# Coordination chemistry of 2,6-dixylyl-4-phenylphosphabarrelene with selected transition metals<sup>†</sup>

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The 2,6-dixylyl-4-phenylphosphabarrelene has been synthesised from the parent phosphinine and its properties as a ligand explored through the preparation and characterisation of the complexes  $W(CO)_5(L)$ ,  $Re(CO)_4(L)Cl$ ,  $(\eta^6$ -cymene)RuCl\_2(L),  $[(\eta^5-Me_3SiC_3H_4)Fe(CO)_2(L)]PF_6$ , Rh(1,5-COD)(L)Cl, Ir(1,5-COD)(L)Cl, and *cis*-Pt(L)\_2Cl\_2, where L = 4-phenyl-2,10-bis-(2,4-dimethylphenyl)-4H-1,4-ethenophospholine (\*PB), cymene = 4-isopropyltoluene,  $\eta^5-Me_3SiC_5H_4$  = trimethylsilylcyclopentadienyl and 1,5-COD = 1,5-cyclooctadiene. The new complexes were characterised by spectroscopic and analytical techniques and, for  $[(\eta^5-Me_3SiC_3H_4)Fe(CO)_2(L)]PF_6$  and Ru( $\eta^6$ -cymene)(L)Cl<sub>2</sub>, by single-crystal X-ray structure determination. The coordination properties of the phosphabarrelene have been established and compared with analogous complexes of triarylphosphines and triarylphosphites. Most spectroscopic and structural indicators suggest that the phosphabarrelene has coordination behaviour similar to that of simple triarylphosphines such as PPh<sub>3</sub>.

# Introduction

Phosphabarrelenes, originally reported by Markl,<sup>1</sup> remain a relatively unexplored class of organophosphorus compound. Breit was the first to investigate metal complexes of phosphabarrelenes during his studies of Rh(I) systems as potential isomerisation/hydroformylation catalysts.<sup>2</sup> Latterly, Le Floch and coworkers have examined the coordination chemistry of heterodonor bi- and tridentate phosphine sulfide phosphabarrelene derivatives in an effort to exploit the perceived unique donor properties of the phosphabarrelenes in catalysis.3 In addition to the study of this ligand type in the rhodium-catalysed hydroformylation of internal alkenes,4 Breit and co-workers have recently synthesised chiral, bidentate phosphite-phosphabarrelene ligands and applied them to rhodium-based asymmetric hydrogenation.<sup>5</sup> Much of this recent focus on phosphabarrelene ligands has been driven by a desire to find ligands that behave similarly to phosphites (or phosphonites) but are less prone to degradation under the reaction conditions commonly required for carbonylation and/or other types of catalysis. Breit identified phosphabenzenes (from which phosphabarrelenes are derived) as good potential candidates to replace phosphites or more traditional tertiary phosphines in rhodium-catalysed hydroformylation.<sup>6</sup> Based on these studies, it was suggested that the phosphinines were more  $\pi$ -acidic than tertiary phosphines and were, therefore, more akin to phosphites in their electronic properties. Breit also investigated the donor properties of phosphabarrelenes by examining  $Rh(CO)(L)_2Cl$  complexes of several phosphabarrelene derivatives. For Rh(1) complexes, this study indicated that the phosphabarrelenes had donor properties best described as lying somewhere between those of triarylphosphines and phosphites.<sup>4</sup>

These studies aside, there are few examples of fully characterised  $\kappa^{1}$  coordinated phosphabarrelene-transition metal complexes. We have an interest in examining the coordination properties of heterocyclic phosphines and have recently investigated aspects of the coordination chemistry of a series of halo-substituted arylphosphinines.<sup>7</sup> As an extension of this work and in order to obtain a more general understanding of the relative donor properties of phosphabarrelenes, we have conducted a systematic survey of the coordination chemistry of a  $\kappa^1$  coordinated triarylphosphabarrelene with a number of transition metal centres. To allow a more direct comparison of phosphabarrelene coordination behaviour for different metals, we have restricted our study to the coordination chemistry of the 2,6-dixylyl-4-phenylphosphabarrelene ligand (<sup>x</sup>PB) originally reported by Breit.<sup>4</sup> The nature of the phosphorusmetal bond has been examined and compared with analogous complexes of triarylphosphines and triarylphosphites and these details are presented here.

# **Results and discussion**

# Tungsten

The mono-phosphabarrelenepentacarbonyltungsten(0) complex  $W(CO)_5({}^{\circ}PB)$ , 1, was formed by the reaction of dixylylphosphabarrelene with the precursor  $W(CO)_5THF$  (Scheme 1). Complex 1 was isolated after recrystallisation and was fully characterised by spectroscopic means. The coordination of the ligand was confirmed by a downfield shift in the  ${}^{31}P{}^{1}H{}$  NMR spectrum of the complex with a singlet being observed at  $\delta_P$  –7.2 ppm

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(compared to  $\delta_{\rm P}$  –58 ppm for the free ligand,  $\Delta \delta_{\rm P}$  = 50.8 ppm) with tungsten satellites (<sup>183</sup>W, 15% abundant,  ${}^{1}J_{P-W} = 265$  Hz). Interestingly, and unlike the analogous complex of the parent phosphinine, only one peak is seen in the  ${}^{31}P{}^{1}H$  NMR spectrum of the complex at room temperature. However, upon cooling the sample to -34 °C this single peak starts to split until two distinct singlets are resolved at  $\delta_{\rm P}$  7.8 and 7.6 ppm at low temperature. As with the analogous phosphinine complex, this observation can be explained by rotamer isomerisation as shown in Fig. 1. The *cis* isomer is defined as that where both *ortho*-methyl groups of the xylyl rings are on the same side of the phosphabarrelene phenyl ring while the trans isomer has the two ortho-methyl groups on opposite sides of the phosphabarrelene ring. When both isomers are observed at low temperature the relative ratios are not 1:1 but approximately 60:40 resembling the situation observed with related dihaloarylphosphinine complexes.<sup>7</sup> Thus, one of the rotamers appears to be thermodynamically more stable but it is not possible to determine from the NMR data alone which one this is. The free energy of activation ( $\Delta G^{\ddagger}_{\ddagger}$ ) for this rotation was determined to be 48 kJ mol<sup>-1</sup> (from variable temperature NMR studies), a value within the range established for M–P rotation in cis-Pt(L)<sub>2</sub>Cl<sub>2</sub> systems (L = 1-*tert*-butylphosphinane).<sup>8</sup>



**Fig. 1** Rotamers of  $W(CO)_5^{x}PB(1)$ .

The  $\Delta G^{\ddagger}$  value for this  $cis \leftrightarrow trans$  interconversion in the W(CO)<sub>5</sub>(dixylylphosphinine) complex was determined to

be 75 kJ mol<sup>-1,7</sup> hence a greater barrier is associated with  $W(CO)_5$ (dixylylphosphinine) compared to  $W(CO)_5$ (<sup>x</sup>PB). The explanation for this resides in the nature of the two donors, the phosphabarrelene being non-planar with a sp<sup>3</sup> hybridised phosphorus compared to a sp<sup>2</sup> hybridised phosphorus centre in the planar phosphinine. Consequently, the dixylyl groups are "pulled back" away from the metal centre in the phosphabarrelene complex alleviating steric congestion and allowing more freedom of rotation than in the dixylylphosphinine complex.

