Synthesis of (1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]octane and derivatives†

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The novel primary phosphine (1*R*,3*S*)-[1,2,2-trimethyl-3-(phosphinomethyl)cyclopentyl]methyl methanesulfonate **3a** (or tosylate **3b**) has been prepared in three steps from (1*R*,3*S*)-camphoric acid with a view to utilising it as a synthon for the preparation of polycyclic phosphines. Efforts to prepare a [3.2.1] bicyclic product by internal cyclisation of **3a** or **3b** under various conditions were unsuccessful, but heating the neat compound at 140 °C for several hours gave the new asymmetric, bicyclic secondary phosphine, (1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]octane (PBO) as its methanesulfonic acid **5a** (or *p*-toluenesulfonic acid **5b**) salt. The cyclisation involves a skeletal rearrangement and occurs with high stereoselectivity to generate two new stereogenic carbon centres and a chiral phosphorus atom. The secondary phosphine was obtained after base treatment of **5a/b** and several derivatives of the phosphine have been synthesised and characterised. Reaction of two mol equivalents of the borane adduct of PBO with α,α′-dichloro-*ortho*-xylene gave the bidentate derivative, *o*-$C_6H_4(CH_2PBO)_2.2BH_3$, **12**, and ultimately *o*-$C_6H_4(CH_2PBO)_2$, **13**. Complexes of **13** with Pd(II), Pt(II), Pt(0) and Mo(0) have been prepared and characterised by spectroscopic and analytical methods including single-crystal X-ray structure determinations of *cis*-Pd{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2, **14**, *cis*-Pt{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2, **15** and $Mo(CO)_4${*o*-$C_6H_4(CH_2PBO)_2$} **17**.

Introduction

The success of phosphorus-containing ligands in homogeneous catalysis is legend.[1] The reasons for this are wide-ranging but relate in the main to the ease with which the electronic and steric properties of the phosphorus donor can be varied through alteration of the groups attached to the P-atom. Furthermore, as the σ-donating/π-accepting properties of such ligands are determined by the nature of the HOMO (lone pair) and LUMO (σ* orbitals) they are sensitive to the intraphosphorus angles. Thus small heterocyclic systems can show unusual electronic and indeed steric properties as a direct consequence of the necessarily constrained X-*P*-X bond angles in these compounds.[2] Cyclic derivatives such as the C_2P phosphiranes and C_3P phosphetanes with typical internal C–P–C angles of ~50° and ~80° are extraordinary while the larger 5- (phospholanes) and 6-membered (phosphinanes) homologues with C–P–C angles of ~94° and 97° produce ligands with features more comparable with related acyclic derivatives.

Recognition of these nuances of phosphacycles has prompted investigation of the nature of their bonding to transition metals especially those commonly employed in homogeneous catalysis.[3] Much of the driving force for the study of the five-membered phospholanes has come from their successful employment in asymmetric catalysis as epitomised by the DuPHOS series of ligands founded by Burk.[4] Although less-well studied, the smaller ring phosphiranes[5] and phosphetanes[6] and larger ring phosphinanes[7] and phosphepanes[3] have been investigated by a number of groups in an effort to understand how ring size can influence coordination behaviour and affect the catalytic behaviour of their metal complexes. Reported examples of bi- and polycyclic systems[8] include the well-established phobane ligands,[9] the 7-phosphabicyclo[2.2.1]heptanes[10] and phosphabarrelenes[11] with aspects of the chemistry of these and many more heterocyclic phosphorus compounds being the subject of a recent comprehensive review.[12]

We have been interested in investigating the donating ability of phosphiranes,[5a] phosphetanes[13] and phosphinanes,[14] both as simple monodentate donors and as part of bi- and multidentate systems. Our early interest in phosphacycles lay in phospholane and phobane chemistry[9a] and has since evolved to include phosphacycles with rigid, inherently chiral frameworks that may have application in asymmetric synthesis.[14] As part of this continuing study we have sought to prepare novel phosphorus containing polycycles (preferably asymmetric) with a view to exploring their coordination properties. The inherently chiral secondary phosphine shown as **4** in Scheme 1 was one such target, however efforts to obtain **4** by typical synthetic protocols have thus far failed. That said, one of these failed routes did furnish a related unexplored [2.2.2] bicyclic phosphacycle namely (1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]octane (PBO), **6**. The present paper details the synthesis of PBO along with the preparation and characterisation of a number of derivatives of the parent phosphacycle including the potentially bidentate ligand α,α′-bis{(1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]octyl}-*o*-xylene, *o*-$C_6H_4(CH_2PBO)_2$, **13**. Some elementary coordination chemistry of α,α′-bis{(1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]octyl}-*o*-xylene with

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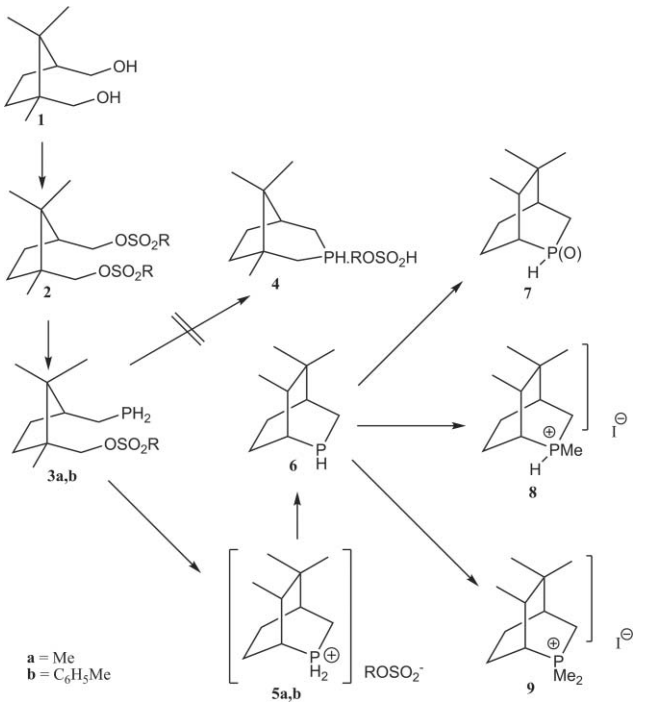


Scheme 1 Synthesis of PBO, **6**, and some derivatives. i) $ROSO_2Cl$, Et_3N, DMAP; ii) $LiP(SiMe_3)_2$, MeOH; iii) 145°, 18 h; iv) Na_2CO_3; v) 3% aq. H_2O_2; vi) MeI, THF, RT; vii) xs MeI, THF, reflux.

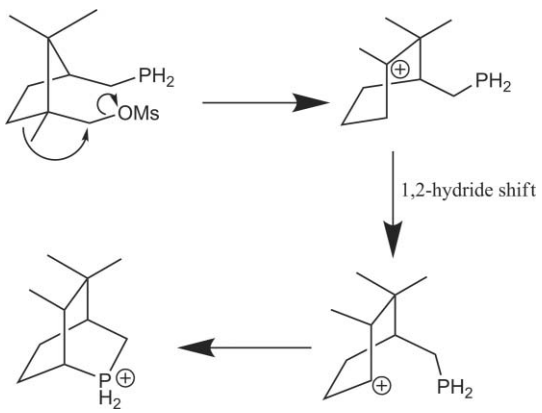
molybdenum(0), palladium(II) and platinum(II/0) is also reported.

Results and discussion

Synthesis of (1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]octane (PBO) and derivatives

The synthesis of (1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]octane, PBO (**6**), is shown in Scheme 1. The starting point for the synthesis is the (1*R*,3*S*)-camphanediol (**1**) obtained by lithium aluminium hydride reduction of (1*R*,3*S*)-camphoric acid. The conversion of the diol to the dimesylate (**2a**) or ditosylate (**2b**) is readily achieved through the DMAP catalysed reaction with the relevant sulfonyl chloride in the presence of base. Subsequent reaction of either **2a** or **2b** with one equivalent of $LiP(SiMe_3)_2$ gives, after protonolysis, (1*R*,3*S*)-[1,2,2-trimethyl-3-(phosphinomethyl)cyclopentyl]methyl methanesulfonate, **3a**, or tosylate, **3b**. The regioselectivity observed in this reaction is typical for this type of skeleton with nucleophilic substitution occurring preferentially at the more open *iso*-butyl carbon rather than the largely unreactive neo-pentyl position. Both **3a** and **3b** were isolated as low-melting waxy solids with ^{31}P resonances around −140 ppm ($^1J_{P-H}$ = 195 Hz) in their ^{31}P NMR spectra as expected for an *iso*-butyl-based primary phosphine.[15] The most distinctive features of the ^1H NMR spectra of **3a/b** are the doublet of multiplets for the phosphine protons centered around 2.60 ppm and the two doublets of an AB coupled system between 3.9 and 4.2 ppm for the diastereomeric protons of the methylene groups α to the sulfonate functionality (see experimental). Attempts to substitute both sulfonates in **2a/b** by reaction with ≥2 mol equivalents of $LiP(SiMe_3)_2$ were unsuccessful leading only to the reclamation of **3a/b** after work-up. Efforts to promote a ring closure to **4** by the addition of organolithium reagents to **3a/b** were also unsuccessful with the formation of red, insoluble precipitates occurring upon addition of the strongly basic organolithium reagent to the phosphino-sulfonate; heating did not lead to dissolution of the solids, which are presumably metal phosphide species, and prolonged reflux led to decomposition.

