

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository: <https://orca.cardiff.ac.uk/id/eprint/118467/>

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Shaw, Paul A., Clarkson, Guy J. and Rourke, Jonathan P. 2016. Long-lived five-coordinate platinum(IV) intermediates: regiospecific C-C coupling. *Organometallics* 35 (21) , pp. 3751-3762.
10.1021/acs.organomet.6b00697

Publishers page: <http://dx.doi.org/10.1021/acs.organomet.6b00697>

Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See <http://orca.cf.ac.uk/policies.html> for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



Long-lived Five-Coordinate Platinum(IV)

Intermediates: Regiospecific C-C Coupling

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

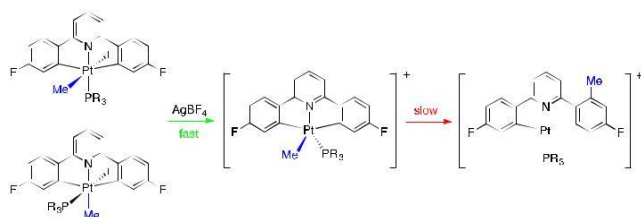
Department of Chemistry, Warwick University, Coventry. UK CV4 7AL.

Email: j.rourke@warwick.ac.uk

Abstract

Three different phosphine derivatives of doubly cyclometallated diphenylpyridine complexes of Pt(II), **1**, were reacted with methyl iodide to give octahedral Pt(IV) complexes, **2**, as two isomers. Treatment of either isomer of complexes **2** with AgBF₄, to abstract iodide, gave long-lived five-coordinate complexes **3**, which could be trapped as pyridine adducts. Complexes **3** underwent a C-C coupling reaction, at a rate that depended on phosphine size, to give a methyl group attached to the original diphenylpyridine. Recyclometallation was then performed and the cycle of reactions was repeated to give a diphenylpyridine doubly methylated on only one phenyl, with complete regiospecificity. NMR was used to demonstrate the geometry of all complexes in solution, with multiple X-ray crystal structures confirming these assignments.

TOC graphic



Introduction

The selective functionalisation of hydrocarbons has yet to be fully realised,¹ and considerable effort has been put into studying model organometallic complexes, such as those of platinum.² Platinum complexes are not just amenable to study, but also have direct relevance to actual processes and some are able to activate methane.³ The most interesting complexes to study are those that are coordinatively unsaturated, as these are often the most reactive. In the context of platinum chemistry, this means three-coordinate platinum(II)⁴ and five-coordinate platinum (IV) complexes.⁵

Bona fide stable five-coordinate platinum complexes have been identified under a variety of circumstances, and can be generated via the abstraction of a halide, usually with a silver salt, from a six-coordinate platinum (IV) starting material. They may also be generated via the addition of a single group to a four-coordinate platinum (II) complex, as part of an electrophilic oxidative addition process,⁶ and have successfully been characterised during the process of halogen oxidation.⁷ Another route to their generation is by the oxidation of a three-coordinate complex.^{4c,8}

The importance of five-coordinate intermediates in the concerted reductive elimination process from six coordinate octahedral complexes is well known and is directly relevant to platinum. The rapid reductive elimination from an unsaturated intermediate has been rationalised theoretically,⁹ 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. This analysis also suggests stereochemical consequences for the reaction and can be used to rationalise which groups end up coupling,¹⁰ with this factor over-riding the perceived kinetic preference for elimination of sp^2 carbons rather than sp^3 .¹¹ Computational work has suggested that, under certain circumstances, i.e. with vinyl groups coupling, the intermediacy of a five-coordinate complex is not necessary for a reductive elimination reaction to occur, though this appears to be an isolated example.¹²

Cyclometallation, one of the oldest methods by which late transition metals can activate C-H bonds,¹³ involves an initial coordination that directs a specific C-H bond to the metal centre, facilitating activation and providing selectivity. Cyclometallation also encompasses some less conventional¹⁴ reactions such as rollover,¹⁵ or transcyclometallation¹⁶ reactions.

Cyclometallated complexes have many uses¹⁷ and are frequently studied as model compounds in fundamental reactions.¹⁸ Our recent contributions to the area include investigating agostic complexes of,^{4f,8b,19} C-H activation by,^{4f,20} and the oxidation and reduction²¹ of a number of cycloplatinated complexes. Some of these results, in particular the reductive coupling that

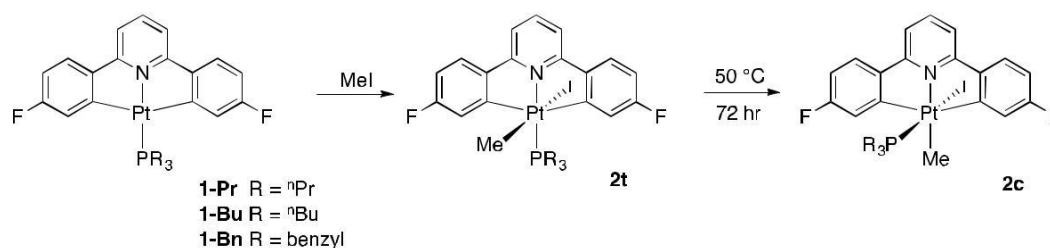
occurs following oxidation, prompted us to revisit some of our earlier work with C[^]N[^]C pincer complexes²² and attempt to oxidise them. Once oxidised, our symmetrical complexes, where both carbons are formally sp² hybridised, have the potential for reductive coupling^{7b,7c,23} but also have a constrained geometry and limited scope for ligand rearrangements. We therefore sought to exploit the constraints the cyclometallated ligand had upon the geometry of the platinum(IV) complex in its reactivity in a reductive elimination reaction. The dependence of the reaction upon the arrangement of the ligating groups can be used to retard the rate of C-C coupling such that five-coordinate intermediates can be seen in solution at room temperature. Furthermore, with unsymmetrical complexes, we were able to demonstrate completely regiospecific C-C coupling.

Results and Discussion

Oxidative addition of methyl iodide

The oxidative addition of methyl iodide to a square planar platinum(II) centre has long been known to take place via an S_N2 type process, as expected for electrophilic reagents.^{6-7,24} The reaction can be thought of attack of the metal centre on the methyl iodide to give a cationic five-coordinate methyl complex which then rapidly combines with the liberated iodide to give a neutral octahedral complex. Normally the spatial arrangement of the existing ligands on the metal centre does not change and the added methyl and iodide groups end up mutually *trans*, though it is possible that the initial octahedral product subsequently isomerises to relieve steric interactions. Thus, when we started from three previously²² reported C[^]N[^]C phosphine complexes, **1-Pr**, **1-Bu** and **1-Bn**, addition of methyl iodide resulted in the expected initial *trans* arrangement of the two incoming groups, followed by a slow isomerisation at room temperature in chloroform solution (taking around 72 hrs at 50 °C), Scheme 1.

Scheme 1



The geometry of the initial and final products can be deduced from NMR data (in particular NOE measurements can be used to identify the positions of the methyl and phosphine groups, relative to the C[^]N[^]C pyridine), and we were also able to grow crystals and solve the structures of both **2t-Pr** and **2c-Bu**, Figures 1 and 2, which allowed us to confirm the

geometries of the two products. We can rationalise the isomerisation of **2t** to **2c** on the basis of a relief of steric strain associated with bringing a large phosphine away from a relatively congested central position to a less congested one above the plane of the diphenylpyridine. Evidence for this strain comes from the N-Pt-P angle of 170.60(9) ° in **2t-Pr** compared with the N-Pt-Me angle of 175.85(19) ° in **2c-Bu**.

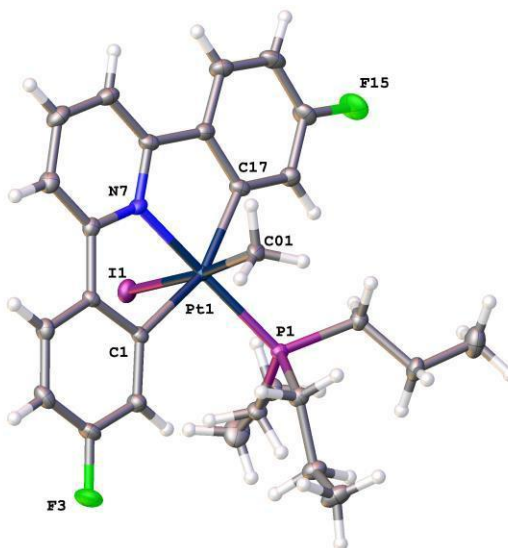


Figure 1: The solid-state structure of **2t-Pr**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): C1-Pt1 2.094(3); P1-Pt1 2.2925(9); C01-Pt1 2.117(4); I1-Pt1 2.7497(3); Pt1-N7 2.037(3); Pt1-C17 2.101(4); C1-Pt1-P1 95.81(10); C1-Pt1-C01 91.40(14); C1-Pt1-I1 89.44(10); C1-Pt1-C17 159.43(15); P1-Pt1-I1 97.72(2); C01-Pt1-P1 87.11(11); C01-Pt1-I1 175.00(11); N7-Pt1-C1 79.96(13); N7-Pt1-P1 170.60(9); N7-Pt1-C01 84.63(14); N7-Pt1-I1 90.67(9); N7-Pt1-C17 79.61(14); C17-Pt1-P1 104.75(11); C17-Pt1-C01 89.05(14); C17-Pt1-I1 88.43(10).

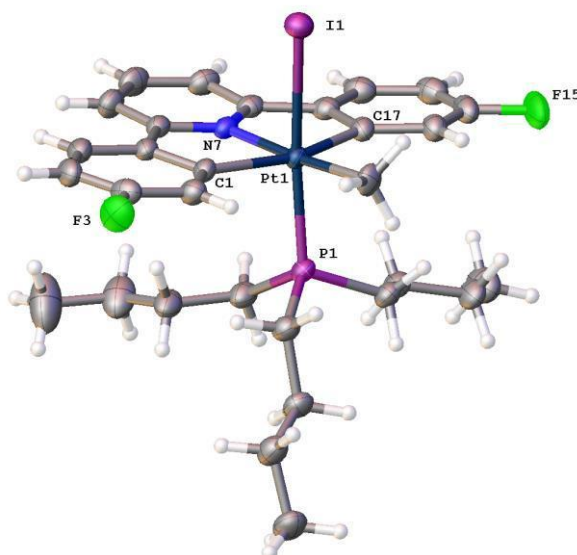
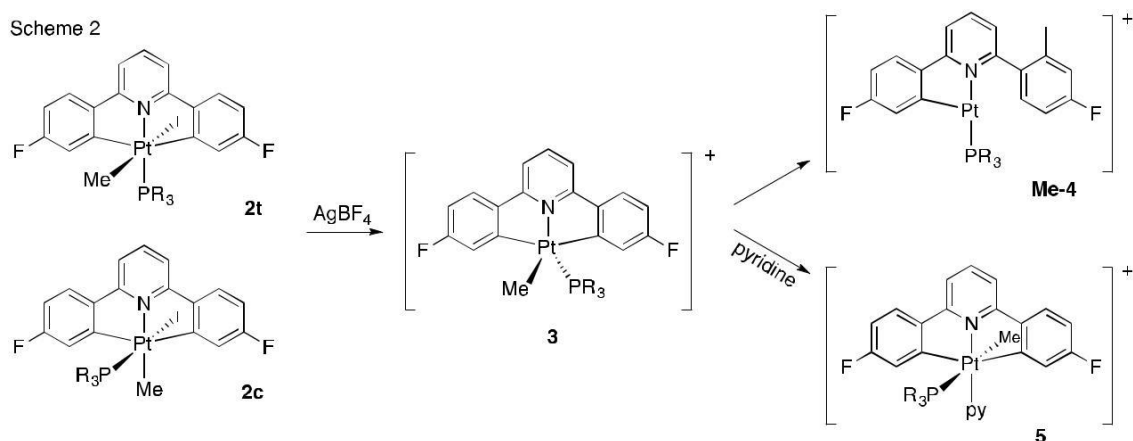


Figure 2: The solid-state structure of **2c-Bu**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt1-I1 2.7108(3); Pt1-C100 2.065(7); Pt1-I2 2.688(3); Pt1-C1 2.091(4); Pt1-N7 2.040(3); Pt1-C17 2.074(4); Pt1-P1 2.2818(11); C100-Pt1-I1 87.38(18); C100-Pt1-C1 101.19(19); C100-Pt1-C17 98.7(2); C100-Pt1-P1 86.93(18); I2-Pt1-I1 87.08(7); C1-Pt1-I1 87.67(11); C1-Pt1-I2 101.38(12); C1-Pt1-P1 94.30(11); N7-Pt1-I1 88.61(9); N7-Pt1-C100 175.85(19); N7-Pt1-I2

175.51(11); N7-Pt1-C1 79.71(14); N7-Pt1-C17 80.15(14); N7-Pt1-P1 97.05(9); C17-Pt1-I1 89.01(11); C17-Pt1-I2 98.49(13); C17-Pt1-C1 159.65(15); C17-Pt1-P1 90.97(11); P1-Pt1-I1 174.25(3); P1-Pt1-I2 87.23(7).

Generating five-coordinate intermediates and C-C coupling

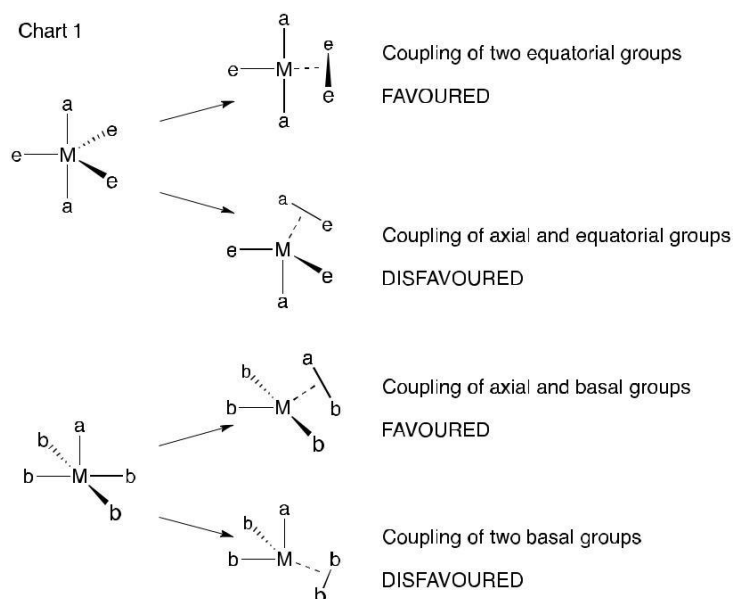
Treatment of either isomer of **2** (or, indeed a mixture) with AgBF_4 , to remove the iodide and generate a five-coordinate species and hence a reductively coupled product, gave the five-coordinate **3** directly. In the case of the propyl and butyl phosphine derivatives, **3-Pr** and **3-Bu**, this species reacted only slowly, taking, respectively, around 5 and 4 hours at room temperature for the reaction to give the C-C coupled product **Me-4**, Scheme 2, to go to completion (at -40°C , there was no appreciable reaction on a timescale of hours). The five-coordinate **3-Pr** and **3-Bu** could clearly be seen in solution and would appear to have trigonal pyramidal structures (NOE measurements indicated that both the phosphine and the methyl group were in proximity to the proton situated between the platinum and the fluorine on the cyclometallated ring this is different to the case for either of **2t** or **2c**, ruling out a square based pyramidal structure). For the benzyl phosphine derivative the reaction was sufficiently fast at room temperature (complete with 1 minute) that **3-Bn** could not be seen in solution by NMR, though it could be trapped out with pyridine to give **5-Bn**, Scheme 2.^{7c} The pyridine trapped complex **5-Bn** initially formed with the incoming pyridine *trans* to the $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$ nitrogen, but slowly isomerised to the isomer with the methyl group *trans* to this nitrogen, a pattern of behaviour that was replicated with the propyl and butyl analogues. There have been reports of C-H activation reactions at platinum that are enhanced by the addition of silver(I),²⁵ but there does not appear to be any effect of that nature here.



The identity of coupled product **Me-4** is clear; there are two signals in the ^{19}F NMR, one with Pt satellites, one without, and the ^1H NMR indicates this geometry. In particular the methyl signal has moved from 1.02 ppm (with Pt satellites at 67 Hz) in **2t-Pr** and from 1.57 ppm (with Pt satellites at 62 Hz) in **2c-Pr** to 2.64 ppm (no satellites) in **Me-4-Pr**. A cationic formulation is suggested from a very intense signal in the positive ion electrospray mass-

spectrometry, and subsequent reactivity confirms this. **Me-4** is formally a three-coordinate species, and might be expected to have a further agostic interaction, either from the proton *ortho* to the pyridine on the methyl substituted phenyl ring, or the methyl group itself, or the alkyl chain of the phosphine. However, we were unable to identify any such interaction in the ^1H NMR or in the ^1H - ^{195}Pt correlation spectrum, even when we reduced the temperature to -60 °C. It is possible that solvent (in particular water) could occupy the fourth coordinate site, but we found no evidence for this, even when we cooled to -60 °C, a temperature at which we might expect any fluxionality or ligand exchange to have been frozen out.^{19a,26} Presumably the additional steric interactions caused by the methyl group on the phenyl ring help to disfavour such interactions.

The reason why the reductive coupling in **3** is relatively slow, and why we were able to identify it at all, relates to the specific requirements needed for the coupling of groups within the five-coordinate intermediate. The original work that rationalised⁹ the rapid reductive elimination from a five-coordinate unsaturated intermediate identified the need for the coupling groups to be part of a three-coordinate planar arrangement of groups, Chart 1.



For a trigonal bipyramidal complex, the reductive coupling of two equatorial groups leads to the electron density being donated into a metal orbital that is only non-bonding in the five-coordinate complex, whereas the coupling of an axial and an equatorial group requires the population of an anti-bonding orbital. Thus in **3** a rapid coupling of the equatorial methyl group with one of the axial phenyl rings is not possible, without some degree of rearrangement of the molecule. The rigidly *mer* coordinating C^NC diphenylpyridine group prevents an easy rearrangement that brings both a phenyl ring and the methyl into equatorial positions, and **3** becomes sufficiently unlabile to persist in solution for several hours.