To understand further the nature of the tungsten–phosphorus bond in W(CO)<sub>5</sub>(<sup>x</sup>PB), the <sup>1</sup>J<sub>P-W</sub> and the carbonyl stretching frequencies of **1** were compared with analogous complexes of phosphines and phosphites. The correlation between the  $\sigma$ -donor/ $\pi$ -acceptor abilities of phosphorus ligands and their <sup>1</sup>J<sub>P-W</sub> values, and/or their v(CO) stretching frequencies in W(CO)<sub>5</sub>(PR<sub>3</sub>) complexes has been studied by Grim and co-workers<sup>9</sup> who showed that there was a correlation between the most intense carbonyl stretching frequency (the E mode) and <sup>1</sup>J<sub>P-W</sub> in phosphine and phosphite complexes of pentacarbonyltungsten.<sup>10</sup> Fig. 2 displays this data in comparison to that of the analogous W(CO)<sub>5</sub>(<sup>x</sup>PB).

The values of the  ${}^{1}J_{P-W}$  coupling constant and the v(CO) (E mode) are 265 Hz and 1942 cm<sup>-1</sup> for 1 placing \*PB between triphenylphosphine and tri-4-tolylphosphine in terms of donor ability. Grim argued that better  $\pi$ -acceptor ligands give a higher v(CO) and a larger  ${}^{1}J_{P-W}$  coupling constant as increased  $\pi$  backbonding to the phosphorus has the effect of shortening the metal-phosphorus bond consequently strengthening the metalphosphorus  $\sigma$ -bond. Larger  ${}^{1}J_{P-W}$  coupling constants were thus interpreted as reflecting a greater  $\pi$ -bonding component in the M–P bond. On this basis, the position of <sup>x</sup>PB in the series suggests that it has  $\pi$ -acceptor abilities (and  $\sigma$ -donor properties) most closely similar to those of simple triarylphosphines. Steric differences between triphenylphosphine and <sup>x</sup>PB might be anticipated and these two influences could be expected to work in opposition. The pendant xylyl groups at the 2 position of the phosphabarrelene core may serve to lengthen and weaken the M-P bond thus reducing  ${}^{1}J_{W-P}$ . Crystallographic studies (herein) indicate that



Fig. 2 E mode stretching frequencies (v) vs. P–W coupling constants (J) in  $W(CO)_5L$  complexes.

triphenylphosphine may, however, be more sterically bulky. Steric influences will also be expected to influence  ${}^{1}J_{P-W}$  coupling constants if such interactions result in compression or expansion of the C–P–C angles. Due to the cyclic nature of the phosphabarrelene ligand, some of the C–P–C bonds are restricted at angles less than 100° (*vide infra*) and it might be anticipated that the lone pair in \*PB has greater 's' character than in PPh<sub>3</sub> giving rise to a larger  ${}^{1}J_{P-W}$  coupling constant in W(CO)<sub>5</sub>(\*PB) compared to W(CO)<sub>5</sub>(PPh<sub>3</sub>). In balance, caution is required in interpreting donor properties by these methods, but it is clear that  ${}^{1}J_{P-W}$  for W(CO)<sub>5</sub>(\*PB) is appreciably smaller than for phosphite complexes.

#### Rhenium

To the best of our knowledge there are no reported complexes of phosphabarrelenes with any of the transition metals of group 7 prompting us to investigate their chemistry. Complex 2 was prepared by refluxing a solution of <sup>x</sup>PB with chloropentacarbonylrhenium(1) in dichloromethane (Scheme 1); the desired complex being obtained as a microcrystalline yellow solid. The  ${}^{31}P{}^{1}H$ NMR spectrum of 2 is a singlet ( $\delta$  -23 ppm) showing the characteristic downfield shift ( $\Delta \delta = 35$  ppm) upon coordination of the phosphabarrelene ligand. In addition, the <sup>1</sup>H NMR spectrum shows a downfield shift for the doublet of doublets associated with the proton at the C-8 position. This is characteristic of coordination of phosphabarrelenes to most transition metal centres, although the magnitude of the coordination shift varies (vide infra). Three carbonyl resonances are observed in the  ${}^{13}C{}^{1}H{}$ NMR spectrum as expected for the two carbonyls cis to the phosphabarrelene and trans to one another, the carbonyl trans to the phosphabarrelene, and the carbonyl trans to the chloride. The carbonyl trans to the phosphabarrelene is identified by a large  ${}^{2}J_{C-P}$  coupling constant of 64 Hz, whereas the CO ligands *cis* to the phosphabarrelene and *trans* to one another have a smaller  ${}^{2}J_{C-P}$ 

The internal C=1=C bond angles of 1 D III 5

coupling constant of around 14 Hz. The unique carbonyl *trans* to the chloride is observed as a broad singlet.

The infrared spectrum of **2** shows four carbonyl stretching frequencies, which agrees with data observed with related complexes of this type<sup>11</sup> and is consistent with a *cis* configuration for the complex.<sup>10</sup> Comparison of **2** with the analogous triphenylphosphine complex reveals a very similar pattern with v(CO) at 2109, 2023, 2005 and 1922 cm<sup>-1</sup> in W(CO)<sub>5</sub>(\*PB) and 2106, 2018, 2002 and 1945 cm<sup>-1</sup> for W(CO)<sub>5</sub>(PPh<sub>3</sub>). Thus, the carbonyl stretching frequencies seem to show that the phosphorus-rhenium bond in **2** is again, in terms of  $\sigma$ -donor and  $\pi$ -acceptor properties, very similar to triphenylphosphine.