Ring-closure was induced upon heating **3a/b** to 140 °C for extended periods (6–18 h) in the absence of solvent. Thus, when either **3a** or **3b** was heated in a Schlenk flask under these conditions, a crystalline solid sublimed in the upper reaches of the flask in addition to some oily, unsublimed material. Spectroscopic analysis of the sublimed solid confirmed that the compound was not the anticipated [3.2.1] cycle shown as **4** in Scheme 1. The $^{31}P\{^1H\}$ NMR spectrum of the crystalline solid recorded in $CDCl_3$ consists of a very broad resonance at δ −65 ppm. Two features of this spectrum are unusual. Firstly, the broad nature of the resonance suggests the existence of an exchange process in solution, presumably a rapid proton exchange between the phosphonium cation and the solvent and/or mesylate(tosylate) anion. Secondly, the position of the resonance is not in the region expected for a protonated secondary phosphonium salt. Indeed, the peak occurs at a chemical shift more appropriate for a secondary phosphine and it appears that proton exchange from the parent phosphine is rapid for the compound even in fairly apolar media. The $^{13}C\{^1H\}$ DEPT NMR spectrum of the sublimed solid revealed the presence of three CH_2 groups and three CH carbons, clearly not in accord with the distribution expected for the [3.2.1] cycle. The forcing conditions of the cyclisation had induced a rearrangement of the bicyclic skeleton to give the [2.2.2] compound as the hydrophosphonium sulfonate (**5a/b**). A putative mechanism for the rearrangement is shown in Scheme 2. The likely intermediate is a tertiary carbocation (formed through loss of the sulfonate group) that rearranges through a 1,2-hydride shift to give the product as shown in the figure. The failure of the phosphine to trap the initially formed carbocation is likely to be a result of steric encumbrance although it may be that the mechanism is more concerted with the hydride migration occurring concomitantly with the loss of the sulfonate. One of the two original stereogenic carbon centres (the bridgehead carbon at position 3) is unaffected by the rearrangement and retains its *S* stereochemistry. The 1-carbon atom of the phosphino-sulfonate is involved in bond breaking and forming with the result that it is no longer a



Scheme 2 Proposed mechanism for the formation of **5a**,**b**.

bridgehead carbon in the product but part of one of the ethane bridges. The transformation appears to be stereoselective with only the 1*R*,4*S*,6*R* isomer of the product being observed (see below). The unsublimed material from the reaction is a mixture of the phosphonium salt and other, apparently oxidised, species resulting from oxygen transfer from the sulfonate to the phosphorus. This mixture, when treated with $LiAlH_4$, gives the secondary phosphine (1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]octane (PBO), **6**, as a sublimable, low-melting solid. The phosphine is obtained as two isomers with ^{31}P NMR chemical shifts of -60.8 (minor) and -79.6 (major) ppm, respectively. The δ_P values are in the region expected for a 6-membered secondary phosphacycle with isobutyl and isopropyl type substituents. The diastereoselectivity is approximately 80 : 20 as deduced from integration of appropriate signals (most notably the CH_3 resonances) in the ^{1}H NMR spectrum (details of which, for the major isomer, are presented in the experimental). Aside from the peaks for the methyl groups, the ^{1}H NMR spectrum is complex with most resonances occurring between 2.0 and 0.5 ppm. The P*H* proton of the major isomer is observed as a doublet of triplets at δ_P 3.04 ppm with $^1J_{H-P}$ of 183.8 Hz and $^2J_{H-H}$ of 10.1 Hz. The relatively large value of 15.4 Hz for the $^2J_{P-C}$ coupling constant to the methine carbon (C6) compared to 8.9 Hz for the methylene group (C7) in the ^{13}C{^{1}H} NMR spectrum suggests that (S_P)-**6** is the major isomer.‡ This is supported by 2D NOESY NMR experiments which show through-space contacts between the P–H proton and the two axial hydrogens of the C3 and C7 methylene groups.

The secondary phosphine, **6**, is unstable in $CDCl_3$ and a solution left standing for 48 h shows only a broad peak at −65 ppm in the ^{31}P{^{1}H} NMR spectrum. This resonance resembles closely that for the phosphonium species **5**. Inspection of the ^{1}H and ^{13}C{^{1}H} NMR spectra of the sample confirms formation of a phosphonium salt and it is clear that the phosphine has abstracted DCl from the $CDCl_3$ to give the P(V) species. Compound **6** is extremely sensitive to oxygen and decomposes very easily on exposure to air to give the secondary phosphine oxide (1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-oxa-2-phosphabicyclo[2.2.2]octane, **7**, which is more readily obtained by oxidation with dilute hydrogen peroxide in a biphasic solvent. The oxide **7** sublimes under high vacuum to give two diastereomers in approximately 2 : 1 ratio as determined by integration of the two distinct signals for the P(O)H protons in the ^{1}H NMR spectrum at δ_P 6.99 (dt, $^1J_{H-P}$ 455 Hz) for the major and δ_P 6.84 (dm, $^1J_{H-P}$ 463 Hz) ppm for the minor isomer.

Phosphine **6** reacts cleanly with a slight molar excess of MeI in THF to give the methylated phosphonium salt **8** as a white precipitate which is isolated as a 70 : 30 diastereomeric mixture in 90% yield. The reaction is extremely rapid, being instantaneous at RT as observed by the immediate precipitation of the salt when the reaction is performed under moderate dilution (1 to 2 M). Heating a THF solution of **6** with a large excess (10-fold) of methyl iodide leads to double methylation of the phosphorus to give **9** as the iodide salt. The salt has been characterised in the solid-state by a single crystal X-ray structure determination as shown in Fig. 1. The bicyclic nature of the phosphine is immediately evident and the chirality of the carbon centres is as expected from the choice of (1*R*,3*S*)-camphoric acid as starting material, thus the full stereochemistry is determined as (1*R*,4*S*,6*R*). The P–C bond lengths to the ring carbons and the methyl carbons are typical at ~1.817(4) Å and 1.789(4) Å but the internal C–P–C bond angle is compressed at 100.43(17)° compared to the remaining intraphosphorus angles which average 111.3(2)°.

‡ This is a result of the lone pair of the phosphorus lying close to the C6 carbon atom [see ref.20].

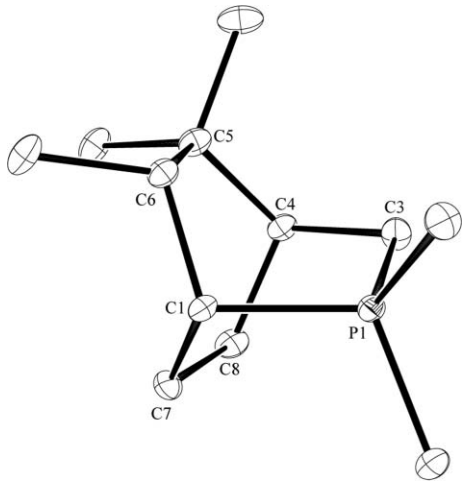
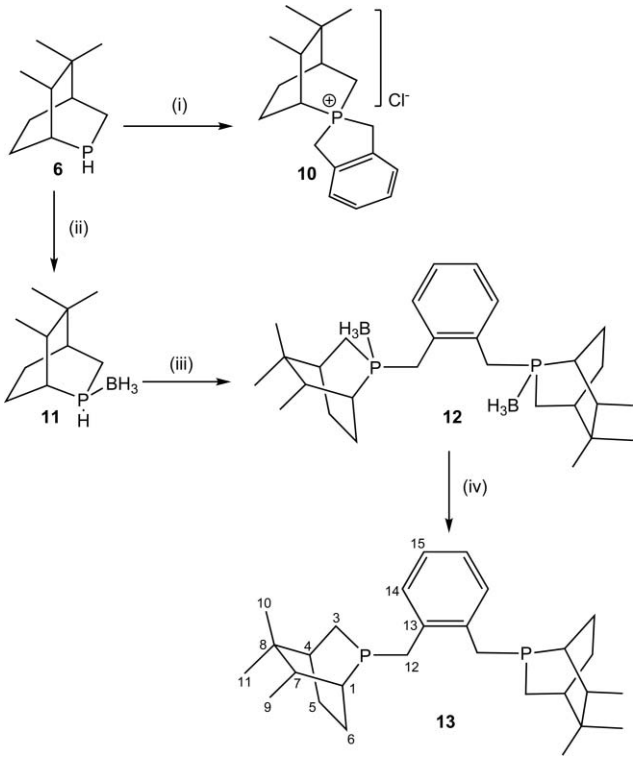


Fig. 1 Ortep view of the molecular structure of the cation **9**.

Synthesis of α,α′-bis{(1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]octyl}-*o*-xylene, *o*-$C_6H_4(CH_2PBO)_2$, 13

An initial premise of the work reported here was to include compound **4** as part of a bidentate system with an *ortho*-xylyl backbone. This choice of backbone reflects another long term interest of our group stemming from early work on 1,2-*bis*(di-*tert*-butylphosphinomethyl)benzene.[16] A continued interest in this linker has been fuelled by the flexible nature of ligands with this backbone which show a wide range of P–M–P bite angles dependent upon, amongst other things, the other substituents at the P-donors.[13,17] Many catalytic cycles have rate determining steps that are strongly influenced by the ligand bite angle and it is the impact that these flexible frameworks may have on the behaviour of the resultant complex(es) that has maintained our interest in these systems. Failure to isolate **4** did not diminish this desire as the unexpected synthesis of PBO presented a similar opportunity to study polycyclic phosphines with an *o*-xylyl bridge.

