# **Coordination chemistry of platinum and palladium in the solid-state:** Synthesis of imidazole and pyrazole complexes<sup>†</sup>

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Solid-state reactions of palladium(II) and platinum(II) chloride complexes with imidazole (Him) and pyrazole (Hpz) or their hydrochloride salts are shown to produce metal complex salts and coordination compounds. Thus,  $K_2[MCl_4]$  or MCl<sub>2</sub> can be ground with imidazolium chloride ([H<sub>2</sub>im]Cl) to produce the salts  $[H_2im]_2[MCl_4]$  (M = Pd, 1; Pt, 5), which can then be dehydrochlorinated in the solid state to produce the coordination compounds *trans*-[PdCl<sub>2</sub>(Him)<sub>2</sub>] **3** or *cis*-[PtCl<sub>2</sub>(Him)<sub>2</sub>] **6**. The complex cis-[PdCl<sub>2</sub>(Him)<sub>2</sub>] 2 is produced when Pd(OAc)<sub>2</sub> is ground with [H<sub>2</sub>im]Cl. Reaction of platinum chloride reagents with imidazole (Him) also produces cis-[PtCl<sub>2</sub>(Him)<sub>2</sub>] 6, but reaction of imidazole with analogous palladium chloride reagents first produces  $[Pd(Him)_4]Cl_2$  4 which then slowly converts to *trans*-[PdCl<sub>2</sub>(Him)<sub>2</sub>] **3**. Grinding pyrazolium chloride with  $K_2[MCl_4]$  produces  $[H_2pz]_2[MCl_4]$  (M = Pd, 7; Pt, 10), which may also be dehydrochlorinated in the solid state to produce the coordination compounds trans-[PdCl<sub>2</sub>(Hpz)<sub>2</sub>] 8 or cis-[PtCl<sub>2</sub>(Hpz)<sub>2</sub>] 11. Grinding K<sub>2</sub>[PdCl<sub>4</sub>] or PdCl<sub>2</sub> with pyrazole gives [Pd(Hpz)<sub>4</sub>]Cl<sub>2</sub> 9, which is then slowly converted into trans-[PdCl<sub>2</sub>(Hpz)<sub>2</sub>] 8. Grinding PtCl<sub>2</sub> with Hpz generates  $[Pt(Hpz)_4]Cl_2$  12, but using  $K_2PtCl_4$  as the metal source does not generate the same product. The single-crystal structures of 8, a new polymorph of 11 and  $[H_2pz]_2[PtCl_6]\cdot 2H_2O$  (isolated as a decomposition product) are reported for the first time, and the structures of 5 and 10 have been solved ab ibitio from XRPD data.

# Introduction

It has long been recognised that salts of the general form  $[AH]_2[MX_n]$ , where AH is a protonated Lewis base (of, for example, a nitrogen-donor ligand A) and [MX<sub>n</sub>] is a metalhalide anion, can be thermally decomposed to yield HCl and the corresponding coordination compound; the decomposition of  $[Hpy]_2[PtCl_6]$  to  $[PtCl_4(py)_2]$  (py = pyridine) in solution was first reported by Anderson in 1855,1 and has been dubbed the 'Anderson rearrangement'.<sup>2</sup> The reaction also occurs in the solid state; an early demonstration was by Balbiano, who showed in 1892 that heating of [H2im]2[PtCl6] to 192 °C generated  $[PtCl_4(Him)_2]$  (Him = imidazole).<sup>3</sup> This area has been extensively studied by Kukushkin and co-workers, who have demonstrated that a variety of compounds of the form  $[AH]_2[MCl_4]$  (M = Pd, Pt) can be thermally decomposed to give cis-[MCl<sub>2</sub>A<sub>2</sub>], and that these compounds often then isomerise to the trans isomers.<sup>2</sup> More recently, we have demonstrated, *inter alia*, that [Hpic]<sub>2</sub>[PtCl<sub>4</sub>] (pic = 4-picoline) can be thermally decomposed in *two* steps to yield firstly [Hpic][PtCl<sub>3</sub>(pic)] and then trans-[PtCl<sub>2</sub>(pic)<sub>2</sub>],<sup>4</sup> and that [4,4'-H<sub>2</sub>bipy][PtCl<sub>4</sub>] gives the coordination polymer trans- ${PtCl_2(4,4'-bipy)}_n$  upon heating.<sup>5</sup> In these cases we have placed emphasis on the pre-organisation of the protonated nitrogen base with the metal halide source (as an anion) through the formation of NH  $\cdots$  Cl hydrogen bonded supramolecular synthons that lead to "crystal engineered" arrangements of the ions. This amounts to a view that crystal engineering, in the classic sense expounded by Schmidt (the topochemical postulate),<sup>6</sup> is important in gaining control over the solid state reactivity of the molecular components of these salts. In this paper we will challenge that orthodoxy and show that, at least in some cases, the transport of reactants in the solid state can be relatively easily achieved, even at room temperature, through mechanical means. This work therefore tests whether these systems have the molecular mobility required for reactivity, in a manner that relates to that cited by Kaupp as being important in his studies of reactivity in the molecular solid state.<sup>7</sup>

Reports have recently begun to appear concerning the solidstate mechanochemical (*i.e.* by grinding) synthesis of compounds of palladium and platinum that have traditionally been synthesised by solution methods, despite the fact that substitution at these metals (especially platinum) is generally slower than at divalent first row metals; in many cases these solid-state methods are more efficient than the traditional ones, or give better selectivity, or both. Examples include the grinding of PPh<sub>3</sub> with PtCl<sub>2</sub> in a ball mill to produce cis-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] in 98% yield, which can subsequently react with solid K<sub>2</sub>CO<sub>3</sub> to give [Pt(CO<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>],<sup>8</sup> and the solvent-free preparation of polymetallic rings and cages by manually grinding 4,4'-bipyridine and  $[Pt(NO_3)_2(en)]$  (en = ethan-1,2-diamine), forming the corresponding square tetraplatinum complex in only 10 min.<sup>9</sup> We therefore have set out to explore the viability of such methods in the controlled preparation of some archetypal metal complexes of platinum and palladium.

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<sup>†</sup> Electronic supplementary information (ESI) available: Complete powder X-ray diffraction patterns for all compounds, TGA traces, and tables of hydrogen bonds. CCDC reference numbers 748472, 748473, 748474, 748475, and 748476. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b919665j



Scheme 1 Reaction chemistry explored in this work.

Herein, we report our studies upon imidazole (Him) and pyrazole (Hpz) complexes of platinum and palladium, demonstrating that combining both thermal and mechanochemical methods can produce a wide array of coordination compounds without recourse to solution chemistry. Scheme 1 summarises the chemistry we set out to explore. In choosing to focus on this chemistry we draw upon previous experience in which some analogous reactions have been achieve using nitrogen ligands such as 4,4'-bipyridine or 4-picoline,<sup>4,5</sup> and on related chemistry of cobalt and zinc.<sup>10</sup>

In this study we compare the behaviour of pyrazole and imidazole in terms of their basicity (as isosteric but rather different bases), and of their nitrogen atom location (and therefore supramolecular chemistry). We also report the use of a wider range of bases to cause dehydrochlorination (beyond KOH as previously used), and of metal complex precursors to the coordination compounds (beyond hydroxides and carbonates). Finally, the variations in metal (Pd *vs.* Pt), precursor (MCl<sub>2</sub> *vs.* K<sub>2</sub>MCl<sub>4</sub>]) and ligand (Hpz *vs.* Him) allow for insight into the reaction mechanism, at least to the level of providing data on the reaction outcomes (composition and isomer) that result.

