

Cite this: *Chem. Sci.*, 2017, 8, 5547

## Reversible C–C bond formation at a triply cyclometallated platinum(IV) centre†

Paul A. Shaw, Guy J. Clarkson and Jonathan P. Rourke \*

The oxidation of the tribenzylphosphine derivative of the doubly cyclometallated platinum(II) complex of diphenylpyridine, **1**, with  $\text{PhICl}_2$  led, as a first step, to the formation of a highly electrophilic metal centre which attacked the benzyl phosphine to give a triply cyclometallated species as the arenium ion. The highly acidic arenium ion protonated unreacted starting **1**, a reaction that could be suppressed by the addition of water, and gave the neutral species **2(t)**. Octahedral complex **2(t)** was induced to reductively couple, with two five-membered rings coupling to give square planar complex **5** containing a nine-membered ring. The crystal structure of **5** showed the nine-membered ring to span *trans* across the square planar metal accompanied by considerable distortion: the P–Pt–N bond angle is  $155.48(5)^\circ$ . Oxidation of **5** with  $\text{PhICl}_2$  resulted in the addition of two chlorides and a change of the nine-membered ring ligand coordination to *cis* at an octahedral centre, still with considerable distortions: the P–Pt–N bond angle in the crystal structure of **6** is  $99.46(5)^\circ$ . Treatment of **2(t)** with  $\text{AgBF}_4$  also induced a coupling to give a nine-membered ring, and the fluxional three coordinate complex **7**. A mono-methylated version of **1**, **Me-1**, was prepared and similar reactions were observed. The presence of the methyl group allowed us to observe selectivity in the coupling reaction to give the nine-membered ring, with two products (**a-Me-7** and **b-Me7**) being initially formed in the ratio 7 : 1. The concentrations of two products changed with time giving a final ratio of 1 : 8 at room temperature (half-life 48 hours), the equilibration being made possible by a reversible C–C bond forming reaction. Reaction of complexes **7** with CO or hydrogen left the nine-membered ring intact, though oxidative degradation resulted in decomplexation of the phosphine donor, accompanied by formation of a P=O group.

Received 27th March 2017  
Accepted 5th June 2017DOI: 10.1039/c7sc01361b  
rsc.li/chemical-science

## Introduction

The making and breaking of carbon–carbon bonds is key to the field of organic chemistry. Transition metals have a considerable role to play in these processes, and two of this century's Nobel Prizes in Chemistry (2005<sup>1</sup> and 2010<sup>2</sup>) were awarded for developments in the formation of, respectively, double and single carbon to carbon bonds, mediated by transition metal catalysts. Even today, control over these processes is far from complete and fundamental mechanistic studies on C–C bond formation and cleavage at a metal centre are still necessary, with both the oxidative addition of a C–C bond, and its microscopic reverse, the reductive elimination of a C–C bond, being studied. Under some circumstances, typically where a strained or

otherwise sterically constrained molecule is used, oxidative addition of the C–C bond is studied.<sup>3</sup> However, normally the energetics are such that the formation of a single carbon–carbon bond from two metal–carbon bonds is strongly favoured, as one strong bond replaces two much weaker ones. This energetic preference, often combined with the difficulty of getting a carbon–carbon bond in close proximity to a metal centre, results in an irreversible elimination reaction, and thus it is the formation of the C–C bond that is studied.<sup>4</sup> In some circumstances, a reversible C–C bond formation/cleavage process is observed, allowing study of both the forward and the reverse reactions.<sup>5</sup>

Organometallic platinum complexes are used in the cyclisation of enynes,<sup>6</sup> but are more commonly the subject of fundamental, mechanistic study.<sup>7</sup> In part this is due to their amenability to study, but it is also due to their relevance to actual processes and their ability to activate methane.<sup>8</sup> Our own work in the area has been to study the oxidation reactions<sup>9</sup> and reductive couplings<sup>10</sup> at cyclometallated platinum. In particular, we have been studying the oxidation of square planar platinum(II) complexes with  $\text{PhICl}_2$ . Oxidation with  $\text{PhICl}_2$  (which can be thought of as a convenient and easy to handle source of  $\text{Cl}_2$ ) is a two step process<sup>11</sup> with initial delivery of a  $\text{Cl}^+$

Department of Chemistry, Warwick University, Coventry, UK CV4 7AL. E-mail: j.rourke@warwick.ac.uk

† Electronic supplementary information (ESI) available: Full experimental details of synthetic procedures, variable temperature NMR spectra for **7** and a comparison of those spectra with those of **5** are available. The data from which the analysis of the equilibrium between **a-Me7** and **b-Me7** was made is included. Full details and discussions of the X-ray structures are available. CCDC 1540378–1540384. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc01361b



generating a very electrophilic metal centre, which would normally then react with a  $\text{Cl}^-$  to complete the oxidation. Thus, for many complexes, the end result is simply the addition of two chloride ligands to the metal centre giving an octahedral  $\text{Pt(IV)}$  centre;<sup>9a,c,10a,b</sup> isomerisation may take place, and this may be assisted by the intermediacy of agostic interactions.<sup>9a,12</sup> However, this electrophilic metal can also react before combining with chloride. Thus, interesting reactions result when the organic groups on the ligand systems can interact with, and intercept, the metal centre. We have observed agostic intermediates at low temperatures (e.g.  $-60^\circ\text{C}$ ) prior to transcyclometallation<sup>13</sup> reactions that lead to cyclometallated alkyl phosphines.<sup>14</sup> Even though the size of the ring containing the agostic interaction could be of different sizes, the cyclometallation selectively gave five-membered rings. Fast intra-molecular C–H activation of aromatic groups (which proceed *via* an electrophilic attack of the metal on an aryl ring), also at low temperature, has also been observed.<sup>9c,15</sup> Crucial to the efficacy of intramolecular electrophilic attack on aryl groups is the size of the ring that is formed. Thus, when the co-ligand is triphenyl phosphine an unfavoured four-membered ring is the only possibility and C–H activation is not observed.<sup>14b</sup> However, a benzyl group on a phosphine ligand would lead to the formation of a favourable five-membered ring and here we report on our

study of such complexes. In addition to the expected electrophilic attack on the benzyl groups, we see a reductive coupling reaction from the newly formed metallacycle, a reaction that is ultimately identified as being reversible.

## Results and discussion

### Tricyclometallation *via* Wheland intermediates

Using our established methodology,<sup>16</sup> doubly cyclometallated  $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$  tribenzylphosphine complex **1** was synthesised and characterised, including by X-ray crystallography, Fig. 1. Oxidation of **1**, with one equivalent of  $\text{PhICl}_2$  proceeds with initial delivery of a  $\text{Cl}^+$  generating a very electrophilic metal centre, which would normally then react with a  $\text{Cl}^-$  to complete the oxidation. However, when **1** was oxidised, in anhydrous chloroform, two products were formed in a 1 : 1 ratio, neither of which was simply the addition of two chlorides to the original complex. The two complexes were separable and were identified and fully characterised, Scheme 1.

The identity of the first product, **2(t)**, became clear from an analysis of the NMR spectra: only one  $^{19}\text{F}$  resonance (with 20 Hz  $^{195}\text{Pt}$  satellites), a single  $^{31}\text{P}$  resonance (satellites at 2649 Hz suggesting  $\text{Pt(IV)}$ <sup>17</sup>), a  $^{195}\text{Pt}$  chemical shift of  $-2911$  ppm (again suggesting  $\text{Pt(IV)}$ <sup>18</sup>), two different aryl protons (integral ratio 2 : 1) with strong coupling to Pt, three different benzyl protons (ratio 2 : 2 : 2) and NOE measurements that showed four of the benzyl protons to be close to the protons on the cyclometallated ring with integral two. All this data pointed towards an intact  $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$  Pt system with an additional cyclometallation to one ring of the phosphine; the structure was definitively confirmed by the solving of the single crystal X-ray structure, Fig. 2. The structure of **2(t)** shows a six-coordinate geometry at platinum, with some distortion away from perfect octahedral: the C–Pt–P angle of the new five-membered metallacycle is  $80.68(10)^\circ$ , the N–Pt–C angles in the cyclometallated diphenyl pyridine are  $79.61(14)^\circ$  and  $79.78(13)^\circ$ , but otherwise there is nothing to indicate major stresses or strains within the molecule.

The identity of the second product, **3**, is clear too: it has a much simpler set of NMR spectra than **2(t)**. Once again the Pt shift ( $-1719$  ppm) indicates  $\text{Pt(IV)}$ , as does the  $^{31}\text{P}$  signal (satellites at 2434 Hz). Two  $^{19}\text{F}$  signals (in the ratio 1 : 1, one with  $^{195}\text{Pt}$  satellites, one without), a set of  $^1\text{H}$  resonances indicating a monocyclometallated diphenyl pyridine (only one H with significant coupling to Pt, six signals of relative integral 1, two with relative integral 2), and a simple set of signals for the tribenzylphosphine (one benzyl resonance, relative integral 6, three aryl signals relative integrals 6 : 6 : 3) suggest structure **3**.

