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Metal Complexes of a Structurally Embellished Phosphinane Ligand: An Assessment of Stereoelectronic Effects

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The stereoelectronic features of the pentacyclic phosphane (1*S*,4*R*,4a*S*,5a*R*,6*R*,9*S*,9a*S*,10a*R*)-4,6,11,11,12,12-hexamethyl-10-phenyldodecahydro-1,4:6,9-dimethanophenoxaphosphinine (phenop) have been explored through a range of empirical methods including single-crystal X-ray structure determinations of the sulfide derivative phenopS (**1**), the selenide phenopSe (**2**), [Fe(CO)$_4$(κ^1-phenop)] (**3**), [W(CO)$_5$(κ^1-phenop)] (**4**) and *trans*-[Rh(κ^1-phenop)(CO)Cl] (**5**). Cone angles derived from the structural data range from 164–203° with the smaller values being observed for the compounds possessing a phenyl group that is orthogonal to the P–Z bond and the larger values for the compounds expressing a parallel phenyl ring orientation. The cone angle data suggest a moderately bulky phosphane comparable, in steric terms, to PCy$_3$. This is further borne out on inspection of the M–P bond lengths which tend towards the longer end of the known scale. Some flexibility is observed in the central ring which approximates to a boat conformation at one extreme and an envelope at the other depending on the nature of the P-substituent. The electronic properties of κ^1-phenop have been assessed using a combination of infrared and NMR spectroscopy. The absolute value of the one-bond coupling constants $^1J_{P\text{-}Se}$ and $^1J_{P\text{-}Rh}$ are very close to those reported for PPh$_3$, suggesting a close analogy between κ^1-phenop and the well known triphenylphosphane. In addition, relevant υ(CO) stretches in the IR spectra of the metal carbonyl complexes also closely mimic those for the analogous complexes containing PPh$_3$. These conclusions are supported by molecular electrostatic potential calculations at the DFT level which place phenop close to PPh$_3$ in terms of lone pair availability.

Introduction

The characterisation of phosphane ligands in terms of their steric and electronic properties is long-established. The seminal paper of Tolman[1] is a constant reference source because of the elegant simplicity and endearing applicability of the methods he employed. Although the methodologies used to measure the steric properties of phosphanes may have altered down the years, the parameter defined by Tolman, i.e. the cone angle, is still universally used for quantifying steric bulk, while the examination of electronic features of phosphanes through their influence on selected properties of other ligands (principally the C–O stretching frequency of bound carbonyl groups) remains a common means of assessing electronic characteristics. These empirical methods are being complemented by computation approaches of ever-increasing sophistication[2] which broadly support the general trends observed by Tolman and others. The modern approach to ligand classification is a more holistic one with an emphasis on the stereoelectronic profiling of phosphanes (and other ligands), nicely encapsulated in the recent review of Fey and Harvey.[3]

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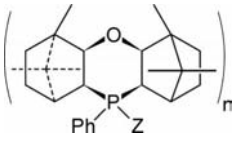
As a consequence of rotational freedom, the cone angle for an acyclic phosphane can vary over an appreciable range, e.g. for triethylphosphane a range from 123.6–159.4° is observed for the relatively large number of structurally characterised complexes containing the ligand.[4] The smallest variations occur with tertiary phosphanes bearing spherically symmetric groups such as tri-*tert*-butylphosphane, and the largest for phosphanes with non-spherical substituents or those bearing aryl substituents. Phosphacycles may not show the same level of flexibility because of their confinement within the ring which will impact on the donating ability of the ligand.[5] The so-called phobane ligands are a good example of bicyclic systems (and are one of the few such classes that have found application in industry) which show isomer-dependent basicity/reactivity allowing the separation of the symmetric and asymmetric forms by selective protonation, oxidation or deformylation.[6] Thus (diastereo)-isomers of phosphacycles can possess different characteristics that can ultimately impact on their coordination ability and/or potential in metal-based catalysis.

Although the number and type of existing phosphorus ligands is legion, structurally elaborate phosphinanes are a relatively rare and understudied class. We have a long-standing interest in bi- and polycyclic phosphanes and their complexation chemistry[7] and prepared recently the rigid, asymmetric 1,4-oxaphosphinane ligand, (1*S*,4*R*,4a*S*,

5a*R*,6*R*,9*S*,9a*S*,10a*R*)-4,6,11,11,12,12-hexamethyl-10-phenyldodecahydro-1,4:6,9-dimethanophenoxaphosphinine, abbreviated as phenop (Scheme 1, Z = lone pair), and reported some aspects of the coordination chemistry of the ligand.[8] Phenop has a framework that consists of three fused six-membered rings, with the central 1,4-oxaphosphinane ring adopting a boat conformation. The two flanking rings are remnants of the 1*R*-camphor starting material and are, therefore, [1.2.2]-bicyclic systems. The ligand can be viewed as a 2,3,5,6-substituted 1,4-oxaphosphinane, a ligand class that has not featured in the chemical literature, although some elaborate derivatives of 2,3,5,6-substituted phosphinanes have been reported.[9] Our earlier work on phenop revealed a propensity for the ligand to undergo cyclometallation when bound to divalent palladium and platinum to such an extent that the only example of monodentate coordination observed with these metals was in the bis(κ^1-phenop)palladium(0) derivative. Therefore, in an effort to quantify the steric and electronic properties of the monodentate phosphane, we sought simple chalcogenide derivatives of phenop as well as metal systems possessing empirical markers to assist assessment of the donating ability of κ^1-phenop but with a lower predilection towards cyclometallation than the aforementioned palladium and platinum systems. To this end we have prepared and examined by single-crystal X-ray structure methods and, where appropriate, IR and NMR spectroscopy, phenopS (**1**), phenopSe (**2**), [Fe(CO)$_4$(κ^1-phenop)] (**3**), [W(CO)$_5$(κ^1-phenop)] (**4**) and *trans*-[Rh(κ^1-phenop)$_2$(CO)Cl] (**5**) (Scheme 1).



Scheme 1. n = 1, Z = S (**1**); n = 1, Z = Se (**2**); n = 1, Z = Fe(CO)$_4$ (**3**); n = 1, Z = W(CO)$_5$ (**4**); n = 2, Z = *trans*-Rh(CO)Cl (**5**).

Results and Discussion

Syntheses and Structure of the Phenop Chalcogenides

The synthesis of phenop proceeds via its oxide derivative which has been structurally characterised previously.[8] The analogous sulfide and selenide derivatives, phenopS (**1**) and phenopSe (**2**), were prepared by heating phenop with the appropriate elemental chalcogenide in toluene. The reactions required a number of days at elevated temperatures to go to completion presumably because of steric encumbrance at the phosphorus. Both compounds are colourless, high melting point solids that crystallise readily from a number of common organic solvents.

The structure of **1**, determined by single crystal X-ray crystallography, is shown in Figure 1. The gross structure compares with that of the oxide and indeed the selenide (see below) as expected for a rigid, fused polycyclic molecule. All the chiral centres have the expected stereochemistry as dictated by the choice of starting material (1*R*-camphor) and the stereoselective nature of the ligand synthesis.[8] In all the structures of the chalcogenides the phenyl group has an orientation where the aryl ring lies parallel to the P–Z bond with a S–P–C$_{ipso}$–C torsion angle of ca. 2° presumably to avoid unfavorable intraligand contacts with the cyclic ligand skeleton. The P–S bond length of 1.9616(10) Å is within the normal range for tertiary phosphane sulfides, as is the heterocyclic C18–P1–C7 bond angle of 102.47(14)°.[10] There is nothing unusual about the remaining C–P–C bond angles, and the P–C bond lengths of 1.846(3) Å (av.) lie between those of phenop {av. 1.861(2) Å}[8b] and phenopO {av. 1.825(2) Å}.[8a] The central ring has the boat conformation with the oxygen and phosphorus atoms at the vertices. There is some flattening in the region of the phosphorus apex as highlighted by O–C–C–P torsion angles averaging 18.4° and a P···O distance of 3.001 Å; this is likely the result of unfavourable contacts between the sulfur atom and a number of hydrogen atoms in the ligand framework (cf. torsion angles and non-bonded P···O distances of 8° and 2.913 Å and 12° and 2.923 Å for the free ligand and phenopO, respectively).[8] The smaller S–P–C$_{ipso}$ bond angle of 109.62(11)° compared to the S–P–C angles of 115.90(11)° and 120.11(12)° for the internal ring C atoms is also a manifestation of this steric hindrance resulting in a distorted tetrahedral environment about the phosphorus. The ring flattening is also evidenced by an increased distance between the P atom and its nearest methyl carbon neighbour (3.685 Å compared to 3.409 Å in phenop).