The fact that coupling does take place at all can probably be attributed to the possibility of a square based pyramidal structure with the phosphine and the C^NC ligand occupying the basal sites, with the methyl group in the axial position. Now, the geometric restrictions on a coupling reaction are such that the axial group can rapidly couple with a basal group, but two basal groups cannot. Thus, with the rigidly *mer* coordinating C^NC diphenylpyridine group and the phosphine in the basal plane, reductive coupling of the methyl group with a phenyl ring can take place. Now the effect of the phosphine on the reaction rate can also be rationalised: the bulkier the phosphine, the more likely the rearrangement to a square based pyramid, with the phosphine in the basal plane. Hence the reaction rates **3-Bn** \gg **3-Bu** > **3-Pr**, which reflect the size of the phosphine, as measured by Tolman cone angle.²⁷

Recyclometallation to give unsymmetrical complexes

The fourth coordinate site of **Me-4** can be filled with halide via the simple expedient of addition of the appropriate sodium halide, Scheme 3. Chloride, bromide and iodide derivatives were isolated and we were able to crystallise and solve the structures of the iodide derivatives of **Me-6-Pr** and **Me-6-Bu**, Figures 3 and 4, As might be expected, the solid state structures of **Me-6-Pr** and **Me-6-Bu** show considerable distortions away from an ideal square planar arrangement with the C-Pt-I bond angles being 151.59(13) and 153.15(8)° respectively, and the N-Pt-P angles being 171.18(10) and 171.06(6)° respectively. Distortions to the bond angles away from 180° of this magnitude are not unheard of.²⁸ The plane of the methylated ring in **Me-6** makes an angle of 50.2° to that of the pyridine ring.

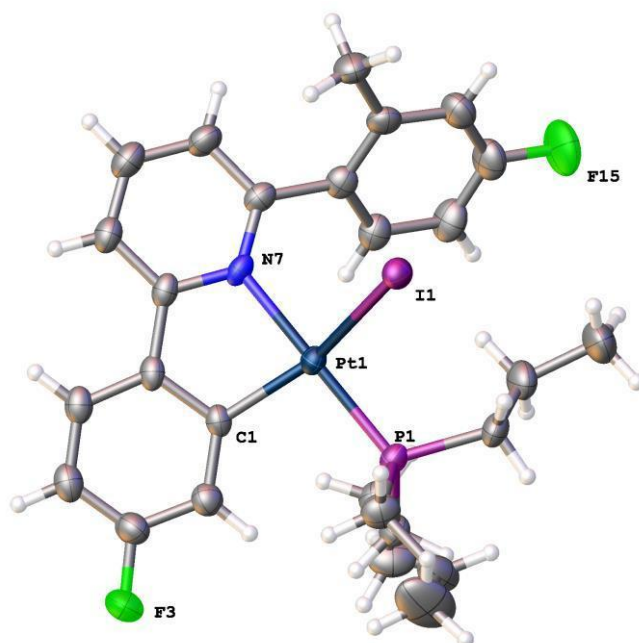


Figure 3: The solid-state structure of **Me-6-Pr**, thermal ellipsoids drawn at 50% probability level.

Selected bond lengths (Å) and angles (°): Pt1-I1 2.7083(3); Pt1-P1 2.2347(11); Pt1-C1 2.015(5); Pt1-N7

2.112(4); P1-Pt1-I1 91.01(3); C1-Pt1-I1 151.59(13); C1-Pt1-P1 98.11(14); C1-Pt1-N7 80.32(17); N7-Pt1-I1 94.41(11); N7-Pt1-P1 171.18(10).

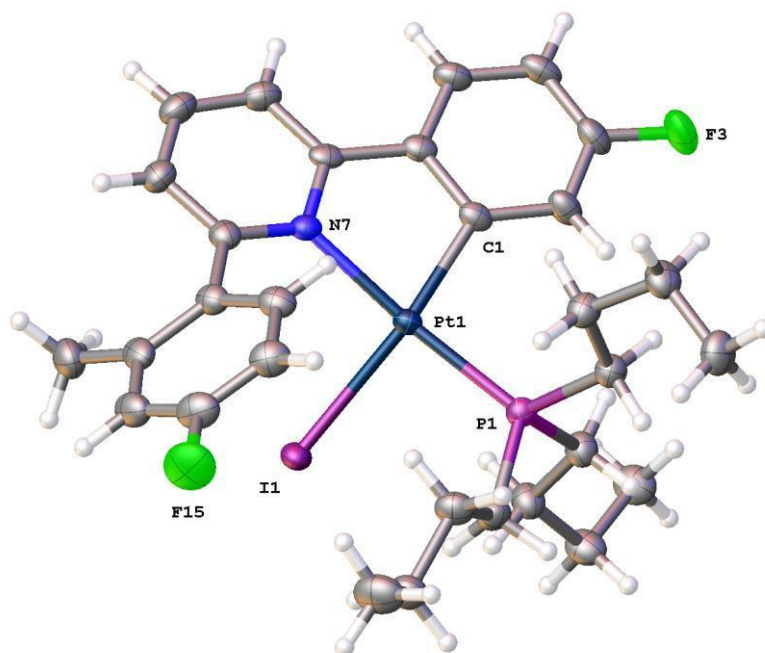
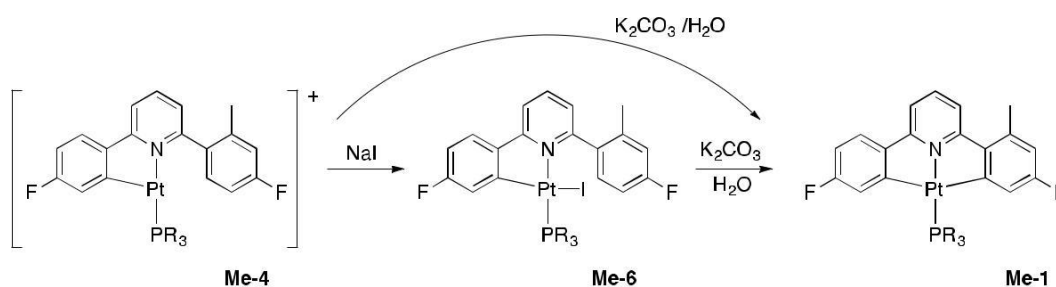


Figure 4: The solid-state structure of **Me-6-Bu**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): C1-Pt1 2.007(3); I1-Pt1 2.7024(2); P1-Pt1 2.2374(8); Pt1-N7 2.122(2); C1-Pt1-I1 153.15(8); C1-Pt1-P1 97.38(9); C1-Pt1-N7 80.52(11); P1-Pt1-I1 92.48(2); N7-Pt1-I1 93.17(6); N7-Pt1-P1 171.06(6).

From derivative **Me-6**, and indeed from the three-coordinate **Me-4**, it is possible to recyclometallate the methyl substituted ring to give doubly cyclometallated C^NC complexes **Me-1**, Scheme 3.^{22a,22b} In this paper we only report the reactions exemplified by the tripropyl phosphine derivative, though it is possible to perform the reaction with the butyl and benzyl phosphine analogues.



Crystals of **Me-1-Pr** were grown and the structure solved, Figure 5, and it is pertinent to note the effect of the additional methyl group, which might be expected to add additional steric crowding. A full comparison of the structure of **Me-1-Pr** with that of **1-Pr** (previously reported by us^{7c}) can be made, but most of these differences are reflected in the two different cyclometallated rings of **Me-1-Pr** and **Me-1-Bu**. Thus, in **Me-1-Pr**, the bond distances and angles in the non-methylated phenyl ring, and its associated metallacycle are all within 0.01 Å and 1°, respectively, of their equivalents in **1-Pr**. However, significant differences in both

bond distances and angles for the methylated ring, and associated metallacycle, compared with the non-methylated ring can be seen. Figures SI8 and SI9 show all the relevant bond lengths and angles, but here we can note that the methylated side of the diphenylpyridine is appreciably more distorted than the non-methylated side. Thus the C-C bond that connects the central pyridine to the phenyl ring is 1.457(9) Å for the non-methylated phenyl, but 1.488(9) Å for the methylated phenyl ring. The angle that this bond makes with the two rings is 121.1(6) and 127.6(6)° on the non-methylated side, but opens up to 123.6(6) and 130.0(6) for the methylated ring. In addition the methyl group has been forced away from the pyridine ring with the angle it makes to the phenyl ring being 124.6(7)°, significantly removed from an ideal 120°. The crowding does not distort the molecule much from planarity: whilst there is a slight bowing of the central C^NC^{Pt} ring system with the platinum 0.27 Å away from plane, none of the carbons are more than 0.07 Å away from it, with the methyl group only 0.166 Å out of plane.

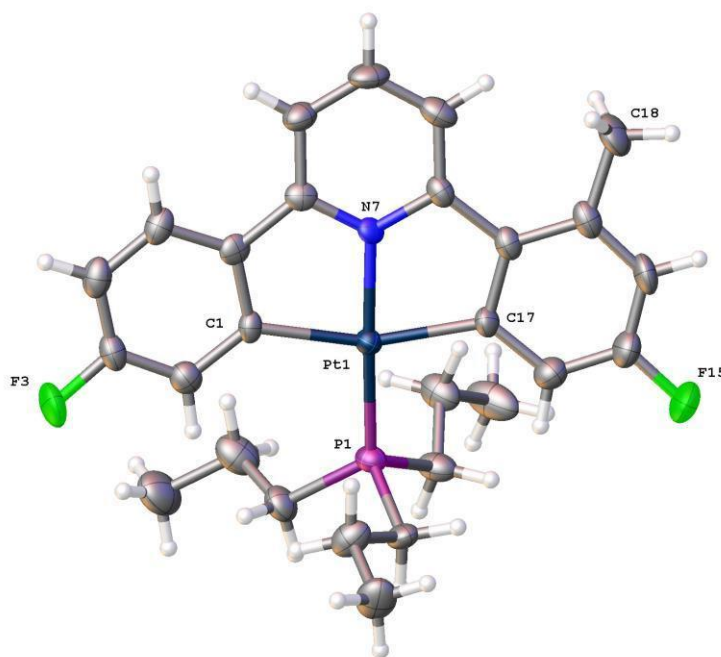


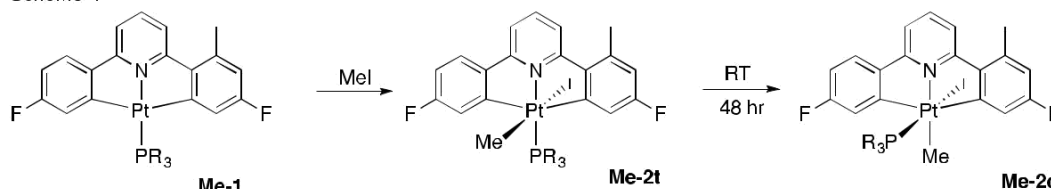
Figure 5: The solid-state structure of **Me-1-Pr**, thermal ellipsoids drawn at 50% probability level.

Selected bond lengths (Å) and angles (°): Pt1-C1 2.074(6); Pt1-P1 2.2298(16); Pt1-N7 2.027(5); Pt1-C17 2.050(6); C1-Pt1-P1 102.18(18); N7-Pt1-C1 80.5(2); N7-Pt1-P1 174.21(15); N7-Pt1-C17 79.9(2); C17-Pt1-C1 159.8(3); C17-Pt1-P1 97.78(18).

Repeating the cycle of reactions

From **Me-1** it is now possible to repeat the sequence of reactions described above. Thus oxidative addition of MeI cleanly gave **Me-2t**, which subsequently isomerised to **Me-2c**. Scheme 4.

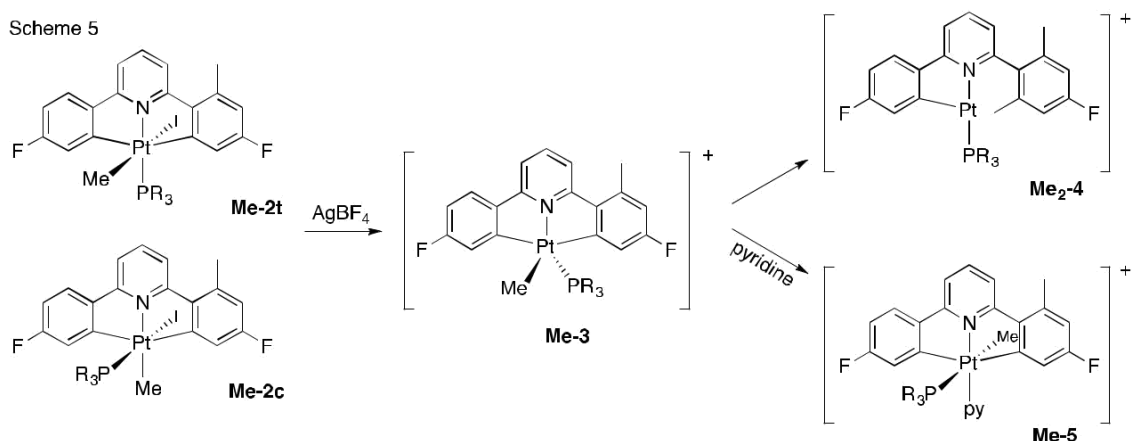
Scheme 4



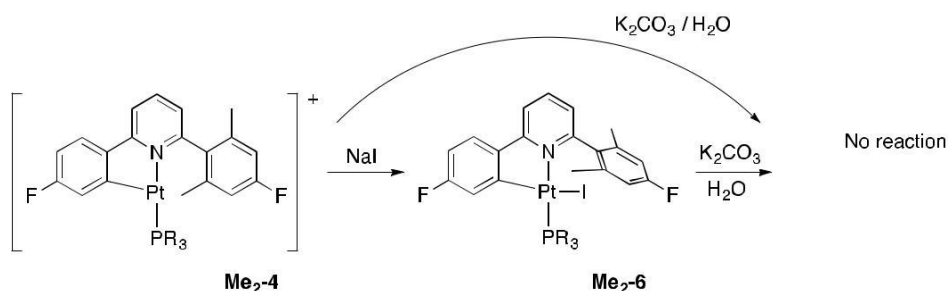
Treatment of either isomer of **Me-2** (or, once again, a mixture) with AgBF₄, now gives intermediate **Me-3**, which again we were able to characterise in solution. Once again, it was possible to trap **Me-3** out, if the reaction was performed with pyridine present, whereupon **Me-5** was formed, Scheme 5. In the absence of pyridine, reductive coupling in **Me-3-Pr** occurred appreciably faster than that of **3-Pr** (only 2 hours to go to completion, compared with 5) and can now result in two possible products: with the methyl group either coupling with the unsubstituted phenyl ring, or with the phenyl ring that already has a methyl group (giving **Me2-4**), Scheme 5.

That only one product does form is absolutely clear from the NMR spectra of the reaction where only one signal is seen in the ³¹P spectrum, only two signals (ratio 1:1, one with satellites, one without) in the ¹⁹F and only one set of signals in the ¹H NMR spectrum. That this product has the doubly methylated phenyl ring of **Me2-4** is unambiguous as the set of signals in ¹H NMR include a singlet of relative intensity six for the methyl groups and a doublet (¹⁹F coupling, but no ¹⁹⁵Pt coupling) of relative intensity two for the aromatic protons of the dimethylated ring. Thus the reaction is completely regiospecific. As the methyl group in **Me-3** would have minimal electronic effect on the C-Pt bond *meta* to it, we can assume that the regiospecificity and the enhanced reaction rate of the coupling of this bond with the methyl group arises from steric factors. Coupling the second methyl group to the already methylated ring breaks the more strained metallacycle free from the platinum and is thus favoured. We can see from the X-ray structures of **Me-1**, Figures 5 and 6, how this side of the molecule is stressed. As the coupled ring is free to rotate away from the plane of the pyridine and the remaining metallacycle, the additional methyl group in **Me2-4** does not impinge upon the rest of the molecule and there is no price to pay for doubly methylating one ring, rather than singly methylating two separate rings.

Scheme 5



Once again, the product of reductive coupling is formally three coordinate, and once again we were unable to identify any solvent or agostic interaction. It was possible to generate the neutral square planar complex **Me2-6** by treating **Me2-4** with NaI, Scheme 6. The crystal structure of **Me2-6-Pr** was solved, Figure 6, and the geometry at the platinum is distorted away from an ideal square planar geometry in a fashion that is similar to the **Me-6** derivatives, with C-Pt-I and N-Pt-P angles of $152.99(6)$ and $169.77(5)^\circ$ respectively. Further evidence for a crowded metal centre in **Me2-6-Pr**, and evidence that the metal centre is even more crowded than in the **Me-6-Pr** complex, comes from a close contact within the molecule: one of the phosphine propyl chain hydrogens is very close to the hydrogen *ortho* to both the Pt and the F in the cyclometallated ring, with an H-H distance of $1.785(1)$ Å. The equivalent distance in **Me-6-Pr** is 2.02 Å, and a discussion of why there might be differences and why these two hydrogens might be so close in **Me2-6-Pr** is included in the SI, as is a picture showing the two structures overlaid (Figure SI12). The plane of the dimethylated ring in **Me2-6-Pr** makes an angle of 64.9° to that of the pyridine ring, up from the equivalent 50.2° in **Me-6-Pr**. Though there are these clear differences in the solid state structures, we note that, in solution, there is very little difference in any of the NMR metrics between **Me-6-Pr** and **Me2-6-Pr** (the respective ^{31}P chemical shifts are -0.10 and -1.60 ppm; the respective ^{31}P - ^{195}Pt coupling constants are 4052 and 4061 Hz; the respective ^{19}F chemical shifts $-112.53/-115.68$ and $-112.83/-116.70$ ppm; both ^{19}F - ^{195}Pt coupling constants are 62 Hz; the respective ^{195}Pt chemical shifts are -3957 and -3946 ppm).



Finally, we were unable to recyclometallate **Me2-4** or **Me2-6** using our standard conditions of mild base and water, presumably because the only available hydrogens are part of an sp^3 hybridised methyl group, rather than the more usual sp^2 hybridised phenyl ring.

