Synthesis of a chelating hexadentate ligand with a P_3N_3 donor set. Crystal and molecular structure of [*OC*-6-22]-[Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]$(PF_6)_3$

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The first structurally authenticated example of a hexadentate chelating tertiary phosphine in which all six donors are bound to a single metal centre is described. The multidentate ligand (R_P*,R_P*,R_P*)- and (R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$ has been prepared in 80% yield *via* the reaction of five equivalents of sodium (2-aminophenyl)phenylphosphide (generated *in situ* from (2-aminophenyl)phenylphosphine and sodium in thf) with 1,1,1-tri(bromomethyl)ethane in thf. The diastereomeric mixture has been complexed to cobalt(III) and the resulting pair of complexes, *viz.* [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]Cl_3 and [CoCl{(R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]Cl_2, separated by ion exchange chromatography. The structure of the former (as the corresponding hexafluorophosphate salt) has been confirmed by X-ray crystallography and clearly shows all six donors of the P_3N_3 ligand coordinated to a single cobalt(III) centre. The related hexadentate ligand with internal N donors and terminal diphenylphosphino groups, *viz.* $CH_3C(CH_2NHC_6H_4PPh_2$-2)$_3$, has also been synthesised, albeit in low yield, *via* the reaction of [Li(tmeda)][2-$NHC_6H_4PPh_2$] (generated *in situ* from (2-aminophenyl)diphenylphosphine, *n*-butyllithium and tmeda in diethyl ether) with 1,1,1-tri(iodomethyl)ethane in thf. No formation of a P_3N_3 ligand has been observed when either Na[2-$PPhC_6H_4NH_2$] or [Li(tmeda)][2-$NHC_6H_4PPh_2$] is reacted with the related tripodal substrate 1,1,1-tris(tolyl-4-sulfonyloxymethyl)ethane in thf. Rather the *P*-methyloxetane (±)-[3-{(2-aminophenyl)phenylphosphinomethyl}]-3-methyloxetane and the sulfonamide 2-(4-$CH_3C_6H_4SO_2$)$NHC_6H_4PPh_2$ and the corresponding *N*-methyloxetane [3-{(2-diphenylphosphinophenyl)aminomethyl}]-3-methyloxetane have been isolated from the respective reactions. The structure of the sulfonamide has been confirmed by an X-ray analysis of the platinum(II) complex *trans*-[PtCl(CH_3){2-$PPh_2C_6H_4NH(SO_2C_6H_4CH_3$-4)}$_2$].

Introduction

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 ligands *via* derivatisation of the amino or diphenylphosphino groups. Reductive cleavage of a phenyl moiety from adpp was readily achieved with three equivalents of lithium in thf to give secondary phosphine (±)-(2-aminophenyl)phenylphosphine, (±)-app, upon hydrolysis.[2,3] The latter was readily metallated with sodium in thf and the resulting metal phosphide alkylated with, for example, CH_3I or $Br(CH_2)_nBr$ (where n = 3–6) to give the bidentate PN ligand (±)-(2-aminophenyl)methylphenylphosphine, (±)-ampp,[2] or the linear quadridentate ligands (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_2)_n(PPhC_6H_4NH_2$-2)$_2$, (R_P*,R_P*)- and (R_P*,S_P*)-C_n-NP_2N.[3,4] Separation of the racemic and meso diastereomers of the linear quadridentate NP_2N ligands and the resolution of (R_P*,R_P*)-C_3-NP_2N was achieved *via* separation by fractional crystallisation of a pair of bis[palladium(II)] complexes containing the respective ligand and orthometallated *N*,*N*-dimethylbenzylamine or (*S*)-dimethyl(1-phenylethyl)amine, respectively.[4] Separation of (R_P*,R_P*)- and (R_P*,S_P*)-C_3-NP_2N has also been demonstrated by complexation to platinum(II).[3] Reductive cleavage of a phenyl moiety from (±)-ampp was similarly achieved using the above conditions and the secondary phosphine (±)-(2-aminophenyl)methylphosphine, (±)-amp, isolated upon hydrolysis.[5] Metallation of the latter with sodium in thf followed by alkylation of the resulting metal phosphide with 1,2-$C_6H_4Cl_2$ gave the 2-chlorophenyl substituted PN ligand (±)-(2-aminophenyl)(2-chlorophenyl)methylphosphine, (±)-acmp. Both (±)-ampp and (±)-acmp were resolved by the method of metal resolution and the antipodes of the latter further reacted with sodium (2-dimethylarsinophenyl)methylarsenide in thf to give optically active multidentate As_2NP and As_4P ligands.[2,5]

Derivatisation of the amino group of adpp has been achieved by complexation to nickel(II) and deprotonation with K_2CO_3, to give the complex *cis*-[Ni(2-$HNC_6H_4PPh_2$)$_2$], followed by reaction with one-half equivalent of 1,3-bis(tolyl-4-sulfonyloxy)propane or 1,2-bis(tolyl-4-sulfonyloxy)ethane, respectively, in toluene to give the linear quadridentate PN_2P ligands $(CH_2)_n(NHC_6H_4PPh_2$-2)$_2$ (where n = 2 or 3) upon decomplexation with aqueous NaCN.[6,7] Higher homologues could not be prepared by this route, however, the analogous PN_2P ligands $(CH_2)_n(NHC_6H_4PPh_2$-2)$_2$ (where n = 4 or 5) were successfully prepared by the Schiff

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base condensation of adpp with the appropriate acid chloride in anhydrous thf in the presence of pyridine followed by reduction with $LiAlH_4$.[8] The latter approach was also used to prepare related linear quadridentate PN_2P ligands containing a variety of linkages between the N atoms by coupling the nitrogen donors of adpp with substrates such as 1,1′-binaphthyl-2,2′-biscarbaldehyde and trimethyl orthoformate.[9] Both of these approaches have been used to convert (R_P*,S_P*)-C_3-NP_2N to macrocyclic P_2N_2 ligands.[10]

In this work derivatisation of both the amino and diphenylphosphino groups of adpp has been investigated as a means of providing a viable synthetic route to hexadentate P_3N_3 ligands of the type $CH_3C(CH_2NHC_6H_4PPh_2\text{-}2)_3$ and $CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$, respectively. The latter exists as a 1 : 3 mixture of (R_P*,R_P*,R_P*) and (R_P*,R_P*,S_P*) diastereomers (see Fig. 1), coordination of the (R_P*,R_P*,R_P*) form of the ligand to cobalt(III) providing the first example of a hexadentate chelating tertiary phosphine in which all six donors are bound to a single metal centre. The (R_P*,R_P*,S_P*) diastereomer is precluded from forming a similar complex as all three stereogenic phosphorus centres need to have the same relative configuration in order for the six donors to be able to bind to the same metal ion. The presence of six phenyl groups on one face of an octahedron also precludes $CH_3C(CH_2NHC_6H_4PPh_2\text{-}2)_3$ from forming a similar complex, however, it was anticipated that derivatisation of the terminal diphenylphosphino groups, using a similar approach to that used for the conversion of adpp to (±)-app, could provide a route to a less sterically hindered analogue capable of coordinating to a single metal ion.

