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# Synthesis spectroscopic and structural properties of transition metal complexes of the *o*-xylyl diphosphine $o-C_6H_4(CH_2PPh_2)_2$

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#### Abstract

The systematic coordination chemistry of the wide-angle diphosphine o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> (L<sup>1</sup>) has been investigated with metal ions from Groups 9–11 in order to explore the consequences of the steric demands of the phosphine and its flexibility towards different oxidation states and coordination geometries. The products isolated include the tetrahedral [CoX<sub>2</sub>(L<sup>1</sup>)] (X = Cl, Br or I), the very distorted square planar [Rh(L<sup>1</sup>)<sub>2</sub>]<sup>+</sup>, [M(cod)(L<sup>1</sup>)]<sup>+</sup> (M = Rh or Ir), square planar [NiX<sub>2</sub>(L<sup>1</sup>)] (X = Cl or Br), [M'Cl<sub>2</sub>(L<sup>1</sup>)] (M' = Pd or Pt), the chloro-bridged [Pd<sub>2</sub>Cl<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>]<sup>2+</sup>, [Pd(L<sup>1</sup>)<sub>2</sub>]<sup>2+</sup>, the tetrahedral [M''(L<sup>1</sup>)<sub>2</sub>]<sup>+</sup> (M'' = Cu, Ag or Au) and the dinuclear [(AuCl)<sub>2</sub>(L<sup>1</sup>)]. Chemical oxidation of some of the complexes are described, giving examples of Co(III), Ni(III) and Pt(IV) species. Where possible the products have been characterised by IR, UV–vis, NMR (<sup>1</sup>H, <sup>31</sup>P, <sup>63</sup>Cu and <sup>195</sup>Pt as appropriate) spectroscopies, mass spectrometry and microanalysis. Crystal structures of six representative examples confirm the coordination environments in particular species and illustrate the steric demands of L<sup>1</sup>. L<sup>1</sup> is a versatile ligand which can readily alter its chelate bite angle to accommodate a range of coordination geometries (the P···P distances within the chelate rings varies by >0.5 Å), and the presence of the rigid aromatic ring in the C<sub>4</sub> backbone leads to some preorganisation favouring *cis* chelation. It also shows a preference for low coordination numbers and this results in some unexpected products.

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#### 1. Introduction

The reaction chemistry of sterically demanding wideangle diphosphines is attracting great interest at present owing to the remarkably high catalytic activities exhibited by some transition metal complexes involving these ligands. Major reactions of interest are Rh-catalysed hydroformylation of alkenes, Ni-catalysed hydrocyanation and Pd-catalysed copolymerisation of CO and alkenes. In particular, the P–M–P bite angle plays an important role in determining the selectivity and rates in these catalytic reactions [1,2]. In previous studies platinum metal complexes incorporating the xylyl diphos-

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phine  $o-C_6H_4(CH_2PPh_2)_2$  have been shown to be active catalysts for several different transformations, e.g., platinum-tin catalysed hydroformylation [3], rhodium-catalysed hydrogenation of CO<sub>2</sub> [4] and iridiumcatalysed hydrogenation of aldehydes [5]. Given the level of interest in these systems, it is surprising that the systematic coordination chemistry of  $L^1$  with transition metal ions has been rather neglected. Initial studies on the complexation of L<sup>1</sup> with medium and low valent late transition metal centres were conducted by Venanzi and co-workers [6,7] who reported the preparations of some mononuclear derivatives and dinuclear halideand hydride-bridged complexes. Example, include the structurally characterised  $[Ag_2X_2(L^1)_2]$  (X = Cl or I) which involve distorted tetrahedral coordination at Ag(I) via two halides and a chelating  $L^1$ , and the Pt(0) complex,  $[Pt(H_2 C=CH_2)(L^1)]$  [8]. Werner et al. [9–11]

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have reported a number of other platinum metal complexes of  $L^1$  with various organic co-ligands, while sulfido- and selenido-Ru and Fe carbonyl clusters, which result from chalcogen transfer from the phosphine sulfide or selenide derivatives of  $L^1$  to the metal centre, have also been reported [12,13].

In this paper we describe a systematic study of the coordination of  $L^1$  with metal ions from Groups 9–11, including their syntheses and spectroscopic properties. The transition metal ions studied adopt square planar, tetrahedral, linear and octahedral coordination geometries and thus allow the ligating properties of the *o*-xylyl diphosphine to be probed. Comparisons are drawn with the ligating properties of the related flexible C<sub>4</sub>-diphosphine, Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub> (dppb), and the more rigid *o*-phenylene derivative *o*-C<sub>6</sub>H<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub>.

#### 2. Results and discussion

The diphosphine  $L^1$  was prepared in high yield as a white solid by a slight modification of the literature method [8] involving reaction of Ph<sub>2</sub>PLi with o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub> in thf solution. In solution  $L^1$  is quite air-sensitive, hence all measurements and subsequent reactions used deoxygenated solutions and Schlenk techniques.

#### 2.1. Co, Rh and Ir complexes

Treatment of an isopropanol solution of CoX<sub>2</sub> (X = Cl, Br or I) with one mol equiv. of  $L^1$  under  $N_2$ affords the distorted tetrahedral  $[CoX_2(L^1)]$  as brightly coloured blue, green or brown-green solids, respectively, in good yield. The formulation follows from the microanalytical data, <sup>1</sup> while magnetic measurements are consistent with high spin Co(II) species. The UV-vis spectra show absorptions consistent with tetrahedral Co(II) [14,15], and the spectra are the same in the solid state and in CH2Cl2 solution. The far IR spectrum of  $[CoCl_2(L^1)]$  shows a broad peak at 318 cm<sup>-1</sup>, consistent with v(Co-Cl). The distorted tetrahedral coordination with one chelating  $L^1$  is confirmed in the solid state by a structure determination on a very small crystal of  $[CoCl_2(L^1)]$  (Fig. 1, Table 1). The Co–P bond distances are 2.3795(16) and 2.4034(16) A, while d(Co-Cl = 2.2045(15) and 2.2165(15) Å.



Fig. 1. View of the structure of  $[CoCl_2(L^1)]$  with numbering scheme adopted. H atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level.

| Table 1      |               |              |                        |           |
|--------------|---------------|--------------|------------------------|-----------|
| Selected bon | d lengths (Å) | and angles ( | <sup>(°)</sup> for [Co | $Cb(L^1)$ |

| 2.2045(15) |
|------------|
| 2.2165(15) |
| 2.3795(16) |
| 2.4034(16) |
| 1.810(5)   |
| 1.811(5)   |
| 1.851(5)   |
| 1.815(5)   |
| 1.817(5)   |
| 1.840(5)   |
|            |
| 109.50(6)  |
| 111.52(6)  |
| 103.26(5)  |
| 114.64(6)  |
| 111.13(6)  |
| 106.18(5)  |
| 106.1(2)   |
| 103.1(2)   |
| 102.0(2)   |
| 115.43(17) |
| 115.45(16) |
| 113.18(17) |
| 104.7(2)   |
| 105.1(2)   |
| 103.7(2)   |
| 107.68(16) |
| 119.13(16) |
| 115.25(17) |
|            |

The related, but more rigid *o*-phenylene diphosphine,  $o-C_6H_4(PPh_2)_2$ , gives planar cations  $[Co\{o-C_6H_4-(PPh_2)_2\}_2][CoX_4]$  and 5-coordinate  $[Co\{o-C_6H_4-(PPh_2)_2\}_2X]^+$  on reaction with Co(II) halides, reflecting

<sup>&</sup>lt;sup>1</sup> We note that microanalytical data for several of the complexes are consistent with there being some  $CH_2Cl_2$  solvent associated with the compounds even after drying in vacuo. For the diamagnetic complexes, there is evidence for  $CH_2Cl_2$  in the <sup>1</sup>H NMR spectra, and indeed four of the crystal structures show two molecules of  $CH_2Cl_2$  (or  $CHCl_3$ ) solvent per metal ion. Thus, we conclude that the steric bulk of the coordinated  $L^1$  probably leaves considerable voids in the lattice which can accommodate solvent molecules.

both the stronger ligand field imposed and the 5-membered chelate rings present [15], whereas larger chelate rings give tetrahedral Co(II) (as in  $[CoX_2(L^1)]$  above) [16]. We note that an early assignment [16] of the product from reaction of CoCl<sub>2</sub> with dppe (Ph<sub>2</sub>PCH<sub>2</sub>-CH<sub>2</sub>PPh<sub>2</sub>) as  $[CoCl_2(dppe)]$  was in error and the compound was subsequently shown to be the phosphine oxide complex [17].

Low temperature oxidation of a  $CH_2Cl_2$  solution of  $[CoCl_2(L^1)]$  with NOCl gives the Co(III) species  $[CoCl_3(L^1)]$  as a deep blue-green solid. The electronic spectrum of this product is characteristic of the rare 5-coordinate geometry and the  $Cl_3P_2$  donor set [18]. The far IR spectrum shows the three Co–Cl bands expected. The Co(III) compound decomposes slowly in  $CH_2Cl_2$  solution at room temperature.

In an attempt to explore the coordination chemistry of rhodium with  $L^1$  we reacted RhCl<sub>3</sub>·3H<sub>2</sub>O with two molar equivalents of  $L^1$  in EtOH solution in the presence of a few drops of 40% aqueous HBF<sub>4</sub>. Stirring at room temperature for approximately 30 min gave an orange solution and concentration of this solution in vacuo afforded an orange solid. The IR spectrum shows peaks associated with coordinated  $L^1$  and BF<sub>4</sub><sup>-</sup> anion. Inspection of the far IR region did not reveal any significant peaks due to Rh–Cl bonds. The electrospray mass spectrum (MeCN) shows peaks with the correct isotope distribution for  $[Rh(L^1)_2]^+$  and  $[Rh(L^1)]^+$ , however again there is no evidence for any Cl containing species or significant higher mass peaks.