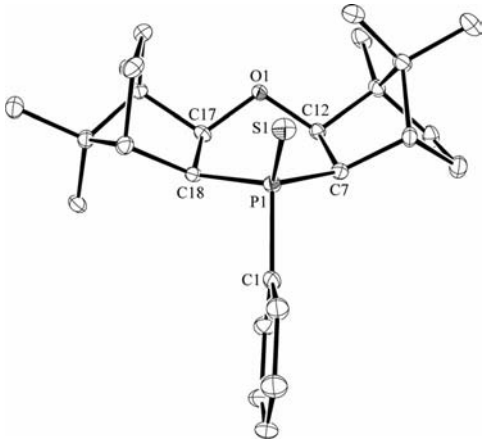


Figure 1. Ortep view of the molecular structure of **1**. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths [Å] and angles[°] for **1**: P1–S1 1.9616(10), P1–C1 1.843(3), P1–C7 1.849(3), P1–C18 1.846(3), C1–P1–S1 109.62(11), C1–P1–C7 105.33(15), C1–P1–C18 101.60(14), C7–P1–C18 102.47(14), C7–P1–S1 109.62(11), C18–P1–S1 120.11(11).

The single-crystal X-ray structure of phenopSe (**2**) is shown in Figure 2. The similarities with the sulfide are immediately obvious, with the parallel orientation of the phenyl group (Se–P–C–C angle of 5°) and axially projecting chalcogenide function. The flattening of the boat conformation of the central ring is more pronounced in phenopSe with an average O–C–C–P angle of 23.0° and an almost coplanar C–C–P–C–C unit. The conformation of the cen-

tral oxaphosphinane ring is better described here as an envelope rather than a true boat and is a consequence of the larger selenium atom impacting on the hydrocarbyl bridges of the polycyclic backbone. However, the Se–P–C bond angles are less disparate here compared to the respective angles in the sulfide and oxide with the value for the Se–P–C_{ipso} angle {111.47(12)°} being closer to those for the remaining two Se–P–C angles {116.71(13) and 117.80(12)°, respectively}. The P–Se bond length of 2.1173(9) Å is typical[11] and the remaining intraligand angles compare with those of the sulfide.

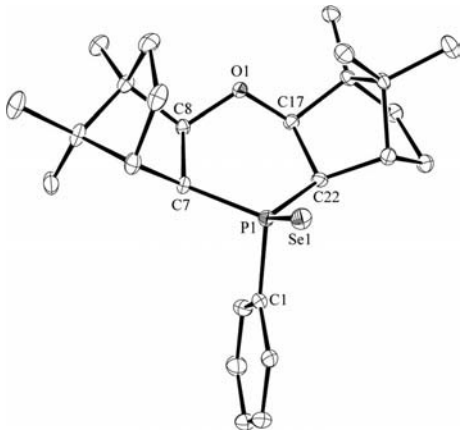


Figure 2. Ortep view of the molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths [Å] and angles[°] for **2**: P1–Se1 2.1173(9), P1–C1 1.830(4), P1–C7 1.849(3), P1–C22 1.848(3), C1–P1–Se1 111.47(12), C1–P1–C7 101.53(15), C1–P1–C22 101.86(16), C7–P1–C22 105.29(15), C7–P1–Se1 117.80(12), C22–P1–Se1 116.71(13).

Syntheses and Structure of the Metal Complexes of Phenop

The complex [Fe(CO)$_4$(κ^1-phenop)] (**3**) was obtained as a bright yellow solid from the 1:1 reaction of $Fe_2(CO)_9$ with phenop in diethyl ether. The complex is air-stable in the solid-state but tends to decompose in solution, so all manipulations of solutions were performed under nitrogen. The complex was crystallised from a mixed solvent of methanol and ethyl acetate at 4 °C. The molecular structure of [Fe(CO)$_4$(κ^1-phenop)] was determined by single-crystal X-ray diffraction and is shown in Figure 3. The complex has the expected trigonal bipyramidal geometry with the phenop bound as a monodentate ligand and occupying one of the axial coordination sites. The CO donors occupy the remaining axial site and the three positions in the trigonal plane. The Fe–P bond lengths average 2.308(2) Å (there are two independent molecules in the asymmetric unit) which compares with the value of 2.306(1) Å in [Fe(CO)$_4${P(*o*-tol)$_3$}],[12] but is longer than that for [Fe(CO)$_4$(PPh$_3$)] {2.244(1) Å}[13] and appreciably shorter than the Fe–P bond length in [Fe(CO)$_4$(P*t*Bu$_3$)] {2.364(1) Å}.[14] The Fe–C bond lengths are typical with the Fe–CO *trans* to phenop being the shortest because of the lower π-acidity of the phosphane compared to CO. The longest Fe–C bond length in [Fe(CO)$_4$(κ^1-phenop)] is associated with the CO that is in close contact with the bulkiest part of the phenop ligand (one of the methyl groups and the dimethylene bridge of the ligand) and there is some steric impact at this carbonyl producing the slightly elongated Fe–C bond. It should be noted that the P–Fe–CO bond angle of 98.5(3)° for this carbonyl is appreciably greater than the same angle for the other two *cis* carbonyl groups {90.4(3)° and 86.2(3)° respectively} confirming the presence of unfavourable contacts at this particular carbonyl. The P–Fe–CO_{trans} angle is 172.7(3)° and the equatorial C–Fe–C angles are 119.1(4), 117.1(4) and 123.5(4)°, respectively, the latter two values being for angles involving the *cis* carbonyl contacted by the bulky part of the ligand as highlighted above.

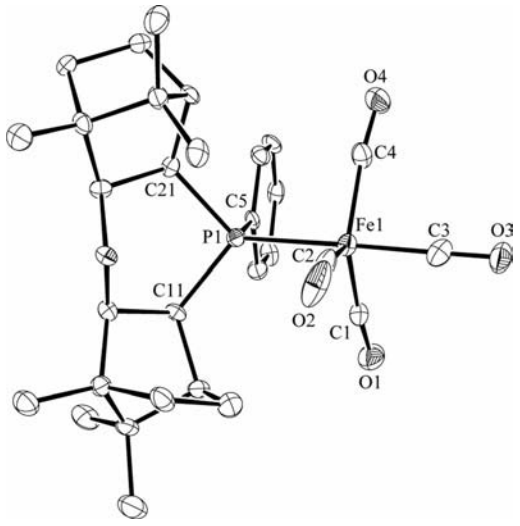


Figure 3. Ortep view of the one of the independent molecules of **3**. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles[°] for **3**: P1–Fe1 2.307(2), P1–C5 1.829(8), P1–C11 1.865(8), P1–C21 1.888(8), Fe1–P1–C5 103.9(3), Fe1–P1–C11 123.6(3), Fe1–P1–C21 125.5(3), C11–P1–C21 99.0(3), P1–Fe1–C3 172.7(3), P1–Fe1–C1 86.2(3), P1–Fe1–C2 98.5(3), P1–Fe1–C4 90.4(3).

The oxaphosphinane ring is again compressed in the iron complex with O–C–C–P dihedral angles averaging 15° and a P···O distance of 3.001 Å, indicating less flattening than in **2**. There is, however, a critical difference between the two structures as the phenyl has the orthogonal orientation in [Fe(CO)$_4$(κ^1-phenop)] as opposed to the parallel arrangement in **2**. As will be discussed later, ring flattening tends to be at its greatest in those compounds where the phenyl ring is parallel. The long non-bonded P···O distance is partly a result of the flattening in the oxaphosphinane ring and partly due to the longer P–C bonds to the carbon atoms in the ring which average 1.874(8) Å. The Fe–P–C angles to the two heterocyclic carbon atoms C11 and C21 are 123.6(3) and 125.5(3)°, respectively, appreciably greater than is typical for non-cyclic tertiary phosphanes. Consequently, the Fe–P–C_{ipso} angle is compressed to 103.9(3)° and it is clear that the phosphorus centre is distorted considerably from a tetrahedral geometry; this will clearly have an influence on the electronic properties of the ligand (see later).

