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Transition Metal-mediated Discrimination between Diastereoisomers of a New Linear P_2N_2 Ligand, L_1; *X*-Ray Structure Analysis of *rac*-L_1, [Pt(*rac*-L_1)Cl]Cl · $2H_2O$, and an Unusual Rh^I Dimer [Rh_2(*rac*-L_1−H)$_2$(CO)$_2$] · $2H_2O$

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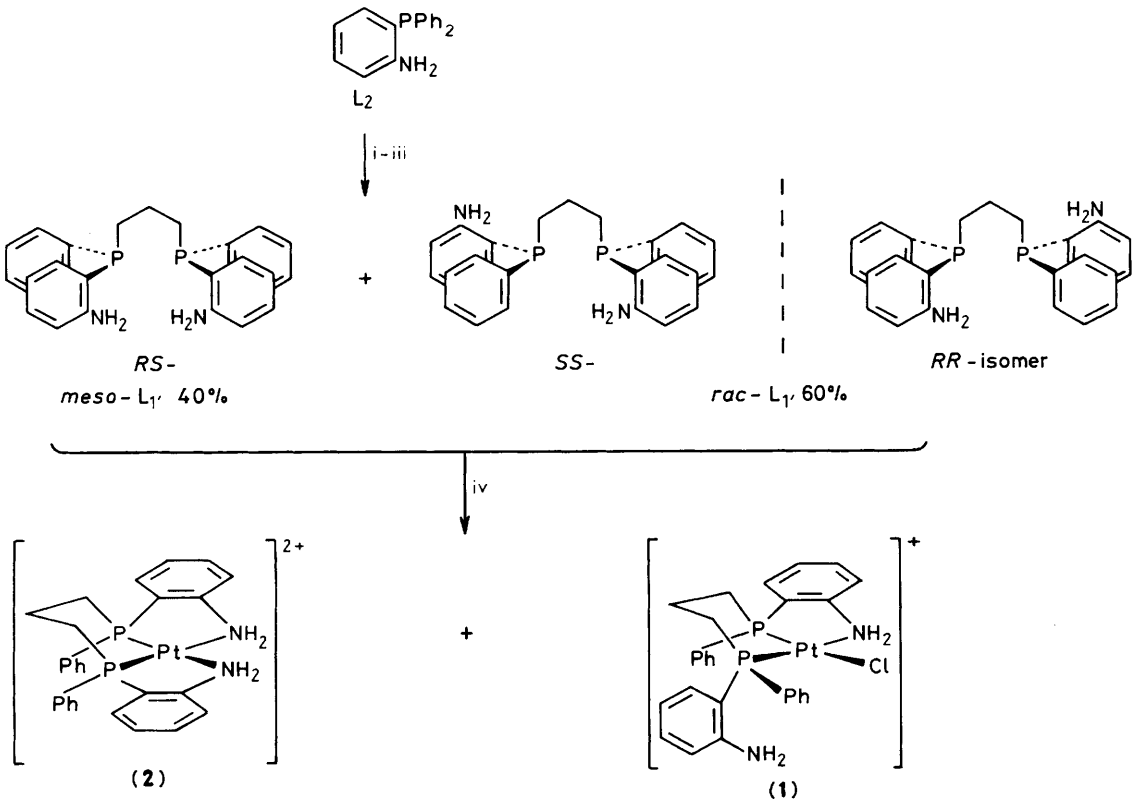
The new linear P_2N_2 ligand 1,3-bis{(*o*-aminophenyl)phenylphosphino}propane, L_1, as synthesised by reaction of (*o*-aminophenyl)diphenylphosphine, L_2, with lithium and 1,3-dichloropropane, forms *racemic* and *meso* isomers with distinctly different stereochemical requirements so that on reaction with $PtCl_2Y_2$ (Y = dimethyl sulphoxide, DMSO, or benzonitrile) they bond in tridentate and tetradentate modes respectively to give the monocationic complex [Pt(*rac*-L_1)Cl]$^+$, (**1**), and the dicationic complex [Pt(*meso*-L_1)]$^{2+}$, (**2**); *X*-ray structure analysis of *rac*-L_1, the chloride salt of (**1**), and the ligand bridged dimer [Rh_2(*rac*-L_1−H)$_2$(CO)$_2$], (**3**), has shown how the stereochemical requirements of this *racemic* ligand lead to unusual modes of co-ordination.