The <sup>1</sup>H NMR spectrum shows the ligand resonances shifted to high frequency upon coordination, while the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of this product is a sharp doublet at +11.6 ppm, indicative of one P environment, with <sup>1</sup>J<sub>RhP</sub> = 140 Hz. This large coupling constant, together with the mass spectrometry data were unexpected for a Rh(III) species, but more in line with the values expected for a planar Rh(I) derivative with more s-orbital character in the Rh(I)–P bond (sp<sup>2</sup>d hybridisation). This result prompted us to seek X-ray structural data to authenticate our assignment of the product as  $[Rh(L^1)_2]BF_4$ .

Orange single crystals were obtained by layering a CHCl<sub>3</sub> solution of the complex with hexane. The structure shows (Fig. 2, Table 2) two chelating  $L^1$  units bound to the Rh centre in a distorted square planar arrangement, with no evidence for other co-ligands. One BF<sub>4</sub><sup>-</sup> anion and two CHCl<sub>3</sub> solvent molecules also occupy general positions in the asymmetric unit, consistent with a Rh(I) complex. The Rh-P bond distances are in the range 2.31–2.34 A. These are in accord with d(Rh-P) in other Rh(I) phosphine complexes, e.g., [RhCl- $(PPh_3)_3$ ]  $d(Rh-P_{transP}) = 2.304-2.338$  Å [19,20]. The sum of the P-Rh-P angles is 370°, indicating a significant tetrahedral distortion, which probably results from the significant steric requirements of the two bulky  $L^{1}$  ligands. The P1...P2 and P3...P4 distances within the chelates are 3.28 and 3.37 Å, and the P1-Rh-P2 and P3-Rh-P4 angles are 90.05(3) and 92.31(3) Å, respectively.

The formation of the bis-diphosphine Rh(I) cation under these reaction conditions is unexpected as this is the method used to obtain the Rh(III) species [RhCl<sub>2</sub>-(L-L)<sub>2</sub>]<sup>+</sup> (L-L = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, o-C<sub>6</sub>H<sub>4</sub>-(PPh<sub>2</sub>)<sub>2</sub>) [21,22]. The different reaction course may also be a consequence of the steric bulk imposed by the wide angle diphosphine L<sup>1</sup>, which disfavours formation of the 6-coordinate Rh(III) dichloro derivative. The preparation of the very well known Wilkinson's compound, [RhCl(PPh<sub>3</sub>)<sub>3</sub>], is however readily achieved by reaction of RhCl<sub>3</sub>·3H<sub>2</sub>O with excess PPh<sub>3</sub> in ethanol [23].

We note also that a CCl<sub>4</sub> suspension of the  $[Rh(L^1)_2]BF_4$  is not oxidised when treated with Cl<sub>2</sub> saturated CCl<sub>4</sub> at room temperature (monitored by <sup>31</sup>P NMR spectroscopy).



Fig. 2. View of the structure of the  $[Rh(L^1)_2]^+$  cation with numbering scheme adopted. H atoms and phenyl rings (except the *ipso* C atoms) are omitted for clarity. Ellipsoids are shown at the 50% probability level.

Table 2

Selected bond lengths (Å) and angles (°) for  $[Rh(L^1)_2]BF_4 \cdot 2CHCl_3$ 

| Bond lengths |            |
|--------------|------------|
| Rh1–P2       | 2.3099(10) |
| Rh1–P1       | 2.3269(10) |
| Rh1–P4       | 2.3352(10) |
| Rh1–P3       | 2.3427(10) |
| P1-C7        | 1.818(4)   |
| P1-C1        | 1.833(4)   |
| P1-C25       | 1.855(4)   |
| P2-C19       | 1.830(4)   |
| P2-C32       | 1.837(4)   |
| P2-C13       | 1.847(4)   |
| P3-C39       | 1.840(4)   |
| P3-C33       | 1.842(4)   |
| P3-C57       | 1.855(4)   |
| P4-C45       | 1.828(4)   |
| P4-C51       | 1.833(4)   |
| P4-C64       | 1.854(4)   |
| Bond angles  |            |
| P2-Rh1-P1    | 90.05(3)   |
| P2-Rh1-P4    | 158.54(3)  |
| P1-Rh1-P4    | 92.70(3)   |
| P2-Rh1-P3    | 93.98(3)   |
| P1-Rh1-P3    | 155.45(4)  |
| P4–Rh1–P3    | 92.31(3)   |
| C7–P1–C1     | 102.58(17) |
| C7–P1–C25    | 97.91(17)  |
| C1-P1-C25    | 102.09(17) |
| C7–P1–Rh1    | 115.19(12) |
| C1–P1–Rh1    | 122.96(12) |
| C25–P1–Rh1   | 112.54(12) |
| C19–P2–C32   | 103.10(16) |
| C19–P2–C13   | 95.41(16)  |
| C32–P2–C13   | 105.02(17) |
| C19–P2–Rh1   | 116.97(12) |
| C32–P2–Rh1   | 119.44(12) |
| C13–P2–Rh1   | 113.61(12) |
| C39–P3–C33   | 98.12(16)  |
| C39–P3–C57   | 103.34(19) |
| C33–P3–C57   | 102.59(17) |
| C39–P3–Rh1   | 104.85(13) |
| C33–P3–Rh1   | 121.61(12) |
| C57–P3–Rh1   | 122.25(12) |
| C45–P4–C51   | 105.85(17) |
| C45–P4–C64   | 96.21(17)  |
| C51-P4-C64   | 99.38(17)  |
| C45–P4–Rh1   | 112.34(13) |
| C51–P4–Rh1   | 121.99(12) |
| C64–P4–Rh1   | 117.36(12) |

The reaction of L<sup>1</sup> with 0.5 mol equiv. of the Rh(I) dimer [Rh<sub>2</sub>Cl<sub>2</sub>(cod)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub> solution in the presence of NH<sub>4</sub>PF<sub>6</sub> yields, after work-up, the Rh(I) species [Rh(cod)(L<sup>1</sup>)]PF<sub>6</sub> as an orange solid in good yield. The IR spectrum confirms the presence of the anionic PF<sub>6</sub><sup>-</sup> as well as coordinated L<sup>1</sup>. Phosphorus-31 NMR spectroscopy of this species shows a sharp doublet at +10.3 ppm (<sup>1</sup>J<sub>RhP</sub> = 146 Hz) and a septet at -145 ppm from the PF<sub>6</sub><sup>-</sup> anion. Evidence for the cod ligation comes from the <sup>1</sup>H NMR spectrum which also confirms a 1:1 L<sup>1</sup>:cod ratio. The Rh–P coupling constant is comparable to that for [Rh(L<sup>1</sup>)<sub>2</sub>]<sup>+</sup> described above, and the

<sup>31</sup>P NMR shift is also similar, further supporting the earlier assignments.

The analogous reaction using  $[Ir_2Cl_2(cod)_2]$  with 0.5 mol equiv. of L<sup>1</sup> in CH<sub>2</sub>Cl<sub>2</sub> and NH<sub>4</sub>PF<sub>6</sub> gives the corresponding Ir(I) complex  $[Ir(cod)(L^1)]PF_6$  as an orangered solid in good yield ( $\delta^{31}P = -1.8$  (L<sup>1</sup>); electrospray MS m/z 775  $[Ir(cod)(L^1)]^+$ .

#### 2.2. Ni, Pd and Pt complexes

The hydrated Ni(II) halides NiX<sub>2</sub>·xH<sub>2</sub>O (X = Cl or Br) react with one mol equiv. of L<sup>1</sup> in isopropanol to give deep red solids with formation [NiX<sub>2</sub>(L<sup>1</sup>)] in good yield. These are similar to the species described previously by Venanzi and co-workers, who assigned them as tetrahedral apparently on the basis that they did not give NMR spectra [7,8]. However, from the diffuse reflectance electronic spectra which show one d–d transition, we assign them as square planar compounds. The far IR spectra show two peaks which are assigned as Ni– X stretching vibrations, indicative of a *cis*-NiX<sub>2</sub> unit. These data, together with <sup>1</sup>H NMR and microanalyses, confirm the assignment of these compounds as square planar Ni(II) species with a chelating L<sup>1</sup> and mutually *cis* halides.

The square planar geometry identified for  $[NiX_2(L^1)]$ is somewhat unexpected given that the corresponding Ni(II) complexes with the flexible dppb ligand,  $[NiX_2(dppb)]$  (also incorporating a 7-membered chelate ring) [24] adopt tetrahedral geometries. Therefore, it appears that the increased rigidity of L<sup>1</sup> over dppb results in a preference for square planar coordination. The *o*phenylene diphosphine in  $[NiX_2\{o-C_6H_4(PPh_2)_2\}]$  (5membered chelate ring) which exerts a strong ligand field, leads to square planar coordination at Ni(II) [25].

An attempt to generate the 5-coordinate Ni(II) species  $[NiI(L^1)_2](CIO_4)$  through reaction of NiI<sub>2</sub> and Ni- $(CIO_4)_2 \cdot 6H_2O$  with four mol equiv. of L<sup>1</sup>, using the method described by Meek and co-workers [26] for other diphosphines was unsuccessful. Similarly, we were unable to isolate the square planar bis-L<sup>1</sup> species  $[Ni(L^1)_2](CIO_4)_2$ .

