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Low-Dimensional Architectures in Isomeric cis-PtCl$_2$(Ph$_2$PCH$_2$N(Ar)CH$_2$PPh$_2$) Complexes Using Regioselective-N(Aryl)-Group Manipulation

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Abstract: The solid-state behaviour of two series of isomeric, phenol-substituted, aminomethylphosphines, as the free ligands and bound to Pt$^{II}$, have been extensively studied using single crystal X-ray crystallography. In the first library, isomeric diphosphines of the type Ph$_2$PCH$_2$N(Ar)CH$_2$PPh$_2$ [1a–e; Ar = C$_6$H$_5$(Me)(OH)] and, in the second library, amide-functionalised, isomeric ligands Ph$_2$PCH$_2$N(CH$_2$O)(NH)(Ar)CH$_2$PPh$_2$ [2a–e; Ar = C$_6$H$_5$(Me)(OH)], were synthesised by reaction of Ph$_2$PCH$_2$OH and the appropriate amine in CH$_3$OH, and isolated as colourless solids or oils in good yield. The non-methyl, substituted diphosphines Ph$_2$PCH$_2$N(CH$_2$O)(NH)(Ar)CH$_2$PPh$_2$ [2f, Ar = 3-C$_6$H$_5$(OH); 2g, Ar = 4-C$_6$H$_5$(OH)] and Ph$_2$PCH$_2$N(Ar)CH$_2$PPh$_2$ [3, Ar = 3-C$_6$H$_5$(OH)] were also prepared for comparative purposes. Reactions of 1a–e, 2a–g, or 3 with PtCl$_2$(η$^4$-cod) afforded the corresponding square-planar complexes 4a–e, 5a–g, and 6 in good to high isolated yields. All new compounds were characterised using a range of spectroscopic ($^1$H, $^3$P/$^1$H), FT–IR) and analytical techniques. Single crystal X-ray structures have been determined for 1a, 1b·CH$_3$OH, 2f·CH$_3$OH, 2g, 3, 4b·(CH$_3$)$_2$SO, 4c·CHCl$_3$, 4d·$^1$H$_2$O, 4e·$^1$CHCl$_3$, 4f·$^1$CH$_2$OH, 5a·$^1$Et$_2$O, 5b, 5c·$^1$H$_2$O, 5d·Et$_2$O, and 6·(CH$_3$)$_2$SO. The free phenolic group in 1b·CH$_3$OH, 2f·CH$_3$OH, 2g, 4b·(CH$_3$)$_2$SO, 5a·$^1$Et$_2$O, 5c·$^1$H$_2$O, and 6·(CH$_3$)$_2$SO exhibits various intra- or intermolecular O–H···X (X = O, N, P, Cl) hydrogen contacts leading to different packing arrangements.

Keywords: amide groups; isomers; late-transition metals; P-ligands; phenols; secondary interactions; single crystal X-ray crystallography

1. Introduction

Tertiary phosphines, and their phospine oxides, have played an important role in the study of supramolecular and self-assembly processes [1–3]. Their synthetic versatility, coupled with ease of substituent modification, has no doubt played a significant contribution over the years. Hydrogen bonding interactions are routinely encountered in supramolecular ligand systems as illustrated by the elegant studies from Breit [4], Keek [5], and others [6,7]. More recently, amongst other common types of non-covalent interactions, those based on halogen bonding [8,9] and H$^+$···H$^-$ have been reported [10].

For a number of years, we [11–16], and others [17–22], have been interested in aminomethylphosphines, readily amenable by Mannich condensation reactions. Such interest stems from the relative ease of accessing P-monodentate ligands based on a P–C–N linker [11,15,16,19,20,22] or P/P-bidentate derivatives bearing a P–C–N–C–P backbone [12–14,17–19,21]. Previously, we have shown that the N-arene group can be easily tuned with, for example, various H-bonding donor/acceptor sites based on –CO$_2$H/OH groups [12–16]. In continuation of these studies, we report here our work on the regioselective positioning of amide/hydroxy and methyl groups within a series of aminomethylphosphines, both as the free ligands and when coordinated to a square-planar Pt(II) metal centre. Our rationale for introducing an –C(O)NH– group is based on the known use of
this functionality in supramolecular chemistry [23] and, furthermore, the recent interest in amide-modified phosphines for their variable coordination chemistry [24–26], binding nitroaromatics [27], and relevance to catalysis based on Pd [28]. Our choice of metal fragment in this work, “cis-PtCl₂”, is based on its capability to support a relatively small bite angle diphosphine ligand in a cis, six-membered ring conformation, and to provide up to two “acceptor” sites for potential H-bonding [29]. For this purpose, we elected to pursue a double Mannich condensation reaction of Ph₂PCH₂OH with a series of isomeric primary amines bearing either OH/CH₃ groups and/or an amide spacer between the arene and P–C–N–C–P backbone (Chart 1).

![Chart 1. Potential modification sites of a Ph₂P–C–N(Ar)–C–PPh₂ backbone.](chart1.png)

2. Results and Discussion

2.1. Ligand Synthesis

We [11–16,29], and others [17,19–22], have previously used Mannich condensations as a versatile method for the synthesis of aminomethylphosphines. Accordingly, two equivalents of Ph₂PCH₂OH were reacted with one equivalent of the amine, for 24 h at r.t. under N₂, yielding the desired phenol-substituted ditertiary phosphines 1a–e and 3 (Scheme 1).

![Scheme 1. Synthesis of 1a–e, 2a–g, and 3.](scheme1.png)
For 1a–e, colourless solids were isolated in 38–97% yields and found to be air stable in the solid state, but oxidise rapidly in solution. Compounds 1a–e and 3 exhibit single resonances in their $^{31}$P{H} NMR spectra (in d$_6$-dmso) around δ(P) = 26 ppm [12–15,29], indicating the presence of only one P$^{III}$ environment. The ligands were also characterised by $^1$H NMR, FT–IR, and elemental analysis (Table 1). In particular, the absence of an NH resonance, in the $^1$H NMR spectra, confirmed that double condensation had occurred.

Table 1. Selected spectroscopic and analytical data for compounds 1a–3.