Yellow [$W(CO)_5(\kappa^1$-phenop)] (**4**) was isolated in good yield from the 1:1 reaction of [$W(CO)_5$(THF)] and phenop in THF. The isolated complex is freely soluble in most common organic solvents, and is air-stable in the solid state. Crystals suitable for single crystal X-ray structure determination were grown from petroleum ether at 4 °C. The structure (Figure 4) has the expected octahedral arrangement of ligands with phenop *trans* to a single carbonyl and the remaining CO donors coplanar. The W–P bond length of 2.6292(10) Å is long for this type of complex when compared to related structurally characterised derivatives such as [$W(CO)_5(PMe_3)$] [2.516(2) Å],[15] [$W(CO)_5(PPh_3)$] [2.545(1) Å][16] and [$W(CO)_5(PCy_3)$] [2.5794(12) Å][17] but is shorter than the value of 2.686 Å observed in the tri-*tert*-butylphosphane analogue.[18] As expected the W–C bond length to the carbonyl carbon *trans* to the phosphane is the shortest at 1.985(5) Å compared to the other W–C bond lengths which are all longer than 2.040 Å. These compare with W–C bond lengths of 2.00(1) Å in [$W(CO)_5(PMe_3)$],[15] 2.006(5) Å in [$W(CO)_5(PPh_3)$],[16] and 1.975 Å in [$W(CO)_5$-(PtBu$_3$)][18] for the carbonyl group *trans* to the phosphane donor. The P–W–C1 and P–W–C5 angles are expanded to 97.89(11)° and 96.44(13)° in **4** because of unfavourable steric contacts with the phenop skeleton resulting in an average W–C–O bond angle of 174.9(4)° for the *cis* carbonyl groups; this value lies between the averages of 179(1)° and 172.7° observed in [$W(CO)_5(PMe_3)$][15] and [$W(CO)_5$-(PtBu$_3$)],[18] respectively. The phenyl orientation is orthogonal, and the W–P–C angles are 124.76(14) and 124.59(13)° for the heterocyclic C atoms and 102.00(13)° for the *ipso* carbon of the phenyl group. The flattening of the boat form of the oxaphosphinane ring is modest as indicated by the average O–C–C–P dihedral angle of 15.8°. The intra-ring P–C bonds are long at 1.879(4) and 1.870(4) Å giving a long P···O non-bonded distance of 3.020 Å.

trans-[$Rh(\kappa^1$-phenop$)_2$(CO)Cl], **5**, was formed in good yield from the reaction of [Rh(1,5-COD)Cl]$_2$ with 4 mol equivalents of phenop in the presence of CO. The complex is soluble in most non-polar organic solvents excepting hexane, but is only poorly soluble in methanol. Crystals suitable for single-crystal X-ray structure determination were obtained upon slow cooling of a solution of the complex in toluene/MeOH (1:1). An Ortep representation of the structure is shown in Figure 5. The complex has the anticipated square-planar geometry with *trans* phosphanes. Some distortion from the square plane is observed, with a P–Rh–P bond angle of 168.49(5)°; the sum of the angles about the metal is 359.95°. Surprisingly, the Cl–Rh–P angles are the most acute and the P–Rh–CO angles the most obtuse of the L–Rh–L angles, a situation that appears contrary to what might be expected on the basis of the relative sizes of the two donors with chloride being larger than CO. The P-phenyl rings are orientated *trans* with respect to the metal square plane. An unexpected feature of the structure involves the orientation of the phenyl rings of the two phenop ligands. It is evident from the examples shown above and previously that there are two favoured orientations for this ring, i.e. the parallel and orthogonal conformers, with the former being favoured by the chalcogenides and the latter favoured by the metal complexes. In **5**, one ligand has a parallel phenyl while the other has an orthogonal phenyl. The parallel conformer has the larger cone angle (see later), yet the Rh–P bond length to the ligand in this orientation is the shortest at 2.3407(19) Å compared to 2.3644(19) Å for the other. These bond lengths are longer than the average of 2.330 Å observed in the several reported structures of *trans*-[$Rh(PPh_3)_2$(CO)Cl],[19] are comparable to the

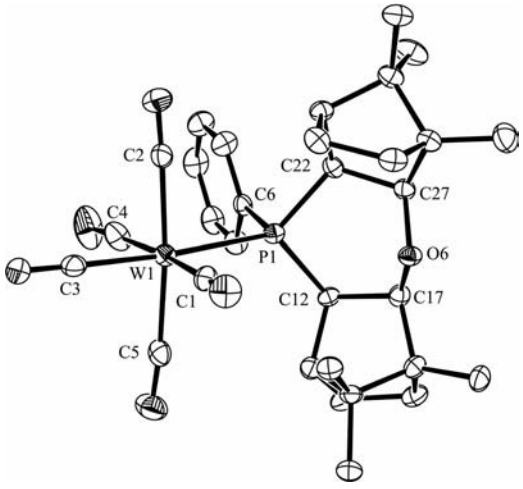


Figure 4. Ortep view of the molecular structure of **4**. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths [Å] and angles[°] for **4**: P1–W1 2.6292(10), P1–C6 1.853(4), P1–C12 1.870(4), P1–C22 1.879(4), W1–P1–C6 102.00(13), W1–P1–C12 124.59(13), W1–P1–C22 124.76(14), C12–P1–C22 100.13(18), P1–W1–C3 174.06(12), P1–W1–C1 97.89(11), P1–W1–C2 88.92(12), P1–W1–C4 88.88(13), P1–W1–C5 96.44(13).

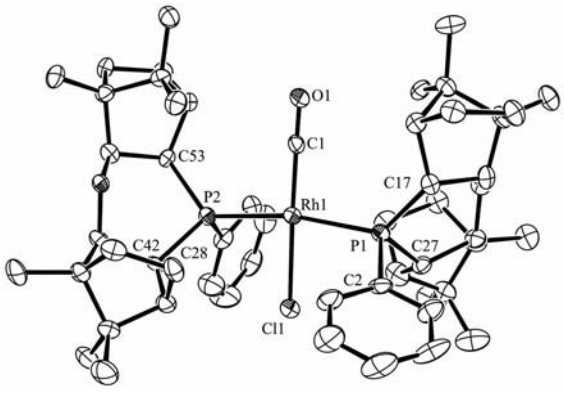


Figure 5. Ortep view of the molecular structure of **5**. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. Selected bond lengths [Å] and angles[°] for **5**: P1–Rh1 2.3407(19), P2–Rh1 2.3644(19), C1–Rh1 1.806(6), Cl1–Rh1 2.3747(16), P1–C2 1.852(6), P1–C17 1.877(7), P1–C27 1.873(6), P2–C28 1.855(7), P2–C42 1.868(6), P2–C53 1.886(6), Rh1–P1–C2 108.5(2), Rh1–P1–C17 127.4(2), Rh1–P1–C27 114.8(2), C17–P1–C27 103.4(3), Rh1–P2–C28 100.6(2), Rh1–P2–C42 119.7(2), Rh1–P2–C53 127.2(2), C42–P2–C53 102.1(3), P1–Rh1–C1 94.3(2), P1–Rh1–Cl1 84.37(6), P2–Rh1–C1 96.9(2), P2–Rh1–Cl1 84.34(6), P1–Rh1–P2 168.49(5), C1–Rh1–Cl1 178.10(19).

average value of 2.355(3)/2.3508(3) Å for the two reported structures of *trans*-[Rh(PCy_3)$_2$(CO)Cl][20] and are shorter than the value of 2.426(1) Å for the tetrahedrally distorted *trans*-[Rh($Pt Bu_3$)$_2$(CO)Cl].[21] There is evidence of increased steric contact at the parallel phenyl group where the Rh–P–C_{ipso} bond angle is 108.5(2)° compared to the second phenop which has a compressed Rh–P–C_{ipso} angle of only 100.6(2)°. Other structural differences between the two phenop ligands include the average Rh–P–C bond angles of 123.4(2)° (parallel conformer) and 121.1(2)° (orthogonal isomer) to the oxaphosphinane C atoms and conformer dependent O–C–C–P dihedral angles of 24.5° and 20.6° for the parallel and orthogonal types respectively. The central six-membered ring has the envelope confomation with the P atom and the four carbon atoms of the ring being close to coplanar for the ligand with the parallel phenyl group; this is highlighted by the long O···P distance of 3.083 Å even though the P–C bond lengths (av. 1.875 Å) are similar to those in the structure of phenop itself. The Rh–Cl and Rh–CO bond lengths of 2.3747(16) and 1.806(6) Å are typical as are the Cl–Rh–CO and Rh–C–O angles which are essentially linear.

Crystallographic Cone Angles

A major thrust of the present work has been to determine cone angle data for κ^1-phenop to enable its categorisation with respect to the large number of known phosphanes. There have been several different approaches employed for the quantification of the steric properties of phosphanes with (largely because of its elegance and simplicity) the seminal work of Tolman remaining pre-eminent.[1] Other methods such as those based on solid angles[22] and ligand profiles[23] are useful alternatives. The use of the crystallographic database to determine so-called crystallographic cone angles,[4,24] is essentially an add-on to Tolman's original idea and provides the basis for our calculation of cone angles for phenop from the crystal data for phenopO, phenopS, phenopSe, Ag_2(κ^1-phenop)$_2$(CF_3SO_3)$_2$, [Fe(CO)$_4$(κ^1-phenop)], [W(CO)$_5$(κ^1-phenop)] and *trans*-[Rh(κ^1-phenop)$_2$(CO)Cl]. As alluded above, the seven compounds fall into two distinct classes; those where the phenyl ring orientates parallel to the P–Z vector {phenopO, PhenopS, phenopSe, Ag_2(κ^1-phenop)$_2$(OTf)$_2$, and one phenop in *trans*-[Rh(κ^1-phenop)$_2$(CO)Cl}] and those where it is orthogonal [{Fe(CO)$_4$(κ^1-phenop)], [W(CO)$_5$(κ^1-phenop)] and the second phenop in [Rh(κ^1-phenop)$_2$(CO)Cl}]. Calculations in the gas phase (see below) show these two conformations to be close in energy for the uncoordinated ligand with a calculated energy difference of 3.68 KJ mol^{-1} in favour of the parallel arrangement. This would suggest that the choice of conformer may be dictated by steric effects (and packing forces in the crystal) with the parallel arrangement being preferred when Z is small and orthogonal when Z is relatively large. The obvious exception to this is in the solid-state structure of the free ligand where the orthogonal orientation is observed even though Z = lone pair. An electronic preference for the orthogonal arrangement in the metal complexes cannot, however, be discounted. A conformational preference is noted in a number of reported metal-phosphinane structures with the parallel orientation being observed in *trans*-Pt(1-phenylphosphinane)$_2$Cl$_2$[25] while the orthogonal arrangement is seen in *trans*-[Ni(4,4-dimethoxy-1-phenylphosphinane)$_2$Cl$_2$[26] and in nickel and palladium complexes of bicyclic derivatives.[27] As a counterpoint, a variety of conformations are noted in complexes of 2,2,6,6-tetrasubstituted 4-keto-1-phenylphosphinanes.[28]

