# Carbene or zwitterion? Competition in organoplatinum complexes

Christopher P. Newman, Guy J. Clarkson, Nathaniel W. Alcock and Jonathan P. Rourke\*

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The reaction of a known dimeric dicarbene complex of platinum with a number of ligands results in four new platinum complexes. The structure of the new complexes is described: one complex must exist as a neutral complex with no charge separation, and the other three are assigned a charge-separated (zwitterionic) structure, rather than a carbene form, on the basis of comparative <sup>13</sup>C NMR shifts.

## Introduction

Numerous zwitterionic organometallic species have been reported in the literature.<sup>1</sup> Often, though, there is only a fine distinction between the formally different resonance structures. One example of a complex that does not exist in the zwitterionic form is the platinum carbene complex that we reported earlier.<sup>2</sup> In this paper, we reported the synthesis of this platinum carbene from the reaction of a 2,6-disubstituted pyridine with potassium tetrachloroplatinate (Scheme 1). The product (1) formed in preference to the cyclometallated compound that might have been expected,<sup>3,4</sup> and exhibits remarkable stability, melting in air without decomposition at 246 °C. Two possible extremes are possible for the compound: a carbene structure (1) and a zwitterionic structure (2). We confirmed the carbene like nature of

Department of Chemistry, University of Warwick, Coventry, UK CV4 7AL. E-mail: j.rourke@warwick.ac.uk; Fax: 44 (0)24 7652 4112; Tel: 44 (0)24 7652 3263 the product on the basis of a short Pt–C bond length (1.9519(9) Å) and the <sup>13</sup>C chemical shift of the carbon attached to the platinum (324.3 ppm). Though we did not speculate on the reasons for the stability of the carbene form of the complex, it is immediately apparent that the additional hydrogen on the nitrogen, and the hydrogen bonding to this hydrogen must play a major role. In this paper we look at the effect of other ligands on the stability of the carbene complex.

## **Results and discussion**

Reaction of platinum carbene (1) with two equivalents of triphenylphosphine per platinum results in the splitting of the dichloride bridge to give a monoplatinum species (3), whereas reaction with one equivalent of ligand per platinum results in the formation of a different monoplatinum species (4), Scheme 2. In practice, however, we saw mixtures of both compounds regardless of how much phosphine we used.



Scheme 1





We consider the reaction with 2 equivalents of phosphine first. Though we do not have an X-ray crystal structure of compound (3) all spectroscopic data are consistent with the formulation shown. The relative sizes of the integrals in the <sup>1</sup>H NMR spectrum indicate two triphenylphosphines present for each diphenylpyridine unit, and the coupling pattern (in particular the singlet for the protons on the pyridine ring) indicate that the substitution pattern on the pyridine ring has not changed. A single peak in the <sup>31</sup>P NMR spectrum indicates a single phosphorous environment (as would be expected with two triphenylphosphine groups mutually *trans*) and the size of the <sup>1</sup>J Pt-P coupling (2870 Hz) suggests P trans to P. Compound (3) does not require the pyridine to be protonated if it is neutral and there is no low field signal in the <sup>1</sup>H NMR spectrum that might have come from such a proton. Thus we are confident that the ring attached to the platinum is best represented as a normal pyridine ring. An analysis of the <sup>13</sup>C NMR spectrum of (3) shows that the carbon directly attached to the platinum resonates at 176.1 ppm. We are able to clearly assign this signal on the basis of it having no protons directly attached and it being a triplet due to coupling to two identical phosphorus atoms ( ${}^{2}J_{PC} = 7$  Hz); coupling to platinum was not seen (either because of the weakness of the sample, or because relaxation due to CSA broadens the satellites). The chemical shift of this carbon is a bit higher than might be expected, but it is not in the region that would indicate a carbene (200+ ppm), and certainly nowhere near the 324 ppm observed for the original complex (1).

When carbene (1) reacts with a single equivalent (per platinum) of triphenylphosphine, complex (4) results. We do have an X-ray crystal structure of (4) (Fig. 1), and whilst there was some disorder in the alkoxy chains leading to a high R value, it does clearly indicate a *cis* arrangement of the two chlorides.