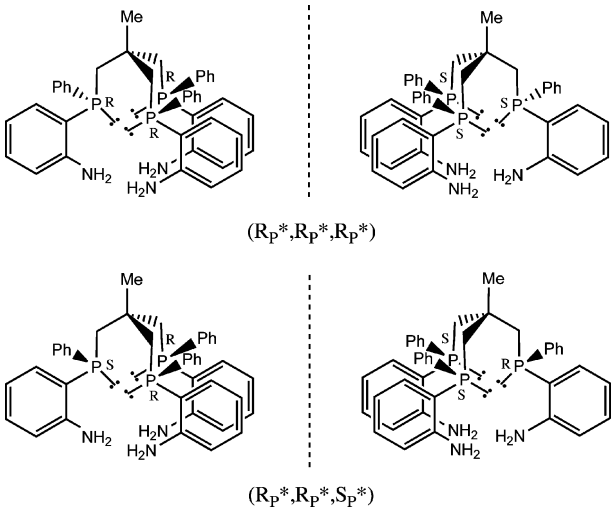
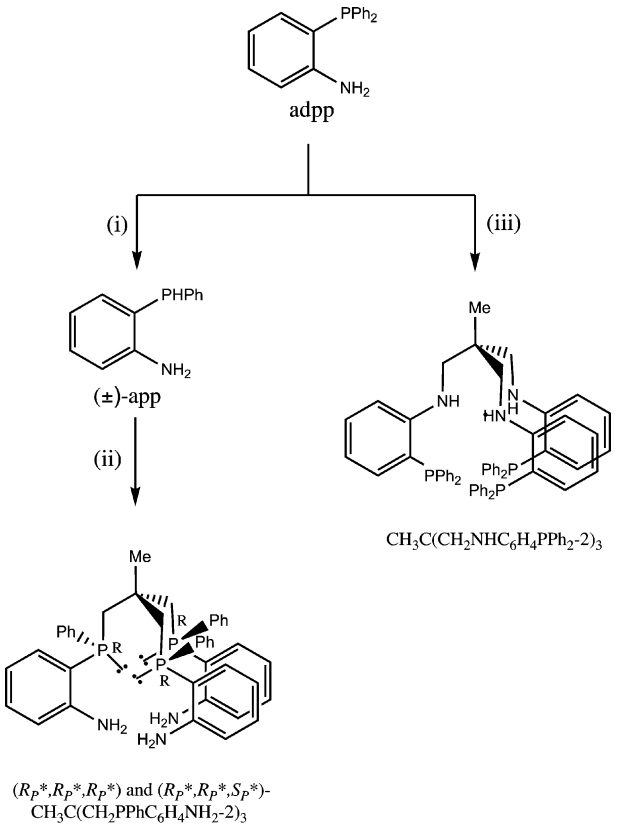


Fig. 1 Stereochemical representation of the tripodal hexadentate ligands (R_P*,R_P*,R_P*)- and (R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$.

Results and discussion

Synthesis of P_3N_3 ligands

Synthesis of the hexadentate P_3N_3 ligands $CH_3C(CH_2NHC_6H_4PPh_2\text{-}2)_3$ and $CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$ was investigated *via* the coupling of [Li(tmeda)][2-$NHC_6H_4PPh_2$] and Na[$PPhC_6H_4NH_2$-2], respectively, with the tripodal substrates $CH_3C(CH_2X)_3$ (where X = Cl, Br, I or OTs) (see Scheme 1). The salt [Li(tmeda)][2-$NHC_6H_4PPh_2$] was isolated in 86% yield



Scheme 1 *Reagents and conditions*: (i) 3 Na, $NH_{3(l)}$; NH_4Cl; (ii) Na, thf; 0.2 $CH_3C(CH_2Br)_3$, thf; (iii) *n*-BuLi, *n*-hexane, diethyl ether, tmeda; 0.33 $CH_3C(CH_2I)_3$, thf.

from the reaction of *n*-butyllithium in *n*-hexane–diethyl ether with adpp followed by the addition of tmeda. The corresponding salt Na[$PPhC_6H_4NH_2$-2] was generated *in situ* from (±)-app and sodium in thf.[2] The secondary phosphine (±)-app was prepared from adpp using three equivalents of sodium in liquid ammonia rather than the standard literature procedure of three equivalents of lithium in thf, followed by hydrolysis. This proved to be a more efficient route to (±)-app since it could be performed on a large scale and routinely gave the product in high yield, in contrast to the lithium reaction where the yield was much more variable and the reaction times significantly longer. Interestingly, whereas essentially completely chemoselective cleavage of a phenyl from the analogous PN ligand (±)-ampp was found using three equivalents of lithium in thf,[5] little selectivity was observed using three equivalents of sodium in liquid ammonia. Rather the crude product consisted of a *ca.* 11 : 9 mixture of the secondary phosphines (±)-amp and (±)-methylphenylphosphine,[11] the latter presumably being formed by cleavage of the 2-aminophenyl group. This result suggests that the amino group of (±)-ampp does not remain completely deprotonated under these reaction conditions. The deprotonation of the amino group in adpp and (±)-ampp on reaction with lithium in thf has previously been proposed to account for the selective cleavage of a phenyl group.[2,5]

The tripodal hexadentate P_3N_3 ligand (R_P*,R_P*,R_P*)- and (R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$ was prepared in 80% yield *via* the dropwise addition of a solution of $CH_3C(CH_2Br)_3$ in

thf to a solution containing five equivalents of Na[$PPhC_6H_4NH_2$-2] in the same solvent at −78 °C, followed by allowing the reaction to proceed at −20 °C for 20 days and ambient temperature for a further 10 days. Significantly lower yields of the P_3N_3 ligand were isolated when the reaction mixture was not kept at −20 °C for several days, three rather than five equivalents of Na[$PPhC_6H_4NH_2$-2] were used, $CH_3C(CH_2Cl)_3$ was used instead of $CH_3C(CH_2Br)_3$, or when the addition of the reagents was reversed *i.e.* addition of the Na[$PPhC_6H_4NH_2$-2] solution to the tripodal substrate in thf. When a stoichiometric amount of Na[$PPhC_6H_4NH_2$-2] was used in the coupling reaction with $CH_3C(CH_2Br)_3$, (R_P*,R_P*,R_P*)- and (R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$ was isolated by column chromatography in only 28% yield. The chromatographic separation yielded two other products, unreacted (±)-app (35%) and the disubstituted product (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_3)_2C(CH_2PPhC_6H_4NH_2$-2)$_2$ (18%). Formation of the latter product can be rationalized in terms of substitution of two of the bromo groups in $CH_3C(CH_2Br)_3$ followed by reduction of the third bromomethyl group. A similar observation has previously been reported for the analogous reaction between sodium (2-dimethylarsinophenyl)methylarsenide and $CH_3C(CH_2Cl)_3$.[12] Here the disubstituted quadridentate As_4 ligands (R_{As}*,R_{As}*)-, (R_{As}*,R_{As}*,r*)- and (R_{As}*,S_{As}*,s*)-$CH_3C(CH_2Cl)(CH_2AsMeC_6H_4AsMe_2$-2)$_2$ were formed when three rather than five equivalents of the sodium arsenide were used in the reaction. Similarly, no evidence for the presence of these disubstituted products was observed when five equivalents of the sodium arsenide was used, the only products formed were the expected hexa(tertiary arsine) (R_{As}*,R_{As}*,R_{As}*)- and (R_{As}*,R_{As}*,S_{As}*)-$CH_3C(CH_2AsMeC_6H_4AsMe_2$-2)$_3$, and a cyclic tetra(tertiary arsine) (R_{As}*,S_{As}*,R_{As}*)-5,6,7,8,9-pentahydro-6-{[(2-dimethylarsinophenyl)methylarsino]methyl}-1,4,6-trimethylbenzo[*b*][1,4]diarsacycloheptane, consistent with complete substitution of the three chloro groups in the substrate.

Evidence for the formation of the related tripodal hexadentate P_3N_3 ligand $CH_3C(CH_2NHC_6H_4PPh_2$-2)$_3$ was found upon heating a mixture of $CH_3C(CH_2I)_3$ and three equivalents of [Li(tmeda)][2-$NHC_6H_4PPh_2$] in toluene under reflux for twelve days. The HR-ESI mass spectrum of the crude reaction product exhibited a molecular ion for $CH_3C(CH_2NHC_6H_4PPh_2$-2)$_3$ [calc. for $C_{59}H_{53}N_3P_3$ $(M - H)^+$: m/z 896.345239; found: 896.347243]. The reaction, however, had not proceeded to any great extent with the crude reaction product being comprised largely of unreacted starting materials. No reaction was observed between [Li(tmeda)][2-$NHC_6H_4PPh_2$] and the related tripodal substrates $CH_3C(CH_2X)_3$ (where X = Cl or Br) under similar conditions.