| Compound a | δ(P) b | δ(H) /OH (NH) | δ(H) /arom. H. | δ(H) /CH$_2$ | δ(H) /CH$_2$ d | δ(H) /CH$_3$ | νOH (νNH) e | Microanalysis (CHN) |
|------------|--------|----------------|----------------|--------------|----------------|--------------|--------------|-------------------|
| 1a (79) | -27.5  | 6.62 | 7.33–7.23, 6.76, 6.69–6.57 | 4.15 (2.4) | 2.10 | 3.098 | Calc. for C$_{33}$H$_{31}$NOP$_2$, C, 76.29; H, 6.01; N, 2.70 |
| 1b (56) | -27.3  | 9.06 | 7.36–7.26, 7.15, 6.50, 6.44 | 3.96 (5.6) | 1.74 | 3.282 | Calc. for C$_{33}$H$_{31}$NOP$_2$.2MeOH, C, 72.03; H, 6.74; N, 2.40 |
| 1c (97) | -27.5  | 8.77 | 7.44–7.22, 6.86, 6.54, 6.48 | 4.09 (3.4) | 2.12 | 3.389 | Calc. for C$_{33}$H$_{31}$NOP$_2$, C, 76.29; H, 6.01; N, 2.70 |
| 1d (38) | -26.7  | 8.63 | 7.40–7.30, 6.55 | 4.02 (3.2) | 1.96 | 3.432 | Calc. for C$_{33}$H$_{31}$NOP$_2$, C, 76.29; H, 6.01; N, 2.70 |
| 1e (96) | -26.4  | 9.06 | 7.49–7.33, 6.85, 6.50, 6.27 | 3.88 (3.6) | 2.08 | 3.387 | Calc. for C$_{33}$H$_{31}$NOP$_2$.MeOH, C, 74.03; H, 6.40; N, 2.54 |
| 2a (81) | -26.0  | 8.15 | 7.77–7.19 | 5.06 | 3.62 (8.0) | 1.19 | - | - |
| 2b (89) | -26.0  | 7.83 | 7.60–7.21 | 5.07 | 3.69 (3.6) | 1.63 | - | - |
| 2c (88) | -26.5 c | 9.34 (8.17) | 7.71–7.19 | 5.27 | 3.61 (4.8) | 1.63 | - | - |
| 2d (65) | -27.1  | 9.05 (8.68) | 7.55–7.32, 6.95, 6.61, 6.41 | 3.69 | 3.81 (4.8) | 2.04 | 3.047 (3228) | Calc. for C$_{35}$H$_{32}$NOP$_2$.2H$_2$O.P$_2$, C, 72.91; H, 5.94; N, 4.86 |
| 2e (80) | -27.1  | 9.29 (9.08) | 7.46–7.35, 7.29, 6.86, 6.15 | 3.73 | 3.82 (4.4) | 2.08 | 3.178 (3317) | Calc. for C$_{35}$H$_{32}$NOP$_2$.2H$_2$O.P$_2$, C, 72.91; H, 5.94; N, 4.86 |
| 2f (70) | -27.5  | 9.31 (9.07) | 7.41–7.03, 6.94, 6.40, 6.30 | 3.69 | 3.77 (4.4) | 3.163 (3283) | Calc. for C$_{34}$H$_{32}$NOP$_2$.2H$_2$O.P$_2$, C, 72.59; H, 5.73; N, 4.98 |
| 2g (85) | -26.8  | 9.09 (8.78) | 7.36–7.25, 6.83, 6.53 | 3.61 | 3.72 (4.4) | 3.300 (3257) | Calc. for C$_{34}$H$_{32}$NOP$_2$.2H$_2$O.P$_2$, C, 72.59; H, 5.73; N, 4.98 |
| 3 (53)  | -27.6  | 9.12 | 7.38–7.31, 6.92, 6.30, 6.13 | 3.85 | - | 3.376 | Calc. for C$_{35}$H$_{32}$NOP$_2$, C, 76.03; H, 5.78; N, 2.77 |

a Isolated yields in parentheses. b Recorded in (CD$_3$)$_2$SO unless otherwise stated. c Recorded in CDCl$_3$. d 2J(PH) coupling in brackets. e Recorded as KBr discs.

The synthesis of ditertiary phosphines, containing a flexible backbone presenting extra donor/acceptor sites with additional H-bonding capability, is described here with the opportunity to enhance solid-state packing behaviour. The precursors for the synthesis of the desired functionalised ditertiary phosphines 2a–g were prepared using, in step (i), 1 equiv. of primary amine, N-carbobenzyloxyglycine (1 equiv.) and dicyclohexylcarbodi-
imide (DCC, 1 equiv.) in THF affording the corresponding carbamates followed by, in step (ii), treatment with Pd/C and cyclohexene in C₂H₅OH, to give the desired primary alkylamines in moderate to good yields [30,31]. Using a similar procedure to that described for 1a–e, the amide-functionalised diphosphines 2a–e were prepared in 65–89% yields by condensation using 1 equiv. of primary amine and two equiv. of Ph₂PCH₂OH at r.t. in CH₂OH (Scheme 1). Furthermore, the phenol-substituted phosphines 2f and 2g were synthesised to investigate what effect, if any, an absent methyl group on the N-arene ring displays. In the case of 2d–g, the diphosphines were obtained as solids whereas 2a–c were obtained as yellow oils that were sufficiently pure to be used in complexation studies. All compounds displayed a single ³¹P NMR resonance around δ(P) −26 ppm [12–15,29] indicating the inclusion of an amide spacer has negligible effect on the ³¹P chemical shift. Other spectroscopic and analytical data are given in Table 1.

2.2. Single Crystal X-ray Studies of 1a, 1b-CH₃OH, 2f-CH₃OH, 2g, and 3

X-ray quality crystals of 1a, 1b-CH₃OH, 2f-CH₃OH, 2g, and 3 were obtained by slow evaporation of a methanol solution, while for 2g diethyl ether was diffused into a deuterochloroform/methanol solution (Table 2).

### Table 2. Details of the X-ray data collections and refinements for compounds 1a, 1b-CH₃OH, 2f-CH₃OH, 2g, and 3.

| Compound | 1a | 1b-CH₃OH | 2f-CH₃OH | 2g | 3 |
|----------|----|----------|----------|----|---|
| Formula  | C₃₀H₂₃NOP₂ | C₃₁H₂₅NO₂P₂ | C₃₁H₂₅N₂O₃P₂ | C₃₅H₂₆N₂O₂P₂ | C₃₂H₂₈NOP₂ |
| M        | 519.53 | 551.57 | 594.60 | 562.55 | 505.50 |
| Crystal dimensions | 0.42 x 0.15 x 0.03 | 0.13 x 0.12 x 0.02 | 0.24 x 0.18 x 0.16 | 0.25 x 0.18 x 0.15 | 0.31 x 0.28 x 0.03 |
| Crystal morphology and colour | Plate, colourless | Block, colourless | Block, colourless | Block, colourless | Plate, colourless |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | P₂₁/n | P₂₁/c | P₅ | ₇ | ₇ |
| a/Å | 17.367(5) | 10.305(3) | 12.6198(3) | 11.6340(10) | 10.5860(4) |
| b/Å | 8.522(2) | 32.8017(10) | 16.2027(4) | 21.7359(10) | 10.7397(4) |
| c/Å | 20.382(6) | 8.5189(2) | 17.8529(4) | 11.6546(10) | 10.5860(4) |
| α/° | 75.5070(14) | 63.1422(6) | 73.1667(6) | 73.1667(6) | 73.1667(6) |
| β/° | 114.673(4) | 92.7318(16) | 73.0760(14) | 93.8717(14) | 93.8717(14) |
| γ/° | 64.0678(10) | 76.4703(14) | 75.5070(14) | 80.4518(7) | 80.4518(7) |
| V/Å³ | 2741.2(13) | 2876.30(14) | 3148.15(13) | 2932.6(4) | 1301.45(9) |
| Z | 4 | 4 | 4 | 4 | 2 |
| χ | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| T/K | 150(2) | 120(2) | 120(2) | 150(2) | 150(2) |
| Density (calcld.)/Mg/m³ | 1.259 | 1.274 | 1.255 | 1.274 | 1.280 |
| μ/µm⁻¹ | 0.185 | 0.183 | 0.176 | 0.182 | 0.193 |
| θ range/° | 2.02–26.60 | 3.03–27.53 | 3.24–25.00 | 1.87–28.82 | 1.59–30.62 |
| Measured reflections | 23,525 | 27,247 | 61,330 | 12,577 | 15,576 |
| Independent reflections | 5708 | 6545 | 11,047 | 6586 | 7814 |
| Observed reflections (F² > 2σ(F²)) | 3115 | 5019 | 7559 | 5293 | 6116 |
| R(F°)/R(F) | 0.124 | 0.058 | 0.095 | 0.039 | 0.027 |
| R(F² > 2σ(F²)) | 0.0743 | 0.0799 | 0.0517 | 0.0389 | 0.0441 |
| wR2 [all data] | 0.2205 | 0.1650 | 0.1220 | 0.0861 | 0.1248 |
| Largest difference map features/eÅ⁻³ | 1.40, −0.49 | 0.46, −0.52 | 0.38, −0.30 | 0.29, −0.16 | 0.51, −0.21 |