# **Results and discussion**

#### Imidazole compounds

The synthesis of the imidazolium salt  $[H_2im]_2[PdCl_4]$  **1** (in 54% yield) has been reported from reaction of  $K_2PdCl_4$  and imidazole in hydrochloric acid.<sup>11</sup> Its crystal structure has also been reported<sup>12</sup> (CSD refcode: RORVOJ), and shown to consist of square planar  $[PdCl_4]^{2-}$  anions and imidazolium cations which are connected into a hydrogen-bonded ribbon along the crystallographic *c*-axis by NH····Cl interactions (see Fig. 1).

We have found that grinding of PdCl<sub>2</sub> and two molar equivalents of imidazolium chloride  $[H_2im]Cl$  results in their conversion to **1**, as a reddish-brown powder of the known structure (as judged by X-ray powder diffraction (XRPD) analysis). Similarly, grinding K<sub>2</sub>PdCl<sub>4</sub> and  $[H_2im]Cl$  affords **1** as an orange polycrystalline powder, whose XRPD pattern confirms that it contains only phase **1** (by comparison with that of RORVOJ) and KCl. Furthermore, exposure of the coordination compounds *cis*-[PdCl<sub>2</sub>(Him)<sub>2</sub>] (**2**) or *trans*-[PdCl<sub>2</sub>(Him)<sub>2</sub>] (**3**) (*vide infra*) to vapour from concentrated hydrochloric acid solution or to



**Fig. 1** The hydrogen-bonded ribbon in  $[H_2im]_2[PdCl_4]$  **1**.



Scheme 2 Synthesis and interconversion of [PdCl<sub>2</sub>(Him)<sub>2</sub>] and [H<sub>2</sub>im]<sub>2</sub>[PdCl<sub>4</sub>].

dry HCl gas in a sealed vessel leads to complete conversion to **1**.

The coordination compounds *cis*-[PdCl<sub>2</sub>(Him)<sub>2</sub>] **2** and *trans*-[PdCl<sub>2</sub>(Him)<sub>2</sub>] **3** are also known,<sup>13</sup> the former synthesised through a (solution) route employing [Pd(C<sub>2</sub>O<sub>4</sub>)(Him)<sub>2</sub>] and the latter directly from reaction of PdCl<sub>2</sub> and imidazole in DMF. Complex **2** is reported to rapidly isomerise to **3** in DMF solution at room temperature,<sup>13</sup> and also in the solid state at between 170 and 230 °C.<sup>14</sup> The crystal structure of **3** has been reported<sup>15</sup> (CSD refcode: TCDIMP01) and consists of molecules linked by NH····Cl hydrogen bonds into a sheet. The crystal structure of **2** has not been reported, although an analysis of its powder pattern has appeared.<sup>16</sup>

We found that it was possible to selectively synthesise **2** or **3** in the solid state (see Scheme 2). Grinding together palladium acetate and two molar equivalents of imidazolium chloride caused the elimination of acetic acid and formation of **2**. The *cis* configuration and the phase crystallised was identified by comparison of the powder pattern for **2** prepared by this method with that of its platinum analogue (Fig. 2); the pattern did not match that previously reported for *cis*-[PdCl<sub>2</sub>(Him)<sub>2</sub>].<sup>16</sup> The *trans*-isomer **3** could be synthesised by heating the salt **1** to 170 °C for 4 h, as previously reported.<sup>14</sup>



Fig. 2 The XRPD pattern for cis-[PdCl<sub>2</sub>(Him)<sub>2</sub>] 2 (bottom) compared with that of cis-[PtCl<sub>2</sub>(Him)<sub>2</sub>] 6 prepared by thermal decomposition of 5 (top).

It was not possible to readily synthesise **2** by grinding of palladium-containing starting materials with imidazole or by deprotonation of the salt **1** with a base. In these cases the reaction mixture always contained  $[Pd(Him)_4]Cl_2$  **4**, along with various other by-products depending upon the stoichiometry used in the reaction (see Scheme 3). Salt **4** is a known compound,<sup>13</sup> and may be deliberately synthesised in the solid state by grinding either PdCl<sub>2</sub> or K<sub>2</sub>PdCl<sub>4</sub> with four molar equivalents of imidazole, although the reaction is rather slow and needs to be left for several days to reach completion. The crystal structure of **4** is not known. Interestingly, after standing for 6 months the powder pattern of the 1 : 1 mixture of [Pd(Him)<sub>4</sub>]Cl<sub>2</sub> **4** and PdCl<sub>2</sub> generated by the 1 : 2 reaction of PdCl<sub>2</sub> with imidazole showed the presence of **3**, indicating that it is possible to form **3** in this manner but that the reaction is rather slow in the solid state.



Scheme 3 Synthetic routes to [Pd(Him)<sub>4</sub>]Cl<sub>2</sub> 4. All products and crystalline by-products have been identified in the XRPD patterns of the appropriate reactions.

Solution synthesis (in 70-75% yield) of the imidazolium tetrachloroplatinate salt  $[H_2im]_2[PtCl_4]$  (5) has been reported,<sup>17</sup> although the crystal structure is not known. We found that grinding of PtCl<sub>2</sub> or K<sub>2</sub>PtCl<sub>4</sub> with imidazolium chloride formed 5 (with KCl in the latter case) as a polycrystalline powder. However, attempts to synthesize 5 by exposing *cis*-[PtCl<sub>2</sub>(Him)<sub>2</sub>] 6 (below) to vapours from concentrated aqueous HCl solution or dry HCl gas were unsuccessful, and no reaction was observed.

Comparison of the experimental XRPD pattern for the mechanochemically synthesized 5 with the pattern calculated from the crystal structure of its palladium analogue  $[H_2im]_2[PdCl_4]$  1

Table 1 Crystal data for 5, 8, 10 β-11 and [H<sub>2</sub>pz]<sub>2</sub>[PtCl<sub>6</sub>]

Crystal Data	5ª	8	<b>10</b> <sup><i>a</i></sup>	β-11	$[H_2pz]_2[PtCl_6] \cdot 2H_2O$
T/K	293(2)	100(2)	293(2)	100(2)	100(2)
Empirical formula	$[C_3H_5N_2]_2[PtCl_4]$	$[PdCl_2(C_3H_4N_2)]$	$[C_3H_5N_2]_2[PtCl_4]$	$[(C_3H_4N_2)_2PtCl_2]$	$[C_3H_5N_2]_2[PtCl_6]\cdot 2H_2O$
Formula weight	475.07	313.46	475.07	402.14	582
Colour	Brown	Yellow	Dark brown	Yellow	Yellow
Morphology	Fine-powder	Block	Powder	Needle	Block
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	2.598	2.150	2.471	2.550	2.366
$\mu/\mathrm{mm}^{-1}$		2.424		13.865	9.634
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a/Å	7.0225(3)	4.0628(5)	8.5229(2)	11.0643(15)	6.8406(2)
b/Å	7.6375(3)	7.2328(7)	7.0222(3)	13.1094(17)	11.1912(4)
c/Å	6.7148(3)	8.3361(8)	7.3333(3)	14.912(2)	11.2366(4)
α (°)	110.2813(19)	93.805(7)	66.635(3)	94.583(8)	84.332(2)
$\beta$ (°)	96.859(2)	99.073(6)	127.557(3)	98.669(8)	76.887(2)
γ (°)	64.110(2)	91.601(7)	105.595(3)	99.749(8)	75.824(2)
$V/Å^3$	303.69(2)	242.05(4)	319.18(2)	2095.0(5)	811.41(5)
λ/Å	1.5406	0.71073	1.5406	0.71073	0.71073
Ζ	1	1	1	8	2
Reflections collected		3731		9564	5527
Unique reflections		1116		9564	5527
<i>R</i> (int)		0.0347		0	0
$wR_2, R_1 (\%)$		6.35, 2.59		22.56, 7.45	8.13, 3.04
" Structure determined f	rom powder diffraction d	lata.			

