

Synthesis and structure of platinum(II) complexes with mixed $\text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2/[\text{Ph}_2\text{PNP}(\text{O})\text{Ph}_2]^-$ or $\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2/[\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}]^-$ hybrid ligands: new $\text{M}-\text{P}-\text{N}-\text{H}\cdots\text{N}-\text{P}$ metallacycles

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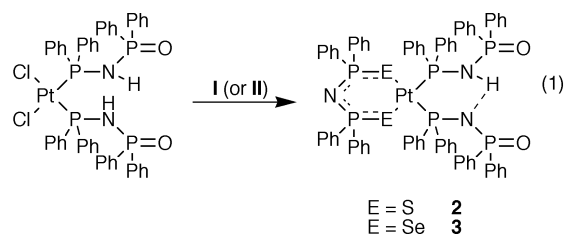
Transmetalation of $\text{K}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$ ($\text{E} = \text{S}$ or Se) with $\text{cis}-[\text{PtCl}_2(\text{HL})_2]$ [$\text{HL} = \text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2$ or $\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2$] gave the mixed platinum(II) compounds $[\text{Pt}\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\text{-E,E'}\}\text{L}(\text{HL})]$ containing one deprotonated $[\text{Ph}_2\text{PNP}(\text{O})\text{Ph}_2]^-$ ligand; X-ray crystallography reveals an unusual pseudo six-membered $\text{Pt}-\text{P}-\text{N}-\text{H}\cdots\text{N}-\text{P}$ metalloring structure.

The chemistry of hybrid ligands, bearing both “hard” (e.g. N, O) and “soft” (e.g. P) donor centres, is an area that has received considerable attention of late.^{1–3} Their ability to co-ordinate catalytically useful transition-metals and subsequent application in several metal-catalysed transformations continues to be demonstrated. Much of their success can be traced to the relatively strong $\text{M}-\text{P}$ bond whilst facile dissociation of N or O from M creates a suitable vacant site. Recently the synthesis and co-ordination chemistry of a new heterodifunctional ligand $\text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2$, HL, was reported.⁴ Two ligating modes exist for this hybrid ligand, the most prevalent is P-ligation although P,O-chelation has frequently been observed.^{4–8} The amine proton in metal co-ordinated compounds of HL can be removed to give $[\text{Ph}_2\text{PNP}(\text{O})\text{Ph}_2]^-$, L. Altogether three different co-ordination types for L have been found namely P-co-ordination, P,O-chelation and P,O-bridging.^{4–8} One feature common with much of the chemistry of P-monodendate complexes of L and HL is the propensity for $\text{N}-\text{H}\cdots\text{X}$ ($\text{X} = \text{Cl}$, Br or O) H-bonding. Here we describe the synthesis and characterisation of two unexpected platinum(II) complexes containing a single deprotonated $[\text{Ph}_2\text{PNP}(\text{O})\text{Ph}_2]^-$ stabilised by an intramolecular H-bond from a neighbouring *cis*-bound $\text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2$ ligand. The hydrogen bonded moiety $\text{M}-\text{P}-\text{N}-\text{H}\cdots\text{N}-\text{P}$ presented here has not, to the best of our knowledge, been reported previously. Related metal complexes with a chelating $\text{M}-\text{P}-\text{O}-\text{H}\cdots\text{O}-\text{P}$ hydrogen bonding array are well known and in many cases the $\text{OH}\cdots\text{O}$ bridge approaches a symmetrical disposition between the two oxygen atoms.⁹ Nixon and co-workers¹⁰ recently described the unusual complex $[\text{PtCl}_2(\text{PMe}_3)(\text{P}_2\text{O}_3\text{C}_3\text{H}_5\text{Bu}_3)]$ which, in the solid state, has a dimeric structure with bridging $\text{M}-\text{P}-\text{O}\cdots\text{H}\cdots\text{O}-\text{P}-\text{M}$ hydrogen bonds.