The reaction of **6** with α,α′-dichloro-*ortho*-xylene led to the isolation of the heterocyclic phosphonium salt, **10** (Scheme 3). The formation of species such as **10** has frustrated attempts to synthesise a number of diphosphines of the type *o*-$C_6H_4(CH_2PR_2)_2$. The use of protecting functions, especially BH_3, is generally used to circumvent the problem of cyclic phosphonium salt formation. PBO can be protected as the borane adduct in the usual way giving PBO.BH_3, **11**, as a mixture of diastereomers (~4 : 1 ratio) as identified from ^{31}P{^{1}H} NMR spectral analysis of the solution where the major four line resonance was observed at δ_P −14.4 ppm ($^1J_{P-B}$ = 45 Hz) and the minor isomer at δ_P −4.3 ppm ($^1J_{P-B}$ = 45 Hz). The PBO.BH_3 adduct was not isolated but converted to the lithium salt *in situ* upon addition of one mole equivalent of n-BuLi at low temperature. Formation of the lithiated species was confirmed from the change in the ^{31}P{^{1}H} NMR spectrum where a major species at −68.4 ppm ($^1J_{P-B}$ = 39 Hz) ppm and a minor at −66.1 ppm ($^1J_{P-B}$ = 40 Hz) were



Scheme 3 i) 0.5 *o*-$C_6H_4(CH_2Cl)_2$; ii) BH_3·THF; iii) n-BuLi, 0.5 *o*-$C_6H_4(CH_2Cl)_2$; iv) HBF_4·Et_2O, aq. Na_2CO_3.

observed in an approximate ratio of 4 : 1 for the deprotonated secondary phosphine-borane compound (Scheme 3). Addition of α,α′-dichloro-*ortho*-xylene to the solution of the borane protected phosphide gave the diphosphine borane, **12**, as a mixture of 2 diastereomers (~8 : 1 ratio) which was deprotected with HBF_4 or 1,4-bis(2-aminoethyl)piperidine as detailed by Livinghouse[18] and Knochel[19] respectively to give **13**. The diphosphine, **13**, was acquired in 80% yield and isolated as a single diastereomer after one recrystallisation from MeOH. The $^{31}P\{^1H\}$ NMR spectrum of **13** consists of a singlet at δ_P −38.4 ppm. Spectroscopic analysis by one- and two-dimensional NMR methods, especially 2D NOESY experiments, revealed that the xylene group is orientated axially and the P-centres have the *R* Chirality as shown in the scheme. Key features of the spectroscopic data that support this conclusion include a large $^2J_{C-P}$ coupling to C6 (21.1 Hz) rather than C7 (2.5 Hz) as a consequence of the proximity of the P lone pair to C6 and NOESY contacts between the methylene protons H12 and the axial H3 and H6 hydrogens.[20] The isolation of the diphosphine as this diastereomer suggests that the stereogenic integrity of the P centre is largely retained during the boronation/deprotonation/deboronation sequence as expressed in the scheme.

Complexes of *o*-$C_6H_4(CH_2PBO)_2$ with Pd(II), Pt(II), Pt(0) and Mo(0)

Reaction of the ligand **13** with Pt(1,5-COD)Cl_2 or K_2PdCl_4 in a 1 : 1 ratio gave complexes of the type *cis*-M{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2 where M = Pd(II), **14**, Pt(II), **15**. Both complexes were obtained as colourless crystals after recrystallisation from acetonitrile. **14** and **15** were only very sparingly soluble in organic solvents such as chloroform and dichloromethane but showed higher solubility in more polar solvents such as methanol and acetone. *Cis*-Pt{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2 shows two AB doublets ($^2J_{P-P}$ = 22.5 Hz) at δ_P = −3.5 and −4.1 ppm in its $^{31}P\{^1H\}$ NMR spectrum at RT indicating asymmetry in the bidentate ligand. Both signals have associated Pt-195 satellites with $^1J_{P-Pt}$ coupling constants of 3310 and 3468 Hz, respectively. The two phosphines are also inequivalent in the related *cis*-Pd{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2 complex as evidenced by the presence of two peaks in the room temperature $^{31}P\{^1H\}$ NMR spectrum but in this case no observable P–P coupling was seen. As is usual for phosphine complexes of Pd(II) and Pt(II), the chemical shift induced upon coordination ($\Delta\delta_P$) is larger for the Pd(II) complex (+ 54 ppm) compared to the analogous Pt(II) species (+ 34 ppm).[21] The lack of C_2 symmetry is a consequence of an asymmetric backbone as shown in the crystal structures of the two complexes (Fig. 2 and 3). The complexes are isostructural with an asymmetric boat conformation for the 7-membered chelate ring as shown in the figures. The sum of the angles about the metal centres are 359.94(4)° for Pd(II) and 359.96(8)° for Pt(II) emphasising the compliance to square planar coordination. The Cl-M-Cl angle is the smallest intrametal angle in both complexes although the distortion from the ideal is small {88.93(4)° for Pd and 86.92(8)° for Pt}. All other metrical data accord with those expected for such systems. The variance of the P–M–P bite angle in these *o*-xylyl backbone diphosphines is of interest. Larger bite angles are observed when the xylyl aryl ring lies flatter to the square plane (for Pd^{2+}, Pt^{2+} and Rh^+ complexes) of the complex, whereas more acute P–M–P angles are observed when the ring is orthogonal to the coordination plane.[13,17b–e,22] More specifically, the closer the methylene carbon atoms of the xylyl group are to being coplanar with the coordination plane, the wider the bite angle. This would appear to be sensitive to the nature of the other substituents on the phosphorus donors with the more obtuse P–M–P angles being observed with bulkier substituents. The low bite angles in **14** and **15** suggest that the [2.2.2] bicyclic framework of the P-donors in the *o*-$C_6H_4(CH_2PBO)_2$ ligand are sterically slight, a feature associated at least in part with the compressed internal C–P–C angles of

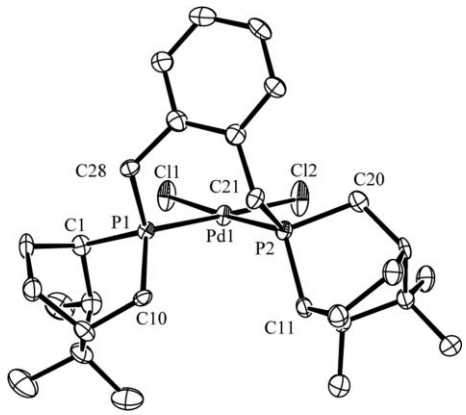


Fig. 2 Ortep view of the molecular structure of **14**. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°) for **14**: Pd1–P1 2.2699(12), Pd1–P2 2.2567(11), Pd1–Cl1 2.3738(11), Pd1–Cl2 2.3405(12), P1–Pd1–P2 89.95(4), P1–Pd1–Cl1 91.28(4), P2–Pd1–Cl2 89.78(4), Cl1–Pd1–Cl2 88.93(4), C1–P1–C10 96.0(2), C11–P2–C20 97.0(2).

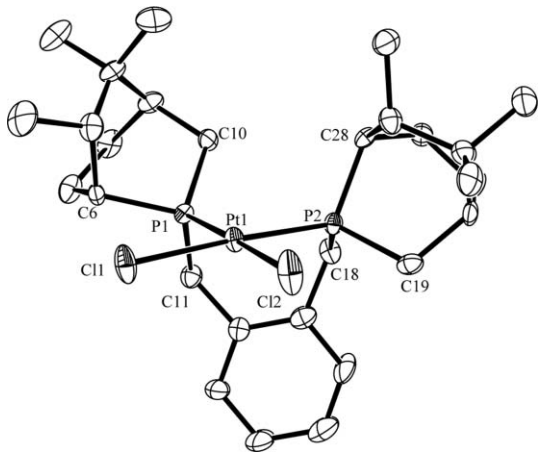


Fig. 3 Ortep view of the molecular structure of **15**. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°) for **15**: Pt1–P1 2.246(2), Pt1–P2 2.239(2), Pt1–Cl1 2.374(2), Pt1–Cl2 2.346(2), P1–Pt1–P2 90.76(8), P1–Pt1–Cl1 91.65(8), P2–Pt1–Cl2 90.63(8), Cl1–Pt1–Cl2 86.92(8), C6-P1–C10 96.9(4), C19–P2–C28 97.3(4).

around 97° for the phosphacycles. Small bite angles have been observed with related *cis*-M{*o*-$C_6H_4(CH_2PR_2)_2$}Cl_2 systems where the P-substituents are not sterically demanding.[13,17b] As alluded above, when the bite angle is small (around 90°) the xylyl aromatic ring tends towards orthogonality to the ML_4 plane; this is clearly the case in the *cis*-M{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2 complexes shown in Fig. 2 and 3 where the aryl ring projects almost vertically over the ML_4 plane. As a consequence, the bicyclic [2.2.2] frameworks of the phosphacycles are forced into a position on the opposing side of the coordination plane to the xylyl backbone such that each potential axial coordination site is quite distinct. The chirality at the phosphorus centres is *S* as deduced previously from the NMR analysis of the free ligand (accepting that the priority of the groups has changed with the lone pair being replaced by the metal). The methylene groups of the xylyl backbone project axially leading to equatorial lone pairs or, in the case of the complexes, equatorial P–M bonds. The P–M–P bond angles are around 90° as anticipated for square planar complexes. These favoured bond angles are quite different from the expanded angles of around 100° observed in the complexes of related ligands with *tert*-butyl substituents and/or other bulky diphosphines containing the *o*-xylyl backbone, but are similar to those reported for a similar system containing phosphetane donors bound to Pd(II).[13] Interestingly, this latter complex shows considerable distortion from square planar geometry unlike the complexes reported here.

