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# Selective C–C coupling at a Pt(IV) centre: 100% preference for $sp^2$ – $sp^3$ over $sp^3$ – $sp^3$ †

Paul A. Shaw and Jonathan P. Rourke  \*

The oxidative addition of three different organic halides RX to the non-symmetric platinum(II) mer-coordinated dicyclopalladated C<sup>^</sup>N<sup>^</sup>C complex **1** yielded short-lived six-coordinate platinum(IV) complexes **2(R)** (R = Me, allyl, Bn), with the incoming groups trans across the platinum centre. A spontaneous reductive coupling reaction then occurred with, in each case, a completely chemoselective  $sp^2$ – $sp^3$  coupling, and exclusively gave **R-3**, with the newly introduced R group bonded to the previously cyclometallated aryl ring. Following a recyclometallation reaction, the oxidative addition/reductive elimination cycle was repeated and gave the same selectivity. A one-pot route to doubly alkylating the aryl ring was developed. The observed selectivity might have been predicted on the normal basis of a steric barrier associated with non-flat  $sp^3$  hybridised groups, but we suggest that it arises from the stereochemistry at the metal, and the orientation of the ligands.

## Introduction

Catalytic processes that result in the general functionalisation of hydrocarbons have yet to be fully realised,<sup>1</sup> and considerable effort is still being invested in the study of model organo-metallic complexes, such as those of platinum.<sup>2</sup> Platinum complexes are not just amenable to study, but also have direct relevance to actual processes as some are able to activate methane.<sup>3</sup> Understanding the selectivity associated with the various steps of a catalytic process is key to the construction of new improved processes, and in this paper we concentrate upon the final step of any process: the reductive elimination of products. In particular, we pay close attention to the selectivity in the carbon–carbon bond forming reaction at a platinum(IV) centre.

When a metal centre has more than two attached groups that could potentially couple, some element of selectivity will come into play. If we just consider carbon bonded groups, one factor that has considerable relevance is the hybridisation of the carbon attached to the metal. Thus, the carbon might be an alkyl group ( $sp^3$  hybridisation), an aryl, alkenyl or vinyl group ( $sp^2$  hybridisation) or an alkynyl ( $sp$  hybridisation). It has long been observed that the coupling of two alkyl groups has the largest energy barrier, and is the slowest process, even though it might result in the most thermodynamically stable

products. This observation can simply be explained with reference to two effects: the first steric and the second electronic.<sup>4</sup> The steric effect arises due to the flat nature of groups other than alkyl reducing the hindrance to the approach of the two coupling groups, whilst the electronic effect relates to the less directional nature of the  $sp^2$  or  $sp$  hybridised orbital (compared with an  $sp^3$  orbital) allowing a greater overlap in the three-centred transition state. Though these effects are reasonably general, it had been observed that there were several conflicting examples in early examples of platinum(IV) chemistry.<sup>5</sup> In more recent years, several platinum examples of the more expected preference for  $sp^2$ – $sp^3$  over  $sp^3$ – $sp^3$  have been observed,<sup>6</sup> and one group has reported a system where the  $sp^2$ – $sp^3$  and  $sp^3$ – $sp^3$  couplings are competitive with each other (a 7 : 1 preference for the former).<sup>7</sup>

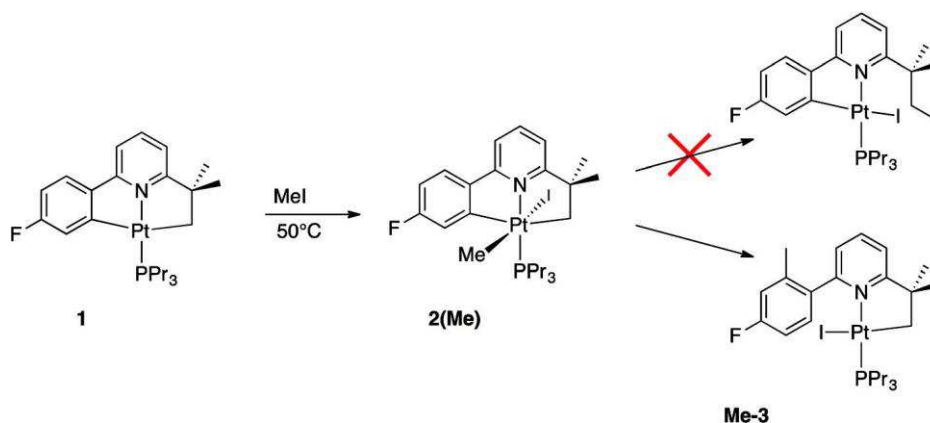
The use of a rigid, or semi-rigid, chelating ligand can lead to selectivity. Thus, whilst the use of a cyclometallated bipyridine restricts the outcome of a reductive elimination to an  $sp^2$ – $sp^3$  coupling (which might have been expected anyway) instead of an  $sp^3$ – $sp^3$  coupling,<sup>8</sup> another group has reported the use of a meridionally coordinating C<sup>^</sup>N<sup>^</sup>N ligand to give exclusive  $sp^3$ – $sp^3$  coupling, rather than  $sp^2$ – $sp^3$  coupling.<sup>9</sup> Both of these examples proceed via a five-coordinate intermediate generated by halide abstraction from a six-coordinate octahedral complex. The rapid reductive elimination from the unsaturated intermediate has been rationalised theoretically,<sup>10</sup> with the analysis also providing additional support for the observed selectivity.

We have recently been expanding our own work on cyclometallated complexes where we have, in the past, investigated agostic interactions of, and the C–H activation by, a number of

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†Electronic supplementary information (ESI) available: NMR spectra for all the compounds, including those recorded at variable temperature, together with their analysis.



Scheme 1

cycloplatinated complexes.<sup>11</sup> Our more recent work now includes studies on both C–Cl<sup>12</sup> and C–C<sup>13</sup> reductive elimination reactions. In this paper we report on the use of a ligand system with a constrained geometry to limit the scope for coupling reactions and were able to demonstrate completely regiospecific C–C coupling.

## Results and discussion

### Oxidative addition of MeI and reductive coupling

Following our published procedure,<sup>11a,e</sup> we were able to isolate the previously unreported tripropylphosphine derivative of the doubly cyclometallated butyl aryl pyridine, complex 1. The oxidative addition of methyl iodide<sup>14</sup> to this complex did not occur at an appreciable rate at room temperature, but proceeded at a respectable rate at 50 °C, whereupon two new products could be observed.

At this temperature, after 30 minutes, 75% of the starting 1 had been consumed, producing the expected six-coordinate 2(Me) (65%) as well as some reductively coupled Me-3 (10%), Scheme 1.† The identities of these two complexes were clear from their NMR spectra. In particular, the six-coordinate Pt(IV) complex 2(Me) had a similar pattern of <sup>1</sup>H resonances to the starting 1, but with the two hydrogens of the cyclometallated alkyl group now being inequivalent (and coupling to each other), as were the two methyls of this group. In addition a new methyl resonance with strong coupling to <sup>195</sup>Pt (~70 Hz, in the <sup>1</sup>H and 563 Hz in the <sup>13</sup>C NMR) was observed, with NOE measurements indicating the expected trans arrangement of this group and the iodide. It proved impossible to isolate 2(Me) free from both the starting 1 and the reductively coupled product Me-3, though short reaction times (e.g. 10 min) could be used to minimise the extent of reductive coupling, though at this point only 25% of the starting 1 had been consumed.

Conversely, longer reaction times (e.g. 1 hour) could be used to ensure all starting 1 had been consumed, though this led to extensive reductive coupling (typically >50%). Thus 2(Me) was only characterised in solution and was never isolated completely pure.

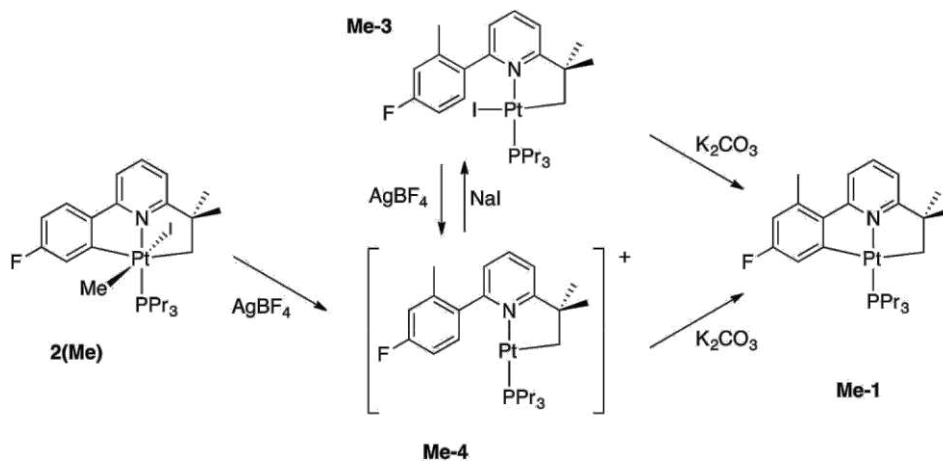
The identity of the reductively coupled product Me-3 was also clear from an analysis of the NMR: the <sup>19</sup>F spectrum consists of a single resonance (no <sup>195</sup>Pt satellites) and the <sup>1</sup>H spectrum shows the cyclometallated alkyl group is still attached to platinum and that the newly introduced methyl group has coupled with the aryl ring. This complex could be isolated and purified; further variable temperature NMR experiments showed that, at room temperature and below, the 2-methyl-4-fluoro-phenyl ring is prevented from freely rotating about its bond to the pyridine (we can estimate the barrier to free rotation to be 63 ± 5 kJ mol<sup>-1</sup>, see ESI†) and this renders the two hydrogens and the two methyls of the cyclometallated group inequivalent on the NMR time scale.