The deep orange-brown, unstable Ni(III) species  $[NiCl_3(L^1)]$  was obtained by NOCl oxidation of  $[NiCl_2(L^1)]$ . The formulation follows from the electronic spectrum, which is characteristic of the 5-coordinate molecule, and the IR spectrum which shows v(Ni-Cl) in the same region as previously reported Ni(III) species [27].

Dissolution of Na<sub>2</sub>[PdCl<sub>4</sub>] in EtOH followed by addition of one mol equiv. of L<sup>1</sup> results in formation of a cream coloured precipitate with formulation [PdCl<sub>2</sub>(L<sup>1</sup>)]. The far IR spectrum of this compound shows two peaks in the region expected for v(Pd–Cl), indicative of a *cis*-PdCl<sub>2</sub> unit. The <sup>1</sup>H NMR spectrum is unexceptional, showing small high frequency shifts upon coordination of L<sup>1</sup>, while the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a singlet at 16.4 ppm, in accord with the data obtained by Venanzi and co-workers [8] and assigned as [PdCl<sub>2</sub>(L<sup>1</sup>)]. The crystal structure of this compound (Fig. 3, Table 3) confirms a distorted square planar coordination environment at Pd(II) through one chelating L<sup>1</sup> ligand and mutually *cis* Cls. The molecule has crystallographic *m* symmetry, with d(Pd-P) = 2.2572(11) and d(Pd-Cl) = 2.3536 Å. The P1-Pd-P1' angle in the chelate of 100.04(6)° is much more obtuse than those seen in the Rh(I) species described above, reflecting the considerable reduction in steric



Fig. 3. View of the structure of  $[PdCl_2(L^1)]$  with numbering scheme adopted. Ellipsoids are drawn at 50% probability and H atoms are omitted for clarity (symmetry operation: ', x, 1/2 - y, z).

Table 3 Selected bond lengths (Å) and angles (°) for  $[PdCl_2(L^1)]$ 

| Selected cond lenguis () and ang |            |
|----------------------------------|------------|
| Bond lengths                     |            |
| Pd1–P1                           | 2.2572(11) |
| Pd1-Cl1                          | 2.3536(11) |
| P1C1                             | 1.813(4)   |
| P1-C7                            | 1.818(4)   |
| P1C13                            | 1.835(4)   |
| Bond angles                      |            |
| P1–Pd1–P1′                       | 100.04(6)  |
| P1-Pd1-Cl1′                      | 174.91(4)  |
| P1–Pd1–Cl1                       | 84.95(4)   |
| Cl1–Pd1–Cl1′                     | 90.04(5)   |
| C1-P1-C7                         | 108.26(19) |
| C1-P1-C13                        | 102.1(2)   |
| C7-P1-C13                        | 103.3(2)   |
| C1–P1–Pd1                        | 111.79(14) |
| C7–P1–Pd1                        | 109.05(14) |
| C13-P1-Pd1                       | 121.43(14) |

Symmetry operation: ', x, 1/2 - y, z.

demand when the metal centre only needs to accommodate one L<sup>1</sup> rather than two. The P1···P1' distance of 3.46 Å is larger than in  $[Rh(L^1)_2]^+$  above.

Attempts to abstract both the Cl's from  $[PdCl_2(L^1)]$  in MeCN solution using 2.1 mol equiv. of TIPF<sub>6</sub> were not successful – the only identifiable Pd-containing species after work-up being the dinuclear  $[Pd_2Cl_2(L^1)_2](PF_6)_2$ . This complex was prepared in good yield by reaction of  $[PdCl_2(NCMe)_2]$  with one mol equiv. of L<sup>1</sup> and one mol equiv. of TIPF<sub>6</sub> in MeCN/CH<sub>2</sub>Cl<sub>2</sub>. Removal of the TlCl precipitate left a light yellow solution from which the complex was obtained as a yellow solid following work-up. The IR, <sup>1</sup>H NMR spectroscopic and microanalytical data are consistent with the formulation  $[Pd_2Cl_2(L^1)_2](PF_6)_2$ . The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of this compound shows a singlet at 27.3 ppm, significantly to high frequency of the mononuclear  $[PdCl_2(L^1)]$ above.

The structure of  $[Pd_2Cl_2(L^1)_2](PF_6)_2$ .  $2CH_2Cl_2$  shows (Fig. 4, Table 4) a dinuclear ( $\mu^2$ -Cl)<sub>2</sub> palladium dication with a chelating L<sup>1</sup> bound to each Pd centre to give a distorted square planar geometry. The dication is centrosymmetric, the centre of inversion in the middle of the Pd\_2Cl\_2 core. The Pd–P bond distances are 2.2481(10) and 2.2657(10) Å, very similar to d(Pd-P)in the mononuclear complex above. The P1–Pd–P2 angle in this species is 98.00(4)° and  $d(P1\cdots P2)$  is 3.41 Å.

The homoleptic bis-ligand ion  $[Pd(L^1)_2]^{2+}$  was subsequently prepared by addition of an aqueous solution of Pd(NO<sub>3</sub>)<sub>2</sub> to two mol equiv. of L<sup>1</sup> in EtOH/CH<sub>2</sub>Cl<sub>2</sub> solution, followed by addition of aqueous HBF<sub>4</sub>. The IR spectrum of the yellow solid isolated shows peaks consistent with coordinated L<sup>1</sup> and ionic BF<sub>4</sub><sup>-</sup>, with no evidence for any remaining nitrate or H<sub>2</sub>O/OH<sup>-</sup> in the product. The <sup>1</sup>H NMR spectrum only shows resonances due to L<sup>1</sup>. These are shifted to high frequency of the 'free' ligand. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of this



Fig. 4. View of the structure of the centrosymmetric  $[Pd_2Cl_2(L^1)_2]^{2+}$  cation with numbering scheme adopted. H atoms are omitted for clarity. Ellipsoids are drawn at 50% probability (symmetry operation: ', - x, 2 - y, 1 - z).

Table 4

Selected bond lengths (Å) and angles (°) for  $[Pd_2Cl_2(L^1)_2](PF_6)_2\cdot 2CH_2Cl_2$ 

| Bond lengths |            |
|--------------|------------|
| Pd1–P1       | 2.2481(10) |
| Pd1–P2       | 2.2657(10) |
| Pd1-Cl1      | 2.3917(10) |
| P1-C1        | 1.818(4)   |
| P1-C7        | 1.821(4)   |
| P1-C25       | 1.821(4)   |
| P2-C13       | 1.802(4)   |
| P2C19        | 1.818(4)   |
| P2-C32       | 1.830(4)   |
| Bond angles  |            |
| P1-Pd1-P2    | 98.00(4)   |
| P1-Pd1-Cl1   | 168.73(4)  |
| P2-Pd1-Cl1   | 90.93(4)   |
| P1-Pd1-Cl1′  | 88.11(4)   |
| P2-Pd1-Cl1′  | 172.66(4)  |
| Cl1–Pd1–Cl1′ | 83.52(4)   |
| Pd1–Cl1–Pd1′ | 96.48(3)   |
| C1-P1-C7     | 106.36(19) |
| C1-P1-C25    | 108.45(19) |
| C7–P1–C25    | 100.83(18) |
| C1–P1–Pd1    | 108.46(14) |
| C7–P1–Pd1    | 109.03(13) |
| C25-P1-Pd1   | 122.51(14) |
| C13-P2-C19   | 107.65(19) |
| C13–P2–C32   | 104.80(18) |
| C19–P2–C32   | 104.87(18) |
| C13–P2–Pd1   | 114.78(14) |
| C19–P2–Pd1   | 103.67(13) |
| C32–P2–Pd1   | 120.10(13) |
|              |            |

Symmetry operation: ', 2 - x, 2 - y, 1 - z.

P<sub>4</sub>-coordinated species shows a singlet at 7.1 ppm. These data, together with microanalyses, are consistent with the formulation  $[Pd(L^1)_2](BF_4)_2$ . The Pd(II) centre is likely to be rather crowded, however this formulation is not unreasonable given the structural evidence for distorted planar  $[Rh(L^1)_2]^+$  cation described above.

The Pt(II) species [PtCl<sub>2</sub>(L<sup>1</sup>)] is formed in high yield by addition of a solution of K<sub>2</sub>[PtCl<sub>4</sub>] to one mol equiv. of L<sup>1</sup> in CH<sub>2</sub>Cl<sub>2</sub>/EtOH. Acetone was then added to give a homogeneous solution which was stirred for 72 h before filtering and concentrating the filtrate in vacuo to give a white solid. The <sup>1</sup>H NMR spectrum is unexceptional and the far IR spectrum shows two peaks, indicating a *cis*-PtCl<sub>2</sub> unit. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a singlet at -1.8 ppm with <sup>195</sup>Pt satellites (J = 3584 Hz), consistent with the literature data [8]. Confirmation that the product is indeed the neutral [PtCl<sub>2</sub>(L<sup>1</sup>)] and not the dinuclear [Pt<sub>2</sub>Cl<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>]Cl<sub>2</sub> (cf. the Pd analogue above) comes from conductivity measurements which show that in MeNO<sub>2</sub> solution the complex is a non-electrolyte. The <sup>195</sup>Pt NMR spectrum shows a triplet at -4503 ppm, in accord with a P<sub>2</sub>Cl<sub>2</sub> donor set at Pt(II) [28].

