Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

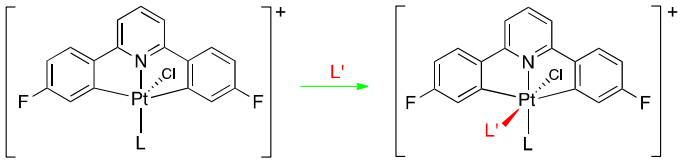
www.rsc.org/dalton

Trapping Five-Coordinate Platinum(IV) Intermediates

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

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

Abstract



The oxidation of three different complexes of the doubly cycloplatinated 2,6-di(4-fluorophenyl)pyridine ligand (namely DMSO, PPh_3 and PPr_3 derivatives, **1a**, **1b** and **1c**, respectively) with the electrophilic oxidant iodobenzenedichloride was studied. In each case oxidation can yield a simple *trans*-dichloro platinum(IV) complex (**2t)**, which subsequently isomerises to the *cis* isomer (**2c**). However, by changing the solvent, or performing the reaction in the presence of an additional ligating species, a five-coordinate intermediate can be trapped out and isolated. Thus, cationic species with additional DMSO or pyridine coordinated could be collected for the DMSO and PPh_3 derivatives. The PPr_3 derivative traps out the reactive five-coordinate species with an agostic interaction that subsequently induces a transcyclometallation reaction to give a complex with a singly cyclometallated pyridine and a cyclometallated phosphine, which was characterised crystallographically, (**6c(c)**).

Introduction

As part of the effort to realise a practical method of selective C-H functionalisation of hydrocarbons,[1] organometallic platinum complexes have been extensively studied.[2] In part this is due to their amenability to study, but it is also due to their relevance to actual processes and their ability to activate methane.[3] Probably the most important 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]

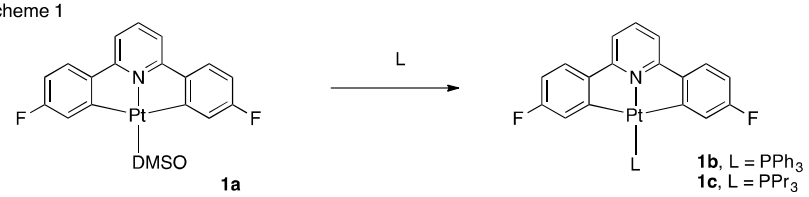
In particular, the importance of five-coordinate intermediates in the concerted reductive elimination process from six coordinate octahedral complexes is well known and is directly relevant to platinum. The rapid reductive elimination from an unsaturated intermediate has been rationalised theoretically,[6] 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,[7] with this factor over-riding the perceived kinetic preference for elimination of sp^2 carbons rather than sp^3.[8] 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.[9] Five-coordinate Pd(IV) complexes have also been shown to activate C-H bonds.[10]

Typically, five-coordinate complexes are generated via the abstraction of a halide, usually with a silver salt, from a six-coordinate platinum (IV) starting material, but in principle, could also be generated via the addition of a single group to a four-coordinate platinum (II) complex, as part of a electrophilic oxidative addition process.[11] Though bona fide stable five-coordinate platinum complexes have been identified under a variety of circumstances,[5b] they have not been successfully characterised during the process of halogen oxidation.[12] Here, we report on the trapping of the five-coordinate complexes that arise through oxidative addition and the characterisation of these complexes.

Results and Discussion

Starting from the previously[13] reported C^N^C DMSO complex (**1a**), we were able to synthesise two further derivatives with the fourth ligand being PPr_3 or PPh_3 (**1b** and **c**, respectively), Scheme 1.

Scheme 1



The single crystal Xray structures of **1b** and **1c** are reported here for the first time, Table 1 and Figures 1 and 2. The oxidation of each of the complexes **1** with iodobenzenedichloride is rapid, taking place in less than one minute, even at temperatures as low as -60 °C. In each case the mechanism of oxidation appears to be the same, that is the expected S_N2 type process for electrophilic reagents.[11-12] This process takes place via a two step mechanism: the initial delivery of a Cl^+ to give a five-coordinate complex, with subsequent addition of a sixth ligand (normally Cl^-). By changing the fourth ligand in complexes **1**, we are able to trap the five-coordinate intermediate and hence change the course of the reaction.

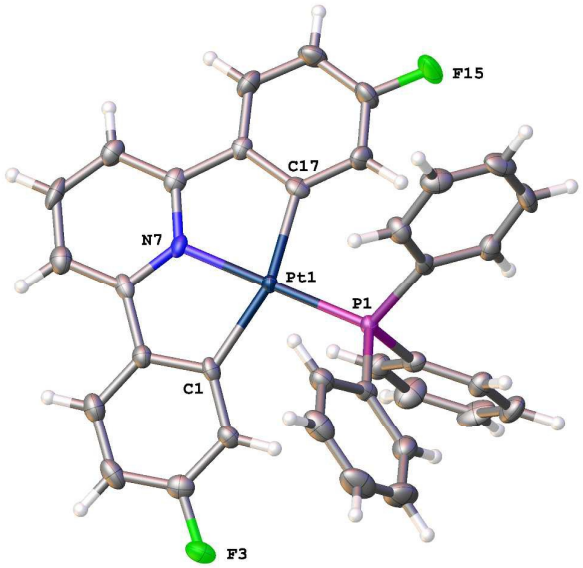


Figure 1: The solid-state structure of **1b**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)-N(7) 2.018(3); Pt(1)-C(1) 2.067(3); Pt(1)-C(17) 2.072(3); Pt(1)-P(1) 2.2294(8); C(1)-C(6) 1.424(4); C(6)-C(7) 1.464(5); N(7)-C(11) 1.350(4); N(7)-C(7) 1.360(4); C(11)-C(12) 1.474(4); C(12)-C(17) 1.420(4); N(7)-Pt(1)-C(1); 80.40(12); N(7)-Pt(1)-C(17) 79.90(11); C(1)-Pt(1)-C(17) 159.24(12); N(7)-Pt(1)-P(1) 178.57(7); C(1)-Pt(1)-P(1) 99.71(9); C(17)-Pt(1)-P(1) 100.15(9); C(6)-C(1)-Pt(1) 111.9(2); C(11)-N(7)-C(7) 123.6(3).

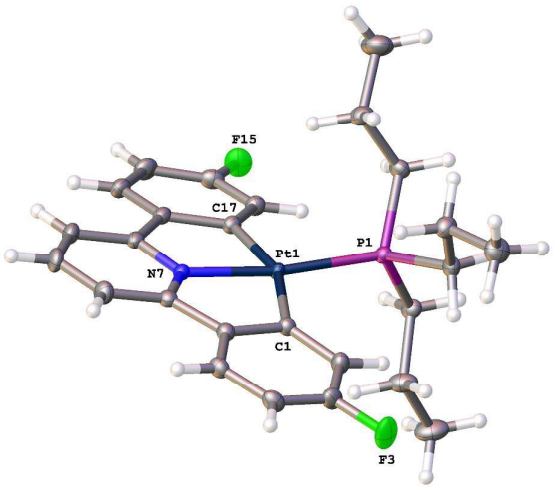
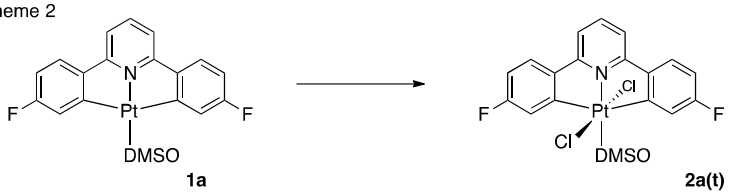


Figure 2: The solid-state structure of **1c**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): C1-Pt1 2.0758(19); P1-Pt1 2.2288(5); Pt1-N7 2.0204(17); Pt1-C17 2.0771(19); C7-N7-Pt1 118.31(13); C7-N7-C11 122.82(18); C6-C1-Pt1 112.20(14); C11-N7-Pt1 118.36(13); C1-Pt1-P1 102.99(6); C1-Pt1-C17 159.00(8); N7-Pt1-C1 79.72(7); N7-Pt1-P1-171.97(5); N7-Pt1-C17-79.96(7); C17-Pt1-P1 97.86(6); C12-C17-Pt1 112.04(14); C16-C17-Pt1 132.48(15).