Complete conversion to the reductively coupled product Me-3 could be induced with extended reaction times (2 hours at 50 °C) or by treatment of the mixture with AgBF<sub>4</sub>, to generate Me-4, followed by treatment with NaI, Scheme 2. Removal of the iodide in Me-3 to generate Me-4 also reduces the impediment to rotation of the 2-methyl-4-fluoro-phenyl ring about its bond to the pyridine: in Me-4 both cyclometallated hydrogens are equivalent in the <sup>1</sup>H NMR (as are the two cyclometallated methyls), with no evidence of any broadening of the signals even upon cooling the sample to -60 °C.

Addition of extra iodide in the form of ten equivalents of tetrabutylammonium iodide had no discernable effect on the rate of either the oxidative addition of MeI to 1 or of the reductive elimination from 2(Me). Similarly, addition of ten equivalents of tetrabutylammonium chloride had no effect on reaction rates nor on the identity of the product: chloride was not incorporated at the expense of iodide. Taken together, these results clearly imply the reductive coupling from 2(Me) is not preceded by loss of iodide, but is an intramolecular process.

The reactions described above are completely clean and at no point do we see any evidence for the sp<sup>3</sup>–sp<sup>3</sup> coupling of

† In the numbering system used, 2(R), (R) refers to the group attached to the metal (either Me, allyl or Bn), whereas the R in R-1 or R2-1 etc. refers to the R group attached to the ligand.



Scheme 2

the methyl group with the cyclometallated t-butyl group: there is complete chemoselectivity for alkyl–aryl coupling.

#### Recyclometallation and a second oxidative addition

Treatment of Me-3 with  $K_2CO_3$ , which acts as a base to remove the HI by-product, induced the recyclometallation reaction to give Me-1, though the process was rather slow, taking around one week at 50 °C.<sup>15</sup> It proved more convenient to treat Me-4 with  $K_2CO_3$ , whereupon a faster reaction (16 h, RT) to generate Me-1 took place. We should note that while the activation of the aryl bond in Me-3 or Me-4 to give a five-membered metalla-cycle is favoured over the formation of a six-membered ring via activation of the alkyl group, examples where this preference has been overridden by other factors have been reported.<sup>6b</sup>

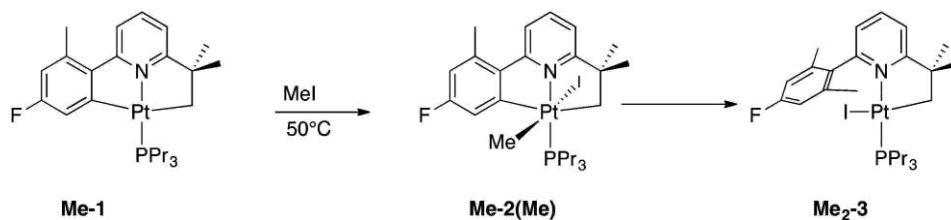
Doubly cyclometallated Me-1 was fully characterised and though we were not able to grow crystals suitable for X-ray analysis, by analogy with the situation with the methylated diphenylpyridine complex,<sup>13c</sup> we would expect a significant degree of steric strain to be associated with the methyl group.

From Me-1, it is now possible to repeat the cycle of reaction described above. Treatment of Me-1 with MeI resulted in an initial reaction to the six-coordinate Me-2(Me) at a similar same rate as before, Scheme 3. Now, however, the reductive coupling reaction to give Me<sub>2</sub>-3 is substantially faster: after 30 minutes 25% of the starting Me-1 remained, but only 5% of the mixture was present as the six-coordinate Me-2(Me), with the remaining 70% present as the coupled Me<sub>2</sub>-3. Again the

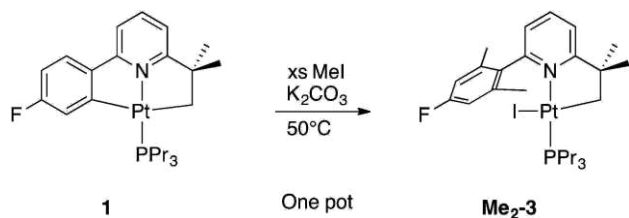
coupling reaction was 100% chemoselective to form the doubly methylated phenyl, with no trace of methylated t-butyl group. The quantities of Me-2(Me) present at any time were only a small fraction of the reaction mixture and the only reliable spectroscopic data we could collect was the  $^{19}F$  and  $^{31}P$  NMR resonances; conversely, Me<sub>2</sub>-3 was fully characterised. Presumably the rotation of the substituted phenyl ring about its bond to the pyridine in Me<sub>2</sub>-3 is even more restricted than in Me-3 but, since the two sides of the ring are now identical, it is impossible to tell from the NMR spectra.

That the rate of MeI addition to Me-1 is not appreciably different from that to 1 is not surprising: the approach of a molecule of MeI to the platinum centre should not be hindered by the remote methyl group, and the platinum centres in both compounds (as evidenced by the  $^{195}Pt$  and  $^{31}P$  shifts and the  $^1J_{Pt-P}$ ) have very similar electronic properties. That the second reductive coupling to give Me<sub>2</sub>-3 is substantially faster than that yields Me-3 is significant. This increase in reaction rate is likely to arise from the unfavourable steric interactions of first methyl group, in Me-2(Me), with the pyridine ring, which are relieved when the reductive coupling occurs, allowing the methylated ring to rotate away.

It also proved possible to combine the sequence of five reactions into a one pot synthetic process. Thus with an excess of methyl iodide and potassium carbonate present, a reaction time of one week, the oxidative addition, reductive coupling, recyclometallation, second oxidative addition and second



Scheme 3



Scheme 4

reductive coupling reactions followed each other sequentially, giving Me<sub>2</sub>-3 as the ultimate product in high purity, Scheme 4.

#### Oxidative addition of other halides

The S<sub>N</sub>2 type oxidative addition reactions shown in the first step of Scheme 1 to be expected with organic halides other than just methyl iodide and we confirmed this with similar behaviour with two other halides: allyl bromide and benzyl bromide, Scheme 5.<sup>14</sup>

The reductive coupling reaction with both allyl and benzyl bromides was, once again, completely selective. The oxidative addition of the allyl bromide occurs at a similar rate to that of methyl iodide (roughly 30% starting 1 remaining after 30 min reaction, compared with 25% with MeI), though the rate of reductive coupling seems to be a bit faster (allyl-3 makes up roughly 15% of the reaction mixture after 30 min, compared with 10% with MeI). The initial oxidative addition of the benzyl bromide occurs at a slower rate to that of methyl iodide (roughly 75% starting 1 remaining after 30 min reaction), and the rate of reductive coupling seems to be similar to that of the allyl compound (Bn-3 makes up roughly 6% of the reaction mixture after 30 min).

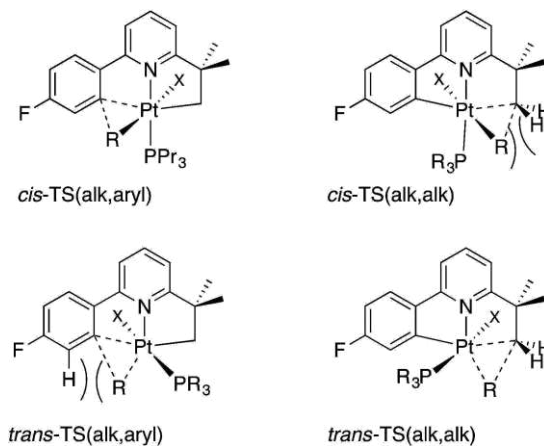
For both allyl-3 and Bn-3, like Me-3, the restricted rotation of the substituted phenyl ring leads to separate resonances for the two cyclometallated hydrogens and the two methyls of the cyclometallated group in the <sup>1</sup>H NMR spectrum. Though we did not follow the reaction through to a doubly substituted

product with allyl bromide, there is no reason to suspect that the reaction would show different behaviour to that seen for methyl iodide; we did, however use the one-pot reaction technique to go through to the doubly substituted product Bn<sub>2</sub>-3.