Treatment of a  $CCl_4$  suspension of  $[PtCl_2(L^1)$  with excess  $Cl_2$  saturated  $CCl_4$  gives the Pt(IV) species

[PtCl<sub>4</sub>(L<sup>1</sup>)] as a yellow solid. This formulation follows from the far IR spectrum and the microanalysis. The Pt(IV) complex readily reverts to [PtCl<sub>2</sub>(L<sup>1</sup>)] in solution (as observed by <sup>31</sup>P NMR spectroscopy), and the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum measured in CH<sub>2</sub>Cl<sub>2</sub> solution in the presence of Cl<sub>2</sub> shows  $\delta$  –4.8, <sup>1</sup>*J*<sub>PtP</sub> = 2170 Hz, consistent with a PtCl<sub>4</sub>(L<sup>1</sup>) composition [28,29]. Similar treatment of [PdCl<sub>2</sub>(L<sup>1</sup>)] did not result in a colour change, and the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum is unchanged.

#### 2.3. Cu, Ag and Au complexes

Reaction of [Cu(NCMe)<sub>4</sub>]BF<sub>4</sub> or AgBF<sub>4</sub> with two molar equivalents of  $L^1$  in  $CH_2Cl_2$  solution in the dark affords colourless solutions from which the homoleptic phosphine complexes  $[Cu(L^1)_2](BF_4)$  and  $[Ag(L^1)_2](BF_4)$ were obtained in high yield. The 2:1 L<sup>1</sup>:M composition follows from microanalyses and from the magnitude of the  ${}^{107/109}$ Ag $-{}^{31}$ P coupling constants in the  ${}^{31}$ P $\{{}^{1}$ H $\}$ NMR spectra - below. Electrospray mass spectrometry (MeCN) shows the only significant species in each case is  $[M(L^{1})_{2}]^{+}$ , with much weaker fragment peaks corresponding to  $[M(L^1)]^+$ . The <sup>1</sup>H NMR spectra for these compounds each show small high frequency shifts in the  $CH_2$  resonance compared to  $L^1$  itself, and the aromatic protons appear as a broad overlapping multiplet. The  ${}^{31}P{}^{1}H{}$  NMR spectrum of the Cu(I) complex shows a single broad resonance at -8.7 ppm, giving a small high frequency coordination shift. A pseudo-tetrahedral bis-L<sup>1</sup> coordination environment at Cu(I) is confirmed by the observation of a broad <sup>63</sup>Cu NMR resonance at +193 ppm which does not change significantly upon cooling. Phosphorus-copper coupling is not observed in either the  ${}^{31}P{}^{1}H$  or  ${}^{63}Cu$  NMR spectra. This chemical shift is typical of a P<sub>4</sub>-donor set at Cu(I) and compares with +150 ppm for [Cu- $(Ph_2PCH_2CH_2PPh_2)_2$ <sup>+</sup> and +231 ppm for  $[Cu(dppp)_2]^+$ , although no <sup>63</sup>Cu NMR resonance has been observed for [Cu(dppb)<sub>2</sub>]<sup>+</sup> between 300 and 175 K, probably due to reversible chelate ring-opening [30]. The  ${}^{31}P{}^{1}H$  NMR spectrum of the Ag(I) complex reveals two overlapping doublets at room temperature at -1.5 ppm, giving  ${}^{1}J({}^{107}\text{Ag}{}^{-31}\text{P}) = 226$  Hz and  ${}^{1}J({}^{109}\text{Ag}{}^{-31}\text{P}) = 257 \text{ Hz}$ , indicating that ligand exchange and/or dissociation are slow on the NMR time-scale. Furthermore, the magnitude of the coupling constants provides a good indication of the coordination environment at Ag. In this species the coupling constants are consistent with tetrahedral P<sub>4</sub>-coordination in solution (compare for example the tetrahedral  $[Ag(dppe)_2]^+$  $J(^{107}\text{Ag}-^{31}\text{P}) = 231$  and  $J(^{109}\text{Ag}-^{31}\text{P}) = 266$  Hz) [31]. The dihalo-bridged complexes  $[Ag_2Cl_2(L^1)_2]$  (distorted tetrahedral P<sub>2</sub>Cl<sub>2</sub> coordination) give  $J(^{107}Ag^{-31}P) =$  359 and  $J(^{109}Ag^{-31}P) =$  413 Hz, small reductions in the J values occur as the Cl is replaced by Br or I [6].

The coordination environment at Ag(I) was subsequently confirmed by a crystal structure determination on  $[Ag(L^{1})_{2}](BF_{4}) \cdot CH_{2}Cl_{2}$ . The structure of the cation shows (Fig. 5, Table 5) two  $L^1$  ligands coordinated in a bidentate manner to Ag(I), giving a distorted tetrahedral coordination environment, consistent with the solution spectroscopic studies. The Ag-P bond distances are in the range 2.47–2.54 Å, while the P1–Ag–P2 and P3– Ag–P4 chelate angles are 102.88(3)° and 104.21(3)°, only slightly larger than those observed in the 1:1 Pd:L<sup>1</sup> complexes above, but some  $10^{\circ}$ -12° larger than in the bis-L<sup>1</sup> complex  $[Rh(L^1)_2]BF_4$ . The obtuse angles within the chelate rings in  $[Ag(L^1)_2]^+$  are also confirmed by the  $P1 \cdots P2$  and  $P3 \cdots P4$  distances of 3.90 and 3.96 Å, respectively. These are over 0.5 Å larger than in  $[Rh(L^{1})_{2}]^{+}$ , reflecting the structural flexibility of the 7-membered chelate ring incorporating the somewhat rigid *o*-xylyl unit.

The structures of the Ag(I) complexes  $[Ag_2X_2(L^1)_2]$ (X = Cl or I) have been described previously. These both show distorted tetrahedral coordination at Ag(I) via two bridging X ligands and a chelating L<sup>1</sup>, with d(Ag-P)very similar to those seen here for  $[Ag(L^1)_2]^+$  (X = Cl: d(Ag-P) = 2.446(1), 2.450(2) Å; X = I: d(Ag-P) =2.487(1), 2.493(2) Å), although the P-Ag-P angles within the chelate rings are closer to the ideal tetrahedral value in the halo-bridged complexes. Again, this probably reflects the reduction in steric bulk when only one L<sup>1</sup> is present on the Ag centre [6].

The analogous Au(I) complex  $[Au(L^1)_2]PF_6$  was obtained in good yield as a white solid by reaction of [AuCl(tht)] with two mol equiv. of L<sup>1</sup> and one mol equiv. of TlPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution. The electrospray mass spectrum reveals a cluster of peaks with the correct isotope distribution at ca. 1145, consistent with  $[Au(L^1)_2]^+$ , with a lower intensity cluster corresponding to a fragment ion derived from loss of one L<sup>1</sup>, while the IR spectrum shows the presence of ionic PF<sub>6</sub><sup>-</sup>, but no



Fig. 5. View of the structure of the  $[Ag(L^1)_2]^+$  cation with numbering scheme adopted. Ellipsoids are drawn at 50% probability and H atoms and phenyl rings (except the *ipso* C atoms) are omitted for clarity.

Table 5 Selected bond lengths (Å) and angles (°) for  $[Ag(L^1)_2]BF_4$ 

| Bond lengths                                 |                          |
|--|--------------------------|
| Ag1-P1                                       | 2.4691(9)                |
| Ag1–P4                                       | 2.4787(9)                |
| Ag1–P2                                       | 2.5222(9)                |
| Ag1–P3                                       | 2.5385(9)                |
| P1-C1  | 1.821(4)                 |
| P1-C7  | 1.827(4)                 |
| P1-C49                                       | 1.856(4)                 |
| P2-C13                                       | 1.825(4)                 |
| P2-C19                                       | 1.829(4)                 |
| P2-C56                                       | 1.856(4)                 |
| P3-C25                                       | 1.830(4)                 |
| P3-C31                                       | 1.833(4)                 |
| P3-C57                                       | 1.857(4)                 |
| P4-C43                                       | 1.821(4)                 |
| P4-C37                                       | 1.826(4)                 |
| P4-C64                                       | 1.863(4)                 |
| Bond angles                                  |                          |
| P1-Ag1-P4                                    | 124.76(3)                |
| P1–Ag1–P2                                    | 102.88(3)                |
| P4–Ag1–P2                                    | 108.32(3)                |
| P1–Ag1–P3                                    | 110.69(3)                |
| P4-Ag1-P3                                    | 104.21(3)                |
| P2–Ag1–P3                                    | 104.37(3)                |
| C1–P1–C7                                     | 101.21(17)               |
| C1–P1–C49                                    | 104.64(16)               |
| C7–P1–C49                                    | 104.40(17)               |
| Cl–Pl–Agl                                    | 117.74(12)               |
| C7–P1–Ag1                                    | 114.77(12)               |
| C49–P1–Agl                                   | 112.52(12)               |
| C13–P2–C19                                   | 102.14(17)               |
| C13–P2–C56                                   | 102.08(16)               |
| C19–P2–C56                                   | 105.35(17)               |
| Cl3–P2–Agl                                   | 123.17(13)               |
| CI9–P2–Agi                                   | 112.89(12)               |
| C56–P2–Agi                                   | 109.45(12)               |
| C25-P3-C31                                   | 101.35(17)               |
| $C_{25} = P_{3} = C_{57}$                    | 104.86(17)               |
| $C_{31} = P_{3} = C_{37}$                    | 100.45(17)               |
| C25-P3-Agi                                   | 112.36(12)               |
| C31-P3-Agi<br>C57 D2 A -1                    | 124.8/(13)               |
| $C_{3/-r_{3}-Ag_{1}}$                        | 110./4(12)<br>104.24(17) |
| C43 - F4 - C57                               | 104.34(17)               |
| $C_{43} = \Gamma_{4} = C_{04}$               | 102.05(16)               |
| $C_{42}$ P4 A $\alpha^1$                     | 102.88(17)<br>110.28(12) |
| $C_{43}$ = $\Gamma_{4}$ = Ag1<br>C 27 D4 Ag1 | 119.38(12)               |
| $C_{1}$ = r4-Agi                             | 110.3/(12)<br>100.72(12) |
| C04-P4-Ag1                                   | 109.72(12)               |

Au–Cl unit. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a singlet at +0.8 ppm due to coordinated L<sup>1</sup> and a septet ( $PF_6^-$ ) at -143.9 ppm with a 4:1 integral ratio. The coordination environment is confirmed from a crystal structure of the complex. The structure of [Au(L<sup>1</sup>)<sub>2</sub>]P-F<sub>6</sub>·2CH<sub>2</sub>Cl<sub>2</sub> shows a distorted tetrahedral cation (Fig. 6, Table 6) derived from two chelating L<sup>1</sup> ligands and giving Au–P bond lengths in the range 2.40–2.43 Å. These bond distances compare very well with the range 2.39–2.42 Å reported for [Au(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]<sup>+</sup> (flattened tetrahedron) [32].