The synthesis of such a square-planar metal complex bearing a *cis* configuration of neutral/deprotonated HL/L ligands appears somewhat challenging. In prior work we showed that reaction of *cis*- $[\text{PtCl}_2(\text{HL})_2]$ **1** with KOBU^t affords the bis-P,O-chelate complex *cis*- $[\text{Pt}\{\text{Ph}_2\text{PNP}(\text{O})\text{Ph}_2\text{-P,O}\}_2]$ ⁴ whilst attempts to prepare $[\text{Pt}\{\text{Ph}_2\text{PNP}(\text{O})\text{Ph}_2\text{-P,O}\}\text{Cl}\{\text{Ph}_2\text{PNP}(\text{O})\text{Ph}_2\text{-P}\}]$ using stoichiometric amounts of KOBU^t were unsuccessful. An insight into how such a

transformation may be accomplished came from recent work describing the synthesis of $[\text{Pt}\{\text{Ph}_2\text{PC}_6\text{H}_4\text{NH-P,N}\}\{\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2\text{-P,N}\}][\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{E})\text{Ph}_2]$.¹¹ Reaction of **1**⁴ with one equivalent of $\text{K}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$ ($\text{E} = \text{S}$ **1**; $\text{E} = \text{Se}$ **2**)^{12,13} gave the new complexes $[\text{Pt}\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\text{-E,E'}\}\text{L}(\text{HL})]$ ($\text{E} = \text{S}$ **2**; $\text{E} = \text{Se}$ **3**) in respectable yields [eqn. (1)].[†] Alternatively when $[\text{PtCl}_2(\text{cod})]$ (*cod* = cycloocta-1,5-diene), HL and **1** (1 : 2 : 1 ratio) were allowed to react in CH_3OH , compound **2** was isolated in slightly higher yield (86%). Whilst the stoichiometry of the reaction necessitates the use of two equivalents of $\text{K}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$ we found that when the reaction was performed on a 1 : 1 ratio of **1** : $\text{K}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$, a cleaner sample [free of $\text{Ph}_2\text{P}(\text{E})\text{NHP}(\text{E})\text{Ph}_2$ as intimated by $^{31}\text{P}\{-^1\text{H}\}$ NMR] was obtained.

The spectroscopic and analytical data are in full agreement with the proposed structures.[‡] Hence the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra for **2** and **3** show three P environments for the P^{III} , P^{O} and P^{E} centres. Presumably in solution the equivalence of the two P^{III} centres may be a consequence of fast proton exchange between the two nitrogen atoms of the neutral HL and deprotonated L ligands. Crystals of **3** suitable for single crystal X-ray crystallography were obtained from CDCl_3 –petroleum ether (bp 60–80 °C).§ The crystal structure of $\text{3}\cdot\text{CHCl}_3$ (Fig. 1) reveals the platinum(II) centre to be co-ordinated by a didentate $[\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2]^-$, a deprotonated $[\text{Ph}_2\text{PNP}(\text{O})\text{Ph}_2]^-$ and a neutral $\text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2$ ligand in an approximately square-planar environment [$\text{Se}(2)-\text{Pt}(1)-\text{P}(6)$ 84.58(8), $\text{Se}(1)-\text{Pt}(1)-\text{P}(4)$ 84.97(8), $\text{P}(4)-\text{Pt}(1)-\text{P}(6)$ 92.8(1) and $\text{Se}(1)-\text{Pt}(1)-\text{Se}(2)$ 98.49(4)°]. The two *cis* $[\text{Ph}_2\text{PNP}(\text{O})\text{Ph}_2]^-$ and $\text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2$ ligands are locked into a six-membered $\text{Pt}-\text{P}-\text{N}-\text{H}\cdots\text{N}-\text{P}$ platinacycle by an intramolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bond [$\text{N}(5)\cdots\text{N}(3)$ 2.78, $\text{H}(5n)\cdots\text{N}(3)$ 2.01 Å, $\text{N}(5)-\text{H}(5n)\cdots\text{N}(3)$ 134°] and which accounts for the *anti* conformation of the NH and PO oxygen in HL. The Pt–Se bond distances [$\text{Pt}(1)-\text{Se}(1)$ 2.521(1), $\text{Pt}(1)-\text{Se}(2)$ 2.520(1) Å] are longer than in the complex $[\text{Pt}\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-Se,Se'}\}_2]\cdot\text{CHCl}_3$ [$\text{Pt}(1)-\text{Se}(1)$ 2.425(2), $\text{Pt}(1)-\text{Se}(2)$ 2.445(2) Å].¹³ The Pt–P [$\text{Pt}(1)-\text{P}(4)$