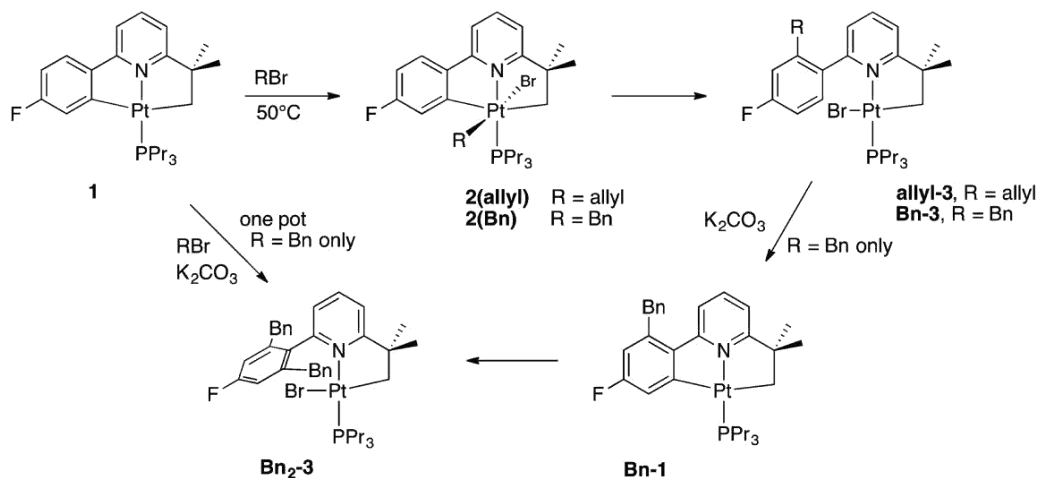
Thus, in all three examples studied, we see a complete selectivity for the sp<sup>2</sup>-sp<sup>3</sup> coupling reaction over the alternative sp<sup>3</sup>-sp<sup>3</sup> coupling.

#### Origins of the selectivity in the sp<sup>2</sup>-sp<sup>3</sup> coupling

We did not perform a detailed computational study, but have sketched likely transition states for the two potential coupling reactions from the six-coordinate 2 in Scheme 6. Thus, when the R group is cis to the nitrogen (as it is in the as-synthesised complexes) it is easy to see that coupling of the R group with the aryl ring, cis-TS(alk,aryl), requires little rearrangement of the two groups. Conversely, there is an immediate steric clash between the R group and one of the hydrogens of the attached alkyl group, and substantial rearrangement of the groups must be required before effective overlap of the orbitals can occur, cis-TS(alk,alk). Hence the selectivity observed makes sense.



Scheme 6



Scheme 5

It is interesting to contemplate what would have happened if the R group had been trans to the nitrogen. Now it is the coupling of the R group with the alkyl group that requires minimal rearrangement, *trans*-TS(alk,alk), with a steric clash (of the R group and the hydrogen ortho to the fluorine) pre-senting itself in the coupling of the R group with the aryl ring, *trans*-TS(alk,aryl). We would predict, therefore, that were this isomer of 2 to be prepared, it would reverse the selectivity we see and undergo an  $sp^3$ - $sp^3$  coupling. Such behaviour has pre-cedent in the reductive elimination of alkyl chloride, rather than aryl chloride, from an analogue of 2.<sup>12</sup>

Finally, we should note that the reductive coupling seen here appears to be spontaneous, and does not need to be stimulated by halide abstraction from the six-coordinate platinum(IV) species. Further evidence for the spontaneous nature of the reductive coupling comes from the lack of any effect on the reductive coupling from the addition of excess halide: neither the rate or the product identity is affected by excess tetrabutylammonium chloride or iodide. Whilst not un-precedented, spontaneous couplings rare<sup>4c,16</sup> but have already been implicated in the reductive elimination of alkyl chloride from similar complexes.<sup>12</sup>

## Conclusions

The oxidative addition of three different organic halides to a non-symmetric platinum(II) mer coordinated dicyclopalladated C<sup>N</sup>^C complex yielded short-lived six-coordinate platinum(IV) complexes. The newly introduced organic fragment had, in each case, an  $sp^3$  hybridised carbon, with the dicyclopalladated ligand being bonded to the platinum centre through two different carbons: an  $sp^2$  hybridised aryl and an  $sp^3$  hybridised alkyl. Thus the coupling of two organic fragments had two competing alternatives. In fact a complete selectivity for an  $sp^2$ - $sp^3$  coupling over a possible  $sp^3$ - $sp^3$  was observed. This selectivity might have been predicted on the normal basis of a steric barrier associated with non-flat  $sp^3$  hybridised groups, but we suggest that it arises from the stereochemistry at the metal and the orientation of the ligands.

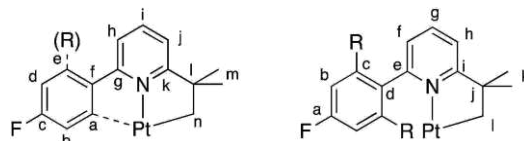
## Experimental

### General

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on Bruker Avance 400, 500 or 600 MHz spectrometers and were recorded at room temperature, in chloroform, unless stated otherwise. <sup>1</sup>H and <sup>13</sup>C signals are referenced to external TMS, assignments being made with the use of decoupling, GOESY and COSY pulse sequences. <sup>19</sup>F and <sup>31</sup>P chemical shifts are quoted from the directly observed signals (referenced to external CFCl<sub>3</sub> and 85% H<sub>3</sub>PO<sub>4</sub>, respectively). <sup>1</sup>H-<sup>195</sup>Pt correlation spectra were recorded using a variant of the HMBC pulse sequence and the <sup>195</sup>Pt chemical shifts reported are taken from these spectra

(referenced to external Na<sub>2</sub>PtCl<sub>6</sub>). All elemental analyses were performed by Warwick Analytical Service. High-resolution mass spectra were recorded from a water/acetonitrile solution (80/20) on a Bruker Maxis plus operating in ESI mode. The DMSO precursor to 1 was prepared as previously reported.<sup>11a,e</sup>

The leftmost labelling scheme was used for all complexes except Me<sub>2</sub>-3 and Bn<sub>2</sub>-3, for which the right hand scheme was used:



### Synthesis of complex 1

50 mg of doubly cyclometallated DMSO precursor complex (0.10 mmol) was dissolved in dry ethylacetate (20 ml), under nitrogen. Separately, also under an atmosphere of nitrogen, tri-propyl phosphine (16 mg, 0.10 mmol, 1 eq.) was dissolved in ethylacetate (20 ml). The solution of phosphine was added slowly to the Pt(II) solution over 10 min at RT and left to stir for a further 10 min. The solvent was then removed and crude product purified by column chromatography on silica, eluting with toluene, to give 1 as a yellow solid (46 mg, 0.08 mmol, 80%).

<sup>1</sup>δ<sub>H</sub> = 7.63 (1H, t, <sup>3</sup>J<sub>H-H</sub> = 8 Hz, H<sub>i</sub>), 7.43 (1H, dd, <sup>3</sup>J<sub>H-H</sub> = 8 Hz, <sup>4</sup>J<sub>H-F</sub> = 5 Hz, H<sub>e</sub>), 7.36 (1H, d, <sup>3</sup>J<sub>H-H</sub> = 8 Hz, H<sub>h</sub>), 7.25 (1H, dd, <sup>3</sup>J<sub>H-F</sub> = 9.5, <sup>4</sup>J<sub>H-H</sub> = 2.5 Hz, <sup>3</sup>J<sub>H-Pt</sub> = 29 Hz, H<sub>b</sub>), 6.93 (1H, d, <sup>3</sup>J<sub>H-H</sub> = 8 Hz, H<sub>j</sub>), 6.67 (1H, td, <sup>3</sup>J<sub>H-H</sub> = <sup>3</sup>J<sub>H-F</sub> = 9.5, <sup>4</sup>J<sub>H-H</sub> = 2.5 Hz, H<sub>d</sub>), 1.86 (6H, m, PCH<sub>2</sub>), 1.78 (2H, s, <sup>2</sup>J<sub>H-H</sub> = 39 Hz, H<sub>n</sub>), 1.56 (6H, m, PCH<sub>2</sub>CH<sub>2</sub>), 1.30 (6H, s, H<sub>m</sub>), 0.97 (9H, t, <sup>3</sup>J<sub>H-H</sub> = 7.5, PCH<sub>2</sub>CH<sub>2</sub>Me) ppm.