As phenop possesses a pseudochiral P-atom, all three substituents on the phosphorus are different but only one (the phenyl group) can rotate freely about a P–C bond. The half angles for the other two substituents are relatively fixed and defined by groups that are remote from the P-donor, i.e. the hydrogens attached to the methyl and methylene groups shown in Figure 6.[29] This is quite distinct from many acyclic tertiary phosphanes where the cone angle is usually defined by half angle relations to hydrogens attached to atoms (usually carbon) β to the phosphorus donor. While such angles can be defined for phenop, we believe the use of the half angles shown in Figure 6 to be more appropriate as these are the regions that impact most on any metal fragment (these are also the groups that undergo C–H activation in the cyclometallated, divalent platinum and palladium complexes);[8] the steric impact of remote groups is known in other phosphanes including heterocyclic derivatives.[30] The cone angles thus determined are collected in Table 1 and it is evident that the values are greatest when small groups are present on the phosphorus (the chalcogenides) as observed in related phospholane complexes.[31] In common with other phosphanes bearing one or more phenyl groups, the cone angle is larger when the phenyl adopts the parallel orientation as exemplified by the two values for each discrete ligand in the bis(phenop) rhodium complex (θ = 175° for ∥ and 165° for the ⊥ arrangement). Within the series of structures that manifest a parallel orientation of the phenyl ring a range of θ values from 203° in phenopO to 175° in the rhodium complex are seen even though the half angles for the phenyl substituent are invariant at 88–89° throughout the series. The differences arise from varying degrees of flattening in the oxaphosphin-

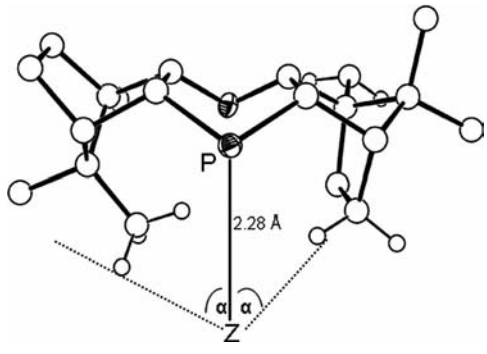


Figure 6. Two of the three angles (α) used to determine the cone angle of the phenop derivatives. The phenyl group has been excluded for the purposes of clarity.

Table 1. Selected geometric data for derivatives of phenop. Bond lengths are in Å and angles in °.

Compound	Cone angle θ[a]	Degree of ring flattening[b]	C–P–C[c]	P–C (av)
phenop		143.6	99.24(10)	1.858(2)
phenopO	203	148.9	101.66(7)	1.8226(16)
1	193	158.4	102.47(14)	1.845(3)
2	185	167.4	105.29(15)	1.839(3)
3	165	152.5	99.2(4)	1.854(8)
4	164	154.5	100.13(18)	1.864(4)
5	175, 165	168.9, 162.0	103.4(3), 102.1(3)	1.867(7), 1.870(7)
$[Ag(phenop)(OTf)]_2$	200, 200	150.3, 147.8	101.1(3), 101.6(3)	1.849(8), 1.844(8)

[a] P–Z vector set to 2.28 Å to allow comparison with the original Tolman values. [b] Defined by the angle between the C–P–C and C–C–C–C planes in the ring. [c] The C–P–C angle within the oxaphosphinane ring.

ane ring (Table 1) which impacts on the half angles represented in Figure 6; these become more acute as the ring approaches the envelope conformation. Ring flattening in the oxaphosphinane ring (measured by the angle of intersection of the C–P–C plane and the C–C–C–C plane within the ring) reflects a change in the conformation from a boat at the lower end of the range (from ≈ 143 to 153°) towards an envelope at higher values, most particularly when the angle is > 155°. No flattening is observed at the oxygen apex of the ozaphosphinane ring with angles of 118 ± 1.5 between the C–C–C–C plane and the C–O–C plane throughout the series. There is, however, no discernible correlation between the extent of flattening at the P apex and the cone angle but the intra-ring C–P–C angle does tend to increase with increased distortion to the envelope conformation. Other general correlations include increased P–C and C–C bond lengths and decreased C–O bond lengths with increased distortion to the envelope conformation. No such flattening was observed in the previously reported cyclometallated complexes of phenop where the central ring adopted the boat conformation with angles of ca. 140° between the C–P–C plane and the C–C–C–C plane.[8] Thus phenop is a moderately bulky phosphane comparable in size to PCy_3 when the phenyl is orthogonal and P(*o*-tolyl)$_3$ when it is parallel. These conclusions are supported by earlier observations such as the isolation of air- and moisture-stable Pd(κ^1-phenop)$_2$.[8]

Spectroscopic and Electronic Properties of 2, 3, 4 and 5

The range of methods used for the assessment of the electronic properties of phosphanes is as wide and varied as those employed for the determination of steric features. Empirical methods include the correlation of NMR chemical shifts and/or appropriate coupling constants and/or infrared (carbonyl) stretching frequencies of selected metal complexes with the donating ability of the phosphane.[1,32] There are also several reliable theoretical approaches that provide useful information on the electronic properties of phosphanes,[2,3] and we have used elements of both approaches to assess the electronic characteristics of phenop.

The magnitude of $^1J_{P\text{-}Z}$ is predominantly determined by the s-character of the orbitals involved in the bond and is thus dependent upon the immediate geometry at phosphorus.[33] Hence caution should be exercised when comparing cyclic phosphanes with acyclic systems as the former are constrained by their inclusion in the phosphacycle. However, $^1J_{P\text{-}Z}$ coupling constants can still provide useful empirical information regarding lone pair availability in a given phosphane as this is also dependent upon the extent of s-character. The range of $^1J_{P\text{-}Se}$ coupling constants for tertiary phosphanes extends from 692 Hz for *t*Bu$_3$PSe as a selenide of a strongly σ-donating phosphane to 817 Hz for {3,5-(CF$_3$)$_2$C$_6$H$_3$}$_3$PSe with electron-withdrawing 3,5-bis-(trifluoromethylphenyl) groups.[11,34] The comparable $^1J_{P\text{-}Se}$ values for **2** (742 Hz) and Ph_3PSe (736 Hz)[34] suggests similar lone pair character in each of the parent phosphanes.

The $^{31}P\{^1H\}$ NMR spectrum of **4** consists of a singlet at δ = –23.1 ppm with satellites due to the 15% of ^{183}W in the sample. The magnitude of the phosphorus-tungsten coupling constant compares with values of 234 Hz for [W(CO)$_5$-{P(*o*-tol)$_3$}],[35] 232 Hz for [W(CO)$_5$(P*t*Bu$_3$)][36] and [W(CO)$_5$(PCy$_3$)],[16] and 240 Hz for [W(CO)$_5$(PPh$_2$Et)][37] but contrasts somewhat with that of 280 Hz seen for [W(CO)$_5$(PPh$_3$)].[36] The solution $^{31}P\{^1H\}$ NMR spectrum of **5** shows a doublet at δ = 6.1 ppm with a $^1J_{P\text{-}Rh}$ coupling constant of 128.0 Hz in addition to minor peaks at δ = 25.0 ppm (doublet, $^1J_{P\text{-}Rh}$ 185.1 Hz) and –36.0 ppm for free ligand. The peak at δ = 25 ppm is identified from its characteristic $^1J_{P\text{-}Rh}$ coupling constant as the dimeric [Rh(κ^1-phenop)(CO)(μ-Cl)]$_2$ species resulting from loss of one phenop ligand from the monomeric bis(ligand) derivative, thus explaining the presence of free ligand in the $^{31}P\{^1H\}$ NMR spectrum. Addition of excess ligand to the solution results in the loss of the resonance at δ_P = 25.0 ppm allowing partial ^1H and $^{13}C\{^1H\}$ NMR spectroscopic characterisation of [Rh(κ^1-phenop)$_2$(CO)Cl] (see Exp. Section). The magnitude of the phosphorus–rhodium coupling constant (128.0 Hz) is typical of this type of complex as confirmed on inspection of the reported values of 129.4, 117.1 and 121.1 Hz for *trans*-[Rh(PPh$_3$)$_2$(CO)Cl], *trans*-[Rh(PEt$_3$)$_2$-(CO)Cl] and *trans*-[Rh(PPhEt$_2$)$_2$(CO)Cl], respectively.[38] It is noteworthy that a related bicyclic 4-silaphosphinane complex has a lower $^1J_{P\text{-}Rh}$ coupling constant of 117.8 Hz[39] while a phenyl-phosphatrioxaadamantane derivative has a higher value of 133 Hz.[40]