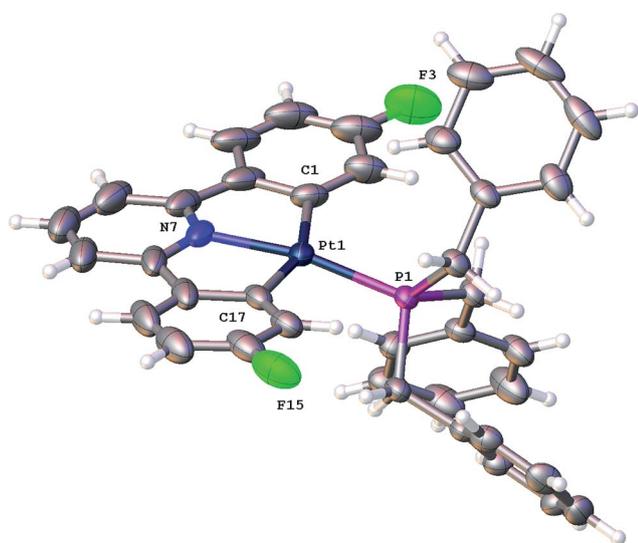
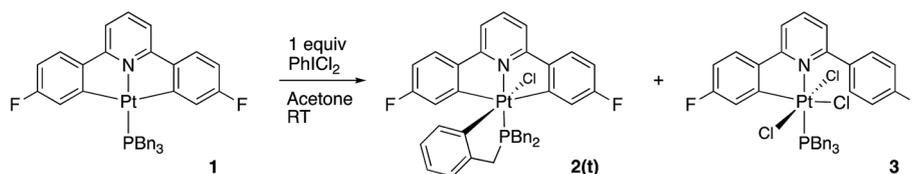


Fig. 1 The solid-state structure of **1**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles ( $^\circ$ ): Pt1–P1 2.2200(8); Pt1–N7 2.033(3); Pt1–C1 2.075(4); Pt1–C17 2.085(4); N7–Pt1–P1 168.72(10); N7–Pt1–C1 80.05(17); N7–Pt1–C17 79.84(16); C1–Pt1–P1 103.82(12); C1–Pt1–C17 159.19(17); C17–Pt1–P1 96.93(11).



Scheme 1



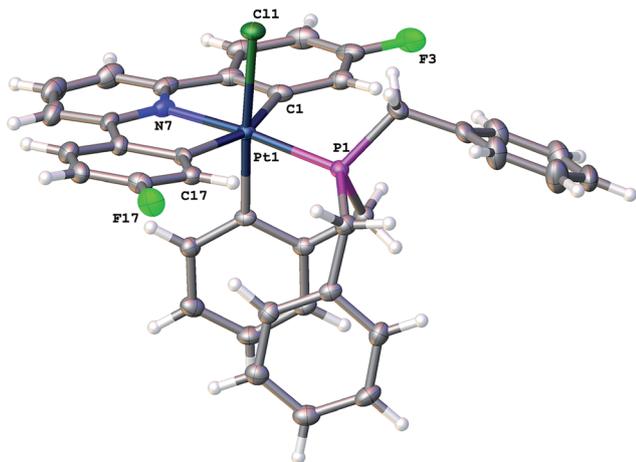


Fig. 2 The solid-state structure of **2(t)**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt1–C11 2.4425(8); Pt1–P1 2.2609(9); Pt1–C1 2.106(3); Pt1–N7 2.039(3); Pt1–C17 2.097(3); Pt1–C20 2.057(3); P1–Pt1–C11 96.45(3); C1–Pt1–C11 91.42(9); C1–Pt1–P1 96.30(11); N7–Pt1–C11 91.88(8); N7–Pt1–P1 170.83(8); N7–Pt1–C1 79.61(14); N7–Pt1–C17 79.78(13); N7–Pt1–C20 90.93(13); C17–Pt1–C11 86.02(9); C17–Pt1–P1 104.57(10); C17–Pt1–C1 159.13(15); C20–Pt1–C11 176.97(10); C20–Pt1–P1 80.68(10); C20–Pt1–C1 87.96(12); C20–Pt1–C17 95.61(12).

Reasoning that the obvious route to this second product, **3**, was oxidation of a mono-cyclometallated platinum(II) species, we repeated the reaction with only half an equivalent of  $\text{PhICl}_2$ , whereupon the products were **2(t)**, as before, and a new platinum(II) species, **4**, with the same pattern of resonances as **3** in the  $^1\text{H}$  NMR spectrum, Scheme 2. For this material, we were able to grow crystals and solve the X-ray structure, confirming our assignment, Fig. 3.

To rationalise the formation of the products, we need to look at the role of the oxidant. As an electrophilic reagent we would expect  $\text{PhICl}_2$  to initially deliver a  $\text{Cl}^+$  to one face of the starting platinum(II) complex **1**.<sup>11</sup> This generates an extremely electrophilic cationic metal centre that can attack the adjacent aryl ring of the benzyl phosphine. This in turn generates a highly acidic arenium ion<sup>19</sup> (Wheland intermediate), which protonates further starting material, it itself rearomatising in the process and forming neutral **2(t)**. Protonation of the platinum(II) complex **1** would result in cleavage of a metal carbon bond, with a final combination with the chloride generated in the initial oxidation giving **4**, Scheme 3. Control experiments show that hydrochloric acid itself, under equivalent conditions, is insufficiently acidic to protonate **1** to give **4**.

Thus, under the conditions we used, the arenium ion protonated unreacted **1** faster than the  $\text{PhICl}_2$  could oxidise **1**,

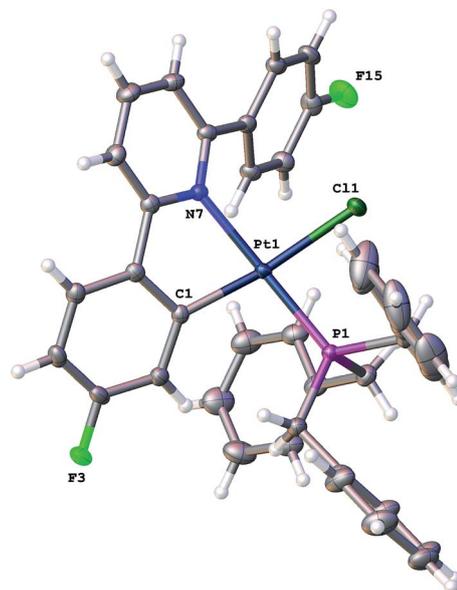


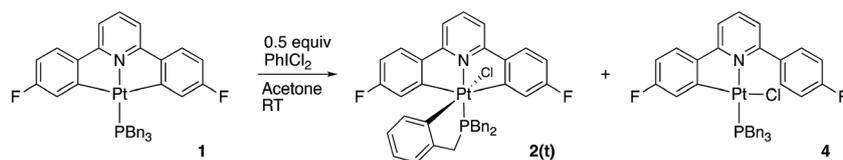
Fig. 3 The solid-state structure of **4**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt1–C11 2.3884(4); Pt1–C1 1.9947(17); Pt1–P1 2.2384(4); Pt1–N7 2.1274(13); C1–Pt1–C11 172.43(5); C1–Pt1–P1 99.70(5); C1–Pt1–N7 79.14(6); P1–Pt1–C11 86.424(16); N7–Pt1–C11 94.32(4); N7–Pt1–P1 174.23(4).

so fast, in fact, that we were unable to observe the arenium ion spectroscopically. So, in order to try and maximise the yield of **2(t)**, we took the simple expedient of adding water, which we expected to be preferentially protonated, allowing all the starting **1** to be oxidised. This strategy worked well, and it proved possible, with an acetone (80%)/water (20%) solvent mixture, and one equivalent of  $\text{PhICl}_2$ , to generate essentially quantitative yields of **2(t)**.