Isolation and crystal structure determination of [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]$(PF_6)_3$

Separation of the (R_P*,R_P*,R_P*) and (R_P*,R_P*,S_P*) forms of $CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$ was achieved by complexation to cobalt(III) followed by ion exchange chromatography to give two complexes, *viz.* [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]Cl_3 and [CoCl{(R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]Cl_2, in yields of 22 and 70%, respectively. Both complexes were readily converted to the corresponding hexafluorophosphate salts, [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]$(PF_6)_3$ and [CoCl{(R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]$(PF_6)_2$, by metathesis with aqueous NH_4PF_6 in methanol and suitable crystals of the former complex for an X-ray analysis were obtained by recrystallisation from isopropyl alcohol–acetone.

The complex [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]$(PF_6)_3$·C_3H_6O is a racemic compound with both Δ and Λ forms of the cation being present in the unit cell. Only the Δ form of the cation is depicted in Fig. 2. Selected bond lengths and angles are given in Table 1.

Table 1 Selected non-hydrogen interatomic distances (Å) and interatomic angles (°) for [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]$(PF_6)_3$·C_3H_6O

Co–P(1)	2.2067(9)	Co–N(1)	2.024(3)
Co–P(2)	2.1958(9)	Co–N(2)	2.048(3)
Co–P(3)	2.1954(9)	Co–N(3)	2.032(2)
P(1)–Co–P(2)	90.27(3)	P(3)–Co–N(2)	174.49(8)
P(2)–Co–P(3)	89.81(3)	P(1)–Co–N(3)	173.85(8)
P(1)–Co–P(3)	89.54(3)	P(2)–Co–N(3)	93.32(8)
P(1)–Co–N(1)	85.48(8)	P(3)–Co–N(3)	85.48(7)
P(2)–Co–N(1)	175.22(8)	N(1)–Co–N(2)	92.4(1)
P(3)–Co–N(1)	92.34(8)	N(1)–Co–N(3)	91.1(1)
P(1)–Co–N(2)	93.58(7)	N(2)–Co–N(3)	91.7(1)
P(2)–Co–N(2)	85.64(8)		

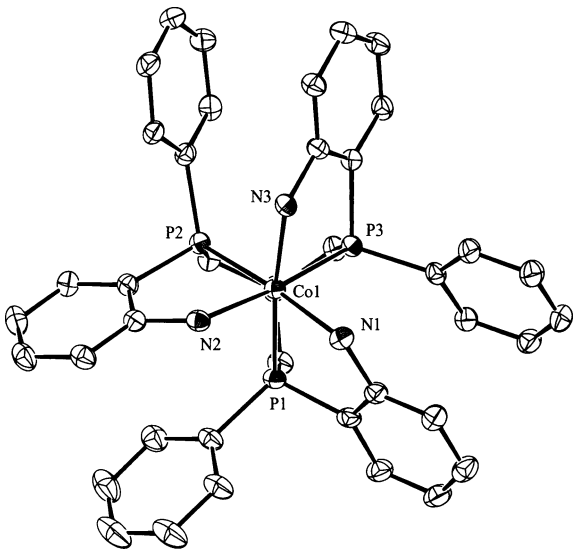


Fig. 2 Molecular structure of the cation [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]$^{3+}$ (ellipsoids show 30% probability levels).

The structural data revealed a C_3 symmetric cation in which all six donor atoms of the P_3N_3 ligand were coordinated to a single cobalt(III) centre in a facial arrangement and the three phosphorus stereocentres had the same relative configuration. The complex had a distorted octahedral geometry, as indicated by the *trans* P–Co(1)–N bond angles which ranged between 173.85 and 175.22°. The Co–P distances (2.21, 2.20, 2.20 Å) and Co–N distances (2.02, 2.05, 2.03 Å) were within the ranges 2.17–2.25 Å and 1.99–2.05 Å, respectively, observed for similar bonds in various mononuclear cobalt(III) complexes.[5,13]

The structural integrity of the cation [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]$^{3+}$ is retained in solution. The

$^{31}P\{^{1}H\}$ NMR spectra of the complexes $[Co\{(R_P^*,R_P^*,R_P^*)\text{-}CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3\}]X_3$ (where X = Cl or PF_6) in CD_3OD revealed a single ^{31}P resonance at δ 54.6 and 55.2, respectively, for the three equivalent phosphorus stereocentres, consistent with the C_3 symmetry of the cation.

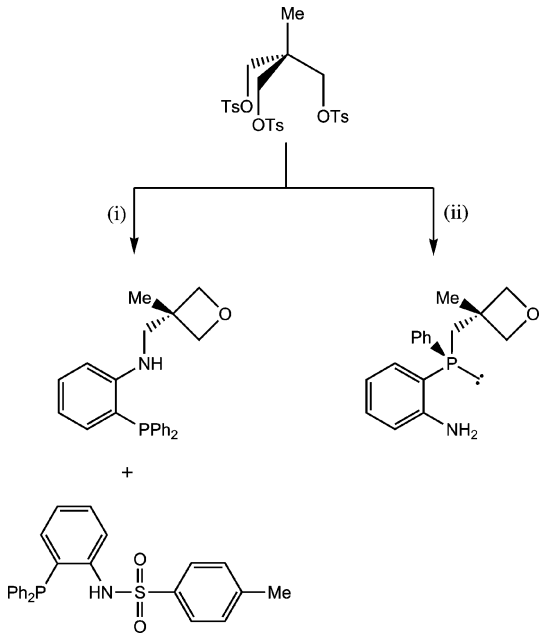
The structure of $[CoCl\{(R_P^*,R_P^*,S_P^*)\text{-}CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3\}](PF_6)_2$ has not been confirmed by X-ray crystallography, however, the formulation given is consistent with analytical data. The P_3N_3 ligand is believed to be coordinated in a pentadentate fashion to the metal centre *via* three P and two N donor atoms with a chloro ligand completing the octahedral arrangement about the cobalt(III) centre. The $^{31}P\{^{1}H\}$ NMR spectrum of the complex in CD_3OD exhibited three broad singlet ^{31}P resonances at δ 18.2, 45.4 and 61.1, consistent with the expected C_1 symmetry of the cation and indicative of all three phosphorus donors of the P_3N_3 ligand being coordinated to the cobalt(III) centre.

Liberation of the P_3N_3 ligand from $[Co\{(R_P^*,R_P^*,R_P^*)\text{-}CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3\}]Cl_3$ and $[CoCl\{(R_P^*,R_P^*,S_P^*)\text{-}CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3\}]Cl_2$ was achieved by treatment of the individual complexes with KCN in refluxing methanol-benzene, however, the cyanolysis caused epimerisation at phosphorus in each case leading to the isolation of a *ca.* 1 : 3 equilibrium mixture of (R_P^*,R_P^*,R_P^*)- and $(R_P^*,R_P^*,S_P^*)\text{-}CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$. The $^{31}P\{^{1}H\}$ NMR spectrum of the liberated P_3N_3 ligand in each case was identical to that recorded for the diastereomeric mixture of (R_P^*,R_P^*,R_P^*)- and $(R_P^*,R_P^*,S_P^*)\text{-}CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$. The epimerisation of the phosphorus stereocentres under these conditions was confirmed by recomplexation of the cyanolysed products to cobalt(III) and separation of the two complexes formed by fractional crystallization from ethanol or ion-exchange chromatography. In each case $[Co\{(R_P^*,R_P^*,R_P^*)\text{-}CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3\}]Cl_3$ and $[CoCl\{(R_P^*,R_P^*,S_P^*)\text{-}CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3\}]Cl_2$ were again obtained in yields of *ca.* 23 and 72%, respectively, indicating that the products of the cyanolysis reactions consisted of a mixture of (R_P^*,R_P^*,S_P^*) and (R_P^*,R_P^*,R_P^*) diastereomers close to the statistical ratio of 3 : 1.