The presence of two stable chiral phosphorus centres in the new potentially tetradentate P_2N_2 ligand L_1 gives rise to two diastereoisomers (*rac* and *meso*). These are readily separated as their complexes with d^8-metal ions in which *rac*-L_1 acts as a tridentate ligand, forming a monocationic complex, while *meso*-L_1 adopts a tetradentate mode of ligation, resulting in a dicationic species.

Thus the product from the reaction of the bidentate ligand



Scheme 1. i, Li, tetrahydrofuran; ii, Cl[CH_2]$_3$Cl; iii, H_2O; iv, PtY_2Cl_2, MeOH, CH_2Cl_2, Y = DMSO or PhCN.

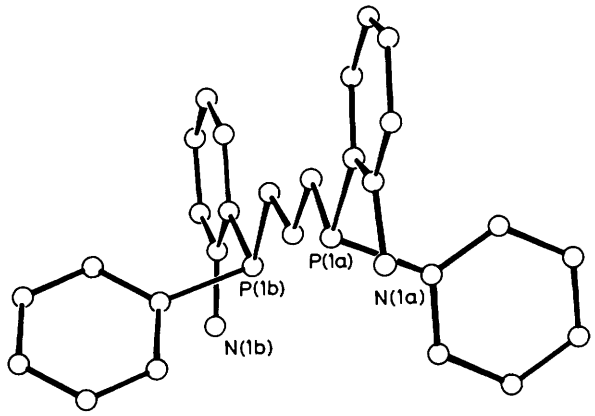


Figure 1. The structure of the *SS* isomer of *rac*-L_1.

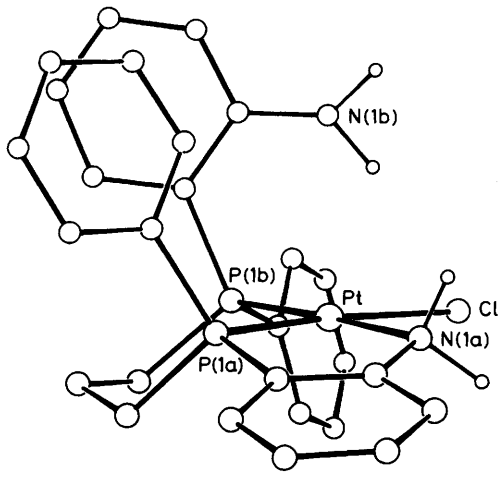
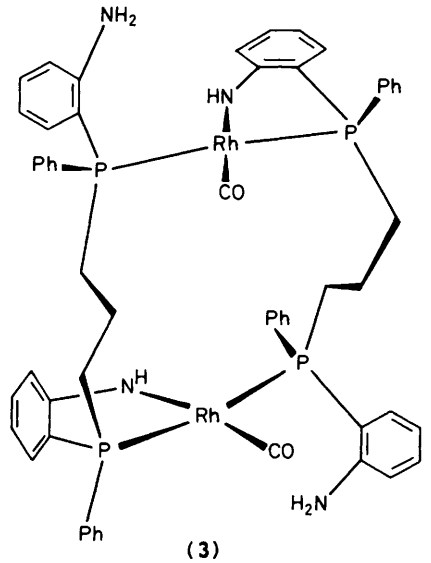


Figure 2. The structure of $[Pt^{II}(rac\text{-}L_1)Cl]Cl \cdot 2H_2O$, (**1**). The platinum to ligand bond distances are Cl, 2.393(3); P(1a), 2.246(3); P(1b), 2.298(3); N(1a), 2.164(8) Å. An amino hydrogen atom on N(1a) is strongly hydrogen bonded to a water molecule with H · · · O 1.93 Å.