Carbonyl stretching frequencies in the infrared spectra of phosphane containing complexes have long been used as a measure of the donating properties of phosphanes. Tolman employed Ni(CO)$_3$(PR$_3$) complexes in his assessment,[1] ob-

serving a lowering of the frequency of the ν(CO) stretch as the σ-basicity of the phosphane increased. The nickel system has been superseded by other less hazardous metal complexes with $[M(PR_3)_2(CO)Cl]$ (M = Rh, Ir) being one of the most common.[40,41] Greater sensitivity to the nature of the phosphane (as indicated by a larger range of values for the carbonyl stretch) is a further advantage of the latter systems.[32e] Complex *trans*-$[Rh(\kappa^1\text{-phenop})_2(CO)Cl]$, **5**, is directly comparable to *trans*-$[Rh(PPh_3)_2(CO)Cl]$ as both share the same value of 1965 cm^{-1} for the carbonyl stretch in their IR spectra.[41] Although less sensitive to phosphane basicity/nucleophilicity and therefore not showing the same range of frequency as the rhodium complexes, the A_1 ν(CO) stretching mode in $[W(CO)_5(PR_3)]$ still acts as an empirical marker for the σ-donating ability of the bound phosphane and the value for the phenop complex is again similar to that for the related triphenylphosphane complex; 2069 and 2071 cm^{-1} respectively.[42] The high energy A_1 vibration in complexes of the type $[Fe(CO)_4(PR_3)]$ is rather insensitive to the nature of the phosphane and therefore not useful. For completeness, the value of 2049 cm^{-1} observed for **3** compares to those of 2053, 2051 and 2049 cm^{-1} for $[Fe(CO)_4(PMe_3)]$,[43] $[Fe(CO)_4(PPh_3)]$,[13] and $[Fe(CO)_4(P\textit{t}Bu_3)]$,[14] respectively.

Apart from the anomalous $^1J_{P\text{-}W}$ coupling constants, all other empirical data suggest that the lone pair in phenop has similar character to that in Ph_3P. In an effort to confirm this, the theoretical approach of Koga[2b] was employed to quantify the electronic features of phenop through application of molecular electrostatic potentials. Using this approach, V_{min} values of –37.4 and –36.3 kcal mol^{-1} are obtained for the parallel and perpendicular phenyl ring orientations, respectively. These values rank phenop alongside PPh_2Me (slightly greater basicity/lone pair availability than PPh_3) in Koga's series of phosphanes. The values for the two conformers are comparable and there appears to be little inherent difference in donor ability between the two.

Conclusions

In conclusion, the donor properties of the pentacyclic phosphane (1*S*,4*R*,4a*S*,5a*R*,6*R*,9*S*,9a*S*,10a*R*)-4,6,11,11,12,12-hexamethyl-10-phenyldodecahydro-1,4:6,9-dimethano phenoxaphosphinine (phenop) have been assessed through synthesis and analysis of a number of derivatives namely phenopS, phenopSe, $[Fe(CO)_4(\kappa^1\text{-phenop})]$, $[W(CO)_5(\kappa^1\text{-phenop})]$, and *trans*-$[Rh(\kappa^1\text{-phenop})_2(CO)Cl]$. A combination of the absolute values of the $^1J_{P\text{-}Se}$ and $^1J_{P\text{-}Rh}$ one-bond coupling constants and the relevant υ(CO) stretching frequencies in the IR spectra of the metal carbonyl complexes suggest a close electronic analogy between κ^1-phenop and triphenylphosphane. This is supported by molecular electrostatic potential calculations at the DFT level which place phenop close to PPh_3 in terms of lone pair availability. Cone angles derived from the structural data cover a range from 164–203° depending to a large part on the relative orientation of the phenyl group with the larger values being observed for those compounds with the phenyl group parallel to the P–Z vector. These data define phenop as a moderately bulky phosphane sterically comparable to PCy_3. The central oxaphosphinane ring is not strictly rigid approximating to a boat conformation at one extreme and an envelope at the other depending on the nature of the P substituent.

Experimental Section

General: 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. Petroleum ether had a boiling range of 40–60 °C. 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 (δ = 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 (δ = 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.[44]

(1*S*,4*R*,4a*S*,5a*R*,6*R*,9*S*,9a*S*,10a*R*)-4,6,11,11,12,12-Hexamethyl-10-phenyldodecahydro-1,4:6,9-dimethanophenoxaphosphinine Sulfide, phenopS (1): A solution of phenop (1 g, 2.52 mmol) and sulfur (0.5 g, excess) in toluene (30 mL) was heated at 60 °C with constant stirring for 96 h. After cooling, the excess sulfur was removed by filtration and the colourless solution concentrated to small volume in vacuo whereupon the desired complex crystallised (occasional contamination of the product by elemental sulfur was observed and care should be employed to ensure complete removal of all the sulfur before crystallising the desired compound). The sulfide was recrystallised from toluene as colourless blocks; yield 0.73 g (68%). A second crop was obtained on concentrating the filtrate; yield 0.17 g (16%, total yield 84%), m.p. 245–247 °C $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = 32.1 (s) ppm. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.87 (m, 2 H, *o*-Ph), 7.45 (m, 3 H, *m*-Ph, *p*-Ph), 3.64 (dd, *J* = 7.4, 3.2 Hz, 1 H, H4a), 3.61 (dd, *J* = 9.0, 2.9 Hz, 1 H, H5a), 3.29 (m, 1 H, *endo*-H8), 2.81 (m, 1 H, H9a), 2.50 (dd, *J* = 10.6, 3.4 Hz, 1 H, H1), 2.32 (dd, *J* = 11.5, 7.5 Hz, 1 H, H10a), 2.09 (t, *J* = 4.0 Hz, 1 H, H9), 1.98 (m, 1 H, *endo*-H7), 1.82 (m, 1 H, *exo*-H2), 1.7–1.4 (m, 2 H), 1.33 (s, 3 H), 1.3–1.0 (m, 3 H), 0.98 (s, 3 H), 0.92 (s, 6 H), 0.83 (s, 3 H), 0.77 (s, 3 H) ppm. ^{13}C DEPT NMR ($CDCl_3$, 100 MHz): δ = 142.6 (d, *J* = 80.0 Hz, C), 130.3 (d, *J* = 2.7 Hz, CH), 130.0 (d, *J* = 8.9 Hz, CH), 128.5 (d, *J* = 11.3 Hz, CH), 89.5 (d, *J* = 5.6 Hz, C4a), 83.3 (d, *J* = 2.9 Hz, C5a), 51.3 (s, C), 50.5 (s, C), 48.8 (d, *J* = 2.9 Hz, CH), 47.5 (s, C), 47.5 (d, *J* = 32.0 Hz, CH), 47.2 (s, CH), 47.2 (s, C), 38.3 (d, *J* = 51.1 Hz, C9a), 33.4 (s, CH_2), 31.0 (d, *J* = 13.2 Hz, CH_2), 27.1 (s, CH_2), 24.4 (s, CH_3), 21.7 (s, CH_3), 20.3 (d, *J* = 4.4 Hz, CH_2), 19.0 (s, CH_3), 19.0 (s, CH_3), 14.3 (s, CH_3), 11.2 (s, CH_3) ppm. $C_{26}H_{37}OPS$ (428.60): calcd. C 72.86, H 8.72; found C 72.7, H 8.6. MS (APCI): 429 (100).