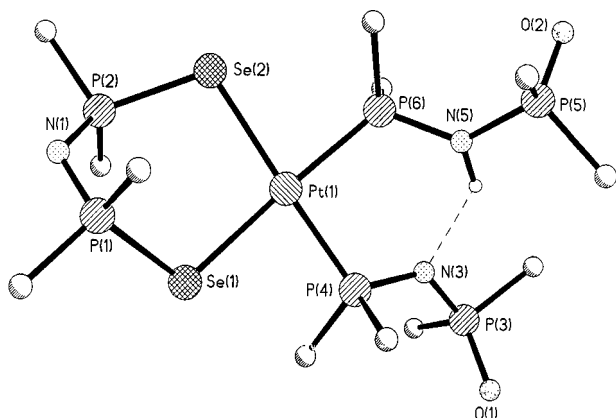


Fig. 1 Crystal structure of $[\text{Pt}\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-Se,Se'}\}\text{-(Ph}_2\text{PNP}(\text{O})\text{Ph}_2\text{-P)}\{\text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2\text{-P}\}]$ **3** (only the *ipso* C atoms shown, C–H hydrogen atoms and solvent molecule omitted for clarity). Selected bond distances (Å) and angles (°): Pt(1)–Se(1) 2.521(1), Pt(1)–Se(2) 2.520(1), Se(1)–P(1) 2.190(3), P(1)–N(1) 1.563(9), N(1)–P(2) 1.605(9), P(2)–Se(2) 2.188(3), Pt(1)–P(4) 2.271(3), Pt(1)–P(6) 2.267(3), P(4)–N(3) 1.643(9), N(3)–P(3) 1.634(9), P(3)–O(1) 1.463(8), P(6)–N(5) 1.643(9), N(5)–P(5) 1.64(1), P(5)–O(2) 1.480(9); Se(1)–Pt(1)–Se(2) 98.49(4), Se(1)–Pt(1)–P(6) 173.57(9), Se(2)–Pt(1)–P(4) 171.55(9), P(4)–Pt(1)–P(6) 92.8(1), Pt(1)–Se(1)–P(1) 103.98(9), Se(1)–P(1)–N(1) 116.2(4), P(1)–N(1)–P(2) 123.8(6), N(1)–P(2)–Se(2) 112.8(4), P(2)–Se(2)–Pt(1) 104.95(9), Pt(1)–P(4)–N(3) 114.0(3), P(4)–N(3)–P(3) 131.9(6), N(3)–P(3)–O(1) 118.4(5), Pt(1)–P(6)–N(5) 116.3(4), P(6)–N(5)–P(5) 132.5(6), N(5)–P(5)–O(2) 117.3(5).

2.271(3), Pt(1)–P(6) 2.267(3) Å] bond lengths are indistinguishable for the protonated/deprotonated ligands and in the range previously documented for complexes with either ligands. Interestingly the P–N/N–P bond distances for the protonated/deprotonated ligands in **3** are similar [P(4)–N(3) 1.643(9), N(3)–P(3) 1.634(9) Å for **L**; P(6)–N(5) 1.643(9), N(5)–P(5) 1.64(1) Å for **HL**] but shorter than in **HL** which exists in the solid state as a H-bonded dimer pair [P(1)–N(1) 1.651(3), P(2)–N(1) 1.707(3) Å].⁴ The P–N–P angles (*ca.* 132°) are somewhat enlarged as would be anticipated for terminal bound ligands. Within the Se–P–N–P–Se metallacycle, the bond lengths and angles are consistent with π delocalisation.

Preliminary experiments suggest that the other N–H proton cannot be removed even with excess NEt_3 . In contrast the metal alkoxides KOBu^t or NaOMe smoothly deprotonate this NH proton affording new phosphorus containing species whose precise identity is currently under investigation and will be reported later.

We recently described that selective deprotonation of a primary N–H amine proton in “ $\text{PtCl}_2(\text{Ph}_2\text{PR})_2$ ” ($\text{R} = o\text{-C}_6\text{H}_4\text{NH}_2$) with the unsymmetrical ligands $\text{K}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{E})\text{Ph}_2]$ ($\text{E} = \text{S}$ or Se) affords the mixed complexes $[\text{Pt}(\text{Ph}_2\text{PC}_6\text{H}_4\text{NH-P,N})(\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2\text{-P,N})][\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{E})\text{Ph}_2]$.¹¹ Likewise **I** reacts similarly with “ $\text{PtCl}_2(\text{Ph}_2\text{PR})_2$ ” (generated *in situ* from $[\text{PtCl}_2(\text{cod})]$ and 2 equivs. Ph_2PR) to give the mixed complex $[\text{Pt}(\text{Ph}_2\text{PC}_6\text{H}_4\text{NH-P,N})(\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2\text{-P,N})][\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]$ **4** in good yield.[†] The corresponding reaction with “ $\text{PdCl}_2(\text{Ph}_2\text{PR})_2$ ” and **I** (or **II**) under analogous conditions gave only the known $[\text{Pd}\{\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\}_2]$ complexes with displacement of both $\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2$ ligands. This difference may reflect the greater lability of palladium(II) over platinum(II). In the crystal structure of **4** (Fig. 2) the molecule is disposed about a crystallographic twofold axis on which Pt(1) and N(3) lie. The platinum(II) centre is *cis* coordinated by a P,N-chelating $\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2$ ligand and a deprotonated $[\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}]^-$ ligand in a near square-planar geometry [N(2)–Pt(1)–P(1) 83.47(13), N(2)–Pt(1)–N(2A) 87.7(3), P(1)–Pt(1)–P(1A) 106.53(6)°]. The $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ anion is perpendicular to the cation and involved in bifurcated hydrogen bonding with the NH protons of the *cis*-coordinated ligands