Fig. 6. View of the structure of the  $[Au(L^1)_2]^+$  cation with numbering scheme adopted. Ellipsoids are drawn at 50% probability and H atoms and phenyl rings (except the *ipso* C atoms) are omitted for clarity.

The chelate angles subtended at Au are  $103.62(2)^{\circ}$ and  $103.65(2)^{\circ}$ , with  $d(P1\cdots P2)$  and  $d(P3\cdots P4) = 3.78$ Å. Comparison of this structure with the Ag(I) analogue above reveals a small but significant shortening of the metal-phosphorus bond distances in the 5d Au(I) complex. Similar observations have been made on other related systems [33].

A similar reaction between [AuCl(tht)] and L<sup>1</sup> in a 2:1 ratio and in the absence of TlPF<sub>6</sub> also gives a white, light sensitive solid. The IR spectrum of this compound clearly indicates the presence of terminal Au–Cl units (319 cm<sup>-1</sup>), and its <sup>31</sup>P{<sup>1</sup>H} NMR spectrum is a singlet at 30.5 ppm, very significantly to high frequency of the PF<sub>6</sub><sup>-</sup> salt above. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the related [Au<sub>2</sub>Cl<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)] displays a similar coordination shift, giving  $\delta$ (<sup>31</sup>P) = +31.5 [32]. These data together with <sup>1</sup>H NMR data confirm the formulation as [(AuCl)<sub>2</sub>(L<sup>1</sup>)], probably involving linear Au–Cl coordination at each P atom of a bridging diphosphine.

#### 3. Conclusions

These results show that  $L^1$  is an effective ligand for a range of late transition metal ions, functioning routinely as a chelating bidentate. The steric demands of  $L^1$  favour the formation of lower coordination numbers, and indeed the only bis-L<sup>1</sup> complexes we have isolated involve either distorted square planar or tetrahedral coordination environments and are sterically quite hindered. This factor may also be responsible for formation of the unusual Cl-bridged dimer  $[Pd_2Cl_2(L^1)_2]^{2+}$ , as the Pd(II) centre can more readily accommodate one  $L^1$ and two relatively small Cl ligands rather than two chelating L<sup>1</sup>'s. The presence of the aromatic unit in the ligand backbone leads to increased rigidity relative to the aliphatic dppb, a greater tendency to chelate, and promotes coordination chemistry more akin to the rigid o-phenylene analogue o-C<sub>6</sub>H<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub>. The flexibility of  $L^1$  is also evident from the wide range of  $P \cdots P$  distances

| Table 6<br>Selected bond lengths (Å) and angle | es (°) for $[Au(L^1)_2]PF_6 \cdot 2CH_2Cl_2$ |
|--|--|
| Bond lengths                                   |  |
| Au1–P4   | 2.4006(7)                                    |
| Au1–P1   | 2.4086(7)                                    |
| Au1–P2   | 2.4255(7)                                    |
| Au1–P3   | 2.4301(7)                                    |
| Cl1-C65  | 1.756(4)                                     |
| Cl2-C65  | 1.746(4)                                     |
| Cl3-C66  | 1.726(6)                                     |
| Cl4-C66  | 1.745(5)                                     |
| P1-C1  | 1.822(3)                                     |
| P1-C7  | 1.824(3)                                     |
| P1-C25   | 1.853(3)                                     |
| P2-C19   | 1.826(3)                                     |
| P2-C13   | 1.830(3)                                     |
| P2-C32   | 1.855(3)                                     |
| P3-C33   | 1.820(3)                                     |
| P3-C39   | 1.828(3)                                     |
| P3-C57   | 1.862(3)                                     |
| P4-C45   | 1.827(3)                                     |
| P4-C51   | 1.830(3)                                     |
| P4-C64   | 1.849(3)                                     |
| Bond angles                                    | 11(1(())                                     |
| P4-AuI-P1                                      | 116.16(2)                                    |
| P4-Au1-P2<br>P1 A-1 P2                         | 115.81(2)                                    |
| P1-Au1-P2<br>P4 Av1 P2                         | 103.62(2)                                    |
| $P_{4} - A_{11} - P_{5}$                       | 105.05(2)                                    |
| $P_1 = A_{11} = P_3$<br>$P_2 = A_{11} = P_3$   | 114.22(2)<br>102.94(2)                       |
| $r_2 - Au_1 - r_3$                             | 102.94(2)                                    |
| $C1_P1_C25$                                    | 101.16(13)                                   |
| C7_P1_C25                                      | 102 43(13)                                   |
| C1_P1_Au1                                      | 116 95(9)                                    |
| C7-P1-Au1                                      | 114 35(9)                                    |
| $C_{25}$ –P1–Au1                               | 114 61(9)                                    |
| C19 = P2 = C13                                 | 101 77(13)                                   |
| C19–P2–C32                                     | 104.33(13)                                   |
| C13–P2–C32                                     | 100.13(13)                                   |
| C19–P2–Au1                                     | 112.74(10)                                   |
| C13–P2–Au1                                     | 122.67(10)                                   |
| C32–P2–Au1                                     | 112.98(10)                                   |
| C33–P3–C39                                     | 102.42(13)                                   |
| C33–P3–C57                                     | 105.29(13)                                   |
| C39–P3–C57                                     | 101.65(13)                                   |
| C33–P3–Au1                                     | 114.18(9)                                    |
| C39–P3–Au1                                     | 117.67(10)                                   |
| C57–P3–Au1                                     | 113.96(9)                                    |
| C45-P4-C51                                     | 103.92(13)                                   |
| C45–P4–C64                                     | 101.18(13)                                   |
| C51-P4-C64                                     | 100.63(13)                                   |
| C45–P4–Au1                                     | 118.84(9)                                    |
| C51–P4–Au1                                     | 117.08(10)                                   |
| C64–P4–Au1                                     | 112.58(9)                                    |

measured within the chelate rings from the six crystal structures.

#### 4. Experimental

Infrared spectra were recorded as either Nujol mulls between CsI plates or as CsI disks using a Perkin–Elmer 983G spectrometer over the range 4000–200 cm<sup>-1</sup>. UV/ vis spectra were recorded either as solids by diffuse reflectance or in CH<sub>2</sub>Cl<sub>2</sub> solution using 1 cm path length quartz cells using a Perkin-Elmer Lambda19 spectrometer. Mass spectra were run by electron impact on a VG-70-SE Normal geometry double focusing spectrometer or by positive ion electrospray (MeCN solution) using a VG Biotech platform. <sup>1</sup>H NMR spectra were recorded using a Bruker AC300 spectrometer. <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H], <sup>63</sup>Cu and <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra were recorded using a Bruker DPX400 spectrometer operating at 100.6, 162.0, 106.11 or 85.62 MHz, respectively, and are referenced to TMS, external 85% H<sub>3</sub>PO<sub>4</sub>, [Cu(NCMe)<sub>4</sub>]BF<sub>4</sub> and 1 mol  $dm^{-3}$  Na<sub>2</sub>[PtCl<sub>6</sub>], respectively. Microanalyses were undertaken by the University of Strathclyde microanalytical service.

Solvents were dried prior to use and all preparations were undertaken using standard Schlenk techniques under a  $N_2$  atmosphere. The ligand  $L^1$  was prepared as described previously [8].

## 4.1. $[CoCl_2(L^1)]$

CoCl<sub>2</sub>·6H<sub>2</sub>O (0.075 g, 0.316 mmol) was dissolved in isopropanol (20 cm<sup>3</sup>). One molar equivalent of L<sup>1</sup> (0.150 g, 0.316 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was added and the reaction mixture was stirred for ca. 30 min. to give a turquoise solid. The solvent was concentrated to ca. 5 cm<sup>3</sup> in vacuo and the solid was collected by filtration, washed with isopropanol and dried in vacuo (yield 67%). Required for [C<sub>32</sub>H<sub>28</sub>Cl<sub>2</sub>CoP<sub>2</sub>]·1/ 4CH<sub>2</sub>Cl<sub>2</sub>: C, 61.9; H, 4.6. Found: C, 62.4; H, 4.3%. UV/vis (diffuse reflectance): v 6120, 7750, 13460, 15080, 16155, 25700 sh cm<sup>-1</sup>; (CH<sub>2</sub>Cl<sub>2</sub> solution): v13590 ( $\varepsilon_{mol}$  1000 cm<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup>), 15625 (900), 16920 (1060) cm<sup>-1</sup>. IR (Nujol mull): v 318 br cm<sup>-1</sup>. Magnetic moment = 4.68  $\mu_{\rm B}$ .