showed the compounds to be isomorphous. This was exploited to refine the crystal structure of **5** against the XRPD data, with starting geometry based on the structure of **1**. The unit cell of **5** is smaller than that of **1** (see Table 1), and the Pt–Cl bonds (2.264(14) and 2.276(15) Å) of **5** marginally shorter than the Pd–Cl bonds (2.3142(15) and 2.3134(15) Å) in **1**. Table 1 compares cell parameters for **1** and **5**.

Solution preparation of *cis*-[PtCl<sub>2</sub>(Him)<sub>2</sub>] **6** has been reported, but was not straightforward and could not be achieved starting from K<sub>2</sub>PtCl<sub>4</sub>.<sup>13</sup> The solid-state synthesis of **6** was the least satisfactory of all the syntheses reported herein; although grinding of PtCl<sub>2</sub> with imidazole led to the formation of the coordination complex **6** (Scheme 4), an unidentified by-product was also formed. Equally, whilst mechanochemical dehydrochlorination of **5** by grinding with Ag<sub>2</sub>O resulted in the formation of **6** + AgCl, use of KOH generated the same unknown by-products as before. Salt **5** could also be converted into **6** by heating for 5 days at 125 °C, contrary to expectations based on the literature,<sup>17</sup> and this proved the cleanest method of synthesis, although heating at higher temperatures also led to small amounts of the *trans* isomer



Scheme 4 Synthesis and interconversion of  $[H_2im]_2[PtCl_4]$  5 and cis-[PtCl\_2(Him)\_2] 6.

being formed. The XRPD pattern of **6** closely resembled that of **2**, suggesting them to be isomorphous (Fig. 2).

#### Pyrazole compounds

The palladium-pyrazolium salt  $[H_2pz]_2[PdCl_4]$  7 has not previously been reported, but we found that grinding of K<sub>2</sub>PdCl<sub>4</sub> with two molar equivalents of pyrazolium chloride affords 7, with two equivalents of KCl as by-product in the former case. The XRPD pattern of 7 synthesised in this manner closely resembles that of its platinum analogue 10, suggesting them to be isostructural. 7 appears to be relatively unstable at room temperature, undergoing spontaneous dehydrochlorination to trans-[PdCl<sub>2</sub>(Hpz)<sub>2</sub>] 8, which makes its isolation as a pure phase difficult; attempting its formation by grinding PdCl<sub>2</sub> with pyrazolium chloride always afforded mixtures containing both 7 and 8. Allowing a sample of 7 to stand at room temperature for a period of weeks leads to its complete conversion to 8, a process which can be accelerated by heating 7 at 125 °C for 4 h, or by grinding 7 with two molar equivalents of potassium tert-butoxide. 8 can also be formed by direct mechanochemical 1:2 reaction of either K<sub>2</sub>PdCl<sub>4</sub> and pyrazole (though the reaction requires ball-milling for 30 min in order to reach completion) or Pd(OAc)<sub>2</sub> and pyrazolium chloride (see Scheme 5).

Although **8** is a known compound,<sup>18,19</sup> its crystal structure has not previously been determined. Single crystals suitable for X-ray diffraction were obtained by the extremely slow evaporation of a dry dichloromethane solution of a sample of **8** prepared by literature solution methods.<sup>19</sup> The structure of the compound consists of discrete centrosymmetric *trans*-[PdCl<sub>2</sub>(Hpz)<sub>2</sub>] molecules, in which the N–Pd–N and Cl–Pd–Cl angles are necessarily 180.0°, and the N(1)-Pd(1)-Cl(1) angle is 89.92(6)°. The palladium–chlorine bond length is 2.3079(6) Å, and the palladium–nitrogen distance is



Scheme 5 Synthesis and interconversion of the palladium pyrazole species  $[H_2pz]_2[PdCl_4]$  (7), trans- $[PdCl_2(Hpz)_2]$  (8) and  $[Pd(Hpz)_4]Cl_2$  (9).

2.028(6) Å. Crystal and structure refinement data are presented in Table 1. The Pd–N distance is close to that of 2.011(2) Å found for a related complex *trans*-[PdCl<sub>2</sub>(HEP)<sub>2</sub>] (HEP = bis-(1-(2-hydroxyethyl)pyrazole).<sup>20</sup> The [PdCl<sub>2</sub>(Hpz)<sub>2</sub>] molecules in **8** are connected into a chain by N–H··· Cl interactions (2.62 Å) between the chloride ligands and the pyrazole NH donors, and there are also shorter intramolecular N–H··· Cl interactions (2.46 Å) (Fig. 3).

Van Kralingen *et al.*<sup>18</sup> observed that **8** exists in more than one polymorphic form, but in our hands preparation of **8** by a wide range of solid state methods (Scheme 5) all led to the formation of just one crystalline form as deduced from XRPD patterns (Fig. 4). However, it is evident from the Fig. 4 that the calculated powder pattern differs from the experimental powder patterns (which were measured at room temperature), especially at higher values of  $2\theta$ , leading us to conclude that there may be some crystallographic changes occurring between the temperature at which the crystal structure and the powder patterns were determined. We have previously seen similar behaviour in imidazole chemistry.<sup>10</sup>

Complex 8 could not be made by grinding pyrazole with  $PdCl_2$  or with  $K_2PdCl_4$  in a mortar and pestle. Such reactions instead produced  $[Pd(Hpz)_4]Cl_2$  9, together with a variety of palladium-containing by-products unless the Hpz:Pd ratio used in the reaction was 4:1. The crystal structure of 9 as a monohydrate has been reported<sup>21</sup> (CSD refcode: IHONAU), and the powder pattern calculated from this closely matches that produced by our solid-state syntheses, though again there apparently are some



**Fig. 4** XRPD patterns for *trans*-[PdCl<sub>2</sub>(Hpz)<sub>2</sub>] **8** (see Scheme 5). Dark blue = calculated from the single crystal structure; green = solution synthesis; brown = thermal elimination from 7; turquoise = Pd(OAc)<sub>2</sub> +  $2[H_2pz]Cl$ ; orange =  $K_2PdCl_4 + 2Hpz$  (ball milling); pink = 7 + 2Bu'OK.

temperature effects in play, and adventitious water has been acquired.