As noted above, the asymmetry observed in the crystal structures is retained in solution with two separate resonances being seen in the $^{31}P\{^1H\}$ NMR spectrum of *cis*-Pd{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2 and an AB pattern for *cis*-Pt{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2 at room temperature; the ^1H and to a lesser extent the $^{13}C\{^1H\}$ NMR spectra are complex at room temperature as a result of this asymmetry in the chelate ring. Heating solutions of the complexes in d_6-dmso leads to coalescence of the two $^{31}P\{^1H\}$ resonances at temperatures of 115 °C for the Pd(II) system and 77 °C for the Pt(II) complex respectively. These values equate to activation energies for the bridge inversion of 77 KJ mol^{-1} for **14** and 71 KJ mol^{-1} for **15**. The ^1H NMR spectra of the complexes are simplified when recorded at temperatures above these coalescence limits as detailed in the experimental section. Temperature-dependent NMR spectra have been reported previously in related systems.[17e]

The Pt(0) complex Pt{*o*-$C_6H_4(CH_2PBO)_2$}(nb), **16**, was prepared from Pt{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2 by the method of Weigand.[23] The complex was obtained as a white solid which was freely soluble in organic solvents and appeared to be stable in the absence of added norbornene unlike most of the complexes reported by Weigand.[23] The $^{31}P\{^1H\}$ NMR spectrum of the complex consists of two AB doublets with a $^2J_{P-P}$ coupling constant of 45 Hz and Pt-195 satellites with a $^1J_{P-Pt}$ coupling constant of 3336 Hz. The AB pattern reflects a lack of symmetry in the complex at room temperature mimicking the pattern observed for the Pt(II) system. Weigand has correlated the $^1J_{P-Pt}$ coupling constants of a number of Pt($R_2P\wedge PR_2$)(nb) species with the bite angle of the diphosphine observing decreasing $|J|$ as the P–Pt–P angle decreases.[23] The value of 3336 Hz observed in the current complex (**16**) is consistent with a bite angle of around 90° according to the correlation of Weigand. This suggests that a conformation similar to that observed in the solid state for *cis*-Pt{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2 is maintained in solution for the Pt(0) complex. However, caution should be exercised in using $^1J_{P-Pt}$ coupling constants as indicators of chelate bite angle as the Pt{*o*-$C_6H_4(CH_2P^tBu_2)_2$}(nb) complex has a $^1J_{P-Pt}$ constant of only 3331 Hz even though the majority of crystal structures containing this ligand show bite angles of >100°.[22a] The $^{13}C\{^1H\}$ NMR spectrum of complex **16** shows a doublet of doublets for the alkenic carbon at δ_C 51.3 ppm with $^2J_{C-P}$ values of 36.3 and 27.2 Hz. These carbons also show Pt-195 satellites with a $^1J_{C-Pt}$ coupling constant of 338 Hz, a value very similar to that of 332 Hz observed for the Pt{*o*-$C_6H_4(CH_2P^tBu_2)_2$}(nb) complex.[22a] The bridgehead methines are observed at δ_C 45.1 ppm with a $^2J_{C-Pt}$ coupling constant of 12.8 Hz again in accord with that observed for the *tert*-butyl derivative.[22a] A doublet at 0.11 ppm ($^2J_{H-H}$ = 8.2 Hz) is observed for a hydrogen of the methylene bridge CH_2 group that resides near the metal suggesting that the norbornene coordinates from the *exo* face of the double bond. Cooling NMR solutions of complex **16** to low temperature (< -35 °C) resulted in four broad peaks in the $^{31}P\{^1H\}$ NMR spectrum at δ_P 7.6, 5.5, -3.1, and -4.0 ppm indicating the presence of two species in solution, both of which have asymmetry in the chelate ring. The most likely explanation for this is the presence of two different alkene rotamers whereby the rotation of the formal C–C double bond about the metal-alkene axis has been slowed to the point that both forms are observed at this low temperature.

The colourless Mo(CO)$_4${*o*-$C_6H_4(CH_2PBO)_2$} complex, **17**, is readily prepared from Mo(CO)$_4$(pip)$_2$ and one mol equivalent of the ligand. The molybdenum complex is much more soluble in hydrochlorocarbons than the Pd(II) or Pt(II) dichloride systems and is readily recrystallised from toluene or 40/60 petroleum ether. Mo(CO)$_4${*o*-$C_6H_4(CH_2PBO)_2$} shows only a singlet in the $^{31}P\{^1H\}$ NMR spectrum at room temperature reflecting a rapid exchange in the xylyl bridge. Upon cooling, the singlet splits into the expected two peaks as the chelate inversion becomes slow on the NMR timescale. The coalescence occurs at −35 °C with an activation barrier to inversion of 45 KJ mol^{-1}. The RT ^1H and $^{13}C\{^1H\}$ NMR

spectra are consequently much simpler than the room temperature spectra for the Pd(II) and Pt(II) complexes allowing full assignment of the spectra for complex **17** (see experimental).

The single-crystal X-ray structure of $Mo(CO)_4\{o\text{-}C_6H_4(CH_2PBO)_2\}$ is shown in Fig. 4. Notwithstanding the fact that **17** is an octahedral complex, many of the features observed in the Pd(II) and Pt(II) complexes are maintained in the structure as shown in Fig. 4. Thus, the 7-membered chelate adopts the asymmetric boat form and the aryl ring of the backbone is forced into an arrangement orthogonal to the $(P\wedge P)Mo(CO)_2$ plane in order to accommodate a P–Mo–P bite angle of 90°. The orientation of the xylyl ring is such that it appears to be involved in a π–π interaction with one of the axial carbonyls (C3) causing the CO ligand to be bent away from the aryl group (Mo–C–O = 170°) with the centroid of the aryl ring 3.214 Å from the midpoint of the C–O bond. The Mo–C bond lengths are shorter to the carbonyl ligands *trans* to the phosphorus donors (Mo–C average 1.988(9) Å) as expected when compared to the mutually *trans* CO groups where Mo–C bond lengths of 2.044(8) Å are observed. The Mo–P bond lengths average 2.541(2) Å and are somewhat shorter than the value of 2.658(6) Å observed in the analogous $Mo(CO)_4\{o\text{-}C_6H_4(CH_2P^tBu_2)_2\}$ system[13] although it should be noted that the P–Mo–P bond angle is slightly expanded in this latter complex {94.161(18)°} compared to that for **17** {87.37(7)°}. Indeed this relatively acute bite angle appears to be a consequence of the π–π interaction noted above. Other phosphacyclic systems with an *o*-xylyl backbone have metric details very similar to those for the complex shown here although the very acute chelate bite and the pronounced π–π interaction are not as evident in these related systems with smaller 4-membered phosphetanes.[13]

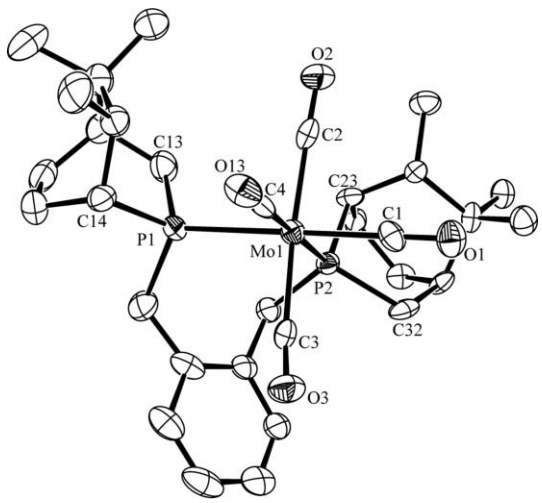


Fig. 4 Ortep view of the molecular structure of **17**. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°) for **17**: Mo1–P1 2.544(2), Mo1–P2 2.534(2), Mo1–C1 1.984(8), Mo1–C2 2.005(8), Mo1–C3 2.064(7), Mo1–C4 1.977(9), C1–O1 1.151(8), C2–O2 1.168(8), C3–O3 1.131(8), C4–O13 1.161(9), P1–Mo1–P2 85.77(7), P1–Mo1–C1 174.4(2), P1–Mo1–C2 91.3(2), P1–Mo1–C3 94.91(19), P1–Mo–C4 93.6(2), P2–Mo1–C1 88.7(2), P2–Mo1–C2 90.5(2), P2–Mo1–C3 94.2(2), P2–Mo1–C4 179.4(2), C2–Mo1–C3 172.5(3), Mo1–C2–O2 175.8(8), Mo1–C3–O3 170.2(7), C13–P1–C14 95.3(3), C23–P2–C32 95.8(3).

Experimental

Methods and materials

All synthetic procedures and manipulations were performed under dry argon or nitrogen using standard Schlenk line techniques. All solvents were freshly distilled from sodium (toluene), sodium/benzophenone (THF) or calcium hydride (acetonitrile, methanol and dichloromethane) under nitrogen before use. All other chemicals were obtained commercially and used as received. The ^{31}P NMR spectra were recorded on a Jeol Eclipse 300 MHz spectrometer operating at 121.7 MHz, and referenced to 85% H_3PO_4 ($\delta = 0$ ppm). ^1H and ^{13}C NMR spectra were obtained using a Bruker 500 MHz spectrometer, operating at 500.0 and 125.8 MHz, respectively, and referenced to tetramethylsilane ($\delta = 0$ ppm). Unless stated otherwise, infrared spectra were recorded as nujol mulls on a Jasco FTIR spectrometer. Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Elemental analyses were performed by Medac Ltd, UK.[24]

Syntheses

(1*R*,3*S*)-(1,2,2-trimethylcyclopentane-1,3-diyl)bis(methylene) dimethanesulfonate, 2a. To a stirred solution of (1,2,2-trimethylcyclopentane-1,3-diyl)dimethanol[25] (3.70 g, 21.47 mmol) and triethylamine (7.3 ml, 2.2 mol equivs) in DCM (70 ml) at −10 °C was added dropwise mesyl chloride (3.66 ml, 2.2 mol equivs) in DCM (20 ml) over 20 min. The mixture was stirred at 0 °C for 1 h then at RT overnight. The mixture was washed successively with 0.5 M HCl (100 ml) then water (2 × 100 ml) and the organic phase dried over magnesium sulfate. After filtering the solvent was removed to give a light yellow oil that crystallised on standing. Yield = 7.05 g (90%). ^1H NMR ($CDCl_3$, 400 MHz) δ 4.20 (1H, dd, $^{2,3}J_{H-H} = 9.6, 6.0$ Hz), 4.08 (2H, m), 3.97 (1H, d, $^2J_{H-H} = 9.5$ Hz), 2.95 (6H, s), 2.27 (1H, m), 1.94 (1H, m), 1.60 (1H, m), 1.49 (2H, m), 1.01 (3H, s), 0.99 (3H, s), 0.80 (3H, s) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 100 MHz) δ 75.2 (CH_2), 71.5 (CH_2), 47.4 (C), 46.9 (CH), 44.5 (C), 37.3 (CH_3), 37.1 (CH_3), 33.4 (CH_2), 25.0 (CH_2), 23.7 (CH_3), 20.7 (CH_3), 20.7 (CH_3), 18.5 (CH_3) ppm. *Anal.*: Calc. for $C_{12}H_{24}O_6S_2$: C, 43.89; H, 7.38%. Found: C, 43.5; H, 7.4%.

