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Di-metallated platinum carbonyl complexes: platinum–platinum interactions in the solid state

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The reaction of a diphenylpyridine with one equivalent of potassium tetrachloroplatinate in ethanoic acid yields a cyclometallated species which can be induced to undergo a second cyclometallation to give a C^N^C tridentate species. Carbonyl derivatives of two such compounds have been structurally characterised. The X-ray structure of the complex $[2,6\text{-}(4'\text{-}C_6H_{13}OC_6H_3)_2C_5H_3NPt(CO)]$, (**1**), obtained using 2,6-bis(4′-hexyloxyphenyl)pyridine, has no unusual features. In contrast, the structure of the complex $[2,6\text{-}(C_6H_4)_2\text{-}4\text{-}(4'\text{-}C_8H_{17}OC_6H_5)C_5H_2NPt(CO)]$, (**2**), which results when using 4-(4′-octyloxy-phenyl)-2,6-diphenylpyridine, has close intermolecular contacts, with a Pt–Pt "bond" of 3.243(1) Å holding the molecules together as dimers. Compound **2** also exists in another form in the solid state, a form that does not appear to contain Pt–Pt bonds.

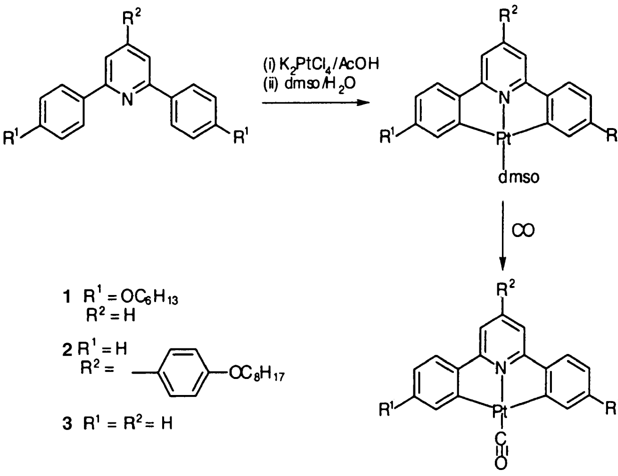
Introduction

Cyclometallation has been both widely studied,[1,2] and widely used,[3,4] but it is still generating much interest. Whilst some researchers have returned to the area of double cyclometallation of the same aromatic ring,[5–10] as pioneered by Trofimenko[11,12] more than a quarter of a century ago, our own use of the reaction has been directed towards the generation of novel cyclopalladated metallomesogens,[5,13–15] and some unusual platinum complexes.[16] Another area of research has been the synthesis of tridentate cyclometallated species where two coordinating groups hold a C–H bond close to the metal and this bond is activated. These are relatively common, thus N^C^N[17] donor sets,[18,19] P^C^P donor sets[20–23] and S^C^S donor sets[24] are well known. Indeed, some groups have used two ligating groups to induce a C–C[25] or C–Si activation.[26] In addition, the use of a chelating N^N donor set to yield N^N^C tridentate cyclometallated species has been reported.[27,28]

Relatively uncommon are double cyclometallations to give complexes with tridentate C^N^C or C^P^C donor sets, which arise when two cyclometallated rings have been formed *via* two C–H activations by the same metal. In two recent papers[29,30] we reported the first high yield synthesis of such tridentate C^N^C compounds of platinum and some of the mechanistic details of the crucial second cyclometallation. Here, we describe the solid state structures of two analogous compounds derived from substituted 2,6-diphenylpyridines.

Results

Using our standard reaction conditions (Scheme 1),[29,30] we were able to isolate the C^N^C doubly cycloplatinated products (**1**) and (**2**) in essentially quantitative yield. Both complexes were analysed by ^1H and ^{13}C NMR spectroscopy, IR, elemental analysis and single crystal X-ray diffraction. The crystals of **1** were yellow. Whilst complex **2** is yellow in solution and as the amorphous powder that results from rapid solvent removal, the crystals suitable for single crystal X-ray diffraction that we were able to grow from chloroform–hexane were red. These red and yellow forms have identical solution NMR and IR spectra, but different solid state IR spectra. In particular, the CO stretch is different when the samples are prepared as KBr discs: in the yellow form, a single band is observed at 2048 cm^{-1}, whereas the red form shows three bands at 2041, 2048 and 2057 cm^{-1}. Heating a sample of the red form results in a change to yellow at around 80 °C (with a corresponding change in the IR spectrum) before melting at 195 °C. Samples of the yellow form change slowly to the red form at room temperature in air.