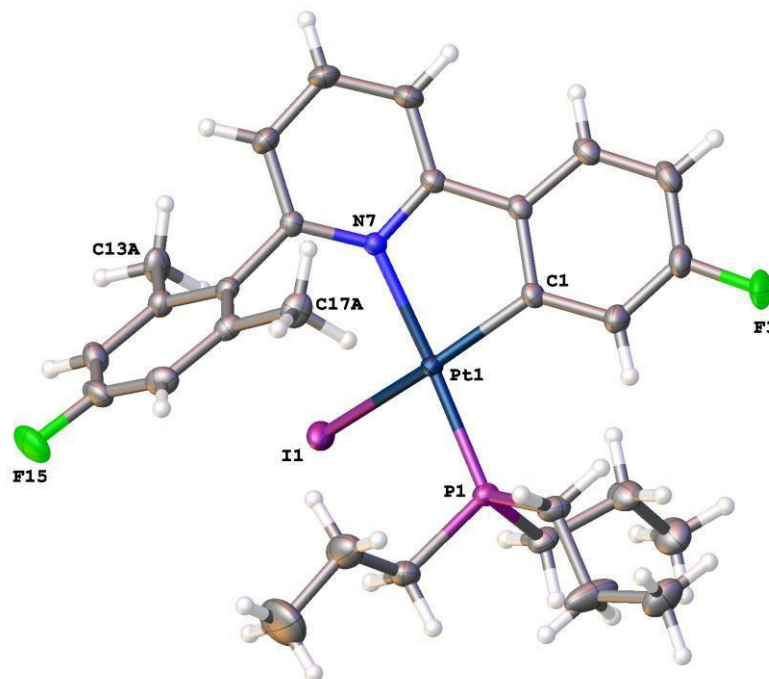


Figure 6: The solid-state structure of **Me2-6-Pr**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt1-I1 2.71245(16); Pt1-P1 2.2454(6); Pt1-C1 2.010(2); Pt1-N7 2.1324(17); P1-Pt1-I1 88.912(15); C1-Pt1-I1 152.99(6); C1-Pt1-P1 99.62(6); C1-Pt1-N7 80.30(7); N7-Pt1-I1 95.71(4); N7-Pt1-P1 169.77(5).

Conclusions

The oxidative addition of methyl iodide to square planar doubly cyclometallated C^N^C Pt(II) complexes gave octahedral Pt(IV) complexes from which it was possible to abstract the coordinated iodide and generate five-coordinate cations. In agreement with theory, these five-coordinate cations were long-lived. This property arises from the rigid C^N^C group, which renders them unable to easily access a geometry that allows the facile coupling of the introduced methyl group with the phenyl of the cyclometallated ligand. This reduced reactivity suggests the five-coordinate complexes have adopted a trigonal bipyramidal geometry, and this is backed up by NMR evidence.

It is therefore possible, by careful choice of ligand geometry, to generate unsaturated complexes, without additional ligand stabilisation, that are sufficiently long-lived that they can be studied in detail. It is also possible to exert some degree of control on the course of subsequent C-C coupling reactions, with our example showing 100% regioselectivity.

Table 1: Xray data

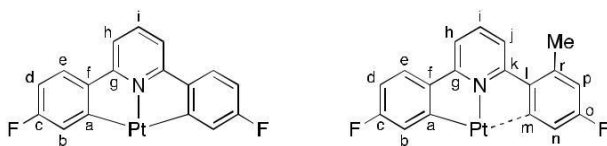
Compound	Me-1-Pr	2t-Pr	2c-Bu	Me-6-Pr	Me-6-Bu	Me2-6-Pr
Empirical formula	C ₂₇ H ₃₂ F ₂ NPt	C ₂₇ H ₃₃ F ₂ INPpt	C _{29.87} H _{38.6} F ₂ I _{1.13} NPt	C ₂₇ H ₃₃ F ₂ INPpt	C ₃₀ H ₃₉ F ₂ INPpt	C ₂₈ H ₃₅ F ₂ INPpt
Formula weight	634.59	762.50	819.53	762.50	804.58	776.53
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /n	P2 ₁ /n	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	9.9623(3)	12.70561(18)	10.2244(3)	17.1855(2)	17.9485(2)	8.56227(7)
b/Å	9.2215(3)	14.9295(3)	17.8517(5)	12.17889(16)	12.31107(18)	17.96588(15)
c/Å	27.2996(8)	13.7143(2)	16.3216(4)	13.62801(18)	13.88543(18)	18.24470(15)
α /°	90	90	90	90	90	90
β /°	100.217(3)	93.1156(13)	94.312(3)	106.9357(13)	110.0913(15)	96.9421(8)
γ /°	90	90	90	90	90	90
Volume/Å ³	2468.17(14)	2597.58(7)	2970.62(13)	2728.64(6)	2881.48(7)	2785.98(4)
Z	4	4	4	4	4	4
$\rho_{\text{calc}}/\text{cm}^3$	1.708	1.950	1.832	1.856	1.855	1.851
μ/mm^{-1}	5.780	6.682	5.987	19.291	6.029	6.232
F(000)	1248.0	1464.0	1584.0	1464.0	1560.0	1496.0
Crystal size/mm ³	0.4 × 0.08 × 0.03 yellow block	0.3 × 0.12 × 0.1 colourless block	0.45 × 0.45 × 0.3 colourless block	0.406 × 0.303 × 0.16 yellow block	0.2 × 0.2 × 0.18 yellow block	0.3 × 0.3 × 0.2 orange block
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	CuK α (λ = 1.54184)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.688 to 65.326	5.056 to 65.242	7.018 to 63.212	9.036 to 156.396	6.454 to 69.214	4.792 to 64.83
	-15 ≤ h ≤ 13	-18 ≤ h ≤ 19	-13 ≤ h ≤ 14	-21 ≤ h ≤ 21	-28 ≤ h ≤ 27	-12 ≤ h ≤ 12
Index ranges	-13 ≤ k ≤ 13	-12 ≤ k ≤ 22	-25 ≤ k ≤ 23	-15 ≤ k ≤ 14	-18 ≤ k ≤ 16	-27 ≤ k ≤ 26
	-41 ≤ l ≤ 39	-19 ≤ l ≤ 20	-24 ≤ l ≤ 22	-16 ≤ l ≤ 17	-22 ≤ l ≤ 21	-27 ≤ l ≤ 27
Reflections collected	24451	19825	34214	26064	56183	85124
Independent reflections	8370 [R _{int} = 0.0602, R _{sigma} = 0.0681]	8654 [R _{int} = 0.0297, R _{sigma} = 0.0414]	9116 [R _{int} = 0.0420, R _{sigma} = 0.0351]	5784 [R _{int} = 0.0576, R _{sigma} = 0.0366]	11614 [R _{int} = 0.0429, R _{sigma} = 0.0369]	9618 [R _{int} = 0.0428, R _{sigma} = 0.0258]
Data/restraints/parameters	8370/0/293	8654/0/302	9116/0/339	5784/0/302	11614/0/329	9618/0/312
Goodness-of-fit on F ²	1.155	1.149	1.043	1.068	1.067	1.054
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0535, wR ₂ = 0.1316	R ₁ = 0.0271, wR ₂ = 0.0672	R ₁ = 0.0342, wR ₂ = 0.0804	R ₁ = 0.0364, wR ₂ = 0.0989	R ₁ = 0.0295, wR ₂ = 0.0571	R ₁ = 0.0223, wR ₂ = 0.0413
Final R indexes [all data]	R ₁ = 0.0811, wR ₂ = 0.1525	R ₁ = 0.0381, wR ₂ = 0.0867	R ₁ = 0.0443, wR ₂ = 0.0856	R ₁ = 0.0380, wR ₂ = 0.1012	R ₁ = 0.0470, wR ₂ = 0.0652	R ₁ = 0.0306, wR ₂ = 0.0437
Largest diff. peak/hole / e Å ⁻³	1.72/-3.42	1.07/-1.99	1.70/-1.50	1.86/-2.05	2.00/-1.34	0.72/-0.84

Experimental

General

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 400, 500 or 600 MHz spectrometers and were recorded at room temperature, in chloroform, unless stated otherwise. ^1H and ^{13}C signals are referenced to external TMS, assignments being made with the use of decoupling, GOESY and COSY pulse sequences. ^{19}F and ^{31}P chemical shifts are quoted from the directly observed signals (referenced to external CFCl_3 and 85% H_3PO_4 , respectively). ^1H - ^{195}Pt correlation spectra were recorded using a variant of the HMBC pulse sequence and the ^{195}Pt chemical shifts reported are taken from these spectra (referenced to external Na_2PtCl_6). All elemental analyses were performed by Warwick Analytical Service. Starting platinum complexes **1** were prepared as previously reported.^{22a,22b}

The following labelling schemes were used for symmetrical and unsymmetrical complexes, as appropriate:



Synthesis of Complexes **2** and **Me-2**

100 mg of **1** or **Me-1** (**1-Pr**: 0.16 mmol; **1-Bu**: 0.15 mmol; **1-Bn**: 0.13 mmol; **Me-1-Pr**: 0.16 mmol) was dissolved in MeI (3 ml) and heated to reflux until full consumption of starting material was observed (**1-Pr**, **1-Bu** and **Me-1**: 1 hour; **1-Bn**: 2 days). The MeI was then removed under vacuum. The residue was then washed with acetone to give a pure mixture of **2t** and **2c**. Longer reaction times (**1-Pr**, **1-Bu** and **Me-1-Pr**: 3 days; **1-Bn**: 2 weeks) gave only **2c** as the product.

Yields (**2t** and **2c** mixture): **2-Pr**: 116 mg, 0.16 mmol, 95%; **2-Bu**: 112 mg, 0.15 mmol, 93%; **2-Bn**: 101 mg, 0.13 mmol, 85%; **Me-2-Pr**: 98 mg, 0.16 mmol, 80%. **2t-Pr** δ_{H} = 7.79 (1H, t, $^3J_{\text{H-H}}$ = 8.5 Hz, Hi), 7.71 (2H, dd, $^3J_{\text{H-H}}$ = 8.5 Hz, $^4J_{\text{H-F}}$ = 5.5 Hz, He), 7.48 (2H, dd, $^3J_{\text{H-H}}$ = 8.5 Hz, $^4J_{\text{H-H}}$ = 2 Hz, Ch), 7.22 (2H, dd, $^3J_{\text{H-F}}$ 10 Hz, $^4J_{\text{H-H}}$ = 2.5 Hz, $^3J_{\text{H-Pt}}$ = 23 Hz, Hb), 6.81 (2H, td, $^3J_{\text{H-H}}$ = $^3J_{\text{H-F}}$ = 8.5 Hz, $^4J_{\text{H-H}}$ = 2.5 Hz, Hd), 1.73 (6H, m, PCH_2CH_2), 2.45 (6H, m, PCH_2), 1.11 (9H, t, $^3J_{\text{H-H}}$ = 7 Hz, $\text{PCH}_2\text{CH}_2\text{Me}$), 1.02 (3H, d, $^3J_{\text{H-P}}$ = 3 Hz, $^1J_{\text{H-Pt}}$ = 67 Hz, PtMe) ppm.

δ_{C} = 3.55 (d, $^2J_{\text{C-P}}$ = 3 Hz, $^1J_{\text{C-Pt}}$ = 516 Hz, PtMe), 14.40 (d, $^3J_{\text{C-P}}$ = 14 Hz, $\text{PCH}_2\text{CH}_2\text{Me}$), 17.58 (d, $^2J_{\text{C-P}}$ = 5 Hz, $^3J_{\text{C-Pt}}$ = 11 Hz, PCH_2CH_2), 25.31 (d, $^1J_{\text{C-P}}$ = 36 Hz, $^2J_{\text{C-Pt}}$ = 23 Hz, PCH_2), 110.05 (d, $^2J_{\text{C-F}}$ = 22 Hz, Cd), 115.06 (d, $^6J_{\text{C-F}}$ = 4 Hz, $^3J_{\text{C-Pt}}$ = 21.5 Hz, Ch), 121.10 (d, $^2J_{\text{C-F}}$ = 18 Hz, $^2J_{\text{C-Pt}}$ = 36 Hz, Cb), 126.62 (d, $^3J_{\text{C-F}}$ = 9 Hz, $^3J_{\text{C-Pt}}$ = 24.5 Hz, Ce), 138.45 (s, Ci), 143.23

(m, Cf), 160.87 (s, $^2J_{C-Pt} = 39$ Hz, Cg), 161.48 (m, $^1J_{C-Pt} = 569$ Hz, Ca), 161.97 (d, $^1J_{C-F} = 254$ Hz, $^3J_{C-Pt} = 40$ Hz, Cc) ppm.

$\delta_F = -110.00$ ($^4J_{F-Pt} = 23$ Hz) ppm. $\delta_P = -22.45$ ($^1J_{P-Pt} = 2650$ Hz) ppm. $\delta_{Pt} = -3520$ ($^1J_{Pt-P} = \sim 2900$ Hz) ppm.

HR-MS (ESI): found 634.1934, calculated 634.1940 = $C_{27}H_{33}F_2PN^{194}Pt = [M-I]^+$.

Elemental analysis found (calculated): C 42.31 (42.53), H 4.27 (4.36), N 1.78 (1.84).

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 1 and Table 1; full details are in the SI.

2t-Bu $\delta_H = 7.71$ (1H, t, $^3J_{H-H} = 8$ Hz, Hi), 7.65 (2H, dd, $^3J_{H-H} = 8.5$ Hz, $^4J_{H-F} = 5.5$ Hz, He), 7.41 (2H, dd, $^3J_{H-H} = 8$ Hz, $^5J_{H-P} = 2$ Hz, Hh), 7.18 (2H, dd, $^3J_{H-F} = 9.5$ Hz, $^4J_{H-H} = 2.5$ Hz, $^3J_{H-Pt} = 22$ Hz, Hb), 6.74 (2H, td, $^3J_{H-H} = ^3J_{H-F} = 8.5$ Hz, $^4J_{H-H} = 2.5$ Hz, Hd), 2.43 (6H, m, PCH_2), 1.63 (6H, m, PCH_2CH_2), 1.46 (6H, m, $PCH_2CH_2CH_2$), 0.97 (3H, d, $^3J_{H-P} = 3$ Hz, $^2J_{H-Pt} = 67$ Hz, PtMe), 0.93 (9H, t, $^3J_{H-H} = 7$ Hz, $PCH_2CH_2CH_2Me$) ppm.

$\delta_C = 3.59$ (d, $^2J_{C-P} = 3$ Hz, $^1J_{C-Pt} = 515$ Hz, PtMe), 12.69 (s, $PCH_2CH_2CH_2Me$), 22.93 (m, $PCH_2, PCH_2CH_2CH_2$), 25.80 (d, $^2J_{C-P} = 5$ Hz, $^3J_{C-Pt} = 10$ Hz, C PCH_2CH_2), 110.06 (d, $^2J_{C-F} = 22$ Hz, Cd), 115.07 (d, $^4J_{C-P} = 4$ Hz, $^3J_{C-Pt} = 20$ Hz, Ch), 121.18 (d, $^2J_{C-F} = 19$ Hz, $^2J_{C-Pt} = 34$ Hz, Cb), 126.64 (d, $^3J_{C-P} = 9$ Hz, $^3J_{C-Pt} = 24$ Hz, Ce), 138.49 (s, Ci), 143.24 (t, $^3J_{C-P} = ^4J_{C-F} = 2$ Hz, $^2J_{C-Pt} = 13$ Hz, Cf), 160.85 (s, $^2J_{C-Pt} = 38$ Hz, Hg), 161.54 (m, $^1J_{C-Pt} = 572$ Hz, Ha), 161.95 (d, $^1J_{C-F} = 253$ Hz, $^3J_{C-Pt} = 38$ Hz, Cc) ppm.

$\delta_F = -109.50$ ($^4J_{F-Pt} = 22$ Hz) ppm. $\delta_P = -21.77$ ($^1J_{P-Pt} = 2644$ Hz) ppm. $\delta_{Pt} = -3517$ ($^1J_{Pt-P} = \sim 2650$ Hz) ppm.

HR-MS (ESI): found 676.2406, 826.1352, calculated 676.2410 = $C_{30}H_{39}F_2NP^{194}Pt = [M-I]^+$, 826.1352 = $C_{30}H_{39}F_2INP^{194}PtNa = [M+Na]^+$.

2t-Bn $\delta_H = 7.89$ (1H, t, $^3J_{H-H} = 8$ Hz, Hi), 7.80 (2H, dd, $^3J_{H-H} = 8.5$ Hz, $^4J_{H-F} = 5.5$ Hz, He), 7.59 (2H, dd, $^3J_{H-H} = 8$ Hz, $^5J_{H-P} = 2$ Hz, $^4J_{H-Pt} = 2$ Hz, Hh), 7.46 (2H, dd, $^3J_{H-F} = 9.5$ Hz, $^4J_{H-H} = 2$ Hz, $^3J_{H-Pt} = 25$ Hz, Hb), 7.29 (9H, m, Bn-*m,p*), 6.89 (2H, td, $^3J_{H-F} = ^3J_{H-H} = 8.5$ Hz, $^4J_{H-H} = 2$ Hz, Hd), 6.83 (6H, d, $^3J_{H-H} = 7.5$ Hz, Bn-*o*), 4.09 (6H, d, $^2J_{H-P} = 10$ Hz, $^3J_{H-Pt} = 20$ Hz, Bn CH_2), 1.31 (3H, d, $^3J_{H-P} = 3$ Hz, $^2J_{H-Pt} = 66$ Hz, PtMe) ppm.

$\delta_F = -109.13$ ($^4J_{F-Pt} = 22.5$ Hz) ppm. $\delta_P = -23.16$ ($^1J_{P-Pt} = 2648$ Hz) ppm. $\delta_{Pt} = -3436$ ($^1J_{Pt-P} = \sim 2700$ Hz) ppm.