### Reductive coupling of two five-membered metallacycles to give nine-membered rings

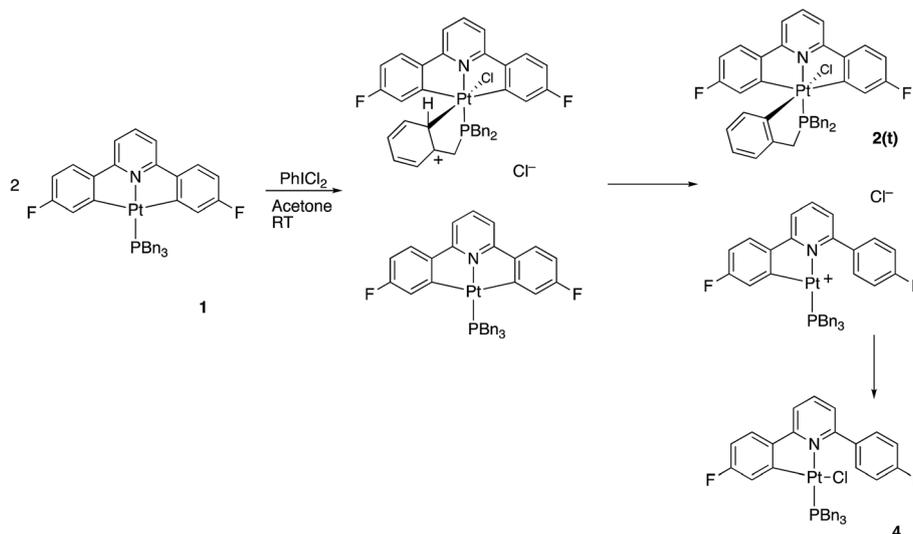
Having maximised the yield of **2(t)**, we set about investigating its reactivity. Simply attempting further purification on a silica column caused isomerisation and the formation of two new complexes, which could be separated by chromatography. One of these new complexes, **2(e)**, is simply the geometric isomer of **2(t)**, where the P and C of the cyclometallated phosphine have exchanged positions. This isomer has the P and N *cis* to each other, and can be rationalised on the basis of bringing the bulky phosphine away from the plane of the cyclometallated diphenylpyridine to a less crowded site above that plane.

Solution NMR data on the other product clearly indicated a platinum(II) species (Pt shift of  $-3985$  ppm,  $^1J_{\text{Pt-P}} = 4552$  Hz),



Scheme 2





Scheme 3

only a singly cyclometallated diphenyl pyridine (two different  $^{19}\text{F}$  resonances, one with Pt satellites, one without) and the joining of the one of the rings of the diphenyl pyridine to one of those of the tribenzyl phosphine (clear from the HMBC  $^{13}\text{C}$  spectrum). A crystal structure, Fig. 4, provided unambiguous evidence for the formation of 5, the complex that forms from the reductive coupling of two of the metal-carbon bonds such that one side of the doubly cyclometallated diphenyl pyridine has coupled to the cyclometallated benzyl group, giving a nine-membered ring, Scheme 4. Typically these two new compounds were separated out at a ratio of 4 : 1, 2(c) : 5.

The nine-membered ring in 5 spans two *trans* coordination sites at the platinum and induces significant distortions away from perfect square planar geometry (the N-Pt-P and C-Pt-Cl bond angles are  $155.83(5)$  and  $158.48(6)$  respectively). The nine-membered ring itself mostly has unexceptional bond lengths and angles, but it is pertinent to note that in addition to the N-Pt-P angle of  $155.83(5)^\circ$ , the Pt-P-C angle is only  $96.81(8)^\circ$ , suggesting the ring is rather tight. The phenyl ring that was derived from the phosphine is located over one side of the square planar platinum, effectively blocking approach to the Pt from that side. A close analysis of the  $^1\text{H}$  NMR spectrum

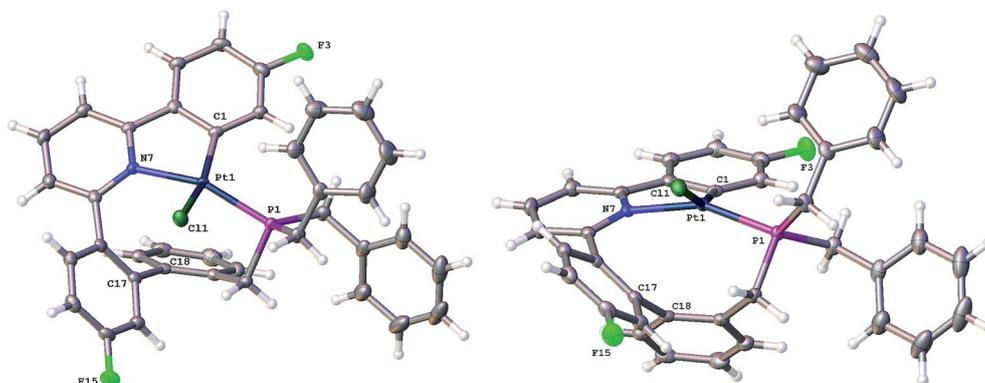
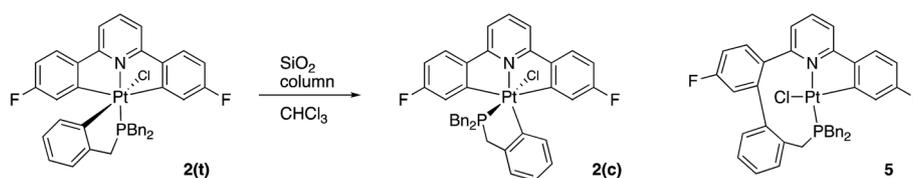


Fig. 4 Two views of the solid-state structure of 5, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles ( $^\circ$ ): C1-Pt1 1.987(2); Cl1-Pt1 2.4001(6); P1-Pt1 2.2346(6); P1-C24 1.857(2); Pt1-N7 2.095(2); C24-P1-Pt1  $96.81(8)$ ; C1-Pt1-Cl1  $158.48(6)$ ; C1-Pt1-P1  $104.44(7)$ ; C1-Pt1-N7  $80.56(9)$ ; P1-Pt1-Cl1  $87.97(2)$ ; N7-Pt1-Cl1  $95.35(6)$ ; N7-Pt1-P1  $155.83(5)$ .



Scheme 4



shows all six of the benzyl protons to be different from each other and variable temperature ( $-60$  to  $+60$  °C) studies shows no broadening of these signals and no hint of any exchange processes.

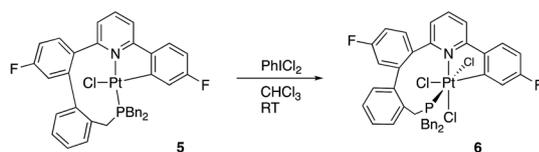
Quite what it is about the silica column that causes the isomerisation is unclear to us (potentially the Lewis acidic silica assists in the removal of the chloride<sup>20</sup>) and, in any event, it is a rather inefficient method of inducing the reductive coupling that gives **5**. Simply heating **2(t)** also gives **2(c)** and **5**, even more inefficiently, as this process is accompanied by significant decomposition. Pure **2(c)** does not transform to **5** either on a column, or upon heating. Once formed **5** is indefinitely stable at room temperature, in solution and in air. It is possible to oxidise it with  $\text{PhICl}_2$  and generate quantitative yields of **6**, simply adding the oxidant at room temperature, Scheme 5. A *cis* relationship for the P and N in the oxidised product is suggested (but cannot be definitively assigned) on the basis of a change in the pattern of the six inequivalent benzyl protons, when compared with **5**.

Crystallisation of **6** and solving the X-ray structure, Fig. 5, confirmed the suggested *cis* P–N geometry. In this arrangement the nine-membered ring seems as if it is on the large side for a *cis* arrangement at the metal with the N–Pt–P and P–C–C bond angles being  $99.46(5)$  and  $122.04(15)^\circ$  respectively. However, given the strains in the nine-membered ring when it was forced into a *trans* arrangement in the square planar **5**, and the positioning of a phenyl ring across one face of the platinum in that complex, it seems unlikely that such a *trans* arrangement could be possible in an octahedral

complex as an additional two chloride ligands need to be accommodated.

A much more efficient, and more readily understandable, method of inducing the reductive coupling of the phenyl pyridine with the benzyl phosphine is the addition of one equivalent of silver tetrafluoroborate to **2(t)**. The silver salt removes the chloride, generating a reactive five-coordinate intermediate,<sup>10d,21</sup> and a reductive coupling reaction between two of the carbon bonded groups takes place. The rapid reductive elimination from an unsaturated intermediate has been rationalised theoretically,<sup>22</sup> with the argument hinging on the fact that the coupling process results in the population of a metal orbital that is only non-bonding in the five-coordinate complex, but anti-bonding in a six-coordinate complex. When the reagents are mixed at  $-40$  °C and warmed up slowly, the reaction starts at around  $-10$  °C and exclusively gives what is presumably the three-coordinate **7** as the tetrafluoroborate salt. Not only does the initial *trans* **2(t)** give this new compound, but so does the *cis* **2(c)** and so does the coupled **5**; subsequent treatment of **7** with NaCl gives **5** in quantitative yield, Scheme 6.