(1*R*,3*S*)-(1,2,2-trimethylcyclopentane-1,3-diyl)bis(methylene) di-*p*-tolylsulfonate, 2b. This was prepared in a similar manner to the dimesylate above. Isolated as a white solid that could be recrystallised from toluene–DCM if desired. Yield = 87%. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.70 (4H, dd, $^2J_{H-H} = 8.1$, $^4J_{H-H} = 1.8$ Hz), 7.28 (4H, d, $^2J_{H-H} = 8.1$ Hz), 3.95 (1H, dd, $^{2,3}J_{H-H} = 9.5, 6.1$ Hz), 3.80 (2H, m), 3.68 (1H, d, $^2J_{H-H} = 9.3$ Hz), 2.38 (6H, s), 2.10 (1H, m), 1.78 (1H, m), 1.39 (1H, m), 1.20 (2H, m), 0.84 (6H, s), 0.54 (3H, s) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 100 MHz) δ 144.9 (C), 144.9 (C), 132.9 (C), 132.9 (C), 129.9 (CH), 129.9 (CH), 127.9 (CH), 127.9 (CH), 75.8 (CH_2), 72.0 (CH_2), 47.3 (C), 46.6 (CH), 44.4 (C), 33.2 (CH_2), 24.8 (CH_2), 23.6 (CH_3), 21.7 (CH_3), 20.7 (CH_3), 18.2 (CH_3) ppm. *Anal.*: Calc. for $C_{24}H_{32}O_6S_2$: C, 59.98; H, 6.73%. Found: C, 60.1; H, 6.8%.

(1*R*,3*S*)-[1,2,2-trimethyl-3-(phosphinomethyl)cyclopentyl]methyl methanesulfonate, 3a. To a stirred solution of $P(SiMe_3)_3$ (1.0 g, 3.99 mmol) in THF (20 ml) was added a solution of MeLi (2.62 ml of a 1.6 M solution, 4.19 mmol) and the mixture stirred at RT overnight. After removing the THF at the pump the resultant

cream solid $LiP(TMS)_2$ was dissolved in diethyl ether (20 ml) and added slowly to a stirred solution of dimesylate (1.31 g, 3.99 mmol) in a 1 : 1 mixture of diethyl ether–THF (30 ml) at −78 °C. After stirring for 1 h at −78 °C, the solution was allowed to reach RT and left stirring overnight. On return, ethanol (1 ml) was added and the mixture stirred for a further 24 h. After filtering, the solution was pumped to dryness and the desired compound dissolved in diethyl ether and filtered off from a small quantity of insoluble salts. The diethyl ether was removed to give a white solid that could be recrystallised from MeOH at low temperature. Yield = 0.82 g (77%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.10 (1H, d, $^2J_{H-H}$ = 9.3 Hz), 3.97 (1H, d, $^2J_{H-H}$ = 9.3 Hz), 2.97 (3H, s), 2.72 (1H, dm, $^1J_{H-P}$ = 195.3 Hz), 2.60 (1H, dm, $^1J_{H-P}$ = 194.8 Hz), 2.01 (1H, m), 1.83 (1H, m), 1.55 (2H, m), 1.38 (1H, m), 1.22 (2H, m), 1.01 (3H, s), 0.87 (3H, s), 0.72 (3H, s) ppm. ^{13}C{^{1}H} DEPT NMR ($CDCl_3$, 125 MHz) δ 76.3 (CH_2), 50.7 (d, $^2J_{C-P}$ = 3.7 Hz, CH), 46.9 (C), 45.5 (d, $^3J_{C-P}$ = 5.2 Hz, C), 37.0 (CH_3), 32.2 (CH_2), 27.5 (CH_2), 22.5 (CH_3), 21.2 (CH_3), 17.9 (CH_3), 14.2 (d, $^1J_{C-P}$ = 7.6 Hz, CH_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): −139.45 ppm.

(1*R*,3*S*)-[1,2,2-trimethyl-3-(phosphinomethyl)cyclopentyl]methyl *p*-tolylsulfonate, 3b. Prepared as detailed above for the mesylate. Yield of white solid = 84%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (2H, dd), 7.28 (2H, d), 3.87 (1H, d, J = 9.23 Hz), 3.71 (1H, d, J = 9.23 Hz), 2.68 (1H, dm, J = 194.95 Hz), 2.55 (1H, dm, $^1J_{H-P}$ = 195.02 Hz), 2.09 (1H, m), 1.92 (1H, m), 1.45 (1H, m), 1.41 (1H, m), 1.25–1.05 (3H, m), 0.88 (3H, s), 0.79 (3H, s), 0.55 (3H, s) ppm. ^{13}C{^{1}H} DEPT NMR ($CDCl_3$, 100 MHz) δ 144.9 (C), 132.9 (C), 132.9 (C), 129.9 (CH), 127.8 (CH), 76.7 (CH_2), 50.8 (d, $^2J_{C-P}$ = 3.8 Hz, CH), 46.9 (C), 45.4 (C), 33.2 (CH_2), 27.5 (CH_2), 22.5 (CH_3), 21.2 (CH_3), 17.8 (CH_3), 14.2 (d, $^1J_{C-P}$ = 7.4, CH_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): −140.43 ppm.

(1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphoniabicyclo[2.2.2]octane methanesulfonate, 5a

The desired compound could be prepared from either the phosphinomesylate or phosphinotosylate; the following procedure is for the methanesulfonate. A solid sample of the phosphinomethanesulfonate **3a** (1 g, 3.76 mmol) was heated to 140° C under N_2 overnight. During this time the desired compound sublimed as a crystalline solid in the upper half of the Schlenk flask. The lower residues were washed away with THF and kept. The crystalline solid was then transferred as a THF solution to a fresh Schlenk and pumped down to a dry solid. Yield = 40%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.80 (3H, s), 2.29 (1H, d br, J = 15.5 Hz), 2.03 (2H, m), 1.90 (2H, m), 1.65 (2H, m), 1.48 (1H, m), 0.97 (3H, dd, $^3J_{H-H}$ = 7.1 Hz, $^4J_{H-P}$ = 1.0 Hz), 0.96 (3H, s), 0.89 (3H, s) ppm. ^{13}C{^{1}H} DEPT NMR ($CDCl_3$, 125 MHz) δ 39.5 (CH_3), 37.7 (CH), 35.6 (d, $^2J_{C-P}$ = 4.8 Hz, CH), 34.0 (C), 29.5 (CH_3), 24.6 (d, $^1J_{C-P}$ = 25.2 Hz, CH), 24.0 (CH_3), 21.8 (d, $^3J_{C-P}$ = 8.2 Hz, CH_2), 17.2 (CH_2), 15.0 (d, $^3J_{C-P}$ = 13.1 Hz, CH_3), 14.2 (d, $^2J_{C-P}$ = 21.7 Hz, CH_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): −65 br ppm.

(1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]octane, PBO, 6. A solid sample of the phosphinomethanesulfonate **3a** (1 g, 3.76 mmol) was heated to 140 °C under N_2 overnight. The resultant mixture was dissolved in THF (30 ml) and added to a stirred suspension of $LiAlH_4$ (1 g, excess) in THF (30 ml) at 0 °C. After stirring overnight at RT, the mixture was hydrolysed by the addition of water (1 ml), 15% aq. NaOH (1 ml) then water (3 ml). The mixture was filtered and the solvent removed in *vacuo* to yield a viscous oil. The desired phosphine was sublimed from the residue upon heating between 50 and 80 °C under high vacuum (0.1 mm Hg). Yield = 0.3 g (47%). ^{1}H NMR ($CDCl_3$, 500 MHz, major isomer) δ 3.04 (1H, d, $^1J_{H-P}$ = 183.8 Hz), 1.75 (1H, m), 1.58 (2H, m), 1.39 (1H, m), 1.25 (2H, m), 1.08 (2H, m), 0.68 (3H, s), 0.66 (3H, d, $^3J_{H-H}$ = 7.3 Hz), 0.64 (3H, s) ppm. ^{13}C{^{1}H} DEPT NMR ($CDCl_3$, 125 MHz, major isomer) δ 38.2 (d, $^1J_{C-P}$ = 15.33 Hz, CH), 36.3 (CH), 34.5 (C), 29.8 (CH_3), 26.3 (CH), 24.4 (CH_3), 22.5 (CH_2), 22.2 (CH_2), 15.6 (d, $^3J_{C-P}$ = 13.1 Hz, CH_3), 14.7 (d, $^2J_{C-P}$ = 8.90 Hz, CH_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): −60.8 (minor), −79.6 (major) ppm.