Additional features of note include a Pt–C distance of 1.989(16) Å and N–O distances of 2.633 and 2.596 Å. The N–O distances are less than the sum of the van der Waals radii of nitrogen and oxygen  $(3.07 \text{ Å})^5$  and similar to the N–O distances of 2.622(9) and 2.720(8) Å observed in the starting carbene complex (1), indicating a hydrogen bonding interaction through a proton



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Fig. 1 The ORTEP of the structure of (4) (ellipsoids at 30% probability). Selected bond lengths (Å) and angles (°): Pt(1)–C(119) 1.989(16), Pt(1)–P(10) 2.219(5), Pt(1)–Cl(1) 2.374(4), Pt(1)–Cl(2) 2.396(4); C(119)–Pt(1)–P(10) 93.3(4), C(119)–Pt(1)–Cl(1) 85.7(4), P(10)–Pt(1)–Cl(1) 178.0(2), C(119)–Pt(1)–Cl(2) 176.7(4), P(10)–Pt(1)–Cl(2) 89.63(16), Cl(1)–Pt(1)–Cl(2) 91.36(15).

on the pyridine nitrogen. The Pt–C distance is longer than that observed in the carbene (1) (though this difference should be treated with caution as it exists on the limit of experimental error), but is not in itself diagnostic of either a Pt–C single or double bond: platinum–carbon single bonds can be found in the literature ranging between ~2.4 and 1.9 Å.<sup>6,7</sup> Spectroscopic data on (4) are revealing: a broad low-field resonance in the <sup>1</sup>H NMR spectrum (12.3 ppm) confirms the presence of a hydrogen on the nitrogen, which is required if the complex is neutral overall, and a singlet in the <sup>31</sup>P NMR spectrum with a <sup>1</sup>J Pt–P coupling (4463 Hz) confirming P *trans* to chloride.

In a similar manner to (1), two resonance structures for (4) are possible, the zwitterionic (4) and the carbene (5), Scheme 3. Whilst



the Pt–C distance is of little use in distinguishing these two forms, the <sup>13</sup>C NMR is: the carbon bonded to the platinum resonates at 177.0 ppm. Once again, we are able to clearly identify this signal on the basis of it having no directly attached protons and it being a doublet due to coupling to phosphorus ( ${}^{2}J_{PC} = 6.5$  Hz); again, coupling to platinum was not seen. The chemical shift value of 177.0 is very similar to that exhibited by complex (3) (171.6 ppm) which has no possibility of exhibiting a carbenoid form. This leads us to conclude that complex (4) exists as the zwitterionic form in solution, not the carbene form.

Two further ligands were used to split the chloride bridged dimeric core present in (1): carbon monoxide and dmso. Both were used in excess, with the carbon monoxide being bubbled through a solution of (1), and (1) being dissolved in dmso, however spectroscopic and elemental analysis data indicates that in both cases only one new ligand was coordinated to the platinum.



The integrals in <sup>1</sup>H NMR spectrum of the dmso complex (6) show the presence of one coordinated DMSO group per diphenylpyridine unit, and that the pyridine nitrogen is protonated (a broad resonance at 12.95 ppm). A  ${}^{3}J_{\rm HPt}$  coupling of 26 Hz gives strong evidence that, similar to triphenylphosphine complex (4), the DMSO coordinates *trans* to chloride.<sup>8,9</sup> The signal for carbon directly bonded to platinum was found at 165.6 ppm in the <sup>13</sup>C NMR spectrum, confirming a zwitterionic structure.

The <sup>1</sup>H NMR spectrum of the carbonyl compound (7) is broadly similar to the mono-triphenylphosphine complex (4) (in terms of the diphenylpyridine signals), and shows that the pyridine nitrogen is protonated with a broad resonance at  $\delta$  10.9 ppm. The carbon spectrum was too weak to see either the metallated carbon or the carbonyl carbon, however the infrared spectrum shows  $v_{\rm CO}$ 2078 cm<sup>-1</sup>, relatively high, and consistent with the CO being *trans* to Cl and not *trans* to C.