* R = Σ||Fo| − |Fc||/Σ|Fo|, *a* wR = Σ[w(Fo² − Fc²)]/Σ[w(Fo²)]¹/².
The geometry around each phosphorus atom is essentially pyramidal as would be anticipated (Figures 1–5). The \( ^{1}P^{III} \) atoms are in an \emph{anti} conformation, presumably to minimise steric repulsions between the phenyl groups. The geometry about the N(1) centre is approx. pyramidal [\( \Sigma(C-N(1)-C) \) angles: \( 337.0(3)^\circ \) for \( 1a \); \( 335(2)^\circ \) for \( 1b \cdot CH_3OH \); \( 335.2(2)/336.6(2)^\circ \) for \( 2f \cdot CH_3OH \); \( 333.7(2)^\circ \) and approximately trigonal planar for \( 3 \) [\( \Sigma(C-N-C) = 359.05(11)^\circ \)]. In \( 1a \) and \( 1b \cdot CH_3OH \), the N-arene ring [C(3) > C(8)] is twisted by ca. \( 88^\circ \) (\( 1a \)) and \( 86^\circ \) (\( 1b \cdot CH_3OH \)) [12,32] such that it is almost perpendicular to the C(1)–N(1)–C(2) plane, whereas for \( 3 \), the twist of the C(1)–N(1)–C(2) fragment is around \( 9^\circ \) from co-planarity with the N-arene group, apparently as a result of the intermolecular H-bonding requirements (\emph{vide infra}).

![Figure 1. Molecular structure of 1a. All hydrogens, except on C(1), C(2) and O(1), have been omitted for clarity.](image)

![Figure 2. Molecular structure of 3 showing a dimer pair. All hydrogens, except on C(1), C(2) and O(1), have been omitted for clarity. Symmetry code: \( A = 1 - x, 1 - y, 1 - z \).](image)
hydroxy group in 2f facilitates 0D dimer formation, as opposed to the chains observed in 1a.

In the IR spectra for 2, bands are observed in the range 3050–3465 cm−1 and also a strong band in the region of 1653–1675 cm−1, indicative of ν(C=O amide).

Figure 3. Crystal structure packing plot for 1b-CH3OH. Most H atoms, two Ph groups per P atom have been omitted for clarity. Symmetry code: A = x, −y + 1/2, z + 1/2.

Figure 4. Dimers of 2f forming R22(16) graph set motifs. Most H atoms omitted for clarity. The second unique molecule which adopts a similar, centrosymmetric motif, is not shown.

Figure 5. Intra- and intermolecular interactions in the crystal structure of 2g. Most H atoms omitted for clarity. Symmetry operator A = x, −y + 3/2, z − 1/2.
2.3. Secondary Interactions in 1a, 1b-CH₃OH, 2f-CH₃OH, 2g, and 3

The synthons observed in the solid state for these highly modular ligands may be dictated by various factors including the nature of the ligand, the flexibility of the P–C–N–C–P backbone, the predisposition of the OH/CH₃ groups about the N-arene ring, and the solvent used in the crystallisation. In order to probe the OH/CH₃ interplay of groups, the crystal structure of 1a, with the –OH group in the ortho position with respect to the N(1) atom, is described first. Ligand 1a crystallises with an intramolecular S(5) [33–35] H-bonded ring with \( d = 2.26(5) \) Å [denoting the hydrogen (H) to acceptor (A) distance in an H-bond D–H⋯A] [36] for the O–H⋯N interaction (Figure 1). The intramolecular H-bonding in 1a limits the dimensionality of the packing of the diphosphine ligand. Therefore, the structure of 1a is essentially zero-dimensional (Table 3).

Table 3. Selected data \((D\cdots A/\text{Å}, \angle D\cdots H\cdots A/\circ)\) for key inter- and intramolecular contacts for compounds 1a, 1b-CH₃OH, 2f-CH₃OH, 2g, and 3.

|          | 1a   | 1b-CH₃OH | 2f-CH₃OH | 2g   | 3    |
|----------|------|----------|----------|------|------|
| O–H⋯N\text{intra}            | 2.745(4), 119(4) |        |         |      |      |
| O–H\text{MeOH}⋯O\text{inter} | 2.844(8), 157    |        |         |      |      |
| O–H\text{MeOH}⋯O\text{MeOH} | 2.781(11), 172   |        |         |      |      |
| O–H⋯P\text{inter}            | 3.432(3), 173    |        |         |      |      |
| O–H⋯(O)C\text{inter}         | 2.671(3), 171(3) | 2.706(4), 167(2) |
| N–H⋯N\text{intra}            | 2.695(3), 114(2) | 2.748(4), 114(3) |

*Values in parentheses are for the second independent molecule.

Compound 3, where the –OH functional group is in the meta position with respect to the tertiary N(1) atom, aggregates in the solid state in such a way that fairly weak hydrogen bonds, O–H⋯P \( d = 2.60(2) \) Å, form between symmetry-related molecules, creating dimers in which two ligands are held in an \( R_2^2(16) \) H-bonding motif (Figure 2). The distance between symmetry-related nitrogen atoms is 8.257 Å. The structure of 3 shows a 0D arrangement.

Compound 1b-CH₃OH, which contains the –OH group in a para position with respect to the N-arene, displays a similar structure to 3 with intramolecular O–H⋯P interactions at \( d = 2.60 \) Å. However, instead of forming dimers, there are 1D zig-zag chains in the \( c \) direction (Figure 3). The \( \text{para} \) hydroxyl oxygen acts as an acceptor for an O–H⋯O intermolecular H-bond from approximately alternate CH₃OH molecules of crystallisation with \( d = 2.05 \) Å. These CH₃OH molecules are 50/50 disordered with the second component H-bonding to its neighbour with \( d = 1.95 \) Å. Selected hydrogen parameters for 1b-CH₃OH are listed in Table 3.

Compound 2f-CH₃OH crystallises with two, similarly behaved, molecules in the asymmetric unit. A pair of H-bonded molecules, related by inversion symmetry, and with \( d = 1.81(3) \) Å for the intermolecular O–H⋯O interaction [1.78(3) Å for molecule 2] affords \( R_2^2(16) \) ring motifs (Figure 4). The intramolecular N–H⋯N S(5) H-bond motif with \( d = 2.25(3) \) Å [2.26(3) Å for molecule 2] results in an intermediate twist angle of 64.23(13)° [but a rather more perpendicular 78.70(8)° for molecule 2] between planes C(1)/N(1)/C(2) and ring C(5) \( > C(10) \) [plane C(35)/N(4)/C(36) and ring C(39) \( > C(44) \) for molecule 2]. The meta hydroxy group in 2f facilitates 0D dimer formation, as opposed to the chains observed in 2g (*vida infra*).

For 2g, molecules form H-bonded, 1D, zig-zag chains in the \( c \) direction via strong O–H⋯O interactions with \( d = 1.83(5) \) Å (Figure 5). The intramolecular N–H⋯N S(5), H-bond motif with \( d = 2.29(3) \) Å again results in an almost perpendicular twist angle of 82.09(15)° between planes C(1)/N(1)/C(2) and arene ring C(5) \( > C(10) \). The para hydroxy group promotes chain formation.
2.4. Dichloroplatinum(II) Complexes of 1a–e, 2a–g, and 3

The synthesis of P,P-chelate complexes cis-PtCl₂(1a–e) [4a–e], cis-PtCl₂(2a–g) [5a–g], and cis-PtCl₂(3) [6] (Chart 2) was achieved by stirring the ligands and PtCl₂(n⁴-cod) (1:1 ratio) in CH₂Cl₂ for 1.5 h with displacement of the cod ligand. The products were isolated in good yields as colourless solids. Downfield shifts of the 31P NMR resonances were observed for all complexes, with ¹J_PtP coupling constants of approx. 3400 Hz, indicative of a cis conformation [29]. This was further supported by two characteristic ν_PtCl IR vibrations in the range of 279–316 cm⁻¹ (Table 4). Furthermore, compounds 4a–e, 5a–g, and 6 present ν(NH) and ν(OH) IR absorptions in the range 3050–3465 cm⁻¹ and also a strong band in the region of 1653–1675 cm⁻¹, indicative of ν(C=O amide).