#### Iron and ruthenium

The cationic  $[(\eta^5-Me_3SiC_5H_4)Fe(CO)_2(^xPB)]^+$  complex (3) was synthesised as its hexafluorophosphate salt by the addition of the phosphabarrelene to a solution of  $[(\eta^5-Me_3SiC_5H_4)-$ Fe(CO)<sub>2</sub>(CH<sub>3</sub>CN)]PF<sub>6</sub> in dichloromethane (Scheme 1). Yellow crystals suitable for X-ray crystallography were obtained by vapour diffusion of diethyl ether to an ethanolic solution of the complex salt; the structure of the cation is shown in Fig. 3. The complex has the three legged piano stool structure common to systems of this type. Comparison with the related [CpFe(CO)<sub>2</sub>PPh<sub>3</sub>]<sup>+</sup> species reveals some differences, notably in the Fe-P bond lengths of 2.2165(12) Å in 3 and 2.2380(15) Å in [CpFe(CO)<sub>2</sub>PPh<sub>3</sub>]<sup>+</sup>.<sup>12</sup> This shorter bond between the phosphabarrelene and the iron centre relative to triphenylphosphine could reflect a slight increase in the  $\pi$ -acceptor properties of the phosphabarrelene (as remarked by Breit<sup>4</sup>) relative to triphenylphosphine although the observed difference may also be due to steric influences of the bulkier PPh<sub>3</sub>. It is noteworthy that the analogous trimethylphosphite complex exhibits a phosphorus-iron bond length of 2.164 Å, significantly shorter than in 3.<sup>13</sup> The internal C–P–C bond angles of <sup>x</sup>PB in 3



Fig. 3 ORTEP view of the cation (3). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% occupancy level. Selected bond lengths (Å): Fe(1)-P(1) 2.2165(12); P(1)-C(21) 1.832(4); P(1)-C(1) 1.852(4); P(1)-C(5) 1.847(4); Fe(1)-C(43) 1.774(5); Fe(1)-C(42) 1.780(5); O(1)-C(42) 1.143(5); O(2)-C(43) 1.138(5). Selected bond angles (°): C(21)-P(1)-Fe(1) 119.14(13); C(1)-P(1)-Fe(1) 119.77(14); C(5)-P(1)-Fe(1) 121.39(14); C(43)-Fe(1)-P(1) 92.27(15); C(42)-Fe(1)-P(1) 95.22(15); O(1)-C(42)-Fe(1) 176.0(4); O(2)-C(43)-Fe(1) 177.1(4).

average 97°, a value very close to that (96°) observed by Breit in the *trans*-Rh(CO)Cl(\*PB)<sub>2</sub> complex.<sup>4</sup> This constraint contributes to the reduced cone angle of 141.4° for the ligand in the current complex (using the method of Mingos).<sup>14</sup>

The  ${}^{31}P{}^{1}H$  NMR spectrum of the iron complex, 3, shows a characteristic upfield coordination shift to  $\delta$  10.6 ppm. The <sup>1</sup>H NMR spectrum was broad at room temperature but sharpened sufficiently upon cooling to -50 °C to allow assignments to be made. The temperature dependence of the <sup>1</sup>H NMR spectrum suggests there is some form of fluxional process present even though no noticeable broadening is observed in the  ${}^{31}P{}^{1}H{}$  NMR spectrum at room temperature indicating that the fluxional process does not involve phosphine exchange at the iron centre and is likely due to restricted rotation of the ligands. The  ${}^{13}C{}^{1}H$  NMR spectrum of 3 is consistent with the structure although assignment of the CO and two of the quaternary carbons was compromised by weak signal intensity. The infrared data for 3 again compare well with the analogous triphenylphosphine complex; 3 exhibits two carbonyl stretching bands at 2055 and 2013 cm<sup>-1</sup>, whereas the triphenylphosphine complex has two bands at 2052 and 2008 cm<sup>-1</sup>, respectively,15 indicating that the phosphabarrelene again exhibits electronic properties similar to those of triphenylphosphine in these iron complexes.

The ( $\eta^6$ -cymene)RuCl<sub>2</sub>(<sup>x</sup>PB) complex, **4**, was prepared from the reaction of the [( $\eta^6$ -cymene)RuCl<sub>2</sub>]<sub>2</sub> dimer with two mol equiv. of the phosphabarrelene in dichloromethane (Scheme 1). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **4** is very broad at room temperature with two peaks centred around 2 ppm. Upon heating to 80 °C these two peaks sharpen to a single peak at  $\delta$  –5.4 ppm; coalescence occurs at 60 °C. Upon cooling, at –50 °C two sharp peaks at  $\delta$  4.5 ppm and  $\delta$  –7.7 ppm are observed in the

 ${}^{31}P{}^{1}H$  NMR spectrum. These observations suggest rotamer isomerisation as was observed with the tungsten carbonyl complex 1;  $\Delta G$  of activation for the rotation was estimated from the NMR experiments to be 60 kJ mol<sup>-1</sup>. It is noteworthy that the peak at  $\delta$  4.5 ppm is considerably more intense than the peak at  $\delta$  -7.7 ppm suggesting that one of the rotamers is thermodynamically favoured over the other as was the case in the (*x*PB)pentacarbonyltungsten(0) complex, 1. These rotamers result from restricted rotation around the phosphorus-ruthenium bond, where, in one of the isomers, the benzene ring of the phosphabarrelene core points towards the cymene ring, while in the other rotamer it points away from the cymene group. Thus, if the cymene is free to rotate on the ruthenium at these temperatures, it is reasonable to suggest that a greater degree of steric relief occurs when the benzene ring points away from the cymene group and it would appear that this configuration would be thermodynamically favoured. This is indeed the orientation seen in the crystal structure of 4 shown in Fig. 4. The complex exhibits a three legged piano stool geometry that is consistent with complexes of this type. Comparison of the phosphorus-ruthenium bond lengths with analogous complexes of tri(meta-tolyl)phosphine<sup>16</sup> and triphenylphosphite<sup>17</sup> gives values of 2.3619 Å for complex 4, 2.379 Å for  $(\eta^{6}$ -cymene)RuCl<sub>2</sub>{P(m-tol)<sub>3</sub>} and 2.264 Å for  $(\eta^{6}\text{-cymene})\text{RuCl}_{2}\{P(OPh)_{3}\}$ . These values follow a similar trend to that noted for the iron(II) systems and reinforces the notion that the phosphabarrelene is similar in behaviour to a triarylphosphine but is not as powerful a  $\pi$ -acid as related phosphites.



Fig. 4 ORTEP view of (4). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% occupancy level. The molecule of dichloromethane has been omitted for clarity. Selected bond lengths (Å): P(1)-Ru(1) 2.3619(12); Cl(1)-Ru(1) 2.4043(12); Cl(2)-Ru(1) 2.4044(12); P(1)-C(1) 1.846(4); P(1)-C(5) 1.852(5); P(1)-C(7) 1.862(4). Selected bond angles (°): P(1)-Ru(1)-Cl(1) 84.15(5); P(1)-Ru(1)-Cl(2) 88.78(5); C(1)-P(1)-Ru(1) 123.09(13); C(5)-P(1)-Ru(1) 121.56(14); C(7)-P(1)-Ru(1) 118.87(14).