L_2[1,2] with lithium followed by addition of 1,3-dichloropropane (Scheme 1), was shown by ^{31}P-{^1H} n.m.r. spectroscopy to consist of an approximately 60 : 40 mixture of the diastereoisomers of L_1.† The structure of the *SS* isomer of *rac*-L_1 is shown in Figure 1.‡ The reaction of the ligand mixture with PtY_2Cl_2 in CH_2Cl_2–MeOH gives two species (Scheme 1). The major species has two chemically inequivalent phosphorus sites† and has been isolated quantitatively by recrystallisation from a 1 : 1 MeOH–1 M HCl solution. *X*-Ray analysis‡ shows that it is the chloride salt of $[Pt(rac\text{-}L_1)Cl]^+$, (**1**), in which the *rac* ligand diastereoisomer is bonded in tridentate mode with one NH_2 group unco-ordinated (Figure 2). The minor species is the chloride salt of the dication $[Pt(meso\text{-}L_1)]^{2+}$, (**2**), in which there is a square planar co-ordination of the *meso*-L_1 ligand so that only one phosphorus environment is detected in the ^{31}P-{^1H} n.m.r. spectrum.† The *meso*-ligand has been obtained in high yield by deprotonating the nitrate salt of the nickel analogue of (**2**) [isolated from the reaction of $Ni(NO_3)_2 \cdot 6H_2O$ with *meso*- and *rac*-L_1 in 90% ethanol] and treating the resulting neutral complex with aqueous cyanide. Reaction of pure *meso*-L_1 with PtY_2Cl_2 gave (**2**) in high yield.



(**3**)

The stereochemical requirements of several linear tetradentate ligands containing two chiral donor atoms have been reported.[3–6] However the chlorides of the monocation (**1**), $[Pt(rac\text{-}L_1)Cl]Cl$ and of the dication (**2**), $[Pt(meso\text{-}L_1)]Cl_2$, provide the first demonstration of ionisation isomerism resulting from tridentate and tetradentate co-ordination of *rac* and *meso* diastereoisomers. Models show that co-ordination of *rac*-L_1 as a tetradentate ligand around a square planar metal ion would result in a strained twist conformation of the six-membered chelate ring, whereas the *meso* isomer gives a favourable chair form.[7] Figure 2 shows that tridentate co-ordination of the *rac* ligand allows this ring to adopt the more favourable chair conformation.

† ^{31}P-{^1H} (36.43 MHz) N.m.r. data (chemical shifts relative to 85% H_3PO_4): *rac*-L_1 (in $CDCl_3$), δ −35.5 p.p.m.; *meso*-L_1 (in $CDCl_3$), δ −35.6 p.p.m.; (**1**) (in 1 : 4 MeOH–CH_2Cl_2), δ −19.9 [J(Pt–P) 2963 Hz], 11.9 p.p.m. [J(Pt–P) 3269, ^2J(P–P) 29 Hz]; (**2**), δ 10.9 p.p.m. [J(Pt–P) 3000 Hz]; (**3**), δ 10.2 [J(Rh–P) 126 Hz], 40.0 p.p.m. [J(Rh–P) 130, ^2J(P–P) 288 Hz]; *cf.* [Rh(CO)(L_2)(L_2−H)] (in CH_2Cl_2), where L_2 is monodentate through phosphorus, and CO is *trans* to amido (ref. 4), δ 23.9 [J(Rh–P) 131 Hz], 47.7 p.p.m. [J(Rh–P) 135, ^2J(P–P) 291 Hz].

‡ *Crystal data*: *rac*-L_1, $C_{27}H_{28}N_2P_2$, from 90% EtOH, M = 442.48, orthorhombic, space group $P2_12_12_1$, a = 22.960(3), b = 7.725(2), c = 13.671(2) Å, U = 2424.8 Å^3, Z = 4, D_c = 1.212 g cm^{-3}, F(000) = 936, μ(Mo-K_α) = 1.55 cm^{-1}, $I/\sigma(I) > 3.0$, present R-factor (for the *SS*-isomer) 0.089 for 701 unique reflections. Changing the stereochemistry of the structure to give the *RR*-isomer resulted in an increase in R to 0.091 confirming that the crystal selected was the *SS*-isomer.

(**1**), $[C_{27}H_{28}ClN_2P_2Pt][Cl] \cdot 2H_2O$, from 1 : 1 MeOH–1 M HCl, M = 744.51, monoclinic, space group $P2_1/c$, a = 12.704(2), b = 12.727(2), c = 20.727(3) Å, β = 92.65(4)°, U = 3347.6 Å^3, Z = 4, D_c = 1.477 g cm^{-3}, F(000) = 1472, μ(Mo-K_α) = 42.77 cm^{-1}, $I/\sigma(I) > 3.0$, present R-factor 0.044 for 3753 unique absorption corrected data.

