Gold(I) and platinum(II) complexes with a new diphosphine ligand based on the cyclotriphosphazene platform†

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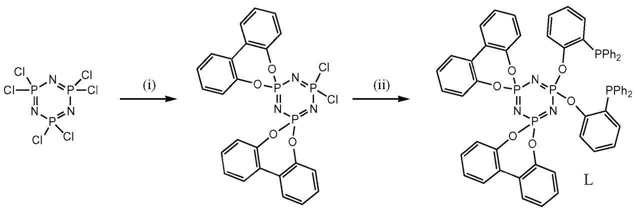
A new diphosphine ligand assembled on the cyclotriphosphazene platform forms linear chelate and dimetallic bridged complexes with Au(I) and a *cis*-chelate complex with Pt(II).

Diphosphines are an important class of ligands due to the application of their metal complexes in many catalytic processes.[1] The development of specifically *trans*-spanning diphosphines for catalytic roles has received much recent attention.[2] In particular, diphosphines with access to wide bite angles are of current interest in rhodium hydroformylation catalysis.[3]

The use of cyclic and linear polyphosphazenes as scaffolds for metal chelators is an area of ongoing interest, mainly due to the potential applications of the polymers.[4] The cyclic compounds are useful small molecule model compounds for the polymeric systems but often exhibit interesting coordination chemistries in their own right. For example, we have recently shown that hexakis(pyridyloxy)cyclotriphosphazene and its 4-methyl derivative are versatile multimodal ligands that exhibit a range of coordination geometries.[5]

In this paper we describe a new diphosphine ligand system, derived from (2-hydroxyphenyl)diphenylphosphine ($HOC_6H_4PPh_2$) and assembled on the cyclotriphosphazene platform (L, Scheme 1). Structural analyses of complexes of L with gold(I) and platinum(II) demonstrate that the ligand has a versatile coordination chemistry, capable of monodentate, linear bidentate and *cis*-bidentate chelating modes. The new ligand differs from related cyclophosphazene ligands derived from (4-oxyphenyl)diphenylphosphine in that the pendant phosphine is *ortho* to the phenoxy linker rather than *para*. Hence these latter ligands favour monodentate coordination.[6]



Scheme 1 Synthesis of **L**. (i) 2,2′-biphenol/K_2CO_3 in acetone, (ii) $HOC_6H_4PPh_2$/NaH in THF.

The phosphazene **L** was prepared from the reaction in THF between two equivalents of $NaOC_6H_4PPh_2$ (generated *in situ* from NaH and $HOC_6H_4PPh_2$) and $[N_3P_3(biph)_2Cl_2]$[7] (biph = 2,2′-biphenolato group). The ^{31}P NMR spectrum of L shows the expected pattern with phosphazene signals at 27.0 (d), 9.6 (t) and the free phosphine singlet at −15.5 ppm. The reaction between L and $AuBF_4$ in CH_3CN/CH_2Cl_2 yielded the complex $[AuL]BF_4$ (**1**).

X-ray quality crystals‡ of **1**·CH_3CN were grown from CH_3CN/Et_2O and the structure of the monocation is shown in Fig. 1. In this complex **L** acts as a bidentate chelating ligand with the gold(I) centre having a slightly distorted linear geometry [P(4)–Au–P(5) 171.99(3)°]. The Au–P bond lengths [2.2542(7) and 2.2643(7) Å] are significantly shorter than those in $[Au(PPh_3)_2]BF_4$ [2.321(3) and 2.322(3) Å][8] which is presumably a consequence of the tethered ligand geometry. No direct interactions between the gold(I) centre and the tetrafluoroborate anion are apparent, although there are short contacts between Au(1) and the oxygen atoms in the (2-oxyphenyl)diphosphine hinges [Au(1)···O(1) and Au(1)···O(2) are *ca.* 3.12 and 3.00 Å, respectively]. The phosphazene ring is essentially planar and the bond lengths and angles in the ring are typical, however, the value of 95.45(10)° for O(1)–P(1)–O(2) is smaller than usual [the mean value of the two spirocyclic O–P–O angles is 103.44°].

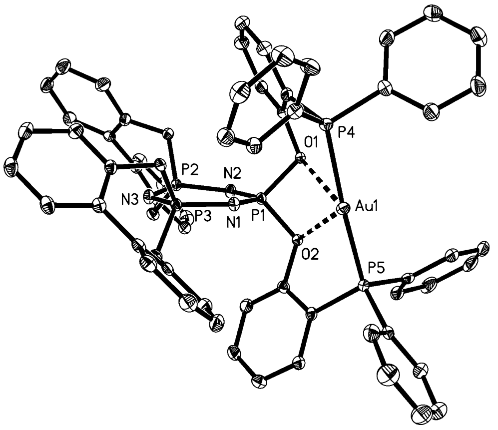


Fig. 1 Ortep diagram of the $[AuL]^+$ cation (ellipsoids are drawn at the 50% probability level). Bond lengths (Å) and angles (°): Au(1)–P(4), 2.2643(7); Au(1)–P(5), 2.2542(7); N(1)–P(1), 1.553(2); N(1)–P(3), 1.548(1); N(2)–P(1), 1.547(2); N(2)–P(2), 1.552(2); N(3)–P(3), 1.544(2); N(3)–P(2), 1.548(2); P(4)–Au(1)–P(5), 171.99(3); O(1)–P(1)–O(2), 95.45(10).