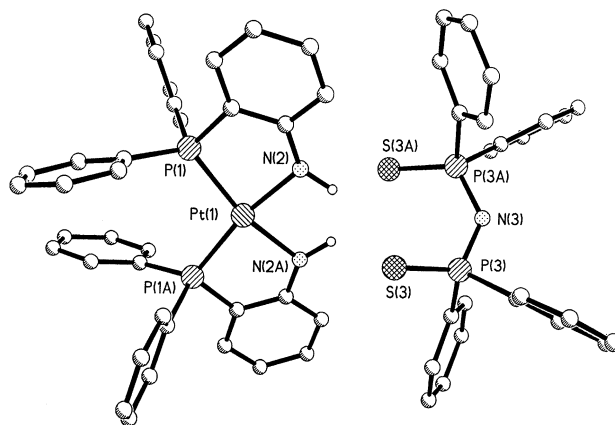


Fig. 2 Crystal structure of $[\text{Pt}(\text{Ph}_2\text{PC}_6\text{H}_4\text{NH-P,N})(\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2\text{-P,N})][\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]$ **4** (C–H hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): Pt(1)–N(2) 2.056(4), Pt(1)–P(1) 2.2481(11), S(3)–P(3) 1.983(2), P(3)–N(3) 1.599(2); N(2)–Pt(1)–N(2A) 87.7(3), N(2)–Pt(1)–P(1), 83.47(13), N(2)–Pt(1)–P(1A) 167.62(12), P(1)–Pt(1)–P(1A) 106.53(6), S(3)–P(3)–N(3), 120.8(2), P(3)–N(3)–P(3A), 133.3(3).

[N(2)···S(3) 3.46, H(2n)···S(3) 2.67 Å, N(2)–H(2n)···S(3) 139°; N(2)···S(3A) 3.43, H(2n)···S(3A) 2.80 Å, N(2)–H(2n)···S(3A) 123°]. In the uncomplexed anion the S–P and N–P bond distances are consistent with delocalisation within the S–P–N–P–S backbone.

In conclusion, we have shown that chloride metathesis of **1** with the potassium salts **I** (or **II**) affords **2** (or **3**) respectively. Further reactivity studies are underway and will be reported in due course.

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Notes and references

[†] Compound **1** was prepared as described in ref. 4. A typical synthesis is illustrated here for compound **2**. To the solids *cis*- $[\text{PtCl}_2\{\text{Ph}_2\text{PNHP}(\text{O})\text{Ph}_2\text{-P}\}_2]$ (0.404 g, 0.378 mmol) and $\text{K}[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]$ (0.185 g, 0.379 mmol) was added CH_3OH (10 cm^3). After stirring the suspension for 3 h, the solid was collected by suction filtration and dried *in vacuo* (0.119 g). This solid was shown by $^{31}\text{P}\{-^1\text{H}\}$ NMR to be **2**. To the filtrate was added dropwise distilled water and the solid **2** precipitated, was collected by suction filtration and dried *in vacuo*. Overall yield: 0.368 g, 66%. In a similar manner **3** was likewise prepared (68%). Compound **4** was synthesised as follows. To a solution of $[\text{PtCl}_2(\text{cod})]$ (cod = cycloocta-1,5-diene) (0.025 g, 0.067 mmol) and $\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2$ (0.037 g, 0.133 mmol) in CH_3OH (1.5 cm^3) was added $\text{K}[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]$ (0.068 g, 0.139 mmol) to give an orange suspension. After stirring the suspension for *ca.* 1 h, the solid was collected by suction filtration. Slow diffusion of CH_3OH into a CHCl_3 solution of this solid over several days gave **4** (0.064 g, 80%).