Careful analysis of the variable temperature NMR spectra does not reveal any loosely bound ligands, such as water or  $\text{BF}_4^-$ , coordinated to **7**, even at  $-60$  °C. It does, however, reveal fluxionality in the compound. At low temperature ( $-60$  °C) all six of the benzyl protons have unique resonances, similar to the situation for **5**. However as the temperature is increased, broadening and merging of signals is observed and the high temperature limit appears to be one in which there are only three signals for the benzyl protons, each of integral two. We can envisage a process whereby the coupled phenyl ring moves from its position above one side of the approximately T-shaped platinum coordination plane to above the other, bringing the newly formed C–C bond past the vacant coordination site, interconverting the appropriate hydrogens as it does so. From the NMR data, we can estimate (see ESI†) the barrier for this interconversion to be of the order of  $62 \pm 8$  kJ mol<sup>-1</sup>. The presence of a chloride in **5** will provide an addition steric barrier



Scheme 5

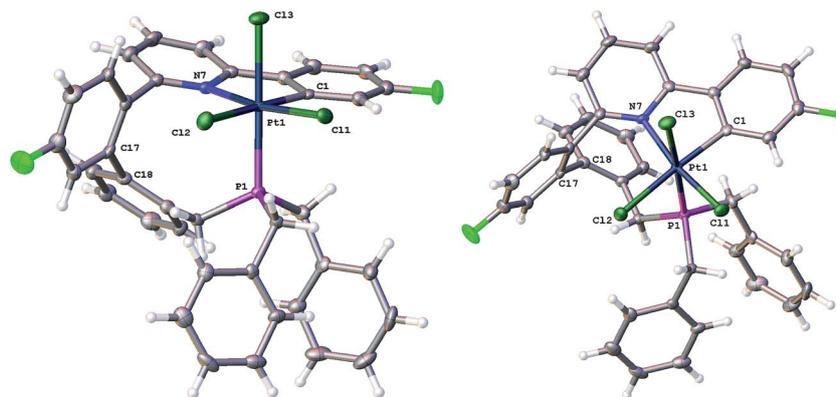
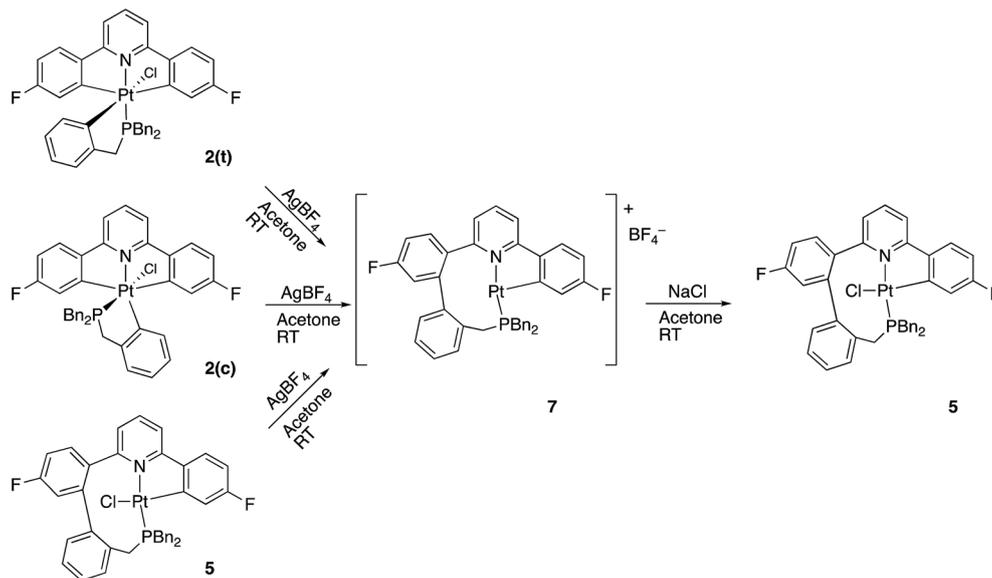


Fig. 5 Two views of the solid-state structure of **6**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt1–Cl1 2.3060(5); Pt1–P1 2.3162(5); Pt1–Cl3 2.3870(5); Pt1–Cl2 2.4175(5); Pt1–N7 2.1070(16); Pt1–C1 2.031(2); Cl1–Pt1–P1 87.370(19); Cl1–Pt1–Cl3 90.032(19); Cl1–Pt1–Cl2 85.42(2); P1–Pt1–Cl3 175.622(19); P1–Pt1–Cl2 84.619(19); Cl3–Pt1–Cl2 91.66(2); N7–Pt1–Cl1 169.78(5); N7–Pt1–P1 99.46(5); N7–Pt1–Cl3 83.59(5); N7–Pt1–Cl2 102.69(5); C1–Pt1–Cl1 90.83(6); C1–Pt1–P1 95.26(6); C1–Pt1–Cl3 88.30(6); C1–Pt1–Cl2 176.26(6); C1–Pt1–N7 81.03(7); C24–P1–Pt1 115.49(7); C23–C24–P1 122.04(15).





Scheme 6

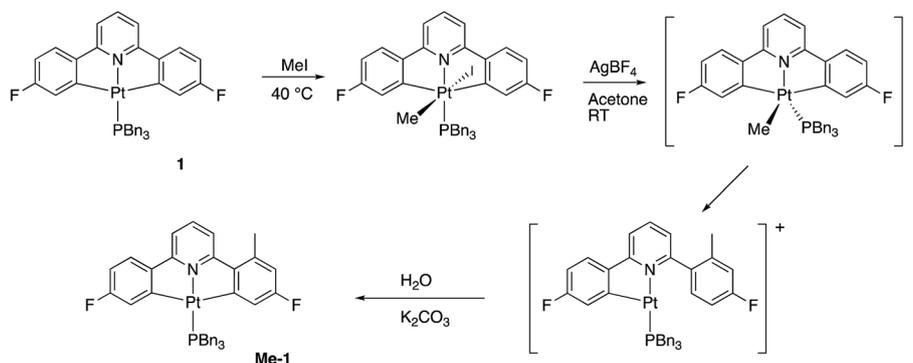
to this process that is sufficient to render it unobservable by NMR; we noted above that all six benzyl proton signals in **5** were inequivalent, with no signs of broadening or an hint of an exchange process over the temperature range  $-60$  to  $+60$  °C. Looking at the X-ray structure of **5**, Fig. 4, it is easy to believe the barrier to interconversion in **5** to be so high that it is insurmountable under normal conditions.

However, an alternative process for the equilibration of the benzyl protons in **7** can be envisaged, one that involves the cleavage of a C–C bond to generate a five-coordinate triply cyclometallated species (*i.e.* **2(t)** without the chloride). If this species were then to reductively couple the benzyl ring with the fluorophenyl ring to which it was not previously coupled (the two fluorophenyl rings are chemically identical in the triply cyclometallated species), the effect would be to exchange the benzyl protons. At first sight this process seems rather unlikely but, as we demonstrate below, it is not impossible, though the energy barrier is too high for it to significantly contribute to the effects we see in the NMR spectra.

### Distinguishing between the two fluoro-phenyl rings: reversible C–C bond formation

Using our previously published methodology<sup>10d</sup> we were able to cleanly synthesise a non-symmetric mono-methylated version of **1**, *i.e.* **Me-1**, Scheme 7. **Me-1** was fully characterised, including solving the X-ray crystal structure, Fig. 6. The presence of a methyl group on one of the fluoro-phenyl rings significantly affects the coupling pattern in the  $^1\text{H}$  NMR of the protons on that ring, and has a minor effect on the  $^{19}\text{F}$  signals; taken together, these differences are sufficient for us to be able to distinguish between reactions on one ring rather than the other. We therefore set about repeating the reactions we had observed with **1** to see how the presence of a methyl group would affect the reactivity, using its presence to distinguish reactions at the two fluoro-phenyl rings, and to elucidate the dynamic behaviour of the intermediates.

The initial reaction with half an equivalent of  $\text{PhICl}_2$  in dry solvent gave the expected **Me-2(t)** and only one of the two possible isomers of **Me-4**, Scheme 8. Protonation of the



Scheme 7



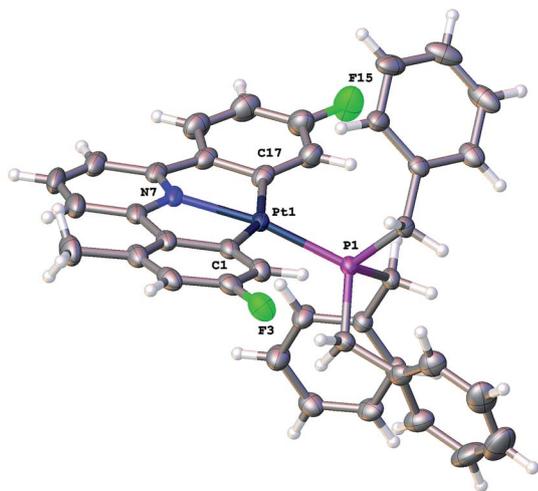


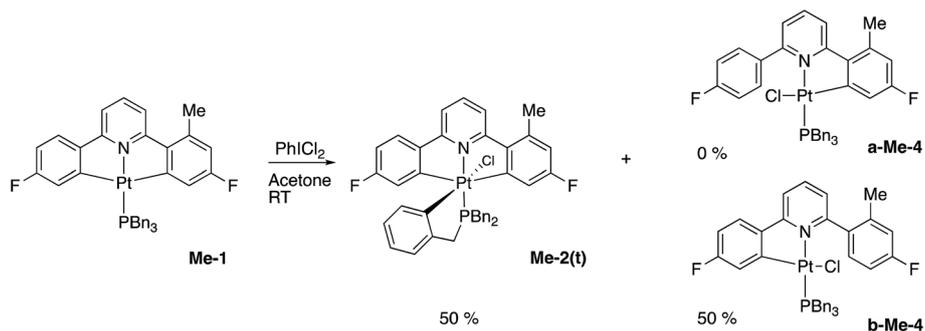
Fig. 6 The solid-state structure of **Me-1**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt1–P1 2.2409(9); Pt1–C1 2.062(4); Pt1–N7 2.029(3); Pt1–C17 2.071(4); C1–Pt1–P1 98.67(11); C1–Pt1–C17 158.79(15); N7–Pt1–P1 169.79(8); N7–Pt1–C1 79.69(14); N7–Pt1–C17 80.22(14); C17–Pt1–P1 102.30(10).