On the basis of the spectroscopic evidence we were able to acquire, we are confident of the assignment of *cis* geometries to both (6) and (7). The question arises as to the nature of the Pt-C bond in carbonyl complex (7): is it the carbene like link seen in (1) or is it a single Pt-C like that in (4)? If we consider the nature of the Pt=C bond in (1), it is apparent that creation of

the  $\pi$ -bond in the Fischer type carbene requires back donation to the carbon from the platinum. This would suggest that the carbene structure would only be observed with electron donating co-ligands on the platinum. This is what is observed with chlorides (good  $\sigma$ - and  $\pi$ -donor ligands). When a chloride is replaced by the poorer electron donor triphenylphosphine as in compound (4), or by dmso as in (6), the carbene structure is not observed. Thus we would expect that the even poorer electron donor, CO, would be even less likely to exhibit a carbene like structure than either the triphenylphosphine or the dmso complexes. We thus assign a zwitterionic structure to (7). It is salient to note that the zwitterionic structure maintains the aromaticity of the pyridine ring, which is not present in the carbene form.

There is one example in the literature of a ruthenium complex that exists in two forms: a metallaquinone (8) or a zwitterionic compound (9), Scheme 4.10 Both forms of this compound are seen, with solvent polarity controlling the position of equilibrium. Thus, in non polar solvents such as benzene the quinoidal form is adopted, the solution is orange and the carbon bonded to ruthenium resonates at 303 ppm. In the more polar methanol the solution becomes yellow and the carbon bonded to ruthenium resonates at 155 ppm. This situation has analogies to ours and provides further support for our use of <sup>13</sup>C chemical shifts to assign a zwitterionic structure rather than a carbene. Certainly these results cast doubt on the assignment of a carbene structure (11) rather than a zwitterionic structure (10) for an organopalladium complex in a recent paper.<sup>11</sup> The assignment in this paper was made on the basis of a <sup>13</sup>C chemical shift of 176.2 ppm for the carbon directly bonded to palladium, Scheme 5.



#### Conclusions

The unequivocal assignment of a non-zwitterionic pyridine structure to triphenylphosphine complex (**3**) allows us to determine the <sup>13</sup>C NMR shift of a carbon directly bonded to a platinum. We have then been able to use this value to assign a zwitterionic structure (**5**), rather than a carbene structure, to another triphenylphosphine derivative. The assignment of the zwitterionic structure to (**5**) allows us to argue that further derivatives also show a zwitterionic structure, as the ligands present in these new examples (dmso and CO) are less likely than triphenylphosphine to stabilise a carbene structure.

## Experimental

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 400 or 500 in CDCl<sub>3</sub> and are referenced to external TMS, assignments being made with the use of decoupling, NOE and the DEPT and COSY pulse sequences. The labelling scheme used in the NMR assignments of all complexes is shown in Fig. 2. All elemental analyses were performed by Warwick Analytical Services. Crystal structures were collected on a Siemens Smart 1 K. Platinum carbene complex (1) was synthesised as we previously reported.<sup>2</sup>



Fig. 2 The labelling scheme used in the NMR assignments of all complexes.

#### Triphenyl phosphine complexes (3) and (4)

Triphenylphosphine (18 mg,  $6.71 \times 10^{-5}$  mol) was added to a solution of platinum carbene (1) (64 mg,  $3.33 \times 10^{-5}$  mol) in CHCl<sub>3</sub>. The mixture was heated at 80 °C for approximately 4 h. After cooling the solution was concentrated *in vacuo* and excess hexane added, precipitating a dark yellow solid. <sup>31</sup> P NMR showed the precipitate to contain three different phosphorus containing compounds. The mixture was eluted on a silica column (5% methanol–95% chloroform). The first fraction contained an unidentified impurity. Fraction 2 contained *cis*-dichloro(2,6-bis(2,4-diheptyloxyphenyl)pyridine)(triphenylphosphine)platinum(II), complex (4); yield: 26 mg, 32% (based on Pt). Fraction 3 contained *trans*-chloro(2,6-bis(2,4-diheptyloxyphenyl)pyridine)bis(triphenylphosphine)platinum(II), complex (3); yield: 25 mg, 27% (based on Pt).