The platinum pyrazolium salt  $[H_2pz]_2[PtCl_4]$  **10** does not appear to have been reported before, but was readily made by grinding of pyrazolium chloride with PtCl<sub>2</sub> or K<sub>2</sub>PtCl<sub>4</sub> (with elimination of KCl once again in the latter case). The crystal structure of **10** is unknown, but comparisons of the X-ray powder diffraction patterns of the samples obtained from both synthetic routes with



Fig. 3 Inter and intramolecular N-H···Cl distances in 8 viewed down the a-axis. Selected bond lengths (Å): Pd-N, 2.0128(2); Pd-Cl 2.3079(6).



Fig. 5 The structure of 10, determined from powder XRD.

that of its palladium analogue 7 showed the salts 7 and 10 to be isomorphous (Fig. 6). Attempts to afford a suitable single crystal of 10 by recrystallization from concentrated HCl solution led to oxidation of the platinum(II) centre to platinum(IV), forming a [PtCl<sub>6</sub>]<sup>2-</sup> anion which crystallised as a hydrated pyrazolium salt {the crystal structure determination of this compound, [H<sub>2</sub>pz]<sub>2</sub>[PtCl<sub>6</sub>]·2H<sub>2</sub>O, is reported in the Supporting Information (see Table 1)}, so the structure of 10 was solved *ab initio* from the powder pattern.

The powder patterns obtained for 10 (see Table 1) were readily indexed as triclinic, with the unit cell volume of 319 Å<sup>3</sup> implying that there was only half of the [H<sub>2</sub>pz]<sub>2</sub>[PtCl<sub>4</sub>] formula unit in the asymmetric unit, and therefore that the [PtCl<sub>4</sub>]<sup>2-</sup> anion must lie on an inversion centre. From this starting point the structure was refined with the  $[H_2pz]^+$  cation as a freely moving rigid body and the platinum atom constrained to the origin, and the resultant crystal structure is shown in Fig. 5. The pyrazole ring makes hydrogen bonds from both NH groups to chloride atoms, and there are also short CH ··· Cl contacts. (The assignment of NH and CH groups within the pyrazolium ring was done on the basis that the shortest H...Cl interaction should be from a NH group, but it is entirely possible that the ring shows some rotational disorder and that all the NH and CH contacts are mixed. However, the arrangement settled upon produces sensible hydrogen-bonding patterns and geometries). The pyrazolium rings are  $\pi$ -stacked, and the overall packing is of ribbons of alternating cations and anions that run along the *a* axis (Fig. 5). These ribbons are then linked to neighbouring ones by intra-strand NH ··· Cl hydrogen bonds.



Fig. 6 Measured powder patterns for  $[H_2pz]_2[PdCl_4]$  7 and  $[H_2pz]_2[PtCl_4]$ 10. Green = 10 from PtCl<sub>2</sub> + 2[H<sub>2</sub>pz]Cl; brown = 10 from K<sub>2</sub>PtCl<sub>4</sub> + 2[H<sub>2</sub>pz]Cl; blue = 10 from calculated structure; red = 7 from K<sub>2</sub>PdCl<sub>4</sub> + 2[H<sub>2</sub>pz]Cl.

Heating a sample of 10 at 125 °C for 4 h in air resulted in the elimination of two molar equivalents of HCl and the subsequent formation of the coordination compound cis-[PtCl<sub>2</sub>(Hpz)<sub>2</sub>] 11. The solid state conversion of 11 into its trans isomer by heating at 110 °C for 8 h has been reported,<sup>22</sup> but in our hands the thermal elimination reaction cleanly generated the cis-isomer. Mechanochemical dehydrochlorination of 10 with Ag<sub>2</sub>O also leads to the formation of 11 (and AgCl). The published crystal structure of 11, previously determined at both room temperature<sup>23</sup> (CSD refcode: VAZWEY01) and low temperature<sup>22</sup> (CSD refcode: VAZWEY) consists of a central platinum(II) cation bonded to two chloride anions and two pyrazole molecules in a slightly distorted square planar cis coordination geometry. Comparison of the XRPD patterns of the products of our solid-state syntheses with a calculated pattern from the room temperature determination<sup>23</sup> showed 11 as prepared by both routes to be the VAZWEY phase.

Mechanochemical dehydrochlorination by grinding of a hydrogen bonded salt of a chlorometallate anions with KOH has been used several times to afford the related coordination compound, and usually produces KCl as a by-product.<sup>5,10</sup> However, this method did not work well for salt [H<sub>2</sub>pz]<sub>2</sub>[PtCl<sub>4</sub>] 10, which on grinding with nominally dry KOH resulted in the formation of K<sub>2</sub>PtCl<sub>4</sub>, trace amounts of the desired product 11 and some uncoordinated pyrazole (pyrazole and  $K_2PtCl_4$  react slowly; vide infra). A similar observation was made when Bu'OK was used as external base, which method produces KCl and t-butanol as the by-products We therefore utilised silver oxide as the external base to eliminate 2 molecules of HCl from 10, forming *cis*-[PtCl<sub>2</sub>(Hpz)<sub>2</sub>] 11 with AgCl and H<sub>2</sub>O as by-products, and avoiding the formation of KCl and the risk of subsequent transformation of the target compound into K<sub>2</sub>PtCl<sub>4</sub> by (formal) reaction of 2 KCl with 11 with elimination of pyrazole. Attempts to convert the coordination compound cis-[PtCl<sub>2</sub>(Hpz)<sub>2</sub>] 11 back into [H<sub>2</sub>pz]<sub>2</sub>[PtCl<sub>4</sub>] 10 by exposure to aqueous HCl vapour or dry HCl gas were unsuccessful (see Scheme 6).

A single crystal of **11** was serendipitously grown from a solution of **10** + 2 KCl in hydrochloric acid that had been left to evaporate, and X-ray structure determination on this revealed a new polymorph of **11** (hereafter  $\beta$ -**11**), which contains 4 unique molecules in its asymmetric unit. These form two pairs which are arranged in a stacked fashion, with the coordination planes about the platinum atom approximately parallel and the platinum centres only 3.6 Å apart (Fig. 7). As noted above, this is not the phase prepared by the solid state methods employed here. The structure of  $\beta$ -**11** is notably less dense than that of the VAZWEY phase (by *ca.* 5%).



Scheme 6 Synthesis and interconversion of platinum pyrazole species  $[H_2pz]_2[PtCl_4]$  10, *cis*- $[PtCl_2(Hpz)_2]$  11, and  $[Pt(Hpz)_4]Cl_2 \cdot H_2O$  12.



Fig. 7 The asymmetric unit of  $\beta$ -11, showing the four molecules of [PtCl<sub>2</sub>(Hpz)<sub>2</sub>] contained therein and their arrangement into pairs.