This result was unexpected given that stereogenic tertiary phosphine centres are usually configurationally stable under these conditions. There have been several reports, however, of the epimerisation of coordinated stereogenic arsenic centres in cobalt(III) complexes containing multidentate arsine ligands.[14,15] For example, Bosnich *et al.* reported the epimerisation of the internal arsenic stereocentres in a cobalt(III) complex containing the linear tetra(tertiary arsine), (R_{As}^*,R_{As}^*)-1,2-bis[(3-dimethylarsinopropyl)phenylarsino]ethane, tetars.[15] The inversion was suggested to occur *via* a five-coordinate arsenic centre similar to the mechanism proposed for the racemization of organoarsonium halides by Horner and Hofer.[16]

Reaction of $Na[2\text{-}PPhC_6H_4NH_2]$ and $[Li(tmeda)][2\text{-}NHC_6H_4PPh_2]$ with 1,1,1-tris(tolyl-4-sulfonyloxymethyl)ethane, $CH_3C(CH_2OTs)_3$

No evidence for the formation of a hexadentate ligand was found when $Na[2\text{-}PPhC_6H_4NH_2]$ (three equivalents) or $[Li(tmeda)][2\text{-}NHC_6H_4PPh_2]$ (five equivalents) were reacted with $CH_3C(CH_2OTs)_3$ in thf (Scheme 2). The key products after hydrolysis were the starting material (±)-app and the *P*-methyloxetane (±)-[3-{(2-aminophenyl)phenylphosphinomethyl}]-3-methyloxetane (67%) from the first reaction and the sulfonamide $2\text{-}(4\text{-}CH_3C_6H_4SO_2)NHC_6H_4PPh_2$ (73%), the *N*-methyloxetane [3-{(2-diphenylphosphinophenyl)aminomethyl}]-3-methyloxetane (52%) and recovered adpp from the second reaction. The corresponding sulfonphosphide (±)-$2\text{-}(4\text{-}CH_3C_6H_4SO_2)PPhC_6H_4NH_2$ was identified in the crude product from the first reaction but could not be isolated in pure form. The $^{31}P\{^{1}H\}$ NMR spectrum of the crude product in $CDCl_3$ contained a singlet resonance at δ 36.8, within the δ 33–45 range for ^{31}P chemical shifts observed for several other sulfonphosphides prepared from lithium diphenylphosphide and the appropriate tosyl chloride,[17] and the mass spectrum contained a peak at m/z 291 ($M - SO_2$) also indicative of the presence of the sulfonphosphide.



Scheme 2 *Reagents and conditions*: (i) 5 [Li(tmeda)][2-$NHC_6H_4PPh_2$] (from *n*-BuLi, *n*-hexane, diethyl ether, tmeda and adpp), thf; (ii) 3 Na[$PPhC_6H_4NH_2$-2] (from (±)-app and Na in thf), thf.

The structure of sulfonamide $2\text{-}(4\text{-}CH_3C_6H_4SO_2)NHC_6H_4PPh_2$ was confirmed by the preparation and subsequent crystal structure determination of the complex *trans*-$[PtClMe\{2\text{-}Ph_2PC_6H_4NH(SO_2C_6H_4CH_3\text{-}4)\}_2]$. The latter was prepared by the reaction of two equivalents of the sulfonamide with [PtClMe(cod)] in thf. The molecular structure of the complex is depicted in Fig. 3 and selected bond lengths and angles are given in Table 2. The structural data clearly shows the presence of two *trans* disposed sulfonamides bound to the platinum(II) centre as unidentate ligands through the phosphorus donor atoms. The *trans* Pt–P bond lengths (2.310 Å) are comparable to those observed in other chloromethylplatinum(II) complexes containing *trans* disposed phosphorus atoms, for example, *trans*-$[PtClMe(PPh_3)_2]$ (2.295, 2.298 Å)[18] *trans*-$[PtClMe(PMePh_2)_2]$ (2.291, 2.292 Å),[19] *trans*-$[PtClMe(PEt_3)_2]$ (2.296 Å)[20] and *trans*-$[PtCl(CH_2CN)(PPh_3)_2]$ (2.308, 2.310 Å).[21] The bond lengths also fall within the range of 2.26–2.33 Å reported for several square planar platinum(II) complexes containing *trans* disposed phosphorus atoms.[22] In addition, the C–S bond length of 1.762 Å is similar to those observed (1.758–1.77 Å) in several related compounds containing

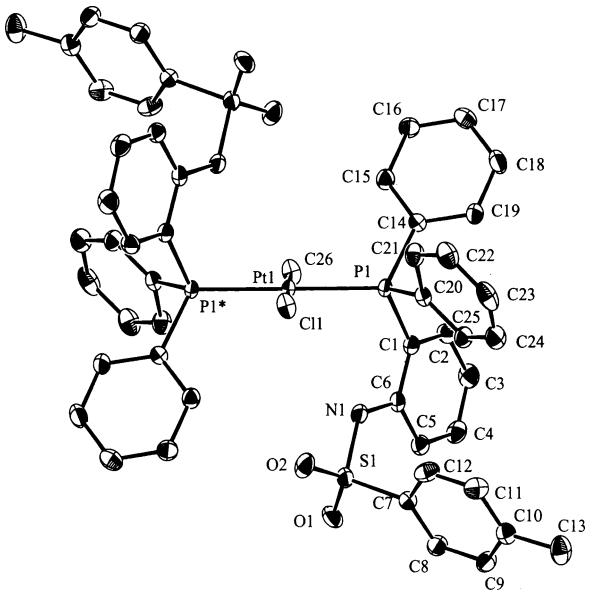


Fig. 3 Molecular structure of the complex [PtClMe{2-$Ph_2PC_6H_4$-$NH(SO_2C_6H_4CH_3$-4)}$_2$] (ellipsoids show 30% probability levels).

Table 2 Selected non-hydrogen interatomic distances (Å) and interatomic angles (°) for [PtClMe{2-$Ph_2PC_6H_4NH(SO_2C_6H_4CH_3$-4)}$_2$]

Pt–Cl	2.358(3)	Pt–C(26)	2.09(2)
Pt–P(1)	2.3102(7)	S(1)–N(1)	1.648(3)
Pt–P(1)[a]	2.3102(7)	S(1)–C(7)	1.762(4)
Cl–Pt–P(1)	91.70(15)	Cl–Pt–C(26)	178.7(10)
Cl–Pt–P(1)[a]	88.30(15)	P(1)–Pt–C(26)	87.6(8)
P(1)–Pt–P(1)[a]	180.0	C(26)–Pt–P(1)[a]	92.4(8)

[a] Indicates an atom generated by the symmetry operation (1 − x, 1 − y, 1 −z).

an arylsulfonyl group.[23] The N–S bond length of 1.648 Å is within the 1.62–1.69 Å range expected for sulfonamides.[24]