2c-Pr $\delta_H = 7.80$ (1H, t, $^3J_{H-H} = 8$ Hz, Hi), 7.74 (2H, dd, $^3J_{H-H} = 8$ Hz, $^4J_{H-F} = 5.5$ Hz, He), 7.53 (2H, d, $^3J_{H-H} = 8$ Hz, Hh), 7.39 (2H, d, $^3J_{H-H} = 8.5$ Hz, $^3J_{H-Pt} = 23$ Hz, Hb), 6.82 (2H, t, $^3J_{H-H} = ^3J_{H-F} = 8$ Hz, Hd), 1.57 (3H, d, $^2J_{H-P} = 3.5$ Hz, $^1J_{H-Pt} = 62$ Hz, PtMe), 1.41 (6H, m, PCH_2), 1.01 (6H, m, PCH_2CH_2), 0.71 (9H, t, $^3J_{H-H} = 7$ Hz, PCH_2CH_2Me) ppm.

δ_C = -15.16 (d, $^2J_{C-P}$ = 5 Hz, $^1J_{C-Pt}$ = 502.5 Hz, PtMe), 15.54 (d, $^3J_{C-P}$ = 15 Hz, PCH₂CH₂Me), 16.52 (d, $^2J_{C-P}$ = 6 Hz, $^3J_{C-Pt}$ = 13 Hz, PCH₂CH₂), 23.09 (d, $^1J_{C-P}$ = 35 Hz, $^2J_{C-Pt}$ = 29 Hz, PCH₂), 111.52 (d $^2J_{C-F}$ = 23.5 Hz, C_d), 115.85 (s, $^3J_{C-Pt}$ = 16 Hz, C_h), 121.15 (d, $^2J_{C-F}$ = 17.5 Hz, $^2J_{C-Pt}$ = 25.5 Hz, C_b), 127.47 (d, $^3J_{C-F}$ = 8 Hz, $^3J_{C-Pt}$ = 23 Hz, C_e), 139.33 (s, C_i), 144.57 (m, C_f), 158.46 (m, $^1J_{C-Pt}$ = 540 Hz, C_a), 161.83 (s, $^2J_{C-Pt}$ = 33.5 Hz, C_g), 163.69 (d, $^1J_{C-F}$ = 256 Hz, $^3J_{C-Pt}$ = 39 Hz, C_c) ppm.

δ_F = -109.00 ($^4J_{F-Pt}$ = 23 Hz) ppm. δ_P = -18.35 ($^1J_{P-Pt}$ = 2482 Hz) ppm. δ_{Pt} = -3901 ($^1J_{Pt-P}$ = ~2730 Hz) ppm.

HR-MS (ESI): found 634.1941, calculated 634.1940 = C₂₇H₃₃F₂PN¹⁹⁴Pt = [M-I]⁺.

Elemental analysis found (calculated): C 42.00 (42.53), H 4.10 (4.36), N 1.74 (1.84).

2c-Bu δ_H = 7.83 (1H, t, $^3J_{H-H}$ = 8 Hz H_i), 7.76 (2H, dd, $^3J_{H-H}$ = 9 Hz, $^4J_{H-F}$ = 5 Hz, H_e), 7.56 (2H, d, $^3J_{H-H}$ = 8 Hz, H_h), 7.40 (2H, dd, $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz, $^3J_{H-Pt}$ = 23 Hz, H_b), 6.85 (2H, dt, $^3J_{H-F}$ = $^3J_{H-H}$ = 9 Hz, $^4J_{H-H}$ = 2 Hz, H_d), 1.59 (3H, d, $^3J_{H-P}$ = 4 Hz, $^3J_{H-Pt}$ = 62 Hz, PtMe), 1.47 (6H, m, PCH₂), 1.10 (6H, m, PCH₂CH₂CH₂), 0.95 (6H, m, PCH₂CH₂), 0.76 (9H, t, $^3J_{H-H}$ = 7 Hz, PCH₂CH₂CH₂Me) ppm.

δ_C = -16.06 (d, $^2J_{C-P}$ = 6 Hz, $^1J_{C-Pt}$ = 503 Hz, PtMe), 12.29 (s, PCH₂CH₂CH₂Me), 19.78 (d, $^1J_{C-P}$ = 35 Hz, $^2J_{C-Pt}$ = 29 Hz, PCH₂), 23.13 (d, $^3J_{C-P}$ = 13 Hz, PCH₂CH₂CH₂), 23.68 (d, $^2J_{C-P}$ = 5.5 Hz, $^3J_{C-Pt}$ = 11 Hz, PCH₂CH₂), 110.51 (d, $^2J_{C-F}$ = 22 Hz, C_d), 114.87 (s, $^3J_{C-Pt}$ = 16 Hz, C_h), 120.18 (d, $^2J_{C-F}$ = 17 Hz, $^2J_{C-Pt}$ = 25 Hz, C_b), 126.45 (d, $^3J_{C-P}$ = 8.5 Hz, $^3J_{C-Pt}$ = 22 Hz, C_e), 138.37 (s, C_i), 143.24 (m, C_f), 157.34 (m, $^1J_{C-Pt}$ = 541 Hz, H_a), 160.80 (s, $^2J_{C-Pt}$ = 29 Hz, H_g), 162.64 (d, $^1J_{C-F}$ = 259 Hz, $^3J_{C-Pt}$ = 39.5 Hz, C_c) ppm.

δ_F = -109.13 ppm ($^4J_{F-Pt}$ = 23 Hz) ppm. δ_P = -18.13 ppm ($^1J_{P-Pt}$ = 2456 Hz) ppm. δ_{Pt} = -3896 ppm ($^1J_{Pt-P}$ = ~3800 Hz) ppm.

HR-MS (ESI): found 676.2398, 826.1340, calculated 676.2410 = C₃₀H₃₉F₂NP¹⁹⁴Pt = [M-I]⁺, 826.1352 = C₃₀H₃₉F₂INNAP¹⁹⁴Pt = [M+Na]⁺.

Elemental analysis found (calculated): 45.96 (44.78), H 5.02 (4.89), N 1.70 (1.74).

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 2 and Table 1; full details are in the SI.

2c-Bn δ_H = 7.76 (2H, dd, $^3J_{H-H}$ = 9 Hz, $^4J_{H-F}$ = 5.5 Hz, H_e), 7.67 (1H, t, $^3J_{H-H}$ = 7.5 Hz, H_i), 7.48 (2H, dd, $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz, $^3J_{H-Pt}$ = 21 Hz, H_b), 7.41 (2H, d, $^3J_{H-H}$ = 7.5 Hz, H_h), 7.11 (3H, t, $^3J_{H-H}$ = 7.5 Hz, Bn-*p*), 6.98 (6H, t, $^3J_{H-H}$ = 7.5 Hz, Bn-*m*), 6.92 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 9 Hz, $^4J_{H-H}$ = 2 Hz, H_d), 5.84 (6H, d, $^3J_{H-H}$ = 7.5 Hz, Bn-*o*), 3.03 (6H, d, $^2J_{H-P}$ = 11 Hz, $^3J_{H-Pt}$ = 23 Hz, BnCH₂), 1.71 (3H, d, $^3J_{H-P}$ = 5 Hz, $^2J_{H-Pt}$ = 61 Hz, PtMe) ppm.

δ_C = -14.02 (d, $^2J_{C-P}$ = 5 Hz, $^1J_{C-Pt}$ = 503 Hz, PtMe), 28.13 (d, $^1J_{C-P}$ = 29 Hz, $^2J_{C-Pt}$ = 29 Hz, BnCH₂), 111.82 (d, $^2J_{C-F}$ = 25 Hz, C_d), 116.26 (s, $^3J_{C-Pt}$ = 16 Hz, C_h), 121.34 (d, $^2J_{C-F}$ = 17.5

Hz, $^2J_{C-Pt} = 22$ Hz, Cb), 127.24 (d, $^5J_{C-P} = 5$ Hz, Bn-*p*), 127.61 (d, $^3J_{C-F} = 8$ Hz, $^3J_{C-Pt} = 23$ Hz, Ce), 128.83, (d, $^4J_{C-P} = 1.5$ Hz, Bn-*m*), 130.08 (d, $^3J_{C-P} = 5$ Hz, Bn-*o*), 131.73 (d, $^2J_{C-P} = 10$ Hz, $^3J_{C-Pt} = 20$ Hz, Bn-*i*), 139.45 (s, Ci), 144.83 (s, $^2J_{C-Pt} = 42$ Hz, Cf), 158.44 (m, $^1J_{C-Pt} = 540$ Hz, Ca), 161.35 (s, $^2J_{C-Pt} = 30$ Hz, Cg), 163.96 (d, $^1J_{C-F} = 259$ Hz, $^3J_{C-F} = 39$ Hz, Cc) ppm. $\delta_F = -108.00$ ($^4J_{F-Pt} = 22.5$ Hz) ppm. $\delta_P = -23.19$ ($^1J_{P-Pt} = 2403$ Hz) ppm. $\delta_{Pt} = -3898$ ($^1J_{Pt-P} = \sim 2450$ Hz) ppm.

HR-MS (ESI): found 779.1920, 928.0864, calculated 778.1940 = $C_{39}H_{33}F_2NP^{194}Pt = [M-I]^+$, 928.0883 = $C_{39}H_{33}F_2NP^{194}PtNa = [M+Na]^+$.

Elemental analysis found (calculated): C 49.98 (51.67), H 3.42 (3.67), N 1.41 (1.54). **Me-2t-Pr** $\delta_H = 7.76$ (1H, t, $^3J_{H-H} = 8$ Hz, Hi), 7.73 (1H, m, Hj), 7.65 (1H, dd, $^3J_{H-H} = 8.5$, $^4J_{H-F} = 5.5$ Hz He), 7.46 (1H, dt, $^3J_{H-H} = 8$ Hz, $^4J_{H-H} = ^5J_{H-P} = 1.5$ Hz, Hh), 7.17 (1H, dd, $^3J_{H-F} = 9.5$ Hz, $^4J_{H-H} = 2.5$, $^3J_{H-Pt} = 21.5$ Hz, Hb), 7.07 (1H, dd, $^3J_{H-F} = 9.5$ Hz, $^4J_{H-H} = 2.5$, $^3J_{H-Pt} = 24.5$ Hz, Hn), 6.75 (1H, td, $^3J_{H-F} = ^3J_{H-H} = 9$ Hz, $^4J_{H-H} = 2.5$, Hd), 6.58 (1H, dd, $^3J_{H-F} = 9.5$ Hz, $^4J_{H-H} = 2.5$, Hp), 2.64 (3H, s, Me), 2.40 (6H, m, PCH_2), 1.67 (6H, m, PCH_2CH_2), 1.05 (9H, dt, $^3J_{H-H} = 7$ Hz, $^4J_{H-P} = 1$ Hz, PCH_2CH_2Me), 0.98 (3H, d, $^3J_{H-P} = 3$ Hz, $^2J_{H-Pt} = 67.5$ Hz, PtMe) ppm. $\delta_C = 4.30$ (d, $^2J_{C-P} = 3$ Hz, $^1J_{C-Pt} = 521.5$ Hz, PtMe), 14.43 (d, $^3J_{C-P} = 15$ Hz, PCH_2CH_2Me), 17.72 (d, $^2J_{C-P} = 5$ Hz, $^3J_{C-Pt} = 10$ Hz, PCH_2CH_2), 23.70 (s, Me), 25.36 (d, $^1J_{C-P} = 35$ Hz, $^2J_{C-Pt} = 22$ Hz, PCH_2), 110.03 (d, $^2J_{C-F} = 22.5$ Hz, Cd), 114.26 (d, $^2J_{C-F} = 20.5$ Hz, Cp), 114.89 (d, $^4J_{C-P} = 4$ Hz, $^3J_{C-Pt} = 21$ Hz, Ch), 119.02 (m, Cn_j), 121.00 (d, $^2J_{C-F} = 18$ Hz, $^2J_{C-Pt} = 33$ Hz, Cb), 126.73 (d, $^3J_{C-F} = 7.5$ Hz, $^2J_{C-Pt} = 23.5$ Hz, Ce), 138.28 (s, Ci), 139.23 (d, $^3J_{C-F} = 8$ Hz, $^3J_{C-Pt} = 25$ Hz, Cq), 141.83 (m, Cl), 143.50 (m, Cf), 160.73 (d, $^1J_{C-F} = 255$ Hz, $^3J_{C-Pt} = 43$ Hz, Co), 161.46 (s, $^2J_{C-Pt} = 39.5$, Cg/k), 161.94 (s, $^2J_{C-Pt} = 37$ Hz, Cg/k), 161.98 (d, $^2J_{C-F} = 254.5$, $^3J_{C-Pt} = 40$ Hz, Cc), 162.56 (m, $^1J_{C-Pt} = 561$ Hz, Ca), 163.68 (m, $^1J_{C-Pt} = 563$ Hz, Cm) ppm. $\delta_F = -109.60$ ($^4J_{F-Pt} = 24.5$ Hz, Fo), -112.18 ($^4J_{F-Pt} = 23$ Hz, Fc) ppm. $\delta_P = -21.56$ ($^1J_{P-Pt} = 2655$ Hz) ppm. $\delta_{Pt} = -3501$ ($^1J_{Pt-P} = \sim 3000$ Hz) ppm.

HR-MS (ESI): found 648.2094, 798.1028, calculated 648.2097 = $C_{28}H_{35}F_2PN^{194}Pt = [M-I]^+$, 798.1039 = $C_{28}H_{35}F_2PNI^{194}PtNa = [M+Na]^+$.

Elemental Analysis calculated (found): C 43.31 (43.24), H 4.54 (4.47), N 1.80 (1.76).

Me-2c-Pr $\delta_H = 7.84$ (2H, m, Hi_j), 7.76 (1H, dd, $^3J_{H-H} = 8.5$ Hz, $^4J_{H-F} = 5$ Hz, He), 7.58 (1H, dd, $^3J_{H-H} = 5.5$ Hz, $^4J_{H-H} = 3$ Hz, Hh), 7.40 (1H, dd, $^3J_{H-F} = 8.5$ Hz, $^4J_{H-H} = 3$ Hz, $^3J_{H-Pt} = 22$ Hz, Hb), 7.32 (1H, dd, $^3J_{H-F} = 7.5$ Hz, $^4J_{H-H} = 2.5$ Hz, $^3J_{H-Pt} = 25$ Hz, Hn), 6.84 (1H, td, $^3J_{H-H} = ^3J_{H-F} = 9$ Hz, $^4J_{H-H} = 2.5$ Hz, Hd), 6.67 (1H, dd, $^3J_{H-F} = 9.5$ Hz, $^4J_{H-H} = 2.5$ Hz, Hp), 2.74 (3H, s, Me), 1.55 (3H, d, $^3J_{H-P} = 4$ Hz, $^2J_{H-Pt} = 62$ Hz, PtMe), 1.41 (6H, m, PCH_2), 1.02 (6H, m, PCH_2CH_2), 0.73 (9H, t, $^3J_{H-H} = 7$ Hz, PCH_2CH_2Me) ppm.

δ_C = -14.22 (d, $^2J_{C-P}$ = 5 Hz, $^1J_{C-Pt}$ = 506 Hz, PtMe), 15.61 (d, $^3J_{C-P}$ = 15 Hz, PCH_2CH_2Me), 16.52 (d, $^2J_{C-P}$ = 5.5 Hz, $^3J_{C-Pt}$ = 12 Hz, PCH_2CH_2), 22.98 (d, $^1J_{C-P}$ = 35 Hz, $^2J_{C-Pt}$ = 29 Hz, PCH_2), 24.42 (s, Me), 111.50 (d, $^2J_{C-F}$ = 23.5 Hz, Cd), 115.62 (m, $C_{h,p}$), 118.67 (d, $^2J_{C-F}$ = 16 Hz, $^2J_{C-Pt}$ = 22 Hz, Cn), 119.87 (s, $^3J_{C-Pt}$ = 15 Hz, Cj), 120.96 (d, $^2J_{C-F}$ = 16 Hz, $^2J_{C-Pt}$ = 25 Hz, Cb), 125.52 (d, $^3J_{C-F}$ = 8.5 Hz, $^3J_{C-Pt}$ = 21 Hz, Ce), 139.09 (s, Ci), 140.35 (d, $^3J_{C-F}$ = 8.5 Hz, Cq), 143.28 (s, Ci), 144.71 (s, Cf), 159.33 (m, $^1J_{C-Pt}$ = 596 Hz, Ca), 160.14 (m, $^1J_{C-Pt}$ = 486 Hz, Cm), 162.31 (d, $^1J_{C-F}$ = 258 Hz, $^3J_{C-Pt}$ = 41 Hz, Co), 162.36 (s, $^2J_{C-Pt}$ = 29 Hz, Ck), 162.72 (s, $^2J_{C-Pt}$ = 29 Hz, Cg), 163.58 (d, $^1J_{C-F}$ = 255 Hz, $^3J_{C-Pt}$ = 41 Hz, Cc) ppm.

δ_F = -109.10 (s, $^4J_{F-Pt}$ = 22 Hz, Fc), -111.63 (s, $^4J_{F-Pt}$ = 23 Hz, Fo) ppm. δ_P = -18.22 ($^1J_{P-Pt}$ = 2520 Hz) ppm. δ_{Pt} = -3910 ($^1J_{Pt-P}$ = ~2550 Hz) ppm.

HR-MS (ESI): found 648.2082, 798.1030, calculated 648.2097 = $C_{28}H_{35}F_2NPt^{194}$ = $[M-I]^+$, 798.1039 = $C_{28}H_{35}F_2INP^{194}PtNa$ = $[M+Na]^+$.

Synthesis of Complexes 3, Me-3, Me-4 and Me2-4

To a suspension of 90 mg of **2** (**2-Pr**: 0.12 mmol; **2-Bu**: 0.11 mmol; **2-Bn**: 0.10 mmol; **Me-2-Pr**: 0.12 mmol), in acetone (5 ml), $AgBF_4$ (30-40 mg) was added. In the case of **2-Pr**, **Me-2-Pr** and **2-Bu**, **3** was characterised in solution before converting to **Me-4** or **Me2-4** (5 and 2 hours respectively). In the case of **2-Bn** conversion to **Me-4-Bn** was complete in less than 5 minutes. The reaction mixture was then filtered to remove AgI, and the solvent removed under vacuum to give **Me-4** and **Me2-4** without further purification.