Mechanochemical grinding of K<sub>2</sub>PtCl<sub>4</sub> or PtCl<sub>2</sub> with pyrazole using a mortar and pestle or ball mill does not lead to 11. Instead, analogously to the palladium system, grinding PtCl<sub>2</sub> with pyrazole (even in a 1:2 ratio) gives  $[Pt(Hpz)_4]Cl_2 \cdot H_2O$  12, which is isomorphous with the palladium compound 9. The reaction is slow, and only reaches a conclusion after standing for about two weeks at room temperature following grinding (XRPD patterns recorded over the course of a fortnight are given in the supplementary information). Unlike the palladium system, however, grinding pyrazole with K<sub>2</sub>PtCl<sub>4</sub> gives a different product to the reaction with  $PtCl_2$ , in a reaction which is even slower (see supplementary information for XRPD patterns). The structure of the product is unknown, but it appears to be neither form of the cis coordination compound 11 (CSD refcode: VAZWEY01)<sup>23</sup> or  $\beta$ -11, nor *trans*-[PtCl<sub>2</sub>(Hpz)<sub>2</sub>] (CSD refcode: NEFXAY),<sup>22</sup> or the constitutional isomer [PtCl<sub>4</sub>][Pt(Hpz)<sub>4</sub>][cis-PtCl<sub>2</sub>(Hpz)<sub>2</sub>] (CSD refcode: XALKOK).24

# **Discussion and conclusions**

It has been shown that:

1. A wide range of solid-state techniques can be used to readily access the hydrogen bonded complexes  $[H_2L]_2[MCl_4]$  ( $H_2L = Him$ ;

M = Pd 1, Pt 5;  $H_2L = Hpz$ ; M = Pd 7, Pt 10) and coordination compounds [MCl<sub>2</sub>(HL)<sub>2</sub>] (HL = Him; M = Pd 2 (*cis*), 3 (*trans*); Pt 6; HL = Hpz; M = Pd 8, Pt 11) without recourse to solvents.

2. Mechanochemical grinding of the hydrochlorides of the ligands (imidazole or pyrazole) with  $K_2PtCl_4$  or  $PtCl_2$  readily gives the tetrachloroplatinate salts **5** and **10**. The X-ray powder diffraction data of these compounds were used to identify their single crystal structures (not known until now). Similarly, reactions of the ligand hydrochloride salts with  $K_2PdCl_4$  afford the crystalline salts **1** and **7**, which are isostructural to **5** and **10** respectively, again with elimination of KCl. The reactions with the tetrachlorometallate salts are interesting, as the position of the salt redistribution reaction  $K_2MCl_4 + 2[H_2L]Cl \rightarrow [H_2L]_2[MCl_4] + 2$  KCl appears to lie well to the right, presumably driven by the formation of KCl.

3. Grinding palladium(II) acetate with ligand hydrochloride salts affords the crystalline  $[PdCl_2(HL)_2]$  coordination compounds with concomitant elimination of acetic acid, without the addition of base, solvent or heating. This proved to be the most convenient way to synthesise *cis*- $[PdCl_2(Him)_2]$  **2** in the solid state.

4. The preparation of *cis*-[PtCl<sub>2</sub>(Him)<sub>2</sub>] **6** by reacting  $K_2$ PtCl<sub>4</sub> and imidazole in solution could not be achieved, but solid-state grinding or ball milling of  $K_2$ PtCl<sub>4</sub> or PtCl<sub>2</sub> with imidazole

affords **6**, though not cleanly. **6** was also obtained by heating of **5** (the best method of preparation) or by mechanochemical grinding of **5** with Ag<sub>2</sub>O. Similarly, thermal and mechanochemical dehydrochlorination of **10** affords *cis*-[PtCl<sub>2</sub>(Hpz)<sub>2</sub>] **11**.

5.  $[PdCl_2(Him)_2]$  can be isolated as both *cis* (2) and *trans* (3) isomers, whilst in contrast  $[PdCl_2(Hpz)_2]$  is always formed as the *trans* isomer 8, irrespective of the synthetic route used.

6. Exposure of the platinum coordination compounds *cis*-[PtCl<sub>2</sub>(HL)<sub>2</sub>] (HL = Him 6, Hpz 11) to vapour from concentrated aqueous HCl or dry HCl gas does not convert them to the salts 5 and 10 even after long periods of exposure. Exposure of *trans*-[PdCl<sub>2</sub>(Hpz)<sub>2</sub>] 8 to HCl did not afford the hydrogen-bonded salt 7 either, but exposure of either *cis*-[PdCl<sub>2</sub>(Him)<sub>2</sub>] 2 or *trans*-[PdCl<sub>2</sub>(Him)<sub>2</sub>] 3 to HCl converts them into 1.

7. Silver oxide  $(Ag_2O)$  can be used as an external base instead of KOH or  $K_2CO_3$  to avoid the formation of KCl and the potential for subsequent formation of  $K_2MCl_4$  (as observed in the mechanochemical dehydrochlorination reactions of the platinum salts). We have also demonstrated that it is possible to use KO<sup>t</sup>Bu as a base in solid-state grinding reactions.

8. Thermal dehydrochlorination from  $[H_2L]_2[MCl_4]$  (M = Pd, Pt;  $H_2L$  = Him, Hpz) takes place smoothly and is a simple and convenient method for the synthesis of the coordination compounds. The process involves the transfer of a proton from the amine to chloride leading to the breaking of the M–Cl bond and the formation of HCl gas. The ligand then occupies the coordination site vacated by the chloride resulting in the formation of M–N bonds.<sup>2</sup>

9. Solid-state preparative methods often seem to produce only one polymorph of a given compound, even when more than one are known. Thus, producing **11** by thermal or mechanochemical dehydrochlorination of **10** gives the VAZWEY phase of **11** only.

The reactions of  $[PtCl_4]^{2^-}$  in aqueous solution with nitrogendonor ligands such as pyridine and amines have been thoroughly studied over many years. When the ligand L has a low *trans*-effect, as is the case for imidazole and pyrazole, then the first stable product is the *cis*-[PtCl\_2L\_2] compound; following replacement of the first chloride of  $[PtCl_4]^{2^-}$  to form the  $[PtCl_3L]^-$  ion; the next chloride to be replaced is one opposite another chloride (owing to the greater *trans*-effect of chloride than L). In the presence of free L, the next compound formed is the tetrakis salt  $[PtL_4]^{2^+}$ , which then reacts slowly with chloride to form the *trans*-[PtCl\_2L\_2] compound; following replacement of the first L to form the  $[PtL_3Cl]^-$  ion, the next L to be replaced is the one opposite the chloride (again owing to the greater *trans*-effect of chloride than L) (Scheme 7).<sup>2</sup>

The solid-state reactions of imidazole and pyrazole with  $MCl_2$ and  $[MCl_4]^{2-}$  that we have reported herein appear to obey the same reaction sequence, and depending upon the relative lability of the compounds various members of the series may be isolated. Given that the lability of palladium is substantially greater than that of platinum, under given reaction conditions the palladium compounds may be expected to progress more readily through the reaction sequence in Scheme 7 than their platinum analogues. Thus, grinding K<sub>2</sub>PdCl<sub>4</sub> and pyrazole gives [Pd(Hpz)<sub>4</sub>]Cl<sub>2</sub> 9 (presumably via unobserved cis-[Pd(Hpz)<sub>2</sub>Cl<sub>2</sub>]), but further reaction can be obtained by ball-milling to give trans-[Pd(Hpz)<sub>2</sub>Cl<sub>2</sub>] 8. The reaction of PtCl<sub>2</sub> with pyrazole affords  $[Pt(Hpz)_4]Cl_2$  12, but this does not then appear to react further to afford *trans*-[Pt(Hpz)<sub>2</sub>Cl<sub>2</sub>]-it is notable that the solution reaction requires 12 to be refluxed in concentrated hydrochloric acid in order to yield the trans isomer,18 indicating that in the solid state at room temperature and without a large excess of chloride ions the reaction is likely to be exceedingly slow. Similar behaviour was observed for the imidazole compounds - in the reaction of PdCl<sub>2</sub> with imidazole, [Pd(Him)<sub>4</sub>]Cl<sub>2</sub> 4 was the product observed initially; though in this case prolonged ball-milling did not cause further reaction, after 6 months peaks due to the product trans- $[Pd(Him)_2Cl_2]$  3 were visible in the powder pattern. The slowness of this reaction compared to the analogous pyrazole chemistry may be attributed to the greater basicity of imidazole compared to pyrazole, and that as a consequence the palladium-imidazole bond is more difficult to break than the palladium-pyrazole bond. As before, in the platinum case there is less progress through the reaction pathway, and the first product cis-[PtCl<sub>2</sub>(Him)<sub>2</sub>] **6** is the only one seen.