Chart 2. Structures of compounds 4a–e, 5a–g, and 6.

Table 4. Selected spectroscopic and analytical data for compounds 4a–6.

| Compound | δ(P) b | δ(H) /OH (NH) | δ(H) /arom. H. | δ(H) /CH₂ | δ(H) /CH₃ | ν_OH (νHN) f | ν_PtCl | Microanalysis (CHN) |
|----------|--------|----------------|----------------|-----------|-----------|--------------|--------|-------------------|
| 4a (98)  | –9.4 d  | 7.89–7.90, 6.68, 6.33 | 4.21          | 3314      | 316, 289  | Calc. for C₃₅H₃₄Cl₂N₂O₂P₂Pt.0.5C₄H₁₀O, C, 50.52; H, 4.47; N, 3.19 |
| 4b (89)  | –4.9 d  | 7.89–7.90, 6.68, 6.33 | 4.21          | 3314      | 316, 289  | Calc. for C₃₃H₃₁Cl₂NOP₂Pt.CH₂Cl₂, C, 46.91; H, 3.82; N, 1.61 |
| 4c (78)  | –8.6 d  | 7.89–7.90, 6.68, 6.33 | 4.21          | 3314      | 316, 289  | Calc. for C₃₃H₃₁Cl₂NOP₂Pt, C, 50.46; H, 4.13; N, 1.83 |
| 4d (98)  | –11.7 d | 7.89–7.90, 6.68, 6.33 | 4.21          | 3314      | 316, 289  | Calc. for C₃₃H₃₁Cl₂NOP₂Pt, C, 50.46; H, 4.13; N, 1.83 |
| 4e (81)  | –7.8 d  | 7.89–7.90, 6.68, 6.33 | 4.21          | 3314      | 316, 289  | Calc. for C₃₃H₃₁Cl₂NOP₂Pt, C, 50.46; H, 4.13; N, 1.83 |
**Table 4. Cont.**

| Compound  | δ(P) a | δ(H)/OH (NH) | δ(H)/arom. H. | δ(H)/CH₂ | δ(H)/CH₃ | νOH (v(NH)) | νPCL | Microanalysis (CHN) |
|-----------|--------|---------------|----------------|----------|-----------|-------------|-------|---------------------|
| 5a (89)   | −9.8 d,e (3398) | 9.45 (8.91) | 7.84–7.80, 7.53–7.44, 6.69 | 3.49 | 4.05 | 2.22 | 3051 (3249) | 305, 283 |
| 5b (65)   | −11.0 d (3397) | 9.16 (8.61) | 7.83–7.80, 7.57–7.41, 7.05, 6.48 | 4.03 | 4.03 | 1.80 | 3050 (3350) | 316, 283 |
| 5c (73)   | −9.9 d (3405) | 9.56 (8.94) | 7.85–7.77, 7.59–7.38, 6.63, 6.51 | 3.17 | 4.05 | 2.17 | 3075 (3347) | 315, 290 |
| 5d (99)   | −9.8 c,d (3406) | 9.17 (8.90) | 7.98–7.50, 6.97–6.84, 6.68, 6.73 | 3.20 | 4.66 | 2.13 | 3323 (3465) | 309, 283 |
| 5e (90)   | −9.7 c,d (3406) | 9.46 (9.21) | 7.94–7.78, 7.54–7.42, 7.09, 6.87, 6.69 | 3.43 | 4.12 | 2.02 | 3287 (3439) | 312, 286 |
| 5f (85)   | −9.5 c,d (3425) | 9.62 (9.36) | 7.91–7.86, 7.60–7.42, 7.05, 6.83, 6.45 | 3.47 | 4.18 | 2.03 | 3053 (3312) | 304, 279 |
| 5g (84)   | −9.5 c,d (3405) | 9.52 (9.31) | 8.01–7.97, 7.70–7.61, 7.34, 6.78 | 3.49 | 4.26 | 2.03 | 3054 (3325) | 311, 287 |
| 6 (89)    | −4.0 d (3436) | 8.45 | 7.45–7.05, 6.89–6.76, 6.31, 6.31 | 4.31 | 4.31 | 2.03 | 3356 (311, 289) | 311, 289 |

a Isolated yields in parentheses. b Recorded in (CD₃)₂SO unless otherwise stated. c Recorded in CDCCl. d] J(PtP) coupling in parentheses. e Recorded in CDCCl/CDCl₂OD. f] Recorded as KBr discs.

2.5. Single Crystal X-ray Studies of Complexes 4b·(CH₃)₂SO, 4c·CHCl₃, 4d·Et₂O, 4e·CHCl₃, 4f·CH₂OH, 4g·Et₂O, 5a·H₂O, 5b·H₂O, 5c·Et₂O, and 6·(CH₃)₂SO

Detailed single crystal X-ray analysis (Tables 5 and 6) of complexes 4b·(CH₃)₂SO, 4c·CHCl₃, 4d·Et₂O, 4e·CHCl₃, 4f·CH₂OH, 5a·Et₂O, 5b·H₂O, 5c·Et₂O, and 6·(CH₃)₂SO shows that the geometry about each Pt(II) centre is approximately square planar [P–Pt–P range 90.23(9)–96.52(3)°] (Tables 7 and 8). The Pt–Cl and Pt–P bond distances are consistent with literature values [29] and the conformation of the Pt–P–C–N–C–P six-membered ring in each complex is best described as a boat. The dihedral angle measured between the P₂C₂ plane and N-arene ring least-squares planes varies between 50.98(12)° [in 6·(CH₃)₂SO] and 90° (in 5d·Et₂O), the difference of ca. 39° may tentatively be explained by the predisposition of the –OH group about the N-arene group and subsequent H-bonding requirements. Upon metal chelation, a degree of freedom, compared with the free ligands 1a, 1b·CH₃OH, 2f·CH₂OH, 2g, and 3 has been removed, as the P–C–N–C–P backbone is locked into a specific conformation. Unfortunately, we were unable to obtain suitable X-ray quality crystals of compounds 4a and 5e–g.
Table 5. Details of the X-ray data collections and refinements for compounds 4b·(CH₃)₂SO, 4c·CHCl₃, 4d·1/2OEt₂, and 4e·1/2CHCl₃·1/2CH₃OH.