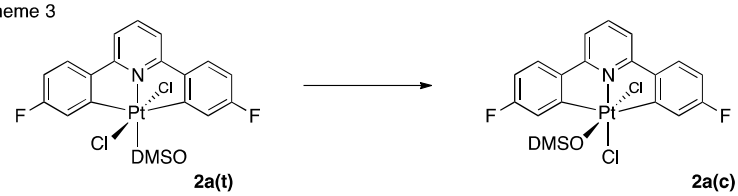
When the fourth ligand is DMSO, i.e. complex **1a**, the reaction proceeds smoothly and cleanly at -40 °C giving the *trans* product, **2a(t)**, Scheme 2.

Scheme 2



The product was identified as this isomer on the basis of solution NMR data (in particular NOE measurements indicated close proximity of the DMSO hydrogens and the H ortho to both Pt and F), and the solving of the single crystal Xray structure, Figure 3. Solutions of **2a(t)** slowly isomerise to the *cis* isomer, Scheme 3, taking around a week for the reaction to go to completion, at room temperature; we were able to crystalise this isomer too, Figure 4. DFT calculations indicate a small (~4 kJmol^{-1}) thermodynamic preference for the *cis* over the *trans*, presumably related to the reduction in steric crowding around the DMSO that accompanies the isomerisation.

Scheme 3



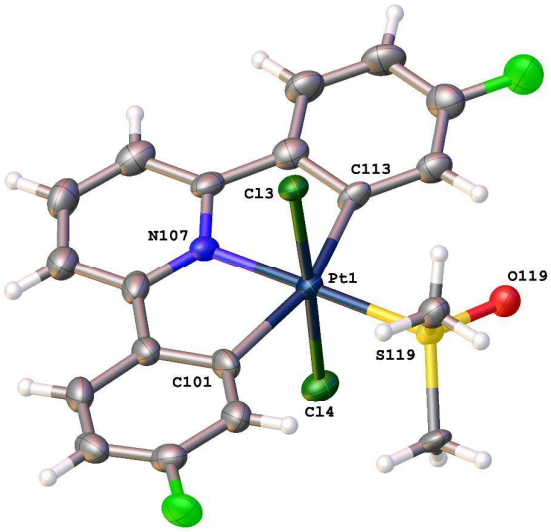


Figure 3: The solid-state structure of **2a(t)**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)-N(107) 2.012(7); Pt(1)-C(113) 2.082(8); Pt(1)-C(101) 2.148(8); Pt(1)-S(119) 2.2891(19); Pt(1)-Cl(3) 2.3265(19); Pt(1)-Cl(4) 2.339(2); N(107)-Pt(1)-C(113) 80.2(3); N(107)-Pt(1)-C(101) 80.8(3); C(113)-Pt(1)-C(101) 160.9(3); N(107)-Pt(1)-S(119) 178.1(2); C(113)-Pt(1)-S(119) 99.2(2); C(101)-Pt(1)-S(119) 99.9(3); Cl(3)-Pt(1)-Cl(4) 177.72(7).

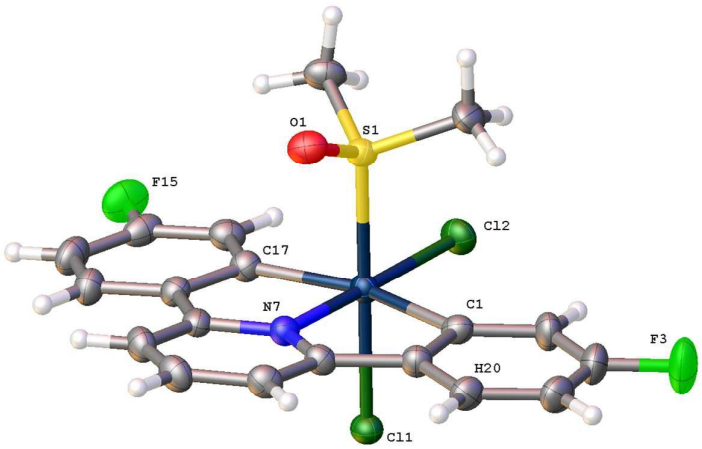
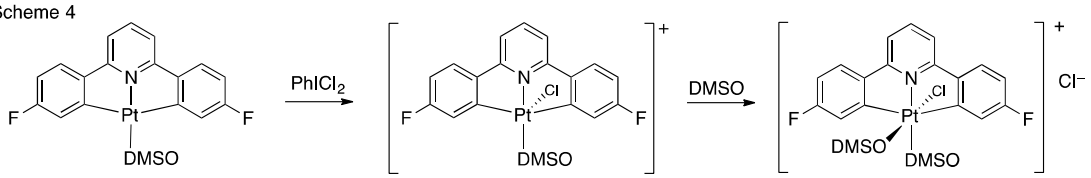


Figure 4: The solid-state structure of **2a(c)**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): C1-Pt1 2.084(5); Cl1-Pt1 2.3367(11); C7-N7 1.353(5); O1-S1-1.465(3); Pt1-S1-2.2752(11); N7-C11 1.364(6); Pt1-Cl6 2.3381(11); Pt1-N7 1.988(4); Pt1-C17 2.080(5); S1-C18 1.766(5); S1-C19 1.772(5); C1-Pt1-Cl1 88.64(13); C1-Pt1-S1 90.83(12); C1-Pt1-Cl6 98.86(13); Cl1-Pt1-Cl6 91.32(4); S1-Pt1-Cl1 178.98(4); S1-Pt1-Cl6 89.63(4); N7-Pt1-C1 81.03(16); N7-Pt1-Cl1 89.69(11); N7-Pt1-S1 89.36(11); N7-Pt1-Cl6 178.98(10); N7-Pt1-C17 81.24(16); C17-Pt1-C1 162.13(19); C17-Pt1-Cl1 89.14(13); C17-Pt1-S1 91.10(13); C17-Pt1-Cl6 98.91(13).

We can account for the initial formation of a *trans* product on the basis of an initial delivery of Cl^+ on one face of the square planar Pt(II) centre followed by the subsequent delivery of a Cl^- to the opposite face, with no rearrangement of the existing ligands. It is, however possible

to trap out a derivative of this five-coordinate intermediate. When we perform the oxidation of **1a** in acetone, in the presence of additional DMSO, a significant (>30%) proportion of the sample precipitates as a salt, identified as containing two DMSO ligands, **4a**, Scheme 4.

Scheme 4

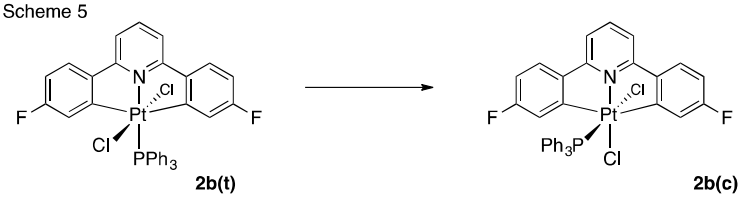


1a **3a** **4a**

Complex **4a** can be redissolved in chloroform and characterised in solution whereupon the formulation depicted can be deduced (in particular ESI mass-spectrometry clearly identifies the composition of the cation, and ^{1}H NMR clearly identifies two different DMSO molecules coordinated the same Pt centre), but we were unable to fully characterise or crystalise the complex as it converts to a mixture of *cis* and *trans* **2a** on a timescale of hours at room temperature.

Turning to the triphenylphosphine complex **1b**, oxidation at -40 °C in acetone results in the clean formation of the *trans* complex **2b(t)** which we were able to isolate and fully characterise. Like its DMSO analogue, this *trans* complex also isomerised to a *cis* complex **2b(c)** on a timescale of days at room temperature, Scheme 5. It is possible to assign *cis* and *trans* geometries to the isomers of **2b** on the basis of spectroscopic data, in particular NMR data that relates to the ^{1}H signal of the hydrogen ortho to both the F and the Pt. Thus this signal is substantially shielded by the proximal PPh_3 group in the *trans* isomer, resonating at 6.58 ppm in **2b(t)** (compare with 5.80 ppm for **1c**) but deshielded and resonating at 7.73 ppm in **2b(c)** when it this located away from the PPh_3 group. NOE measurements also confirm the assignment of *cis* and *trans* geometries.