platinum centre, will be followed by aryl-Pt cleavage and could take place with either aryl ring, however we would expect **b-Me-4** to be favoured thermodynamically over **a-Me-4**, as cleavage of the methylated metallacycle would allow a release of a steric

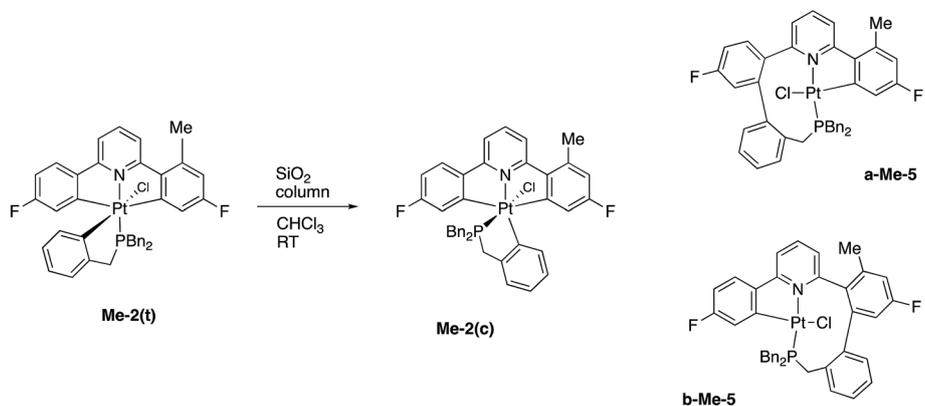
clash associated with the methyl group and the pyridine. That it is indeed the only product formed is, however, due to a lower energy pathway to that isomer, rather than the thermodynamic preference, as we would not expect the two compounds to be in equilibrium with each other under the reaction conditions used. As the methyl group will be electron releasing, in comparison to a hydrogen, perhaps it is the more electron rich nature of this ring that means it preferentially takes place in what is a reductive coupling reaction.

In a similar fashion to the chemistry reported earlier, column chromatography induces an isomerisation reaction with **Me-2(t)** giving three compounds, the methyl analogues of **2(c)** and two coupled products, **a-Me-5** and **b-Me-5**, Scheme 9, approximate ratio 6 : 1 : 1, respectively. Though it proved impossible to completely separate **a-Me-5** and **b-Me-5** from each other, samples enriched in one isomer over the other allowed complete sets of solution data on each to be acquired. Given that these two **Me-5** compounds were formed by this method in only low yields *via* an indeterminate mechanism, we should not read too much into the fact that they formed in roughly equal quantities. What we can do, though, is note that the relative proportions of these two isomers in solution does not change, whatever that proportion is, even after 1 month at 50 °C; this clearly implies an irreversible coupling reaction in their formation.

In contrast, and more interesting, is the chemistry we observe when we attempt the reaction of the triply-



Scheme 8



Scheme 9



cyclometallated **Me-2(t)** with  $\text{AgBF}_4$ . The first step of the reaction will be to generate a five-coordinate intermediate from which one of the aryl rings will couple with the cyclometallated phosphine, Scheme 10. Unlike the earlier situation, Scheme 6, we can now distinguish exactly which fluoro-phenyl ring the benzyl group couples with.

Once again we can see that **b-Me-7** will be thermodynamically favoured, but it is in fact **a-Me-7** that is formed preferentially (rough ratio **a** : **b** = 7 : 1) when the reaction is carried out at room temperature. Quite what causes this selectivity is unclear, but it is reproducible. Presumably the presence of the methyl group has a tangible influence of the orientation of the three metallacycles and this subtly affects the activation energies of the two competing coupling reactions, with the result that we get the product distribution observed.

It is also clear that, in solution, the proportions of the two isomers changes with time: the concentration of **a-Me-7** decreases with a corresponding increase in the concentration of **b-Me-7** and an equilibrium exists between the two of them, Fig. 7. A full analysis is given in the ESI,<sup>†</sup> and we only need to note here that the reaction exhibits first order kinetics with a half-life of around 48 hours at room temperature and a final position of equilibrium of around 1 : 7.5, **a** : **b**.

The only sensible intermediate between the two isomers is the triply cyclometallated cation that forms when chloride is abstracted from **Me-2(t)**, *i.e.* the coupling reaction is reversible. The three coordinate complexes **7** have a vacant site at platinum, and we know from the variable temperature  $^1\text{H}$  NMR data recorded on the non-methylated complexes that the nine-membered ring system is flipping in conformation on an NMR timescale, and that this process must bring the appropriate C–C bond right across the vacant site, so such a reaction makes sense. In addition, we know that the nine-membered ring is strained, so that the balance of energies does not so clearly lie on the side of the reductively coupled product (a C–C bond, part of a strained nine-membered ring), compared with two five-membered rings with two Pt–C bonds. Earlier, Scheme 9, we had noted that there is no interchange between the **a** and

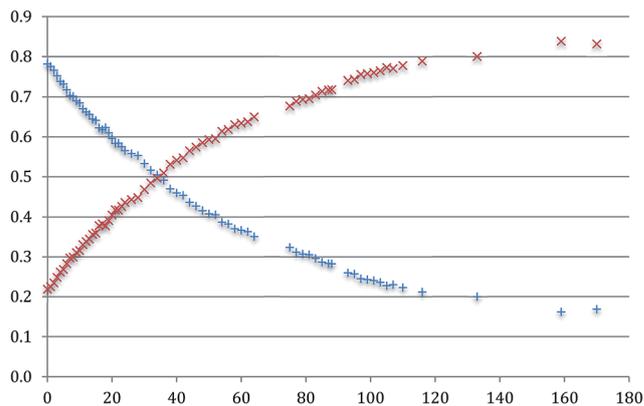
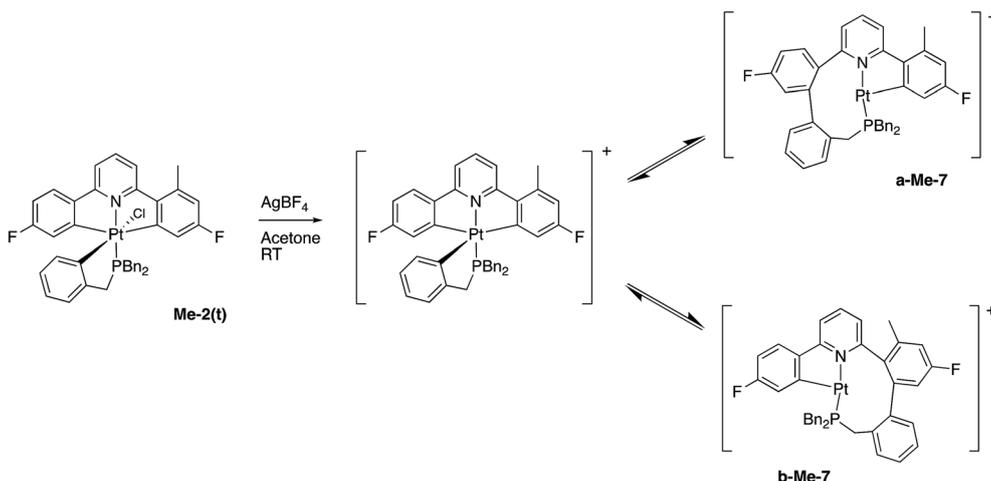


Fig. 7 The change in the normalised concentrations of **a-Me-7** (+) and **b-Me-7** (x) with respect to time (hours).