| Compound  | 4b·(CH₃)₂SO | 4c·CHCl₃ | 4d·1/2OEt₂ | 4e·1/2CHCl₃·1/2CH₃OH |
|-----------|-------------|----------|------------|---------------------|
| Formula   | C₃₅H₃₇Cl₂NO₂P₂PtS | C₃₄H₃₅Cl₅NOP₂Pt | C₃₅H₃₆Cl₅NO₁.₅P₂Pt | C₃₄H₃₅Cl₅NO₁.₅P₂Pt |
| M         | 863.64      | 1014.98  | 904.88     | 822.58              |
| Crystal dimensions | 0.19 × 0.02 × 0.01 | 0.30 × 0.18 × 0.04 | 0.13 × 0.06 × 0.03 | 0.15 × 0.04 × 0.02 |
| Crystal morphology and colour | Needle, colourless | Plate, colourless | Lath, colourless | Needle, colourless |
| Crystal system | Tetragonal | Monoclinic | Monoclinic | Monoclinic |
| Space group | P₄₃ | P2₁/n | P2₁/n | P2₁/n |
| a/Å        | 11.373(3)  | 11.6938(4) | 15.7344(4) | 21.4521(4) |
| b/Å        | 16.7052(6) | 17.0714(6) | 12.5164(2) | 12.5164(2) |
| c/Å        | 26.773(6)  | 18.2242(7) | 13.9632(5) | 24.5837(4) |
| α/°        | 99.7066(6) | 92.0800(4) | 92.2343(5) | 92.2343(5) |
| β/°        | 92.6753(8) | 92.0800(4) | 92.2343(5) | 92.2343(5) |
| γ/°        | 99.7066(6) | 92.0800(4) | 92.2343(5) | 92.2343(5) |
| V/Å³       | 3463(2)    | 3509.1(2) | 3748.2(2) | 6595.78(19) |
| Z          | 4          | 4         | 4          | 8               |
| Density (calcd.)/Mg/m³ | 1.657 | 1.713 | 1.458 | 1.735 |
| μ/mm⁻¹     | 4.391      | 4.500     | 3.425     | 4.666 |
| θ range/°  | 1.79–26.09 | 1.67–31.09 | 1.78–31.10 | 2.94–27.49 |
| Measured reflections | 29848 | 32600 | 48268 | 84353 |
| Independent reflections | 6852 | 10997 | 13239 | 15063 |
| Observed reflections | 5560 | 8926 | 10198 | 12905 |
| R[F² > 2σ(F²)] a | 0.110 | 0.043 | 0.039 | 0.049 |
| wR2[all data] b | 0.0473 | 0.0303 | 0.0266 | 0.0561 |
| Largest difference map features/eÅ⁻³ | 1.43, −0.91 | 1.29, −1.08 | 0.84, −0.67 | 1.64, −1.48 |

Table 6. Details of the X-ray data collections and refinements for compounds 5a·1/2OEt₂, 5b, 5c·1/2H₂O, 5d·OEt₂, and 6(CH₃)₂SO.

| Compound  | 5a·1/2OEt₂ | 5b | 5c·1/2H₂O | 5d·OEt₂ | 6·(CH₃)₂SO |
|-----------|------------|----|-----------|---------|------------|
| Formula   | C₃₅H₃₇Cl₂NO₂P₂O₂Pt | C₃₅H₃₇Cl₂NO₂P₂O₂Pt | C₃₅H₃₆Cl₂N₂O₂P₂Pt | C₃₅H₃₆Cl₂N₂O₂P₂Pt | C₃₅H₃₆Cl₂N₂O₂P₂Pt |
| M         | 879.63     | 879.63 | 842.57 | 916.69 | 849.62 |
| Crystal dimensions | 0.12 × 0.06 × 0.05 | 0.05 × 0.02 × 0.01 | 0.09 × 0.05 × 0.02 | 0.13 × 0.12 × 0.02 | 0.32 × 0.11 × 0.02 |
| Crystal morphology and colour | Block, colourless | Plate, colourless | Plate, colourless | Plate, colourless | Needle, colourless |
| Crystal system | Trigonal | Monoclinic | Triclinic | Orthorhombic | Monoclinic |
| Space group | P₃₁ | P2₁/n | PT | Pbcm | P2₁/n |
| a/Å        | 24.3688(7) | 18.2384(7) | 8.4021(6) | 10.125(6) | 9.7763(4) |
| b/Å        | 18.2384(7) | 17.0714(6) | 10.3896(3) | 19.7900(11) | 13.0930(5) |
| c/Å        | 35.0821(6) | 32.805(2) | 21.8810(15) | 18.407(10) | 25.8715(10) |
| α/°        | 99.7066(6) | 106.6253(8) | 92.3830(10) | 97.9841(9) | 95.1690(6) |
| β/°        | 92.6753(8) | 106.6253(8) | 92.3830(10) | 97.9841(9) | 95.1690(6) |
| γ/°        | 99.7066(6) | 106.6253(8) | 92.3830(10) | 97.9841(9) | 95.1690(6) |
| V/Å³       | 5480.5(4)  | 3280.5(2) | 1804.5(2) | 3688(4) | 3288.1(2) |
| Z          | 4          | 4         | 4         | 4       | 4         |
| Density (calcd.)/Mg/m³ | 1.79 | 1.713 | 1.458 | 1.735 | 1.735 |
| μ/mm⁻¹     | 5.266      | 4.225     | 3.561     | 4.077   | 4.609     |
| θ range/°  | 3.69–33.17 | 1.19–31.01 | 2.71–30.94 | 2.01–25.00 | 1.58–30.64 |
| Measured reflections | 48822 | 37553 | 22910 | 25092 | 38887 |
Table 6. Cont.

| Compound       | 5a·\(\frac{1}{2}\)OEt₂ | 5b | 5c·\(\frac{1}{2}\)H₂O | 5d·OEt₂ | 6·(CH₃)₂SO |
|----------------|------------------------|----|---------------------|---------|------------|
| Independent reflections | 19,298                | 10,642 | 12,184             | 3357    | 10,104     |
| Observed reflections | 17,145                | 8283  | 10,104             | 2051    | 7753       |
| \(F² > 2 \sigma(F²)\) |                       |      |                     |         |            |
| \(R_{\text{int}}\) | 0.071                  | 0.063 | 0.053              | 0.1504  | 0.0572     |
| \(wR₂\) [all data] | 0.0542                 | 0.0363 | 0.0507             | 0.0746  | 0.0356     |
| Largest difference map features/eÅ\(^{-3}\) | 1.59, -1.71           | 1.40, -1.47 | 2.34, -3.46 | 2.77, -1.91 | 1.97, -1.50 |

\(^a\) \(R = \sum |F_o| - |F_c| / \sum |F_o|\), \(^b\) \(wR₂ = \sum w(F_o² - F_c²)^2 / \sum w(F_o²)^2\)^\(^1/2\).

Table 7. Selected bond distances and angles for dichloroplatinum(II) compounds 4b·(CH₃)₂SO, 4c·CHCl₃, 4d, and 4e·\(\frac{1}{2}\)CHCl₃·\(\frac{1}{2}\)CH₃OH.

| Bond Length (Å) | 4b·(CH₃)₂SO | 4c·CHCl₃ | 4d | 4e·\(\frac{1}{2}\)CHCl₃·\(\frac{1}{2}\)MeOH \(^a\) |
|-----------------|-------------|-----------|----|---------------------------------|
| Pt(1)–Pt(1)    | 2.223(4)    | 2.226(6)  | 2.225(7) | 2.238(18) [2.235(18)] |
| Pt(1)–Pt(2)    | 2.225(4)    | 2.2186(7) | 2.214(6)  | 2.245(18) [2.246(18)] |
| Pt(1)–Cl(1)    | 2.358(4)    | 2.3625(6) | 2.3558(6) | 2.3560(18) [2.3574(17)] |
| Pt(1)–Cl(2)    | 2.359(4)    | 2.3464(6) | 2.3553(6) | 2.3694(17) [2.3616(18)] |

Bond angle (°)

| Cl(1)–Pt(1)–P(1) | 87.91(14) | 86.06(2)  | 87.63(2) | 87.30(7) [86.87(7)] |
| Cl(1)–Pt(2)–P(2) | 174.97(15)| 176.00(2) | 175.93(2) | 176.50(7) [176.84(7)] |
| Cl(1)–Pt(1)–Cl(2)| 88.95(13) | 88.98(2)  | 90.43(2) | 88.13(7) [87.34(7)] |
| Cl(2)–Pt(1)–P(1) | 176.97(15)| 174.73(2) | 177.81(2) | 169.14(7) [170.73(7)] |
| P(1)–Pt(1)–P(2)  | 96.35(14) | 96.07(3)  | 96.42(2) | 96.17(7) [95.95(7)] |

\(^a\) Values in parentheses are for the second independent molecule.