4.2.  $[CoCl_3(L^1)]$ 

Treatment of a CH<sub>2</sub>Cl<sub>2</sub> solution of  $[CoCl_2(L^1)]$  with a stream of NOCl at ca. -15 °C leads to immediate formation of a deep green-blue solution which, upon pumping to dryness in vacuo affords a green-blue solid. IR (Nujol mull): v 349, 321, 311 cm<sup>-1</sup>. UV/vis (CH<sub>2</sub>Cl<sub>2</sub> solution): v 6580, 16130, 16530 sh, 28570 cm<sup>-1</sup>.

### 4.3. $[CoBr_2(L^1)]$

Method as above, but using  $CoBr_2 \cdot 6H_2O$ . Green solid (yield 62%). Required for  $[C_{32}H_{28}Br_2CoP_2]$ : C, 55.4; H, 4.1. Found: C, 55.4; H, 3.7%. UV/vis (diffuse reflectance): v 6540, 7605, 13265, 15130, 15875 cm<sup>-1</sup>; (CH<sub>2</sub>Cl<sub>2</sub> solution): 13280 ( $\varepsilon_{mol}$  1580 cm<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup>), 15040 (1560), 16050 (1460) cm<sup>-1</sup>. IR (Nujol mull): v 243 br cm<sup>-1</sup>. Magnetic moment = 4.41  $\mu_B$ . 4.4.  $[CoI_2(L^1)]$ 

Method as above, but using CoI<sub>2</sub>. Brown-green solid (yield 55%). Required for  $[C_{32}H_{28}CoI_2P_2] \cdot 1.5CH_2Cl_2$ : C, 44.0; H, 3.4. Found: C, 43.7; H, 3.1%. UV/vis (diffuse reflectance): *v* 6610, 7350, 12770, 14045, 14730, 20830 sh, 2500 sh cm<sup>-1</sup>; (CH<sub>2</sub>Cl<sub>2</sub> solution): 12805 ( $\varepsilon_{mol}$  920 cm<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup>), 13965 (885), 14840 (770) cm<sup>-1</sup>. Magnetic moment = 4.84  $\mu_{\rm B}$ .

## 4.5. $[Rh(L^1)_2]BF_4$

RhCl<sub>3</sub>·3H<sub>2</sub>O (0.0416 g, 0.158 mmol) was dissolved in EtOH (20 cm<sup>3</sup>). Two equivalents of L<sup>1</sup> (0.15 g, 0.316 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was then added, together with 40% aqueous HBF<sub>4</sub> (1 cm<sup>3</sup>). The resulting mixture was stirred at room temperature for 30 min. Concentrating the mixture in vacuo gave an orange precipitate, which was filtered, washed with diethyl ether and dried in vacuo (yield 52%). Required for [C<sub>64</sub>H<sub>56</sub>BF<sub>4</sub>P<sub>4</sub>Rh]·2CHCl<sub>3</sub>: C, 57.5; H, 4.2. Found: C, C, 58.3; H, 4.6%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.00–7.40 (m) [40H] (Ph), 6.90 (m) [4H] (o-C<sub>6</sub>H<sub>4</sub>), 6.35 (m) [4H] (o- $C_6H_4$ ), 3.65 (br s) [8H] (CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR  $(CH_2Cl_2/CDCl_3)$ : 11.6 ppm (d,  ${}^{1}J_{RhP} = 140$  Hz). IR spectrum (Nujol mull): v 1060 s, 506 s cm<sup>-1</sup>. Electrospray MS (MeCN): m/z 1051  $[Rh(L^1)_2]^+$ , 557  $[Rh(L^1)]^+$ , 475  $[L^1 + H]^+$ .

## 4.6. $[Rh(cod)(L^{1})]PF_{6}$

[RhCl(cod)]<sub>2</sub> (0.077 g, 0.158 mmol) was dissolved in a degassed solution of  $CH_2Cl_2$  (20 cm<sup>3</sup>).  $NH_4PF_6$  (0.057 g, 0.35 mmol) and  $L^1$  (0.15 g, 0.316 mmol) were added to the mixture and the reaction was stirred under nitrogen for 30 min. The reaction mixture changed from yellow to red and the white precipitate (NH<sub>4</sub>Cl) was filtered off. The solution was reduced in volume to  $\sim 5 \text{ cm}^3$  in vacuo. Upon addition of diethyl ether (10 cm<sup>3</sup>) an orange precipitate formed which was filtered and washed with diethyl ether  $(2 \times 10 \text{ cm}^3)$ . The orange solid (0.145 g, 55%) was dried in vacuo. Required for [C<sub>40</sub>H<sub>40</sub>F<sub>6</sub>P<sub>3</sub>Rh]·1/2CH<sub>2</sub>Cl<sub>2</sub>: C, 55.7; H, 4.7. Found: C, 56.1; H, 3.9%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.70–7.50 (m) [20H] (Ph), 6.85 (m) [2H] (o-C<sub>6</sub>H<sub>4</sub>), 6.40 (m) [2H] (o-C<sub>6</sub>H<sub>4</sub>), 4.40 (br m) [4H] (cod CH), 3.90 (br m) [4H]  $(L^{1}CH_{2}), 2.0-2.2 \text{ (m) } [8H] \text{ (cod } CH_{2}). {}^{31}P{}^{1}H} \text{ NMR}$  $(CH_2Cl_2/CDCl_3)$ : 10.3 ppm (d,  ${}^{1}J_{RhP} = 146$  Hz) [2P], -143.8 (septet, PF<sub>6</sub><sup>-</sup>) [1P]. IR (Nujol mull): 840 s, 557 s  $cm^{-1}$ .

# 4.7. $[Ir(cod)(L^1)]PF_6$

Method as above, using  $[Ir_2Cl_2(cod)_2]$ , giving an orange-red solid (yield 55%). Required for  $[C_{40}H_{40}F_6IrP_3] \cdot CH_2Cl_2$ : C, 49.0; H, 4.2. Found: C, 48.3; H, 3.7%. <sup>1</sup>H NMR (CDCl\_3):  $\delta$  7.70–7.30 (m) [20H] (Ph), 6.85 (m) [2H] (o-C<sub>6</sub>H<sub>4</sub>), 6.40 (m) [2H] (o-C<sub>6</sub>H<sub>4</sub>), 4.18 (br m) [4H] (cod CH), 3.92 (br m) [4H] (L<sup>1</sup>CH<sub>2</sub>), 1.7–2.0 (m) [8H] (cod CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub>): -1.8 ppm (s) [2P], -143.8 (septet, PF<sub>6</sub><sup>-</sup>) [1P]. IR (Nujol mull): 841 s, 557 s cm<sup>-1</sup>. Electrospray MS (MeCN): m/z 775 [Ir(cod)(L<sup>1</sup>)]<sup>+</sup>.

## 4.8. $[NiCl_2(L^1)]$

NiCl<sub>2</sub>·6H<sub>2</sub>O (0.075 g, 0.316 mmol) was dissolved in isopropanol (20 cm<sup>3</sup>) and one mol equiv. of L<sup>1</sup> (0.15 g, 0.316 mmol) was added. Stirring the reaction mixture for 1 h afforded a deep pink solid which was filtered and dried in vacuo. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub> gave a deep pink solid (yield 76%). Required for [C<sub>32</sub>H<sub>28</sub>Cl<sub>2</sub>NiP<sub>2</sub>]·1.5CH<sub>2</sub>Cl<sub>2</sub>: C, 55.0; H, 4.3. Found: C, 55.5; H, 5.0%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.90–7.40 (br m) [20H] (Ph), 6.70 (br m) [2H] (*o*-C<sub>6</sub>H<sub>4</sub>), 6.30 (br m) [2H] (*o*-C<sub>6</sub>H<sub>4</sub>), 3.40 (br m) [4H] (CH<sub>2</sub>) ppm. UV/vis (diffuse reflectance): 20325, 29415, 37310 cm<sup>-1</sup>; (CH<sub>2</sub>Cl<sub>2</sub> solution): 20410 ( $\varepsilon_{mol}$  510 cm<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup>). IR (Nujol mull): v 337 m, 322 m cm<sup>-1</sup>.

## 4.9. $[NiCl_3(L^1)]$

Treatment of a CH<sub>2</sub>Cl<sub>2</sub> solution of [NiCl<sub>2</sub>(L<sup>1</sup>)] with a stream of NOCl at ca. -50 °C gave a deep orangebrown solution, from which an orange brown solid was obtained upon pumping to dryness in vacuo. IR (Nujol mull): v 340, 312, 300 sh cm<sup>-1</sup>. UV/vis (CH<sub>2</sub>Cl<sub>2</sub> solution): 12 900 v br, 21 050, 28 570 cm<sup>-1</sup>.