One unexpected result is that reactions of pyrazole with PtCl<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub> do not produce the same product; in the former case the product is [Pt(Hpz)<sub>4</sub>]Cl<sub>2</sub> **12**, but in the latter an unidentified phase is slowly formed. This also explains why grinding [H<sub>2</sub>pz]<sub>2</sub>[PtCl<sub>4</sub>] **10** with KOH does not yield *cis*-[Pt(Hpz)<sub>2</sub>Cl<sub>2</sub>] **11**, and actually gives an insight into the mechanism of the reaction. The fact that K<sub>2</sub>PtCl<sub>4</sub> and free pyrazole are observed indicates that the first step of the reaction is deprotonation of the [H<sub>2</sub>pz]<sup>+</sup> rather than abstraction of a chloride ion from the [PtCl<sub>4</sub>]<sup>2-</sup> ion. The reaction only proceeds if a base that is also a potent chloride abstractor (Ag<sub>2</sub>O) is used; presumably, pyrazole is not a strong enough Lewis base to displace chloride from [PtCl<sub>4</sub>]<sup>2-</sup>.

We see no reason why the reactions reported above should not be extended to related systems. Substituted imidazole and pyrazole compounds of palladium and platinum are often of interest in polymerisation studies or as anticancer agents,<sup>25-27</sup> and it should be possible to synthesise them using the solid-state methods reported above. It is normally the case that the *cis* isomers exhibit much higher antitumour activity than the *trans*, and so methods that allow synthesis of particular isomers are especially useful.<sup>28</sup> We also note that compound  $[H_2pz]_2[PtCl_4]$  **10** has recently been implicated as an active species in the Shilov-type activation of methane in ionic liquids, the hydrogen bonding between anion and cation being particularly important in preventing catalyst degradation,<sup>29</sup> and that bis(imidazolium) tetrachloropalladate species are active catalyst precursors for Suzuki-Miyaura crosscoupling reactions.<sup>30</sup>

$$[MCl_4]^{2^2} \xrightarrow{+2L} cis-[MCl_2HL_2] \xrightarrow{+2L} [ML_4]Cl_2 \xrightarrow{-2L} trans-[MCl_2L_2]$$

Scheme 7 The sequence that leads to the formation of *trans* compounds from the reaction of metal-chloride precursors with ligands of low *trans*-effect.

Our aim in reporting this work is to try and draw the attention of the chemistry community to the fact that many coordination compounds can be synthesised simply by grinding together appropriate starting materials. Many of the synthetic pathways reported herein generate the platinum or palladium-containing products as mixtures with potassium chloride (or in some cases, silver chloride). We have not attempted further purification of these compounds as we have deliberately limited the scope of this paper to solid-state chemistry and methods of analysis, but in many cases simply washing the mixture with water will remove the KCl by-product. If feasible, the best option if the procedures outlined above are to prove useful synthetic pathways to starting materials for further synthetic transformations might be to simply ignore the presence of the AgCl or KCl by-products and use the compounds as mixtures, removing the by-product at a later stage. Nevertheless, every one of the compounds presented in this paper (apart from 8, which spontaneously decomposes) can be synthesised as a singlephase solid (with no by-products) by solid-state methods in one or two steps from commercially available starting materials (this requires the use of the  $MCl_2$  or  $M(OAc)_2$  species as the metal source, as using K<sub>2</sub>MCl<sub>4</sub> necessarily leaves KCl behind).

# Experimental

#### Synthesis

Samples were ground by hand using an agate mortar and pestle in air. Ball milling was performed in a Retsch MM 200 ball mill (mixer mill) for the specified times at 30 Hz. All reagents were purchased from Aldrich, Strem or Lancaster and used without further purification. Product samples were dried *in vacuo* or in the oven at 50 °C. The PtCl<sub>2</sub> used was purchased from Aldrich and shown by XRPD to be of the  $\beta$ -phase.<sup>31</sup>

*n.b.* The reactions reported below did not all produce pure samples of the desired product; the results section above should be consulted for further details.

[H<sub>2</sub>im]<sub>2</sub>[PdCl<sub>4</sub>] (1). Mechanochemical synthesis: Using PdCl<sub>2</sub>: 177 mg (1 mmol) of PdCl<sub>2</sub> and 209 mg (2 mmol) of imidazolium chloride were ground in an agate mortar. This resulted in the formation of a hygroscopic reddish-brown powder. Microanalytical data (%) for [C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>]<sub>2</sub>[PdCl<sub>4</sub>], Calculated: C, 18.65; H, 2.61; N, 14.50. Found C, 18.88; H, 2.69; N, 14.65. Using  $K_2PdCl_4$ : 163 mg (0.5 mmol) of  $K_2PdCl_4$  and 105 mg (1 mmol) of imidazolium chloride were ground in an agate mortar. This resulted in the formation of an orange polycrystalline powder, which XRPD revealed to contain KCl. Microanalytical data (%) for [C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>]<sub>2</sub>[PdCl<sub>4</sub>] + 2 KCl, Calculated: C, 13.46; H, 1.88; N, 10.46. Found C, 13.82; H, 2.17; N, 10.90. Vapour absorption: A vial containing 25 mg of *cis*-[PdCl<sub>2</sub>(Him)<sub>2</sub>] 2 was placed in a jar containing concentrated aqueous HCl. The yellow powder became orange after a few minutes and finally reddish-brown. The reaction took 48 h to reach completeness. Microanalytical data (%) for [C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>]<sub>2</sub>[PdCl<sub>4</sub>], Calculated: C, 18.65; H, 2.61; N, 14.50. Found C, 18.71; H, 2.54; N, 14.27. Similar conversion occurred when *trans*-[PdCl<sub>2</sub>(Him)<sub>2</sub>] **3** was exposed to dry HCl gas, but there was no colour change observed.

cis-[PdCl<sub>2</sub>(Him)<sub>2</sub>] (2). Mechanochemical synthesis: 225 mg (1 mmol) of Pd(OAc)<sub>2</sub> was ground with 209 mg (2 mmol)

of imidazolium chloride in an agate mortar, forming **2** as a yellow polycrystalline solid. This was dried *in vacuo* to evaporate any remaining acetic acid. Microanalytical data (%) for  $[PdCl_2(C_3H_4N_2)_2]$ , Calculated: C, 22.99; H, 2.57; N, 17.87. Found C, 23.19; H, 2.81; N, 17.57.

*trans*-[PdCl<sub>2</sub>(Him)<sub>2</sub>] (3). *Thermal elimination*: 3 was synthesized from 1 as reported.<sup>14</sup> Microanalytical data (%) for [PdCl<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>]: Calculated: C, 22.99; H, 2.57; N, 17.87 Found C, 22.58; H, 2.53; N, 17.75.