Scheme 5



2b(t) **2b(c)**

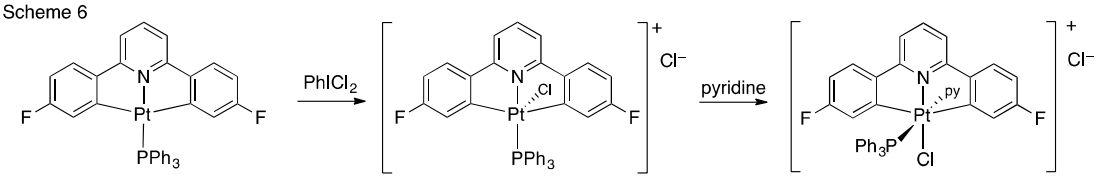
However, oxidation of the triphenylphosphine complex **1b** at -40 °C in chloroform results in clean formation of a different platinum(IV) complex, one that we were unable to isolate. Upon warming up towards room temperature, this new complex began to transform into the *trans* complex **2b(t)** and thence into the *cis* complex **2b(c)**.

This initial product of oxidation is clearly a Pt(IV) species (^{195}Pt shift of -2339 ppm, a ^{31}P-^{195}Pt coupling constant of 2806 Hz) and symmetrical (a single ^{19}F resonance, with satellites, with the appropriate pattern of ^{1}H signals, resembling that of **1b**, **2b(t)** or **2b(c)**). We believe

the evidence points to it being the five-coordinate cationic intermediate, **3b**, potentially stabilised by solvent or water. It should be noted that we found no evidence for coordinated solvent or water by NMR, even when we cooled to -60 °C, a temperature at which we might expect any fluxionality or ligand exchange to have been frozen out.[14] We can justify the identification of this complex in chloroform, but not in acetone, as arising from the superior solvation of the chloride anion by chloroform.[15] Coupling this factor with the large steric bulk of the triphenylphosphine ligand, which will hinder the combination of the platinum centre with the final chloride, suggests why we were able to identify this intermediate.

The intermediate **3b** will persist in chloroform solution for a matter of hours at low temperature and we thus sought to trap it out as a cation with another neutral ligand to give a complex like **4a**. We unable to do so with acetonitrile or DMSO but successful when excess pyridine was added, Scheme 6.

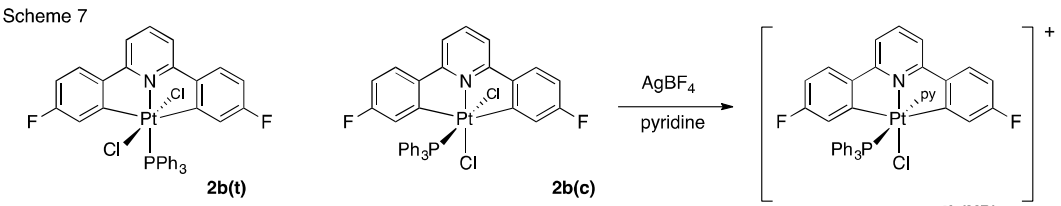
Scheme 6



1b **3b** **4b(NP)t**

Thus another new complex, with the same pattern of NMR resonances, but with the addition of pyridine signals (including clear satellites on the hydrogens adjacent to the nitrogen), could be isolated. The relative positions of the pyridine and phosphine ligands could be determined by NOE measurements and its cationic nature was apparent from the intensity of the ion in the electrospray mass spectrometry. Addition of excess pyridine to a solution of **1b** in chloroform before oxidation gives rise to the same pyridine adduct directly. We also sought to generate this pyridine complex by the treatment of **2b(c)** and **2b(t)** (separately) with $AgBF_4$ in acetone solution, in the presence of pyridine, and indeed we were able to isolate the same material in both cases, Scheme 7.

Scheme 7

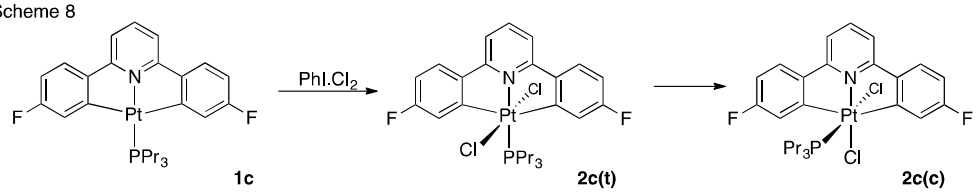


2b(t) **2b(c)** **4b(NP)t**

Finally, the oxidation of the tripropylphosphine complex **1c** is more complicated than that of either the DMSO complex **1a** or the triphenylphosphine complex **1b**, but again a five-coordinate intermediate can be trapped out. Complex **1c** does, however, follow a similar path to that of the analogous tributylphosphine complex, as reported by us earlier.[16] Thus, when the tripropylphosphine complex **1c** is oxidised at -40 °C in acetone, the reaction gives the

trans Pt(IV) product **2c(t)**, with none of the *cis* isomer **2c(c)** to which it subsequently slowly isomerises to, Scheme 8.

Scheme 8



Both *cis* and *trans* **2c** products were characterised in solution, and **2c(c)** was further fully characterised, including by crystalography, Figure 5. Heating of **2c(c)** does not result in further reaction. A trace amount of another product is also observed at -40 °C in acetone, and the formation of this can be favoured with the use of a different solvent.

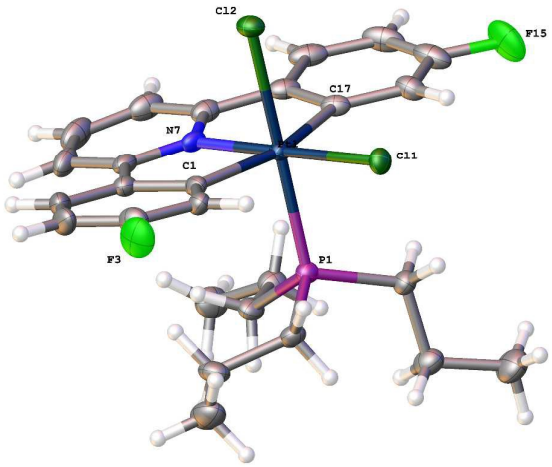
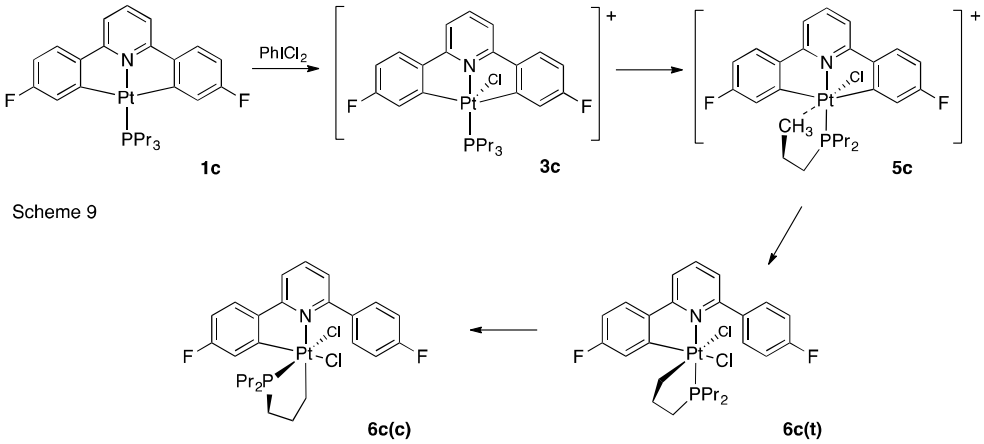


Figure 5: The solid-state structure of **2c(c)**, thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pt1-P1 2.2944(11); Pt1-Cl2 2.4116(10); Pt1-C1 2.069(4); Pt1-C17 2.083(4); Pt1-N7 1.981(3); Pt1-Cl1 2.3282(10); C11-N7 1.352(6); C7-N7 1.364(6); P1-Pt1-Cl2 175.49(4); P1-Pt1-Cl1 85.53(4); C1-Pt1-P1 91.42(11); C1-Pt1-Cl2 85.48(10); C1-Pt1-C17 162.32(17); C1-Pt1-Cl1 97.86(12); C17-Pt1-P1 93.94(11); C17-Pt1-Cl2 89.98(11); C17-Pt1-Cl1 99.34(13); N7-Pt1-P1 95.28(10); N7-Pt1-Cl2 87.51(10); N7-Pt1-C1 81.56(15); N7-Pt1-C17 81.18(16); N7-Pt1-Cl1 179.01(10); Cl1-Pt1-Cl2 91.65(4).