## 4.10. $[NiBr_2(L^1)]$

Prepared as above with NiBr<sub>2</sub>·3H<sub>2</sub>O (0.086 g, 0.316 mmol) and L<sup>1</sup> (0.15 g, 0.316 mmol) to afford a brick red solid (yield 87%). Required for  $[C_{32}H_{28}Br_2Ni-P_2]$ ·1.5CH<sub>2</sub>Cl<sub>2</sub>: C, 49.0; H, 3.8. Found: C, 48.3; H, 4.9%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.70–7.50 (br m) [24H] (Ar–CH), 3.80 (br m) [4H] (CH<sub>2</sub>) ppm. UV/vis (diffuse reflectance): 19600, 24040, 29240 cm<sup>-1</sup>; (CH<sub>2</sub>Cl<sub>2</sub> solution): 19920 ( $\epsilon_{mol}$  450 cm<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup>), 25000 (1485), 30675 (3140) cm<sup>-1</sup>. IR (Nujol mull): 282 w, 262 cm<sup>-1</sup>.

# 4.11. $[PdCl_2(L^1)]$

Na<sub>2</sub>PdCl<sub>4</sub> (0.093 g, 0.316 mmol) was dissolved in EtOH (20 cm<sup>3</sup>). One equivalent of L<sup>1</sup> (0.15 g, 0.316 mmol) was added in EtOH ( $\sim$ 5 cm<sup>3</sup>). The reaction mixture was stirred overnight, and a pale cream precipitate formed. After filtering and drying in vacuo a cream solid (yield 58%) was recovered. Required for [C<sub>32</sub>-H<sub>28</sub>Cl<sub>2</sub>P<sub>2</sub>Pd]·CH<sub>2</sub>Cl<sub>2</sub>: C, 53.8; H, 4.1. Found: C, 54.2; H, 4.2%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.85–7.98 (m), 7.44–

7.60 (m) [20H] (Ph), 6.88 (m) [2H] (o-C<sub>6</sub>H<sub>4</sub>), 6.15 (m) [2H] (o-C<sub>6</sub>H<sub>4</sub>), 3.75 (br d, J = 10 Hz) [4H] (CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  16.4 ppm. IR (CsI disk): v 3064 w, 2971 w, 2933 w, 1586 w, 1481 m, 1433 s, 1360 m, 1188 w, 1103 s, 1073 w, 1027 w, 1000 m, 867 w, 837 m, 746 s, 700 s, 504 s, 452 w, 316 m, 304 m cm<sup>-1</sup>.

## 4.12. $[Pd_2Cl_2(L^1)_2](PF_6)_2$

PdCl<sub>2</sub> (0.056 g, 0.316 mmol) was dissolved in MeCN  $(20 \text{ cm}^3)$ , by refluxing for 1 h. One equivalent of L<sup>1</sup> (0.15) g, 0.316 mmol) was added to the reaction mixture, followed by, one equivalent of  $TlPF_6$  (0.11 g, 0.316 mmol). The resulting reaction mixture was stirred overnight and then filtered. The yellow filtrate was reduced to  $\sim 5 \text{ cm}^3$ . Cold diethyl ether ( $\sim 10 \text{ cm}^3$ ) was added dropwise to precipitate a yellow solid, which was filtered and dried in vacuo (yield 44%). Required for  $[C_{64}H_{56}Cl_2F_{12}P_6Pd_2]$ : C, 50.5; H, 3.7. Found: C, 50.9; H, 3.8%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.40–7.90 (m) [40H], (Ph), 6.80 (m) [4H] (o- $C_6H_4$ ), 6.20 (m) [4H] (o- $C_6H_4$ ), 3.90 (br d, J = 12 Hz) [8H], (CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  27.3 (s) [4P] (-P-Ph), -143.7 (septet) [2P] (PF<sub>6</sub><sup>-</sup>) ppm. IR (CsI disk): v 3082 w, 3067 w, 3031 w, 2932 w, 1587 w, 1485 w, 1437 s, 1356 m, 1185 w, 1167 w, 1106 m, 1068 w, 1002 m, 843 br s, 777 m, 746 m, 696 m, 561 s, 501 m, 457 m, 374 w, 315 m cm<sup>-1</sup>. Electrospray MS (MeCN): m/z 617 [PdCl(L<sup>1</sup>)]<sup>+</sup>, 658 [PdCl(L<sup>1</sup>)(MeCN)]<sup>+</sup>.

# 4.13. $[Pd(L^1)_2](BF_4)_2$

L<sup>1</sup> (0.15 g, 0.316 mmol) was dissolved in a mixture of EtOH (20 cm<sup>3</sup>) and CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>). Pd(NO<sub>3</sub>)<sub>2</sub> (0.036 g, 0.158 mmol) was dissolved in deionised H<sub>2</sub>O (~10 cm<sup>3</sup>) and added forming an orange solution. An excess of 40% aqueous HBF<sub>4</sub> (2 cm<sup>3</sup>) was then added, and the reaction was stirred for 1 h. The solution was reduced in volume until a yellow precipitate formed which was filtered and dried in vacuo (yield 69%). Required for [C<sub>64</sub>H<sub>56</sub>B<sub>2</sub>F<sub>8</sub>P<sub>4</sub>Pd]: C, 62.5; H, 4.6. Found: C, 63.0; H, 4.9%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.30–7.80 (m) [40H] (Ph), 6.20–6.80 (m) [8H] (*o*-C<sub>6</sub>H<sub>4</sub>), 3.70 (br m) ppm [8H] (CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  7.1 ppm. IR (Nujol mull): *v* 1067 s, 505 s cm<sup>-1</sup>.

## 4.14. $[PtCl_2(L^1)]$

 $K_2PtCl_4$  (0.13 g, 0.316 mmol) was dissolved in deionised  $H_2O$  (10 cm<sup>3</sup>) and added to EtOH (20 cm<sup>3</sup>) whilst stirring. One equivalent of L<sup>1</sup> (0.15 g, 0.316 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was added. The reaction mixture was stirred for 3 h, and the subsequent two layers were combined with the addition of acetone (10 cm<sup>3</sup>). After stirring for 72 h, the mixture was filtered and then reduced in volume until a cream precipitate formed

85

which was filtered and dried in vacuo (yield 98%). Required for  $[C_{32}H_{28}Cl_2P_2Pt]$ : C, 51.9; H, 3.8. Found: C, 51.1; H, 3.9%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.90–8.00 (m), 7.45–7.60 (m) [20H] (Ph), 6.90 (m) [2H] (o-C<sub>6</sub>H<sub>4</sub>), 6.20 (m) [2H] (o-C<sub>6</sub>H<sub>4</sub>), 3.95 (br d, J = 11 Hz) [4H] (CH<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  –1.8 ppm, <sup>1</sup> $J_{Pt-P} = 3584$  Hz. <sup>195</sup>Pt NMR: -4503 (t, <sup>1</sup> $J_{PtP} = 3584$ Hz). IR (Nujol mull): v 326 w, 304 w cm<sup>-1</sup>. Conductivity  $\Lambda_M/\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> (10<sup>-3</sup> mol dm<sup>-3</sup> MeNO<sub>2</sub>): 11.0. Electrospray MS (MeCN): m/z 745 [PtCl(L<sup>1</sup>)(MeCN)]<sup>+</sup>.

## 4.15. $[PtCl_4(L^1)]$

Treatment of a CH<sub>2</sub>Cl<sub>2</sub> solution of [PtCl<sub>2</sub>(L<sup>1</sup>)] with Cl<sub>2</sub> in CCl<sub>4</sub> gave a bright yellow solution, which upon concentrating in vacuo gave a bright yellow solid. Required for [C<sub>32</sub>H<sub>28</sub>Cl<sub>4</sub>P<sub>2</sub>Pt]·CH<sub>2</sub>Cl<sub>2</sub>: C, 44.2; H, 3.4. Found: C, 44.8; H, 3.4%. <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  –4.8 ppm, <sup>1</sup>J<sub>Pt-P</sub> = 2160 Hz. IR (Nujol mull):  $\nu$  344, 299, 288 cm<sup>-1</sup>.

## 4.16. $[Cu(L^1)_2](BF_4)$

[Cu(NCMe)<sub>4</sub>](BF<sub>4</sub>) (0.044 g, 0.158 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) and stirred. Two equivalents of  $L^1$  (0.15 g, 0.316 mmol) were added, and the reaction was stirred for 2 h. The solution was reduced in volume to  $\sim 5 \text{ cm}^3$  and hexane (15 cm<sup>3</sup>) was added to precipitate a solid. This was filtered and the white solid (vield 92%) was dried in vacuo. Required for [C<sub>64</sub>H<sub>56</sub>BCuF<sub>4</sub>P<sub>4</sub>]·2CH<sub>2</sub>Cl<sub>2</sub>: C, 62.5; H, 4.8. Found: C, 62.5; H, 4.9%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.70–6.80 (br m) [44H] (Ar–CH), 6.30 (br m) [4H] (*o*-C<sub>6</sub>H<sub>4</sub>) 3.65 (br m) [8H] (CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$  -8.7 (s) ppm. <sup>63</sup>Cu NMR:  $\delta$  +193 ppm. Electrospray MS (MeCN): m/z1011 [Cu(L<sup>1</sup>)<sub>2</sub>]<sup>+</sup>, 578 [Cu(L<sup>1</sup>)](MeCN)]<sup>+</sup>, 537 [Cu(L<sup>1</sup>)]<sup>+</sup>. IR (CsI disk): v 3059 w, 2964 w, 2927 w, 1590 w, 1482 m, 1437 s, 1359 w, 1272 w, 1186 m, 1159 w, 1096 s, 1062 br s, 1003 w, 865 m, 842 m, 766 m, 735 s, 700 s, 504 s, 486 s, 445 w, 342 w cm<sup>-1</sup>.