Scheme 1

The X-ray structure of **1** is largely as expected (Fig. 1): the main part of the molecule (the diphenylpyridine and the Pt–CO moiety) is flat (RMS deviation from planarity 0.013 Å), bond lengths and angles are not unusual and there are no significant intermolecular interactions arising from the packing arrangement, though the ends of the aliphatic chains do end up reasonably close to each other (the CH_3 groups are separated by 3.76 Å).

By contrast, the solid state structure of compound **2** (red form) is dramatically different. The structure is unusual, though not unprecedented, in that it exists in dimers, held together with a Pt–Pt "bond", Fig. 2 and 3. The molecular cores (pyridine, the two metallated aromatic rings and the platinum carbonyl) are nearly, but not totally flat. The platinum carbonyls are bent

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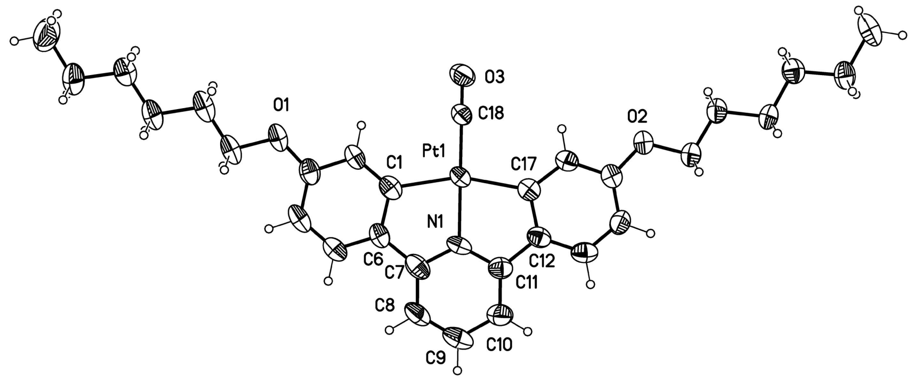

Fig. 1 The crystal structure of **1**. Selected bond lengths (Å) and angles (°): Pt(1)–C(18) 1.827(6), Pt(1)–N(1) 2.007(5), Pt(1)–C(17) 2.055(6), Pt(1)–C(1) 2.070(6), N(1)–C(7) 1.375(7), N(1)–C(11) 1.381(8), C(18)–O(3) 1.152(7), C(1)–C(6) 1.437(8), C(6)–C(7) 1.441(9), C(7)–C(8) 1.386(9), C(8)–C(9) 1.386(10), C(9)–C(10) 1.407(9), C(10)–C(11) 1.374(9), C(11)–C(12) 1.448(8), C(12)–C(17) 1.425(8), C(18)–Pt(1)–N(1) 178.8(2), C(18)–Pt(1)–C(17) 99.3(2), C(17)–Pt(1)–N(1) 80.4(2), C(18)–Pt(1)–C(1) 100.1(3), C(1)–Pt(1)–N(1) 80.2(2), O(3)–C(18)–Pt(1) 179.6(5).

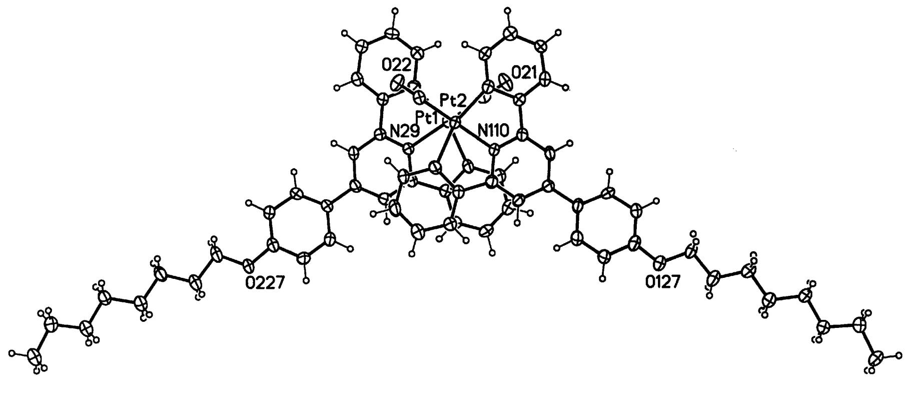

Fig. 2 Top view the crystal structure of **2**.