3-Pr δ_H (Acetone- d_6) = 8.20 (1H, t, $^3J_{H-H}$ = 8 Hz, Hi), 8.10 (2H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 5.5 Hz, He), 8.05 (2H, d, $^3J_{H-H}$ = 8 Hz, Hh), 7.47 (2H, dd, $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2.5 Hz, $^3J_{H-Pt}$ = 21 Hz, Hb), 7.09 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2.5 Hz, Hd), 1.86 (6H, m, PCH_2), 1.60 (3H, s, $^2J_{H-Pt}$ = 55 Hz, PtMe), 1.20 (6H, m, PCH_2CH_2), 0.75 (9H, t, $^3J_{H-H}$ = 7 Hz, PCH_2CH_2Me) ppm.

δ_C (Acetone- d_6) = -4.37 (d, $^2J_{C-P}$ = 6 Hz, $^1J_{C-Pt}$ = 508 Hz, PtMe), 14.51 (d, $^3J_{C-P}$ = 15 Hz, PCH_2CH_2Me), 16.30 (d, $^2J_{C-P}$ = 5 Hz, $^3J_{C-Pt}$ = 15 Hz, PCH_2CH_2), 23.09 (d, $^1J_{C-P}$ = 42 Hz, $^2J_{C-Pt}$ = 34.5 Hz, PCH_2), 113.02 (d, $^2J_{C-F}$ = 23.5 Hz, Cd), 117.81 (s, $^3J_{C-Pt}$ = 14 Hz, Ch), 120.45 (d, $^2J_{C-F}$ = 18 Hz, $^2J_{C-Pt}$ = 27 Hz, Cb), 128.73 (d, $^3J_{C-F}$ = 8.5 Hz, $^3J_{C-Pt}$ = 21 Hz, Ce), 142.26 (s, Ci), 146.11 (m, Cf), 160.40 (m, Ca), 161.50 (s, $^2J_{C-Pt}$ = 29 Hz, Cg), 164.02 (d, $^1J_{C-F}$ = 256 Hz, $^3J_{C-Pt}$ = 39 Hz, Cc) ppm.

δ_F (Acetone- d_6) = -110.00 ($^4J_{F-Pt}$ = 19 Hz) ppm. δ_P (Acetone- d_6) = 1.89 ($^1J_{P-Pt}$ = 3076 Hz) ppm. $^1J_{Pt}$ (Acetone- d_6) = -2930 ($^1J_{Pt-P}$ = ~3300 Hz) ppm. HR-MS (ESI):

found 634.1938, calculated 634.1940 = $C_{27}H_{33}F_2PN^{194}Pt$ = $[M]^+$.

3-Bu δ_{H} (Acetone- d_6) = 8.08 (1H, t, $^3J_{\text{H-H}} = 8$ Hz, H_i), 7.99 (2H, dd, $^3J_{\text{H-H}} = 8.5$ Hz, $^4J_{\text{H-F}} = 5$ Hz, H_e), 7.94 (2H, $^3J_{\text{H-H}} = 8$ Hz, H_h), 7.35 (2H, dd, $^3J_{\text{H-H}} = 8.5$ Hz, $^4J_{\text{H-F}} = 3$ Hz, $^3J_{\text{H-Pt}} = 21$ Hz, H_b), 6.97 (2H, td, $^3J_{\text{H-H}} = ^3J_{\text{H-F}} = 8.5$ Hz, $^4J_{\text{H-H}} = 3$ Hz, H_d), 1.71 (6H, m, PCH_2), 1.48 (3H, s, $^2J_{\text{H-H}} = 55$ Hz, PtMe), 1.01 (6H, m, PCH_2CH_2), 0.77 (6H, m, $\text{PCH}_2\text{CH}_2\text{CH}_2$), 0.61 (9H, t, $^3J_{\text{H-H}} = 6.5$ Hz, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{Me}$) ppm.

δ_{F} (Acetone- d_6) = -110.05 ($^4J_{\text{F-Pt}} = 19$ Hz) ppm. δ_{P} (Acetone- d_6) = 2.54 ($^1J_{\text{P-Pt}} = 3115$ Hz) ppm.

δ_{Pt} (Acetone- d_6) = -3725 ($^1J_{\text{Pt-P}} = \sim 3150$ Hz) ppm.

Me-3-Pr δ_{H} (233K, Acetone- d_6) = 8.23 (2H, m, $\text{H}_{i,j}$), 8.16 (2H, m, $\text{H}_{e,h}$), 7.47 (1H, dd, $^3J_{\text{H-F}} = 8$ Hz, $^4J_{\text{H-H}} = 2$ Hz, $^3J_{\text{H-Pt}} = \sim 20$ Hz, H_b), 7.36 (1H, dd, $^3J_{\text{H-F}} = 7$ Hz, $^4J_{\text{H-H}} = 2$ Hz, $^3J_{\text{H-Pt}} = \sim 20$ Hz, H_n), 7.13 (1H, td, $^3J_{\text{H-F}} = 8.5$ Hz, $^4J_{\text{H-H}} = 2$ Hz, H_d), 7.01 (1H, dd, $^3J_{\text{H-F}} = 10$ Hz, $^4J_{\text{H-H}} = 2$ Hz, H_p), 2.82 (3H s, Me), 1.81 (6H, m, PCH_2), 1.52 (3H, s, $^2J_{\text{H-Pt}} = 53$ Hz, PtMe), 1.12 (6H, m, PCH_2CH_2), 0.70 (9H, t, $^3J_{\text{H-H}} = 7$ Hz, $\text{PCH}_2\text{CH}_2\text{Me}$) ppm.

δ_{C} (233K, Acetone- d_6) = -3.78 (s, $^1J_{\text{C-Pt}} = 521$ Hz, PtMe), 14.80 (d, $^3J_{\text{C-P}} = 18$ Hz, $\text{PCH}_2\text{CH}_2\text{Me}$), 16.30 (s, PCH_2CH_2), 23.55 (s, Me), 24.42 (d, $^1J_{\text{C-P}} = 42$ Hz, $^2J_{\text{C-Pt}} = 36$ Hz, PCH_2), 113.09 (d, $^2J_{\text{C-F}} = 23$ Hz, C_d), 116.75 (d, $^2J_{\text{C-F}} = 23$ Hz, C_p), 117.84 (m, $\text{C}_{h,n}$), 120.36 (d, $^2J_{\text{C-F}} = 18$ Hz, C_b), 121.92 (s, C_j), 128.93 (d, $^3J_{\text{C-F}} = 7$ Hz, C_e), 141.83 (d, $^3J_{\text{C-F}} = \text{Hz}$, C_q), 142.19 (s, C_i), 144.52 (s, C_i), 146.18 (C_f), 161.33 (m, $^1J_{\text{C-Pt}} = 530$ Hz, C_m), 161.55 (s, C_g), 161.71 (m, $^1J_{\text{C-Pt}} = 526$ Hz, C_a), 162.31 (s, $^2J_{\text{C-Pt}} = \text{Hz}$, C_k), 162.48 (d, $^1J_{\text{C-F}} = 256$ Hz, $^3J_{\text{C-Pt}} = 34$ Hz, C_o), 163.91 (d, $^1J_{\text{C-F}} = 255$ Hz, $^3J_{\text{C-Pt}} = 30$ Hz, C_c) ppm.

δ_{F} (Acetone- d_6) = -110.00 ($^4J_{\text{F-Pt}} = 18$ Hz), -112.33 ($^4J_{\text{F-Pt}} = 21$ Hz) ppm. δ_{P} (233K, Acetone- d_6) = 1.36 ($^1J_{\text{P-Pt}} = 3109$ Hz) ppm. δ_{Pt} (233K, Acetone- d_6) = -2971 ($^1J_{\text{Pt-P}} = \sim 3150$ Hz) ppm.

Me-4-Pr δ_{H} (Acetone- d_6) = 8.31 – 8.24 (2H, m, $\text{H}_{h,i}$), 7.99 (1H, dd, $^3J_{\text{H-H}} = 8.5$ Hz, $^4J_{\text{H-F}} = 6$ Hz, H_e), 7.77 (1H, dd, $^3J_{\text{H-H}} = 8.5$ Hz, $^4J_{\text{H-F}} = 6$ Hz, H_m), 7.61 (1H, dt, $^3J_{\text{H-H}} = 7$ Hz, $^4J_{\text{H-H}} = ^5J_{\text{H-P}} = 1.5$ Hz, H_j), 7.27 – 7.20 (2H, m, $\text{H}_{p,n}$), 7.05 (1H, td, $^3J_{\text{H-H}} = ^3J_{\text{H-F}} = 8.5$ Hz, $^4J_{\text{H-H}} = 2.5$ Hz, H_d), 7.01 (1H, dt, $^3J_{\text{H-F}} = 10$ Hz, $^4J_{\text{H-H}} = ^4J_{\text{H-P}} = 2.5$ Hz, H_b), 2.64 (3H, s, Me), 1.92 (6H, m, PCH_2), 1.66 (6H, m, PCH_2CH_2), 1.02 (9H, t, $^3J_{\text{H-H}} = 7.5$ Hz, $\text{PCH}_2\text{CH}_2\text{Me}$) ppm.

δ_{C} (Acetone- d_6) = 14.78 (d, $^3J_{\text{C-P}} = 15$ Hz, $\text{PCH}_2\text{CH}_2\text{Me}$), 18.12 (s, $^3J_{\text{C-Pt}} = 28$ Hz, PCH_2CH_2), 20.38 (s, Me), 24.60 (d, $^1J_{\text{C-P}} = 36$ Hz, $^2J_{\text{C-Pt}} = 36$ Hz, PCH_2), 112.05 (d, $^2J_{\text{C-F}} = 22$ Hz, C_d), 113.63 (d, $^2J_{\text{C-F}} = 22$ Hz, C_p), 117.73 (d, $^2J_{\text{C-F}} = 22$ Hz, C_n), 118.33 (s, $^3J_{\text{C-Pt}} = 20$ Hz, C_h), 121.47 (dd, $^2J_{\text{C-F}} = 21$ Hz, $^3J_{\text{C-P}} = 6$ Hz, C_b), 125.96 (d, $^4J_{\text{C-P}} = 3$ Hz, $^3J_{\text{C-Pt}} = 14$ Hz, C_j), 127.22 ($^2J_{\text{C-F}} = 10$ Hz, C_e), 128.91 (t, $^2J_{\text{C-P}} = ^3J_{\text{C-F}} = 7$ Hz, C_a), 132.46 (d, $^3J_{\text{C-F}} = 9$ Hz, C_m), 134.06 (d, $^4J_{\text{C-F}} = 3$ Hz, C_f), 139.13 (d, $^3J_{\text{C-F}} = 9$ Hz, C_q), 141.27 (s, C_i), 142.47 (d, $^4J_{\text{C-F}} = 2$ Hz, C_l), 158.83 (s, C_k), 162.10 (dd, $^1J_{\text{C-F}} = 253$ Hz, $^4J_{\text{C-P}} = 3$ Hz, C_c), 162.51 (d, $^4J_{\text{C-P}} = 4$ Hz, C_g), 163.27 (d, $^1J_{\text{C-F}} = 248$ Hz, C_o) ppm.

δ_F (Acetone- d_6) = -110.54 ($^4J_{F-Pt}$ = 61 Hz), -113.18 ppm. δ_P (Acetone- d_6) = 4.43 ($^1J_{P-Pt}$ = 4018 Hz) ppm. δ_{Pt} (Acetone- d_6) = -3829 ($^1J_{Pt-P}$ = ~4100 Hz) ppm. HR-MS (ESI): found 634.1940, calculated 634.1940 = $C_{27}H_{33}F_2PN^{194}Pt$ = $[M]^+$.

Me-4-Bu δ_H (Acetone- d_6) = 8.14 (2H, m, $H_{h,i}$), 7.85 (1H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-J}$ = 6 Hz, H_e), 7.66 (1H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-J}$ = 6 Hz, H_m), 7.49 (1H, d, $^3J_{H-H}$ = 7.5 Hz, H_j), 7.11 (2H, m, $H_{n,p}$), 6.91 (2H, m, $H_{b,d}$), 2.53 (3H, s, Me), 1.83 (6H, m, PCH_2), 1.50 (6H, m, PCH_2CH_2), 1.30 (6H, m, $PCH_2CH_2CH_2$), 0.77 (9H, t, $^3J_{H-H}$ = 7 Hz, $PCH_2CH_2CH_2Me$) ppm. δ_C (Acetone- d_6) = 12.95 (s, $PCH_2CH_2CH_2Me$), 20.47 (s, Me), 22.08 (d, $^1J_{C-P}$ = 38 Hz, $^2J_{C-Pt}$ = 38 Hz, PCH_2), 23.63 (d, $^3J_{C-P}$ = 14 Hz, $PCH_2CH_2CH_2$), 26.50 (d, $^2J_{C-P}$ = 2.5 Hz, $^3J_{C-Pt}$ = 21 Hz, PCH_2CH_2), 111.98 (d, $^2J_{C-F}$ = 23 Hz, C_d), 113.62 (d, $^2J_{C-F}$ = 23 Hz, C_n), 117.82 (d, $^2J_{C-F}$ = 22 Hz, C_p), 118.27 (s, C_h), 121.42 (dd, $^2J_{C-F}$ = 21.5 Hz, $^3J_{C-P}$ = 7 Hz, $^2J_{C-Pt}$ = ~120 Hz, C_b), 125.90 (d, $^4J_{C-P}$ = 3 Hz, C_j), 127.14 (d, $^3J_{C-F}$ = 8.5 Hz, C_e), 129.35 (m, C_a), 132.43 (d, $^3J_{C-F}$ = 8 Hz, C_m), 134.08 (s, C_i), 139.16 (d, $^3J_{C-F}$ = 8 Hz, C_q), 141.16 (s, C_i), 142.36 (s, C_g), 158.79 (s, C_k), 162.11 (dd, $^1J_{C-F}$ = 253 Hz, $^4J_{C-P}$ = 3 Hz, C_c), 162.58 (d, $^3J_{C-P}$ = 2.5 Hz, C_g), 163.33 (d, $^1J_{C-F}$ = 249 Hz, C_o) ppm.

δ_F (Acetone- d_6) = -110.62 ($^4J_{F-Pt}$ = 63 Hz), -113.04 ppm. δ_P (Acetone- d_6) = 5.69 ($^1J_{P-Pt}$ = 4042 Hz) ppm. δ_{Pt} (Acetone- d_6) = -3830 ($^1J_{Pt-P}$ = ~3950 Hz) ppm.

HR-MS (ESI): found 676.2409, calculated 676.2410 = $C_{30}H_{39}F_2NP^{194}Pt$ = $[M]^+$.

Me-4-Bn δ_H (Acetone- d_6) = 8.27 (2H, d, $^3J_{H-H}$ = 8 Hz, $H_{h,j}$), 8.01 (1H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 6 Hz, H_e), 7.67 (1H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 6 Hz, H_m), 7.58 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 7.31 (15H, m, $Bn-o,m,p$), 7.23 (1H, dd, $^3J_{H-F}$ = 10 Hz, $^4J_{H-H}$ = 2 Hz, H_p), 7.14 (1H, dt, $^3J_{H-F}$ = 10 Hz, $^4J_{H-H}$ = $^4J_{H-P}$ = 2.5 Hz, H_b), 7.07 (2H, m, $H_{d,n}$), 3.51 (6H, t, $^2J_{H-H}$ = $^2J_{H-P}$ = 12.5 Hz, $^3J_{H-Pt}$ = ~45 Hz, $BnCH_2$), 2.49 (3H, s, Me) ppm.

δ_C (Acetone- d_6) = 20.55 (s, Me), 29.40 (m, $BnCH_2$), 112.38 (d, $^2J_{C-F}$ = 22 Hz, C_d), 113.63 (d, $^2J_{C-F}$ = 19 Hz, C_n), 117.79 (d, $^2J_{C-F}$ = 25 Hz, C_p), 118.50 (s, C_h), 122.43 (dd, $^2J_{C-F}$ = 21 Hz, $^3J_{C-P}$ = 5 Hz, $^2J_{C-Pt}$ = ~90 Hz, C_b), 125.97 (d, $^5J_{C-P}$ = 3 Hz, C_i), 127.13 (d, $^5J_{C-P}$ = 3 Hz, $Bn-p$), 127.40 (d, $^3J_{C-F}$ = 9 Hz, C_e), 128.69 (s, $Bn-m$), 130.41 (d, $^3J_{C-P}$ = 6 Hz, $Bn-o$), 132.63 (d, $^3J_{C-F}$ = 8 Hz, C_m), 133.29 (d, $^2J_{C-P}$ = 5 Hz, $Bn-i$), 133.71 (d, $^4J_{C-F}$ = 2 Hz, C_l), 139.01 (d, $^3J_{C-F}$ = 8.5 Hz, C_q), 141.40 (s, C_j), 142.32 (d, $^4J_{C-F}$ = 2 Hz, C_f), 158.46 (s, H_k), 162.02 (dd, $^1J_{C-F}$ = 253 Hz, $^4J_{C-P}$ = 2 Hz, C_c), 162.55 (d, $^3J_{C-P}$ = 2.5 Hz, C_g), 163.04 (d, $^1J_{C-F}$ = 248 Hz, C_o) ppm.

δ_F (Acetone- d_6) = -109.44 ($^4J_{F-Pt}$ = 64 Hz), -112.64 ppm. δ_P (Acetone- d_6) = 9.40 ($^1J_{P-Pt}$ = 4200 Hz) ppm. δ_{Pt} (Acetone- d_6) = -3796 ($^1J_{Pt-P}$ = ~4250 Hz) ppm. HR-MS (ESI): found 778.1946, calculated 778.1940 = $C_{39}H_{33}F_2NP^{194}Pt$ = $[M]^+$.

Me2-4-Pr δ_H = 7.96 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 7.79 (1H, d, $^3J_{H-H}$ = 8 Hz, H_h), 7.54 (1H, dd, $^3J_{H-H}$ = 9 Hz, $^4J_{H-F}$ = 6.5 Hz, H_e), 7.06 (1H, d, $^3J_{H-H}$ = 8 Hz, H_j), 6.96 (2H, d, $^3J_{H-F}$ = 9 Hz, H_n),

6.93 (1H, td, $^3J_{H-F} = ^3J_{H-H} = 8.5$ Hz, $^4J_{H-H} = 2$ Hz, Hd), 6.72 (1H, dt, $^3J_{H-F} = 10$ Hz, $^4J_{H-H} = ^4J_{H-P} = 2$ Hz, Hb), 2.25 (6H, s, Me), 1.79 (6H, m, PCH₂), 1.49 (6H, m, PCH₂CH₂), 0.95 (9H, t, $^3J_{H-H} = 7.5$ Hz, PCH₂CH₂Me) ppm.