*cis*-Dichloro(2,6-bis(2,4-diheptyloxyphenyl)pyridine)(triphenylphosphine)platinum(II) (4).  $\delta_{\rm H}$  (CDCl<sub>3</sub>): 12.3 (br t, 1H, H<sub>q</sub>); 7.7 (d, 2H, <sup>4</sup>J<sub>HH</sub> 2 Hz, H<sub>b</sub>); 7.65 (m, 6H, PPh<sub>3</sub>); 7.3 (d, 2H, <sup>3</sup>J<sub>HH</sub> 9 Hz, H<sub>e</sub>); 7.15 (m, 9H, PPh<sub>3</sub>); 6.5 (dd, 2H, <sup>3</sup>J<sub>HH</sub> 9 Hz, <sup>4</sup>J<sub>HH</sub> 2 Hz, H<sub>f</sub>); 6.45 (d, 2H, <sup>4</sup>J<sub>HH</sub> 2 Hz, H<sub>b</sub>); 3.9 (t, 8H, <sup>3</sup>J<sub>HH</sub> 7 Hz, H<sub>j,j\*</sub>); 1.72 (m, 4H, H<sub>k</sub>); 1.52 (m, 4H, H<sub>k\*</sub>); 1.4 (m, 4H, H<sub>1</sub>); 1.3 (m, 4H, H<sub>m</sub>); 1.25 (m, 8H, H<sub>n.0</sub>); 1.1 (m, 4H, H<sub>I\*</sub>); 1.05 (m, 4H, H<sub>o\*</sub>); 0.95 (m, 4H, H<sub>m\*</sub>); 0.85 (m, 6H, H<sub>p</sub>); 0.8 (m, 4H, H<sub>n\*</sub>); 0.7 (m, 6H, H<sub>p\*</sub>).  $\delta_{\rm C}$  (CDCl<sub>3</sub>): 177.0 (d, <sup>2</sup>J<sub>PC</sub> = 6.5 Hz, C<sub>a</sub>); 161.8 (C<sub>i</sub>); 156.3 (C<sub>g</sub>); 142.3 (C<sub>c</sub>); 133.8 (C<sub>x</sub>); 132.0 (C<sub>b</sub>); 130.5 (C<sub>e</sub>); 129.7 (C<sub>v</sub>); 129.2 (C<sub>z</sub>); 26.8 (C<sub>y</sub>); 110.5 (C<sub>d</sub>); 105.6 (C<sub>f</sub>); 99.3 (C<sub>h</sub>); 68.3 (C<sub>j</sub>); 67.4 (C<sub>j\*</sub>); 30.5 (C<sub>n.n\*</sub>); 28.1 (C<sub>k,k\*,LI\*</sub>); 24.8 (C<sub>m</sub>); 21.6 (C<sub>m\*,0.0\*</sub>); 13.1 (C<sub>p.p\*</sub>).  $\delta_{\rm P}$  (CDCl<sub>3</sub>): 14.4 (<sup>1</sup>J<sub>(PPt)</sub> 4463 Hz). MS (LSIMS): *m/z* 1216 (M<sup>+</sup>). Microanalysis (%): Found (expected): C 61.6 (62.2); H 6.2 (7.0); N 0.8 (1.2).