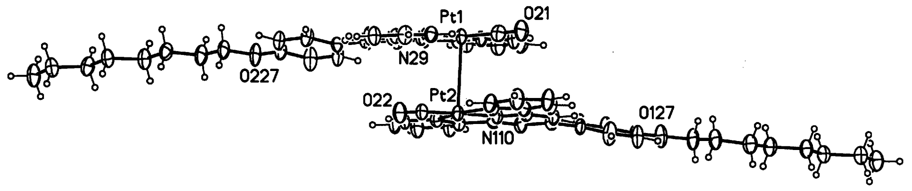

Fig. 3 Side view the crystal structure of **2**.

slightly out of the plane, with the Pt atoms 0.057 and 0.034 Å out of this plane, the carbonyl carbons 0.15 and 0.13 Å out and the carbonyl oxygens 0.23 and 0.25 Å out. These deviations from planarity result in the Pt–CO vectors pointing 3.4 and 4.3° out of the plane, with both vectors pointing away from the other molecule in the dimer. The metallated phenyl rings are distorted slightly away from the mean plane, with a bowing of 3.0, 2.5, 2.4 and 1.6° in towards the centre of the dimer. The two core planes are at an angle of 6.0° to each other, with the Pt–Pt vector making angles of 86.9 and 84.0° to the two planes. The two molecules in the dimer are rotated by an angle of 110° with respect to each other. The platinum–platinum distance is 3.243(1) Å, and the unmetallated phenyls are twisted by 16.8 and 17.0° with respect to the core plane. The bond lengths and angles within the molecules are all very similar to those in **1** and to those we have observed in similar compounds.[29,30] The platinums in adjacent dimers are separated by 6.17 Å at an angle of 53.5° to the Pt–Pt bond in the dimer giving rise to a zigzag along the extended platinum chain.

In addition to the interactions within the dimer, the dimers themselves appear to be weakly associated. Whilst the platinums within the cores are separated from those in the next dimer by a distance of 6.17 Å along the *c* axis of the unit cell, the extended chains of the substituted pyridines are much closer. In fact, the hydrocarbon chains of adjacent dimers are parallel, with H–H distances of around 2.5 Å, (Fig. 4). Whilst the H–H distance might be regarded as artificial, since the hydrogens are placed in the crystal structure at calculated positions, the extended nature of the carbon chains results in hydrogen positions that can be treated with confidence. The chains of adjacent dimers also interleave along the *b* axis of the unit cell, again with H–H contacts down to 2.5 Å (Fig. 5).

Discussion

Ostensibly very similar, compounds **1** and **2** have quite different solid state structures. Whilst the bond lengths and angles observed in both crystal structures are very similar and comparable to those we have observed in similar compounds,[29,30] dimer formation in the solid state structure of **2** distinguishes them and is of more interest. Whereas crystals of **1** were yellow, those of **2** were red. This red colour has long been recognised as indicative of strong Pt–Pt interactions in the solid state.[31,32] Solutions of **2** are yellow and, since the solution NMR spectrum shows no unexpected features or unusual chemical shifts, we are confident that the dimers do not persist in solution. In addition, this red form (with 3 distinct CO stretches in the solid state KBr IR spectrum) can be converted to a yellow form (with a single CO stretch in the solid state KBr IR spectrum) by the simple expedient of heating to 80 °C. This yellow form slowly converts back to the red form at room temperature, and we were unable to obtain an X-ray crystal structure of the former.