The formation of sulfonamide 2-(4-$CH_3C_6H_4SO_2$)NHC_6H_4-PPh_2 can be rationalized in terms of thiophilic attack by the lithium reagent [Li(tmeda)][2-$NHC_6H_4PPh_2$] on the substrate $CH_3C(CH_2OTs)_3$, the resulting alkoxide cyclising to give an oxetane intermediate, 3-(tolyl-4-sulfonyloxy)methyl-3-methyloxetane (see Fig. 4). The latter presumably reacts further with a second equivalent of the lithium reagent to give the *N*-methyloxetane [3-{(2-diphenylphosphinophenyl)aminomethyl}]-3-methyloxetane, *via* substitution at carbon with displacement of a tosylate. The reaction of organolithium compounds with arylsulfonates has previously been reported to proceed by thiophilic attack, rather than by substitution at carbon with displacement of a tosylate.[25,26] Moreover, steric crowding in the tripodal tritosylate would presumably hinder access of the amide nucleophile to the electrophilic carbon centre and prevent the substitution of tosylate, resulting in nucleophilic attack at the more accessible sulfur center. Steric crowding is greatly diminished in the proposed oxetane intermediate and hence substitution of tosylate by the lithium reagent presumably ensues to give the *N*-methyloxetane product. A similar mechanism was proposed to account for the formation of related compounds containing an oxetane ring, *viz.* 3-methoxymethyl-3-methyloxetane, 3-(2-methoxyethoxymethyl)-3-methyloxetane, and 3-(2-methoxyethoxymethyl)-3-methyloxetane in the attempted preparation of hexaethers by the nucleophilic substitution of $CH_3C(CH_2OTs)_3$ with sodium alkoxides.[26]

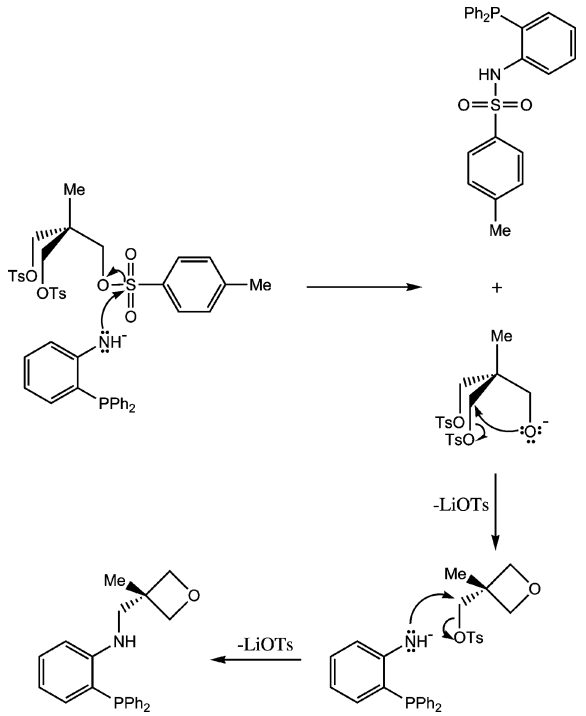


Fig. 4 Proposed mechanism of formation of sulfonamide 2-(4-$CH_3C_6H_4SO_2$)$NHC_6H_4PPh_2$ and *N*-methyloxetane [3-{(2-diphenylphosphinophenyl)aminomethyl}]-3-methyloxetane.

The formation of *P*-methyloxetane (±)-[3-{(2-aminophenyl)-phenylphosphinomethyl}]-3-methyloxetane can be rationalized in a similar manner. Thiophilic attack by Na[2-$PPhC_6H_4NH_2$] on the substrate $CH_3C(CH_2OTs)_3$ would lead to the formation of the sulfonphosphide (±)-2-(4-$CH_3C_6H_4SO_2$)$PPhC_6H_4NH_2$ and the same oxetane intermediate, 3-(tolyl-4-sulfonyloxy)methyl-3-methyloxetane. Subsequent reaction of the latter with Na[2-$PPhC_6H_4NH_2$] presumably proceeds *via* substitution at carbon with displacement of a tosylate to give the *P*-methyloxetane.

Conclusion

The first example of a structurally authenticated complex containing a chelating hexadentate tertiary phosphine in which all six donor atoms are bound to a single metal centre has been described, *viz.* [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4$-NH_2-2)$_3$}]$(PF_6)_3$. The P_3N_3 ligand was isolated in high yield *via* the reaction of $CH_3C(CH_2Br)_3$ with five equivalents of Na[$PPhC_6H_4NH_2$-2] in thf and the two diastereomeric forms of the ligand separated by complexation to cobalt(III) followed by column chromatography. Two complexes were isolated, *viz.* [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]Cl_3 and [CoCl{(R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2$-2)$_3$}]Cl_2, and subsequently converted to the corresponding hexafluorophosphate salts by metathesis with aqueous NH_4PF_6. Unfortunately the diastereomerically pure ligand could not be removed from the cobalt(III) centre in a stereospecific manner, a *ca.* 3 : 1 equilibrium mixture of the (R_P*,R_P*,S_P*) and (R_P*,R_P*,R_P*)

forms of the ligand, respectively, being isolated when either of the two complexes was treated with KCN in refluxing methanol–benzene. Current work is focussing on capping the three facial nitrogen donors in $[Co\{(R_P^*,R_P^*,R_P^*)\text{-}CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3\}](PF_6)_3$ to give the first example of a P_3N_3 cryptand.

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 ($^{31}P\{^1H\}$) or 75 MHz ($^{13}C\{^1H\}$). 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 $^{13}C\{^1H\}$ and external 85% aqueous H_3PO_4 for $^{31}P\{^1H\}$. Melting 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 microanalytical 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. GC-EIMS spectra were recorded on a Hewlett-Packard G1800A GCD mass spectrometer on a HP-5 column [(crosslinked 5% phenyl methyl silicone) 30 m × 0.25 mm × 0.25 mm film thickness], using helium as the carrier gas (1 mL min^{-1}), with a temperature gradient rising between 5–15 °C per minute as appropriate and operating between 100 and 330 °C using positive ion detection. Mass spectra are recorded in mass/charge ratios (m/z).

The compounds (2-aminophenyl)diphenylphosphine,[1] [*SP*-4-2]-chloro(cycloocta-1,5-diene)methylplatinum(II),[27] 1-chloro-2,2-di(chloromethyl)propane, $CH_3C(CH_2Cl)_3$,[28] 2,2-di(tolyl-4-sulfonyloxymethyl)-1-(tolyl-4-sulfonyloxy)propane, $CH_3C(CH_2OTs)_3$,[29] 1-bromo-2,2-di(bromomethyl)propane, $CH_3C(CH_2Br)_3$,[29] and 2,2-di(iodomethyl)-1-iodopropane, $CH_3C(CH_2I)_3$,[30] were prepared by literature procedures.

Preparations

(±)-(2-Aminophenyl)phenylphosphine, (±)-app. Ammonia (1200 mL) was condensed onto adpp (80.0 g, 0.288 mol). Sodium foil (19.9 g, 0.865 mol) was added piecewise to the stirred solution. The reaction was allowed to stir in the cold for 2 h. Solid ammonium chloride was added until the colour discharged and the reaction mixture stirred overnight under nitrogen to allow the ammonia to evaporate. Water (300 mL) and dichloromethane (200 mL) were added to the residue. The resulting phases were separated and the aqueous phase extracted further with dichloromethane (2 × 200 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed *via* distillation under nitrogen at 1 atm. Distillation of the crude oil under reduced pressure gave the product as a colourless viscous oil (54.8 g, 95%), bp 122 °C, 0.05 mm Hg. Analytical data for the secondary phosphine was identical to that previously reported.[2]

(R_P^*,R_P^*,R_P^*)- and (R_P^*,R_P^*,S_P^*)-1,1,1-tris{(2-aminophenyl)-phenylphosphinomethyl}ethane, (R_P^*,R_P^*,R_P^*)- and (R_P^*,R_P^*,S_P^*)-$CH_3C(CH_2PhPC_6H_4NH_2\text{-}2)_3$.