[‡] Selected spectroscopic data for complexes **2–4**. For **2**: $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3 , referenced to 85% H_3PO_4): δ 37.6, $^1J(\text{PtP})$ 3890 (PPh_2N); 34.2, $^2J(\text{PtP})$ 61, $^3J(\text{PP})$ 8 (Ph_2PS); 16.8, $^3J(\text{PtP})$ 147, $^2J(\text{PP})$ 29 Hz (Ph_2PO). $^{195}\text{Pt}\{-^1\text{H}\}$ NMR [referenced to external H_2PtCl_6 (in $\text{D}_2\text{O-HCl}$)]: δ –4548. ^1H NMR: δ 10.40 (NH), 7.99–6.92 (arom. H). IR (KBr): 3667 (ν_{OH}), 3333, 3215 (ν_{NH}), 578, 572 cm^{-1} (ν_{PS}). FAB MS: m/z 1447 (M^+). $\text{C}_{72}\text{H}_{61}\text{N}_3\text{O}_2\text{P}_6\text{S}_2\text{Pt} \cdot \text{H}_2\text{O}$ requires C 59.10, H 4.40, N 2.85. Found C 58.70, H 4.20, N 2.80%. For **3**: $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 36.1, $^1J(\text{PtP})$ 3853 (PPh_2N); 26.4, $^1J(\text{PSe})$ 520, $^2J(\text{PtP})$ 66, $^3J(\text{PP})$ 12.5 (Ph_2PSe); 16.5, $^3J(\text{PtP})$ 141, $^2J(\text{PP})$ 30 Hz (Ph_2PO). $^{195}\text{Pt}\{-^1\text{H}\}$ NMR: δ –4689. ^1H NMR: δ 10.50 (NH), 8.05–6.94 (arom. H). IR (KBr): 3668 (ν_{OH}), 3332, 3213 (ν_{NH}), 540 cm^{-1} (ν_{PSe}). FAB MS: m/z 1539 (M^+). $\text{C}_{72}\text{H}_{61}\text{N}_3\text{O}_2\text{P}_6\text{Se}_2\text{Pt} \cdot \text{H}_2\text{O}$ requires C 55.55, H 4.10, N 2.70. Found C 55.25, H 3.95, N 2.75%. For **4**: $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 50.4 (SPPH_2); 27.5, $^1J(\text{PtP})$ 3075 Hz (PPh_2). $^{195}\text{Pt}\{-^1\text{H}\}$ NMR: δ –4496. ^1H NMR: δ 8.02–6.56 (arom. H, NH_2),

NH). IR (KBr): 3341 (ν_{NH}), 578 cm^{-1} (ν_{PS}). ES MS: m/z 1198 (MH^+). $\text{C}_{60}\text{H}_{51}\text{N}_3\text{P}_4\text{S}_2\text{Pt}$ requires C 60.20, H 4.30, N 3.50. Found C 60.05, H 4.15, N 3.55%.

§ Crystal data for **3**: $\text{C}_{72}\text{H}_{61}\text{N}_3\text{O}_2\text{P}_6\text{PtSe}_2 \cdot \text{CHCl}_3$, M 1658.52, monoclinic, space group $P2_1/n$, $a = 24.754(3)$, $b = 31.372(9)$, $c = 11.241(5)$ Å, $\beta = 103.19(2)^\circ$; $U = 8500(5)$ Å³, $D_c = 1.296$ g cm⁻³, $\lambda(\text{Cu-K}\alpha) = 1.54178$ Å, $Z = 4$, $\mu = 6.195$ mm⁻¹, $T = 293$ K, $R1 = 0.058$ for 12958 unique reflections. Crystal data for **4**: $\text{C}_{60}\text{H}_{51}\text{N}_3\text{P}_4\text{PtS}_2$, M 1197.13, monoclinic, space group $C2/c$, $a = 18.1036(1)$, $b = 14.8333(3)$, $c = 19.6519(4)$ Å, $\beta = 101.81(1)^\circ$; $U = 5165.5(2)$ Å³, $D_c = 1.539$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $Z = 4$, $\mu = 2.965$ mm⁻¹, $T = 293(2)$ K, $R1 = 0.0314$ for 3712 unique reflections. Data were collected either on a Rigaku AFC7S or Bruker SMART diffractometer. The N–H proton in compound **3** was located from a ΔF map, whilst in compound **4**, the remaining N–H proton could not be located because of static disorder and crystallographic symmetry. CCDC reference number 440/160.

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