The crystallographic cone angle of  $145.3^{\circ}$  for the phosphabarrelene in complex 4 compares to that calculated for the iron complex 3 but is somewhat smaller than the value of  $161^{\circ}$  quoted for the *trans*-Rh(CO)Cl(\*PB)<sub>2</sub> complex 4. Although direct comparison with PPh<sub>3</sub> complexes may be inappropriate as PPh<sub>3</sub> shows cone angle values that extend from approximately  $129^{\circ}$  to around  $168^{\circ}$ , it is noteworthy that a large number of triphenylphosphine complexes have cone angles of ~ $145^{\circ}$ . All these values are lower than the ~ $175^{\circ}$  cone angle of the directly comparable di(*o*-tolyl)phenylphosphine largely as a consequence of the 'tied-back' C–P–C bond angles in the constrained phosphabarrelene. It would appear therefore that \*PB has steric and electronic properties similar to those of triarylphosphines (particularly PPh<sub>3</sub>).

#### **Rhodium and iridium**

The Rh(1,5-COD)(\*PB)Cl complex 5 was synthesised by addition of 2 equiv. of the phosphabarrelene ligand to [Rh(1,5-(COD)Cl]<sub>2</sub> in dichloromethane (Scheme 1). Complex 5 was isolated as a yellow solid and characterised by spectroscopic means. The  ${}^{31}P{}^{1}H{}$ NMR spectrum shows a downfield shifted doublet at  $\delta$  –17.5 ppm, with a  ${}^{1}J_{P-Rh}$  coupling constant of 160 Hz. Again, coordination is confirmed in the <sup>1</sup>H NMR spectrum by the characteristic downfield shift (from  $\delta$  7.82 ppm to  $\delta$  8.77 ppm) of the C-8 proton. The  ${}^{1}J_{P-Rh}$  coupling constant in 5 compares with a value of 152 Hz for the analogous triphenylphosphine complex.<sup>18</sup> The analogous iridium(I) complex Ir(1,5-COD)(xPB)Cl, 6, was made in the same way as the rhodium complex 5 (Scheme 1). The  ${}^{31}P{}^{1}H$  NMR spectrum of the yellow compound gives a singlet at  $\delta$  –24.1 ppm, and the <sup>1</sup>H NMR spectrum shows the downfield shifted doublet of doublets for the proton on the C-8 position of the phosphabarrelene ring at  $\delta$  8.76 ppm. These data aside, the remaining spectroscopic details are unremarkable.

#### Platinum

The cis-Pt(xPB)2Cl2 complex 7 was synthesised by reaction of 2 equiv. of the phosphabarrelene ligand with Pt(NCPh)<sub>2</sub>Cl<sub>2</sub> in dichloromethane (Scheme 1). Complex 7 is, to the best of our knowledge, the first phosphabarrelene complex of its type to be characterised by spectroscopic means. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum exhibits the coordinated downfield singlet at -27.8 ppm, with corresponding <sup>195</sup>Pt satellites ( ${}^{1}J_{P-Pt}$  coupling constant of 3860 Hz.) The <sup>1</sup>H NMR spectrum also shows the characteristic coordination shift for the C-8 proton on the phosphabarrelene ring from  $\delta$  7.82 ppm to  $\delta$  8.60 ppm. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum alludes to the *cis* configuration of the complex. This reasoning is based upon two observations; firstly the C-2 and C-6 carbons on the phosphabarrelene ring appear as doublets rather than triplets and, secondly they show an increased  $J_{C-P}$  coupling constant of 38 Hz. Further evidence for the cis assignment for complex 7 comes from comparison of the  ${}^{1}J_{P-Pt}$  coupling constant in 7 with related phosphine complexes. It is reported that, for any given phosphine, the magnitude of this coupling constant is sensitive to the geometry of the complex. For example, cis-Pt{P(p-tolyl)<sub>3</sub>}<sub>2</sub>Cl<sub>2</sub> has a  ${}^{1}J_{P-Pt}$  coupling constant of 3627 Hz, whereas in *trans*-Pt{P(*p*tolyl)<sub>3</sub>}<sub>2</sub>Cl<sub>2</sub> it is 2650 Hz.<sup>19</sup> This highlights an established trend for phosphine complexes of the type  $Pt(PR_3)_2Cl_2$ , where  ${}^1J_{P-Pt}$  values are characteristically in the order of 1000 Hz greater in the cis isomer compared to the trans form, which relates to the higher trans influence of a phosphine donor relative to chloride. Hence, as the  ${}^{1}J_{P-Pt}$  coupling constant of complex 7 (3860 Hz) is close to the values recorded for cis-Pt{P(p-tolyl)<sub>3</sub>}<sub>2</sub>Cl<sub>2</sub> (3627 Hz), and cis-Pt(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (3673 Hz),<sup>20</sup> it can be concluded that the likely geometry of 7 is cis. See Fig. 5 for comparison of the current complex with known phosphine systems.



Fig. 5  ${}^{-1}J_{P-Pt}$  coupling constants for complexes of the type *cis*-(L)<sub>2</sub>PtCl<sub>2</sub>.

In common with the rhodium complex 5, the phosphorus-metal coupling constant in complex 7 is slightly higher at 3860 Hz than the analogous triphenylphosphine complex where a value of 3673 Hz is observed. The magnitude of  ${}^{1}J_{P-M}$  coupling is largely dominated by the Fermi contact term and hence the extent of s orbital character in the M-P bond. Furthermore, there tends to be, in the absence of complicating steric effects,<sup>21</sup> an increase in the absolute value of  ${}^{1}J_{P-M}$  as the M–P bond length decreases.<sup>22</sup> Thus the higher  $\pi$ -acceptor ability of the phosphabarrelene combined with a greater degree of s orbital character in the phosphorus lone pair of <sup>x</sup>PB results in the enhanced  ${}^{1}J_{P-Pt}$  coupling constant for 7. The former point is supported by the work of Grim and coworkers<sup>23</sup> who postulate that there is a trend in the  ${}^{1}J_{P-Pt}$  coupling constants on going from alkyl to aryl phosphines. Thus, they state that for  $PR_nPh_{3-n}$  as *n* decreases the absolute value of the  ${}^{1}J_{P-Pt}$  coupling constant increases, *i.e.*  $\pi$ -acidity increases as more phenyl groups are introduced on the phosphine and the values of the observed  ${}^{1}J_{P-Pt}$  coupling constant increase accordingly. There remains, however, a marked distinction between the absolute values of the  ${}^{1}J_{P-Pt}$  coupling constants for phosphines (including <sup>x</sup>PB) compared to typical phosphites which are larger as a consequence of shorter M-P bond lengths and increased 's' electron density in the bonds.24,25

In conclusion, several complexes of the di-xylylphosphabarrelene, \*PB, have been synthesised and characterised. Spectroscopic indicators suggest that \*PB behaves in a similar fashion to triarylphosphines as a donor to metal centres. A close comparison between the data for the \*PB complexes and related PPh<sub>3</sub> complexes is noted, although cone angles for the more rigid \*PB ligand from two crystal structures are less than those observed at the higher extreme for the more rotationally free PPh<sub>3</sub> system.