(i) Via reaction of $CH_3C(CH_2Br)_3$ with five equivalents of sodium (2-aminophenyl)phenylphosphide. Secondary phosphine (±)-app (2.24 g, 0.0112 mol) was dissolved in thf (40 mL) and sodium foil (0.256 g, 0.0112 mol) added piecewise to the stirred solution. The reaction mixture was stirred overnight. The resulting red metal phosphide solution was cooled to −78 °C and $CH_3C(CH_2Br)_3$ (0.689 g, 2.23 mmol) in thf (20 mL) added dropwise to the stirred solution. The reaction mixture was allowed to warm slowly to −20 °C and stirred at this temperature for a further 20 d after which time the reaction mixture was allowed to warm to room temperature and stirred at this temperature for a further 10 d. Solid ammonium chloride (2 g) followed by water (2 mL) were added. The solvent was removed under reduced pressure and the residual oil dissolved in water (40 mL) and dichloromethane (30 mL). The resulting phases were separated and the aqueous phase extracted with further dichloromethane (2 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The residual oil was distilled under reduced pressure to remove the unreacted secondary phosphine (±)-app (0.92 g, 41%), bp 128–130 °C, 0.07 mmHg. ^{1}H and $^{31}P\{^1H\}$ NMR spectra identical to that of an authentic sample. The residue was triturated using *n*-pentane (30 mL) to give (R_P^*,R_P^*,R_P^*)- and (R_P^*,R_P^*,S_P^*)-$CH_3C(CH_2PhPC_6H_4NH_2\text{-}2)_3$ as a white microcrystalline solid. The latter was filtered off, washed with *n*-pentane (2 × 3 mL) and dried *in vacuo* (1.20 g, 80%). (Found: C, 69.81; H, 6.38; N, 5.71. Calc. for $C_{41}H_{42}P_3N_3{\cdot}2H_2O$: C, 69.77; H, 6.57; N, 5.95%). ^{1}H NMR (CD_2Cl_2): δ 0.94 (s, 3 H, CH_3); 2.34 (m, 6 H, PCH_2); 4.20 (br s, 6 H, NH_2); 6.52–7.47 (m, 27 H, *aromatics*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −46.1 (s, 3 P); −46.4 (s, 3 P). $^{13}C\{^1H\}$ APT NMR (CD_2Cl_2): δ 28.9 (m, 1 C, CH_3C_q); 38.9 (m, 1 C, CH_3C_q); 42.0 (m, 3 C, PCH_2C_q); 115.5–151.0 (m, 27 C, *aromatics*). LR-EI MS: m/z 669 $(M)^+$, 592 $(M - Ph)^+$, 577 $(M - C_6H_5CH_3)^+$, 469 $(M - PhPC_6H_4NH_2)^+$. HR-EI MS: Found for $(M)^+$ 669.2604 (calc. for $C_{41}H_{42}N_3P_3$: 669.2592).

(ii) Via reaction of $CH_3C(CH_2Br)_3$ with three equivalents of sodium (2-aminophenyl)phenylphosphide. Secondary phosphine (±)-app (1.62 g, 8.06 mmol) was dissolved in thf (40 mL) and sodium foil (0.185 g, 8.06 mmol) added piecewise to the stirred solution. The reaction mixture was stirred at room temperature for 48 h. The resulting red metal phosphide solution was cooled to −78 °C and 1,1,1-tris(bromomethyl)ethane (0.829 g, 2.69 mmol) in thf (20 mL) added dropwise to the stirred solution. The reaction mixture was allowed to warm to room temperature and stirred for 7 d. The reaction mixture was refluxed in thf for 4 d during which time the colour discharged. Solid ammonium chloride (2 g) followed by water (2 mL) were added. The solvent was removed under reduced pressure and the residual oil dissolved in water (40 mL) and dichloromethane (30 mL). The resulting phases were separated and the aqueous phase extracted with further dichloromethane (2 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The residual oil (1.42 g) was separated

on a silica column (19 × 2.5 cm, silica gel 70–230 mesh, eluent petroleum spirit (bp 40–60 °C)–dichloromethane, gradient 90 : 10 → 0 : 100) under nitrogen to give three fractions. Fraction 1: (±)-app (0.303 g, 35% based on starting (±)-app). ^{1}H NMR and ^{31}P{^{1}H} NMR spectra identical to an authentic sample. Fraction 2: (R_P*,R_P*)- and (R_P*,S_P*)-$(CH_3)_2C(CH_2PPhC_6H_4NH_2\text{-}2)_2$ (0.23 g, 18%). ^{1}H NMR (CD_2Cl_2): δ 1.27 (s, 6 H, CH_3C); 2.54 (m, 4 H, PCH_2); 4.37 (br s, 4 H, NH_2); 6.82–7.66 (m, 18 H, *aromatics*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −44.5 (s, 2 P). LR-EI MS: *m*/*z* 470 $(M)^+$, 393 $(M - Ph)^+$, 378 $(393 - Me)^+$, 322 $(M - C_8H_7PN)^+$, 271 $(M - PhPC_6H_4NH)^+$, 200 $(M - CH_2C(Me)_2CH_2PhPC_6H_4NH_2)^+$. Fraction 3: ($R_P$*,$R_P$*,$R_P$*)- and ($R_P$*,$R_P$*,$S_P$*)-$CH_3C(CH_2PhPC_6H_4NH_2\text{-}2)_3$ (0.50 g, 28%). ^{1}H NMR and ^{31}P{^{1}H} NMR spectra identical to an authentic sample.

[*OC*-6-22-(R_P*,R_P*,R_P*)]-[1,1,1-Tris{(2-aminophenyl)phenylphosphinomethyl}ethane-N_3P_3]cobalt(III) chloride, [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$}]$Cl_3$ and [*OC*-6-23-(R_P*,R_P*,S_P*)]-chloro-[1,1,1-tris{(2-aminophenyl)phenylphosphinomethyl}ethane-N_2P_3]cobalt(III) chloride, [CoCl{(R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$}]$Cl_2$. The P_3N_3 hexadentate ligand (R_P*,R_P*,R_P*)- and (R_P*,R_P*,S_P*)-$CH_3C(CH_2PhPC_6H_4NH_2\text{-}2)_3$ (2.75 g, 4.12 mmol) was dissolved in hot methanol (30 mL). Hexaaquacobalt(II) chloride (1.71 g, 7.19 mmol) in methanol (20 mL) was added and the reaction mixture refluxed gently for 1 h. Hydrochloric acid (6 mL) was added and air drawn through the solution for a period of 4 h. The solvent was removed from the brown solution and the residue dried *in vacuo*. The residue (4.40 g) was dissolved in the minimum volume of methanol (60 mL) and the resulting brown solution loaded onto an ion-exchange column [270 × 25 mm, Dowex 50WX8, cation exchange resin]. The column was eluted with HCl–methanol (1 mol L^{-1}, elution rate *ca*. 2 mL min^{-1}). The first compound eluted was unchanged hexaaquacobalt(II) chloride (0.70 g). A red band eluted from the column was [CoCl{(R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$}]$Cl_2$ exclusively (2.41 g, 70% based on (R_P*,R_P*,R_P*)- and (R_P*,R_P*,S_P*)-$CH_3C(CH_2PhPC_6H_4NH_2\text{-}2)_3$). ^{1}H NMR ($CD_3OD$): δ 1.94 (br s, 2 H, CH_3); 2.87 (m, 6 H, PCH_2); 6.44–7.75 (m, 27 H, *aromatics*). ^{31}P{^{1}H} NMR (CD_3OD): δ 60.3 (br s, 1 P); 44.5 (br s, 1 P); 18.7 (br s, 1 P). The last fraction was collected with HCl–methanol (3 mol L^{-1}, elution rate *ca*. 2 mL min^{-1}) and contained exclusively [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$}]$Cl_3$ (0.76 g, 22% based on (R_P*,R_P*,R_P*)- and (R_P*,R_P*,S_P*)-$CH_3C(CH_2PhPC_6H_4NH_2\text{-}2)_3$). ^{1}H NMR ($CD_3OD$): δ 2.05 (d, 3 H, CH_3); 3.08 (br s, 6 H, PCH_2); 6.69–7.65 (m, 27 H, *aromatics*). ^{31}P{^{1}H} NMR (CD_3OD): δ 54.6 (br s, 3 P).