Thus, when the oxidation is carried out in chloroform at -60 °C, other products, representing around 40% of the sample, form; the remaining 60% is **2c(t)**. Again this pattern of behaviour was observed with the tributylphosphine derivative. The first product that we assume to form is the agostic complex **5c** which transforms into **6c(t)** in a matter of minutes, even at -60 °C, Scheme 9. We were only able to obtain limited spectroscopic data on **5c**, but the ^{31}P shift of 51.0 in particular suggests that the phosphine is now part of a chelating ring,[17] and calls to mind the agostic complex that the tributylphosphine forms under equivalent reaction conditions.[16] With the tributylphosphine it was clear that it was the terminal methyl group of the chain that interacted with the central platinum, and this rearranged at around -40 °C to

form a five-membered metalacycle containing the phosphine. With the propyl complex **5c** it is presumably again the terminal methyl that interacts with the metal but now it does not need to rearrange before it reacts to give the five-membered metalacycle, and this is presumably the reason it reacts more quickly than the butyl analogue. The new complex formed at -60 °C, **6c(t)**, is reasonably stable at room temperature and in air, but does convert to another species if it is simply left in solution for more than a few days at room temperature and it proved difficult to purify via chromatography; thus we were unable to completely characterise it. Certain pieces of spectroscopic data could be identified and confirm an unsymmetrical diphenylpyridine system (two ^{19}F resonances, one with satellites, one without), a ^{31}P shift (47.86 ppm) indicative of chelate ring formation,[17] the platinum still in oxidation state +4 (^{195}Pt shift of -2667) and a direct platinum bond to one of the alkyl groups of the phosphine. Spectroscopic data suggests, but is not definitive, that the phosphine is *trans* to the pyridine nitrogen. We were, however, able to purify by chromatography and fully characterise the new species that **6c(t)** transforms to and the identity of this final species helps to confirm our suggestions, Scheme 9. This final species is stable in air and at room temperature.



Scheme 9

All the salient features of the structure of this final complex can be deduced from the NMR data, particularly when compared with the analogous tributylphosphine complex[16] (a Pt chemical shift of -2780 indicating Pt(IV); a ^{31}P chemical shift of 42.68 indicating one of the propyl chains has reacted to form a cyclometallated ring, no visible coupling of this P to the protons in the cyclometallated aryl ring, suggesting the P is *cis* to the pyridine; two ^{19}F resonances, one with Pt satellites, one without; two alkyl proton resonances, each integral one, coupling strongly to each other and to the a Pt with a large coupling constant; the close proximity of one of these two in space to the aryl proton adjacent to Pt and F on the cyclometallated fluorophenyl ring) and we believe it to be **6c(c)** in Scheme 9. Mass spectral data suggests the complex is not cationic and therefore has the sixth site of its octahedral geometry occupied by a further chloride. Final confirmation of the structure comes from the

Xray structure, Figure 6, which does indeed show a singly cyclometallated diphenyl pyridine ring system, a singly cyclometallated phosphine, with the P *cis* to the N, and finally two further chlorides.

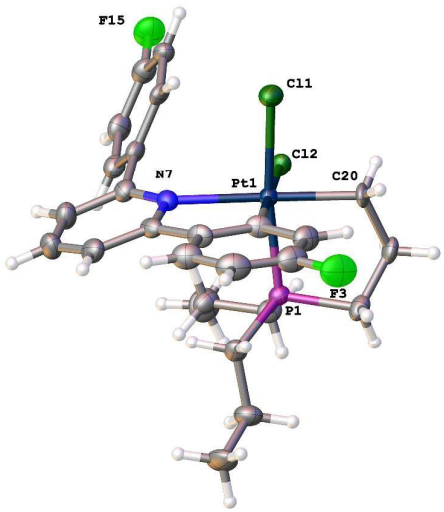


Figure 6: The solid-state structure of **6c(c)**, thermal ellipsoids drawn at 50% probability level**.** Selected bond lengths (Å) and angles (°): Pt1-Cl1 2.3953(15); Pt1-Cl2 2.4072(16); Pt1-C1 2.030(7); Pt1-N7 2.246(5); Pt1-P1 2.2650(15); Pt1-C20 2.076(6); C18-P1 1.828(6); C18-C19 1.480(16); Cl1-Pt1-Cl2 91.68(6); C1-Pt1-Cl1 89.54(19); C1-Pt1-Cl2 178.72(19); C1-Pt1-N7 79.7(3); C1-Pt1-P1 87.46(19); C1-Pt1-C20 96.2(3); N7-Pt1-Cl1 91.74(14); N7-Pt1-Cl2 100.66(15); N7-Pt1-P1 95.20(14); P1-Pt1-Cl1 171.83(5); P1-Pt1-Cl2 91.29(6); C20-Pt1-Cl1 87.93(19); C20-Pt1-Cl2 83.4(2); C20-Pt1-N7 175.9(3); C20-Pt1-P1 84.84(19).

The formation of this tripropylphosphine complex can be thought of as exactly like that of the DMSO and triphenylphosphine compexes, but with the agostic interaction of the alkyl chain internally trapping the five-coordinate intermediate. The subsequent reaction of the agostically trapped five-coordinate complex to give **6c(t)** and ultimately **6c(c)** is an example of a transcyclometallation reaction.[18] Such reactions involve the exchange of one cyclometallated ligand by another and have been known for some time,[19] and used to considerable effect, for instance to induce multiple[20] or chiral[21] cyclometallations. The effect of the reaction **5c** to **6c(t)** is to exchange one five-membered cyclometallated ring containing an aryl group with another five-membered ring containing an alkyl chain. We saw the same chemistry with the tributyl phosphine and rationalised the exchange as replacing two adjoining five membered metallacycles which strain and distort the coordinating pyridine ring in **5c** with two independent five membered metallacycles without any cumulative strain in complex **6c(t)**, even though there has been an exchange of an aryl-Pt bond for a notionally weaker alkyl-Pt bond. We have previously noted a similar type of exchange in mono-cyclometallated complexes.[22] The subsequent isomerisation of **6c(t)** to **6c(c)**, is presumably brought about be by the further relief of steric strain as it brings the large PPr_2 fragment away

from a relatively congested central position to a less congested one above the plane of the diphenylpyridine. The crystal structure of **6c(c)** provides evidence for its relatively unstrained nature: the three angles through the central platinum, N-Pt-C, P-Pt-Cl, Cl-Pt-Cl are 175.9(3), 171.83(5) and 178.72(19) ° respectively, Figure 6.

Once again we can account for the differing behaviour in chloroform and acetone as arising from the superior solvation of the chloride anion by chloroform.[15] Thus, by keeping the chloride which is released from the iodobenzene dichloride oxidant away from the platinum it allows the alkyl chain of the phosphine to coordinate and hence react.

Conclusions

The oxidation reactions of our three platinum (II) complexes with iodobenzenedichloride all proceed via a two step reaction giving a five-coordinated intermediate. In each case we have been able to trap out the intermediate with another ligating species and temporarily stabilise it. When an external ligand is added (e.g. DMSO with the DMSO complexes, or pyridine with the triphenyl phosphine) a cationic species is generated and, if the counter ion is non-coordinating (e.g. BF_4^-), it is possible to isolate new species. When the trapping agent is the internal alkyl chain of a previously coordinated ligand (i.e. the propyl chain of PPr_3) the intermediate complex is an agostic one and, rather than the agostic interaction being displaced by another ligating group, a reaction occurs. This reaction results in the cleavage of a C-H bond with the formation of a new Pt-C bond. It is therefore possible, by careful choice of ligands and conditions, to trap out the reactive five-coordinate and exert some degree of control as the course of subsequent reactivity.