Molecules containing Pt–Pt bonds like that observed in the solid state structure of the red form of **2** have considerable precedent; a search of the Cambridge Crystallographic Database[33] reveals 105 structures with Pt–Pt distances between 3 and 3.5 Å. In our case, the two molecules in the dimer are rotated by an angle of 110° with respect to each other, which appears to allow one of the C–H bonds in each half of the dimer to be positioned over the pyridine ring with all the aromatic rings in the other half of the dimer, avoiding repulsive interactions.[34] This arrangement also allows an electrostatic interaction between the carbonyl in one half of the dimer and a phenyl ring in the other half of the dimer.[35] Other examples of cyclometallated platinum carbonyl compounds with short Pt–Pt distances have not shown interactions between the carbonyls and the aromatic rings, suggesting that this interaction is not dominant.[36] The fact that the Pt–Pt vector is so nearly perpendicular to the planes of the two halves of the dimer suggests that the Pt–Pt interaction is indeed a major factor in the bonding in the dimer.[35] This type of bonding between the two platinums can be rationalised in part as arising from the overlap of $5d_{z^2}$ and $6p_z$ orbitals.[37] The separation of 3.243(1) Å is similar to that of 3.28(1) Å seen in the N^N^C tridentate complex that platinum forms with 6-phenyl-2,2′-bipyridine, though in that example the Pt–Pt bond was inclined at 80.5° to the cyclometallated planes.[27] The platinums in adjacent dimers are separated by 6.17 Å at an angle of 53.5° to the Pt–Pt bond in the dimer giving rise to a zigzag along the platinum chain, as has been observed before.[38]

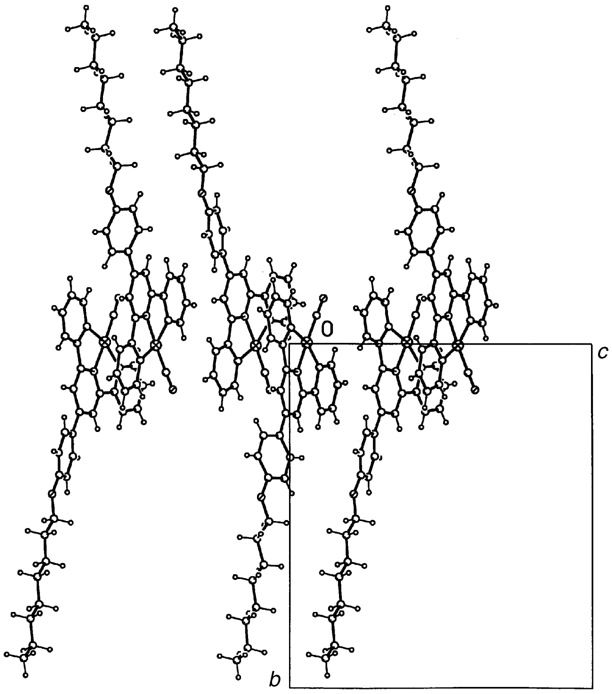

Fig. 4 View of the packing within the crystal structure of **2** showing the parallel hydrocarbon chains of adjacent dimers.

The interactions observed between the hydrocarbon chains within the solid state structure of **2** are reminiscent of those found in lipid bilayers, though it is difficult to quantify their contribution to the stability of our structure. What we do know is that the structure of both **1** and of the simple 2,6-diphenylpyridine platinum carbonyl complex **3**[30] shows no significant intermolecular interactions in the solid state. Neither the Pt–Pt bond seen in **2** or the hydrocarbon chain interactions are present in either crystal structure. The unsubstituted diphenylpyridine compound **3** must have very similar electronic properties, at least around the platinum, to the Kröhnke-derived compound **2**. Thus, we believe that it is the interactions between the hydrocarbon chains in **2** which are, in some way, assisting the organisation of the molecules so as to induce formation of the platinum–platinum bond. We also know that the red form of **2**, with its Pt–Pt interaction, is unstable with respect to the yellow form (which we believe lacks close Pt–Pt interactions) at temperatures above 80 °C. Presumably, the monomeric yellow form is entropically favoured over the red one: at higher temperatures this is sufficient to disrupt the more ordered nature of the red crystalline form, overcoming any enthalpic contributions the Pt–Pt interactions might make. Thus, it is clear that the balance between the presence or otherwise of a platinum–platinum bond can be a very delicate one.

Experimental

General

All chemicals were used as supplied, unless otherwise noted. The substituted diphenylpyridines were synthesised *via* the palladium-catalysed coupling of a Grignard reagent with 2,6-dichloropyridine,[39] the standard Kröhnke route,[40] or its solventless version.[41] All elemental analyses were performed by Warwick Analytical Service.