(**3**), $[C_{28}H_{25}N_2OP_2Rh]_2 \cdot 2H_2O$, from CH_2Cl_2–Bu^nOH, M = 1208.79, monoclinic, space group $C2/c$, a = 22.435(3), b = 18.018(3), c = 14.073(3) Å, β = 105.00(4)°, U = 5494.94 Å^3, Z = 4, D_c = 1.461 g cm^{-3}, F(000) = 2464, μ(Mo-K_α) = 4.22 cm^{-1}, $I/\sigma(I) > 3.0$, present R-factor 0.058 for 2611 unique reflections. Data were collected on a Philips PW1100 diffractometer in the θ range 3—25° and using Mo-K_α radiation. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

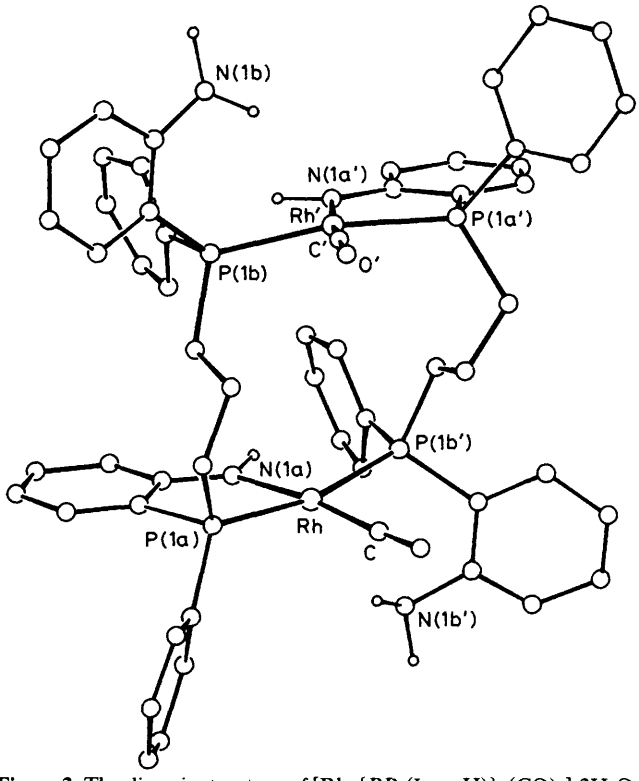


Figure 3. The dimeric structure of $[Rh_2\{RR\text{-}(L_1 - H)\}_2(CO)_2]\cdot 2H_2O$, (**3**). The dimer has crystallographic 2-fold symmetry. The rhodium to ligand bond distances are P(1a), 2.288(3); P(1b'), 2.309(3); C, 1.834(13); and N(1a), 2.040(9) Å. Each dimeric unit is linked, across inversion centres, to two other dimer units by hydrogen bonding (between a hydrogen of the free amino group of one dimer and the co-ordinated amido group of the adjacent dimer). Thus the structure can be thought of as consisting of polymeric chains with alternate dimer subunits of opposite chirality; the dimer chains are separated by chains of hydrogen bonded water molecules.

A further illustration of a tridentate mode of co-ordination for *rac*-L_1 is provided by the unusual ligand bridged dimeric compound $[Rh_2(rac\text{-}L_1-H)_2(CO)_2]$, (**3**).§ This was prepared by deprotonation of the product of the reaction of $[Rh(CO)_2Cl_2]^+$ with the mixture of *rac*- and *meso*-L_1. In this case tridentate ligation around a single metal centre would lead to an unfavourable *trans* arrangement of the carbonyl and phosphine groups. The molecule has C_2 symmetry with each P_2N_2 ligand bonded to one rhodium atom through a PN chelate ring and to a second rhodium atom through the second phosphine donor, with the fourth, amino, donor group unco-ordinated, as shown in Figure 3.‡

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§ *Mass spectrum:* (**3**), *m/z* 1086 ($M-CO,-2H$).