(1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-oxa-phosphabicyclo[2.2.2]octane, 7. A solution of **6** (100 mg) in DCM was stirred with a 3% aqueous solution of hydrogen peroxide for 30 mins. The organic phase was isolated, dried over $MgSO_4$, filtered and the volatiles removed to leave a colourless oil. A pure sample of the desired compound was obtained as a low melting solid after sublimation under high vacuum (0.1 mm Hg). Yield = 70%. ^{1}H NMR ($CDCl_3$, 400 MHz, major isomer) δ 6.99 (1H, dt, $^1J_{H-P}$ = 454.6 Hz, $^3J_{H-H}$ = 3.5 Hz), 2.3–1.0 (9H, m), 1.03 (3H, s), 0.99 (3H, d, $^3J_{H-H}$ = 5.80 Hz), 0.89 (3H, s) ppm. ^{1}H NMR ($CDCl_3$, 400 MHz, minor isomer) δ 6.84 (1H, d, $^1J_{H-P}$ = 463.0 Hz) 2.3–1.0 (9H, m), 0.99 (3H, d, $^3J_{H-H}$ = 6.30 Hz), 0.92 (3H, s), 0.85 (3H, s) ppm. ^{13}C{^{1}H} DEPT NMR ($CDCl_3$, 125 MHz, major isomer) δ 38.5 (d, $^2J_{C-P}$ = 4.7 Hz, CH), 34.2 (s, C), 33.4 (d, $^1J_{C-P}$ = 61.3 Hz, CH), 31.6 (CH), 29.5 (CH_3), 29.1 (d, $^1J_{C-P}$ = 53.8, CH_2), 24.5 (CH_3), 21.3 (d, $^3J_{C-P}$ = 10.9 Hz, CH_2), 15.1 (d, $^3J_{C-P}$ = 12.9 Hz, CH_3), 14.2 (CH_2) ppm. ^{13}C{^{1}H} DEPT NMR ($CDCl_3$, 125 MHz, minor isomer) δ 38.4 (d, $^2J_{C-P}$ = 5.1 Hz, CH), 33.9 (C), 33.1 (d, $^1J_{C-P}$ = 64.0 Hz, CH), 31.6 (CH), 29.9 (CH_3), 29.7 (d, $^1J_{C-P}$ = 54.2, CH_2), 24.0 (CH_3), 22.1 (d, $^3J_{C-P}$ = 11.4 Hz, CH_2), 14.6 (d, $^3J_{C-P}$ = 17.0 Hz, CH_3), 12.1 (d, $^2J_{C-P}$ = 5.8 Hz, CH_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): 34.7 (minor), 34.3 (major) ppm.

(1*R*,4*S*,6*R*)-2,5,5,6-tetramethyl-2-phosphoniabicyclo[2.2.2]octane iodide, 8. To a solution of PBO (200 mg, 1.17 mmol) in THF (30 ml) was added MeI (0.5 ml) and the mixture left at 4 °C overnight. On return the white precipitate was isolated by filtration and dried at the pump. Yield = 227 mg (62%). ^{1}H NMR ($CDCl_3$, 500 MHz, major isomer) δ 7.70 (1H, dm, $^1J_{H-P}$ = 517.67 Hz), 2.91 (1H, m), 2.46 (1H, dt, J = 11.3, 2.5 Hz), 2.22 (3H, dd, $^2J_{C-P}$ = 15.0 Hz, $^3J_{H-H}$ = 5.3 Hz), 2.10 (1H, m), 1.99 (2H, m), 1.82 (2H, m), 1.65 (2H, m), 1.05 (3H, dd, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-P}$ = 1.3 Hz), 0.97 (3H, s), 0.93 (3H, s) ppm. ^{13}C{^{1}H} DEPT NMR ($CDCl_3$, 125 MHz, major isomer) δ 36.3 (d, $^2J_{C-P}$ = 5.2 Hz, CH), 33.9 (C), 33.7 (d, $^2J_{C-P}$ = 2.5 Hz, CH), 29.4 (CH_3), 26.2 (d, $^1J_{C-P}$ = 47.9 Hz, CH), 23.9 (d, $^1J_{C-P}$ = 43.4 Hz, CH_2), 15.0 (d, $^2J_{C-P}$ = 4.4 Hz, CH_2), 14.4 (d, $^3J_{C-P}$ = 14.0 Hz, CH_3), 4.1 (d, $^1J_{C-P}$ = 52.0 Hz, CH_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): 2.7 (minor), 1.4 (major) ppm. *Anal*.: Calc. for $C_{11}H_{22}PI$: C, 42.32; H, 7.12%. Found: C, 42.2; H, 6.8%.

(1*R*,4*S*,6*R*)-2,2,5,5,6-pentamethyl-2-phosphoniabicyclo[2.2.2]-octane iodide monohydrate, 9. To a solution of PBO (200 mg, 1.17 mmol) in THF (30 ml) was added MeI (2 ml) and the mixture refluxed for 2 h. After cooling the white precipitate was isolated

by filtration in air and dried at the pump. The compound was recrystallised from MeCN. Yield = 388 mg (96%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.41 (3H, m), 2.33 (3H, d, $^2J_{H-P}$ = 3.2 Hz), 2.29 (3H, d, $^2J_{H-P}$ = 3.1 Hz), 2.2-1.7 (5H, m), 1.44 (1H, m), 1.09 (3H, d, $^3J_{H-H}$ = 7.0 Hz), 0.97 (3H, s), 0.93 (3H, s) ppm. ^{13}C{^{1}H} DEPT NMR ($CDCl_3$, 125 MHz) δ 36.8 (d, $^2J_{C-P}$ = 5.1 Hz, CH), 34.3 (d, $^2J_{C-P}$ = 1.8 Hz, CH), 33.6 (C), 29.6 (CH_3), 27.6 (d, $^1J_{C-P}$ = 48.8 Hz, CH), 24.1 (CH_3), 23.7 (d, $^1J_{C-P}$ = 44.5 Hz, CH_2), 21.0 (d, $^3J_{C-P}$ = 11.9 Hz, CH_2), 14.5 (d, $^3J_{C-P}$ = 14.2 Hz, CH_3), 13.3 (d, $^2J_{C-P}$ = 4.7 Hz, CH_2), 10.0 (d, $^1J_{C-P}$ = 49.5 Hz, CH_3), 8.7 (d, $^1J_{C-P}$ = 52.5 Hz, CH_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): 25.2 ppm. *Anal.*: Calc. for $C_{12}H_{26}OPI$: C, 41.86; H, 7.63%. Found: C, 41.9; H, 7.4%.

α,α′-bis{(1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]-octyl}-*o*-xylene diborane, *o*-$C_6H_4(CH_2PBO)_2.2BH_3$, 12. To a solution of PBO (600 mg, 3.51 mmol) in THF (30 ml) at −78 °C was added 1.1 mol equivalents of BH_3·THF (3.9 ml of a 1 M solution) and the mixture stirred for 20 min at this temperature before the cold bath was removed and the solution stirred for a further 20 min. After re-cooling to −78 °C, 1.1 mol equivalents of n-BuLi (1.4 ml of a 2.5 M solution in hexanes) were added and the solution stirred for another 20 min at this temperature and then a further 20 min after the cold bath was removed. The solution was again cooled to −78 °C before a solution of α,α′-dichloro-*o*-xylene (0.3 g, 1.75 mmol) in THF (20 ml) was added dropwise. The solution was left to slowly reach room temperature and then left stirring overnight. All volatiles were removed at the pump and the residue partitioned between DCM and water. The organic phase was isolated, dried ($MgSO_4$), filtered and the solvent removed in *vacuo*. The resultant sticky solid was stirred with Et_2O (20 ml) to give a free-flowing white solid. Yield = 370 mg (45%). A second crop was obtained after cooling the Et_2O filtrate to −35 °C. Yield = 140 mg (17%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.10 (4H, m), 3.39 (2H, m), 3.24 (2H, dd, $^2J_{H-H}$ = 15.0, $^2J_{H-P}$ = 10.0 Hz), 2.16 (2H, m), 2.1–1.8 (8H, m), 1.60 (4H, m), 1.42 (4H, m), 0.94 (3H, d, $^3J_{H-H}$ = 7.27 Hz), 0.92 (3H, s), 0.89 (3H, s) ppm. ^{13}C{^{1}H} DEPT NMR ($CDCl_3$, 125 MHz) δ 133.3 (d, $^2J_{C-P}$ = 3.8 Hz, C), 130.6 (s, CH), 127.0 (s, CH), 37.5 (d, $^2J_{C-P}$ = 5.2 Hz, CH), 34.5 (d, $^2J_{C-P}$ = 2.2 Hz, CH), 33.9 (s, C), 29.5 (s, CH_3), 29.4 (d, $^1J_{C-P}$ = 23.8 Hz, CH_2), 28.9 (d, $^1J_{C-P}$ = 30.8 Hz, CH), 24.7 (s, CH_3), 23.0 (d, $^1J_{C-P}$ = 28.8 Hz, CH_2), 22.1 (d, $^3J_{C-P}$ = 8.8 Hz, CH_2), 15.1 (d, $^3J_{C-P}$ = 13.6 Hz, CH_3), 14.3 (d, $^2J_{C-P}$ = 7.5 Hz, CH_2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz): 10.3 (br m) ppm. *Anal.*: Calc. for $C_{28}H_{52}P_2B_2$: C, 71.19; H, 11.12%. Found: C, 70.7; H, 10.9%.