**b** isomers of **Me-5**, reinforcing the fact that the vacant site at platinum is crucial for the reversible reaction.

Nine-membered rings have considerable precedence in the literature, though there are only seven crystal structures of transition metal complexes with one P and one N donor reported; of these, six are of chiral spiro iridium phosphine complexes used for enantioselective transformations<sup>23</sup> and the last one is of a dirhenium phosphino-fullerene.<sup>24</sup> There are rather more nine-membered rings where both donors to the metal are nitrogen. In some of the crystal structures of these  $\kappa^2\text{N}$  donors the donors span *trans*<sup>25</sup> coordination sites, some *cis*<sup>26</sup> and there is one example where a change from *trans* to *cis* occurs upon addition of CO.<sup>27</sup> The formation of the eight-membered linkage that becomes the nine-membered metallacycle from two equal sized rings does not appear to have been seen before with two different cyclometallated ligands (as in the phosphine and pyridine reported here), but has been seen with two identical ligands. Thus, reported examples include the coupling of two cyclometallated phenylpyridines to give a nine-membered metal containing ring,<sup>25a,27</sup> and a similar coupling but where the coupled product detaches from the metal.<sup>28</sup> One



of these examples also illustrates the fine balance that is present: the coupling of two five-membered cyclometallated phenylpyridines to give a nine-membered ring is favourable when the metal is palladium, but not when it is platinum.<sup>25a</sup> In our case, the fine balance shows up as a reversible reaction: though the coupling of the two five membered rings is thermodynamically favoured, it is not so favoured as to present an insurmountable barrier to its reverse.

We had also earlier raised the possibility of the reversible C–C bond forming reaction in **7** being responsible for the exchange processes seen in the <sup>1</sup>H NMR of the benzyl protons. We can now discount such a process as it is obvious that the timescale of the chemical exchange (48 hour half-life) is far too slow to be responsible for the interconversion of NMR signals.

### Other reactions of the nine-membered ring species

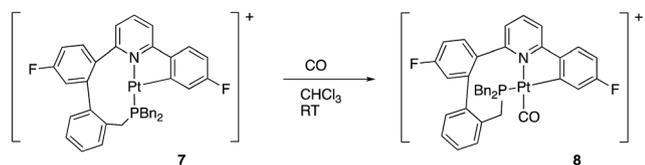
We noted above, Scheme 6, that complex **7** reacted with chloride ions to give **5**, and this reaction is general: bromide or iodide gave equivalent complexes. The reaction of **7** with other potential ligands was not fully explored, but we did note that reaction did occur with CO and H<sub>2</sub>. Carbon monoxide reacted rapidly (<1 min reaction time) and cleanly giving **8**, Scheme 11.

The coordination of CO to **7** to give **8** was immediately obvious from a colour change and from the IR spectrum, where a strong band at 2097 cm<sup>-1</sup> indicates a coordinated carbonyl. A *cis* arrangement of the P and N donors was indicated from the solution NMR data, with a resolvable <sup>5</sup>J of 6 Hz between the P and F nuclei. Such couplings are only visible when these two groups are *trans* to each other across

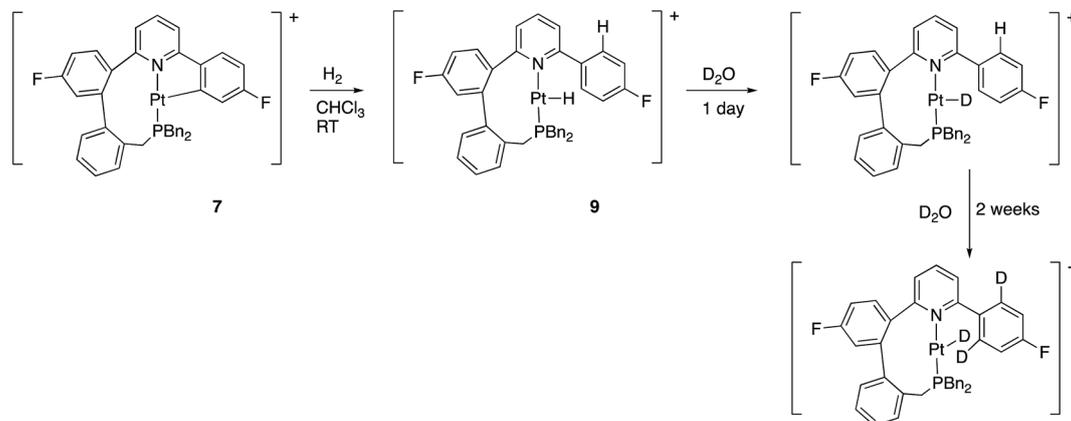
the metal centre: for comparison, in all the other complexes described in this paper, the P and the fluorinated ring are *cis* to each other and no coupling is resolvable. Presumably this *cis* arrangement of the P and N donors is more strained than the *trans* arrangement seen in **5**, otherwise it too would have this arrangement. The preferred geometry in **8** can be understood, though, on the basis of keeping two C donor ligands from coordinating *trans* to each other, a phenomenon sometimes referred to as “transphobia”.<sup>29</sup> It is interesting to note that we have therefore observed three coordination modes for the monocyclometallated coupled ligand: a *fac* coordination in **6**, and two *mer* coordination modes, one with the P and N *cis*, **8**, but more commonly with the P and N *trans*, **5** and **7**. In each of these modes there appears to be some difficulty in accommodating the nine-membered ring, and this ring ultimately proves to be the site where further reaction takes place, Scheme 13 below.

Reaction with hydrogen gas is also rapid, with only one new species seen by NMR. The new species is clearly a hydride, and not a dihydrogen complex: in the <sup>1</sup>H NMR spectrum there is a new resonance, relative integral one, at -24.34 ppm with <sup>1</sup>J<sub>H–Pt</sub> = 1230 Hz. Further analysis of the NMR spectra shows the previously cyclometallated phenyl ring to be free (no coupling between <sup>195</sup>Pt and <sup>19</sup>F, two resonances ratio 2 : 2 in the <sup>1</sup>H NMR spectrum), and we can formulate this compound as **9**, Scheme 12. The new hydride species exchanged H for D on treatment with D<sub>2</sub>O, and then, more slowly, the two hydrogens in the fluorinated ring, *ortho* to the bond to the coordinated pyridine. Whilst the first process can simply be seen as reversible protonation reaction, the second process implies a reversible cyclometallation process.

Though solutions of the all the coordinatively saturated complexes appear to survive for several weeks or more at room temperature and in air, the unsaturated **Me-7** does change over that sort of timescale, in chloroform solution and in air. The reaction is not completely clean, with multiple peaks visible in the solution NMR spectra, but we were able to isolate crystals from one reaction mixture, Fig. 8. The X-ray structure determined from the crystals revealed a molecule that no longer has



Scheme 11



Scheme 12



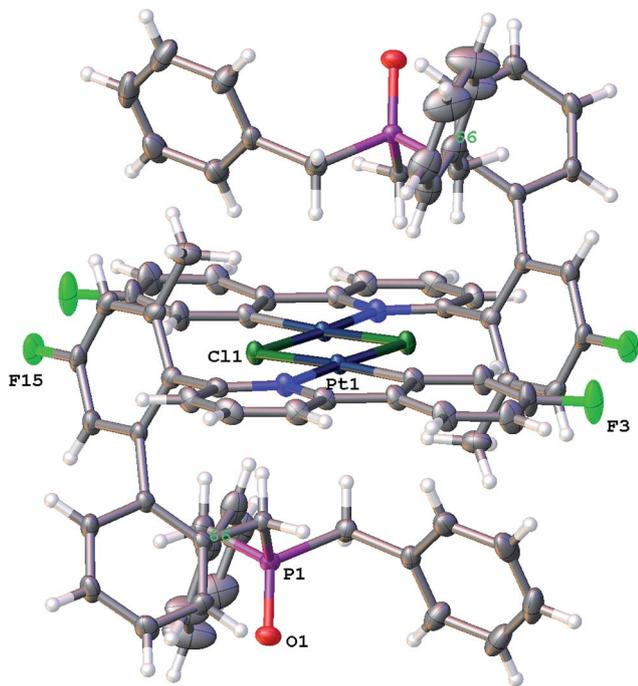


Fig. 8 The solid-state structure of **10**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): C1–Pt1 1.968(4); C1–C2 1.406(6); C1–C6 1.401(5); O1–P1 1.490(3); Pt1–Cl1<sup>1</sup> 2.4607(9); Pt1–Cl1 2.2982(9); Pt1–N7 2.052(3); C1–Pt1–Cl1 93.50(12); C1–Pt1–Cl1<sup>1</sup> 171.00(13); C1–Pt1–N7 81.59(15); Cl1–Pt1–Cl1<sup>1</sup> 79.15(3); N7–Pt1–Cl1<sup>1</sup> 105.73(9); N7–Pt1–Cl1 175.09(9).

the phosphine coordinated (it has become oxidised), but with the original cyclometallated ring still intact, the addition of chloride and a dimeric structure completes the square planar coordination at platinum, Scheme 13. Such a material is completely consistent with the dominant peaks in the NMR spectra and can be thought of as being favoured by the release of strain from breaking the nine-membered ring. The X-ray structure of **10** shows the central core of the molecule to have bond lengths and angles very similar to those found in similar analogues.<sup>9a,9c,16b,30</sup>

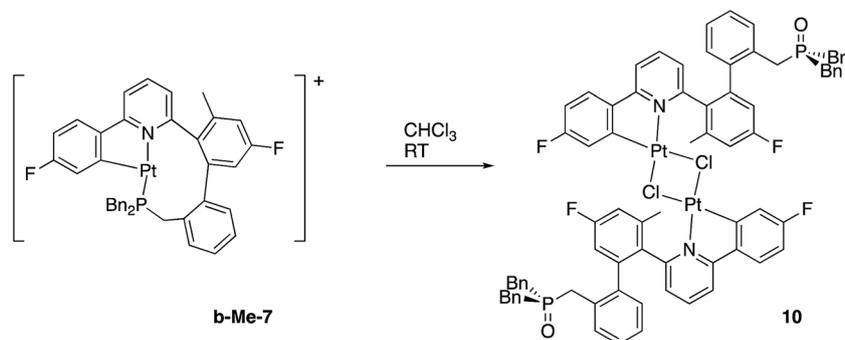
Though we did not isolate and purify a similar material from the non-methylated **7**, it too degrades to something with similar NMR spectra and we can expect the majority product to be the non-methylated analogue of **10**.