δ<sub>C</sub> = 14.79 (d, <sup>3</sup>J<sub>C-P</sub> = 15.5 Hz, PCH<sub>2</sub>CH<sub>2</sub>Me), 15.63 (s, <sup>3</sup>J<sub>C-Pt</sub> = 32.5 Hz, PCH<sub>2</sub>CH<sub>2</sub>), 26.14 (d, <sup>1</sup>J<sub>C-P</sub> = 35.63, <sup>2</sup>J<sub>C-Pt</sub> = 37.5 Hz, PCH<sub>2</sub>), 33.11 (s, <sup>3</sup>J<sub>C-Pt</sub> = 18.5 Hz, C<sub>m</sub>), 34.79 (d, <sup>2</sup>J<sub>C-P</sub> = 6 Hz, <sup>1</sup>J<sub>C-Pt</sub> = 466 Hz, C<sub>n</sub>), 51.52 (d, <sup>3</sup>J<sub>C-P</sub> = 3.5 Hz, <sup>2</sup>J<sub>C-Pt</sub> = 21 Hz, C<sub>i</sub>), 108.05 (d, <sup>2</sup>J<sub>C-F</sub> = 22 Hz, C<sub>d</sub>), 114.28 (d, <sup>4</sup>J<sub>C-P</sub> = 3 Hz, <sup>3</sup>J<sub>C-Pt</sub> = 25.5 Hz, C<sub>h</sub>), 117.50 (d, <sup>4</sup>J<sub>C-P</sub> = 2.5 Hz, <sup>3</sup>J<sub>C-Pt</sub> = 33 Hz, C<sub>j</sub>), 122.31 (d, <sup>2</sup>J<sub>C-F</sub> = 15 Hz, <sup>2</sup>J<sub>C-Pt</sub> = 64.5 Hz, C<sub>b</sub>), 124.77 (d, <sup>3</sup>J<sub>C-F</sub> = 9 Hz, <sup>3</sup>J<sub>C-Pt</sub> = 30 Hz, C<sub>e</sub>), 136.76 (s, C<sub>i</sub>), 145.20 (m, <sup>2</sup>J<sub>C-Pt</sub> = 26 Hz, C<sub>f</sub>), 163.22 (s, <sup>2</sup>J<sub>C-Pt</sub> = 52 Hz, H<sub>g</sub>), 163.72 (d, <sup>2</sup>J<sub>C-F</sub> = 254.5 Hz, <sup>3</sup>J<sub>C-Pt</sub> = 52 Hz, C<sub>c</sub>), 173.95 (m, <sup>1</sup>J<sub>C-Pt</sub> = 686 Hz, C<sub>a</sub>), 176.22 (s, <sup>2</sup>J<sub>C-Pt</sub> = 19 Hz, H<sub>k</sub>) ppm.

δ<sub>F</sub> = -111.69 (<sup>4</sup>J<sub>F-Pt</sub> = 26.5 Hz) ppm. δ<sub>P</sub> = 0.44 (<sup>1</sup>J<sub>P-Pt</sub> = 3813 Hz) ppm. δ<sub>Pt</sub> = -4026 (d, <sup>1</sup>J<sub>Pt-P</sub> = ~3700 Hz) ppm.

HR-MS (ESI): found 582.2186, calculated 582.2191 = C<sub>24</sub>H<sub>35</sub>FNP<sup>194</sup>Pt = [M]<sup>+</sup>.

Elemental analysis found (calculated): C 49.54 (49.48), H 6.07 (6.06), N 2.26 (2.40).

### Synthesis of 2(Me), 2(allyl), 2(Bn), Me-3, allyl-3 and Bn-3

2(Me) and Me-3 MeI (20 μl, excess), was added to a solution of 1 (46 mg, 0.08 mmol) in CDCl<sub>3</sub> and heated (50 °C, 1 hour) to give full conversion to Me-3. The solvent was removed to give pure Me-3 (58 mg, 0.08 mmol, 100%). If reaction time was

reduced to 30 min, it was possible to identify 2(Me) by NMR analysis, but it was not possible to purify it.

The allyl and benzyl versions, were synthesised in a similar procedure.

2(Me)  $\delta_H = 7.67$  (2H, m,  $H_{i,e}$ ),  $7.50$  (1H, d,  $^3J_{H-H} = 7$  Hz,  $H_h$ ),  $7.26$  (1H, dd,  $^3J_{H-F} = 9$  Hz,  $^4J_{H-H} = 2.5$  Hz,  $^3J_{H-Pt} = 25$  Hz,  $H_b$ ),  $6.86$  (1H, d,  $^3J_{H-H} = 7$  Hz,  $H_h$ ),  $6.70$  (1H, td,  $^3J_{H-H} = ^3J_{H-F} = 8.5$  Hz,  $^4J_{H-H} = 2.5$  Hz,  $H_d$ ),  $3.13$  (1H, d,  $^2J_{H-H} = 10.5$  Hz,  $^2J_{H-Pt} = 60$  Hz,  $H_n$ ),  $2.17$  (6H, m,  $PCH_2$ ),  $1.69$  (1H, dd,  $^2J_{H-H} = 10.5$  Hz,  $^3J_{H-P} = 2$  Hz,  $^2J_{H-Pt} = 20$  Hz,  $H_n$ ),  $1.60$  (6H, m,  $PCH_2CH_2$ ),  $1.56$  (3H, s,  $H_m$ ),  $1.31$  (3H, s,  $H_m$ ),  $1.01$  (12H, m, PtMe,  $PCH_2CH_2Me$ ) ppm.

$\delta_C = 5.03$  (d,  $^2J_{C-P} = 4$  Hz,  $^1J_{C-Pt} = 563$  Hz, PtMe),  $14.54$  (d,  $^3J_{C-P} = 14.5$  Hz,  $PCH_2CH_2Me$ ),  $16.83$  ( $^2J_{C-P} = 3$  Hz,  $PCH_2CH_2$ ),  $25.36$  (d,  $^1J_{C-P} = 37$  Hz,  $^2J_{C-Pt} = 24$  Hz,  $PCH_2$ ),  $29.74$  (d,  $^2J_{C-P} = 3$  Hz,  $^1J_{C-Pt} = 388$  Hz,  $C_n$ ),  $32.71$  (s,  $C_m$ ),  $35.49$  (s,  $C_m$ ),  $52.16$  (s,  $C_i$ ),  $109.30$  (d,  $^2J_{C-F} = 25$  Hz,  $C_d$ ),  $116.27$  (s,  $C_h$ ),  $119.56$  (s,  $^3J_{C-Pt} = 28$  Hz,  $C_j$ ),  $121.58$  (d,  $^2J_{C-F} = 17$  Hz,  $^2J_{C-Pt} = 34$  Hz,  $C_b$ ),  $126.05$  (d,  $^3J_{C-F} = 9$  Hz,  $^3J_{C-Pt} = 22$  Hz,  $C_e$ ),  $137.20$  (s,  $C_i$ ),  $143.19$  (s,  $C_f$ ),  $160.00$  (s,  $^2J_{C-Pt} = 31$  Hz,  $C_g$ ),  $162.38$  (d,  $^1J_{C-F} = 255$  Hz,  $^3J_{C-Pt} = 39$  Hz,  $C_c$ ),  $167.94$  (m,  $^1J_{C-Pt} = 536$  Hz,  $C_a$ ),  $175.88$  (s,  $^2J_{C-Pt} = 48$  Hz,  $C_k$ ) ppm.

$\delta_F = -110.33$  ( $^4J_{F-Pt} = 22$  Hz) ppm.  $\delta_P = -22.00$  ( $^1J_{P-Pt} = 2704$  Hz) ppm.  $\delta_{Pt} = -3500$  (d,  $^1J_{Pt-P} = \sim 2750$  Hz) ppm.

HR-MS (ESI): found 596.2348, calculated 596.2347 =  $C_{25}H_{38}FNP^{194}Pt = [M - I]^+$ .

2(allyl)  $\delta_F = -110.58$  ( $^4J_{F-Pt} = 21.5$  Hz) ppm.  $\delta_P = -20.86$  ( $^1J_{Pt-P} = 2770$  Hz) ppm.

2(Bn)  $\delta_F = -110.78$  ( $^4J_{F-Pt} = 22$  Hz) ppm.  $\delta_P = -21.17$  ( $^1J_{Pt-P} = 2772$  Hz) ppm.

Me-3  $\delta_H = 7.70$  (1H, t,  $^3J_{H-H} = ^3J_{H-H} = 8$  Hz,  $H_i$ ),  $7.65$  (1H, dd,  $^3J_{H-H} = 8.5$  Hz,  $^4J_{H-F} = 6$  Hz,  $H_a$ ),  $6.16$  (2H, m,  $H_{h,j}$ ),  $6.86$  (1H, dd,  $^3J_{H-H} = 10$  Hz,  $^4J_{H-H} = 2.5$  Hz,  $H_d$ ),  $6.80$  (1H, td,  $^3J_{H-H} = ^3J_{H-F} = 8$  Hz,  $^4J_{H-H} = 2.5$  Hz,  $H_b$ ),  $2.45$  (3H, s, Me),  $1.77$  (6H, m,  $PCH_2$ ),  $1.49$  (14H, m,  $H_{m,n}$ ,  $PCH_2CH_2$ ),  $0.95$  (9H, t,  $^3J_{H-H} = 7$  Hz,  $PCH_2CH_2Me$ ) ppm.