Table 8. Selected bond distances and angles for dichloroplatinum(II) compounds 5a·\(\frac{1}{2}\)OEt₂, 5b, 5c·\(\frac{1}{2}\)H₂O, 5d·OEt₂, and 6·(CH₃)₂SO.

| Bond Length (Å) | 5a·\(\frac{1}{2}\)OEt₂ \(^a\) | 5b | 5c·\(\frac{1}{2}\)H₂O | 5d·OEt₂ | 6·(CH₃)₂SO |
|-----------------|------------------------|----|---------------------|---------|------------|
| Pt(1)–Pt(1)    | 2.233(3) [2.234(3)]    | 2.2172(9) | 2.2268(12) | 2.220(3)  | 2.2219(9) |
| Pt(1)–Pt(2)    | 2.230(3) [2.229(3)]    | 2.2249(9) | 2.2196(12) | 2.228(3)  | 2.2288(9) |
| Pt(1)–Cl(1)    | 2.381(3) [2.378(3)]    | 2.3685(9) | 2.347(4) \(^b\) | 2.348(3)  | 2.3421(9) |
| Pt(1)–Cl(2)    | 2.361(3) [2.365(3)]    | 2.3425(9) | 2.3638(12) | 2.3618(10)|            |

Bond angle (°)

| Cl(1)–Pt(1)–P(1) | 86.31(10) [86.48(10)] | 85.73(3) | 92.55(11) | 89.98(12) | 88.81(3) |
| Cl(1)–Pt(1)–P(2) | 177.81(12) [177.51(12)] | 176.29(3) | 167.1(2)  | 176.96(13) | 173.98(3) |
| Cl(1)–Pt(1)–Cl(2) | 90.20(13) [90.16(13)] | 89.33(3) | 88.17(11) | 87.38(17) | 88.78(4) |
| Cl(2)–Pt(1)–P(2) | 87.75(14) [87.51(13)] | 88.31(3) | 87.76(4)  | 89.98(12) | 87.17(3) |
| Cl(2)–Pt(1)–P(1) | 175.76(12) [175.67(12)] | 174.72(3) | 178.70(5) | 176.96(13) | 174.52(4) |
| P(1)–Pt(1)–P(2)  | 90.20(13) [95.81(11)] | 96.52(3) | 91.30(4)  | 92.62(17) | 94.83(3) |

\(^a\) Values in parentheses are for the second independent molecule. \(^b\) 2-fold disorder. \(^c\) Molecule lies on a mirror plane.

Despite the ortho position of the hydroxy group in 4c·CHCl₃, molecules do not form an intramolecular S(5) O–H⋯⋅N interaction as seen in 1a (Figure 1), instead forming a bifurcated H-bond with the two coordinated chloride ligands of an adjacent molecule (Figure 6). This generates a 1D chain, and also attracts a bifurcated H-bonded chloroform...
molecule. There are somewhat asymmetric distances \( d \) for H(1C) to Cl(1) and Cl(2) are 2.45(4) and 2.76(4) Å, while those from H(34) to Cl(1) and Cl(2) are 2.66 and 2.86 Å, so are also asymmetric. The twist angle between planes \( \text{P}(1)/\text{P}(2)/\text{C}(1)/\text{C}(2) \) and ring \( \text{C}(3) > \text{C}(8) \) is 84.83(8)°, so is almost perpendicular. Atoms N(1) and Pt(1) lie 0.795(4) and 0.024(2) Å away from the \( \text{P}(1)/\text{P}(2)/\text{C}(1)/\text{C}(2) \) plane, respectively. The hinge angle across the \( \text{P}(1)--\text{P}(2) \) vector is 2.51(5)°. Selected hydrogen bonding geometric parameters for 4c·CHCl\(_3\) are shown in Table 9.

![Figure 6. H-bonded packing arrangement in the crystal structure of 4c·CHCl\(_3\). Most H atoms omitted for clarity. Symmetry operator A = x+\( \frac{1}{2} \), –y+\( \frac{1}{2} \), z+\( \frac{1}{2} \).](image)

**Table 9.** Selected data (\( D \cdots A / \AA, \angle D--H--A/° \)) for key inter- and intramolecular contacts for compounds 4b·(CH\(_3\))\(_2\)SO, 4c·CHCl\(_3\), 4e·½CHCl\(_3\), 1/2CH\(_3\)OH, 5a·½OEt\(_2\), 5b, 5c·1/2H\(_2\)O, 5d·OEt\(_2\), and 6·(CH\(_3\))\(_2\)SO.

|                  | 4b·(CH\(_3\))\(_2\)SO | 4c·CHCl\(_3\) | 4e·1/2CHCl\(_3\) | 5a·1/2OEt\(_2\) | 5b       | 5c·1/2H\(_2\)O | 5d·OEt\(_2\) | 6·(CH\(_3\))\(_2\)SO |
|------------------|------------------------|--------------|------------------|-----------------|----------|----------------|--------------|----------------------|
| O–H···(O)C\(_{\text{inter}}\) |                         |              |                  |                 |          |                |              |                      |
| N–H···N\(_{\text{intra}}\)   |                         |              |                  |                 |          |                |              |                      |
| O–H\(_{\text{inter}}\)···O\(_{\text{MeOH}}\) | 2.624(10), 160 | 3.145(2), 145(3), 3.361(2), 133(3) | 3.197(6), 160(9) | 3.065(3), 161(5) |          |                |              |                      |
| O–H\(_{\text{inter}}\)···ClPt | 2.716(17), 170 |                       |                  |                 |          |                |              | 1.79(2), 173(5)     |
| N–H\(_{\text{inter}}\)···ClPt |                       | 3.328(12), 145(16) | 3.320(11), 159(16) | 2.596(13), 157   | 3.505(15), 138(6) |
| O–H···(O)C\(_{\text{intra}}\) |                       | 2.610(13), 175(20) |                  |                 |          |                |              |                      |

\(^a\) Values in parentheses are for the second independent molecule. \(^b\) For the major disorder component; 2.658(12), 117 for the minor component.

Compound 6·(CH\(_3\))\(_2\)SO, in which the –OH group is meta to the N-arene group H-bonds to the DMSO molecule of crystallisation resulting in a 0D structure (Figure 7). The distance \( d \) for this H-bond is 1.79(2) Å. The twist angle between plane \( \text{P}(1)/\text{P}(2)/\text{C}(1)/\text{C}(2) \) and ring \( \text{C}(3) > \text{C}(8) \) is 50.98(12)°. Atoms N(1) and Pt(1) lie 0.758(4) and 0.404(2) Å away from the \( \text{P}(1)/\text{P}(2)/\text{C}(1)/\text{C}(2) \) plane, respectively, so is more chair-shaped than some of the
other platinum(II) complexes reported here. The hinge angle across the P(1)–P(2) vector is 11.87(13)°.

For 4d, ½Et₂O (Figure 8) a molecule of badly disordered diethyl ether, modelled by the Platon Squeeze procedure, is not shown, but is in the vicinity of the hydroxy group and may H-bond to it resulting in a 0D structure. The twist angle between plane P(1)/P(2)/C(1)/C(2) and ring C(3) > C(8) is 67.82(7)°. Atoms N(1) and Pt(1) lie 0.797(3) and 0.2378(16) Å away from the P(1)/P(2)/C(1)/C(2) plane, respectively. The hinge angle across the P(1)–P(2) vector is 9.20(9)°.

The crystal structure of 4b∙(CH₃)₂SO shows the hydroxy group H-bonding to the (CH₃)₂SO molecule of crystallisation. Most H-atoms omitted for clarity.

Figure 7. Crystal structure of 6∙(CH₃)₂SO showing the hydroxyl group H-bonding to the (CH₃)₂SO molecule of crystallisation. Most H-atoms omitted for clarity.

Figure 8. Crystal structure of 4d∙½Et₂O. Most H atoms and the disordered OEt₂ molecule omitted for clarity.