## Conclusions

The oxidation reactions of a doubly cyclometallated platinum(II) complex of diphenylpyridine with iodobenzenedichloride leads, as a first step, to the formation of a highly electrophilic metal centre. Given the presence of an adjacent aryl ring, this is followed by intramolecular electrophilic attack on that ring to give a triply cyclometallated species. In contrast, had the ligand had an alkyl group, a transcyclometallation<sup>13</sup> reaction, as we saw with tributyl<sup>14a</sup> or tripropyl<sup>14b</sup> phosphine would have occurred. The cyclometallation itself generates a highly acidic arenium ion as an intermediate; this intermediate is sufficiently reactive to protonate unreacted starting platinum(II) material, faster than it can be oxidised, though this reaction can be suppressed by the addition of an alternative substrate for protonation (in fact, simply adding water is sufficient).

Once formed, the triply cyclometallated complex, with three five-membered metallacycles, can be induced to react, with two of those rings coupling to give a strained nine-membered ring. When the nine-membered ring spans *trans* across a square planar platinum with two further ligands, it appears to be conformationally rigid and not prone to any reversible cleavage. However, when it is part of a coordinatively unsaturated square plane, not only is the ring flipping from one side of the metal centre to the other, but the newly formed C–C bond is reversibly breaking to reform the two five-membered rings before reforming the nine-membered ring. A kinetic analysis from the <sup>1</sup>H NMR data showed the reaction to be first order, with a rate constant of 0.0145 h<sup>-1</sup> at 298 K. We can rationalise the reversible nature of the reaction in terms of the ring strain of the nine-membered ring reducing the favourability of the coupling to such an extent that it does not present an insurmountable barrier to its reverse.

A *cis* configuration of the nine-membered ring was seen with the octahedral coordination at the metal that results from oxidation of the square planar Pt(II). However all of the complexes with the nine-membered ring suffer from steric strain to some degree, though further reaction of the three coordinate complexes (**7**) with CO or hydrogen left the ring intact. Oxidative degradation did result in decomplexation of the phosphine donor, accompanied by formation of a P=O group.



Scheme 13



## Conflict of interest

The authors declare no competing financial interests.

## Acknowledgements

We thank EPSRC for a DTG award to PAS and support from Advantage West Midlands (AWM) (part funded by the European Regional Development Fund) for the purchase of a high resolution mass spectrometer and the XRD system that was used to solve the crystal structures.

## References

- (a) Y. Chauvin, *Adv. Synth. Catal.*, 2007, **349**, 27–33; (b) R. H. Grubbs, *Adv. Synth. Catal.*, 2007, **349**, 34–40; (c) R. R. Schrock, *Adv. Synth. Catal.*, 2007, **349**, 41–53.
- (a) A. Suzuki, *Angew. Chem., Int. Ed.*, 2011, **50**, 6722–6737; (b) C. Seechurn, M. O. Kitching, T. J. Colacot and V. Snieckus, *Angew. Chem., Int. Ed.*, 2012, **51**, 5062–5085.
- (a) M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759; (b) H. Salem, Y. Ben-David, L. J. W. Shimon and D. Milstein, *Organometallics*, 2006, **25**, 2292–2300; (c) M. Montag, I. Efremenko, Y. Diskin-Posner, Y. Ben-David, J. M. L. Martin and D. Milstein, *Organometallics*, 2012, **31**, 505–512; (d) B. L. Edelbach, R. J. Lachicotte and W. D. Jones, *J. Am. Chem. Soc.*, 1998, **120**, 2843–2853; (e) W. D. Jones, *Mechanistic Studies of Transition Metal-Mediated C–C Bond Activation*, in *C–C Bond Activation*, ed. G. Dong, Springer-Verlag: Berlin, 2014, Vol. 346, pp. 1–31; (f) A. Barretta, F. G. N. Cloke, A. Feigenbaum, M. L. H. Green, A. Gourdon and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1981, 156–158; (g) R. H. Crabtree, R. P. Dion, D. J. Gibboni, D. V. McGrath and E. M. Holt, *J. Am. Chem. Soc.*, 1986, **108**, 7222–7227; (h) Z. Lu, C. H. Jun, S. R. Degala, M. P. Sigalas, O. Eisenstein and R. H. Crabtree, *Organometallics*, 1995, **14**, 1168–1175; (i) A. B. Chaplin, J. C. Green and A. S. Weller, *J. Am. Chem. Soc.*, 2011, **133**, 13162–13168; (j) M. Murakami and N. Ishida, *J. Am. Chem. Soc.*, 2016, **138**, 13759–13769.
- (a) D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 624–655; (b) A. S. K. Hashmi, L. Schwarz, J. H. Choi and T. M. Frost, *Angew. Chem., Int. Ed.*, 2000, **39**, 2285–2288; (c) W. Shi, C. Liu and A. W. Lei, *Chem. Soc. Rev.*, 2011, **40**, 2761–2776; (d) P. van Leeuwen, P. C. J. Kamer, J. N. H. Reek and P. Dierkes, *Chem. Rev.*, 2000, **100**, 2741–2769; (e) S. Shekhar and J. F. Hartwig, *J. Am. Chem. Soc.*, 2004, **126**, 13016–13027; (f) K. I. Goldberg, J. Yan and E. M. Breitung, *J. Am. Chem. Soc.*, 1995, **117**, 6889–6896; (g) J. Procelewska, A. Zahl, G. Liehr, R. van Eldik, N. A. Smythe, B. S. Williams and K. I. Goldberg, *Inorg. Chem.*, 2005, **44**, 7732–7742; (h) R. Ghosh, X. W. Zhang, P. Achord, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *J. Am. Chem. Soc.*, 2007, **129**, 853–866; (i) M. A. Bennett, S. K. Bhargava, D. C. R. Hockless, L. L. Welling and A. C. Willis, *J. Am. Chem. Soc.*, 1996, **118**, 10469–10478; (j) E. G. Bowes, S. Pal and J. A. Love, *J. Am. Chem. Soc.*, 2015, **137**, 16004–16007; (k) M. Crespo, C. M. Anderson, N. Kfoury, M. Font-Bardia and T. Calvet, *Organometallics*, 2012, **31**, 4401–4404; (l) C. M. Anderson, M. Crespo, N. Kfoury, M. A. Weinstein and J. M. Tanski, *Organometallics*, 2013, **32**, 4199–4207; (m) A. Ariafard, Z. Ejehi, H. Sadrara, T. Mehrabi, S. Etaati, A. Moradzadeh, M. Moshtaghi, H. Nosrati, N. J. Brookes and B. F. Yates, *Organometallics*, 2011, **30**, 422–432.
- (a) M. Albrecht, A. L. Spek and G. van Koten, *J. Am. Chem. Soc.*, 2001, **123**, 7233–7246; (b) C. Carmen, H. Atienza, C. Milsman, S. P. Semproni, Z. R. Turner and P. J. Chirik, *Inorg. Chem.*, 2013, **52**, 5403–5417; (c) T. R. Dugan, E. Bill, K. C. MacLeod, G. J. Christian, R. E. Cowley, W. W. Brennessel, S. F. Ye, F. Neese and P. L. Holland, *J. Am. Chem. Soc.*, 2012, **134**, 20352–20364; (d) J. J. Garcia, N. M. Brunkan and W. D. Jones, *J. Am. Chem. Soc.*, 2002, **124**, 9547–9555; (e) M. J. Monreal and P. L. Diaconescu, *J. Am. Chem. Soc.*, 2010, **132**, 7676–7683; (f) M. Montag, J. Zhang and D. Milstein, *J. Am. Chem. Soc.*, 2012, **134**, 10325–10328; (g) M. H. Shaw, N. G. McCreanor, W. G. Whittingham and J. F. Bower, *J. Am. Chem. Soc.*, 2015, **137**, 463–468.
- (a) M. Mendez, M. P. Munoz, C. Nevado, D. J. Cardenas and A. M. Echavarren, *J. Am. Chem. Soc.*, 2001, **123**, 10511–10520; (b) P. Y. Toullec, C. M. Chao, Q. Chen, S. Gladiali, J. P. Genet and V. Michelet, *Adv. Synth. Catal.*, 2008, **350**, 2401–2408; (c) L. M. Zhang, J. W. Sun and S. A. Kozmin, *Adv. Synth. Catal.*, 2006, **348**, 2271–2296.
- (a) M. Lersch and M. Tilset, *Chem. Rev.*, 2005, **105**, 2471–2526; (b) L. Johansson, M. Tilset, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2000, **122**, 10846–10855; (c) J. S. Owen, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2006, **128**, 2005–2016; (d) H. A. Zhong, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2002, **124**, 1378–1399; (e) B. L. Madison, S. B. Thyme, S. Keene and B. S. Williams, *J. Am. Chem. Soc.*, 2007, **129**, 9538–9539; (f) D. M. Crumpton-Bregel and K. I. Goldberg, *J. Am. Chem. Soc.*, 2003, **125**, 9442–9456; (g) M. P. Jensen, D. D. Wick, S. Reinartz, P. S. White, J. L. Templeton and K. I. Goldberg, *J. Am. Chem. Soc.*, 2003, **125**, 8614–8624; (h) B. S. Williams, A. W. Holland and K. I. Goldberg, *J. Am. Chem. Soc.*, 1998, **121**, 252–253; (i) G. S. Hill and R. J. Puddephatt, *Organometallics*, 1998, **17**, 1478–1486; (j) J. D. Scott and R. J. Puddephatt, *Organometallics*, 1983, **2**, 1643–1648; (k) F. Zhang, E. M. Prokopchuk, M. E. Broczkowski, M. C. Jennings and R. J. Puddephatt, *Organometallics*, 2006, **25**, 1583–1591.
- (a) R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh and H. Fujii, *Science*, 1998, **280**, 560–564; (b) A. Caballero and P. J. Perez, *Chem. Soc. Rev.*, 2013, **42**, 8809–8820.
- (a) S. H. Crosby, G. J. Clarkson, R. J. Deeth and J. P. Rourke, *Organometallics*, 2010, **29**, 1966–1976; (b) S. H. Crosby, G. J. Clarkson, R. J. Deeth and J. P. Rourke, *Dalton Trans.*, 2011, **40**, 1227–1229; (c) J. Mamtora, S. H. Crosby, C. P. Newman, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2008, **27**, 5559–5565.