(600 MHz) Note that at 298 K  $PCH_2$  is broader than normal, without its characteristic shape. See ESI.†  $H_m$  is split into two broad peaks separated by 85 Hz. At 328 K,  $H_m$  has coalesced to form one broad lump hidden under  $PCH_2CH_2$ , and  $PCH_2$  has regained its characteristic shape. Lowering the temperature to 268 K,  $H_m$  now comprises of two distinct peaks (1.44 and 1.66). Two new peaks also appear which correspond to  $H_n$ . These peaks are at 1.74 (1H, dd,  $^2J_{H-H} = 10$  Hz,  $^3J_{H-P} = 3.5$  Hz) and 2.21 (1H, d,  $^2J_{H-H} = 10$  Hz,  $^2J_{H-Pt} = \sim 43$  Hz) which were pre-viously hidden under  $PCH_2CH_2$ . Lowering the temperature further to 238 K we see  $PCH_2$  beginning to separate into 2 peaks. Using a separation of 131 Hz and a coalescence temperature of 313 K for  $H_m$  we can calculate a barrier of  $62.9$   $\text{kJ mol}^{-1}$ ; a coalescence temperature of 298 would equate to a barrier of  $59.9$   $\text{kJ mol}^{-1}$ ; variations in the peak separation make a similar difference in calculated value, hence our estimate of an uncertainty of  $\pm 5$   $\text{kJ mol}^{-1}$ .

$\delta_C = 14.68$  (d,  $^3J_{C-P} = 15$  Hz,  $PCH_2CH_2Me$ ),  $16.96$  (s,  $^3J_{C-Pt} = 35$  Hz,  $PCH_2CH_2$ ),  $20.67$  (s, Me),  $26.49$  (d,  $^1J_{C-P} = 38$  Hz,  $^2J_{C-Pt} = 38$  Hz,  $PCH_2$ ),  $31.58$  (d,  $^2J_{C-P} = 4$  Hz,  $^1J_{C-Pt} = 727$  Hz,  $C_n$ ),  $48.83$

(s,  $C_i$ ),  $110.64$  (d,  $^2J_{C-F} = 20$  Hz,  $C_b$ ),  $116.18$  (d,  $^2J_{C-F} = 22$  Hz,  $C_d$ ),  $118.35$  (s,  $^3J_{C-Pt} = 20$  Hz,  $C_j$ ),  $124.57$  (d,  $^4J_{C-P} = 4$  Hz,  $C_h$ ),  $134.56$  (d,  $^3J_{C-F} = 10$  Hz,  $C_a$ ),  $135.9$  (s,  $C_i$ ),  $136.91$  (d,  $^4J_{C-F} = 8$  Hz,  $C_f$ ),  $138.31$  (d,  $^3J_{C-F} = 3$  Hz,  $C_e$ ),  $159.57$  (s,  $C_k$ ),  $162.22$  (d,  $^1J_{C-F} = 251$  Hz,  $C_c$ ),  $173.30$  (d,  $^3J_{C-P} = 3$  Hz,  $C_g$ ) ppm. Note that at 298 K  $C_m$  does not show a resonance. This is probably due to broadness of this peak at this temperature.

$\delta_F = -113.28$  ppm.  $\delta_P = -2.05$  ( $^1J_{P-Pt} = 4303$  Hz) ppm.  $\delta_{Pt} = -4339$  (d,  $^1J_{Pt-P} = \sim 4300$  Hz) ppm.

HR-MS (ESI): found 596.2353, calculated 596.2347 =  $C_{25}H_{38}FNP^{194}Pt = [M - I]^+$ .

Elemental analysis found (calculated): C 41.54 (41.44), H 5.26 (5.29), N 1.78 (1.93).

Allyl-3  $\delta_H = 7.76$  (1H, t,  $^3J_{H-H} = 7.5$  Hz,  $H_i$ ),  $7.63$  (1H, dd,  $^3J_{H-H} = 8$  Hz,  $^4J_{H-F} = 6$  Hz,  $H_a$ ),  $7.26$  (1H, d,  $^3J_{H-H} = 7.5$  Hz,  $H_j$ ),  $7.23$  (1H, d,  $^3J_{H-H} = 7.5$  Hz,  $H_h$ ),  $6.98$  (1H, dd,  $^3J_{H-F} = 10$  Hz,  $^4J_{H-H} = 2$  Hz,  $H_d$ ),  $6.90$  (1H, td,  $^3J_{H-H} = ^3J_{H-F} = 8$  Hz,  $^4J_{H-H} = 2$  Hz,  $H_b$ ),  $5.99$  (1H, ddt,  $^3J_{H-H_{trans}} = 17$  Hz,  $^3J_{H-H_{cis}} = 10$  Hz,  $^3J_{H-H} = 6.5$  Hz,  $H_{allyl}$ ),  $5.06$  (1H, dd,  $^3J_{H-H} = 10$  Hz,  $^3J_{H-H} = 1.5$  Hz,  $H_{allyl}$ ),  $5.01$  (1H, dd,  $^3J_{H-H} = 17$  Hz,  $^3J_{H-H} = 1.5$  Hz,  $H_{allyl}$ ),  $3.69$  (2H, d,  $^3J_{H-H} = 6.5$  Hz,  $H_{allyl}$ ),  $2.05$  (1H, d,  $^2J_{H-H} = 9.5$  Hz,  $^2J_{H-Pt} = 60$  Hz,  $H_n$ ),  $1.77$  (6H, m,  $PCH_2$ ),  $1.68$  (1H, d,  $^2J_{H-H} = 9.5$  Hz,  $H_n$ ),  $1.63$  (3H, s,  $H_m$ ),  $1.58$  (6H, m,  $PCH_2CH_2$ ),  $1.48$  (3H, s,  $H_m$ ),  $1.01$  (9H, t,  $^3J_{H-H} = 6$  Hz,  $PCH_2CH_2Me$ ) ppm.

Note that at 298 K both  $H_m$  and  $H_n$  have separated into two peaks each, separated by 75 Hz and 183 Hz respectively (600 MHz spectrometer).

$\delta_C = 15.73$  (d,  $^3J_{C-P} = 15$  Hz,  $PCH_2CH_2Me$ ),  $17.91$  (s,  $^3J_{C-Pt} = 32$  Hz,  $PCH_2CH_2$ ),  $26.27$  (d,  $^1J_{C-P} = 37$  Hz,  $^2J_{C-Pt} = 46$  Hz,  $PCH_2$ ),  $27.39$  (d,  $^2J_{C-P} = 5$  Hz,  $^1J_{C-Pt} = 746$  Hz,  $C_n$ ),  $32.58$  (s,  $^3J_{C-Pt} = 59$  Hz,  $H_m$ ),  $34.07$  (s,  $^3J_{C-Pt} = 33$  Hz,  $H_m$ ),  $38.49$  (s,  $C_{allyl}$ ),  $49.72$  (s,  $^2J_{C-Pt} = 23.5$  Hz,  $C_i$ ),  $112.08$  (d,  $^2J_{C-F} = \text{Hz}$ ,  $C_b$ ),  $115.96$  (d,  $^2J_{C-F} = \text{Hz}$ ,  $C_d$ ),  $116.37$  (s,  $C_{allyl}$ ),  $119.62$  (s,  $^3J_{C-Pt} = 25$  Hz,  $C_j$ ),  $125.67$  (d,  $^4J_{C-P} = 4$  Hz,  $C_h$ ),  $132.71$  (d,  $^3J_{C-F} = 9.5$  Hz,  $C_h$ ),  $136.95$  (m,  $C_f$ ),  $137.05$  (m,  $C_{allyl}$ ),  $141.01$  (d,  $^3J_{C-F} = 8.5$  Hz,  $C_e$ ),  $159.90$  (s,  $C_g$ ),  $163.21$  (d,  $^1J_{C-F} = 249$  Hz,  $C_c$ ),  $174.60$  (s,  $C_k$ ) ppm.

$\delta_F = -113.00$  ppm.  $\delta_P = -1.2$  ( $^1J_{P-Pt} = 4330$  Hz) ppm.  $\delta_{Pt} = -4214$  (d,  $^1J_{Pt-P} = \sim 4350$  Hz) ppm.

HR-MS (ESI): found 622.2493, calculated 622.2504 =  $C_{27}H_{40}FNP^{194}Pt = [M - Br]^+$ .

Bn-3  $\delta_H = 7.57$  (2H, m,  $H_{a,i}$ ),  $7.14$  (3H, m,  $H_j$ , Bn-m),  $7.08$  (1H, m, Bn-p),  $7.05$  (2H, d,  $^3J_{H-H} = 7.5$  Hz, Bn-o),  $6.99$  (2H, d,  $^3J_{H-H} = 7.5$  Hz,  $H_h$ ),  $6.85$  (1H, td,  $^3J_{H-H} = ^3J_{H-F} = 8.5$  Hz,  $^4J_{H-H} = 2.5$  Hz,  $H_b$ ),  $6.70$  (1H, td,  $^3J_{H-F} = 10$  Hz,  $^4J_{H-H} = 2.5$  Hz,  $H_b$ ),  $4.41$  (1H, d,  $^2J_{H-H} = 16.5$  Hz,  $H_o$ ),  $2.41$  (1H, d,  $^2J_{H-H} = 16.5$  Hz, Bn- $CH_2$ ),  $1.93$  (1H, d,  $^2J_{H-H} = 10.5$  Hz,  $^2J_{H-Pt} = 51$  Hz,  $H_n$ ),  $1.72$  (7H, m,  $H_n$ ,  $PCH_2$ ),  $1.53$  (9H, m,  $H_m$ ,  $PCH_2CH_2$ ),  $1.43$  (3H, s,  $H_m$ ),  $0.96$  (9H, t,  $^3J_{H-H} = 7$  Hz,  $PCH_2CH_2Me$ ) ppm.