The crystal structure of 4b∙(CH₃)₂SO shows the hydroxy group H-bonding to the DMSO molecule of crystallisation (Figure 9a). The distance d for this H-bond is 1.89 Å. The twist angle between plane P(1)/P(2)/C(1)/C(2) and ring C(3) > C(8) is 72.2(4)°. Atoms N(1) and Pt(1) lie 0.758(4) and 0.404(2) Å away from the P(1)/P(2)/C(1)/C(2) plane, respectively. The hinge angle across the P(1)–P(2) vector is 9.20(9)°.

Selected hydrogen bonding parameters for 4b∙(CH₃)₂SO are shown in Table 9.
Figure 9. (a) Crystal structure of 4b·(CH$_3$)$_2$SO showing the hydroxyl group H-bonding to the DMSO molecule of crystallisation. Most H-atoms removed for clarity. (b) Packing interactions in the crystal structure of 4b·(CH$_3$)$_2$SO. Most H atoms omitted for clarity. Symmetry operator A = y − 1, 1 − x, ¼ + z.

For compound 4e·$\frac{1}{2}$CHCl$_3$·$\frac{1}{2}$CH$_3$OH there are two independent Pt complexes, one CH$_3$OH, and one CHCl$_3$ in the asymmetric unit. Both Pt complexes form 1D chains aligned parallel to $b$, but these chains are different (Figure 10). The chain involving Pt(2) forms simple O–H⋯Cl H-bonds with the adjacent molecules via the para hydroxy group with $d$ = 2.39(4) Å. For the chain involving the Pt(1)-containing molecules, the intermolecular H-bond has an inserted methanol molecule. The distances, $d$, are 2.32(5) and 1.82 Å for H(3)⋯Cl(2) and H(1A)⋯O(3), respectively. Atoms N(1)/N(2) and Pt(1)/Pt(2) lie 0.765(9)/0.798(9) and 0.424(5)/0.364(5) Å away from the P(1)/P(2)/C(1)/C(2) or P(3)/P(4)/C(34)/C(35) planes, respectively. So, as in 6·(CH$_3$)$_2$SO, the core 6-membered Pt–P–C–N–C–P rings adopt more chair-shaped conformations. The hinge angles across the P(1)–P(2)/P(3)–P(4) vectors are 13.44(16)/12.47(16)$^\circ$. The twist angles between planes P(1)/P(2)/C(1)/C(2) or P(3)/P(4)/C(34)/C(35) and rings C(3) > C(8) or C(36) > C(41) are 88.17(19)/54.62(15)$^\circ$. So, while the other geometric parameters are similar between the two molecules, this twist angle is significantly different.
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![Figure 10](image-url)

**Figure 10.** H-bonded packing motifs in the crystal structure of 4e·½CHCl₃·½CH₃OH. Most H atoms, two Ph groups per P atom, and the disordered chloroform of crystallisation which is not involved in any significant intermolecular interactions, are omitted for clarity. Symmetry operators are x, y − 1, z and x, y + 1, z.

In 5c, the amide and ring atoms from C(4) > C(11) are disordered over two sets of almost equally occupied positions. The disorder highlights two or more chain-forming possibilities for this structure, analogous to that observed in 4e·½CHCl₃·½CH₃OH, with one possibility being simple (hydroxyl)O–H–O(amide) links (Figure 11a), while the other, shown in Figure 11b, shows an alternative, water-inserted linkage. There is also likely to be some alternation of these motifs, given the random disorder and approx. 25% occupancy observed for water atom O(3). Unlike almost all of the other structures herein, the core 6-membered Pt–P–C–N–C–P ring adopts a conformation with atoms Pt(1)/P(1)/P(1)/C(2) being in a plane and atoms C(1) and N(2) being 1.021(6) and 1.237(6) Å, respectively, away from that plane. There is no C=O···HN intermolecular H-bonding observed between molecules. Instead, the amide NH forms a bifurcated H-bond with the two neighbouring acceptor atoms N(1) and the *ortho* hydroxyl O(2) with d = 2.37 and 2.28 Å, respectively, while d = 2.89 Å for H(2)···O(1A).

![Figure 11](image-url)

**Figure 11.** Most H atoms and 2 Ph groups per P atom have been omitted for clarity. (a) Packing motif 1 in the crystal structure of 5c. Symmetry operator A = x + 1, y, z. (b) Packing motif 2 in the crystal structure of 5c. The true structure is most likely an alternation of motifs 1 and 2. Symmetry operator A = x + 1, y, z.
In the second motif, adjacent molecules have an inserted water molecule in the H-bond pattern (Figure 11b). The amide NH again forms a bifurcated H-bond with the two neighbouring acceptor atoms N(1) and O(2X) with $d = 2.14$ and 2.25 Å, respectively, while $d = 2.89$ Å for H(2X)···O(3), which is a little long, and $d$ for O(3)···O(1XA) = 2.21(3) Å, which is rather short. The distance $d$ from water oxygen O(3) to O(1A), however, is entirely reasonable for an H-bond at 2.74 Å, suggesting a predominantly alternating pattern between the two disorder options is most likely.

Complex 5a·½Et$_2$O was crystallised from a diethyl ether solution, including half a solvent molecule per complex molecule in the crystal lattice. There are two Pt complexes and two, half-occupied, Et$_2$O solvent molecules of crystallisation in the asymmetric unit. The packing adopted by this second complex with an ortho hydroxyl group is very different to 5c (Figure 12). Here there is no intramolecular N–H···N H-bond, instead the ortho hydroxyl forms an intramolecular H-bond with the amide oxygen with $d = 1.80$ and 1.77(4) Å in the molecules containing Pt(1) and Pt(2), respectively. This does leave the two unique amide NH atoms free to form intermolecular interactions, which they do via highly asymmetric, bifurcated H-bonds with the coordinated chloride ligands on adjacent Pt complexes. From H(2) $d = 2.60(11)$ and 2.95(13) Å to Cl(3) and Cl(4), respectively, while $d = 2.52(7)$ and 3.12(15) Å from H(4) to Cl(1A) and Cl(2A), respectively. N(1)/N(3) and Pt(1)/Pt(2) lie 0.771(13)/0.781(14) and 0.349(8)/0.346(8) Å out of the planes P(1)/P(2)/C(1)/C(2) and P(3)/P(4)/C(37)/C(38), respectively. The twist angle between planes P(1)/P(2)/C(1)/C(2) and P(3)/P(4)/C(37)/C(38) relative to the rings C(5) > C(10) and C(41) > C(46) are 51.3(5) and 51.71(4)$^\circ$, respectively. Hinge angles across P(1)–P(2) and P(3)–P(4) are 12.3(5) and 12.0(4)$^\circ$, respectively. Differences between the two systems involving ortho hydroxyl groups are the position of the methyl ring substituent in the meta or para position, and the co-crystallised solvent being a small amount of water or Et$_2$O. Either, or both of these differences might account for the different intra- and intermolecular packing motifs observed. Selected hydrogen bonding parameters for 5a·½Et$_2$O are shown in Table 9.

![Figure 12. Packing motif in the crystal structure of 5a·½Et$_2$O. Most H atoms, two Ph groups per P atom and the two, half-occupied, Et$_2$O molecules have been omitted for clarity.](image-url)
Pt–P–C–N–C–P 6-membered ring. The meta hydroxyl group is not involved in the chain propagating intermolecular interactions and points into a cleft between a pair of Ph rings. It does not make an H-bond with the solvent of crystallisation.