[*OC*-6-22-(R_P*,R_P*,R_P*)]-[1,1,1-Tris{(2-aminophenyl)phenylphosphinomethyl}ethane-N_3P_3]cobalt(III) hexafluorophosphate, [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$}]$(PF_6)_3$. A solution of ammonium hexafluorophosphate (0.12 g, 0.74 mmol) in water (20 mL) was added slowly to a solution of [Co{(R_P*,R_P*,R_P*)-$CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$}]$Cl_3$ (0.05 g, 0.06 mmol) in methanol (5 mL) and left standing overnight. The resulting yellow precipitate was collected and washed with water (3 × 5 mL). The complex was recrystallised from acetone–isopropyl alcohol to give yellow crystals (0.038 g, 55%), mp 245 °C (decomp.) (Found: C, 41.81; H, 3.71; N, 3.53. Calc. for $C_{41}H_{42}P_3N_3CoP_3F_{18}\cdot H_2O$: C, 41.68; H, 3.75; N, 3.56%). ^{1}H NMR ($(CD_3)_2CO$): δ 2.22 (s, 3 H, CH_3); 3.35 (br s, 3 H, PCHH); 3.44 (br s, 3 H, PCHH); 6.03–7.98 (m, 33 H, *aromatics* & NH_2). ^{31}P{^{1}H} NMR: δ 55.2 (br s, 3 P).

[*OC*-6-23-(R_P*,R_P*,S_P*)]-Chloro[1,1,1-tris{(2-aminophenyl)-phenylphosphinomethyl}ethane-N_2P_3]cobalt(III) hexafluorophosphate, [CoCl{(R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$}]$(PF_6)_2$. A solution of ammonium hexafluorophosphate (0.15 g, 0.92 mmol) in water (7 mL) was added slowly to a solution of [CoCl{(R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$}]$Cl_2$ (0.08 g, 0.096 mmol) in methanol (4 mL) and left standing overnight. The resulting orange precipitate was collected, washed with water (3 × 5 mL) and dried *in vacuo* (0.06 g, 59%), mp 215–216 °C (Found: C, 46.74; H, 4.24; N, 3.79; Co, 5.11; Cl, 2.91; F, 19.92. Calc. for $C_{41}H_{42}N_3P_5CoClF_{12}\cdot EtOH$: C, 46.94; H, 4.40; N, 3.82; Co, 5.36; Cl, 3.22; F, 20.72%). ^{1}H NMR (CD_3OD): δ 1.93 (s, 3 H, CCH_3); 2.87 (m, 6 H, PCH_2); 6.45–7.80 (m, 27 H, *aromatics*). ^{31}P{^{1}H} NMR (CD_3OD): δ 18.2 (br s, P); 45.4 (br s, P); 61.1 (br s, P). LR-ESI MS: *m*/*z* 1055 $([CoLCl]^{2+} + 2PF_6^- + H^+)^+$, 1039 $([CoLCl]^{2+} + 2PF_6^- - Me)^+$, 873 $([CoL]^{3+} + PF_6^-)^+$, 858 $([CoL]^{3+} + PF_6^- - Me)^+$, 726 $([CoL]^{3+} - 2H)^+$ where L = (R_P*,R_P*,S_P*)-$CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3$.

Reaction of [Li(tmeda)][2-$NHC_6H_4PPh_2$] with $CH_3C(CH_2OTs)_3$. Isolation of (2-diphenylphosphinophenyl)tolyl-4-sulfonamide, 2-(4-$CH_3C_6H_4SO_2$)$NHC_6H_4PPh_2$, and [3-{(2-diphenylphosphinophenyl)aminomethyl}]-3-methyloxetane. A solution of *n*-butyllithium in *n*-hexane (25 mL, 1.6 M, 0.0399 mol) was added to dry diethyl ether (120 mL) and the solution cooled to 0 °C. Solid adpp (11.09 g, 0.0399 mol) was added to the stirred solution followed by tmeda (4.65 g, 0.0399 mol). The solution was decanted off the resulting white solid of [Li(tmeda)][2-$NHC_6H_4PPh_2$], the latter washed with diethyl ether (5 × 50 mL) and dried *in vacuo* (13.7 g, 86%). The latter (13.7 g, 0.040 mol) was suspended in benzene (100 mL) and $CH_3C(CH_2OTs)_3$ (4.66 g, 8.00 mmol) added to the stirred suspension. The reaction mixture was heated under reflux for 12 d and cooled to ambient temperature. Aqueous ammonium chloride solution (100 mL, 20% w/v) was added, the resulting two phases separated and the aqueous phase extracted with dichloromethane (3 × 70 mL). The combined organic phases were dried ($MgSO_4$), filtered and the solvent removed *via* distillation under argon at 1 atm. The crude yellow oil was dried *in vacuo*. Yield 11.2 g. The oily product was extracted with hot methanol (4 × 50 mL). The combined methanol extracts were left standing at ambient temperature for 4 h and the white solid formed filtered off, washed with cold methanol (3 × 3 mL) and dried to give the sulfonamide as white microcrystals (2.22 g, 64% based on tritosylate, 1 : 1), mp 140–140.5 °C. ^{1}H NMR (CD_2Cl_2): δ 2.30 (s, 3 H, CH_3); 6.87–7.87 (m, 19 H, *aromatics* and NH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −26.2 (s, 1 P). ^{13}C{^{1}H} NMR (CD_2Cl_2): 21.7 (s, 1 C, CH_3), 121.3–144.2 (m, 24 C, *aromatics*). *m*/*z* 431 $(M)^+$, 367 $(M - SO_2)^+$, 276 $(M - SO_2C_6H_4Me)^+$, 183 $(M - NHSO_2C_6H_4Me)^+$.

The residual material was separated on a silica column (15 × 2.5 cm, silica gel 70–230 mesh, eluent petroleum spirit (bp 40–60 °C)–dichloromethane, gradient 90 : 10 → 0 : 100) under nitrogen to give three fractions. Fraction 1: adpp (4.1 g, 37% based on starting adpp, 43% based on [Li(tmeda)][2-$NHC_6H_4PPh_2$]). ^{1}H NMR and ^{31}P{^{1}H} NMR spectra identical to an authentic sample. Fraction 2: sulfonamide (0.3 g, 9%). ^{1}H NMR and ^{31}P{^{1}H} NMR spectra identical to an authentic sample. Fraction 3: oxetane (1.5 g,

Table 3 Crystallographic data for the complexes $[Co\{(R_P^*,R_P^*,R_P^*)\text{-}CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3\}](PF_6)_3\cdot C_3H_6O$, **A**, and *trans*-$[PtClMe\{2\text{-}Ph_2PC_6H_4NH(SO_2C_6H_4CH_3\text{-}4)\}_2]$, **B**

	A	**B**
Empirical formula	$C_{41}H_{42}Co\,F_{18}N_3P_6\cdot C_3H_6O$	$C_{51}H_{47}ClN_2O_4P_2PtS_2$
M	1221.62	1108.55
T/K	200	200
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
Crystal size/mm	0.52 × 0.30 × 0.03	0.46 × 0.11 × 0.05
a/Å	27.1248(3)	11.1852(2)
b/Å	10.8041(1)	17.7100(3)
c/Å	34.2865(4)	11.7952(1)
β/°	92.1000(4)	92.8833(8)
V/Å^3	10041.2(2)	2333.55(6)
Z	8	2
D_c/g cm^{-3}	1.616	1.578
μ/mm^{-1}	0.639	3.269
Reflections collected	62384	50772
Independent reflections	8844	5360
Indep. observed reflections	5526 ($I > 2\sigma(I)$)	3107 ($I > 3\sigma(I)$)
R_{int}	0.08	0.05
Final R, R_w	0.0350, 0.0382	0.0227, 0.0259
2θ Range/°	6–50	6–55
Parameters	658	292