## 4.17. $[Ag(L^1)_2](BF_4)$

AgBF<sub>4</sub> (0.031 g, 0.158 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) in a foil wrapped reaction vessel to exclude light, at 0 °C. Two equivalents of L<sup>1</sup> (0.15 g, 0.316 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and added dropwise whilst stirring to the reaction mixture, keeping the temperature at 0 °C. After stirring for 2 h, the white precipitate was recovered by filtration, and dried in vacuo to afford a white solid (yield 82%). The solid was stored in a foil wrapped container to exclude light. Required for [C<sub>64</sub>H<sub>56</sub>AgBF<sub>4</sub>P<sub>4</sub>]·1.5CH<sub>2</sub>Cl<sub>2</sub>: C, 61.9; H, 4.7. Found: C, 62.4; H, 5.1%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.95–7.30 (m) [40H] (Ph), 6.65 (br m) [4H] (*o*-C<sub>6</sub>H<sub>4</sub>), 6.20 (br m) [4H] (*o*-C<sub>6</sub>H<sub>4</sub>), 3.65 (br s) [8H] (CH<sub>2</sub>) ppm.

<sup>31</sup>P {<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  -1.5 (2×d, <sup>1</sup>J<sub>107Ag-31P</sub> = 226 Hz, <sup>1</sup>J<sub>109Ag-31P</sub> = 257 Hz). Electrospray MS (MeCN): *m*/*z* 1055 [<sup>107</sup>Ag(L<sup>1</sup>)<sub>2</sub>]<sup>+</sup>, 1057 [<sup>109</sup>Ag(L<sup>1</sup>)<sub>2</sub>]<sup>+</sup>. IR (Nujol mull): *v* 1059 m, 504 m cm<sup>-1</sup>.

# 4.18. $[Au(L^1)_2]PF_6$

 $L^1$  (0.15 g, 0.316 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>). AuCl(tht) (0.051 g, 0.158 mmol) was added to the reaction vessel, followed by TlPF<sub>6</sub> (0.055 g, 0.158 mmol). The vessel was wrapped in foil to exclude light. This was stirred for 1 h, and filtered to remove TICl. The volume was reduced to  $\sim 5 \text{ cm}^3$  and a white precipitate formed, which was filtered and dried in vacuo. The resulting fine white powder (yield 66%) was stored in a sample bottle excluding light. Required for [C<sub>64</sub>H<sub>56</sub>AuF<sub>6</sub>P<sub>5</sub>]·CH<sub>2</sub>Cl<sub>2</sub>: C, 56.7; H, 4.2. Found: C, 57.3; H, 3.9%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.10–7.35 (m) [40H] (Ph), 6.40 (m) [4H] (o-C<sub>6</sub>H<sub>4</sub>), 5.83 (m) [4H] (o- $C_6H_4$ ), 3.75 (br s) [8H], (CH<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR  $(CH_2Cl_2/CDCl_3)$ :  $\delta$  0.8 (s) [4P] (P-Ph), -143.9 (sep) [1P] (PF<sub>6</sub>) ppm. Electrospray MS (MeCN): m/z 1145  $[Au(L^1)_2]^+$ , 671  $[Au(L^1)]^+$ . IR (Nujol mull): v 850 br s, 560 s cm<sup>-1</sup>.

## 4.19. $[(AuCl)_2(L^1)]$

L<sup>1</sup> (0.072 g, 0.152 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>). AuCl(tht) (0.098 g, 0.304 mmol) was added and the vessel was wrapped in foil to exclude light. The reaction mixture was stirred for 30 min at room temperature, and then reduced in volume to ~5 cm<sup>3</sup>. The resulting white precipitate was filtered and dried in vacuo to afford a fine white powder (yield 23%), which was placed in a foil wrapped container. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.30–7.60 (m) [20H] (Ph), 6.86 (m) [2H] (*o*-C<sub>6</sub>H<sub>4</sub>), 6.35 (m) [2H] (*o*-C<sub>6</sub>H<sub>4</sub>), 3.92 (br) [4H] (CH<sub>2</sub>) ppm. <sup>31</sup>P {<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  30.5 (s) ppm. IR (Nujol mull): v 319 m cm<sup>-1</sup>.

#### 5. X-ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 7. Small blue crystals of  $[CoCl_2(L^1)]$  were obtained by vapour diffusion of diethyl ether into a  $CH_2Cl_2$  solution of the complex. Orange crystals of  $[Rh(L^1)_2]BF_4 \cdot 2CHCl_3$  were obtained by liquid diffusion of hexane into a solution of the complex in CHCl<sub>3</sub>, while yellow crystals of  $[PdCl_2(L^1)] \cdot 2CH_2Cl_2$  and  $[Pd_2Cl_2(L^1)_2](PF_6)_2$  and colourless crystals of  $[Ag(L^1)_2]BF_4 \cdot 2CH_2Cl_2$  and  $[Au(L^1)_2]PF_6 \cdot 2CH_2Cl_2$  were grown by liquid diffusion of hexane into a  $CH_2Cl_2$  solution of the appropriate complex. Data collection used a Nonius Kappa CCD diffractometer (T = 120 K) and with graphite-monochromated

| Crystallographic parameters                                    |                                   |  |                                 |                                 |                                   |                                   |
|--|-----------------------------------|--|---------------------------------|---------------------------------|-----------------------------------|-----------------------------------|
| Complex  | $[CoCl_2(L^1)]$                   | $[Rh(L^1)_2]BF_4 \cdot 2CHCl_3$  | $[PdCl_2(L^1)] \cdot 2CH_2Cl_2$ | $[Pd_2Cl_2(L^1)_2](PF_6)_2$     | $[Ag(L^1)_2]BF_4 \cdot 2CH_2Cl_2$ | $[Au(L^1)_2]PF_6 \cdot 2CH_2CI_2$ |
| Formula  | $C_{32}H_{28}Cl_2CoP_2$           | $\mathrm{C}_{66}\mathrm{H}_{58}\mathrm{B}\mathrm{Cl}_{6}\mathrm{F}_{4}\mathrm{P}_{4}\mathrm{Rh}$ | $C_{34}H_{32}Cl_6P_2Pd$         | $C_{64}H_{56}Cl_2F_{12}P_6Pd_2$ | $C_{66}H_{60}AgBCl_4 F_4P_4$      | C66H60AuCl4F6P5                   |
| M  | 604.31                            | 1377.42  | 821.72                          | 1522.61                         | 1313.50                           | 1460.76                           |
| Crystal system   | monoclinic                        | monoclinic   | monoclinic                      | triclinic                       | triclinic                         | monoclinic                        |
| Space group  | $P2_1/c$                          | $P2_1/c$   | $P2_1/m$                        | $P\overline{1}$                 | $P\overline{1}$                   | $P2_1/n$                          |
| <i>ι</i> (Å)   | 8.431(3)                          | 12.5675(2)   | 10.0854(7)                      | 9.6898(4)                       | 11.8886(3)                        | 11.32970(10)                      |
| 5 (Å)  | 18.217(3)                         | 24.5759(7)   | 17.7620(15)                     | 13.1151(7)                      | 14.8588(3)                        | 24.0180(3)                        |
| <sub>2</sub> (Å)   | 18.075(5)                         | 20.1428(6)   | 10.5702(7)                      | 13.8233(7)                      | 17.5104(4)                        | 22.8978(2)                        |
| (°) x  | 90                                | 90   | 06                              | 66.043(2)                       | 85.0570(10)                       | 90                                |
| g (°)  | 93.54(2)                          | 100.595(2)   | 115.727(4)                      | 86.115(3)                       | 89.6220(10)                       | 93.7570(10)                       |
| (°)<br>V   | 90                                | 06   | 06                              | 75.645(3)                       | 86.0290(10)                       | 90                                |
| $U(\mathbf{\mathring{A}}^3)$                                   | 2770.8(13)                        | 6115.2(3)  | 1705.8(2)                       | 1554.17(13)                     | 3074.28(12)                       | 6217.48(11)                       |
| Z  | 4                                 | 4  | 2                               | 1                               | 1                                 | 4                                 |
| $u(Mo K\alpha) (cm^{-1})$                                      | 9.49                              | 7.00   | 11.32                           | 8.96                            | 6.58                              | 2.726                             |
| Unique reflections   | 6330                              | 13 925   | 3756                            | 7038                            | 14004                             | 14231                             |
| Number of parameters   | 334                               | 739  | 202                             | 388                             | 721                               | 739                               |
| $R_1 \left[ I_0 > 2\sigma(I_0) \right]$                        | 0.0692                            | 0.0570   | 0.0539                          | 0.0512                          | 0.0571                            | 0.0301                            |
| R <sub>1</sub> [all data]                                      | 0.1668                            | 0.1041   | 0.0746                          | 0.0751                          | 0.0775                            | 0.0425                            |
| $vR_2 \left[ I_0 > 2\sigma(I_0) \right]$                       | 0.1172                            | 0.1082   | 0.1116                          | 0.1041                          | 0.1393                            | 0.0642                            |
| $wR_2$ [all data]  | 0.1464                            | 0.1236   | 0.1202                          | 0.1142                          | 0.1527                            | 0.0694                            |
| $\mathbf{R}_{1} = \sum   F_{o}  -  F_{c}  _{i} / \sum  F_{o} $ | $wR_2 = [\sum_w (F_o^2 - F_o^2)]$ | $\sum_{i=1}^{2} \sum wF_{oi}^{4} = \sum_{i=1}^{2} \sum wF_{oi}^{4}$                              |                                 |                                 |                                   |                                   |

#### 6. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 240478 (Co), 240479 (Rh), 240480 (Pd monomer), 240481 (Pd dimer), 240482 (Ag), 240483 (Au). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CD2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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