Note that at 298 K the Bn- $CH_2$ ,  $H_m$  and  $H_n$  resonances have separated into 2 peaks each, separated by 103, 60 and 102 Hz respectively (600 MHz spectrometer). See ESI.† By 328 K, multiplicity is lost in all cases due to broadening of the peaks. Using a separation of 102 Hz and a coalescence temperature of 338 K we can calculate a barrier of  $68.0$   $\text{kJ mol}^{-1}$ ; in line with our previous calculation our estimate of the uncertainty in this is  $\pm 5$   $\text{kJ mol}^{-1}$ .

$\delta_C = 15.70$  (d,  $^3J_{C-P} = 14.5$  Hz,  $PCH_2CH_2Me$ ),  $17.89$  (s,  $^3J_{C-Pt} = 31$  Hz,  $PCH_2CH_2$ ),  $26.22$  (d,  $^3J_{C-P} = 38$  Hz,  $^2J_{C-Pt} = 38$  Hz,  $PCH_2$ ),  $27.57$  (d,  $^2J_{C-P} = 5$  Hz,  $^1J_{C-Pt} = 741$  Hz,  $C_n$ ),  $32.83$  (s,  $C_m$ ),  $33.81$  (s,  $C_m$ ),  $40.05$  (s,  $Bn-CH_2$ ),  $49.66$  (s,  $C_i$ ),  $112.13$  (d,  $^2J_{C-F} = 20$  Hz,  $C_b$ ),  $116.64$  (d,  $^2J_{C-F} = 21$  Hz,  $C_d$ ),  $119.64$  (s,  $^3J_{C-Pt} = 24$  Hz,  $C_j$ ),  $125.69$  (d,  $^4J_{C-P} = 3.5$  Hz,  $C_h$ ),  $125.98$  (s,  $Bn-p$ ),  $128.32$  (s,  $Bn-m$ ),  $129.26$  (s,  $Bn-o$ ),  $132.94$  (d,  $^3J_{C-F} = 8.5$  Hz,  $C_a$ ),  $136.94$  (d,  $^3J_{C-F} = 3$  Hz,  $C_f$ ),  $137.03$  (s,  $C_i$ ),  $140.33$  (s,  $Bn-i$ ),  $142.12$  (d,  $^3J_{C-F} = 8$  Hz,  $C_b$ ),  $159.95$  (s,  $C_g$ ),  $163.13$  (d,  $^1J_{C-F} = 247$  Hz,  $C_c$ ),  $174.49$  (d,  $^2J_{C-P} = 3$  Hz,  $C_k$ ) ppm.

Note that at 298 K  $C_m$  is split into 2 peaks separated by 114 Hz (500 MHz spectrometer).

$\delta_F = -112.82$  ppm.  $\delta_P = -1.05$  ( $^1J_{P-Pt} = 4318$  Hz) ppm.  $\delta_{Pt} = -4219$  (d,  $^1J_{Pt-P} = \sim 4300$  Hz) ppm.

HR-MS (ESI): found 672.2657, calculated 672.2660 =  $C_{31}H_{42}FNP^{194}Pt = [M - Br]^+$ .

Elemental analysis found (calculated): C 46.75 (49.14), H 6.06 (5.62), N 1.49 (1.86).

#### Synthesis of Me-4

To solution of complex Me-3 (10 mg, 0.014 mmol) in acetone (0.6 ml) at room temperature,  $AgBF_4$  was added (3.7 mg, 0.019 mmol, 1.4 eq.) giving full conversion. Complex Me-4 was not isolated, and only characterised in solution.

Me-4  $\delta_H$  (acetone- $d_6$ ) = 8.11 (1H, t,  $^3J_{H-H} = 8$  Hz,  $H_i$ ), 7.59 (2H, m,  $H_{j,a}$ ), 7.40 (1H, d,  $^3J_{H-H} = 8$  Hz,  $H_h$ ), 7.04 (2H, m,  $H_{b,d}$ ), 2.42 (3H, s, Me), 2.00 (2H, m,  $^2J_{H-Pt} = \sim 32$  Hz,  $H_n$ ), 1.54 (12H, m,  $PCH_2$ ,  $PCH_2CH_2$ ), 0.91 (9H, t,  $^3J_{H-H} = 7$  Hz,  $PCH_2CH_2Me$ ) ppm.

$\delta_C = 15.01$  (d,  $^3J_{C-P} = 15.5$  Hz,  $PCH_2CH_2Me$ ),  $16.61$  (d,  $^2J_{C-P} = 5.5$  Hz,  $^1J_{C-Pt} = 765$  Hz,  $C_n$ ),  $17.45$  (s,  $^3J_{C-Pt} = 30$  Hz,  $PCH_2CH_2$ ),  $20.03$  (s, Me),  $24.77$  (d,  $^1J_{C-P} = 38$  Hz,  $^2J_{C-Pt} = 42$  Hz,  $PCH_2$ ),  $31.21$  (s,  $C_m$ ),  $49.68$  (s,  $C_i$ ),  $113.04$  (d,  $^2J_{C-F} = 25$  Hz,  $C_b$ ),  $117.25$  (d,  $^2J_{C-F} = 22$  Hz,  $C_d$ ),  $121.13$  (s,  $C_j$ ),  $125.93$  (s,  $C_h$ ),  $131.83$  (d,  $^3J_{C-F} = 8.5$  Hz,  $C_a$ ),  $134.63$  (s,  $C_f$ ),  $139.07$  (d,  $^3J_{C-F} = 8.5$  Hz,  $C_e$ ),  $140.10$  (s,  $C_i$ ),  $158.35$  (s,  $C_g$ ),  $163.02$  (d,  $^1J_{C-F} = 245$  Hz,  $C_c$ ),  $173.43$  (s,  $C_k$ ) ppm.

$\delta_F$  (acetone- $d_6$ ) = -114.13 ppm.  $\delta_P$  (acetone- $d_6$ ) = 3.00 ( $^1J_{P-Pt} = 4272$  Hz) ppm.  $\delta_{Pt}$  (acetone- $d_6$ ) = -4116 (d,  $^1J_{Pt-P} = \sim 4400$  Hz) ppm.

HR-MS (ESI): found 596.2349, calculated 596.2347 =  $C_{25}H_{38}FNP^{194}Pt = [M]^+$ .

#### Synthesis of Me-1 and Bn-1

Me-1 To a solution of complex Me-3 (58 mg, 0.08 mmol) in chloroform (10 ml), was added a solution of  $K_2CO_3$  (0.5 g) in water (2 ml); the mixture was then stirred (3 days). The solvent were removed and the crude product purified by chromatography on silica, eluting with chloroform (45 mg, 0.075 mmol, 94%).

Bn-1 was prepared in an similar fashion.

Me-1  $\delta_H = 7.71$  (2H, m,  $H_{h,i}$ ),  $7.25$  (1H, m,  $H_b$ ),  $7.02$  (1H, d,  $^3J_{H-H} = 8.5$  Hz,  $H_j$ ),  $6.56$  (1H, dd,  $^3J_{H-H} = 9.5$  Hz,  $^5J_{H-P} = 2$  Hz,  $H_d$ ),  $2.63$  (3H, s, Me),  $1.92$  (6H, m,  $PCH_2$ ),  $1.81$  (2H, s,  $^2J_{H-Pt} = 37$  Hz,  $H_n$ ),  $1.62$  (6H, m,  $PCH_2CH_2$ ),  $1.37$  (6H, s,  $H_m$ ),  $1.04$  (9H, t,  $^3J_{H-H} = 7$  Hz,  $PCH_2CH_2Me$ ) ppm.