For compound 5b, the para position of the hydroxyl group facilitates 1D chain formation, forming an H-bond with one of the chloride ligands on an adjacent molecule with $d = 2.09(6)$ Å (Figure 14). The amide NH here forms the familiar, but not universal, H-bond with the amine N(1) with $d = 2.29(5)$ Å. The twist angle between the P(1)/P(2)/C(1)/C(2) plane and the ring C(5) > C(10) = $68.39(12)^\circ$. The hinge angle at P(1)–P(1A) = $4.95(10)^\circ$. Atoms N(1) and Pt(1) lie 0.810(4) and 0.164(3) Å away from the P(1)/P(2)/C(1)/C(2) plane, respectively.

In summary, we have shown that the position of the OH/CH$_3$ groups with respect to the N-arene, the inclusion of an amide spacer, and the solvent used in the crystallisation can dictate the solid-state packing behaviour of both non coordinated and cis-PtCl$_2$ bound diphosphine ligands. Unsurprisingly, the use of highly polar solvents (DMSO, CH$_3$OH) in this study has been shown to play an important role in disrupting packing behaviour. Our work reinforces the importance of substituent effects, not only those commonly associated with –PR$_2$ groups which may be alkyl or aryl based [37,38], but also those functional moieties positioned on the arene group of the central tertiary amine.

### 4. Conclusions

In summary, we have shown that the position of the OH/CH$_3$ groups with respect to the N-arene, the inclusion of an amide spacer, and the solvent used in the crystallisation can dictate the solid-state packing behaviour of both non coordinated and cis-PtCl$_2$ bound diphosphine ligands. Unsurprisingly, the use of highly polar solvents (DMSO, CH$_3$OH) in this study has been shown to play an important role in disrupting packing behaviour. Our work reinforces the importance of substituent effects, not only those commonly associated with –PR$_2$ groups which may be alkyl or aryl based [37,38], but also those functional moieties positioned on the arene group of the central tertiary amine.

### 4. Materials and Methods

#### 4.1. General Procedures

The synthesis of ligands 1a–e, 2a–g, and 3 were undertaken using standard Schlenk-line techniques and an inert nitrogen atmosphere. Ph$_2$PCH$_2$OH was prepared according to a known procedure [39]. All coordination reactions were carried out in air, using reagent grade quality solvents. The compound PtCl$_2$(η$^4$-cod) (cod = cycloocta-1,5-diene) was...
prepared according to a known procedure [40]. All other chemicals were obtained from commercial sources and used directly without further purification.

4.2. Instrumentation

Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum 100S (4000–250 cm$^{-1}$ range) Fourier-Transform spectrometer. $^1$H NMR spectra (400 MHz) were recorded on a Bruker DPX-400 spectrometer with chemical shifts (δ) in ppm to high frequency of Si(CH$_3$)$_4$ and coupling constants (J) in Hz. $^{31}$P[$^1$H] NMR (162 MHz) spectra were recorded on a Bruker DPX-400 spectrometer with chemical shifts (δ) in ppm to high frequency of 85% H$_3$PO$_4$. NMR spectra were measured in CDCl$_3$ or (CD$_3$)$_2$SO at 298 K. Elemental analyses (Perkin-Elmer 2400 CHN Elemental Analyser) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

4.3. Preparation of Ligands 1a–e, 2a–g, and 3

The following general procedure was used for the synthesis of 1a–e, 2a–g, and 3. A mixture of Ph$_2$PCH$_2$OH (2 equiv.) and the appropriate amine (1 equiv.) in CH$_2$OH (20 mL) was stirred under N$_2$ for 24 h. The volume of the solution was evaporated to ca. 2–3 mL, under reduced pressure, to afford the desired ligands which were collected by suction filtration (except 2a–c) and dried in vacuo. Isolated yields in range 73–99%. Characterising details are given in Table 1.

4.4. Preparation of cis-Dichloroplatinum(II) Phosphine Complexes 4a–e, 5a–g, and 6

The following general procedure was used for the synthesis of 4a–e, 5a–g, and 6. To a solution of PtCl$_2$(η$^3$-cod) (1 equiv.) in CH$_2$Cl$_2$ (5 mL) was added a solution of the appropriate ligand (1 equiv.) in CH$_2$OH (5 mL). The colourless (or pale yellow) solution was stirred for 30 min at r.t., evaporated to ca. 2–3 mL under reduced pressure, and diethyl ether (10 mL) added. The solids were collected by suction filtration and dried in vacuo. Isolated yields in range 73–99%. Characterising details are given in Table 4.

4.5. Single Crystal X-ray Crystallography

Suitable crystals of 1a, 1b·CH$_3$OH, 2f·CH$_3$OH 3, 4b·(CH$_3$)$_2$SO, 4c·CHCl$_3$, 4d 4e·$^1$CHCl$_3$·$^1$CH$_2$OH, 5d·Et$_2$O, and 6·(CH$_3$)$_2$SO, were collected using a Bruker or Bruker-Nonius APEX 2 CCD diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. Data for compounds 5b and 5c·$^1$H$_2$O, were collected using a Bruker APEX 2 CCD diffractometer using synchrotron radiation at Daresbury SRS Station 9.8 or 16.2 SMX for 5a·$^1$Et$_2$O. Data for compound 2g was collected using a Bruker SMART 1000 CCD diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. All structures were solved by direct methods [except structures 4b·(CH$_3$)$_2$SO, 5a·$^1$Et$_2$O, and 5b which were solved using Patterson synthesis] and refined by full-matrix least-squares methods on F$^2$. All CH atoms were placed in geometrically calculated positions and were refined using a riding model (aryl C–H 0.95 Å, methyl C–H 0.98 Å, methylene C–H 0.99 Å. Where data quality allowed, OH and NH atom coordinates and U$_{eq}$ were freely refined, or refined with mild geometrical restraints; otherwise, they were placed geometrically with O/N–H = 0.84 Å. U$_{eq}$(H) values were set to be 1.2 times U$_{eq}$ of the carrier atom for aryl CH and NH, and 1.5 times U$_{eq}$ of the carrier atom for OH and CH$_3$. Throughout the text and tabulated data, where H atom geometry does not include a SU, the coordinates were
constrained. Unless stated, all structural determinations proceeded without the need for restraints or disorder modelling. Where disorder was modelled it was supported with appropriate geometrical and \( U \) value restraints. In 1b·CH\(_3\)OH, the methanol was modelled as disordered over two equally occupied sets of positions. In 2f·CH\(_3\)OH the methanol was modelled using the Platon Squeeze procedure [41]. Compound 3 was found to contain a disordered methanol and was modelled over two sets of positions, each at half weight. In 4d·Et\(_2\)O, atoms C(1) > C(7) and N(1) were modelled with \( U \) value restraints. The Et\(_2\)O was modelled using Platon Squeeze due to significant disorder. In 4e·CHCl\(_3\)·CH\(_3\)OH the chloroform molecule was modelled over two sets of positions with major occupancy 57.1(7)% Restraints were applied to that molecule and also ring C(55) > C(60). In 5a·Et\(_2\)O three Ph rings were modelled as disordered over two sets of positions with occupancies close to 50%. Restraints were applied to these rings and also the two half-occupancy Et\(_2\)O solvent molecules of crystallisation. In 5c·H\(_2\)O, atoms C(11) and C(3) > C(11), O(1), O(2) and N(1) were modelled as split over two sets of positions with major occupancy 56(4) and 50.9(6)%, respectively and restraints were applied. In 5d·Et\(_2\)O the Et\(_2\)O was modelled as a diffuse area of electron density by the Platon Squeeze procedure and restraints were applied to atoms C(1) > C(10), C(11) > C(22) and N(2) O(2). In 6·(CH\(_3\))\(_2\)SO the DMSO was modelled with restraints as disordered over two sets of positions with major component 71.0(5)% and with C(33) coincident for both components Programs used during data collection, refinement and production of graphics were Bruker SMART, Bruker APEX 2, SAINT, SHELXTL, COLLECT, DENZO and local programs [41–51]. CCDC 2101643–2101656 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures (accessed on 3 November 2021).

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