The reaction between **L** and two equivalents of [Au(tht)Cl] (tht = tetrahydrothiophene) in $CHCl_3$ produces the complex $[(AuCl)_2L]$ (**2**). Crystals§ of **2**·2.7$CHCl_3$ were grown by vapour diffusion of pentane into the $CHCl_3$ solution and the structure of **2** is shown in Fig. 2. In this complex, **L** acts as a bridging ligand, coordinating through both phosphine arms to the AuCl centres.

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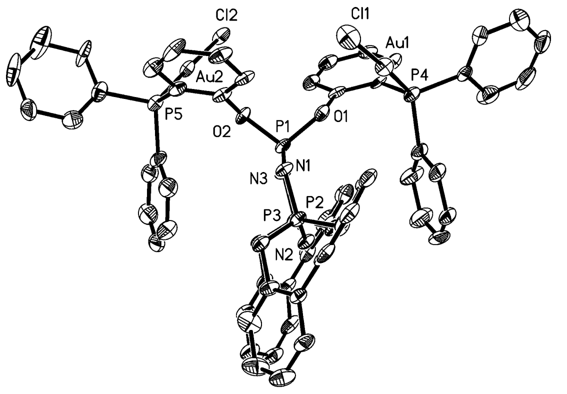

Fig. 2 Ortep diagram of $[(AuCl)_2L]$ (ellipsoids are drawn at the 50% probability level). Selected bond lengths (Å) and angles (°): Au(1)–P(4), 2.2256(19); Au(1)–P(5), 2.2244(19); Au(1)–Cl(1)2.282(2); Au(2)–Cl(2), 2.2890(18); N(1)–P(1), 1.571(5); N(1)–P(2), 1.584(5); N(2)–P(2) 1.577(6); N(2)–P(3), 1.582(5); N(3)–P(1), 1.572(6); N(3)–P(3), 1.573(5); P(4)–Au(1)–Cl(1), 176.21(7); P(5)–Au(2)–Cl(2), 176.73(6); O(1)–P(1)–O(2), 103.0(2).

The P–Au–Cl angles are nearly linear [176.73(6) and 176.21(7)°] and the Au–P and Au–Cl bond lengths are typical.

The phosphine arms in **2** are orientated such that the Au(I) centres lie *ca.* 2.27 and 3.54 Å above and below the mean plane of the phosphazene ring. Consequently the Au(I) atoms are ~7.75 Å apart and the closest Au···Au approach between adjacent molecules is ~5.77 Å indicating that are no strong aurophilic interactions in **2** as reported for many other digold complexes of diphosphines.[9] There is a weak interaction between Au(1) and O(1) [Au(1)···O(1) 3.20 Å] although the Au(2)···O(2) distance at 3.35 Å is greater.

The reaction of **L** with $[Pt(COD)Cl_2]$ in CH_2Cl_2 affords the complex $[PtLCl_2]$ (**3**) and crystals¶ of **3**·4CH_3CN (Fig. 3) were grown from an acetonitrile solution. In this complex the ligand coordinates as a *cis*-chelate diphosphine with a bite angle of 100.21(10)° giving a distorted square planar geometry about the Pt(II) centre. The phosphazene ring is significantly more distorted in this structure than **1** and **2**, with P(2) and N(1) lying ~0.17 and ~0.16 Å above and below the mean plane.

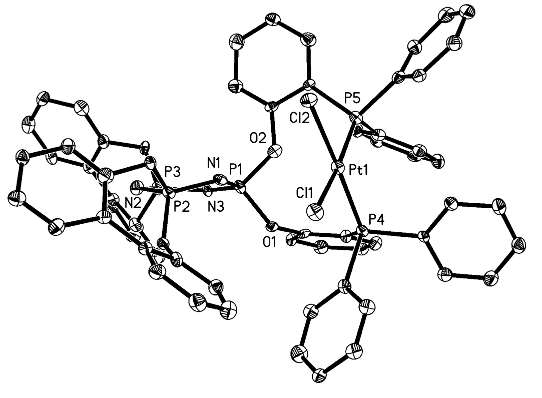

Fig. 3 Ortep diagram of $[PtLCl_2]$ (ellipsoids are drawn at the 50% probability level). Selected bond lengths (Å) and angles (°): Pt(1)–P(4), 2.261(3); Pt(1)–P(5), 2.266(3); Pt(1)–Cl(1), 2.334(3); Pt(1)–Cl(2), 2.358(3); N(1)–P(1), 1.600(9); N(1)–P(2), 1.586(8); N(2)–P(2) 1.577(9); N(2)–P(3), 1.602(9); N(3)–P(1), 1.578(8); N(3)–P(3), 1.567(8); P(4)–Au(1)–P(5), 100.21(10); Cl(1)–Pt(1)–Cl(2), 87.85(9); O(1)–P(1)–O(2), 97.1(4).