# Experimental

The new compounds were synthesised under nitrogen using standard inert atmosphere (Schlenk) techniques. Complexes 1–7 were handled as air and moisture sensitive compounds for manipulation. Solvents were freshly distilled from sodium or calcium hydride under nitrogen before use. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on Jeol Eclipse 300 and Bruker DPX500 spectrometers operating at 121.7 and 202.5 MHz, respectively, and referenced to 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta = 0$  ppm). <sup>1</sup>H (400.8 MHz) spectra were obtained on a Bruker DPX400 spectrometer was used as indicated. <sup>13</sup>C{<sup>1</sup>H} (125.8 MHz) NMR spectra were obtained on a Bruker DPX500 spectrometer and are referenced to tetramethylsilane ( $\delta = 0$  ppm). Infrared spectra were recorded either in

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solution or as Nujol Mulls on a Nicolet 510 FT-IR spectrophotometer. Accurate mass spectra were recorded on a Waters LCT Premier XE mass spectrometer, the protonated form of leucine enkephalin C<sub>28</sub>H<sub>38</sub>N<sub>5</sub>O<sub>7</sub> (MW 556.2271) was used as the lock mass/internal standard. 4-phenyl-2,10-bis-(2,4-dimethylphenyl)-4H-1,4-ethenophospholine (xPB) was prepared by the method of Breit.<sup>4</sup> All other chemicals were of reagent grade and used as supplied unless otherwise stated. All new compounds have been characterised by a combination of spectroscopic and high resolution mass spectrometry. Microanalyses were performed by Medac Ltd UK. The accuracy of the analytical data was impaired by the presence of a persistent non-phosphorus containing by-product that was carried through from the ligand synthesis. Exhaustive crystallisation and/or chromatography of the complexes did remove much of this unwanted material and the resultant microanalytical data are somewhat outside the usual limits. In addition, compounds 3 and 4 have been characterised crystallographically.

# [4-Phenyl-2,10-bis-(2,4-dimethylphenyl)-4H-1,4ethenophospholine]-pentacarbonyltungsten(0), 1

A solution of <sup>x</sup>PB (0.1 g, 0.22 mmol) in THF (5 mL) was added to a solution of W(CO)<sub>5</sub>THF (70 mg, 0.22 mmol) in THF (10 mL) and the reaction mixture stirred at room temperature for 18 h. After removing the solvent in vacuo the crude material was washed with cold 40: 60 petroleum ether and the residue recrystallised from 40 : 60 petroleum ether to give 1 as a yellow solid. Yield = 0.15 g (87%). <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, CDCl<sub>3</sub>):  $\delta = -7.23$  (s with <sup>183</sup>W satellites,  ${}^{1}J_{P-W} = 265 \text{ Hz}$ ) ppm.  ${}^{1}\text{H}$  NMR (400.8 MHz, CDCl<sub>3</sub>):  $\delta = 2.21$  (s, 12H, CH<sub>3</sub>), 6.52 (d, 1H, J = 7.7 Hz, Ar–H), 6.91 (m, 5H, Ar–H), 7.01 (t, 1H, J = 7.6 Hz, Ar–H), 7.16 (m, 2H, Ar–H), 7.39 (t, 1H, J = 7.3 Hz, Ar–H), 7.48 (t, 2H, J = 7.9 Hz, Ar–H), 7.56 (d, 2H, J = 7.5 Hz, Ar–H), 7.73 (d, 2H, J = 17.3 Hz, CH3/5), 7.97 (dd, 1H,  $J_{\text{H-H}} = 4.0 \text{ Hz}$ ,  $J_{\text{H-P}} = 12.0 \text{ Hz}$ , CH-8) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 21.13$  (s, CH<sub>3</sub>), 61.79 (d, J =8.8 Hz, C), 124.66 (d, J = 12.6 Hz, CH), 124.86 (d, J = 3.8 Hz, CH), 126.30 (s, C), 126.44 (s, CH), 127.70 (s, CH), 127.97 (s, CH), 128.70 (s, CH), 128.86 (s, C), 129.02 (s, CH), 129.23 (s, CH), 131.02 (s, CH), 131.16 (s, CH), 131.53 (d, J = 18.9 Hz, CH), 134.90 (d, J = 13.8 Hz, C), 136.09 (s, C), 138.32 (s, C), 139.86 (s, C), 150.23 (s, C), 191.15 (d, J = 62.9 Hz, trans-CO), 194.88 (d, J = 7.5 Hz, cis-CO) ppm. IR (hexane): 2073.9 (w, CO), 1985.7 (w, CO), 1941.6 (s, CO), 1261.0, 1099.1, 1016.4, 858.0, 739.7 cm<sup>-1</sup>. Anal. calcd for C<sub>38</sub>H<sub>29</sub>O<sub>5</sub>PW: C 58.47, H 3.75%. Found: C 57.5, H 3.5%.

# [4-Phenyl-2,10-bis-(2,4-dimethylphenyl)-4H-1,4ethenophospholine]-tetracarbonyl(chloro)-rhenium(1), 2

To a solution of chloropentacarbonyl-rhenium(1) (80 mg, 0.22 mmol) in dichloromethane (10 mL) was added the phosphabarrelene (0.1 g, 0.22 mmol) in dichloromethane (10 mL) and the reaction mixture subsequently refluxed for 18 h. After cooling the volatile materials were removed *in vacuo* and the desired compound extracted into 40 : 60 petroleum ether (20 mL). After filtering, the desired complex was precipitated as a yellow solid upon cooling. Yield = 83 mg (48%). <sup>31</sup>P{<sup>1</sup>H} NMR (121.7 MHz, CDCl<sub>3</sub>):  $\delta$  = -21.90 (s) ppm. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.21 (s, 12H, CH<sub>3</sub>), 6.52 (d, 1H, *J* = 8.0 Hz, Ar–H), 6.91 (m, 3H, Ar–H), 7.00 (t, 2H, *J* = 7.6 Hz, Ar–H), 7.13 (m,