Synthesis of [{2,6-bis(4′-hexyloxyphenyl)pyridine}Pt(CO)] (1)

Potassium tetrachloroplatinate (103 mg, 0.239 mmol) was added to a solution of 2,6-bis(4′-hexyloxyphenyl)pyridine (99 mg, 0.239 mmol) in glacial acetic acid (125 ml). The reaction was stirred at 100 °C until the red platinum salt was no longer visible (3 days). The reaction mixture was concentrated to 10 ml and then filtered, yielding a yellow powder which was washed with water, acetone and diethyl ether. This powder was dissolved in hot dmso (1 ml), the solution allowed to cool, and the product precipitated with water (1 ml) giving a yellow crystalline material. These crystals were dissolved in chloroform and CO gas bubbled through the solution. The solvent was removed to yield the yellow product. Yield 135 mg (88%, 0.210 mmol). δ_H (400 MHz, $CDCl_3$): 7.50 (1H, t, ^3J 8.0, central pyridine),

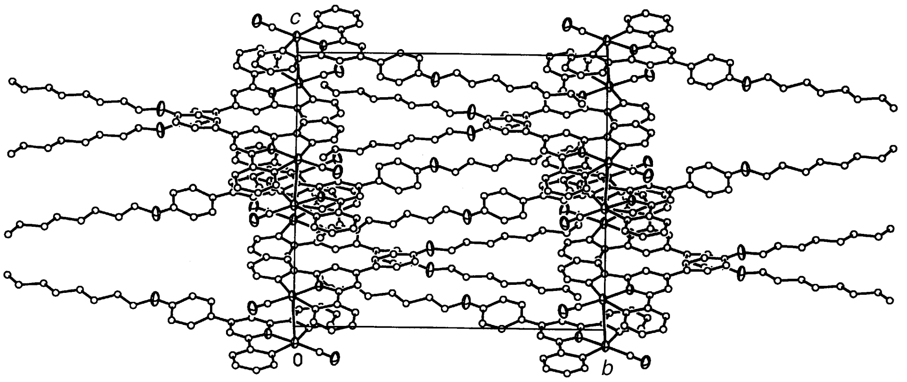

Fig. 5 View of the packing within the crystal structure of **2** showing the interleaving of the hydrocarbon chains along the *b* axis.

7.35 (2H, d, ^3J 8.8, cycloplatinated ring, *meta* to Pt), 7.19 (2H, d, ^4J 2.5, ^3J(H,Pt) 36, cycloplatinated ring, *ortho* to Pt), 6.99 (2H, d, ^3J 8.0, pyridine), 6.59 (2H, dd, ^3J 8.8, ^4J 2.5, cycloplatinated ring, *para* to Pt), 3.99 (4H, t, ^3J 6.7, OCH_2), 1.84–1.41 (16H, m), 0.98 (6H, t, *J* 7.0 Hz, CH_3). δ_C ($CDCl_3$): 206.9 (s, CO). FT-IR (KBr disc): ν(C–O) 2042 cm^{-1}. Elemental analysis: found (expected) C 55.5 (55.2), H 5.4 (5.4), N 2.1 (2.2%).

Synthesis of [{4-(4′-octyloxyphenyl)-2,6-diphenylpyridine}-Pt(CO)] (2)