$\delta_C = 23.63$ (d, $^3J_{C-P} = 15.5$ Hz, PCH₂CH₂Me), 18.16 (d, $^2J_{C-P} = 2$ Hz, $^3J_{C-P} = 17$ Hz, PCH₂CH₂), 20.84 (s, Me), 24.20 (d, $^1J_{C-P} = 36.5$ Hz, $^2J_{C-Pt} = 48$ Hz, PCH₂), 112.05 (d, $^2J_{C-F} = 22.5$ Hz, Cd), 116.16 05 (d, $^2J_{C-F} = 20.5$ Hz, Cn), 118.13 (s, Hh), 121.77 (dd, $^2J_{C-F} = 21$ Hz, $^3J_{C-P} = 6$ Hz, Cb), 126.18 (d, $^4J_{C-P} = 4.5$ Hz, Cj), 126.42 (d, $^3J_{C-F} = 9$ Hz, Ce), 129.46 (t, $^2J_{C-P} = ^3J_{C-F} = 8$ Hz, $^1J_{C-Pt} = 686$ Hz, Ca), 131.70 (d, $^4J_{C-F} = 2.5$ Hz, Cl), 140.00 (d, $^3J_{C-F} = 8.5$ Hz, Cm), 140.31 (s, Ci), 141.79 (d, $^4J_{C-F} = 2.5$ Hz, Cf), 158.32 (s, Ck), 162.5 (dd, $^1J_{C-F} = 254$ Hz, $^4J_{C-P} = 2$ Hz, Cc), 163.10 (d, $^1J_{C-F} = 253$ Hz, Co), 163.65 (d, $^3J_{C-P} = 2.5$ Hz, Cg) ppm.

$\delta_F = -108.56, -108.58$ ($^4J_{F-Pt} = 57$ Hz) ppm. $\delta_P = 3.66$ ($^1J_{P-Pt} = 4148$ Hz) ppm. $\delta_{Pt} = -3903$ ($^1J_{Pt-P} = \sim 4300$ Hz) ppm.

HR-MS (ESI): found 648.2091, calculated 648.2097 = C₂₈H₃₅F₂PN¹⁹⁴Pt = [M]⁺.

Synthesis of Complexes 5 and Me-5

To a suspension of 10mg of **2** (**2-Pr**: 0.013 mmol; **2-Bn**: 0.011 mmol; **Me-2**: 0.013 mmol) in acetone (5 ml), an excess of pyridine was added (~10 mg). An excess of AgBF₄ (5-10 mg) was then added, resulting in immediate precipitation of AgI. After 30 min stirring, the mixture was filtered and the filtrate dispersed in 10 ml of dichloromethane. The pyridine was removed by washing with water. The organic layer was then dried with MgSO₄, and solvent removed under vacuum to give **5c-Pr**, **5c-Bn** and **Me-5-Pr**.

5t-Pr δ_H (Acetone-d₆) $\delta = 8.68$ (m, $^3J_{H-Pt} = 40$ Hz, Py-o), 7.61 (dd, $^3J_{H-F} = 9.5$ Hz, $^4J_{H-H} = 2.5$ Hz, Hb), 7.20 (td, $^3J_{H-F} = ^3J_{H-H} = 8.5$, $^4J_{H-H} = 2.5$ Hz, Hd), 2.50 (m, PCH₂), 1.70 (m, PCH₂CH₂), 1.06 (d, $^3J_{H-P} = 3.5$ Hz, $^2J_{H-Pt} = 66$ Hz, PtMe), 1.02 (td, $^3J_{H-H} = 7$ Hz, $^4J_{H-P} = 1$ Hz, PCH₂CH₂Me) ppm.

δ_F (Acetone-d₆) $\delta = -107.87$ ($^4J_{F-Pt} = 20.5$ Hz) ppm. δ_P (Acetone-d₆) $\delta = -16.74$ ($^1J_{P-Pt} = 2600$ Hz) ppm. δ_{Pt} (Acetone-d₆) $\delta = -2838$ ($^1J_{Pt-P} = \sim 3000$ Hz) ppm.

5c-Pr δ_H (Acetone-d₆) = 8.10 (1H, t, $^3J_{H-H} = 8$ Hz, Hi), 7.90 (2H, dd, $^3J_{H-H} = 8.5$ Hz, $^4J_{H-H} = 5$ Hz, He), 7.87 (2H, m, $^3J_{H-Pt} = 26$ Hz, Py-o), 7.80 (2H, d, $^3J_{H-H} = 8$ Hz, Hb), 7.70 (1H, t, $^3J_{H-H} = 7$ Hz, Py-p), 7.24 (2H, dd, $^3J_{H-F} = 8$ Hz, $^4J_{H-H} = 2.5$ Hz, $^3J_{H-Pt} = 20.5$ Hz, Hb), 7.15 (2H, t, $^3J_{H-H} = 7$ Hz, Py-o), 7.01 (2H, td, $^3J_{H-H} = ^3J_{H-F} = 8.5$ Hz, $^4J_{H-H} = 2.5$ Hz, Hd), 1.54 (6H, m, PCH₂), 1.16 (3H, d, $^3J_{H-P} = 2$ Hz, $^2J_{H-Pt} = 56$ Hz, PtMe), 0.99 (6H, m, PCH₂CH₂), 0.71 (9H, td, $^3J_{H-H} = 7$ Hz, $^4J_{H-P} = 1.5$ Hz, PCH₂CH₂Me) ppm.

δ_C (Acetone-d₆) = -5.18 (d, $^2J_{C-P} = 5.5$ Hz, $^1J_{C-Pt} = 538$ Hz, PtMe), 14.48 (d, $^3J_{C-P} = 16$ Hz, PCH₂CH₂Me), 15.71 (d, $^2J_{C-P} = 5.5$ Hz, $^3J_{C-Pt} = 11$ Hz, PCH₂CH₂), 23.72 (d, $^1J_{C-P} = 39$ Hz, $^2J_{C-Pt}$

$\text{Pt} = 28 \text{ Hz}$, PCH_2), 112.96 (d, $^2\text{J}_{\text{C-F}} = 22.5 \text{ Hz}$, C_d), 117.48 (s, $^3\text{J}_{\text{C-Pt}} = 14 \text{ Hz}$, C_h), 118.67 (d, $^2\text{J}_{\text{C-F}} = 18.5 \text{ Hz}$, $^2\text{J}_{\text{C-Pt}} = 18 \text{ Hz}$, C_b), 125.66 (d, $^4\text{J}_{\text{C-P}} = 3.5$, $^3\text{J}_{\text{C-Pt}} = 18.5 \text{ Hz}$, Py-m), 128.67 (d, $^3\text{J}_{\text{C-F}} = 8.5 \text{ Hz}$, $^3\text{J}_{\text{C-Pt}} = 17 \text{ Hz}$, C_e), 138.84 (s, Py-p), 141.78 (s, C_a), 143.47 (d, $^4\text{J}_{\text{C-F}} = 2.5 \text{ Hz}$, C_d), 148.09 (s, $^2\text{J}_{\text{C-Pt}} = 8.5 \text{ Hz}$, Py-o), 159.40 (m, $^1\text{J}_{\text{C-Pt}} = 547 \text{ Hz}$, C_a), 159.49 (s, $^2\text{J}_{\text{C-Pt}} = 30 \text{ Hz}$, C_g), 163.39 (d, $^1\text{J}_{\text{C-F}} = 260 \text{ Hz}$, $^3\text{J}_{\text{C-Pt}} = 38 \text{ Hz}$, C_c) ppm.

δ_{F} (Acetone- d_6) = -106.06 ($^4\text{J}_{\text{F-Pt}} = 20 \text{ Hz}$) ppm. δ_{P} (Acetone- d_6) = -9.05 ($^1\text{J}_{\text{P-Pt}} = 2645 \text{ Hz}$) ppm. δ_{Pt} (Acetone- d_6) = -3111 ($^1\text{J}_{\text{Pt-P}} = \sim 2850 \text{ Hz}$) ppm.

HR-MS (ESI): found 634.1940, 713.2371, calculated 634.1940 = $\text{C}_{27}\text{H}_{33}\text{F}_2\text{PN}^{194}\text{Pt} = [\text{M-Py}]^+$, 713.2362 = $\text{C}_{32}\text{H}_{38}\text{F}_2\text{PN}_2^{194}\text{Pt} = [\text{M}]^+$.

5c-Bn $\delta_{\text{H}} = 7.95$ (5H, m, $\text{H}_{i,e}$, Py-o), 7.79 (1H, t, $^3\text{J}_{\text{H-H}} = 8 \text{ Hz}$, Py-p), 7.66 (2H, d, $^3\text{J}_{\text{H-H}} = 8 \text{ Hz}$, H_h), 7.42 (2H, dd, $^3\text{J}_{\text{H-F}} = 8 \text{ Hz}$, $^4\text{J}_{\text{H-H}} = 2 \text{ Hz}$, $^3\text{J}_{\text{H-Pt}} = 16 \text{ Hz}$, H_b), 7.26 (2H, m, Py-m), 7.16 (5H, m, H_d , Bn-p), 7.03 (6H, t, $^3\text{J}_{\text{H-H}} = 7.5 \text{ Hz}$, Bn-m), 5.97 (6H, d, $^3\text{J}_{\text{H-H}} = 7.5 \text{ Hz}$, Bn-o), 3.25 (6H, d, $^2\text{J}_{\text{H-P}} = 11.5 \text{ Hz}$, $^3\text{J}_{\text{H-Pt}} = 21 \text{ Hz}$, BnCH_2), 1.43 (3H, d, $^3\text{J}_{\text{H-P}} = 2 \text{ Hz}$, $^2\text{J}_{\text{H-Pt}} = 56 \text{ Hz}$, PtMe) ppm.

$\delta_{\text{C}} = -4.08$ (d, $^2\text{J}_{\text{C-P}} = 6.5 \text{ Hz}$, PtMe), 29.19 (d, $^1\text{J}_{\text{C-P}} = 35 \text{ Hz}$, $^2\text{J}_{\text{C-Pt}} = 31 \text{ Hz}$, BnCH_2), 113.15 (d, $^2\text{J}_{\text{C-F}} = 23 \text{ Hz}$, C_d), 117.81 (s, C_h), 118.89 (d, $^2\text{J}_{\text{C-F}} = 17.5 \text{ Hz}$, $^2\text{J}_{\text{C-Pt}} = 17.5 \text{ Hz}$, C_b), 125.84 (d, $^4\text{J}_{\text{C-P}} = 2.5 \text{ Hz}$, $^3\text{J}_{\text{C-Pt}} = 17.5 \text{ Hz}$, Py-m), 126.94 (d, $^4\text{J}_{\text{C-P}} = 2.5 \text{ Hz}$, Bn-p), 128.27 (d, $^3\text{J}_{\text{C-P}} = 7 \text{ Hz}$, Bn-m), 128.87 (m, C_e , Bn-o), 129.71 (d, $^2\text{J}_{\text{C-P}} = 9 \text{ Hz}$, $^3\text{J}_{\text{C-Pt}} = 9 \text{ Hz}$, Bn-i), 139.10 (s, Py-p), 141.91 (s, Py-o), 144.05 (s, C_f), 148.17 (s, C_i), 158.91 (s, $^2\text{J}_{\text{C-Pt}} = 28 \text{ Hz}$, C_g), 159.24 (m, $^1\text{J}_{\text{C-Pt}} = 542 \text{ Hz}$, C_a), 163.57 (d, $^1\text{J}_{\text{C-F}} = 257 \text{ Hz}$, $^3\text{J}_{\text{C-Pt}} = 31 \text{ Hz}$, C_c) ppm.

$\delta_{\text{F}} = -105.29$ ($^4\text{J}_{\text{F-Pt}} = 19 \text{ Hz}$) ppm. $\delta_{\text{P}} = -13.24$ ($^1\text{J}_{\text{P-Pt}} = 2639 \text{ Hz}$) ppm. $\delta_{\text{Pt}} = -3086$ ($^1\text{J}_{\text{Pt-P}} = \sim 2600 \text{ Hz}$) ppm.

HR-MS (ESI): found 857.2369, calculated 857.2362 = $\text{C}_{44}\text{H}_{38}\text{F}_2\text{N}_2\text{P}^{194}\text{Pt} = [\text{M}]^+$. **Me-5t-Pr**

δ_{H} (Acetone- d_6) = 8.38 (2H, $^3\text{J}_{\text{H-H}} = 5.39 \text{ Hz}$, $^3\text{J}_{\text{H-Pt}} = \sim 16 \text{ Hz}$, Py-o), 7.59 (1H, m, H_b), 7.48 (1H, m, H_n), 7.18 (1H, td, $^3\text{J}_{\text{H-F}} = 8.5 \text{ Hz}$, $^4\text{J}_{\text{H-H}} = 2 \text{ Hz}$, H_d), 7.05 (1H, d, $^3\text{J}_{\text{H-F}} = 8.5 \text{ Hz}$, H_p), 2.81 (3H, s, Me), 2.47 (6H, m, PCH_2), 1.69 (6H, m, PCH_2CH_2), 1.40 (3H, s, $^2\text{J}_{\text{H-Pt}} = 57 \text{ Hz}$, PtMe) 1.01 (9H, t, $^3\text{J}_{\text{H-H}} = 7 \text{ Hz}$, $\text{PCH}_2\text{CH}_2\text{Me}$) ppm.

δ_{F} (Acetone- d_6) = -107.98 ($^4\text{J}_{\text{F-Pt}} = 21 \text{ Hz}$), -110.83 ($^4\text{J}_{\text{F-Pt}} = 21.5 \text{ Hz}$) ppm. δ_{P} (Acetone- d_6) = -16.78 ($^1\text{J}_{\text{P-Pt}} = 2589 \text{ Hz}$) ppm. δ_{Pt} (Acetone- d_6) = -2824 ($^1\text{J}_{\text{Pt-P}} = \sim 2600 \text{ Hz}$) ppm.

Me-5c-Pr $\delta_{\text{H}} = 8.14$ (1H, t, $^3\text{J}_{\text{H-H}} = 7.5 \text{ Hz}$, H_i), 8.04 (1H, d, $^3\text{J}_{\text{H-H}} = 7.5 \text{ Hz}$, H_j), 7.94 (3H, m, H_e , Py-o), 7.87 (1H, d, $^3\text{J}_{\text{H-H}} = 7.5 \text{ Hz}$, H_h), 7.79 (1 H, t, $^3\text{J}_{\text{H-H}} = 7.5 \text{ Hz}$, Py-p), 7.32 (1H, dd, $^3\text{J}_{\text{H-F}} = 8 \text{ Hz}$, $^4\text{J}_{\text{H-H}} = 2.5 \text{ Hz}$, $^3\text{J}_{\text{H-Pt}} = 16 \text{ Hz}$, H_b), 7.22 (3H, m, H_n , Py-m), 7.06 (1H, td, $^3\text{J}_{\text{H-H}} = 3\text{J}_{\text{H-F}} = 9 \text{ Hz}$, $^4\text{J}_{\text{H-H}} = 2.5 \text{ Hz}$, H_d), 6.87 (1H, dd, $^3\text{J}_{\text{H-F}} = 9.5 \text{ Hz}$, $^4\text{J}_{\text{H-H}} = 2 \text{ Hz}$, H_p), 2.79 (3H, s, Me), 1.58 (6H, m, PCH_2), 1.20 (3H, s, $^2\text{J}_{\text{H-Pt}} = 55.71 \text{ Hz}$, PtMe), 1.05 (6H, m, PCH_2CH_2), 0.77 (9H, t, $^3\text{J}_{\text{H-H}} = 7 \text{ Hz}$, $\text{PCH}_2\text{CH}_2\text{Me}$) ppm.

$\delta_F = -105.85$ ($^4J_{F-Pt} = 20$ Hz, F_c), -108.45 ($^4J_{Pt-F} = 22.5$ Hz, F_o) ppm. $\delta_P = -9.03$ ($^1J_{P-Pt} = 2666$ Hz) ppm. $\delta_{Pt} = -3122$ ($^1J_{Pt-P} = \sim 2850$ Hz) ppm.

HR-MS (ESI): found 648.2105, 727.2518, calculated 648.2096 = $C_{28}H_{35}F_2NP^{194}Pt = [M-Py]^+$, 727.2532 = $C_{33}H_{40}F_2N_2P^{194}Pt = [M]^+$.

Synthesis of Complexes Me-6 and Me2-6

NaI (10 mg) was added to an acetone solution (10 ml) of **Me-4** or **Me2-4** from above, and the mixture stirred (24 hr). Solvent was removed, leaving an orange oil. Purification by column chromatography on silica, loading and eluting with toluene gave the pure **Me-6** or **Me2-6**.

Yields: **Me-6-Pr**: 83 mg, 0.10 mmol, 95%; **Me-6-Bu**: 87 mg, 0.11 mmol, 97%; **Me-6-Bn**: 86 mg, 0.10 mmol, 95%; **Me2-6-Pr**: 88 mg, 0.12 mmol, 98%.

In a similar fashion chloride and bromide derivatives of **Me-6-Pr** were synthesised. **Me-6-Pr-I** δ_H (Acetone- d_6) = 8.08 (2H, m, $H_{i,j}$), 7.92 (1H, dd, $^3J_{H-H} = 8.5$ Hz, $^4J_{H-F} = 6$ Hz, H_e), 7.74 (1H, dd, $^3J_{H-H} = 8$ Hz, $^4J_{H-F} = 5.5$ Hz, H_m), 7.54 (1H, d, $^3J_{H-H} = 6.5$ Hz, H_b), 7.14 (1H, dt, $^3J_{H-F} = 10.5$ Hz, $^4J_{H-H} = ^4J_{H-P} = 2.5$ Hz, $^3J_{H-Pt} = 62$ Hz, H_b), 7.05 (2H, m, $H_{p,n}$), 6.98 (1H, td, $^3J_{H-H} = ^3J_{H-F} = 8.5$ Hz, $^4J_{H-H} = 2.5$ Hz, H_d), 2.60 (3H, s, Me), 2.15 (6H, m, PCH_2), 1.69 (6H, m, PCH_2CH_2), 0.99 (9H, t, $^3J_{H-H} = 7.5$ Hz, PCH_2CH_2Me) ppm.