(1*S*,4*R*,4a*S*,5a*R*,6*R*,9*S*,9a*S*,10a*R*)-4,6,11,11,12,12-Hexamethyl-10-phenyldodecahydro-1,4:6,9-dimethanophenoxaphosphinine Selenide, phenopSe (2): A solution of phenop (1 g, 2.52 mmol) and selenium (0.22 g, 2.77 mmol) in toluene (15 mL) was heated near reflux with

constant stirring for 72 h. After cooling, the excess selenium was removed by filtration and the slightly pink solution taken to dryness. The slightly pink solid was recrystallised from ethanol as fine, fibrous needles; yield 0.85 g (71%). A second crop was obtained on reducing the volume of solvent; yield 0.22 g (18%, total yield 89%), m.p. 253–255 °C. Crystals suitable for single crystal X-ray structure determination were grown from acetone by slow evaporation at 4 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = 21.5 (s) with ^{77}Se satellites ($^1J_{P\text{-}Se}$ = 742 Hz) ppm. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.81 (m, 2 H, *o*-Ph), 7.38 (m, 3 H, *m*-Ph, *p*-Ph), 3.59 (dd, *J* = 7.2, 3.2 Hz, 1 H, H4a), 3.53 (dd, *J* = 7.5, 4.0 Hz, 1 H, H5a), 3.21 (m, 1 H, *endo*-H8), 2.86 (m, 1 H, H9a), 2.51 (dd, *J* = 11.3, 3.6 Hz, 1 H, H1), 2.34 (dd, *J* = 12.0, 7.2 Hz, 1 H, H10a), 2.05 (t, *J* = 4.3 Hz, 1 H, H9), 1.92 (m, 1 H, *endo*-H7), 1.77 (m, 1 H, *exo*-H2), 1.55 (m obscured, 1 H, *exo*-H3), 1.46 (m obscured, 1 H, *exo*-H8), 1.28 (s, 3 H), 1.15 (m, 1 H, *exo*-H7), 1.07 (m, 1 H, *endo*-H3), 0.98 (s, 3 H), 0.95 (m obscured, 1 H, *endo*-H2), 0.91 (s, 3 H), 0.90 (s, 3 H), 0.87 (s, 3 H), 0.83 (s, 3 H) ppm. ^{13}C DEPT NMR ($CDCl_3$, 100 MHz): δ = 142.0 (d, *J* = 72.0 Hz, C), 130.4 (d, *J* = 9.0 Hz, CH), 130.2 (d, *J* = 2.6 Hz, CH), 128.6 (d, *J* = 11.2 Hz, CH), 89.2 (d, *J* = 5.7 Hz, C4a), 82.8 (d, *J* = 2.9 Hz, C5a), 51.7 (s, C), 50.7 (s, C), 49.5 (s, CH), 49.0 (s, CH), 47.3 (s, C), 47.2 (obscured, C), 46.0 (d, *J* = 36.8 Hz, C10a), 37.5 (d, *J* = 43.1 Hz, C9a), 33.4 (s, CH_2), 30.8 (d, *J* = 13.5 Hz, CH_2), 27.3 (s, CH_2), 24.8 (s, CH_3), 21.7 (s, CH_3), 20.3 (d, *J* = 4.4 Hz, CH_2), 19.3 (s, CH_3), 19.1 (s, CH_3), 14.5 (s, CH_3), 11.2 (s, CH_3) ppm. $C_{26}H_{37}OPSe$ (475.56): calcd. C 65.66, H 7.89; found C 65.4, H 7.9. MS (APCI): 477 (100).

[(1*S*,4*R*,4a*S*,5a*R*,6*R*,9*S*,9a*S*,10a*R*)-4,6,11,11,12,12-Hexamethyl-10-phenyldodecahydro-1,4:6,9-dimethanophenoxaphosphinine]tetracarbonyliron(0), [Fe(κ¹-phenop)(CO)₄] (3): A solution of phenop (93 mg, 2.34×10^{-4} mol) and $Fe_2(CO)_9$ (85 mg, 2.34 × 10–4 mol) in diethyl ether (20 mL) was stirred in the absence of light for 18 h. On return, the mixture was filtered and the solvent removed in vacuo to yield a pale green solid. The solid was dissolved in petroleum ether and passes through a small plug of neutral alumina. After concentrating to about 3 mL, the solution was left at –33 °C whereupon the desired compound crystallised as yellow prisms; yield 120 mg (91%). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz): δ = 42.9 (s) ppm. ^1H NMR (C_6D_6, 500 MHz): δ = 7.85 (t, *J* = 8.0 Hz, 2 H, *o*-Ph), 7.24 (obscured, 2 H, *m*-Ph), 7.09 (t, *J* = 7.3 Hz, 1 H, *m*-Ph), 3.39 (d, *J* = 8.2 Hz, 1 H, H4a), 3.27 (d, *J* = 7.0 Hz, 1 H, H5a), 2.98 (m, 1 H, H9a), 2.78 (dd, *J* = 9.4, 3.6 Hz, 1 H, H1), 2.71 (m, 1 H, *endo*-H8), 2.45 (t, *J* = 4.2 Hz, 1 H, H9), 2.41 (dd, *J* = 14.6, 7.1 Hz, 1 H, H10a), 2.19 (m, 1 H, H7), 1.82 (m br, 2 H, H2, *exo*-H8), 1.53 (s, 3 H), 1.47 (t, *J* = 11.9 Hz, 1 H, H3), 1.34 (m, 1 H, H7), 1.04 (s, 3 H), 1.01 (m obscured, 2 H, H2, H3), 0.99 (s, 3 H), 0.87 (s, 3 H), 0.86 (s, 3 H), 0.70 (s, 3 H) ppm. ^{13}C DEPT NMR (C_6D_6, 125.8 MHz): δ = 213.3 (d, *J* = 16.7 Hz, CO), 149.6 (d, *J* = 47.6 Hz, C), 128.6 (d, *J* = 7.8 Hz, CH), 127.7 (s, CH), 127.5 (d, *J* = 8.9 Hz, CH), 87.6 (d, *J* = 5.2 Hz, C4a), 81.4 (d, *J* = 3.1 Hz, C5a), 50.6 (d, *J* = 4.2 Hz, C1), 49.7 (s, C9), 49.0 (d, *J* = 13.8 Hz, C), 46.3 (d, *J* = 13.7 Hz, C), 46.2 (s, C), 45.6 (d, *J* = 12.0 Hz, C10a), 40.2 (d, *J* = 19.8 Hz, C9a), 32.1 (s, C3), 30.1 (d, *J* = 11.3 Hz, C2), 26.4 (s, C7), 23.7 (s, CH_3), 21.1 (d, *J* = 6.4 Hz, C8), 20.1 (s, CH_3), 17.9 (s, CH_3), 17.8 (s, CH_3), 12.9 (s, CH_3), 10.0 (s, CH_3) ppm. $C_{30}H_{37}O_5PFe$ (564.49): calcd. C 63.83, H 6.62; found C 63.3, H 6.5. MS (APCI): 565 (10). IR: $\tilde{\nu}_{CO}$ (hexane) = 2049 (s), 1975 (s), 1947 (s), 1935 (s) cm^{-1}.

[(1*S*,4*R*,4a*S*,5a*R*,6*R*,9*S*,9a*S*,10a*R*)-4,6,11,11,12,12-Hexamethyl-10-phenyldodecahydro-1,4:6,9-dimethanophenoxaphosphinine]-pentacarbonyltungsten(0), [W(κ¹-phenop)(CO)₅] (4): A solution of phenop (0.248 g, 6.25×10^{-4} mol) in THF (25 mL) was added to a solution of $[W(CO)_5(THF)]$ (prepared in situ from 0.22 g, 6.25×10^{-4} mol, of tungsten hexacarbonyl in THF, 100 mL, by ultraviolet photolysis) and the solution stirred for 48 h. On return, the solvent was removed in vacuo and the pale yellow solid extracted into petroleum ether. Concentration of the solution resulted in precipitation of the desired complex. Recrystallisation was effected from petroleum ether at 4 °C; yield 0.30 g (67%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ = –23.1 (s) with ^{183}W satellites ($^1J_{P\text{-}W}$ = 232 Hz) ppm. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.36 (m, 2 H, *o*-Ph), 7.19 (m, 3 H, *m*-Ph, *p*-Ph), 3.38 (dd, *J* = 7.7, 2.0 Hz, 1 H, H4a), 3.34 (d, *J* = 9.0 Hz, 1 H, H5a), 2.93 (m, 1 H, H9a), 2.53 (dd, *J* = 10.0, 3.9 Hz, 1 H, H1), 2.50 (obscured, 1 H, *endo*-H8), 2.46 (dd, *J* = 14.3, 7.5 Hz, 1 H, H10a), 2.22 (t, *J* = 4.3 Hz, 1 H, H9), 1.96 (m, 1 H, H2), 1.83 (m, 1 H, H7), 1.75 (m, 1 H, *exo*-H8), 1.57 (dt, *J* = 13.0, 3.4 Hz, 1 H, H3), 1.28 (m obscured, 2 H, H2, H7), 1.27 (s, 3 H), 1.09 (m, 1 H, H3), 0.96 (s, 3 H), 0.88 (s, 3 H), 0.87 (s, 3 H), 0.86 (s, 3 H), 0.83 (s, 3 H) ppm. ^{13}C DEPT NMR ($CDCl_3$, 100 MHz): δ = 199.3 (d, *J* = 23.8 Hz, CO), 198.0 (d, *J* = 6.4, $^1J_{C\text{-}W}$ = 127.5 Hz, CO), 153.9 (d, *J* = 35.0 Hz, C), 128.8 (d, *J* = 7.4 Hz, CH), 127.9 (s, CH), 127.7 (d, *J* = 8.1 Hz, CH), 89.7 (d, *J* = 4.4 Hz, C4a), 83.5 (d, *J* = 2.5 Hz, C5a), 50.8 (d, *J* = 7.1 Hz, C1), 50.4 (s, C9), 50.0 (s, C), 48.0 (s, C), 47.2 (d, *J* = 10.3 Hz, C), 46.3 (d, *J* = 10.3 Hz, C10a), 41.9 (d, *J* = 16.7 Hz, C9a), 33.8 (s, C3), 30.1 (d, *J* = 11.8 Hz, C2), 27.5 (s, C7), 24.7 (d, *J* = 5.1 Hz, CH_3), 23.5 (d, *J* = 10.0 Hz, C8), 20.7 (s, CH_3), 19.5 (s, CH_3), 19.2 (s, CH_3), 14.2 (s, CH_3), 11.0 (s, CH_3) ppm. $C_{31}H_{37}O_6PW$ (720.49): calcd. C 51.67; H, 5.19; found C, 51.3; H, 5.0. MS (APCI): 610 [M – 4CO, 15%]. IR: $\tilde{\nu}_{CO}$ (hexane) = 2069 (w), 1944 (s), 1931 (vs) cm^{-1}.

