf (350 mL). Lithium wire (0.44 g, 63.4 mmol) was added piece wise to the stirred solution and the reaction mixture stirred for 7 d at ambient temperature. Saturated ammonium chloride solution (50 mL) was added and the solvent removed under reduced pressure. The residue was dissolved in water (50 mL) and dichloromethane (150 mL) and the resulting phases separated. The aqueous phase was extracted further with dichloromethane (2 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give an off-white solid (3.60 g, 99%). ^1H NMR ($CDCl_3$): δ 1.52 (m, 2 H, NCH_2CH_2); 2.82 (m, 4 H, NCH_2); 4.06 (bs, 2 H, N*H*); 5.07 (d, 2 H, $^1J_{PH}$ = 220 Hz, P*H*); 6.41–7.43 (m, 18 H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ –60.3 (s, 1 P); –60.5 (s, 1 P). LR-EI MS: *m/z* 442 $(M)^+$, 333 $(M–PHPh)^+$, 242 $(333–C_6H_5NH)^+$, 201 $(242–HNCH_2CH_2CH_3)^+$.

(R_P*,R_P*)- and (R_P*,S_P*)-1,3-Bis[1-{3-phenyl-1,3-dihydrobenzo[1,3]azaphosphol-2-one}]propane, (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_2)_3$(pbap)$_2$, 13.

Method 1. Triphosgene (0.68 g, 2.29 mmol) was dissolved in thf (40 mL) and a solution of (R_P*,R_P*)- and (R_P*,S_P*)-CH_2[$CH_2NHC_6H_4PHPh$]$_2$, **14** (1.51 g, 3.41 mmol) in thf (60 mL) was added dropwise to the stirred solution at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred overnight. The solvent was removed under reduced pressure to leave pale yellow oil that was crystallised by trituration with *n*-pentane (10 mL) to give pale yellow crystals. These were filtered off, washed with *n*-pentane (2 × 5 mL) and dried *in vacuo* (1.22 g, 72%), mp 69 °C. ^1H NMR ($CDCl_3$): δ 1.90 (m, 2 H, C-CH_2-C), 3.72 (m, 4 H, 2 × NCH_2), 6.69–7.45 (m, 18 H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ –36.7 (s, 2 P). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.5 (s, 1 C, C-*C*H_2-C), 38.9 (s, 2 C, 2 × N*C*H_2),110.9–145.0 (m, 24 C, aromatics), 183.8 (d, 2 C, $^1J_{PC}$ = 9.7 Hz, C=O). LR-EI MS: *m/z* 494 $(M)^+$, 267 $(M - (\pm)$-pbap$)^+$. HR-EI MS: Found for $(M)^+$ 494.1312 (calc. for $C_{29}H_{24}N_2O_2P_2$: 494.1313). IR (thin film) cm^{-1}: ν(C–H) 2945–3053 (m); ν(C=O) 1655 (s); δ(N–H) 1589 (m); $\nu(P–C)_{asym}$ 1453 (s); $\nu(P–C)_{sym}$ 1059 (m).

Method 2. Azaphospholone **4** (0.25 g, 1.10 mmol) was dissolved in thf (2 mL) and excess KOBu^t (0.25 g, 2.20 mmol) was added to the stirred solution. The reaction mixture was stirred for 0.5 h. 1,3-Dibromopropane (0.14 g, 0.69 mmol) was added and the reaction mixture stirred for 5 d. The solvent was removed under reduced pressure. Dichloromethane (30 mL) and water (20 mL) were added, the organic layer separated and the aqueous phase extracted twice with dichloromethane (2 × 5 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The residue was triturated with *n*-pentane (2 mL) to give a light yellow solid (0.18 g, 65%). NMR spectra were identical to that described above.