δ_C (Acetone- d_6) = 14.96 (d, $^3J_{C-P} = 15$ Hz, PCH_2CH_2Me), 1.58 (s, $^3J_{C-Pt} = 30$ Hz, PCH_2CH_2), 21.5 (s, Me), 29.32 (m, PCH_2), 110.02 (d, $^2J_{C-F} = 23$ Hz, C_d), 111.71 (d, $^2J_{C-F} = 20$ Hz, C_n), 117.09 (m, $C_{j,p}$), 119.42 (dd, $^2J_{C-F} = 19$ Hz, $^3J_{C-P} = 5$ Hz, $^2J_{C-Pt} = 107$ Hz, C_b), 125.135 (d, $^4J_{C-P} = 2.5$ Hz, C_h), 126.67 (d, $^3J_{C-F} = 8$ Hz, $^3J_{C-Pt} = 48$ Hz, C_e), 133.25 (d, $^3J_{C-F} = 9$ Hz, C_m), 138.42 (s, C_i), 138.46 (s, C_l), 139.76 ($^3J_{C-F} = 8$ Hz, C_q), 142.35 (d, $^4J_{C-F} = 2$ Hz, C_i), 148.71 (t, $^3J_{C-P} = ^4J_{C-F} = 5$ Hz, $^1J_{C-Pt} = 1139$ Hz, C_a), 161.03 (s, C_g), 162.25 (dd, $^1J_{C-F} = 252$ Hz, $^4J_{C-P} = 2.5$ Hz, $^3J_{C-Pt} = 36$ Hz, C_c), 163.09 (d, $^3J_{C-P} = 3$ Hz, $^2J_{C-Pt} = 72$ Hz, C_g), 163.45 (d, $^1J_{C-P} = 246$ Hz, C_o) ppm.

δ_F (Acetone- d_6) = -112.40 ($^4J_{F-Pt} = 64$ Hz), -115.07 ppm. δ_P (Acetone- d_6) = -1.20 ($^1J_{P-Pt} = 4000$ Hz) ppm. δ_{Pt} (Acetone- d_6) = -3946 ($^1J_{Pt-P} = \sim 4000$ Hz) ppm.

HR-MS (ESI): found 634.1928, calculated 634.1940 = $C_{27}H_{33}F_2NP^{194}Pt = [M-I]^+$.

Elemental analysis found (calculated): C 43.20 (42.53), H 4.40 (4.36), N 1.76 (1.84).

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 3 and Table 1; full details are in the SI.

Me-6-Pr-Br δ_H (Acetone- d_6) = 8.07 (2H, m, $H_{h,i}$), 7.88 (1H, t, $^3J_{H-H} = ^4J_{H-F} = 6$ Hz, H_e), 7.57 (1H, t, $^3J_{H-H} = ^4J_{H-F} = 6$ Hz, H_m), 7.51 (1H, d, $^3J_{H-H} = 7$ Hz, H_j), 7.14 (1H, d, $^3J_{H-F} = 10$ Hz, $^3J_{H-Pt} = 65$ Hz, H_b), 6.97 (3H, m, $H_{d,n,p}$), 2.57 (3H, s, Me), 2.07 (6H, m, PCH_2), 1.65 (6H, m, PCH_2CH_2), 1.00 (9H, t, $^3J_{H-H} = 7$ Hz, PCH_2CH_2Me) ppm.

δ_{C} (Acetone- d_6) = 14.95 (d, $^3J_{\text{C-P}} = 16$ Hz, $\text{PCH}_2\text{CH}_2\text{Me}$), 18.38 (s, $^3J_{\text{C-Pt}} = 25$ Hz, PCH_2CH_2), 21.13 (s, Me), 27.43 (d, $^1J_{\text{C-P}} = 38$ Hz, $^2J_{\text{C-Pt}} = 38$ Hz, PCH_2), 109.85 (d, $^2J_{\text{C-F}} = 23.5$ Hz, Cd), 111.47 (d, $^2J_{\text{C-F}} = 21$ Hz, Cn), 116.61 (m, $\text{C}_{\text{p,h}}$), 120.42 (d, $^2J_{\text{C-F}} = 20$ Hz, $^2J_{\text{C-Pt}} = 102$ Hz, Cb), 125.10 (s Cj), 126.71 (d, $^3J_{\text{C-F}} = 9.5$ Hz, $^3J_{\text{C-Pt}} = 54$ Hz, Ce), 133.31 (d, $^3J_{\text{C-F}} = 9$ Hz, Cm), 137.75 (s, Ci), 138.76 (s, Ci), 139.58 (d, $^3J_{\text{C-F}} = 8.5$ Hz, Cq), 143.10 (s, Cf), 147.19 (m, Ca), 160.99 (s, Ck), 162.21 (d, $^1J_{\text{C-F}} = 250$ Hz, Cc), 163.02 (d, $^1J_{\text{C-F}} = 244$ Hz, Co), 163.74 (m, Cg) ppm.

δ_{F} (Acetone- d_6) = -112.83 ($^4J_{\text{F-Pt}} = 62$ Hz), -115.68 ppm. δ_{P} (Acetone- d_6) = -1.60 ($^1J_{\text{P-Pt}} = 4061$ Hz) ppm. δ_{Pt} (Acetone- d_6) = -3879 ($^1J_{\text{Pt-P}} = \sim 4100$ Hz) ppm.

HR-MS (ESI): found 634.1941, calculated 634.1940 = $\text{C}_{27}\text{H}_{33}\text{F}_2\text{NPt}^{194}\text{Pt} = [\text{M-Br}]^+$. **Me-6-Pr-Cl** ^1H (Acetone- d_6) δ = 8.09 (1H, t, $^3J_{\text{H-H}} = 8$ Hz, Hi), 8.03 (1H, d, $^3J_{\text{H-H}} = 8$ Hz, Hh), 7.85 (1H, dd, $^3J_{\text{H-H}} = 8.5$ Hz, $^4J_{\text{H-F}} = 6$ Hz, He), 7.46 (2H, m, H_{j,m}), 7.13 (1H, dt, $^3J_{\text{H-H}} = 10.5$ Hz, $^4J_{\text{H-H}} = ^4J_{\text{H-P}} = 5$ Hz, $^3J_{\text{H-Pt}} = 65$ Hz, Hb), 6.96 (2H, m, H_{n,p}), 6.91 (1H, td, $^3J_{\text{H-H}} = ^3J_{\text{H-F}} = 8.5$ Hz, $^4J_{\text{H-H}} = 2.5$ Hz, Hd), 2.54 (3H, s, Me), 1.99 (6H, m, PCH_2), 1.62 (6H, m, PCH_2CH_2), 0.99 (9H, t, $^3J_{\text{H-H}} = 7.5$ Hz, $\text{PCH}_2\text{CH}_2\text{Me}$) ppm.

^{13}C (Acetone- d_6) = 14.92 (d, $^3J_{\text{C-P}} = 15.5$ Hz, $\text{PCH}_2\text{CH}_2\text{Me}$), 18.17 (s, $^3J_{\text{C-Pt}} = 30.5$ Hz, PCH_2CH_2), 20.81 (s, Me), 26.12 (d, $^1J_{\text{C-P}} = 37.5$ Hz, $^2J_{\text{C-Pt}} = 37.5$ Hz, PCH_2), 109.67 (d, $^2J_{\text{C-F}} = 23.5$ Hz, Cd), 111.37 (d, $^2J_{\text{C-F}} = 21$ Hz, Cn), 116.32 (d, $^2J_{\text{C-F}} = 21$ Hz, Cp), 116.50 (s, $^4J_{\text{C-Pt}} = 20$ Hz, Ch), 121.03 (dd, $^2J_{\text{C-F}} = 19$ Hz, $^3J_{\text{C-P}} = 4$ Hz, $^2J_{\text{C-Pt}} = 96$ Hz, Cb), 125.08 (d, $^4J_{\text{C-P}} = 4.5$ Hz, $^4J_{\text{C-Pt}} = 17$ Hz, Cj), 126.73 (d, $^3J_{\text{C-F}} = 9.5$ Hz, $^3J_{\text{C-Pt}} = 46$ Hz, Ce), 133.00 (d, $^3J_{\text{C-F}} = 9$ Hz, Cm), 137.23 (d, $^4J_{\text{C-F}} = 3$ Hz, Ci), 138.95 (s, Ci), 139.25 (d, $^3J_{\text{C-F}} = 8.5$ Hz, Cq), 143.50 (d, $^4J_{\text{C-F}} = 3$ Hz, Cf), 146.79 (t, $^3J_{\text{C-F}} = ^2J_{\text{C-P}} = 7$ Hz, $^1J_{\text{C-Pt}} = 1081$ Hz, Ca), 160.84 (s, Ck), 162.40 (dd, $^1J_{\text{C-F}} = 251$ Hz, $^4J_{\text{C-P}} = 2.5$ Hz, Cc), 162.93 (d, $^1J_{\text{C-F}} = 244.5$ Hz, Co), 164.20 (d, $^3J_{\text{C-P}} = 3$ Hz, Cg) ppm. ^{19}F (Acetone- d_6) = -113.11 ($^4J_{\text{F-Pt}} = 64$ Hz), -116.05 ppm. ^{31}P (Acetone- d_6) = -1.10 ($^1J_{\text{P-Pt}} = 4083$ Hz) ppm. ^{195}Pt (Acetone- d_6) = -3847 ($^1J_{\text{Pt-P}} = \sim 4150$ Hz) ppm.

HR-MS (ESI): found 634.1940, calculated 634.1940 = $\text{C}_{23}\text{H}_{33}\text{F}_2\text{NPt}^{194}\text{Pt} = [\text{M-Cl}]^+$.

Me-6-Bu δ_{H} = 7.83 (1H, t, $^3J_{\text{H-H}} = 8$ Hz, Hi), 7.70 (2H, m, H_{h,m}), 7.64 (1H, dd, $^3J_{\text{H-H}} = 8$ Hz, $^4J_{\text{H-F}} = 5.5$ Hz, He), 7.29 (d, $^3J_{\text{H-H}} = 8$ Hz, Hj), 7.06 (1H, dt, $^3J_{\text{H-F}} = 10.5$ Hz, $^4J_{\text{H-H}} = ^4J_{\text{H-P}} = 2.5$ Hz, $^3J_{\text{H-Pt}} = 64$ Hz, Hb), 6.98 (1H, dd, $^3J_{\text{H-F}} = 10$ Hz, $^4J_{\text{H-H}} = 2.5$ Hz, Hp), 6.90 (2H, m, H_{d,n}), 2.60 (3H, s, Me), 2.08 (6H, m, PCH_2), 1.57 (6H, m, PCH_2CH_2), 1.40 (6H, m, $\text{PCH}_2\text{CH}_2\text{CH}_2$), 0.90 (9H, t, $^3J_{\text{H-H}} = 7.5$ Hz, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{Me}$) ppm.

δ_{C} = 13.69 (s, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 22.21 (s, Me), 24.00 (d, $^3J_{\text{C-P}} = 14$ Hz, $\text{PCH}_2\text{CH}_2\text{CH}_2$), 26.76 (d, $^1J_{\text{C-P}} = 38$ Hz, $^2J_{\text{C-Pt}} = 38$ Hz, PCH_2), 27.06 (s, $^3J_{\text{C-Pt}} = 24$ Hz, PCH_2CH_2), 110.31 (d, $^2J_{\text{C-F}} = 23$ Hz, Cd), 111.91 (d, $^2J_{\text{C-F}} = 21$ Hz, Cn), 116.48 (s, Ch), 117.55 (d, $^2J_{\text{C-F}} = 22$ Hz, Cp), 119.62 (dd, $^2J_{\text{C-F}} = 19$ Hz, $^3J_{\text{C-P}} = 5$ Hz, $^2J_{\text{C-Pt}} = 104$ Hz, Cb), 124.78 (d, $^4J_{\text{C-P}} = 4$ Hz, Cj),

126.09 (d, $^3J_{C-F} = 9$ Hz, C_p), 133.08 (d, $^3J_{C-F} = 9$ Hz, C_m), 137.52 (s, H_i), 138.19 (s, C_i), 139.65 (d, $^3J_{C-F} = 8$ Hz, C_q), 142.22 (s, C_f), 148.63 (t, $^2J_{C-P} = ^3J_{C-F} = 5$ Hz, $^1J_{C-Pt} = 1128$ Hz, H_a), 161.31 (s, C_k), 162.17 (dd, $^1J_{C-F} = 252$ Hz, $^4J_{C-P} = 4$ Hz, H_c), 163.31 (d, $^3J_{C-P} = 4$ Hz, C_g), 163.46 (d, $^1J_{C-F} = 250$ Hz, C_o) ppm.
 $\delta_F = -111.05$ ($^4J_{F-Pt} = 63$ Hz), -112.65 ppm. $\delta_P = -1.10$ ($^1J_{P-Pt} = 4005$ Hz) ppm. $\delta_{Pt} = -3967$ ($^1J_{Pt-P} = \sim 4050$ Hz) ppm.

HR-MS (ESI): found 676.2415, calculated 676.2410 = C₃₀H₃₉F₂NP¹⁹⁴Pt = [M-I]⁺.

Elemental analysis, expected (result): C 44.78 (44.99), H 4.89 (4.91), N 1.74 (1.65).

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 4 and Table 1; full details are in the SI.

Me-6-Bn $\delta_H = 7.79$ (1H, t, $^3J_{H-H} = 8$ Hz, H_i), 7.67 (1H, dd, $^3J_{H-H} = 9$ Hz, $^4J_{H-F} = 6$ Hz, H_m), 7.61 (1H, d, $^3J_{H-H} = 9$ Hz, H_h), 7.42 (1H, dd, $^3J_{H-H} = 9$ Hz, $^4J_{H-F} = 6$ Hz, H_e), 7.32 (6H, m, Bn-*o*), 7.24 (1H, d, $^3J_{H-H} = 9$ Hz, H_j), 7.12 (9H, m, Bn-*m,p*), 6.92 (1H, dd, $^3J_{H-F} =$ Hz, $^4J_{H-H} =$ Hz, H_p), 6.67 (1H, td, $^3J_{H-H} = ^3J_{H-F} = 8.5$ Hz, $^4J_{H-H} = 2.5$ Hz, H_n), 6.59 (1H, td, $^3J_{H-H} = ^3J_{H-F} = 8.5$ Hz, $^4J_{H-H} = 2.5$ Hz, H_n), 6.15 (1H, dt, $^3J_{H-F} = 10.5$ Hz, $^4J_{H-H} = ^4J_{H-P} = 2.5$ Hz, $^3J_{H-Pt} = \sim 60$ Hz, H_b), 3.45 (6H, m, BnCH₂)*, 2.55 (2H, s, Me) ppm.

*At 298 K, this peak has separated into 2 broad peaks, separated by 320 Hz, and FWHM 55 Hz. At 278 K the broad beaks have begun to show multiplicity as two triplets, now 423 Hz apart. At 333 K there is a single broad peak at 3.60 FWHM ~ 100 Hz.

$\delta_C = 21.07$ (s, Me), 31.15 (d, $^1J_{C-P} = 35$ Hz, $^2J_{C-Pt} = 35$ Hz, BnCH₂), 109.18 (d, $^2J_{C-F} = 23.5$ Hz, C_d), 110.80 (d, $^2J_{C-F} = 23.5$ Hz, C_n), 115.62 (s, C_h), 116.71 (d, $^2J_{C-F} = 21.5$ Hz, C_p), 119.16 (dd, $^2J_{C-F} = 20$ Hz, $^3J_{C-P} = 4$ Hz, $^2J_{C-Pt} = \sim 115$ Hz, C_b), 123.39 (d, $^4J_{C-P} = 5.5$ Hz, C_j), 124.05 (d, $^2J_{C-F} = 9$ Hz, C_e), 125.86 (d, $^5J_{C-P} = 2$ Hz, Bn-*p*), 127.32 (d, $^4J_{C-P} = 2.5$ Hz, Bn-*m*), 129.28 (d, $^3J_{C-P} = 7$ Hz, Bn-*o*), 131.60 (d, $^3J_{C-F} = 9$ Hz, C_m), 132.60 (d, $^2J_{C-P} = 6.5$ Hz, Bn-*i*), 136.56 (s, C_i), 136.69 (s, C_i), 138.68 (d, $^3J_{C-F} = 8$ Hz, C_q), 139.82 (s, C_f), 147.25 (dd, $^2J_{C-F} = 5.5$ Hz, $^3J_{C-P} = 3.5$ Hz, $^2J_{H-Pt} = 1140$ Hz, C_a), 159.83 (s, C_k), 160.66 (dd, $^1J_{C-F} = 254$ Hz, $^4J_{C-P} = 3$ Hz, C_c), 162.41 (d, $^3J_{C-P} = 3$ Hz, C_g), 162.51 (d, $^1J_{C-F} = 248$ Hz, C_o) ppm.

$\delta_F = -109.02$ ($^4J_{F-Pt} = 63$ Hz), -111.76 ppm. $\delta_P = -0.30$ ($^1J_{P-Pt} = 4180$ Hz) ppm. $\delta_{Pt} = -3857$ ($^1J_{Pt-P} = \sim 4150$ Hz) ppm.

HR-MS (ESI): found 778.1925, calculated 778.1940 = C₃₉H₃₃F₂NP¹⁹⁴Pt = [M-I]⁺.