$\delta_C = 14.81$  (d,  $^3J_{C-P} = 14.5$  Hz,  $PCH_2CH_2Me$ ),  $17.27$  (s,  $^3J_{C-Pt} = 32$  Hz,  $PCH_2CH_2$ ),  $23.73$  (s, Me),  $26.01$  (d,  $^1J_{C-P} = 35$  Hz,  $^2J_{C-Pt} = 35$  Hz,  $PCH_2$ ),  $33.36$  (s,  $^3J_{C-Pt} = 18$  Hz,  $C_m$ ),  $35.18$  (d,  $^2J_{C-P} = 6.5$  Hz,  $^1J_{C-Pt} = 460$  Hz,  $C_n$ ),  $51.43$  (d,  $^3J_{C-P} = 4$  Hz,  $C_i$ ),  $112.42$  (d,  $^3J_{C-F} = 21.5$  Hz,  $C_d$ ),  $117.06$  (d,  $^4J_{C-P} = 3$  Hz,  $^3J_{C-Pt} = 31$  Hz,  $C_h$ ),  $118.36$  (d,  $^4J_{C-P} = 3$  Hz,  $^3J_{C-Pt} = 23$  Hz,  $C_j$ ),  $120.13$  (d,  $^2J_{C-F} = 14$  Hz,  $^2J_{C-Pt} = 60$  Hz,  $C_b$ ),  $136.42$  (s,  $C_i$ ),  $137.37$  (d,  $^3J_{C-F} = 7.5$  Hz,  $^3J_{C-Pt} = 31$  Hz,  $C_e$ ),  $143.77$  (s,  $^2J_{C-Pt} = 29$  Hz,  $C_f$ ),  $162.55$  (d,  $^1J_{C-F} = 254$  Hz,  $^3J_{C-Pt} = 55$  Hz,  $C_c$ ),  $163.69$  (s,  $^2J_{C-Pt} = 54$  Hz,  $C_g$ ),  $175.35$  (m,  $^1J_{C-Pt} = 680$  Hz,  $C_a$ ),  $177.22$  (s,  $^2J_{C-Pt} = 54.5$  Hz,  $C_k$ ) ppm.

$\delta_F = -114.13$  ( $^4J_{F-Pt} = 28$  Hz) ppm.  $\delta_P = 0.96$  ( $^1J_{P-Pt} = 3820$  Hz) ppm.  $\delta_{Pt} = -3995$  (d,  $^1J_{Pt-P} = \sim 3900$  Hz) ppm.

HR-MS (ESI): found 604.2003, calculated 604.2010 =  $C_{25}H_{37}FNP^{194}Pt = [M]^+$ .

Elemental analysis found (calculated): C 50.83 (50.33), H 6.43 (6.25), N 2.19 (2.35).

Bn-1  $\delta_H = 7.55$  (1H, t,  $^3J_{H-H} = 7.5$  Hz,  $H_i$ ),  $7.41$  (1H, d,  $^3J_{H-H} = 7.5$  Hz,  $H_h$ ),  $7.35$  (d, 1H,  $^3J_{H-F} = 8$  Hz,  $^4J_{H-H} = 2$  Hz,  $^3J_{H-Pt} = \#20$  Hz,  $H_b$ ),  $7.31$  (3H, m,  $Bn-m,p$ ),  $7.20$  (2H, d,  $^3J_{H-H} = 8.5$  Hz,  $Bn-o$ ),  $6.98$  (1H, d,  $^3J_{H-H} = 7.5$  Hz,  $H_j$ ),  $6.51$  (1H, dd,  $^3J_{H-F} = 10$  Hz,  $^4J_{H-H} = 2$  Hz,  $H_d$ ),  $4.34$  (2H, s,  $Bn-CH_2$ ),  $1.95$  (6H, m,  $PCH_2$ ),  $1.83$  (2H, s,  $^2J_{H-Pt} = 37$  Hz,  $H_n$ ),  $1.66$  (6H, m,  $PCH_2CH_2$ ),  $1.38$  (6H, s,  $C_m$ ),  $1.07$  (9H, t,  $^3J_{H-H} = 7$  Hz,  $PCH_2CH_2Me$ ) ppm.

$\delta_C = 14.79$  (d,  $^3J_{C-P} = 14$  Hz,  $PCH_2CH_2Me$ ),  $17.26$  (s,  $^3J_{C-Pt} = 30.5$  Hz,  $PCH_2CH_2$ ),  $26.00$  (d,  $^1J_{C-P} = 36$  Hz,  $^2J_{C-Pt} = 36$  Hz,  $PCH_2$ ),  $33.36$  (s,  $^3J_{C-Pt} = 17$  Hz,  $C_m$ ),  $35.17$  (s,  $C_n$ ),  $40.86$  (s,  $Bn-CH_2$ ),  $51.44$  (s,  $C_i$ ),  $112.69$  (d,  $^2J_{C-F} = 24$  Hz,  $C_d$ ),  $117.35$  (s,  $C_j$ ),  $118.52$  (s,  $C_h$ ),  $120.83$  (d,  $^2J_{C-F} = 16$  Hz,  $C_b$ ),  $125.29$  (s,  $Bn-p$ ),  $127.69$  (s,  $Bn-o,m$ ),  $136.46$  (s,  $C_i$ ),  $138.82$  (s,  $Bn-i$ ),  $144.28$  (s,  $C_f$ ),  $162.82$  (s,  $C_g$ ),  $162.85$  (d,  $^1J_{C-F} = 253$  Hz,  $C_c$ ),  $175.66$  (m,  $C_a$ ),  $177.07$  (s,  $C_k$ ) ppm.

$\delta_F = -113.66$  ( $^4J_{F-Pt} = 26.5$  Hz) ppm.  $\delta_P = 0.86$  ( $^1J_{P-Pt} = 3813$  Hz) ppm.  $\delta_{Pt} = -3987$  (d,  $^1J_{Pt-P} = \sim 3850$  Hz) ppm.

Mass spec: found 672.2661, calculated 672.2660 =  $C_{31}H_{41}FNP^{194}Pt = [M]^+$ .

#### Synthesis of Me-2(Me) and Me2-3

MeI (20  $\mu$ l, excess), was added to a solution of Me-1 (10 mg, 0.016 mmol) in  $CDCl_3$  and heated (50  $^\circ$ C, 1 hour) to give full conversion to Me2-3. The solvent was removed to give pure Me2-3 (12 mg, 0.016 mmol, 100%). If reaction time was reduced to 30 min, it was possible to identify key NMR resonances for Me-2(Me), but it was not possible to purify it.

Me-2(Me)  $\delta_F = -113.19$  ppm.  $\delta_P = -19.77$  ppm.

Me2-3  $\delta_H = 7.80$  (1H, t,  $^3J_{H-H} = 8$  Hz,  $H_g$ ),  $7.27$  (1H, d,  $^3J_{H-H} = 8$  Hz,  $H_h$ ),  $7.08$  (1H, d,  $^3J_{H-H} = 8$  Hz,  $H_f$ ),  $6.73$  (2H, d,  $^3J_{H-F} = 9.5$  Hz,  $H_b$ ),  $2.35$  (6H, s, Me),  $1.83$  (8H, m,  $H_i$ ,  $PCH_2$ ),  $1.56$  (12H, m,  $H_k$ ,  $PCH_2CH_2$ ),  $0.99$  (9H, t,  $^3J_{H-H} = 7$  Hz,  $PCH_2CH_2Me$ ) ppm.

$\delta_C = 15.76$  (d,  $^3J_{C-P} = 18$  Hz,  $PCH_2CH_2Me$ ),  $18.00$  (s,  $^3J_{C-Pt} = 30$  Hz,  $PCH_2CH_2$ ),  $22.24$  (s, Me),  $27.57$  (d,  $^1J_{C-P} = 35$  Hz,  $^2J_{C-Pt} = 48$  Hz,  $PCH_2$ ),  $33.23$  (s,  $^3J_{C-Pt} = 44$  Hz,  $C_k$ ),  $35.16$  (s,  $^1J_{C-Pt} = 727$  Hz,  $C_i$ ),  $49.98$  (s,  $C_j$ ),  $114.22$  (d,  $^2J_{C-F} = 23$  Hz,  $C_b$ ),  $119.42$  (s,  $C_h$ ),  $126.44$  (s,  $C_f$ ),  $136.86$  (s,  $C_d$ ),  $137.44$  (s,  $C_g$ ),  $139.83$  (d,



$^3\text{J}_{\text{C-F}} = 10$  Hz, C<sub>c</sub>), 160.69 (s, C<sub>e</sub>), 162.80 (d,  $^1\text{J}_{\text{C-F}} = 254$  Hz, C<sub>a</sub>), 174.32 (s, C<sub>i</sub>) ppm.

$\delta_{\text{F}} = -114.84$  ppm.  $\delta_{\text{P}} = -1.80$  ( $^1\text{J}_{\text{P-Pt}} = 4292$  Hz) ppm.  $\delta_{\text{Pt}} = -4382$  (d,  $^1\text{J}_{\text{Pt-P}} = \sim 4300$  Hz) ppm.

HR-MS (ESI): found 610.2508, calculated 610.2504 = C<sub>26</sub>H<sub>40</sub>FNP<sup>194</sup>Pt = [M - I]<sup>+</sup>.

Elemental analysis found (calculated): C 43.85 (42.28), H 5.73 (5.46), N 1.85 (1.90).

### One pot synthesis of Me<sub>2</sub>-3 and Bn<sub>2</sub>-3

**Me<sub>2</sub>-3** To solution of 1 (25 mg, 0.043 mmol) in chloroform (0.6 ml) was added MeI (20  $\mu$ l, excess) and 2 M aqueous K<sub>2</sub>CO<sub>3</sub> (0.08 ml). The reaction mixture was then heated with stirring (50 °C, 1 week). The water layer was decanted off, and the solvent and excess MeI removed. The product was purified by column chromatography on silica, elution was with toluene, giving pure Me<sub>2</sub>-3 (29 mg, 0.04 mmol, 92%).