2H, Ar–H), 7.41 (d, 2H, J = 7.2 Hz, Ar–H), 7.48 (t, 2H, J = 7.4 Hz, Ar–H), 7.55 (d, 2H, J = 7.4 Hz, Ar–H), 7.79 (d, 2H, J = 19.3 Hz, CH3/5), 8.48 (b dd, 1H,  $J_{H-P} = 9.25$  Hz, CH-8) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = 20.09$  (s br, CH<sub>3</sub>), 60.75 (d, J = 10.1 Hz, C), 123.47 (d, J = 12.6 Hz, CH), 124.03 (s, CH), 126.86 (s, CH), 127.09 (s, CH), 127.44 (s, CH), 127.58 (s, CH), 128.01 (s, CH), 130.22 (s, CH), 132.02 (d, J = 12.6 Hz, CH), 137.62 (s, CH), 138.32 (s, CH), 146.08 (br, C), 148.13 (br, C), 148.46 (br, C), 148.63 (br, C), 150.63 (br, C), 151.14 (br, C), 178.29 (s br, CO), 180.89 (d, J = 64.2 Hz, *trans*-CO), 182.31 (d, J = 13.8 Hz, *cis*-CO) ppm. IR (hexane): 2109.8 (m, CO), 2023.9 (s, CO), 2005.6 (s, CO), 1922.7 (s, b, CO), 1261.2, 1096.3, 1014.4, 734.8 cm<sup>-1</sup>. ES mass spectrum: (m/z) 755.1363 [M – CI]<sup>+</sup>. Anal. calcd for C<sub>37</sub>H<sub>29</sub>O<sub>4</sub>PCIRe: C 56.23, H 3.71%. Found: C 54.9, H 3.4%.

## (η<sup>5</sup>-Trimethylsilylcyclopentadienyl)[4-phenyl-2,10-bis-(2,4dimethylphenyl)-4H-1,4-ethenophospholine]-dicarbonyliron(II) hexafluorophosphate, 3

To a solution of  $(\eta^5$ -trimethylsilylcyclopentadienyl)(dicarbonyl)-(acetonitrile)-iron(II) hexafluorophosphate (96 mg, 0.22 mmol) in dichloromethane (10 mL) was added \*PB (0.1 g, 0.22 mmol) in dichloromethane (10 mL) and the reaction mixture stirred for 18 h. After removing the volatile materials in vacuo, the desired compound was isolated from the solid residue by crystallisation via vapour diffusion of diethyl ether into an ethanolic solution of the crude product. Yield = 40 mg (21%).  ${}^{31}P{}^{1}H{}$  NMR (202.5 MHz, CDCl<sub>3</sub>):  $\delta = 10.59$  (s), -144.17 (septet,  $J_{P-F} = 713$  Hz,  $PF_6^{-}$ ) ppm. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>, 223 K):  $\delta = 0.15$  (s, 9H, SiMe<sub>3</sub>), 2.16 (s, 6H, CH<sub>3</sub>), 2.31 (s, 6H, CH<sub>3</sub>), 4.07 (br, 2H, Cp-H), 4.37 (br, 2H, Cp-H), 6.62 (br, m, 1H, Ar-H), 6.89 (br, m, 1H, Ar-H), 7.10 (br, m, 8H, Ar-H), 7.60 (br, m, 6H, Ar-H), 8.00 (br, m, 1H, Ar–H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 1.04$ (s, SiMe<sub>3</sub>), 20.92 (s, CH<sub>3</sub>), 21.02 (s, CH<sub>3</sub>), 21.13 (s, CH<sub>3</sub>), 21.15 (s, CH<sub>3</sub>), 65.90 (s, C, Cp), 71.10 (s, CH, Cp), 72.80 (s, CH, Cp), 123.93 (s, CH), 124.07 (s, C), 126.46 (s, CH), 126.61 (s, CH), 127.46 (s, CH), 128.93 (s, CH), 129.01 (s, CH), 129.28 (s, CH), 131.01 (s, CH), 131.17 (s, CH), 135.25 (s, C), 136.38 (s, C), 136.98 (s, C), 138.17 (s, C), 149.68 (d, J = 4.0 Hz, C), 150.91 (br, CH) ppm. IR (dichloromethane): 2054.8 (CO), 2013.3 (CO), 1261.2, 1095.4, 1019.2, 734.8 cm<sup>-1</sup>. ES mass spectrum: (m/z) 705.2022 [M]<sup>+</sup>. Anal. calcd for C43H42O2P2SiF6Fe: C 60.70, H 4.99%. Found: C 60.4, H 4.9%.

# $(\eta^{6}\text{-Cymene})[4\text{-phenyl-2,}10\text{-bis-(2,}4\text{-dimethylphenyl})\text{-}4\text{H-1,}4\text{-}ethenophospholine}](dichloro)ruthenium(II), 4$

To a solution of bis( $\eta^6$ -cymene)tetrachlorodiruthenium(II) (134 mg, 0.22 mmol) in dichloromethane (10 mL) was added <sup>s</sup>PB (0.2 g, 0.44 mmol) in dichloromethane (10 mL) and the reaction mixture allowed to stir at room temperature for 18 h. Subsequently, the solution was evaporated to dryness *in vacuo*, washed with 40 : 60 petroleum ether and the resulting yellow solid crystallised from dichloromethane–methanol. Yield = 0.25 g (74%). <sup>31</sup>P{<sup>1</sup>H} NMR (121.7 MHz, CDCl<sub>3</sub>, 353 K):  $\delta$  = -5.46 (s) ppm. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.01 (s, 3H, CH<sub>3</sub>), 1.16 (d, 3H, J = 6.7 Hz, CH<sub>3</sub>), 1.21 (d, 3H, J = 6.8 Hz, CH<sub>3</sub>), 2.08 (s, 3H, CH<sub>3</sub>), 2.24 (s, 6H, CH<sub>3</sub>), 2.85 (septet, 1H, J = 6.9 Hz, CH), 5.26 (d, 2H, J = 5.9 Hz, CH), 5.40 (d, 2H, J = 6.0 Hz, CH), 6.34 (d,