α,α′-bis{(1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]-octyl}-*o*-xylene, *o*-$C_6H_4(CH_2PBO)_2$, 13. To a solution of **12** (500 mg, 1.06 mmol) in DCM (100 ml) was added HBF_4·Et_2O (1.7 ml) and the mixture stirred for 24 h before being added dropwise to a degassed saturated aqueous solution of Na_2CO_3. After stirring for 2 h, the organic phase was isolated and dried over $MgSO_4$. After filtering, the volatiles were removed in *vacuo* to give a white solid that was recrytallised from MeOH at −35 °C. Yield = 375 mg (80%). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.08 (2H, m, H13), 6.97 (2H, m, H14), 3.29 (2H, dd, $^2J_{H-H}$ = 13.4, $^2J_{H-P}$ = 1.5 Hz, H12), 3.11 (2H, dd, $^2J_{H-H}$ = 13.4, $^2J_{H-P}$ = 1.3 Hz, H12), 2.02 (2H, ddt, $^2J_{H-P}$ = 25.2, $^2J_{H-H}$ = 14.3, $^3J_{H-H}$ = 2.8 Hz, H3eq), 1.91 (4H, m, H7), 1.80 (4H, m, H6, H8), 1.50 (2H, m, H8), 1.39 (6H, m, H3ax, H4, H1), 0.97 (6H, s, H10/11), 0.95 (6H, d, $^3J_{H-H}$ = 6.7 Hz, H9), 0.93 (6H, H10/11) ppm. ^{13}C{^{1}H} DEPT NMR (C_6D_6, 125 MHz) δ 137.5 (t, $^{2,3}J_{C-P}$ = 3.8 Hz, C), 130.5 (d, $^3J_{C-P}$ = 5.0 Hz, CH), 126.0 (s, CH), 40.1 (d, $^2J_{C-P}$ = 21.1 Hz, C6), 37.6 (d, $^2J_{C-P}$ = 1.9 Hz, C4), 33.6 (s, C5), 32.7 (dd, $^1J_{C-P}$ = 25.0, $^5J_{C-P}$ = 9.8 Hz, C12), 30.3 (s, C10/11), 29.0 (d, $^1J_{C-P}$ = 12.7 Hz, C1), 24.5 (s, C10/11), 23.1 (d, $^3J_{C-P}$ = 1.7 Hz, C8), 21.8 (d, $^1J_{C-P}$ = 17.2 Hz, C3), 15.5 (d, $^3J_{C-P}$ = 15.3 Hz, C9), 15.0 (d, $^2J_{C-P}$ = 2.5 Hz, C7) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 121.7 MHz): −38.4 (s) ppm.

***cis*-Pd{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2·MeCN, 14.** A mixture of Na_2PdCl_4 (97 mg, 0.33 mmol) and **13** (145 mg, 0.33 mmol) in EtOH (15 ml) was refluxed for 12 h during which time an off-white precipitate formed. The solid was filtered off and recrystallised from MeCN as colourless blocks. Yield = 171 mg (78%). ^{1}H NMR {$(CD_3)_2SO$, 500 MHz, 393 K} δ 7.35 (2H, s br), 7.28 (2H, m), 3.52 (4H), 2.88 (4H, br), 2.13 (4H, m), 2.02 (6H, m), 1.67 (4H, m), 0.99 (6H, s), 0.96 (6H, d, $^3J_{H-H}$ = 7.1 Hz), 0.91 (6H, s) ppm. ^{13}C{^{1}H} DEPT NMR {$(CD_3)_2SO$, 125.8 MHz} δ 136.1 (d, $^2J_{C-P}$ = 4.6 Hz, C), 133.0 (t, $^{2,3}J_{C-P}$ = 4.0 Hz, C), 131.0 (d br, $^3J_{C-P}$ = 5.6 Hz, CH), 130.2 (d br, CH), 127.6 (d, $^3J_{C-P}$ = 3.5 Hz, CH), 127.4 (s, CH), 38.4 (d, $^2J_{C-P}$ = 6.4 Hz, CH), 38.2 (d, $^2J_{C-P}$ = 6.4 Hz, CH), 36.9 (s, CH), 34.6 (s br, CH), 33.3 (s, C), 33.2 (dd, $^1J_{C-P}$ = 25.7, $^3J_{C-P}$ = 4.2 Hz, CH_2), 32.6 (s, C), 32.0 (d, $^1J_{C-P}$ = 23.1 Hz, CH_2), 31.9 (d, $^1J_{C-P}$ = 19.5 Hz, CH_2), 30.5 (d, $^1J_{C-P}$ = 31.4 Hz, CH), 29.4 (s, CH_3), 28.2 (s, CH_3), 27.5 (dd, $^1J_{C-P}$ = 21.3, $^3J_{C-P}$ = 4.8 Hz, CH), 24.2 (s, CH_3), 23.8 (s, CH_3), 22.2 (d br, $^3J_{C-P}$ = 21.2 Hz, CH_2), 20.8 (d, $^3J_{C-P}$ = 7.9 Hz, CH_2), 20.6 (d, $^3J_{C-P}$ = 7.8 Hz, CH_2), 15.0 (d, $^2J_{C-P}$ = 8.0 Hz, CH_2), 14.9 (d, $^3J_{C-P}$ = 13.5 Hz, CH_3), 14.1 (d, $^2J_{C-P}$ = 6.3 Hz, CH_2), 13.6 (d, $^3J_{C-P}$ = 16.3 Hz, CH_3) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.7 MHz): 17.0 (s), 15.4 (s) ppm. MS: 618 (M^+, 30%), 602 ($M_2L_2Cl_3^{2+}$, 100%). IR (KBr): 2949 vs, 2871 vs, 1472 s, 1447 s, 1410 s, 1390 s, 1367 m, 1228 m, 1193 m, 1072 s, 1012 s, 911 m, 871 m, 849 s, 809 s, 784 s, 771 s, 652 m, 504 m, 460 m, 408 m cm^{-1}. *Anal.*: Calc. for $C_{30}H_{47}P_2NPdCl_2$: C, 54.51; H, 7.18; N, 2.12%. Found: C, 54.3; H, 7.1; N, 2.3%.

***cis*-Pt{*o*-$C_6H_4(CH_2PBO)_2$}Cl_2·MeCN, 15.** A solution of Pt(1,5-COD)Cl_2 (85 mg, 0.23 mmol) and **13** (106 mg, 0.24 mmol) in DCM (20 ml) was stirred at RT for 18 h, after which time the volatiles were removed in *vacuo* and the white solid recrystallised from hot MeCN as colourless blocks. Yield = 162 mg (94%). ^{1}H NMR {$(CD_3)_2SO$, 500 MHz, 363 K} δ 7.28 (2H, br), 7.19 (2H, m), 3.60 (5H, br), 2.15–1.50 (15H, m br), 0.99 (6H, s), 0.95 (6H, d, $^3J_{H-H}$ = 7.1 Hz), 0.91 (6H, s) ppm. ^{13}C{^{1}H} DEPT NMR {$(CD_3)_2SO$, 125.8 MHz} δ 137.4 (s, C), 133.8 (s, C), 131.2 (s, CH), 130.4 (s, CH), 127.6 (s, CH), 127.3 (s, CH), 38.7 (d, $^2J_{C-P}$ = 5.8 Hz, CH), 38.4 (d, $^2J_{C-P}$ = 5.8 Hz, CH), 36.7 (s, CH), 34.6 (s, CH), 33.8 (s, C), 33.2 (s, C), 33.4 (d, $^1J_{C-P}$ = 27.6 Hz, CH_2), 32.6 (d, $^1J_{C-P}$ = 31.3 Hz, CH), 32.5 (d, $^1J_{C-P}$ = 27.3 Hz, CH_2), 29.9 (s, CH_3), 28.7 (s, CH_3), 28.7 (d, $^1J_{C-P}$ = 37.6 Hz, CH), 24.8 (s, CH_3), 24.3 (s, CH_3), 21.3 (d, $^3J_{C-P}$ = 8.1 Hz, CH_2), 21.2 (d, $^3J_{C-P}$ = 9.4 Hz, CH_2), 19.4 (d, $^1J_{C-P}$ = 31.6 Hz, CH_2), 15.4 (d, $^3J_{C-P}$ = 13.8 Hz, CH_3), 15.2 (d, $^2J_{C-P}$ = 4.7 Hz, CH_2), 14.2 (d, $^2J_{C-P}$ = 4.5 Hz, CH_2), 14.1 (d, $^3J_{C-P}$ = 15.0 Hz, CH_3) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.7 MHz): -3.5 (d, $^2J_{P-P}$ = 22.5 Hz, $^1J_{P-Pt}$ = 3310 Hz), −4.1 (d, $^2J_{P-P}$ = 22.5 Hz, $^1J_{P-Pt}$ = 3468 Hz) ppm. MS: 707 (M^+, 85%). IR (KBr): 2952 vs, 2876 vs, 1474 s, 1458 s, 1411 m, 1388 s, 1365 m, 1263 w, 1232 w, 1192 w, 1064 s, 1011 m, 913 m, 872 m, 850 s, 810 s, 784 m, 768 s, 733 m, 653 m, 508 m, 460 m cm^{-1}. *Anal.*: Calc. for $C_{30}H_{47}P_2NPtCl_2$: C, 48.06; H, 6.33; N, 1.87%. Found: C, 47.7; H, 6.3; N, 1.7%.