Bn<sub>2</sub>-3 was prepared in a similar fashion.

**Bn<sub>2</sub>-3**  $\delta_{\text{H}} = 7.32$  (1H, t,  $^3\text{J}_{\text{H-H}} = 8.5$  Hz, H<sub>g</sub>), 7.07 (7H, m, H<sub>h</sub>, Bn-m,p), 6.91 (4H, d,  $^3\text{J}_{\text{H-H}} = 8$  Hz, Bn-o), 6.61 (2H, d,  $^3\text{J}_{\text{H-F}} = 10$  Hz, H<sub>b</sub>), 6.53 (2H, d,  $^3\text{J}_{\text{H-H}} = 8.5$  Hz, H<sub>f</sub>), 4.16 (2H, d,  $^2\text{J}_{\text{H-H}} = 16$  Hz, Bn-CH<sub>2</sub>), 4.09 (2H, d,  $^2\text{J}_{\text{H-H}} = 16$  Hz, Bn-CH<sub>2</sub>), 1.75 (8H, m, H<sub>i</sub>, PCH<sub>2</sub>), 1.55 (6H, m, PCH<sub>2</sub>CH<sub>2</sub>), 1.52 (6H, m, H<sub>k</sub>), 0.96 (9H, t,  $^3\text{J}_{\text{H-H}} = 7$  Hz, PCH<sub>2</sub>CH<sub>2</sub>Me) ppm.

$\delta_{\text{C}} = 15.80$  (d,  $^3\text{J}_{\text{C-P}} = 16$  Hz, PCH<sub>2</sub>CH<sub>2</sub>Me), 18.02 (s,  $^3\text{J}_{\text{C-Pt}} = 27$  Hz, PCH<sub>2</sub>CH<sub>2</sub>), 26.35 (d,  $^1\text{J}_{\text{C-P}} = 37$  Hz,  $^2\text{J}_{\text{C-Pt}} = 34$  Hz, PCH<sub>2</sub>), 29.50 (d,  $^2\text{J}_{\text{C-P}} = 4$  Hz, C<sub>i</sub>), 33.40 (s, C<sub>k</sub>), 40.69 (s, C<sub>m</sub>), 49.60 (s, C<sub>j</sub>), 114.56 (d,  $^2\text{J}_{\text{C-F}} = 22$  Hz, C<sub>b</sub>), 119.66 (s, C<sub>f</sub>), 125.88 (s, Bn-p), 127.26 (s, C<sub>h</sub>), 128.18 (s, Bn-m), 129.09 (s, Bn-o), 135.83 (s, C<sub>d</sub>), 136.81 (s, C<sub>g</sub>), 140.44 (s, C<sub>n</sub>), 143.01 (d,  $^3\text{J}_{\text{C-F}} = 8$  Hz, C<sub>c</sub>), 159.11 (s, C<sub>e</sub>), 162.85 (d,  $^1\text{J}_{\text{C-F}} = 247$  Hz, C<sub>a</sub>), 174.50 (s, C<sub>i</sub>) ppm.

$\delta_{\text{F}} = -113.65$  ppm.  $\delta_{\text{P}} = -0.93$  ( $^1\text{J}_{\text{P-Pt}} = 4298$  Hz) ppm.  $\delta_{\text{Pt}} = -4250$  (d,  $^1\text{J}_{\text{Pt-P}} = \sim 4300$  Hz) ppm.

HR-MS (ESI): found 762.3137, calculated 762.3130 = C<sub>38</sub>H<sub>48</sub>FNP<sup>194</sup>Pt = [M - Br]<sup>+</sup>.

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## References

- (a) A. E. Shilov and G. B. Shul'pin, *Chem. Rev.*, 1997, 97, 2879–2932; (b) A. S. Goldman and K. I. Goldberg, in *Activation and Functionalization of C-H Bonds*, ed. K. I. Goldberg and A. S. Goldman, ACS, Washington DC, 2004, vol. 885, ACS Symposium Series; (c) D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev.*, 2010, 110, 624–655; (d) J. Wencel-Delord, T. Droge, F. Liu and F. Glorius, *Chem. Soc. Rev.*, 2011, 40, 4740–4761; (e) B. G. Hashiguchi, S. M. Bischof, M. M. Konnick and R. A. Periana, *Acc. Chem. Res.*, 2012, 45, 885–898; (f) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord and F. Glorius, *Angew. Chem., Int. Ed.*, 2012, 51, 10236–10254; (g) J. F. Hartwig and M. A. Larsen, *ACS Cent. Sci.*, 2016, 2, 281–292; (h) J. A. Labinger and J. E. Bercaw, *Nature*, 2002, 417, 507–514.
- M. Lersch and M. Tilset, *Chem. Rev.*, 2005, 105, 2471–2526.
- (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) J. J. Low and W. A. Goddard, *J. Am. Chem. Soc.*, 1986, 108, 6115–6128; (b) P. M. Maitlis, H. C. Long, R. Quyoum, M. L. Turner and Z.-Q. Wang, *Chem. Commun.*, 1996, 1–8; (c) 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) J. K. Jawad and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1977, 892–893; (b) J. K. Jawad, R. J. Puddephatt and M. A. Stalteri, *Inorg. Chem.*, 1982, 21, 332–337; (c) M. P. Brown, R. J. Puddephatt, C. E. E. Upton and S. W. Lavington, *J. Chem. Soc., Dalton Trans.*, 1974, 1613–1618; (d) K. I. Goldberg, J. Yan and E. M. Breitung, *J. Am. Chem. Soc.*, 1995, 117, 6889–6896.
- (a) M. Crespo, C. M. Anderson, N. Kfoury, M. Font-Bardia and T. Calvet, *Organometallics*, 2012, 31, 4401–4404; (b) C. M. Anderson, M. Crespo, N. Kfoury, M. A. Weinstein and J. M. Tanski, *Organometallics*, 2013, 32, 4199–4207; (c) C. M. Anderson, M. W. Greenberg, L. Spano, L. Servatius and J. M. Tanski, *J. Organomet. Chem.*, 2016, 819, 27–36.
- B. L. Madison, S. B. Thyme, S. Keene and B. S. Williams, *J. Am. Chem. Soc.*, 2007, 129, 9538–9539.
- A. Zucca, L. Maidich, L. Canu, G. L. Petretto, S. Stoccoro, M. A. Cinellu, G. J. Clarkson and J. P. Rourke, *Chem. – Eur. J.*, 2014, 20, 5501–5510.
- E. G. Bowes, S. Pal and J. A. Love, *J. Am. Chem. Soc.*, 2015, 137, 16004–16007.
- (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.
- (a) S. H. Crosby, G. J. Clarkson and J. P. Rourke, *J. Am. Chem. Soc.*, 2009, 131, 14142–14143; (b) S. H. Crosby, G. J. Clarkson, R. J. Deeth and J. P. Rourke, *Organometallics*, 2010, 29, 1966–1976; (c) S. H. Crosby, G. J. Clarkson, R. J. Deeth and J. P. Rourke, *Dalton Trans.*, 2011, 40, 1227–1229; (d) H. R. Thomas, R. J. Deeth, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2011, 30, 5641–5648; (e) S. H. Crosby, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2011, 30, 3603–3609; (f) J. Mamtara, S. H. Crosby, C. P. Newman, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2008, 27, 5559–5565.
- (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.

- 13 (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, 11397–11406; (c) P. A. Shaw, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2016, 35, 3751–3762.
- 14 (a) M. Crespo and R. J. Puddephatt, *Organometallics*, 1987, 6, 2548–2550; (b) L. M. Rendina and R. J. Puddephatt, *Chem. Rev.*, 1997, 97, 1735–1754; (c) J. A. Labinger, *Organometallics*, 2015, 34, 4784–4795.
- 15 (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; (c) C. P. Newman, G. W. V. Cave, M. Wong, W. Errington, N. W. Alcock and J. P. Rourke, *J. Chem. Soc., Dalton Trans.*, 2001, 2678–2682.
- 16 (a) D. M. Crumpton-Bregel and K. I. Goldberg, *J. Am. Chem. Soc.*, 2003, 125, 9442–9456; (b) J. R. Khusnutdinova, L. L. Newman, P. Y. Zavalij, Y. F. Lam and A. N. Vedernikov, *J. Am. Chem. Soc.*, 2008, 130, 2174–2175; (c) A. Vigalok, *Acc. Chem. Res.*, 2015, 48, 238–247; (d) T. Calvet, M. Crespo, M. Font-Bardia, S. Jansat and M. Martinez, *Organometallics*, 2012, 31, 4367–4373; (e) C. Gallego, M. Martinez and V. S. Safont, *Organometallics*, 2007, 26, 527–537.