1H, J = 6.5 Hz, Ar–H), 6.82 (t, 1H, J = 6.5 Hz, Ar–H), 6.93 (m, 6H, Ar–H), 7.37 (t, 2H, J = 7.1 Hz, Ar–H), 7.45 (t, 2H, J = 7.6 Hz, Ar–H), 7.53 (d, 2H, J = Ar–H), 7.69 (d, 2H, J = 17.5 Hz, CH3/5), 8.85 (s, 1H, Ar–H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 19.25$  (s, CH<sub>3</sub>), 21.27 (s, CH<sub>3</sub>), 21.52 (s, CH<sub>3</sub>), 22.30 (s, CH<sub>3</sub>), 30.69 (s, CH<sub>3</sub>), 60.64 (s, C), 80.77 (s, CH), 81.48 (s, CH), 96.82 (s, C), 101.25 (s, C), 123.35 (d, J = 10.1 Hz, CH), 123.60 (s, CH), 126.13 (s, CH), 126.68 (s, CH), 127.81 (s, CH), 128.69 (s, CH), 129.12 (s, CH), 130.90 (s, CH), 135.82 (s, C), 136.88 (s, CH), 137.60 (s, C), 140.18 (s, C), 151.10 (s, C), 153.56 (s, CH) ppm. IR (Nujol): 1260.3, 1093.4, 1027.9, 806.1, 724.1 cm<sup>-1</sup>. ES mass spectrum: (*m*/*z*) 768.2087 [M – Cl + CH<sub>3</sub>CN]<sup>+</sup>. Anal. calcd for C<sub>43</sub>H<sub>43</sub>PCl<sub>2</sub>Ru: C 67.70, H 5.69%. Found: C 66.4, H 5.4%.

#### (1,5-Cyclooctadiene)[4-phenyl-2,10-bis-(2,4-dimethylphenyl)-4H-1,4-ethenophospholine]chloro-rhodium(1), 5

To a solution of  $[Rh(1,5-COD)Cl]_2$  (0.15 mg, 0.22 mmol) in dichloromethane (10 mL) was added \*PB (0.2 g, 0.44 mmol) in dichloromethane (10 mL) and the reaction mixture stirred for 18 h. After removal of all volatile materials in vacuo, the resulting yellow solid was washed with cold 40 : 60 petroleum ether. The desired compound was obtained as a bright yellow solid upon crystallisation from 40 : 60 petroleum ether. Yield = 70 mg (40%). <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, CDCl<sub>3</sub>):  $\delta = -17.52$  (d,  $J_{P-Rh} = 160.8$ Hz) ppm. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.66$  (m, 4H, CH<sub>2</sub>), 2.12 (s, 6H, CH<sub>3</sub>), 2.23 (s, 6H, CH<sub>3</sub>), 2.41 (m, 4H, CH<sub>2</sub>), 3.27 (s, 2H, CH), 5.13 (s, 2H, CH), 6.39 (d, 1H, J = 7.8 Hz, Ar-H), 6.95 (m, 3H, Ar-H), 7.06 (dt, 1H, J = 7.3 Hz, 2.1 Hz, Ar-H), 7.18 (m, 3H, Ar–H), 7.38 (m, 2H, Ar–H), 7.46 (t, 2H, J = 8.0 Hz, Ar–H), 7.54 (d, 2H, J = 7.7 Hz, Ar–H), 7.58 (d, 2H, J = 16.3 Hz, CH3/5), 8.77 (dd, 1H, J = 9.7 Hz, 7.8 Hz, CH-8) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 21.18$  (s, CH<sub>3</sub>), 21.40 (s, CH<sub>3</sub>), 28.03 (s, CH<sub>2</sub>), 32.67 (s, CH<sub>2</sub>), 43.48 (s, CH), 69.24 (d, J = 12.6 Hz, C), 103.99 (d, J = 12.6 Hz, CH), 123.96 (s, CH), 124.03 (s, CH), 126.25 (s, CH), 127.06 (s, CH), 127.77 (s, CH), 128.69 (s, CH), 129.12 (s, CH), 129.62 (d, J = 5.0 Hz, CH), 130.56 (s, CH), 131.21(s, C), 134.32 (d, J = 18.9 Hz, CH), 135.59 (s, C), 136.19 (d, J = 13.8 Hz, C), 137.47 (s, C), 140.24 (s, C), 149.59 (d, J = 18.9 Hz, C2/6), 151.81 (d, J = 3.8 Hz, CH), 152.50 (s, C) ppm. IR (hexane): 1260.6, 1096.9, 1020.1, 801.8, 722.3 cm<sup>-1</sup>. ES mass spectrum: (m/z)708.2251 [M – Cl + CH<sub>3</sub>CN]<sup>+</sup>. Anal. calcd for  $C_{41}H_{41}PClRh$ : C 70.03, H 5.89%. Found: C 69.0, H 5.5%.

#### (1,5-Cyclooctadiene)[4-phenyl-2,10-bis-(2,4-dimethylphenyl)-4H-1,4-ethenophospholine]chloroiridium(1), 6

The Ir complex, **6**, was synthesised as for the rhodium complex above using [Ir(1,5-COD)Cl]<sub>2</sub> (0.15 mg, 0.22 mmol) and <sup>x</sup>PB (0.2 g, 0.44 mmol) in dichloromethane (20 mL). The desired compound was isolated as a yellow solid. Yield = 70 mg (40%). <sup>31</sup>P NMR (202.5 MHz, CDCl<sub>3</sub>):  $\delta = -24.09$  (s) ppm. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.21$  (m, 4H, CH<sub>2</sub>), 1.52 (m, 4H, CH<sub>2</sub>), 2.09 (s, 6H, CH<sub>3</sub>), 2.22 (s, 6H, CH<sub>3</sub>), 2.93 (dd, 2H, J = 6.6 Hz, 3.4 Hz, CH), 4.73 (m, 2H, CH), 6.42 (d, 1H, J = 7.6 Hz, Ar–H), 6.92 (m, 4H, Ar–H), 7.10 (d, 2H, J = 7.6 Hz, Ar–H), 7.37 (t, 2H, J = 7.2 Hz, Ar–H), 7.45 (t, 3H, J = 7.5 Hz, Ar–H), 7.53 (d, 2H, J = 7.8 Hz, Ar–H), 7.63 (d, 2H, J = 18.3 Hz, CH3/5), 8.76 (dd, 1H, J = 10.5 Hz, 7.3 Hz, CH-8) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz,

CDCl<sub>3</sub>):  $\delta = 21.19$  (s, CH<sub>3</sub>), 21.44 (s, CH<sub>3</sub>), 28.45 (s, CH<sub>2</sub>), 33.58 (s, CH<sub>2</sub>), 52.51 (s, CH), 60.98 (d, J = 11.3 Hz, C), 93.60 (d, J = 15.1 Hz, CH), 124.02 (d, J = 12.6 Hz, CH), 124.85 (d, J = 1.3 Hz, CH), 126.13 (s, CH), 127.14 (s, CH), 127.83 (s, CH), 128.68 (s, CH), 129.15 (s, CH), 129.60 (d, J = 5.0 Hz, CH), 130.47 (s, CH), 132.71 (s, C), 133.85 (d, J = 16.4 Hz, CH), 135.75 (d, J = 3.8 Hz, C), 136.03 (d, J = 12.6 Hz, C), 137.43 (t, J = 15.1 Hz, C), 140.14 (s, C), 149.51 (d, J = 3.8 Hz, C) ppm. IR (hexane): 1260.3, 1091.9, 1019.0, 803.3, 722.2 cm<sup>-1</sup>. ES mass spectrum: (m/z) 798.2815 [M - Cl + CH<sub>3</sub>CN]<sup>+</sup>. Anal. calcd for C<sub>41</sub>H<sub>41</sub>PCIIr: C 62.14, H 5.23%. Found: C 61.8, H 5.3%.