***trans*-Bis[(1*S*,4*R*,4a*S*,5a*R*,6*R*,9*S*,9a*S*,10a*R*)-4,6,11,11,12,12-Hexamethyl-10-phenyldodecahydro-1,4:6,9-dimethanophenoxaphosphinine]chlorocarbonylrhodium(I), *trans*-[Rh(κ¹-phenop)₂(CO)Cl] (5):** Carbon monoxide was slowly bubbled through a solution of bis(1,5-cyclooctadiene)chlororhodium(I) dimer (0.19 mmol) in hexane (20 mL) over a period of 2 h. The volatiles were removed in vacuo, the solid residue dissolved in hexane (20 mL) containing phenop (150 mg, 0.38 mmol) and CO passed through the resultant solution for a further 1 h. Volatiles were again removed at the pump, and the sticky residue heated to near boiling in MeOH (20 mL) whereupon a microcrystalline yellow solid precipitated. The solid was isolated by filtration and recrystallised from toluene/MeOH (1:1, 20 mL) at 4 °C; yield 152 mg (84%). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz): δ = 6.1 (d, $^1J_{P\text{-}Rh}$ = 128.0 Hz) ppm. ^1H NMR (C_6D_6, 500 MHz): δ = 8.07 (4 H, *o*-Ph), 7.33–7.15 (obscured, 6 H, *m*,*p*-Ph), 3.48 (d, *J* = 10.5 Hz, 2 H, H4a), 3.22 (d, *J* = 7.1 Hz, 2 H, H5a), 3.20 (m obscured, 4 H), 3.15 (m br, 2 H), 2.44 (m, 2 H), 2.37 (m, 2 H), 1.97 (m br, 2 H), 1.85–1.75 (obscured, 4 H), 1.77 (s, 6 H), 1.50 (m br, 4 H), 1.15 (m, 2 H), 1.12 (s, 6 H), 1.10 (m obscured, 2 H), 1.07 (s, 6 H), 1.00 (s, 6 H), 0.98 (s, 6 H), 0.84 (s, 6 H) ppm. ^{13}C DEPT NMR (C_6D_6, 125.8 MHz): δ = 146.0 (t, *J* = 20.8 Hz, C), 130.8 (t, *J* = 5.0 Hz, CH), 127.0–126.4 (obscured, 2× CH), 87.0 (s, C4a), 81.9 (s, C5a), 49.6 (s, C), 49.2 (s, CH), 49.1 (s, C), 48.7 (s, CH), 48.1 (d, *J* = 7.3 Hz, CH), 46.4 (s, C), 44.5 (t, *J* = 5.3 Hz, C), 37.6 (d, *J* = 12.5 Hz, CH), 31.9 (s, CH_2), 30.0 (t, *J* = 5.3 Hz, CH_2), 26.9 (s, CH_2), 24.5 (t, *J* = 5.2 Hz, CH_2), 22.1 (s, CH_3), 19.9 (s, CH_3), 18.1 (s, CH_3), 17.9 (s, CH_3), 13.1 (s, CH_3), 10.2 (s, CH_3) ppm. $C_{53}H_{74}O_3P_2ClRh$ (959.56): calcd. C 66.34; H, 7.79; found C, 66.5; H, 7.8. MS (APCI): 924 [M – Cl, 60%], 499 [Rh(phenop), 20%]. IR: $\tilde{\nu}_{CO}$ (KBr) = 1965 (s) cm^{-1}.

Crystallography: Data collection was carried out on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromated Mo-K_α radiation, λ(Mo-K_α) = 0.71073 Å. The instrument was equipped with an Oxford Cryosystems cooling apparatus. Data collection and cell refinement were carried out using COLLECT[45] and HKL SCALEPACK.[46] Data reduction was applied using

HKL DENZO and SCALEPACK.[46] The structures were solved by direct methods (Sir92)[47] and refined with SHELX-97.[48] Absorption corrections were performed using SORTAV.[49] 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 U_{eq} 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.

CCDC-789203 (for **1**), -799142 (for **2**), -789205 (for **3**), 789206 (for **4**) and 789207 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: All DFT calculations were performed using the Gaussian03 suite of programs.[50] Separate geometry optimisation of parallel and perpendicular orientations of phenop were carried out at the B3LYP/6-31G(d,p) level,[51] as in the work of Koga.[2b] Both orientations were found to be stable minima in the gas phase, as confirmed by harmonic frequency calculation. Molecular electrostatic potential, *V*, on a cube in the vicinity of P was extracted from the resulting density and the value of V_{min} corresponding to the lone pair located.

[1] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 31.

[2] a) K. D. Cooney, T. R. Cundari, N. W. Hoffman, K. A. Pittard, M. D. Temple, Y. Zhao, *J. Am. Chem. Soc.* **2003**, *125*, 4318; b) C. H. Suresh, N. Koga, *Inorg. Chem.* **2002**, *41*, 1573; c) N. Fey, *Dalton Trans.* **2010**, *39*, 296; d) W. P. Giering, A. Prock, A. L. Fernandez, *Inorg. Chem.* **2003**, *42*, 8033; e) M. R. Wilson, A. Prock, W. P. Giering, A. L. Fernandez, C. M. Haar, S. P. Nolan, B. M. Foxman, *Organometallics* **2002**, *21*, 2758; f) K. A. Bunten, A. J. Poë, *New J. Chem.* **2006**, *30*, 1638; g) K. A. Bunten, A. J. Poë, T. A. Stromnova, *Dalton Trans.* **2005**, 3780; h) L. Chen, A. J. Poë, *Coord. Chem. Rev.* **1995**, *143*, 265; i) A. M. Gillespie, K. A. Pittard, T. R. Cundari, D. P. White, *Internet Electronic J. Mol. Des.* **2002**, *1*, 242; j) C. H. Suresh, *Inorg. Chem.* **2006**, *45*, 4982; k) J. Mathew, T. Tinto, C. H. Suresh, *Inorg. Chem.* **2007**, *46*, 10800; l) N. Fey, A. Tsipis, S. E. Harris, J. N. Harvey, A. G. Orpen, R. A. Mansson, *Chem. Eur. J.* **2006**, *12*, 291.

[3] N. Fey, A. G. Orpen, J. N. Harvey, *Coord. Chem. Rev.* **2009**, *253*, 704.

[4] T. E. Müller, M. P. Mingos, *Trans. Met. Chem.* **1995**, *20*, 533.

[5] R. A. Baber, M. F. Haddow, A. J. Middleton, A. G. Orpen, P. G. Pringle, A. Haynes, G. L. Williams, R. Papp, *Organometallics* **2007**, *26*, 713.

[6] M. Carreira, M. Charernsuk, M. Eberhard, N. Fey, R. van Ginkel, A. Hamilton, W. P. Mul, A. G. Orpen, H. Phetmung, P. G. Pringle, *J. Am. Chem. Soc.* **2009**, *131*, 3078.

[7] a) S. J. Coles, P. G. Edwards, M. B. Hursthouse, K. M. A. Malik, J. L. Thick, R. P. Tooze, *J. Chem. Soc., Dalton Trans.* **1997**, 1821; b) P. G. Edwards, S. J. Paisey, R. P. Tooze, *J. Chem. Soc. Perkin Trans. 1* **2000**, 3122.

[8] a) R. Haigh, K. M. A. Malik, P. D. Newman, *Chem. Commun.* **2002**, 2558; b) K. M. A. Malik, P. D. Newman, *Dalton Trans.* **2003**, 3516.