**[Pd(Him)<sub>4</sub>]Cl<sub>2</sub> (4).** Mechanochemical synthesis: Using  $K_2PdCl_4$ and imidazole (1:4): 163 mg (0.5 mmol) of  $K_2PdCl_4$  was forcefully ground with 136 mg (2 mmol) of imidazole forming **4** + 2 KCl as bright white polycrystalline powder. It takes 48 h after grinding for the reaction to reach completion. Microanalytical data (%), Calculated for [Pd(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]Cl<sub>2</sub> + 2 KCl: C, 24.07; H, 2.69; N, 18.71. Found C, 23.83; H, 2.78; N, 17.36. Using PdCl<sub>2</sub> and imidazole (1:4): 89 mg (0.5 mmol) of PdCl<sub>2</sub> was forcefully ground with 136 mg (2 mmol) of imidazole forming **4** as a white polycrystalline powder. The reaction takes about 5 days after grinding to reach completion. Microanalytical data (%), Calculated for [Pd(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]Cl<sub>2</sub>: C, 32.05; H, 3.59; N, 24.92. Found C, 32.30; H, 3.62; N, 24.83.

**[H<sub>2</sub>im]<sub>2</sub>[PtCl<sub>4</sub>] (5).** Mechanochemical synthesis: Using PtCl<sub>2</sub>: 266 mg (1 mmol) of PtCl<sub>2</sub> and 209 mg (2 mmol) of imidazolium chloride were ground in an agate mortar. The resulting ochre polycrystalline powder of **5** was analysed using XRPD. Microanalytical data (%) for  $[C_3H_5N_2]_2[PtCl_4]$ , Calculated: C, 15.17; H, 2.12; N, 11.79. Found C, 15.14; H, 2.19; N, 11.35. Using  $K_2PtCl_4$ : 208 mg (0.5 mmol) of  $K_2PtCl_4$  and 105 mg (1 mmol) of imidazolium chloride were forcefully ground in an agate mortar. This resulted in the formation of an orange polycrystalline powder, and X-ray diffraction pattern on the powder revealed the presence of KCl in the product. Microanalytical data (%) for  $[C_3H_5N_2]_2[PtCl_4] + 2$  KCl, Calculated: C, 11.55; H, 1.61; N, 8.98. Found C, 11.93; H, 2.00; N, 8.53.

*cis*-[PtCl<sub>2</sub>(Him)<sub>2</sub>] (6). *Mechanochemical reaction: Using PtCl*<sub>2</sub> and imidazole: 266 mg (1 mmol) of PtCl<sub>2</sub> and 136 mg (2 mmol) of imidazole were forcefully ground in an agate mortar, resulting in the formation an olive-green polycrystalline powder. Microanalytical data (%) for [PtCl<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>], Calculated: C, 17.92; H, 2.01; N, 13.93. Found C, 17.87; H, 2.15; N, 13.95. Thermal elimination: 48 mg (0.1 mmol) of 5 was heated under vacuum at 125 °C for 5 days. This resulted in a colour change from brown to light grey. Microanalytical data (%) for  $[PtCl_2(C_3H_4N_2)_2]$ : Calculated: C, 17.92; H, 2.01; N, 13.93. Found C, 18.04; H, 2.17; N, 13.67. Mechanochemical elimination  $(Ag_2O)$ : 48 mg (0.1 mmol) of 5 was forcefully ground with 23 mg (0.1 mmol) of Ag<sub>2</sub>O. The reaction proceeded with a visible colour change from dark brown to grey, and water was removed in vacuo. Microanalytical data (%) for  $[PtCl_2(C_3H_4N_2)_2] + 2AgCl, Calculated: C, 10.46; H, 1.17; N, 8.13.$ Found C, 10.48; H, 1.18; N, 8.47.

 $[H_2pz]_2[PdCl_4]$  (7). Mechanochemical synthesis. Using  $PdCl_2$ : 177 mg (1 mmol) of PdCl<sub>2</sub> and 209 mg (2 mmol) of pyrazolium chloride were ground in an agate mortar. This resulted in the formation of 7 as a reddish-brown polycrystalline powder. Microanalytical data (%) for  $[C_3H_5N_2]_2[PdCl_4]$ , Calculated: C, 18.65; H, 2.61; N, 14.50. Found C, 18.35; H, 2.61; N, 14.63. Using  $K_2PdCl_4$ : 163 mg (0.5 mmol) of  $K_2PdCl_4$  and 105 mg (1 mmol) of pyrazolium chloride were ground in an agate mortar. This resulted in the formation of an orange polycrystalline powder, which XRPD revealed to contain KCl. Microanalytical data (%) for  $[C_3H_5N_2]_2[PdCl_4] + 2$  KCl, Calculated: C, 13.46; H, 1.88; N, 10.46. Found C, 14.07; H, 2.03; N, 10.67.

trans-[PdCl<sub>2</sub>(Hpz)<sub>2</sub>] (8). Mechanochemical synthesis: Using  $K_2PdCl_4$  and pyrazole: 163 mg (0.5 mmol) of  $K_2PdCl_4$  and 68 mg (1 mmol) of pyrazole were ball milled for 30 min forming an orange polycrystalline powder of 8. Microanalytical data (%) for [PdCl<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>] + 2 KCl, Calculated: C, 15.58; H, 1.74; N, 12.11. Found C, 15.99; H, 1.96; N, 11.96. Using Pd(OAc)<sub>2</sub> and  $[H_2pz]Cl$ : 225 mg (1 mmol) of Pd(OAc)<sub>2</sub> was ground with 209 mg (2 mmol) of pyrazolium chloride in an agate mortar forming 8 as a yellow-orange polycrystalline powder. This was dried in vacuo to evaporate any remaining acetic acid. Microanalytical data (%) for [PdCl<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>], Calculated: C, 22.99; H, 2.57; N, 17.87. Found C, 23.79; H, 2.81; N, 17.65. Solution synthesis: The title compound was prepared as previously reported.<sup>19</sup> Microanalytical data (%) for [PdCl<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>]: Calculated: C, 22.99; H, 2.57; N, 17.87 Found C, 23.08; H, 2.75; N, 18.24. Thermal elimination: 39 mg (0.1 mmol) of 7 was heated to 125 °C for 4 h. The elimination of 2HCl was accomplished with a colour change from dark orange to yellow. Microanalytical data (%) for  $[PdCl_2(C_3H_4N_2)_2]$ : Calculated: C, 22.99; H, 2.57; N, 17.87. Found C, 23.44; H, 2.69; N, 17.16. Mechanochemical elimination: 39 mg (0.1 mmol) of [H<sub>2</sub>pz]<sub>2</sub>[PdCl<sub>4</sub>] 7 was forcefully ground with 22 mg (0.2 mmol) of t-BuOK forming a grey polycrystalline powder, which was dried *in vacuo* to remove excess t-butanol. Microanalytical data (%), Calculated for  $[PdCl_2(C_3H_4N_2)_2] + 2$  KCl: C, 15.58; H, 1.74; N, 12.11. Found C, 15.29; H, 1.95; N, 11.98.