52% based on tritosylate). ^{1}H NMR (CD_2Cl_2): δ 1.14 (s, 3 H, CH_3); 3.26 (m, 2 H, CH_2N); 4.21 (m, 4 H, OCH_2); 4.58 (br s, 1 H, NH); 6.61–7.36 (m, 14 H, *aromatics*). ^{31}P{^{1}H} NMR (CD_2Cl_2): −19.4 (s, 1 P). ^{13}C{^{1}H} (CD_2Cl_2): δ 22.0 (s, 1 C, CH_3), 40.0 (s, 1 C, C_q), 51.3 (s, 1 C, CH_2N), 80.5 (s, 2 C, CH_2O), 110.4–151.2 (m, 18 C, *aromatics*). LR-EI MS: m/z 361 (M)$^+$, 346 (M − Me)$^+$, 316 (M − C_2H_5O)$^+$, 290 (M − C_4H_7O)$^+$, 276 (M − C_5H_9O)$^+$. HR-EI MS: Found (M)$^+$ 361.1589 (calc. for $C_{23}H_{24}NOP$: 361.1596).

[*SP*-4-3]-Chlorobis{(2-diphenylphosphinophenyl)tolyl-4-sulfonylamide-*P*}methylplatinum(II), *trans*-[PtClMe{2-$Ph_2PC_6H_4NH(SO_2C_6H_4CH_3$-4)}$_2$]. The sulfonamide 2-(4-$CH_3C_6H_4SO_2$)-$NHC_6H_4PPh_2$ (0.117 g, 0.273 mmol) was dissolved in dry thf (10 mL). The complex [PtClMe(cod)] (0.048 g, 0.137 mmol) in thf (10 mL) was added dropwise to the stirred solution. The reaction mixture was stirred for 30 min and *n*-pentane (40 mL) added. The white precipitate that formed was filtered off, washed with *n*-pentane (2 × 2 mL) followed by diethyl ether (2 × 2 mL) and dried *in vacuo* (0.12 g, 80%), mp 195–196 °C (decomp.) (Found: C, 54.39; H, 4.31; N, 2.15. Calc. for $C_{51}H_{47}P_2N_2O_4S_2PtCl\cdot H_2O$: C, 54.37; H, 4.38; N, 2.48%). ^{1}H NMR (CD_2Cl_2): δ 0.27 (t, 3 H, $^2J_{PtH}$ = 78 Hz, $^3J_{PH}$ = 13 Hz, PtCH_3); 2.38 (s, 3 H, CH_3); 7.04–7.70 (m, 36 H, *aromatics*); 9.33 (s, 1 H, NH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 22.7 (s, 2 P, $^1J_{PtP}$ = 2916 Hz). ^{13}C{^{1}H} APT (CD_2Cl_2): δ 1.14 (s, 1 C, Pt*Me*), 21.7 (s, 2 C, C*Me*), 120.0–144.1 (m, 18 C, *aromatics*).

Reaction of Na[2-$PPhC_6H_4NH_2$] with $CH_3C(CH_2OTs)_3$. Isolation of (±)-[3-{(2-aminophenyl)phenylphosphino}]-3-methyloxetane. Secondary phosphine (±)-app (0.833 g, 4.14 mmol) was dissolved in thf (40 mL) and sodium foil (0.105 g, 4.14 mmol) added piecewise to the stirred solution. The reaction mixture was stirred overnight. The resulting red metal phosphide solution was cooled to −78 °C and $CH_3C(CH_2OTs)_3$ (0.804 g, 1.37 mmol) in thf (20 mL) added slowly dropwise to the stirred solution. The reaction mixture was allowed to warm to room temperature and stirred for 3 days. Solid ammonium chloride (2 g) followed by water (2 mL) were added. The solvent was removed under reduced pressure and the residual oil dissolved in water (30 mL) and dichloromethane (20 mL). The resulting phases were separated and the aqueous phase extracted further with dichloromethane (2 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The residual oil (0.63 g) was separated on a silica column (12 × 2.5 cm, silica gel 70–230 mesh, eluent petroleum spirit (bp 40–60 °C)–dichloromethane, gradient 90 : 10 → 0 : 100) under nitrogen to give two fractions. Fraction 1: (±)-app (0.29 g, 35% based on starting (±)-app). ^{1}H NMR and ^{31}P{^{1}H} NMR identical to an authentic sample. Fraction **2**, oxetane (0.26 g, 67% based on tritosylate). ^{1}H NMR (CD_2Cl_2): δ 1.29 (s, 3 H, CH_3); 2.38 (m, 2 H, PCH_2); 4.10 (d, 1 H, $^2J_{HH}$ = 5.8 Hz, OCH_a); 4.14 (d, 1 H, $^2J_{HH}$ = 5.7 Hz, OCH_b); 4.28 (d, 1 H, $^2J_{HH}$ = 5.8 Hz, OCH_c); 4.30 (d, 1 H, $^2J_{HH}$ = 5.8 Hz, OCH_d); 4.20 (br s, 2 H, NH_2); 6.52–7.38 (m, 9 H, *aromatics*). ^{31}P{^{1}H} NMR (CD_2Cl_2): −41.7 (s, 1 P). ^{13}C{^{1}H}APT (CD_2Cl_2): δ 25.5 (d, 1 C, $^3J_{CP}$ = 16.4 Hz, CH_3), 37.3 (d, 1 C, $^1J_{PC}$ = 13.1 Hz, PCH_2), 39.4 (d, 1 C, $^2J_{PC}$ = 15.6 Hz, CH_3C_q), 83.4 (m, 2 C, CH_2O), 115.6–150.9 (m, 12 C, *aromatics*). LR-EI MS: m/z 285 (M)$^+$, 270 (M − Me)$^+$, 254 (M − CH_3O)$^+$, 200 (M − C_5H_9O)$^+$. HR-EI MS m/z: Found 285.1284 ($C_{17}H_{20}NOP$ requires 285.1283).

X-Ray crystallography

X-Ray diffraction data for $[Co\{(R_P^*,R_P^*,R_P^*)\text{-}CH_3C(CH_2PPhC_6H_4NH_2\text{-}2)_3\}](PF_6)_3\cdot C_3H_6O$, **A**, and *trans*-$[PtClMe\{2\text{-}Ph_2PC_6H_4NH(SO_2C_6H_4CH_3\text{-}4)\}_2]$, **B**, 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*.[31,32] Analytical absorption corrections were applied to the data for both **A** and **B** (max./min. transmission factors 0.981/0.807 and 0.858/0.431, respectively).[33,34]

B is centred on a crystallographic inversion centre. The structure of **B** was initially refined with two chloro groups bound to the

platinum(II) centre. However, the displacement parameters of the Cl atom were larger than those of the Pt and P atoms and there was a major peak in a difference electron density map between the Pt and Cl atoms which was consistent with the presence of statistically disordered Cl and methyl groups. This has previously been reported for the related complexes *trans*-[PtClMe(PR_3)$_2$] (where R = Et or Ph).[20,35] To model this effect C(26) was included between the Pt and Cl atoms; both C(26) and the Cl atom were assigned occupancies of 0.5 and constrained to have equal displacement parameters. Initially the Pt–C and Pt–Cl distances were restrained to values reported for related complexes that did not have the Cl/Me disorder,[18,36] but for the final cycles of refinement the restraints were removed. Distances and angles involving the Cl and C(26) atoms are probably not reliable as these sites are only separated by 0.27(2) Å.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607847h

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