Table 1

	1b	1c	2a(t)	2a(c)	2c(c)	6c(c)
Crystal form	yellow block	yellow block	yellow plate	yellow block	yellow plate	yellow plate
Dimensions/mm	0.40×0.10×0.10	0.45×0.28×0.2	0.12x0.08x0.01	0.35 × 0.2 × 0.1	0.2 × 0.2 × 0.08	0.4 × 0.1 × 0.02
Emp. Formula	$C_{35}H_{24}F_2NPPt$	$C_{26}H_{30}F_2NPPt$	$C_{20}H_{16}Cl_5F_2NOPtS$	$C_{20}H_{16}Cl_5F_2NOPtS$	$C_{26}H_{30}Cl_2F_2NPPt$	$C_{29.5}H_{34}Cl_2F_2NPPt$
Mw	722.61	620.57	728.74	728.74	691.47	737.53
Crystal system	orthorhombic	triclinic	triclinic	triclinic	orthorhombic	orthorhombic
Space group	Pbca	P-1	P-1	P-1	$Pna2_1$	Aea2
a/Å	18.6702(4)	8.97222(14)	8.39188(17)	8.1160(4)	18.3851(2)	18.2105(2)
b/Å	7.6361(3)	9.20765(17)	12.5024(3)	10.4007(5)	12.6327(2)	17.91980(10)
c/Å	37.4789(12)	15.2259(3)	22.3193(5)	14.6707(6)	11.03420(10)	17.59350(10)
α/°	90	106.6101(16)	85.0481(18)	78.098(4)	90	90
β/°	90	92.0547(13)	80.9008(18)	79.630(4)	90	90
γ/°	90	106.6725(15)	83.9730(17)	75.596(4)	90	90
U/Å^3	5343.3(3)	1145.14(4)	2293.65(9)	1162.80(9)	2562.73(5)	5741.26(8)
T/K	100(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Z	8	2	4	2	4	8
D_{calc}/Mg m^{-3}	1.797	1.800	2.110	2.081	1.792	1.707
F(000)	2816	608.0	1392	696	1352	2904
μ(MoKα)/mm^{-1}	5.353	6.226	18.793	6.728	5.776	11.649
θ max/°	32.65	32.30	33.30	32.35	30.522	78.949
Refl. Measured	25129	34899	14891	14646	31888	16968
Unique data	8837	7678	8080	7417	7234	4983
*R*1 [$I > 2\sigma(I)$]	0.0372	0.0194	0.0568	0.0414	0.0223	0.0264
*wR*2	0.0565	0.0428	0.1385	0.1082	0.0412	0.0656
Data/rest/param	8837/0/361	7678/0/283	8080/9/580	7417/0/282	7234/1/301	4983/1/360

Supporting Information

Full details and discussions of the Xray structures are available. CIF files are also available to download from the CCDC, reference numbers: 1481768-1481773. DFT optimized structures of **2a(t)** and **2a(c)** are available as is the variable temperature ^{1}H NMR spectrum of **6c(c)**.

Acknowledgements

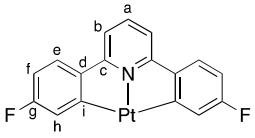
We thank EPSRC for a DTG award to PAS and support from Advantage West Midlands (AWM) (part funded by the European Regional Development Fund) for the purchase of a high resolution mass spectrometer and the XRD system that was used to solve the crystal structures.

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. ^{1}H 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). ^{1}H-^{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 complex **1a** was prepared as previously reported.[13]

The following labelling scheme was used for all symmetrical C^N^CPt complexes:



Synthesis of complexes 1b, 1c.

The following general method was used for both derivatives: to a solution of [(2,6-di(4-fluorophenyl)pyridine)Pt(DMSO)] **1a** (54 mg, 1.00×10^{-4} mol) in chloroform (1 ml) at room temperature was added a chloroform solution of 1 equivalent of the appropriate phosphine (26.3 mg, 16.1 mg, respectively). The mixture was stirred for five minutes before solvent and liberated DMSO were removed under high vacuum. If necessary, column chromatography (chloroform on silica) was used to purify the products. Yields: **1b** 68 mg, 9.41×10^{-5} mol, 94%, **1c** 57 mg, 9.19×10^{-5} mol, 92 %.

1b PPh_3

δ_H = 7.80 (6H, m, P(C*H*)$_2$(CH)$_2$CH), 7.60 (1H, t, $^{3}J_{H\text{-}H}$ = 8 Hz, H_a), 7.42 (3H, m, P(CH)$_2$(CH)$_2$C*H*), 7.40 (2H, dd, $^{3}J_{H\text{-}H}$ = 8.5, $^{4}J_{H\text{-}F}$ = 5 Hz, H_e), 7.39 (6H, m, P(CH)$_2$(C*H*)$_2$CH), 7.18 (2H, d, $^{3}J_{H\text{-}H}$ = 8 Hz, H_b), 6.54 (2H, td, $^{3}J_{H\text{-}H}$ = $^{3}J_{H\text{-}F}$ = 8.5, $^{4}J_{H\text{-}H}$ = 2.5 Hz, H_f), 5.80 (2H, dd, $^{3}J_{H\text{-}F}$ = 10, $^{4}J_{H\text{-}H}$ = 2.5, $^{3}J_{H\text{-}Pt}$ = 42 Hz H_h).

δ_C = 167.58 (m, C_i), 164.39 (C_g), 163.07 (d $^{2}J_{C\text{-}F}$ = 254 Hz, C_c), 146.72 (C_d), 140.44 (C_a), 135.43 (d, $^{3}J_{C\text{-}P}$ = 12 Hz, *o*-PPh_3), 131.45 (d, $^{3}J_{C\text{-}P}$ = 58 Hz, *ipso*-PPh_3), 130.84 (*p*-PPh_3), 128.33 (d, $^{3}J_{C\text{-}F}$ = 11 Hz, C_e), 125.38 (d, $^{2}J_{C\text{-}P}$ = 8 Hz, *m*-PPh_3), 124.57 (d $^{2}J_{C\text{-}F}$ = 18 Hz, C_h), 114.40 (C_b), 110.46 (d $^{2}J_{C\text{-}F}$ = 23 Hz, C_f).

δ_F = -110.11 ($^{4}J_{F\text{-}Pt}$ = 29 Hz). δ_F (233K, acetone-d_6) : -111.02 ($^{4}J_{F\text{-}Pt}$ = 27.2 Hz).

δ_P = 27.44 ($^{1}J_{P\text{-}Pt}$ = 4020 Hz) δ_P (233K, acetone-d_6) : 25.18, δ_{Pt} : -4323 ppm (d, ~4010 Hz)

Elemental Analysis. Found (expected for $C_{35}H_{24}F_2NPPt$): C 57.9 (58.17), H 3.6 (3.35), N 1.9 (1.94)

HR-MS (ESI): found *m/z* 722.1318, calc for $C_{35}H_{25}F_2NP^{194}Pt$ = 722.1319 (MH^+)

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

1c PPr_3

δ_H = 7.58 (1H, t, ^3J = 8 Hz, H_a), 7.47 (2H, dd, ^3J = 8.5, $^4J_{H-F}$ = 6 Hz, H_e), 7.22 (4H, m, $H_{b,h}$), 6.73 (2H, dt, $^3J_{H-F}$ = $^3J_{H-H}$ = 8.5 Hz, $^3J_{H-H}$ = 2.7 Hz, H_f), 2.09 (6H, m, PCH_2), 1.66 (6H, m, H_k PCH_2CH_2), 1.05 (9H, t, $^3J_{H-H}$ = 7.5 Hz, CH_3).

δ_C = 15.72 (d, $^3J_{C-P}$ = 16 Hz, CH_3), 17.61 (s, $^3J_{C-Pt}$ = 31.5 Hz, PCH_2CH_2), 26 (d, $^1J_{C-P}$ = 35 Hz, $^2J_{C-Pt}$ = 34 Hz, PCH_2), 109.34 (d, $^2J_{C-F}$ = 23 Hz, C_f), 113.46 (d, $^6J_{C-F}$ = 3 Hz, $^3J_{C-Pt}$ = 27 Hz, C_b), 123.12 (d, $^2J_{C-F}$ = 17 Hz, $^2J_{C-Pt}$ = 64, C_h), 124.88 (d, $^3J_{C-F}$ = 8.5 Hz, $^3J_{C-Pt}$ = 31 Hz, C_e), 139 (s, C_a), 146.07 (m, $^2J_{C-Pt}$ = 26 Hz, C_d), 163.34 (d, $^1J_{C-F}$ = 255 Hz, $^3J_{C-Pt}$ = 54 Hz, C_g), 163.98 (s, $^2J_{C-Pt}$ = 67 Hz, C_c), 167.80 (d, $^3J_{C-F}$ = 8 Hz, $^1J_{C-Pt}$ = 718 Hz, C_i).

δ_F = -111.44 ($^4J_{F-Pt}$ = 28 Hz). δ_P = 1.34 ($^1J_{P-Pt}$ = 3712 Hz). δ_{Pt} = -4212 ($^1J_{Pt-P}$ = ~3700 Hz).

Elemental Analysis. Found (expected for $C_{26}H_{30}F_2NPPt$) C 50.04 (50.32), H 4.84 (4.87), N 2.27 (2.26)

HR-MS (ESI): found *m/z* 620.1783, calc for $C_{26}H_{30}F_2NP^{194}Pt$, $[M]^+$ = 620.1782.