### *cis*-Di[4-phenyl-2,10-bis-(2,4-dimethylphenyl)-4H-1,4-ethenophospholine]dichloroplatinum(II), 7

To a solution of bis-(benzonitrile)dichloroplatinum(II) (0.10 g, 0. 22 mmol) in dichloromethane (10 mL) was added \*PB (0.2 g, 0.44 mmol) and the reaction mixture stirred for 18 h. After evaporation of volatile materials in vacuo, the resulting yellow material was recrystallised from THF to yield 7 as a white solid. Yield = 0.13 g (57%). <sup>31</sup>P NMR (121.7 MHz, CDCl<sub>3</sub>):  $\delta = -27.78$ (s with <sup>195</sup>Pt satellites,  ${}^{1}J_{P-Pt} = 3860$  Hz) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.97$  (s, 12H, CH<sub>3</sub>), 2.24 (s, 12H, CH<sub>3</sub>), 6.46 (d, 2H, J = 7.2 Hz, Ar–H), 6.73 (d, 4H, J = 7.4 Hz, Ar–H), 6.82 (m, 4H, Ar–H), 6.97(m, 8H, Ar–H), 7.29 (d, 4H, J = 7.3 Hz, Ar–H), 7.40 (m, 10H, Ar–H), 8.60 (dd, 2H, J = 12.1 Hz, 7.5 Hz, CH-8) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 20.99$  (s, CH<sub>3</sub>), 21.60 (s, CH<sub>3</sub>), 60.95 (d, J = 16.4 Hz, C), 124.26 (d, J = 5.0 Hz, CH), 124.58 (d, J = 12.6 Hz, CH), 126.80 (s, CH), 128.49 (s, CH), 128.83(s, CH), 129.13 (s, C), 129.31 (s, CH), 131.05 (s, CH), 132.97 (s, CH), 134.38 (s, C), 134.47 (s, CH), 135.32 (s, CH), 135.93 (s, C), 138.30 (s, C), 139.16 (s, C), 147.21 (d, J = 37.7 Hz, C2/6), 151.46 (s, C), 152.61 (s, CH) ppm. IR (Nujol): 1260.3, 1096.3, 1022.1, 806.1, 761.7, 701.0 cm<sup>-1</sup>. Anal. calcd for C<sub>66</sub>H<sub>58</sub>P<sub>2</sub>Cl<sub>2</sub>Pt: C 67.22, H 4.97%. Found: C 66.1, H 4.6%.

# Crystallography

All single-crystal X-ray data was collected at 150 K on a Bruker/Nonius Kappa CCD diffractometer using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å), equipped with an Oxford Cryostream cooling apparatus. The data was corrected for Lorentz and polarization effects and for absorption using SORTAV.<sup>26</sup> Structure solution was achieved by Patterson methods (Dirdiff-99 program system<sup>27</sup>) and refined by full-matrix least-squares on  $F^2$  (SHELXL-97<sup>28</sup>) with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in idealised positions and allowed to ride on the relevant carbon 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. Molecular structures in the figures were drawn with Ortep 3.0 for Windows (version 1.08).<sup>29</sup> Data collection and refinement parameters: Compound 3:  $C_{43}H_{42}FeO_2PSi \cdot PF_6$ , FW = 850.65 g mol<sup>-1</sup>, T = 150(2) K,  $\lambda = 0.71073$  Å, orthorhombic,  $Pna2_1, a = 17.285(4)$  Å, b = 18.104(4) Å, c = 12.811(3) Å, V =4008.8(14) Å<sup>3</sup>, Z = 4,  $\rho$ (calcd) = 1.409 Mg m<sup>-3</sup>, crystal size =  $0.25 \times 0.22 \times 0.20$  mm<sup>3</sup>, reflections collected = 21 094, independent reflections = 7708, R(int) = 0.045, Parameters = 504,  $R_1$  [ $I > 2 \sigma$  (I)] = 0.053,  $wR_2$  [ $I > 2 \sigma$  (I)] = 0.13,  $R_1$  (all data) = 0.066,  $wR_2$  (all data) = 0.13, Flack parameter = 0.01(2). Compound 4: C<sub>43</sub>H<sub>43</sub>Cl<sub>2</sub>PRu·0.5(CH<sub>2</sub>Cl<sub>2</sub>), FW = 805.18 g mol<sup>-1</sup>, T = 150(2) K,  $\lambda = 0.71073$  Å, triclinic,  $P\overline{1}$ , a = 10.238(2) Å, b = 13.693(3) Å, c = 16.451(3) Å,  $\alpha = 107.20(3)^{\circ}$ ,  $\beta = 103.59(3)^{\circ}$ ,  $\gamma = 106.38(3)^{\circ}$ , V = 1982.2(7) Å<sup>3</sup>, Z = 2,  $\rho(\text{calcd}) = 1.349$  Mg m<sup>-3</sup>, crystal size = 0.35 × 0.25 × 0.15 mm<sup>3</sup>, reflections collected = 13 631, independent reflections = 7520,  $R_{\text{int}} = 0.035$ , parameters = 458,  $R_1[I > 2\sigma(I)] = 0.053$ ,  $wR_2$  [ $I > 2\sigma(I)$ ] = 0.14,  $R_1$  (all data) = 0.067,  $wR_2$  (all data) = 0.15.

# Conclusions

We have surveyed the coordination chemistry of 2,6-dixylyl-4phenylphosphabarrelene (<sup>x</sup>PB) with a number of transition metals, hence extending the range of known phosphabarrelene-transition metal complexes. We report for the first time a number of isolated phosphabarrelene complexes ranging from group 6 to group 11. The coordination chemistry of the phosphabarrelene ligand has been established, identifying it as electronically similar to triarylphosphine analogues but sterically slightly less bulky; cone angles have been established in two cases. Rotameric isomerism is observed in a number of complexes and appears to be common.

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