Me2-6-Pr δ_H (Acetone-d₆) = 8.16 (2H, m, H_{h,i}), 7.94 (1H, dd, $^3J_{H-H} = 8.5$ Hz, $^4J_{H-F} = 6$ Hz, H_e), 7.30 (1H, d, $^3J_{H-H} = 8.1$ Hz, H_j), 7.09 (1H, dt, $^3J_{H-F} = 11$ Hz, $^4J_{H-H} = ^4J_{H-P} = 2.5$ Hz, $^3J_{H-Pt} = 66$ Hz, H_b), 6.96 (2H, td, $^3J_{H-H} = ^3J_{H-F} = 8.5$ Hz, $^4J_{H-H} = 2.5$ Hz, H_d), 6.79 (2H, d, $^3J_{H-F} = 8.5$ Hz, H_n), 2.40 (6H, s, Me), 2.13 (6H, m, PCH₂), 1.64 (6H, m, PCH₂CH₂), 0.95 (9H, t, $^3J_{H-H} = 7$ Hz, PCH₂CH₂Me) ppm.

δ_C (Acetone- d_6) = 15.09 (d, $^3J_{C-P}$ = 16 Hz, PCH_2CH_2Me), 18.58 (s, $^3J_{C-Pt}$ = 31 Hz, PCH_2CH_2), 22.00 (s, Me), 29.56 (m, PCH_2), 110.09 (d, $^2J_{C-F}$ = 21.5 Hz, C_c), 113.98 (d, $^2J_{C-F}$ = 21.5 Hz, C_o), 118.13 (s, C_h), 119.46 (dd, $^2J_{C-F}$ = 18.5 Hz, $^3J_{C-P}$ = 5 Hz, $^2J_{C-Pt}$ = 100 Hz, C_b), 126.41 (s, C_j), 126.93 (d, $^3J_{C-F}$ = 9.5 Hz, $^3J_{C-Pt}$ = 46 Hz, C_e), 137.43 (d, $^4J_{C-F}$ = 3 Hz, C_i), 139.03 (s, C_i), 140.25 (d, $^3J_{C-F}$ = 9 Hz, C_m), 142.21 (d, $^4J_{C-F}$ = 2 Hz, C_f), 149.84 (t, $^2J_{C-P}$ = $^3J_{C-F}$ = 5 Hz, $^1J_{C-Pt}$ = 1129 Hz, C_a), 160.37 (s, C_k), 162.50 (dd, $^1J_{C-F}$ = 3.5 Hz, $^4J_{C-P}$ = 253 Hz, C_c), 162.74 (d, $^1J_{C-F}$ = 244 Hz, C_o), 163.50 (m, C_g) ppm.

δ_F (Acetone- d_6) = -112.53 (broad peak FWHM 60Hz), -116.70 ppm. δ_P (Acetone- d_6) = -0.10 ($^1J_{P-Pt}$ = 4052 Hz) ppm. δ_{Pt} (Acetone- d_6) = -3957 ($^1J_{Pt-P}$ = ~4250 Hz) ppm. HR-MS (ESI): found 648.2093, calculated 648.2096 = $C_{28}H_{35}FNPt^{194}Pt = [M-I]^+$.

Elemental analysis result (expected): C 43.31 (42.29), H 4.54 (4.33), N 1.80 (1.69).

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 6 and Table 1; full details are in the SI.

Synthesis of Complex Me-1-Pr

To a solution of 100mg (0.13 mmol) **Me-4-Pr** in chloroform (10 ml), 2M K_2CO_3 (1 ml) was added. The mixture was left to stir (24 hr), and the chloroform layer separated from the aqueous layer. The organic solution was dried ($MgSO_4$) and solvent removed under vacuum. The crude product was then purified by column chromatography on silica, loading and eluting with toluene to give pure **Me-1-Pr** (76 mg, 0.12 mmol, 93%).

δ_H = 7.53 (1H, t, $^3J_{H-H}$ = 8 Hz, H_i), 7.41 (1H, d, $^3J_{H-H}$ = 8 Hz, H_j), 7.38 (1H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 5.5 Hz, H_e), 7.16 (1H, d, $^3J_{H-H}$ = 8 Hz, H_h), 7.14 (1H, dd, $^3J_{H-F}$ = 10 Hz, $^4J_{H-H}$ = 2.5 Hz, $^3J_{H-Pt}$ = 32 Hz, H_b), 7.07 (1H, dd, $^3J_{H-F}$ = 9 Hz, $^4J_{H-H}$ = 2 Hz, $^3J_{H-Pt}$ = 36 Hz, H_n), 6.65 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_d), 6.47 (1H, dd, $^3J_{H-F}$ = 10 Hz, $^4J_{H-H}$ = 2 Hz, H_p), 2.51 (3H, s, Me), 2.00 (6H, m, PCH_2), 1.58 (6H, m, PCH_2CH_2), 0.96 (9H, t, $^3J_{H-H}$ = 7.5 Hz, PCH_2CH_2Me) ppm.

δ_C = 14.70 (d, $^3J_{C-P}$ = 15 Hz, PCH_2CH_2Me), 17.63 (s, $^3J_{C-Pt}$ = 34 Hz, PCH_2CH_2), 23.45 (s, Me), 25.93 (d, $^1J_{C-P}$ = 36 Hz, $^2J_{C-Pt}$ = 34 Hz, PCH_2), 109.24 (d, $^2J_{C-F}$ = 23 Hz, C_d), 113.37 (d, $^4J_{C-P}$ = 3 Hz, $^3J_{C-Pt}$ = 26 Hz, C_j), 113.51 (d, $^2J_{C-F}$ = 22 Hz, C_p), 117.80 (d, $^4J_{C-P}$ = 3 Hz, $^3J_{C-Pt}$ = 26 Hz, C_h), 120.91 (dd, $^2J_{C-F}$ = 16 Hz, $^3J_{C-P}$ = 2 Hz, $^2J_{C-Pt}$ = 58 Hz, C_n), 122.88 (d, $^2J_{C-F}$ = 16.5 Hz, $^2J_{C-Pt}$ = 64 Hz, C_b), 124.97 (d, $^3J_{C-F}$ = 8.5 Hz, $^3J_{C-Pt}$ = 30 Hz, C_e), 137.47 (d, $^3J_{C-F}$ = 8 Hz, C_q), 138.47 (s, C_i), 144.79 (t, $^3J_{C-P}$ = $^4J_{C-F}$ = 2.5 Hz, $^2J_{C-Pt}$ = 35 Hz, C_l), 146.12 (t, $^3J_{C-P}$ = $^4J_{C-F}$ = 2.5 Hz, $^2J_{C-Pt}$ = 26 Hz, C_f), 162.11 (d, $^1J_{C-F}$ = 254 Hz, $^3J_{C-Pt}$ = 57 Hz, C_o), 163.28 (d, $^1J_{C-F}$ = 253 Hz, $^3J_{C-Pt}$ = 50 Hz, C_c), 164.44 (s, $^2J_{C-Pt}$ = 70 Hz, $C_{k/g}$), 164.68 (s, $^2J_{C-Pt}$ = 60 Hz, $C_{k/g}$), 168.94 (m, $^1J_{C-Pt}$ = 704 Hz, $C_{a/m}$), 169.40 (m, $^1J_{C-Pt}$ = 704 Hz, $C_{a/n}$) ppm.

$\delta_F = -111.01$ ($^4J_{F-Pt} = 24$ Hz, F_c), -113.45 ($^4J_{F-Pt} = 27.5$ Hz, F_o) ppm. $\delta_P = 2.70$ ($^1J_{P-Pt} = 3733$ Hz) ppm. $\delta_{Pt} = -4200$ ($^1J_{Pt-P} = \sim 3800$ Hz) ppm.

HR-MS (ESI): found 634.1940, calculated 634.1940 = $C_{27}H_{32}F_2PN^{194}Pt = [M]^+$.

Elemental analysis found (calculated): C 51.07 (51.10), H 5.05 (5.08), N 2.03 (2.21).

Crystals suitable for Xray analysis were grown by the slow evaporation of solvent from a chloroform solution, Figure 5 and Table 1; full details are in the SI.

Supporting Information

Full details and discussions of the Xray structures are available. CIF files are also available to download from the CCDC, reference numbers: .

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.

The authors declare no competing financial interests.

References

- (1) (a) Shilov, A. E.; Shul'pin, G. B., *Chem. Rev.* **1997**, *97*, 2879. (b) Goldman, A. S.; Goldberg, K. I., In *Activation and Functionalization of C-H Bonds*, Goldberg, K. I.; Goldman, A. S., Eds. ACS: Washington DC, 2004; Vol. ACS Symposium Series vol 885. (c) Colby, D. A.; Bergman, R. G.; Ellman, J. A., *Chem. Rev.* **2010**, *110*, 624. (d) Wencel-Delord, J.; Droge, T.; Liu, F.; Glorius, F., *Chem. Soc. Rev.* **2011**, *40*, 4740. (e) Hashiguchi, B. G.; Bischof, S. M.; Konnick, M. M.; Periana, R. A., *Acc. Chem. Res.* **2012**, *45*, 885. (f) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F., *Angew. Chem., Int. Ed.* **2012**, *51*, 10236. (g) Hartwig, J. F.; Larsen, M. A., *ACS Cent. Sci.* **2016**, *2*, 281. (h) Labinger, J. A.; Bercaw, J. E., *Nature* **2002**, *417*, 507.
- (2) Lersch, M.; Tilset, M., *Chem. Rev.* **2005**, *105*, 2471.
- (3) (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H., *Science* **1998**, *280*, 560. (b) Caballero, A.; Perez, P. J., *Chem. Soc. Rev.* **2013**, *42*, 8809.
- (4) (a) Scott, J. D.; Puddephatt, R. J., *Organometallics* **1983**, *2*, 1643. (b) Roselló-Merino, M.; Rivada-Wheelaghan, O.; Ortuño, M. A.; Vidossich, P.; Díez, J.; Lledós, A.; Conejero, S., *Organometallics* **2014**, *33*, 3746. (c) Rivada-Wheelaghan, O.; Roselló-Merino, M.; Díez, J.; Maya, C.; López-Serrano, J.; Conejero, S., *Organometallics* **2014**, *33*, 5944. (d) Campos, J.; Ortega-Moreno, L.; Conejero, S.; Peloso, R.; López-Serrano, J.; Maya, C.; Carmona, E., *Chem. Eur. J.* **2015**, *21*, 8883. (e) Werlé, C.; Bailly, C.; Karmazin-Brelot, L.; Le Goff, X.-F.; Ricard, L.; Djukic, J.-P., *J. Am. Chem. Soc.* **2013**, *135*, 17839. (f) Crosby, S. H.; Clarkson, G. J.; Rourke, J. P., *J. Am. Chem. Soc.* **2009**, *131*, 14142.

- (5) (a) Hill, G. S.; Yap, G. P. A.; Puddephatt, R. J., *Organometallics* **1999**, *18*, 1408. (b) Zhao, S. B.; Wu, G.; Wang, S., *Organometallics* **2008**, *27*, 1030. (c) Grice, K. A.; Scheuermann, M. L.; Goldberg, K. I., *Top. Organomet. Chem.* **2011**, *35*, 1. (d) Vigalok, A., *Acc. Chem. Res.* **2015**, *48*, 238.
- (6) Rendina, L. M.; Puddephatt, R. J., *Chem. Rev.* **1997**, *97*, 1735.
- (7) (a) Forniés, J.; Martín, A.; Navarro, R.; Sicilia, V.; Villarroja, P., *Organometallics* **1996**, *15*, 1826. (b) Shaw, P. A.; Phillips, J. M.; Newman, C. P.; Clarkson, G. J.; Rourke, J. P., *Chem. Commun.* **2015**, *51*, 8365. (c) Shaw, P. A.; Phillips, J. M.; Clarkson, G. J.; Rourke, J. P., *Dalton Trans.* **2016**, 11397.
- (8) (a) Rivada-Wheelaghan, O.; Ortuño, M. A.; Díez, J.; García-Garrido, S. E.; Maya, C.; Lledós, A.; Conejero, S., *J. Am. Chem. Soc.* **2012**, *134*, 15261. (b) Crosby, S. H.; Clarkson, G. J.; Deeth, R. J.; Rourke, J. P., *Dalton Trans.* **2011**, *40*, 1227.
- (9) (a) Tatsumi, K.; Hoffman, R.; Yamamoto, A.; Stille, J. K., *Bull. Chem. Soc. Jpn* **1981**, *54*, 1857. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M. H., *Orbital Interactions in Chemistry*. Wiley and Sons Inc: 1985.
- (10) (a) Bowes, E. G.; Pal, S.; Love, J. A., *J. Am. Chem. Soc.* **2015**, *137*, 16004. (b) Zucca, A.; Maidich, L.; Canu, L.; Petretto, G. L.; Stoccoro, S.; Cinellu, M. A.; Clarkson, G. J.; Rourke, J. P., *Chem. Eur. J.* **2014**, *20*, 5501.
- (11) Madison, B. L.; Thyme, S. B.; Keene, S.; Williams, B. S., *J. Am. Chem. Soc.* **2007**, *129*, 9538.
- (12) Ariaifard, A.; Ejehi, Z.; Sadrara, H.; Mehrabi, T.; Etaati, S.; Moradzadeh, A.; Moshtaghi, M.; Nosrati, H.; Brookes, N. J.; Yates, B. F., *Organometallics* **2011**, *30*, 422.
- (13) Albrecht, M., *Chem. Rev.* **2009**, *110*, 576.
- (14) Omae, I., *Curr. Org. Chem.* **2014**, *18*, 2776.
- (15) (a) Minghetti, G.; Stoccoro, S.; Cinellu, M. A.; Soro, B.; Zucca, A., *Organometallics* **2003**, *22*, 4770. (b) Minghetti, G.; Stoccoro, S.; Cinellu, M. A.; Petretto, G. L.; Zucca, A., *Organometallics* **2008**, *27*, 3415. (c) Crosby, S. H.; Clarkson, G. J.; Rourke, J. P., *Organometallics* **2011**, *30*, 3603.
- (16) (a) Albrecht, M.; Dani, P.; Lutz, M.; Spek, A. L.; Koten, G. v., *J. Am. Chem. Soc.* **2000**, *122*, 11822. (b) Ryabov, A. D.; Yatsimirsky, A. K., *Inorg. Chem.* **1984**, *23*, 789. (c) Ryabov, A. D., *Inorg. Chem.* **1987**, *26*, 1252.
- (17) (a) Omae, I., *Coord. Chem. Rev.* **2004**, *248*, 995. (b) Jenkins, D. M.; Bernhard, S., *Inorg. Chem.* **2010**, *49*, 11297. (c) Omae, I., *Coord. Chem. Rev.* **2016**, *310*, 154.
- (18) (a) Butschke, B.; Schroöder, D.; Schwarz, H., *Organometallics* **2009**, *28*, 4340. (b) Crespo, M.; Martínez, M.; Nabavizadeh, S. M.; Rashidi, M., *Coord. Chem. Rev.* **2014**, *279*, 115. (c) Anderson, C. M.; Greenberg, M. W.; Spano, L.; Servatius, L.; Tanski, J. M., *J. Organomet. Chem.* **2016**, *819*, 27. (d) Nahaei, A.; Rasekh, A.; Rashidi, M.; Hosseini, F. N.; Nabavizadeh, S. M., *J. Organomet. Chem.* **2016**, *815–816*, 35. (e) Juliá, F.; González-Herrero, P., *J. Am. Chem. Soc.* **2016**, *138*, 5276.
- (19) (a) Crosby, S. H.; Clarkson, G. J.; Deeth, R. J.; Rourke, J. P., *Organometallics* **2010**, *29*, 1966. (b) Thomas, H. R.; Deeth, R. J.; Clarkson, G. J.; Rourke, J. P., *Organometallics* **2011**, *30*, 5641.
- (20) (a) Newman, C. P.; Casey-Green, K.; Clarkson, G. J.; Cave, G. W. V.; Errington, W.; Rourke, J. P., *Dalton Trans.* **2007**, 3170. (b) Mamtora, J.; Crosby, S. H.; Newman, C. P.; Clarkson, G. J.; Rourke, J. P., *Organometallics* **2008**, *27*, 5559.
- (21) (a) Crosby, S. H.; Thomas, H. R.; Clarkson, G. J.; Rourke, J. P., *Chem. Commun.* **2012**, *48*, 5775. (b) Crosby, S. H.; Clarkson, G. J.; Rourke, J. P., *Organometallics* **2012**, *31*, 7256.
- (22) (a) Cave, G. W. V.; Alcock, N. W.; Rourke, J. P., *Organometallics* **1999**, *18*, 1801. (b) Cave, G. W. V.; Fanizzi, F. P.; Deeth, R. J.; Errington, W.; Rourke, J. P.,

- Organometallics* **2000**, *19*, 1355. (c) Newman, C. P.; Cave, G. W. V.; Wong, M.; Errington, W.; Alcock, N. W.; Rourke, J. P., *J. Chem. Soc., Dalton Trans.* **2001**, 2678.
- (23) Crespo, M.; Anderson, C. M.; Kfoury, N.; Font-Bardia, M.; Calvet, T., *Organometallics* **2012**, *31*, 4401.
- (24) (a) Labinger, J. A., *Organometallics* **2015**, *34*, 4784. (b) Crespo, M.; Puddephatt, R. J., *Organometallics* **1987**, *6*, 2548.
- (25) Lohr, T. L.; Piers, W. E.; Sgro, M. J.; Parvez, M., *Dalton Trans.* **2014**, *43*, 13858.
- (26) Newman, C. P.; Deeth, R. J.; Clarkson, G. J.; Rourke, J. P., *Organometallics* **2007**, *26*, 6225.
- (27) Bilbrey, J. A.; Kazez, A. H.; Locklin, J.; Allen, W. D., *J. Comput. Chem.* **2013**, *34*, 1189.
- (28) (a) Bröring, M.; Kleeberg, C., *Z. Anorg. Allg. Chem.* **2007**, *633*, 2210. (b) Štěpnička, P.; Solařová, H.; Císařová, I., *J. Organomet. Chem.* **2011**, *696*, 3727. (c) Szyszko, B.; Latos-Grażyński, L.; Szterenberg, L., *Angew. Chem., Int. Ed.* **2011**, *50*, 6587. (d) Andrew, R. E.; Chaplin, A. B., *Dalton Trans.* **2014**, *43*, 1413.