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

Oxidation of complexes 1a, 1b, 1c

In a typical procedure, 10mg of complex **1** (1.86×10^{-5} mol, 1.38×10^{-5} mol, 1.61×10^{-5} mol, respectively) was dissolved in chloroform (1 ml) and the solution cooled to -40 °C. One equivalent of solid $PhICl_2$ (5.1 mg, 3.5 mg, 4.4 mg, respectively) was added and the mixture thoroughly mixed by shaking. After allowing to warm to room temperature the solvent was removed under vacuum, the resulting solid washed with hexane and then recrystallised from chloroform, or purified by column chromatography (chloroform on silica). Yields: **1a** 9.5 mg, 1.76×10^{-5} mol, 95%; **1b** 8.3 mg, 1.14×10^{-5} mol, 83%; **1c** 9.1 mg, 1.47×10^{-5} mol, 91%.

DMSO complexes 2a(t) and 2a(c)

Oxidation of **1a** gave **2a(t)** directly.

2a(t) δ_H : 7.87 (1H, t, $^3J_{H-H}$ = 8Hz, H_a), 7.73 (2H, dd, $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz, $^3J_{H-Pt}$ = 36 Hz, H_h), 7.56 (2H, $^3J_{H-H}$ = 9, $^4J_{H-F}$ = 5 Hz, H_e), 7.52 (2H, d, J_{H-H} = 8 Hz, H_b), 6.92 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 9Hz, $^4J_{H-H}$ = 3Hz, H_f), 3.86 (6H, s, $^3J_{H-Pt}$ = 16 Hz, DMSO). NOE: Irradiation of DMSO protons enhances H_h and vice versa; no other enhancements observed with these irradiations.

δ_F ($CDCl_3$): -105.90 ($^4J_{F-Pt}$ = 14 Hz), δ_F (acetone d_6) = -108.39 ($^4J_{F-Pt}$ = 16 Hz). δ_{Pt} = -2072

ppm.

Elemental Analysis. Found (expected for $C_{19}H_{15}Cl_2F_2NOPtS$): C 36.9 (37.45), H 2.2 (2.48), N 2.6 (2.30).

HR-MS (ESI): found *m/z* 607.9924, calc for $C_{19}H_{16}F_2{}^{35}Cl_2NO^{194}PtS$ = 607.9913 (MH^+).

Crystals of **2a(t)** suitable for Xray analysis were grown from the evaporation of solvent from a chloroform solution, Fig 3 and Table 1; full details are in the SI.

The *trans* isomer **2a(t)** slowly (over the course of several days) converted to the *cis* isomer **2a(c)**.

2a(c) δ_H 7.85 (1H, t, $^3J_{H-H}$ = 8 Hz, H_a), 7.77 (2H, dd, $^3J_{H-F}$ = 7.5 Hz, $^4J_{H-H}$ = 2.5 Hz, $^3J_{H-Pt}$ = 32 Hz, H_h), 7.74 (2H, dd, $^3J_{H-H}$ = 9, $^4J_{H-F}$ = 5 Hz, H_e), 7.50 (2H, d, $^3J_{H-H}$ = 8 Hz, H_b), 6.99 (2H, td, $^3J_{H-F}$ = $^3J_{H-H}$ = 8.5, $^4J_{H-H}$ = 2.5 Hz H_f), 3.26 (6H, s, $^3J_{H-Pt}$ = 17 Hz, DMSO). nOe: No visible enhancement of H_h when DMSO protons irradiated and vice versa.

δ_F ($CDCl_3$): -105.27 ($^4J_{F-Pt}$ = 12 Hz), δ_F (acetone d_6) = -108.21 ($^4J_{F-Pt}$ = 13 Hz). δ_{Pt} = -2126 ppm.

HR-MS (ESI): found *m/z* 607.9926 calc for $C_{19}H_{16}F_2{}^{35}Cl_2NO^{194}PtS$ = 607.9913 (MH^+).

Crystals of **2a(c)** suitable for Xray analysis were grown from the evaporation of solvent from a chloroform solution, Fig 4 and Table 1; full details are in the SI.

double-DMSO 4a

δ_H (acetone-d_6) = 7.87 (1H, dd, $^3J_{H-F}$ = 9 Hz, $^4J_{H-H}$ = 2.5 Hz, $^3J_{H-Pt}$ = 26Hz), 4.13 (6H, t, $^3J_{H-Pt}$ =14 Hz, H_j), 3.36 (6H, t, $^3J_{H-Pt}$ =20 Hz, H_k).

δ_F ($CDCl_3$) = -102.42 ($^4J_{F-Pt}$ = 13 Hz), δ_F (acetone d_6) = -105.39 ($^4J_{F-Pt}$ = 15 Hz). δ_{Pt} = -2098 ppm.

HR-MS (ESI): found *m/z* 650.0289, calc for $C_{21}H_{21}{}^{35}ClF_2NO_2{}^{194}PtS_2$ [M^+] 650.0297.

PPh_3 complexes 2b(t), 2b(c), 3b and pyridine adduct 4b(NP)t

Oxidation of **1b** in acetone gave **2b(t)** directly.

2b(t) δ_H = 7.94 (6H, dd, $^3J_{H-P}$ = 12 Hz, $^4J_{H-H}$ = 8 Hz, P(C*H*)$_2$(CH)$_2$CH)), 7.85 (1H, t, $^3J_{H-H}$ = 8 Hz, H_a), 7.70 (2H, dd, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 5.5 Hz H_e), 7.56 (2H, d, $^3J_{H-H}$ = 8 Hz, H_b), 7.51 (3H, tt, P(CH)$_2$(CH)$_2$C*H*)), 7.44 (6H, td , $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 3 Hz, P(CH)$_2$(C*H*)$_2$CH)), 6.78 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_f), 6.58 (2H, dd, $^3J_{H-F}$ = 9 Hz, $^4J_{H-H}$ = 2 Hz, H_h).

δ_F ($CDCl_3$) = -107.91 ($^4J_{F-Pt}$ = 16 Hz), δ_F (acetone d_6) = -108.87 ($^4J_{F-Pt}$ = 17 Hz). δ_P : -4.09 ($^1J_{P-Pt}$ = 2470 Hz). δ_{Pt} : -2323 ppm (d, ~2450 Hz).

Anal. Found (expected for $C_{35}H_{24}Cl_2F_2NPPt$): C 52.4 (52.98), H 3.1 (3.05), N 1.6 (1.77)

HR-MS (ESI): found *m/z* 756.0921, calc for $C_{35}H_{24}{}^{35}ClF_2NP^{194}Pt$ = 756.0930 ($M\text{-}Cl^+$)

The *trans* isomer **2b(t)** slowly (over the course of several days) converted to the *cis* isomer **2b(c)**.

2b(c) δ_H : 7.73 (2H, dd, $^3J_{H-F}$ = 9, $^4J_{H-H}$ = 2, $^3J_{H-Pt}$ = 32Hz H_h), 7.43 (1H, t, $^3J_{H-H}$ = 8 Hz, H_a) 7.41 (2H, dd, $^3J_{H-H}$ = 8.5, $^4J_{H-F}$ = 5 Hz, H_e), 7.36 (9H, m, P(C*H*)$_2$(CH)$_2$C*H*)), 7.18 (6H, m, P(CH)$_2$(C*H*)$_2$CH)), 7.05 (2H, d, $^3J_{H-H}$ = 8 Hz, H_b), 6.77 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2.5Hz, H_f).

δ_F -106.25 ($^4J_{F-Pt}$ = 14 Hz). δ_P : -7.95 ($^1J_{P-Pt}$ = 2460 Hz). δ_{Pt} : -2573 (d, 2460 Hz).

Elemental Analysis. Found (expected for $C_{35}H_{24}Cl_2F_2NPPt$): C 52.6 (52.98), H 3.2 (3.05), N 1.8 (1.77)

HR-MS (ESI): found *m/z* 756.0928, calc for $C_{35}H_{24}{}^{35}ClF_2NP^{194}Pt$ = 756.0930 (M-Cl^+)

Oxidation of **1b** in chloroform gave five-co-ordinate **3b**

3b δ_H (233 K) = 8.08 (1H, t, $^3J_{H-H}$ = 8 Hz, H_a), 7.80 (6H, br dd, $^3J_{H-H}$ = 8Hz, *o*-PPh_3), 7.60 (2H, dd, $^3J_{H-H}$ = 9 Hz, $^4J_{H-F}$ = 6Hz, H_e), 7.57 (3H, br t, $^3J_{H-H}$ = 8 Hz, *p*-PPh_3), 7.51 (2H, d, $^3J_{H-H}$ = 8 Hz, H_b), 7.47 (6H, td, $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 2 Hz, *m*-PPh_3), 6.87 (2H, br dt, $^3J_{H-F}$ = 10, $^4J_{H-H}$ = $^4J_{H-P}$ = 2 Hz Hz, H_h), 6.84 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz, H_f).