[9] a) M. Bode, G. Schnakenburg, J. Daniels, A. Marinetti, R. Streubel, *Organometallics* **2010**, *29*, 656; b) R. Streubel, M. Bode, G. Von Frantzius, C. Hrib, P. G. Jones, A. Monsees, *Organometallics* **2007**, *26*, 1371; c) N. H. T. Huy, S. Hao, L. Ricard, F. Mathey, *Organometallics* **2006**, *25*, 3152; d) N. Hoffmann, C. Wismach, L. Ernst, H.-M. Schiebel, P. G. Jones, *Eur. J. Inorg. Chem.* **2003**, 1815.

[10] a) A. T. McPhail, J. C. H. Steele, *J. Chem. Soc., Dalton Trans.* **1972**, 2680; b) L. D. Field, I. P. Thomas, P. Turner, T. W. Hambley, *Aust. J. Chem.* **2000**, *53*, 541; c) A. Polas, J. D. E. T. Wilton-Ely, A. M. Z. Slawin, D. F. Foster, P. J. Steynberg, M. J. Green, D. J. Cole-Hamilton, *Dalton Trans.* **2003**, 4669.

[11] a) D. W. Allen, I. W. Nowell, B. F. Taylor, *J. Chem. Soc., Dalton Trans.* **1985**, 2505; b) A. Muller, S. Otto, A. Roodt, *Dalton Trans.* **2008**, 650; c) R. P. Pinnell, C. A. Megerle, S. L. Manatt, P. A. Kroon, *J. Am. Chem. Soc.* **1973**, *95*, 977.

[12] J. A. S. Howell, M. G. Palin, P. McArdle, D. Cunningham, Z. Goldschmidt, H. E. Gottlieb, D. Hezroni-Langerman, *Inorg. Chem.* **1993**, *32*, 3493.

[13] P. E. Riley, R. E. Davis, *Inorg. Chem.* **1980**, *19*, 159.

[14] J. Pickardt, L. Rösch, H. Schumann, *J. Organomet. Chem.* **1976**, *107*, 241.

[15] F. A. Cotton, D. J. Darensbourg, B. W. S. Kolthammer, *Inorg. Chem.* **1981**, *20*, 4440.

[16] M. J. Aroney, I. E. Buys, M. S. Davies, T. W. Hambley, *J. Chem. Soc., Dalton Trans.* **1994**, 2827.

[17] O. Demircan, S. Özkar, D. Ulku, L. T. Yildirim, *J. Organomet. Chem.* **2003**, *688*, 68.

[18] J. Pickhardt, L. Rosch, H. Schumann, *Z. Anorg. Allg. Chem.* **1976**, *426*, 66.

[19] a) A. Del Pra, G. Zanotti, P. Segala, *Cryst. Struct. Commun.* **1979**, *8*, 959; b) A. Ceriotti, G. Ciani, A. Sironi, *J. Organomet. Chem.* **1983**, *247*, 345; c) A. L. Rheingold, S. J. Geib, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *43*, 784.

[20] a) M. L. Clarke, G. L. Holliday, A. M. Z. Slawin, J. D. Woolins, *J. Chem. Soc., Dalton Trans.* **2002**, 1093; b) M. R. Wilson, A. Prock, W. P. Geiring, A. L. Fernandez, C. M. Haar, S. P. Nolan, B. M. Foxman, *Organometallics* **2002**, *21*, 2758.

[21] R. L. Harlow, S. A. Westcott, D. L. Thorn, R. T. Baker, *Inorg. Chem.* **1992**, *31*, 323.

[22] a) D. White, C. B. Tavener, P. G. L. Leach, N. J. Coville, *J. Organomet. Chem.* **1994**, *478*, 205; b) D. White, N. J. Coville, *Adv. Organometallic. Chem.* **1994**, *36*, 95; c) A. Immirzi, A. Musco, *Inorg. Chim. Acta* **1977**, *25*, L41; d) I. A. Guzei, M. Wendt, *Dalton Trans.* **2006**, 3991.

[23] J. D. Smith, J. D. Oliver, *Inorg. Chem.* **1978**, *17*, 2585.

[24] T. L. Brown, K. J. Lee, *Coord. Chem. Rev.* **1993**, *128*, 89.

[25] R. A. Baber, M. F. Haddow, A. J. Middleton, A. G. Orpen, P. G. Pringle, A. Haynes, G. L. Williams, R. Papp, *Organometallics* **2007**, *26*, 713.

[26] A. T. McPhail, J. C. H. Steele, *J. Chem. Soc., Dalton Trans.* **1972**, 2680.

[27] a) A. E. Smith, *Inorg. Chem.* **1972**, *11*, 3017; b) S. J. Coles, P. G. Edwards, M. B. Hursthouse, K. M. A. Malik, J. L. Thick, R. P. Tooze, *J. Chem. Soc., Dalton Trans.* **1997**, 1821.

[28] R. Doherty, M. F. Haddow, Z. A. Harrison, A. G. Orpen, P. G. Pringle, A. Turner, R. L. Wingad, *Dalton Trans.* **2006**, 4310.

[29] The positions of the hydrogens used for the cone angle calculations were not determined crystallography but fixed using the afix command in SHELX. As for most cone angle data derived from structures determined by single crystal X-ray techniques, this introduces a slight error in the half-angles most particularly for the angle defined by the methyl group in our case.

[30] a) Y. Ohzu, K. Goto, T. Kawashima, *Angew. Chem.* **2003**, *115*, 5892; b) S. V. Bobrov, A. A. Karasik, O. G. Sinyashin, *Phosphorus Sulfur Relat. Elem.* **1999**, *144*, 289.

[31] J. H. Shin, B. M. Bridgewater, D. G. Churchill, G. Parkin, *Inorg. Chem.* **2001**, *40*, 5626.

[32] a) A. M. Trzeciak, J. J. Ziólkowski, *Inorg. Chim. Acta* **1985**, *96*, 15; b) T. T. Derencsényi, *Inorg. Chem.* **1981**, *20*, 665; c) S. Vastag, B. Heil, L. Marko, *J. Mol. Catal.* **1979**, *5*, 189; d) S. O. Grim, D. A. Wheatland, W. McFarlane, *J. Am. Chem. Soc.* **1967**, *89*, 5573; e) A. Roodt, S. Otto, G. Steyl, *Coord. Chem. Rev.* **2003**, *245*, 121.

[33] a) P. G. Waddell, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2010**, *39*, 8620; b) D. W. Allen, B. F. Taylor, *J. Chem. Soc., Dalton Trans.* **1982**, 51; c) J. G. Verkade, L. D. Quin (Eds.), *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis, Organic Compounds and Metal Complexes*, VCH, Weinheim, **1986**.

[34] a) D. J. Adams, J. A. Bennett, D. Duncan, E. G. Hope, J. Hopewell, A. M. Stuart, A. J. West, *Polyhedron* **2007**, *26*, 1505; b) P. A. W. Dean, L. Polensek, *Can. J. Chem.* **1980**, *58*, 1627.
[35] J. A. S. Howell, P. C. Yates, M. G. Palin, P. McArdle, D. Cunningham, Z. Goldschmidt, H. E. Gottlieb, D. Hezroni-Langerman, *J. Chem. Soc., Dalton Trans.* **1993**, 2775.
[36] R. G. Goel, W. O. Ogini, R. Schrivastava, *J. Organomet. Chem.* **1981**, *214*, 405.
[37] S. O. Grim, P. R. McAllister, R. M. Singer, *J. Chem. Soc. C* **1969**, 38.
[38] P. E. Garrou, G. E. Hartwell, *Inorg. Chem.* **1976**, *15*, 646.
[39] A. Ochida, G. Hamasaka, Y. Yamauchi, S. Kawamorita, N. Oshima, K. Hara, H. Ohmiya, M. Sawamura, *Organometallics* **2008**, *27*, 5494.
[40] R. A. Baber, M. L. Clarke, K. M. Heslop, A. C. Marr, A. G. Orpen, P. G. Pringle, A. Ward, D. E. Zambrano-Williams, *Dalton Trans.* **2005**, 1079.
[41] a) M. L. Clarke, G. L. Holliday, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **2002**, 1093; b) M. L. Clarke, J. J. R. Frew, *Organometallic Chemistry, Specialist Peridic Rev.* **2009**, *35*, 19.
[42] J. L. Male, R. K. Pomeroy, D. R. Tyler, *Organometallics* **1997**, *16*, 3431.
[43] M. van Rentergen, G. P. van der Kelen, E. C. Claeys, *J. Mol. Struct.* **1982**, *80*, 317.
[44] *Medac LTD, Alpha 319*, Chobham Business Centre, Chertsey Road, Chobham, Surrey, UK GU24 8JB.
[45] *COLLECT*, Nonius BV, **1998**, Delft, The Netherlands.
[46] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307.
[47] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343.
[48] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
[49] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
[50] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Revision C.02, Gaussian, Inc., Wallingford, CT, **2004**.
[51] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; c) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724; d) M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163.

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