*trans*-Chloro(2,6-bis(2,4-diheptyloxyphenyl)pyridine)bis(triphenylphosphine)platinum(II) (3).  $\delta_{\rm H}$  (CDCl<sub>3</sub>): 7.6 (m, 12H, PPh<sub>3</sub>); 7.3 (s, 2H, H<sub>b</sub>); 7.25 (m, 18H, PPh<sub>3</sub>); 6.9 (d, 2H <sup>3</sup>J<sub>HH</sub> 9 Hz, H<sub>c</sub>); 6.5 (dd, 2H, <sup>3</sup>J<sub>HH</sub> 9 Hz, <sup>4</sup>J<sub>HH</sub> 2 Hz, H<sub>f</sub>); 6.45 (d, 2H, <sup>4</sup>J<sub>HH</sub> 2 Hz, H<sub>b</sub>); 3.95 (m, 8H, H<sub>j,j\*</sub>); 1.7 (m, 4H, H<sub>k</sub>); 1.5 (m, 4H, H<sub>k\*</sub>); 1.35 (m, 4H, H<sub>1</sub>); 1.3 (m, 4H, H<sub>m</sub>); 1.25 (m, 8H, H<sub>n</sub>, <sub>o</sub>); 1.1 (m, 8H, H<sub>1\*,o</sub>\*); 1.0 (m, 4H, H<sub>m</sub>\*); 0.9 (m, 4H, H<sub>n</sub>\*); 0.85 (m, 6H, H<sub>p</sub>); 0.75 (m, 6H, H<sub>p</sub>\*).  $\delta_{\rm C}$  (CDCl<sub>3</sub>): 176.1 (t, <sup>2</sup>*J*<sub>PC</sub> = 7 Hz, C<sub>a</sub>); 164.2 (C<sub>i</sub>); 152.7 (C<sub>g</sub>); 148.2 (C<sub>c</sub>); 134.9 (C<sub>x</sub>); 131.6 (C<sub>b</sub>); 131.1 (C<sub>c</sub>); 129.8 (C<sub>y</sub>); 128.9 (C<sub>z</sub>); 127.6 (C<sub>y</sub>); 110.2 (C<sub>d</sub>); 104.3 (C<sub>f</sub>); 97.8 (C<sub>h</sub>); 67.4 (C<sub>j</sub>); 66.5 (C<sub>j</sub>\*); 30.1 (C<sub>n,n</sub>\*); 28.0 (C<sub>k,k\*,1,1</sub>\*); 24.4 (C<sub>m</sub>); 21.0 (C<sub>m\*,o,o</sub>\*); 12.9 (C<sub>p,p</sub>\*).  $\delta_{\rm P}$  (CDCl<sub>3</sub>): 23.6 (<sup>1</sup>*J*<sub>PPt</sub> 2870 Hz). MS (LSIMS): *m/z* 1180 (M<sup>+</sup> – PPh<sub>3</sub>). Microanalysis (%): Found (expected): C 66.9 (67.5); H 6.6 (6.9); N 0.7 (1.0).

#### *Cis*-Dichloro(2,6-bis(2,4diheptyloxyphenyl)pyridine)(dmso)platinum (6)

A sample of platinum carbene (1) (40 mg,  $2.08 \times 10^{-5}$  mol) was dissolved in DMSO (3 ml) and heated at 50 °C for 15 h. Upon cooling, the mixture was flooded with water and extracted with dichloromethane. The organic washings were washed with water and dried over MgSO<sub>4</sub>. Concentration of the solution followed by addition of diethyl ether resulted in precipitation of the *cis*-dichloro(2,6-bis(2,4-diheptyloxyphenyl)pyridine)(dmso)-platinum product which was collected by filtration. Yield: 34 mg, 78% (based on Pt).