δ_F (233 K) = -108.27 ($^4J_{F-Pt}$ = 17 Hz). δ_P (233 K) = 9.44 ($^1J_{P-Pt}$ = 2806Hz). δ_{Pt} (233 K) = -2339 ppm (d, $^1J_{P-Pt} \approx$ 2900Hz)

Pyridine complexes **4b(NP)** were made either by addition of excess pyridine directly to **3b**, or by treating **2b(c)** and **2b(t)** with $AgBF_4$ in acetone solution, in the presence of excess pyridine.

4b(NP)t

δ_H = 8.41 (2H, ddd, $^3J_{H-H}$ = 7 Hz, $^4J_{H-P}$ = 5.5 Hz, $^4J_{H-H}$ = 1 Hz, $^3J_{H-Pt}$ = 24 Hz, *o*-py), 7.98 (2H, m, H_a and *p*-py), 7.94 (2H, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-F}$ = 5 Hz, H_e), 7.75 (2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-Pt}$ = 8 Hz, H_b), 7.64 (2H, $^3J_{H-F}$ = 7.5 Hz, $^4J_{H-H}$ =2.5 Hz, $^3J_{H-Pt}$ = 24 Hz, H_h), 7.59 (3H, t, $^3J_{H-H}$ = 7.5 Hz, *p*-PPh_3), 7.55 (6H, dd, $^3J_{H-P}$ = 12.5, $^3J_{H-H}$ = 7.5 Hz, *o*-PPh_3), 7.45 (2H, td, $^3J_{H-H}$ = $^3J_{H-H}$ = 7 Hz, $^4J_{H-P}$ = 1 Hz, *m*-py), 7.40 (6H, td, $^3J_{H-H}$ = $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-P}$ = 3.5 Hz, *m*-PPh_3), 7.08 (2H, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5, $^4J_{H-H}$ = 2.5 Hz, H_f) ppm. NOE: no real effects on each other upon irradiation of *o*-PPh_3, *o*-py or H_h.

δ_F = -106.26 ($^4J_{F-Pt}$ = 14 Hz). δ_P = -11.23 ($^1J_{P-Pt}$ = 2395 Hz). δ_{Pt} = -2362 (d, $^1J_{Pt-P}$ = ~2500 Hz) ppm.

HR-MS (ESI): found *m/z* 756.0935, calc for $C_{35}H_{24}{}^{35}ClF_2NP^{194}Pt$ = 756.0930 (M-py^+)

found *m/z* 836.1350, calc for $C_{40}H_{29}ClF_2N_2P^{194}Pt$ = 835.1346 (M^+)

PPr_3 complexes 2c(t) and 2c(c)

Oxidation of **1c** in acetone gave **2c(t)** directly.

2c(t) δ_H = 7.81 (1H, t, $^3J_{H-H}$ = 8 Hz, H_a), 7.73 (2H, dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-F}$ = 5 Hz, H_e), 7.53 (2H, dd, $^3J_{H-H}$ = 8 Hz, $^5J_{H-P}$ = 2 Hz, H_b), 7.26 (2H, dd, $^3J_{H-F}$ = 9 Hz, $^4J_{H-H}$ = 2 Hz, $^3J_{H-Pt}$ = 20 Hz, H_h), 6.88 ((2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz, H_f), 2.47 (6H, m, PC*H*$_2$), 1.81 (6H, m, PCH$_2$C*H*$_2$), 1.12 (9H, td, $^3J_{H-H}$ = 7 Hz, $^4J_{H-P}$ = 1.5 Hz, CH_3) ppm.

δ_C = 15.26-15.55 (m, CH_3), 17.85 (d, $^2J_{C-P}$ = 5 Hz, PCH$_2$*C*H$_2$), 24.10 (d, $^1J_{C-P}$ = 36 Hz, $^2J_{C-Pt}$ = 18 Hz, P*C*H$_2$), 112.09 (d, $^3J_{C-F}$ = 22 Hz, C_f), 116.86 (d, $^4J_{C-P}$ = 4 Hz, C_b), 121.71 (d, $^2J_{C-F}$ = 19 Hz, $^2J_{C-Pt}$ = 21 Hz, C_h), 128.01 (d, $^3J_{C-F}$ = 8 Hz, C_e), 140.42 (s, C_a), 144.15 (t, $^4J_{C-F}$ = $^3J_{C-P}$ = 3 Hz, C_d), 159.63 (m, $^1J_{C-Pt}$ = 512 Hz, C_i), 161.58 (m, $^3J_{C-Pt}$ = 30 Hz, C_c), 163.20 (d, $^1J_{C-F}$ = 258 Hz, $^3J_{C-Pt}$ = 28 Hz, C_g) ppm.

δ_F = -108.06 (s, $^4J_{F-Pt}$ = 14 Hz) ppm. δ_P = -13.96 (s, $^1J_{P-Pt}$ = 2310 Hz) ppm. δ_{Pt} = -2282 (d, $^1J_{Pt-P}$ = ~2300 Hz) ppm.

The *trans* isomer **2c(t)** converted to the *cis* isomer **2b(c)** over several hours at room temp.

2c(c) δ_H = 7.83 (3H, m, $H_{a,h}$), 7.71 (2H, dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-F}$ = 4 Hz, H_e), 7.51 (2H, d, $^3J_{H-H}$ = 8 Hz, H_b), 6.94 (2H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz, H_f), 1.71 (6H, m, PC*H*$_2$), 1.10 (6H, m, PCH$_2$C*H*$_2$), 0.76 (9H, td, $^3J_{H-H}$ = 7 Hz, CH_3) ppm.

^{13}C (500 MHz) δ = 15.40-15.58 (m, CH_3), 16.72 (d, $^2J_{C-P}$ = 6 Hz, PCH$_2$*C*H$_2$), 24.30 (d, $^1J_{C-P}$ = 37 Hz, $^2J_{C-Pt}$ = 24 Hz, P*C*H$_2$), 112.88 (d, $^3J_{C-F}$ = 24 Hz, C_f), 116.35 (d, $^4J_{C-Pt}$ = 31.5 Hz, C_b), 120.98 (d, $^2J_{C-F}$ = 19 Hz, $^2J_{C-Pt}$ = 19 Hz, C_h), 127.63 (d, $^3J_{C-F}$ = 8 Hz, $^3J_{C-Pt}$ = 22 Hz, C_e), 141.10 (s, C_a), 141.70 (d, $^4J_{C-F}$ = 2 Hz, $^2J_{C-Pt}$ = 28 Hz C_d), 162.67 (m, $^3J_{C-Pt}$ = 35 Hz, C_c), 163.78 (m, $^1J_{C-Pt}$ = 512 Hz, C_i),164.90 (d, $^1J_{C-F}$ = 260 Hz, $^3J_{C-Pt}$ = 28 Hz, C_g) ppm.

δ_F = -105.57 (s, $^4J_{F-Pt}$ = 15 Hz) ppm. δ_P = -1.42 (s, $^1J_{P-Pt}$ = 2342 Hz) ppm. δ_{Pt} = -2625 (d, $^1J_{Pt-P}$ = ~2300 Hz) ppm.

Elemental Analysis. Found (expected for $C_{26}H_{30}F_2PNPt$): C 44.32 (45.16); H 4.12 (4.37); N 1.93 (2.03).

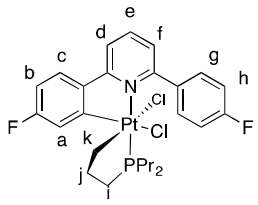
HR-MS (ESI): found *m/z* 654.1382, calculated = 654.1393 = $C_{26}H_{30}F_2PN^{194}Pt$ $[M-Cl]^+$; 712.0978, calculated = 712.0979 = $C_{26}H_{30}F_2PNNa^{194}Pt$ $[M+Na]^+$

Crystals of **2c(c)** suitable for Xray analysis were grown from the evaporation of solvent from a chloroform solution, Fig 5 and Table 1; full details are in the SI.

Complexes 5c, 6c(t) and 6c(c)

Oxidation of **1c** in chloroform gave agostic **5c** for which has a ^{31}P shift of 51.0 ppm at -60 °C. Proton signals could be observed, but could not be assigned.

Agostic **5c** transforms to **6c(t)** within minutes at -60 °C, but only incomplete (though absolutely characteristic) data could be obtained in solution as **6c(t)** transforms to **6c(t)** and could not be isolated as a pure material.