To explore further the potential for **L** to act as a *cis*-bidentate diphosphine, its reaction with the $[M(CO)_4(pip)_2]$ precursors (M = W or Mo, pip = piperidine) was examined. Complexes of stoichiometry $[W(CO)_4L]$ (**4**) and $[Mo(CO)_4L]$ (**5**) were isolated after column chromatography and characterised by microanalytical, NMR and IR data. The *cis*-coordination mode is anticipated from the characteristic pattern[10] of carbonyl IR stretching frequencies [ν(CO) cm^{-1}: 2020, 1918, 1892, and 1866 in **4**; 2023, 1932, 1900 and 1868 in **5**].

The linear bidentate preference of **L** with Au(I) is interesting since the Au(I) complexes of ligands that could form chelate rings of a similar size (for example, the aliphatic carbon bridged diphosphines) exhibit the monodentate bridging mode.[11] The linear chelating mode is comparable with the *trans*-spanning behaviour in complexes of more rigid diphosphines[2] although the structures presented here demonstrate that a flexible bite angle is available to **L** that can vary between 100.21(10) and 171.99(3)°. To our knowledge these complexes are the first structurally characterised cyclotriphosphazene derivatives containing diphenylphosphine substituents and are also the first structurally characterised gold complexes of phosphazene based ligands. We are currently investigating the coordination chemistry of **L** and derivatives with other metal ions.

CCDC reference numbers 287631–287633.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517309b

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Notes and references

‡ Crystal data for $C_{62}H_{47}AuBF_4N_4O_6P_3$: M = 1382.66, triclinic, space group P-1, a = 12.2010(1), b = 14.2978(1), c = 17.6740(1) Å, α = 69.287(1), β = 83.074(1), γ = 67.942(1)°, U = 2672.54(3) Å^3, T = 83 K, Z = 2, D_c = 1.718 g cm^{-3}, $F(000)$ = 1380, μ(Mo-K) = 2.977 mm^{-1}, 27712 reflections measured (2.30 < 2θ < 51.72), 115701 unique (R_{int} = 0.0627). Refinement of 749 parameters converged at R_1 = 0.0254 [observed data: 10643 $|F_o| > 4\sigma(F_o)$], $wR(F^2)$ = 0.0637 (all data).

§ Crystal data for $C_{62.7}H_{46.7}Au_2Cl_{10.1}N_3O_6P_5$: M = 1845.06, triclinic, space group P-1, a = 13.8387(1), b = 14.0919(1), c = 18.3886(1) Å, α = 93.237(1), β = 104.527(1), γ = 100.185(1)°, U = 3397.49(6) Å^3, T = 83 K, Z = 2, D_c = 1.803 g cm^{-3}, $F(000)$ = 1793, μ(Mo-K) = 4.880 mm^{-1}, 30919 reflections measured (2.46 < 2θ < 54.08), 12898 unique (R_{int} = 0.024). For the solution of **2**·2.7$CHCl_3$, the electron density of disordered $CHCl_3$ was removed from the unit cell using PLATON/SQUEEZE. Approximately 2.7 molecules of $CHCl_3$ per cell were removed (314 e^- per cell and 869 Å^3 was left by the void). Refinement of 703 parameters converged at R_1 = 0.0498 [observed data: 9596 $|F_o| > 4\sigma(F_o)$], $wR(F^2)$ = 0.1295 (all data).

¶ Crystal data for $C_{68}H_{56}Cl_2N_7O_6P_5Pt$: M = 1488.04, monoclinic, space group $P2(1)/c$, a = 13.5768(2), b = 11.1807(2), c = 42.2143(2) Å, β = 98.811(1)°, U = 6348.60(15) Å^3, T = 83 K, Z = 4, D_c = 1.557 g cm^{-3}, $F(000)$ = 2992, μ(Mo-K) = 2.480 mm^{-1}, 28324 reflections measured (5.78 < 2θ < 46.52), 9094 unique (R_{int} = 0.1263). Refinement of 806 parameters converged at R_1 = 0.0660 [observed data: 5816 $|F_o| > 4\sigma(F_o)$], $wR(F^2)$ = 0.1384 (all data).

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