**[Pd(Hpz),]Cl<sub>2</sub> (9).** Using  $K_2PdCl_4$  and pyrazole (1:4): 163 mg (0.5 mmol) of  $K_2PdCl_4$  was forcefully ground with 136 mg (2 mmol) of pyrazole forming **9** + 2 KCl as off-white polycrystalline powder. Microanalytical data (%), Calculated for [Pd(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]Cl<sub>2</sub> + 2 KCl: C, 24.07; H, 2.69; N, 18.71. Found C, 23.87; H, 2.78; N, 18.18. Using PdCl<sub>2</sub> and pyrazole (1:4): 89 mg (0.5 mmol) of PdCl<sub>2</sub> and 136 mg (2 mmol) of pyrazole were forcefully ground in an agate mortar, resulting in the formation of **9** as a grey polycrystalline powder. The reaction is slow and takes a few weeks to reach completion whilst standing at room temperature. Microanalytical data (%) for [Pd(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]Cl<sub>2</sub> Calculated: C, 32.05; H, 3.59; N, 24.92. Found C, 32.24; H, 3.64; N, 25.23.

**[H<sub>2</sub>pz]<sub>2</sub>[PtCl<sub>4</sub>] (10).** Mechanochemical synthesis using PtCl<sub>2</sub>: 266 mg (1 mmol) of PtCl<sub>2</sub> and 209 mg (2 mmol) of pyrazolium chloride were ground in an agate mortar leading to the formation of a dark brown polycrystalline powder. Microanalytical data (%) for  $[C_3H_5N_2]_2$ [PtCl<sub>4</sub>], Calculated: C, 15.17; H, 2.12; N, 11.79. Found C, 15.15; H, 2.14; N, 11.34. Mechanochemical synthesis using  $K_2PtCl_4$ : 208 mg (0.5 mmol) of  $K_2PtCl_4$  and 105 mg (1 mmol) of pyrazolium chloride were ground in an agate mortar. This resulted in the formation of an orange polycrystalline powder. Microanalytical data (%) for  $[C_3H_5N_2]_2$ [PtCl<sub>4</sub>] + 2 KCl, Calculated: C, 11.55; H, 1.61; N, 8.98. Found C, 11.28; H, 1.47; N, 8.53. *cis*-[PtCl<sub>2</sub>(Hpz)<sub>2</sub>] (11). *Thermal elimination*: 47.5 mg (0.1 mmol) of  $[C_3H_3N_2]_2$ [PtCl<sub>4</sub>] **10** was heated to 125 °C for 4 h, the dark brown powder becoming light grey. The XRPD pattern measured for the product matches with that calculated from the computed crystal structure of *cis*-[PtCl<sub>2</sub>(Hpz)<sub>2</sub>]. Microanalytical data (%) for [PtCl<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>]: Calculated: C, 17.92; H, 2.01; N, 13.93. Found C, 17.41; H, 1.97; N, 13.53. *Mechanochemical elimination* ( $Ag_2O$ ): 48 mg (0.1 mmol) of [C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>]<sub>2</sub>[PtCl<sub>4</sub>] **10** was forcefully ground with 23 mg (0.2 mmol) of Ag<sub>2</sub>O. The reaction proceeded with a visible colour change from dark brown to grey and excess water was removed *in vacuo*. Microanalytical data (%) for [PtCl<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>] + 2AgCl, Calculated: C, 10.46; H, 1.17; N, 8.13. Found C, 10.48; H, 1.18; N, 8.47.

**[Pt(Hpz)<sub>4</sub>]Cl<sub>2</sub> (12).** Using  $K_2PtCl_4$  and pyrazole (1:4): 208 mg (0.5 mmol) of  $K_2PtCl_4$  were forcefully ground with 136 mg (2 mmol) of pyrazole, forming an unknown phase + 2 KCl as a pink polycrystalline powder. Microanalytical data (%), Calculated for [Pt(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]Cl<sub>2</sub> + 2 KCl: C, 20.97; H, 2.35; N, 16.30. Found C, 21.04; H, 2.76; N, 16.28. Using PtCl<sub>2</sub> and pyrazole (1:4): 133 mg (0.5 mmol) of PtCl<sub>2</sub> and 136 mg (2 mmol) of pyrazole were forcefully ground in an agate mortar, resulting in the formation of **12** as a beige polycrystalline powder. The reaction is slow and takes about a week to reach completion whilst standing at room temperature. Microanalytical data (%) for [(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>PtCl<sub>2</sub>]·H<sub>2</sub>O, Calculated: C, 25.91; H, 3.26; N, 20.14. Found C, 25.69; H, 3.07; N, 19.63.

 $[H_2pz]_2[PtCl_6]\cdot 2H_2O$ . A small amount of dark brown 10 was dissolved in 5 ml of concentrated HCl solution. This was allowed to evaporate slowly at room temperature and after a few days yellow prismatic crystals were obtained.

## X-ray powder diffraction analysis

All crystalline phases were analysed at room temperature by powder X-ray diffraction on a Bruker D8 diffractometer using Cu-K $\alpha$  X-radiation. In all the cases the experimental pattern matches that calculated on the basis of the single crystal structure determination at room temperature (if known). The powder patterns of the products of mechanochemical eliminations show an extra peak at  $2\theta = 28^{\circ}$  due to the presence of KCl.

A model of  $[H_2im]_2[PtCl_4]$  **5**, was created from the crystal structure of  $[H_2im]_2[PdCl_4]$  **1** by replacing palladium with platinum. The positions of the chlorine atoms were allowed to vary, but those of the carbon, nitrogen and hydrogen atoms relative to each other were fixed (the position of platinum is constrained by symmetry). The isotropic displacement parameter was fixed at reasonable values for all atoms. Refinement was carried out using the FullProf suite of programmes<sup>32</sup> using Gaussian peak profiles in the range from 10-40° in 2 $\theta$ .

The powder pattern of **10** was indexed using the program DASH.<sup>33</sup> Rigid models of the  $[PtCl_4]^{2-}$  anion (with a geometry taken from the structure of  $[H_2pz]_2[PtCl_6]\cdot 2H_2O$  by removal of two chloride atoms from the anion) and a pyrazolium cation (from the same source) were then placed in the unit cell by simulated annealing using the same program. Final refinement was carried out using FullProf as above; the position of the platinum atom is again constrained by symmetry, but the chloride atoms were

allowed to move freely. The location of the pyrazolium cation was fixed.

#### X-ray single crystal analysis

X-ray data for **8**, β-**11** and  $[H_2pz]_2[PtCl_6]·2H_2O$  were collected at 100 K on a Bruker APEX diffractometer using Mo-Kα X-radiation. Data for **8** were corrected for absorption using empirical methods (SADABS)<sup>34</sup> based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles. The crystals used for the structural determinations of β-**11** and  $[H_2pz]_2[PtCl_6]·2H_2O$  were both twinned; the components were identified using the program "cell now" and integrated and merged using SAINT (both from the APEX2 suite of programs), and corrected for absorption using TWINABS. Crystal structures were solved and refined against all  $F^2$  values using the SHELXTL suite of programs.<sup>35</sup> Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters.

## Thermogravimetric analysis

Thermal analysis of the samples was carried out on a Perkin-Elmer STA 6000 simultaneous thermal analyzer between 50 and 500 °C at the heating rate of 5 °C min<sup>-1</sup>. Data was analyzed using Pyris thermal analysis software. TGA traces are shown in the Supporting Information.†

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