- 10 (a) S. H. Crosby, H. R. Thomas, G. J. Clarkson and J. P. Rourke, *Chem. Commun.*, 2012, **48**, 5775–5777; (b) S. H. Crosby, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2012, **31**, 7256–7263; (c) P. A. Shaw and J. P. Rourke, *Dalton Trans.*, 2017, **46**, 4768–4776; (d) P. A. Shaw, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2016, **35**, 3751–3762.
- 11 L. M. Rendina and R. J. Puddephatt, *Chem. Rev.*, 1997, **97**, 1735–1754.
- 12 (a) H. R. Thomas, R. J. Deeth, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2011, **30**, 5641–5648; (b) S. H. Crosby, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2011, **30**, 3603–3609.
- 13 (a) A. D. Ryabov and A. K. Yatsimirsky, *Inorg. Chem.*, 1984, **23**, 789–790; (b) A. D. Ryabov, *Inorg. Chem.*, 1987, **26**, 1252–1260; (c) M. Albrecht, P. Dani, M. Lutz, A. L. Spek and G. v. Koten, *J. Am. Chem. Soc.*, 2000, **122**, 11822–11833.
- 14 (a) P. A. Shaw, J. M. Phillips, C. P. Newman, G. J. Clarkson and J. P. Rourke, *Chem. Commun.*, 2015, **51**, 8365–8368; (b) P. A. Shaw, J. M. Phillips, G. J. Clarkson and J. P. Rourke, *Dalton Trans.*, 2016, **45**, 11397–11406.
- 15 (a) K. L. Hull, E. L. Lanni and M. S. Sanford, *J. Am. Chem. Soc.*, 2006, **128**, 14047–14049; (b) S. R. Whitfield and M. S. Sanford, *Organometallics*, 2008, **27**, 1683–1689; (c) J. M. Racowski, N. D. Ball and M. S. Sanford, *J. Am. Chem. Soc.*, 2011, **133**, 18022–18025.
- 16 (a) G. W. V. Cave, N. W. Alcock and J. P. Rourke, *Organometallics*, 1999, **18**, 1801–1803; (b) G. W. V. Cave, F. P. Fanizzi, R. J. Deeth, W. Errington and J. P. Rourke, *Organometallics*, 2000, **19**, 1355–1364.
- 17 P. S. Pregosin and R. W. Kunz, *<sup>31</sup>P and <sup>13</sup>C NMR of Transition Metal Phosphine Complexes*, Springer-Verlag: Berlin, 1979.
- 18 (a) P. S. Pregosin, *Coord. Chem. Rev.*, 1982, **44**, 247–291; (b) E. Gabano, E. Marengo, M. Bobba, E. Robotti, C. Cassino, M. Botta and D. Osella, *Coord. Chem. Rev.*, 2006, **250**, 2158–2174.
- 19 S. Fornarini and M. E. Crestoni, *Acc. Chem. Res.*, 1998, **31**, 827–834.
- 20 (a) A. S. K. Hashmi, J. W. Bats, J. H. Choi and L. Schwarz, *Tetrahedron Lett.*, 1998, **39**, 7491–7494; (b) G. W. Kabalka and R. M. Pagni, *Tetrahedron*, 1997, **53**, 7999–8065.
- 21 (a) S. B. Zhao, G. Wu and S. Wang, *Organometallics*, 2008, **27**, 1030–1033; (b) K. A. Grice, M. L. Scheuermann and K. I. Goldberg, *Top. Organomet. Chem.*, 2011, **35**, 1–28; (c) A. Vigalok, *Acc. Chem. Res.*, 2015, **48**, 238–247.
- 22 (a) K. Tatsumi, R. Hoffman, A. Yamamoto and J. K. Stille, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1857; (b) T. A. Albright, J. K. Burdett and M. H. Whangbo, *Orbital Interactions in Chemistry*, Wiley and Sons Inc, 1985.
- 23 (a) S. Li, S.-F. Zhu, J.-H. Xie, S. Song, C.-M. Zhang and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2010, **132**, 1172–1179; (b) S.-F. Zhu, Y.-B. Yu, S. Li, L.-X. Wang and Q.-L. Zhou, *Angew. Chem., Int. Ed.*, 2012, **51**, 8872–8875; (c) C. Guo, D.-W. Sun, S. Yang, S.-J. Mao, X.-H. Xu, S.-F. Zhu and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 90–93; (d) Y.-B. Yu, L. Cheng, Y.-P. Li, Y. Fu, S.-F. Zhu and Q.-L. Zhou, *Chem. Commun.*, 2016, **52**, 4812–4815; (e) S.-F. Zhu, J.-B. Xie, Y.-Z. Zhang, S. Li and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2006, **128**, 12886–12891.
- 24 C.-H. Chen and W.-Y. Yeh, *Dalton Trans.*, 2013, **42**, 2488–2494.
- 25 (a) R. Corbo, D. C. Georgiou, D. J. D. Wilson and J. L. Dutton, *Inorg. Chem.*, 2014, **53**, 1690–1698; (b) N. Wang, T. M. McCormick, S.-B. Ko and S. Wang, *Eur. J. Inorg. Chem.*, 2012, **2012**, 4463–4469.
- 26 (a) R. Tan, P. Jia, Y. Rao, W. Jia, A. Hadzovic, Q. Yu, X. Li and D. Song, *Organometallics*, 2008, **27**, 6614–6622; (b) R. Tan and D. Song, *Inorg. Chem.*, 2011, **50**, 10614–10622.
- 27 O. Saavedra-Díaz, R. Cerón-Camacho, S. Hernández, A. D. Ryabov and R. Le Lagadec, *Eur. J. Inorg. Chem.*, 2008, **2008**, 4866–4869.
- 28 S. R. Whitfield and M. S. Sanford, *J. Am. Chem. Soc.*, 2007, **129**, 15142–15143.
- 29 (a) J. Vicente, A. Arcas, D. Bautista and P. G. Jones, *Organometallics*, 1997, **16**, 2127–2138; (b) J. Vicente, J. A. Abad, A. D. Frankland and M. C. R. de Arellano, *Chem.–Eur. J.*, 1999, **5**, 3066–3075.
- 30 C. P. Newman, K. Casey-Green, G. J. Clarkson, G. W. V. Cave, W. Errington and J. P. Rourke, *Dalton Trans.*, 2007, 3170–3182.