[*SP*-4-2-(R_P*,S_P*)]-Chloromethylbis{3-phenyl-1,3-dihydrobenzo-[1,3]aza-phosphol-2-one-P}platinum(II), [PtClMe(4)$_2$]. A solution of the complex [PtClMe(cod)] (0.19 g, 0.537 mmol) in thf (15 mL) was added dropwise to a stirred solution of **4** (0.24 g, 1.06 mmol) in thf (10 mL). The reaction mixture was stirred for 0.5 h and *n*-pentane (40 mL) was added. The resulting very pale yellow precipitate was filtered off, washed with *n*-pentane (2 × 2 mL) followed by diethyl ether (2 × 2 mL) and dried *in vacuo* (0.35 g, 95%), mp > 230 °C. (Found: C, 45.63; H, 3.35; N, 3.84. Calc. for $C_{27}H_{23}ClN_2O_2P_2Pt.0.5H_2O$: C, 45.74; H, 3.41; N, 3.95%.) ^1H NMR [$(CD_3)_2SO$)]: δ 1.16 (bs, 3 H, $^3J_{PtH}$ = 51 Hz, Pt*Me*), 7.32–8.51 (m, 18 H, aromatics), 11.16 (d, 1 H, $^3J_{PH}$ = 13 Hz, N*H*), 11.65 (d, 1 H, $^3J_{PH}$ = 17 Hz, N*H*). $^{31}P\{^1H\}$ NMR [$(CD_3)_2SO$)]: δ –5.0 (d, 1 P, $^2J_{PP}$ = 15 Hz, $^1J_{PtP}$ = 4310 Hz), 1.3 (d, 1 P, $^2J_{PP}$ = 15 Hz, $^1J_{PtP}$ = 1625 Hz).

[*SP*-4-2-(R_P*,S_P*)]-Chloromethylbis{N-methyl-3-phenyl-1,3-dihydrobenzo[1,3]aza-phosphol-2-one-P}platinum(II), [PtClMe(9)$_2$]. A solution of the complex [PtClMe(cod)] (0.12 g, 0.34 mmol) in thf (15 mL) was added dropwise to a stirred solution of **9** (0.16 g, 0.68 mmol) in thf (10 mL). The reaction mixture was stirred for 0.5 h and *n*-pentane (40 mL) was added. The resulting very pale yellow precipitate was filtered off, washed with *n*-pentane (2 × 2 mL) followed by diethyl ether (2 × 2 mL) and dried *in vacuo* (0.13 g, 53%), mp > 230 °C. (Found: C, 47.59; H, 3.82; N, 3.85. Calc. for $C_{29}H_{27}ClN_2O_2P_2Pt$: C, 47.84; H, 3.74; N, 3.85%). ^1H NMR [$(CD_3)_2SO$)]: δ 0.66 (bs, 3 H, Pt*Me*), 2.62 (s, 3 H, N*Me*), 2.91 (s, 3 H, N*Me*), 7.14–8.13 (m, 18 H, aromatics). $^{31}P\{^1H\}$ NMR [$(CD_3)_2SO$)]: δ –5.2 (d, 1 P, $^2J_{PP}$ = 14 Hz,$^1J_{PtP}$ = 4357 Hz), 0.6 (d, 1 P, $^2J_{PP}$ = 14 Hz, $^1J_{PtP}$ = 1621 Hz).

[*SP*-4-2-(R_P*,S_P*)]-Chloromethylbis{N-benzyl-3-phenyl-1,3-dihydrobenzo[1,3]aza-phosphol-2-one-P}platinum(II), [PtClMe(10)$_2$]. A solution of the complex [PtClMe(cod)] (0.084 g, 0.24 mmol) in thf (10 mL) was added dropwise to a stirred solution of **10** (0.15 g, 0.47 mmol) in thf (10 mL). The reaction mixture was stirred for 0.5 h and *n*-pentane (40 mL) was added. The resulting very pale yellow precipitate was filtered off, washed with *n*-pentane (2 × 2 mL) followed by diethyl ether (2 × 2 mL) and dried *in vacuo* (0.12 g, 57%), mp > 230 °C. (Found: C, 55.31; H, 4.04; N, 3.39. Calc. for $C_{41}H_{35}ClN_2O_2P_2Pt.0.5H_2O$: C, 55.37; H, 4.08; N, 3.15%.) ^1H NMR [$(CD_3)_2SO$)]: δ 0.33 (bs, 3 H, Pt*Me*), 3.91, 4.03 (ABq, 2 H, $^2J_{HH}$ = 18 Hz, NCH_2Ph), 4.13, 4.25 (ABq, 2 H, $^2J_{HH}$ = 18 H,z NCH_2Ph), 6.58–7.77 (m, 18 H, aromatics). $^{31}P\{^1H\}$ NMR [$(CD_3)_2SO$)]: δ –4.7 (d, 1 P, $^2J_{PP}$ = 15 Hz, $^1J_{PtP}$ = 4362 Hz), 1.7 (d, 1 P, $^2J_{PP}$ = 14 Hz,$^1J_{PtP}$ = 1621 Hz).