Table 1 Details of X-ray crystallographic data collection for the compounds **9**, **14**, **15** and **17**

	9	**14**	**15**	**17**
Empirical formula	$C_{12}H_{24}PI$	$C_{30}H_{47}Cl_2NP_2Pd$	$C_{30}H_{47}Cl_2NP_2Pt$	$C_{71}H_{96}O_8P_4Mo_2$
Formula weight	326.18	660.93	749.62	1393.24
Crystal system	Orthorhomibic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a/Å	7.1710(2)	7.8766(2)	7.92200(10)	17.118(3)
b/Å	10.4460(3)	18.4788(4)	21.3381(3)	8.9172(18)
c/Å	18.5870(5)	21.4062(6)	18.4545(3)	22.259(5)
β (°)				97.60(3)
U/Å^3	1392.32(7)	3115.67(14)	3119.56(8)	3367.9(12)
Z	4	4	4	2
D_c/Mg m^{-3}	1.556	1.409	1.596	1.374
F(000)	656.0	1376	1504	1460
θ range/°	2.93 to 27.50	2.91 to 27.48	2.92 to 27.5	2.94 to 27.48
Index ranges	$-8 \le h \le 9$, $-13 \le k \le 13$, $-24 \le l \le 24$	$-10 \le h \le 10$, $-23 \le k \le 23$, $-27 \le l \le 27$	$-10 \le h \le 10$, $-27 \le k \le 27$, $-23 \le l \le 23$	$-22 \le h \le 22$, $-11 \le k \le 11$, $-28 \le l \le 28$
Reflections collected	7691	20635	24594	44591
Independent reflections	3068	7042	7129	15091
R_{int}	0.0848	0.0914	0.1288	0.1279
Data/restraints/parameters	3068/0/132	7042/0/332	7129/0/332	15091/235/806
Goodness of fit on F^2	1.042	1.046	1.039	1.031
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0317, 0.0823	0.0500, 0.0873	0.0560, 0.1273	0.0669, 0.1356
(all data)	0.0348, 0.0836	0.0747, 0.0968	0.0664, 0.1342	0.1204, 0.1565
Largest difference peak				
And hole/e Å^{-3}	0.414 and –0.555	0.559 and –0.934	1.828, –3.370	0.755, –1.169
Flack parameter	–0.09(3)	–0.02(3)	–0.021(9)	–0.03(4)

Pt{*o*-C$_6$H$_4$(CH$_2$PBO)$_2$}(nb), 16. The compound was prepared according to the method of Weigand.[23] Crystallised by vapour diffusion of 40/60 petroleum ether into a THF solution of **16**. Yield = 52%. ^{1}H NMR (C_7D_8, 500 MHz): δ 6.98 (1H, s), 6.80 (3H, m), 3.29 (2H, m), 2.85 (2H, m), 2.64 (2H, d, J = 18.8 Hz), 2.50 (2H, m), 2.10 (3H, m), 1.85-1.05 (20H, m), 0.90 (3H, s), 0.84 (6H, s), 0.75 (3H, d, $^3J_{H-H}$ = 7.0 Hz), 0.68 (6H, s), 0.53 (1H, m), 0.12 (1H, d, J = 7.5 Hz) ppm. ^{13}C{^{1}H} DEPT NMR (C_7D_8, 125.1 MHz): δ 129.5 (s, CH), 128.9 (s, CH), 128.0 (s, CH), 126.0 (s, CH), 51.3 (dd, $^2J_{C-P}$ = 36.3, 27.2 Hz, $^1J_{C-Pt}$ = 338 Hz, CH), 45.1 (vt, $^3J_{C-P}$ = 4.0 Hz, $^2J_{C-Pt}$ = 12.8 Hz, CH), 40.8 (s, $^3J_{C-Pt}$ = 58.9 Hz, CH_2), 38.9 (s, CH), 36.8 (t, $^{1,3}J_{C-P}$ = 18.9 Hz, CH_2), 35.6 (s br, CH), 33.8 (d, $^1J_{C-P}$ = 8.1 Hz, C), 33.2 (m, CH), 32.2 (d, $^1J_{C-P}$ = 19.6 Hz, CH_2), 31.9 (d, $^1J_{C-P}$ = 19.6 Hz, CH_2), 29.9 (vt, J = 9.2 Hz, CH_2), 29.4 (s, CH_3), 29.2 (s, CH_3), 29.2 (obs, CH_2), 24.3 (d, $^3J_{C-P}$ = 4.8 Hz, CH_3), 22.5 (s, CH_2), 16.0 (s, CH_2), 15.0 (d, $^3J_{C-P}$ = 13.8 Hz, CH_3), 14.7 (d, $^3J_{C-P}$ = 15.0 Hz, CH_3) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 121.7 MHz, 323 K): 3.1 (d, $^2J_{P-P}$ = 45 Hz, $^1J_{P-Pt}$ = 3336 Hz), 1.6 (d, $^2J_{P-P}$ = 45 Hz, $^1J_{P-Pt}$ = 3336 Hz) ppm. MS: 732 (M$^+$, 100%). *Anal.*: Calc. for $C_{38}H_{54}P_2Pt$: C, 64.64; H, 7.72%. Found: C, 63.5; H, 7.4%.

Mo(CO)$_4${*o*-C$_6$H$_4$(CH$_2$PBO)$_2$}, 17. A solution of Mo(CO)$_4$(pip)$_2$ (68 mg, 0.18 mmol) and **13** (80 mg, 0.18 mmol) in DCM (20 ml) was stirred at RT overnight. The volatiles were removed at the pump and the off-white solid residue dissolved in the minimum amount of toluene. Storage at –25 °C over several days gave colourless needles which were isolated by filtration. Yield = 50 mg (43%). A second crop was obtained upon dilution of the toluene solution with 40/60 petroleum ether. Yield = 53 mg (45%). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.11 (2H, m, H15), 7.06 (2H, m, H14), 3.27 (2H, d br, $^2J_{H-H}$ = 11.9, H12), 3.00 (2H, br, H12), 2.18 (2H, d br, $^2J_{H-H}$ = 14.8 Hz, H3eq), 2.08 (4H, m, H6, H7eq), 1.93 (2H, m, H7ax), 1.86 (2H, m, H8eq), 1.72 (2H, m, H3ax), 1.56 (2H, m, H4), 1.48 (2H, m, H8ax), 1.33 (2H, s br, H1), 1.00 (6H, d, $^3J_{H-H}$ = 7.1 Hz, H9), 0.97 (6H, s, H10/11), 0.96 (6H, H10/11) ppm. ^{13}C{^{1}H} DEPT NMR (CD_2Cl_2, 125 MHz) δ 213.9 (t, $^2J_{C-P}$ = 7.6 Hz, CO), 207.6 (m, CO), 136.8 (s, C13), 130.2 (s, C14), 127.3 (s, C15), 38.6 (s, C4), 36.6 (s, C6), 36.1 (s, C12), 34.4 (t, $^1J_{C-P}$ = 9.1 Hz, C1), 33.7 (s, C5), 30.0 (t, $^1J_{C-P}$ = 11.3 Hz, C3), 28.7 (s, C10/11), 24.4 (s, C10/11), 21.9 (s, C8), 15.8 (s, C7), 14.2 (d, $^3J_{C-P}$ = 7.2 Hz, C9) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.7 MHz): 9.8 (s) ppm. MS: 652 (M$^+$, 25%). IR (KBr): 2962 m, 2008 s, 1906 vs, 1883 vs, 1855 vs, 1261 s, 1093 s, 1011 s, 803 s, 762 m, 617 s, 584 s, 500 w, 460 m, 413 s cm^{-1}. *Anal.*: Calc. for $C_{32}H_{44}P_2O_4Mo$: C, 59.08; H, 6.82%. Found: C, 58.4; H, 7.0%.

Crystallography

Data collection was carried out on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromoated Mo-Kα radiation (λ(Mo-Kα) = 0.71073 Å). The instrument was equipped with an Oxford Cryosystems cooling apparatus. Data collection and cell refinement were carried out using COLLECT[26] and HKL SCALEPACK.[27] Data reduction was applied using HKL DENZO and SCALEPACK.[26] The structures were solved using direct methods (Sir92)[28] and refined with SHELX-97.[29] Absorption corrections were performed using SORTAV.[30] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were inserted in idealised positions with Uiso set at 1.2 or 1.5 times the Ueq of the parent atom. In the final cycles of refinement, a weighting scheme that gave a relatively flat analysis of variance was introduced and refinement continued until convergence was reached. The Mo structure included a toluene molecule within the lattice framework which was disordered over two discrete positions. The details of the data collection and structure solution are collected in Table 1.

Conclusions

In conclusion, (1*R*,4*S*,6*R*)-5,5,6-trimethyl-2-phosphabicyclo-[2.2.2]octane, PBO, has been prepared stereoselectively from (1*R*,3*S*)-[1,2,2-trimethyl-3-(phosphinomethyl)cyclopentyl]methyl methanesulfonate or the corresponding tosylate. The [2.2.2] bicyclic product results from a rearrangement of the original skeleton under the somewhat harsh reaction conditions. Several derivatives of the phosphacycle have been prepared and characterised including a bidentate ligand with an *ortho*-xylyl backbone. This latter ligand has been coordinated to Pd(II), Pt(II), Pt(0) and Mo(0) and the resultant complexes fully characterised. The bite angle of the ligand conforms to the ideal 90° for the divalent palladium and platinum complexes and the zerovalent molybdenum complex as determined by single crystal X-ray structure analysis of the respective complexes; adherence to a 90° P-M-P angle forces the aryl ring of the xylyl backbone into an orientation roughly perpendicular to the ML_4 coordination plane for Pd(II) and Pt(II) and into close proximity to one of the carbonyl ligands in the Mo(0) system. A similar arrangement is suggested for the zerovalent platinum species, Pt{*o*-$C_6H_4(CH_2PBO)_2$}(nb) based on the $^1J_{P-Pt}$ value.

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