 $\delta_{\rm H}$  (CDCl<sub>3</sub>): 12.9 (br, 1H, H<sub>q</sub>); 8.1 (s, 2H,  $^3J_{\rm HPt}$  43 Hz, H<sub>b</sub>); 7.7 (d, 2H,  $^3J_{\rm HH}$  7 Hz, H<sub>e</sub>); 6.6 (dd, 2H,  $^3J_{\rm HH}$  7 Hz,  $^4J_{\rm HH}$  2 Hz, H<sub>f</sub>); 6.5 (d, 2H,  $^4J_{\rm HH}$  2 Hz, H<sub>b</sub>); 4.0 (m, 8H, H<sub>j,j\*</sub>); 3.55 (s, 6H,  $^3J_{\rm HPt}$  26 Hz, dmso); 1.7 (m, 4H, H<sub>k</sub>); 1.6 (m, 4H, H<sub>k\*</sub>); 1.4 (m, 4H, H<sub>1</sub>); 1.3 (m, 12H, H<sub>m,n,o</sub>); 1.1 (m, 4H, H<sub>I\*</sub>); 1.05 (m, 4H, H<sub>o\*</sub>); 1.0 (m, 4H, H<sub>a\*</sub>); 0.9 (m, 4H, H<sub>m\*</sub>); 0.85 (m, 6H, H<sub>p</sub>); 0.7 (m, 6H, H<sub>p\*</sub>).  $\delta_{\rm C}$  (CDCl<sub>3</sub>): 165.6 (C<sub>a</sub>); 161.2 (C<sub>i</sub>); 155.6 (C<sub>g</sub>); 143.8 (C<sub>d</sub>); 132.4 (C<sub>o</sub>); 113.1 (C<sub>o</sub>); 111.6 (C<sub>b</sub>); 105.9 (C<sub>f</sub>); 99.2 (C<sub>h</sub>); 69.4 (C<sub>j</sub>); 67.8 (C<sub>j\*</sub>); 46.8 (C<sub>r</sub>); 31.3 (C<sub>m/m\*-o'o\*</sub>); 30.1 (C<sub>k,k\*</sub>); 26.5 (C<sub>1</sub>); 23.0 (C<sub>1\*</sub>); 14.6 (C<sub>p,p\*</sub>). MS (LSIMS): *m/z* 1032 (M<sup>+</sup>). Microanalysis (%): found (expected) C 53.9 (54.7); H 6.9 (7.3); N 1.1 (1.4).

## *cis*-Dichloro(2,6-bis(2,4diheptyloxyphenyl)pyridine)(carbonyl)platinum (7)

A sample of platinum carbene (1) (40 mg,  $2.08 \times 10^{-5}$  mol) was dissolved in chloroform and gaseous carbon monoxide bubbled through for 90 min. The solvent was removed and the remaining residue was run down a column of silica with CHCl<sub>3</sub> as the eluent. A brownish band contained the *cis*-dichloro(2,6-bis(2,4-diheptyloxyphenyl)pyridine)(carbonyl)platinum product. Yield: 24 mg, 59% (based on Pt).

$$\begin{split} &\delta_{\rm H} \, ({\rm CDCl_3}): \, 10.85 \, ({\rm br}, \, 1H, \, {\rm H_q}); \, 7.5 \, ({\rm d}, \, 2H, \, {}^3J_{\rm HH} \, 9 \, {\rm Hz}, \, {\rm H_e}); \, 6.55 \\ &({\rm s}, \, 2H, \, {\rm H_b}); \, 6.5 \, ({\rm d}, \, 2H, \, {}^3J_{\rm HH} \, 9 \, {\rm Hz} \, {}^4J_{\rm HH} \, 2 \, {\rm Hz}, \, {\rm H_f}); \, 6.4 \, ({\rm d}, \, 2H, \, {}^4J_{\rm HH} \\ &2 \, {\rm Hz}, \, {\rm H_h}); \, 3.9 \, ({\rm t}, \, 8H, \, {}^3J_{\rm HH} \, 6 \, {\rm Hz}, \, {\rm H_{j,j}*}); \, 1.7 \, ({\rm m}, \, 4H, \, {\rm H_k}); \, 1.55 \, ({\rm m}, \\ &4H, \, {\rm H_{k^*}}); \, 1.4 \, ({\rm m}, \, 4H, \, {\rm H_l}); \, 1.25 \, ({\rm m}, \, 12H, \, {\rm H_{m, n, o}}); \, 1.15 \, ({\rm m}, \, 4H, \\ &{\rm H_{l^*}}); \, 1.05 \, ({\rm m}, \, 4H, \, {\rm H_o^*}); \, 1.0 \, ({\rm m}, \, 4H, \, {\rm H_{n^*}}); \, 0.9 \, ({\rm m}, \, 4H, \, {\rm H_{m^*}}); \, 0.85 \\ &({\rm m}, \, 6H, \, {\rm H_p}); \, 0.75 \, ({\rm m}, \, 6H, \, {\rm H_{p^*}}). \, \delta_{\rm C} \, ({\rm CDCl_3}): \, 162.0 \, ({\rm C_l}); \, 157.3 \, ({\rm C_g}); \\ 146.4 \, ({\rm C_d}); \, 131.1 \, ({\rm C_c}); \, 114.3 \, ({\rm C_c}); \, 114.2 \, ({\rm C_b}); \, 106.6 \, ({\rm C_f}); \, 100.5 \, ({\rm C_h}); \\ 69.7 \, ({\rm C_j}); \, 68.210 \, ({\rm C_{j^*}}); \, 32.8 \, ({\rm Cm/m^* o/o^*}); \, 29.3 \, ({\rm C_{k,k^*}}); \, 26.1 \, ({\rm C_l}); \, 22.7 \\ &({\rm C_{l^*}}); \, 14.2 \, ({\rm C_{p, p^*}}). \, {\rm MS} \, ({\rm LSIMS}): \, m/z \, 983 \, ({\rm M^+}). \, {\rm Microanalysis} \, (\%): \\ {\rm found} \, ({\rm expected}): {\rm C} \, 55.7 \, (56.3); \, {\rm H} \, 6.9 \, (7.1); \, {\rm N} \, 1.3 \, (1.4). \, {\rm IR} \, ({\rm CHCl_3} \\ {\rm solution}): \, 2078 \, {\rm cm^{-1}} \, ({\rm CO} \, {\rm stretch}). \end{split}$$