[*SP*-4-2-(R_P*,S_P*)]-Dichlorobis{3-phenyl-1,3-dihydrobenzo-[1,3]aza-phosphol-2-one-P}palladium(II), [PdCl$_2$(4)$_2$]. A solution of $Li_2[PdCl_4]$ in methanol was prepared by reacting $PdCl_2$ (0.2025 g, 1.14 mmol) with excess anhydrous LiCl (0.50 g, 11.8 mmol) in methanol (30 mL). The mixture was stirred for 1 h and the resulting reddish-brown solution filtered through Celite. A solution of **4** (0.5189 g, 2.28 mmol) in methanol (10 mL) was added to the filtrate. The resulting golden yellow precipitate was filtered off, washed with diethyl ether (2 × 2 mL) and dried *in vacuo* (0.49 g, 68%), mp > 230 °C. (Found: C, 48.37; H, 3.21; N, 4.29. Calc. for $C_{26}H_{20}Cl_2N_2O_2P_2Pd.H_2O$: C, 48.06; H, 3.41; N, 4.31%.) ^1H NMR [$(CD_3)_2SO$)]: δ 6.92–8.25 (m, 18 H, aromatics), 11.16

Table 3 Crystallographic data for the complexes *cis*-[PtClMe(**4**)$_2$] and *cis*-[PdCl$_2$(**4**)$_2$]

	cis-[PtClMe(**4**)$_2$]	*cis*-[PdCl$_2$(**4**)$_2$]
Empirical formula	$C_{27}H_{23}ClN_2O_2P_2Pt.2C_3H_8O$	$C_{26}H_{20}Cl_2N_2O_2P_2Pd.1.66CH_4O.1.34\ H_2O$
M	820.17	709.02
T/K	200	200
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$
Crystal size/mm	$0.36 \times 0.13 \times 0.05$	$0.40 \times 0.08 \times 0.03$
a/Å	15.4641(2)	8.6093(2)
b/Å	12.9680(2)	11.3301(3)
c/Å	18.4124(3)	16.3435(5)
α/°		81.4299(12)
β/°	113.4788(9)	83.0012(16)
γ/°		77.0439(16)
V/Å^3	3386.69(9)	1529.80(7)
Z	4	2
D_c/g cm^{-3}	1.609	1.528
μ/mm^{-1}	4.37	0.92
Reflections collected	69 517	34 432
Independent reflections	7756	7035
Independent observed reflections	5069 ($I > 3\sigma(I)$)	4819 ($I > 3\sigma(I)$)
R_{int}	0.041	0.043
Final R, R_w	0.026, 0.030	0.028, 0.033
2θ range/°	6–55	6–55
Parameters	395	400

(d, 1 H, $^3J_{PH}$ = 12 Hz, N*H*). ^{31}P{^{1}H} NMR [(CD$_3$)$_2$SO)]: δ 28.9 (s, 2 P).

X-Ray crystallography

X-Ray diffraction data for *cis*-[PtClMe(**4**)$_2$] and *cis*-[PdCl$_2$(**4**)$_2$] were obtained on a Nonius Kappa CCD diffractometer using Mo Kα radiation. Details of the data collections, solutions and refinements are given in Table 3. The structures were solved using *SIR*92 and refined using *CRYSTALS*.[9,10] Analytical absorption corrections were applied to the data for both *cis*-[PtClMe(**4**)$_2$] and *cis*-[PdCl$_2$(**4**)$_2$] (max./min. transmission factors 0.803/0.347 and 0.969/0.794, respectively).[11,12]

Initial solution of the structure of *cis*-[PtClMe(**4**)$_2$] revealed that the two non-phosphine sites on the Pt atom were of very similar size. When incorporated as two Cl atoms their displacement parameters were much larger than those of adjacent atoms; when assigned to be two C atoms their displacement parameters were very small. This suggested that the chloro and methyl groups were disordered on the two sites. Attempts to get them to refine to separate positions were not successful. This has previously been reported for the related complexes *trans*-[PtClMe{2-Ph$_2$PC$_6$H$_4$NH(SO$_2$C$_6$H$_4$CH$_3$-4)}$_2$] and *trans*-[PtClMe(PR$_3$)$_2$] (where R = Et or Ph).[6,13,14] To model this effect Cl and C atoms of occupancy 0.5 were placed at each site and constraints were imposed on their positional and anisotropic displacement factors so they would remain identical during further refinement. The relative occupancies of Cl *versus* C were refined.

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