Potassium tetrachloroplatinate (94 mg, 0.225 mmol) was added to a solution of 4-(4′-octyloxyphenyl)-2,6-diphenylpyridine (109 mg, 0.250 mmol) in glacial acetic acid (125 ml). The reaction was stirred at 80 °C until the red platinum salt was no longer visible (3 days). The reaction mixture was concentrated to 10 ml and then filtered, yielding a yellow powder which was washed with water, acetone and diethyl ether. This powder was dissolved in hot dmso (1 ml), the solution allowed to cool, and the product precipitated with water (1 ml) giving a yellow crystalline material. These crystals were dissolved in chloroform and CO gas bubbled through the solution, the colour remaining yellow. When the solvent was removed rapidly, a yellow amorphous powder resulted, whereas slow removal of solvent yielded a red microcrystalline product. Both red and yellow forms had identical solution state properties (IR, NMR) but different solid state properties (IR). Heating the red form to 80 °C caused it to turn yellow with a corresponding change in the solid state IR. Yield 143 mg (97%, 0.218 mmol). δ_H (400 MHz, $CDCl_3$): 7.57 (2H, AA′XX′, phenyl, *meta* to OC_8H_{17} chain), 7.50 (2H, dd, ^3J 7.5, ^4J 1.5, ^3J(Pt–H) 38, phenyl, *ortho* to Pt), 7.39 (2H, dd, ^3J 7.5, ^4J 1.5, phenyl, *meta* to Pt, *ortho* to pyridine), 7.23 (2H, s, pyridine) 7.14 (2H, dt, ^3J 7.5, ^4J 1.5, phenyl, *meta* to Pt, *para* to pyridine), 7.06 (2H, dt, ^3J 7.5, ^4J 1.5, phenyl, *para* to Pt), 6.99 (2H, AA′XX′, phenyl, *ortho* to OC_8H_{17} chain), 4.01 (2H, t, ^3J 7.0, OCH_2), 1.80 (2H, m, OCH_2CH_2), 1.51 (10H, m, chain), 0.89 (3H, t, ^3J 7.0 Hz, CH_3). δ_C ($CDCl_3$): 209.7 (s, CO). FT-IR: yellow form (KBr disc) ν(C–O) 2048 cm^{-1}; red form (KBr disc) ν(C–O) 2041, 2048 and 2057 cm^{-1}, ($CDCl_3$ solution) ν(C–O) 2062 cm^{-1}. Elemental analysis: found (expected) C 58.2 (58.5), H 4.4 (4.8), N 2.1 (2.1). Mp = 195 °C.

X-Ray crystallographic study of 1

Crystals suitable for structural analysis were grown from ethyl acetate. A yellow prism (dimensions 0.40 × 0.38 × 0.24 mm) was mounted with oil on a thin quartz fibre. Data were collected at 180(2) K using a Siemens SMART CCD area-detector diffractometer. Crystal data for **1**: $C_{30}H_{35}O_3NPt$, *M* = 652.68, triclinic, space group $P\bar{1}$, *a* = 10.0566(5), *b* = 11.7161(6), *c* = 13.8432(8) Å, *a* = 68.794(1), *β* = 69.218(1), *γ* = 64.736(1)°, *U* = 1335.75(12) Å^3, *Z* = 2, *D*(calc.) = 1.623 Mg m^{-3}. Refinement was by full matrix least-squares on F^2 for 7048 reflection positions using SHELXL-96[42] with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which the H atom is attached (or 1.5 for methyl H atoms). The weighting scheme was calculated using $w = 1/[\sigma^2(F_o^2) + (0.0357P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Goodness-of-fit on F^2 was 0.935, *R*1[for 3993 reflections with $I > 2\sigma(I)$] = 0.0354, *wR*2 = 0.0749. Data/parameters 4865/318. Largest difference Fourier peak and hole 1.911 and −1.671 e Å^{-3}; the only large peaks are near the Pt atoms.

X-Ray crystallographic study of 2

Crystals suitable for structural analysis were grown from chloroform–hexane. A red prism (dimensions 0.25 × 0.25 × 0.2 mm) was mounted with oil on a thin quartz fibre. Data were collected at 180(2) K using a Siemens SMART CCD area-detector diffractometer. Crystal data for **3**: $C_{32}H_{31}O_2NPt$, *M* = 656.67, monoclinic, space group *C*2/*c*, *a* = 32.1213(4), *b* = 19.17320(10), *c* = 17.0303(3) Å, *β* = 97.5690(10)°, *U* = 10397.0(2) Å^3, *Z* = 16, *D*(calc.) = 1.678 Mg m^{-3}. Refinement was by full matrix least-squares on F^2 for 32811 reflection positions using SHELXL-96[42] with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which the H atom is attached (or 1.5 for methyl H atoms). The weighting scheme was calculated using *w* = $1/[\sigma^2(F_o^2) + (0.0297P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Goodness-of-fit on F^2 was 0.943, *R*1 [for 7326 reflections with $I > 2\sigma(I)$] = 0.0381, *wR*2 = 0.0799. Data/parameters 12731/649. Largest difference Fourier peak and hole 1.228 and −1.398 e Å^{-3}; the only large peaks are near the Pt atoms.

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See http://www.rsc.org/suppdata/dt/b1/b105073g/ for crystallographic data in CIF or other electronic format.

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