#### Crystal structure data for compound (5)

Colourless plates  $0.16 \times 0.12 \times 0.04$  mm,  $C_{63}H_{84}Cl_2NO_4PPt$ , M = 1216.27, triclinic, space group  $P\bar{1}$ ; a = 11.9888(3), b = 13.3067(4),

c = 21.2775(6) Å,  $a = 75.4120(10)^{\circ}$ ,  $\beta = 85.0940(10)^{\circ}$ ,  $\gamma = 66.880(2)^{\circ}$ ;  $D_c = 1.337$  Mg m<sup>-3</sup>, U = 3020.82(15) Å<sup>3</sup> (by least-squares refinement on 2891 reflection positions), T = 180(2) K,  $\lambda = 0.71073$  Å, Z = 2, F(000) = 1256;  $\mu$ (Mo-K $\alpha$ ) = 2.482 mm<sup>-1</sup>. Maximum  $\theta$  was 29.46°. The *hkl* ranges were -7/14, -13/15, -25/25. 15439 reflections measured, 10273 unique ( $R_{int} = 0.1747$ ). Absorption correction semi-empirical from equivalents; minimum and maximum transmission factors: 0.5998, 0.90723.

No systematic absences; space group  $P\overline{1}$  was chosen on the basis of intensity statistics and shown to be correct by successful refinement. The structure was solved in P1 by direct methods using SHELXS12 and then the inversion centre located; additional light atoms were found by Fourier methods. One chain was found to be disordered, some of the partly-occupied positions coinciding with those in the alternative position related by symmetry. Rather than model these as overlapped atoms, both chains were included completely at partial occupancy. The occupancy was refined but converged to about 0.5, as is required for such alternating positions; it was then held at 0.5. The possibility of a superlattice with ordered molecules was considered but no evidence for this was seen. Refinement was by full-matrix least squares on  $F^2$  for 2851 reflection positions using SHELXTL. Hydrogen atoms were added at calculated positions, including all disordered positions, and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms apart from the disordered chain and some terminal chain atoms with high displacement parameters; Hatoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the Hatom is attached. The weighting scheme was calculated using  $w = 1/[\sigma^2(F_o^2) + (0.0455P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Goodness of fit on  $F^2 = 0.878$ ; R1 [for 3225 reflections with  $I > 2\sigma(I)$ ] = 0.0898, wR2 = 0.2044. Data/restraints/parameters 10273/22/626. Largest difference Fourier peak and hole 1.178 and -1.137 e Å<sup>-3</sup>. The largest peaks are all close to the Pt atom. The relatively high *R*-value is not unexpected in view of the high thermal motion of the chains and the partial disorder.

CCDC reference number 294673.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517874f

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