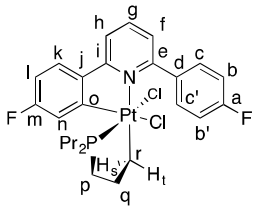


6c(t)

δ_H = 7.93 (1H, t, $^3J_{H-H}$ = 8Hz, H_e), 7.84 (1H, d, $^3J_{H-H}$ = 8Hz, $H_{d/f}$), 7.31 (1H, d, $^3J_{H-H}$ = 8Hz, $H_{d/f}$), 7.07 (1H, dt, $^3J_{H-F}$, 10 Hz, $^4J_{H-H}$ = $^4J_{H-P}$ = 2 Hz, H_a), 3.09 (1H, dt, $^2J_{H-H}$ = $^3J_{H-H}$ = 6.5 Hz, $^2J_{H-H}$ = 102 Hz, H_j), 2.37 (1H, m, $^2J_{H-Pt}$ = 56 Hz, H_j), 1.09 (3H, td, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-P}$ = 1 Hz, H_{Me}), 0.98 (3H, td, $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 1.5 Hz, H_{Me}) ppm.

δ_F = -109.54 ($^4J_{F-Pt}$ = 45 Hz), -111.90 ppm. δ_P = 47.86 ($^1J_{P-Pt}$ = 3129 Hz) ppm. δ_{Pt} = -2667 ($^1J_{Pt-P}$ = ~3300 Hz) ppm.

6c(c) was collected from the reaction solution after allowing to stand at room temperature overnight. The solvent was removed, the product washed with hexane and recrystallised from chloroform.



6c(c)

δ_H = 7.94 (2H, m, $H_{f,h}$), 7.87 (2H, m, H_c)*, 7.79 (1H, dd, $^3J_{H-H}$ = 9 Hz, $^4J_{H-F}$ = 6 Hz, H_k), 7.63 (1H, dd, $^3J_{H-H}$ = 5.5, 3 Hz, H_g), 7.30 (1H, $^3J_{H-F}$ = 10 Hz, $^4J_{H-H}$ = 3 Hz, $^3J_{H-Pt}$ = 47 Hz, H_n), 7.19 (2H, dd, $^3J_{H-F}$ = $^3J_{H-H}$ = 8.5 Hz, H_b)**, 7.01 (1H, td, $^3J_{H-H}$ = $^3J_{H-F}$ = 8.5 Hz, $^4J_{H-H}$ = 2.5 Hz, H_l), 3.70 (1H, m, $^2J_{H-Pt}$ = 95 Hz, H_s), 3.10 (1H, m, $^2J_{H-Pt}$ = 65 Hz, H_t)***, 2.06 (2H, m, H_{P-CH2}), 1.64 (2H, m, H_q), 1.36 – 1.17 (2H, m, H_p), 0.99 (4H, m, MeCH_2), 0.94 – 0.79 (5H, m, Me,PCH_2), 0.64 (3H, t, $^3J_{H-H}$ = 7 Hz, Me) ppm.

δ_C = 15.52 (d, $^3J_{C-Pt}$ = 8 Hz, C_{Me}), 15.65 (d, $^3J_{C-P}$ = 6 Hz, C_{Me}), 16.29 (d, $^2J_{C-P}$ = 6 Hz, $^3J_{C-Pt}$ = 24 Hz, MeCH_2), 16.53 (d,$^2J_{C-P}$ = 5 Hz, $^3J_{C-Pt}$ = 11 Hz, MeCH_2), 21.88 (d, $^1J_{C-P}$ = 33 Hz, $^2J_{C-Pt}$ = 42 Hz, PCH_2), (d, $^1J_{C-P}$ = 35 Hz, $^2J_{C-Pt}$ = 20 Hz, PCH_2), 26.45 (d, $^1J_{C-P}$ = 40 Hz, $^2J_{C-Pt}$ = 86 Hz, C_p), 28.56 (d, $^2J_{C-P}$ = 3 Hz, C_q), 37.82 (s, $^1J_{C-Pt}$ = 554 Hz, C_r), 122.89 (d, $^2J_{C-F}$ = 23 Hz, C_l), 115.05 (d, $^2J_{C-F}$ = 21 Hz, $C_{b,b'}$), 116.51 (d, $^2J_{C-F}$ = 21 Hz, $^2J_{C-Pt}$ = 42 Hz, C_n), 118.12 (s, $^3J_{C-Pt}$ = 11 Hz, C_h), 125.90 (s, C_g), 128.00 (d, $^3J_{C-F}$ = 9 Hz, $^3J_{C-Pt}$ = 40 Hz, C_k), 135.54 (d, $^4J_{C-F}$ = 3 Hz, C_d), 138.60 (d, $^4J_{C-F}$ = 2 Hz, C_j), 139.09 (s, C_f), 140.51 (dd, $^3J_{C-F}$ = 7 Hz, $^2J_{C-P}$ = 2 Hz, $^1J_{C-Pt}$ = 841 Hz, C_o), 162.10 (s, $^3J_{C-Pt}$ = 50 Hz, C_i), 163.81 (d, $^1J_{C-F}$ = 249 Hz, C_a), 163.88 ($^1J_{C-F}$ = 256 Hz, $^3J_{C-Pt}$ = 75 Hz, C_m), 163.97 (s, C_e) ppm.

^{19}F (376 MHz) δ_F = -107.23 (s, $^4J_{F-Pt}$ = 45 Hz), -112.12 ppm. δ_P = 42.68, (s, $^1J_{P-Pt}$ = 2938 Hz) ppm. δ_{Pt} = -2780 (d, $^1J_{Pt-P}$ = ~3300 Hz) ppm.

*very broad lump at 298 K. By 208 K on 400MHz spectrometer, H_c and $H_{c'}$ have become separate proton environments. Coupling to the adjacent proton, H_b, can be observed by COSY at 218 K. At 208 K the peak is now a broad triplet (J_{H-H} = 5.3 Hz, separation of peaks = 505 Hz, centre = 7.86 ppm. Even by 328 K, the peak has not coalesced to form a single peak, instead a broad peak remains (width at half height = 21 Hz). COSY at 328K shows Coupling to H_b.

**At room temperature, and even down to 268 K, this peak is a triplet on a 400 MHz spectrometer. The peak moves slightly to greater ppm with a decrease in temperature. By 208 K the triplet has decoalesced into 2 peaks. Peak positions makes it difficult to work out the width at half height, but the peaks are separated by around 25 Hz.

***irradiation of this peak shows enhancement of H_n.

The VT-NMR spectra are available as SI.

Elemental Analysis. Found (expected for $C_{26}H_{30}Cl_2F_2PNPt$): C 44.73 (45.16), H 4.23 (4.37), N 1.98 (2.03).

HR-MS (ESI): found *m/z* 654.1390, calculated = 654.1393 = $C_{26}H_{30}ClF_2PN^{194}Pt$ $[M\text{-}Cl]^+$.

DFT Calculations

All DFT calculations used the Amsterdam density functional (ADF) code version 2008.01.[23] The general features available in ADF have been described.[24] Here, we have used scalar zero-order regular approximation (ZORA) relativistic corrections with the OPBE functional[25] and the supplied frozen-core, triple-ζ plus polarisation ZORA basis sets. Solvation effects were included via the conductor-like screening model (COSMO) as implemented in ADF. Default SCF and geometry optimisation convergence criteria were used.

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.

(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) Roselló-Merino, M.; Rivada-Wheelaghan, O.; Ortuño, M. A.; Vidossich, P.; Díez, J.; Lledós, A.; Conejero, S., *Organometallics* **2014,** *33*, 3746. (b) Rivada-Wheelaghan, O.; Roselló-Merino, M.; Díez, J.; Maya, C.; López-Serrano, J.; Conejero, S., *Organometallics* **2014,** *33*, 5944. (c) Campos, J.; Ortega-Moreno, L.; Conejero, S.; Peloso, R.; López-Serrano, J.; Maya, C.; Carmona, E., *Chem. Eur. J.* **2015,** *21*, 8883. (d) Werlé, C.; Bailly, C.; Karmazin-Brelot, L.; Le Goff, X.-F.; Ricard, L.; Djukic, J.-P., *J. Am. Chem. Soc.* **2013,** *135*, 17839.

(5) (a) Zhao, S. B.; Wu, G.; Wang, S., *Organometallics* **2008,** *27*, 1030. (b) Grice, K. A.; Scheuermann, M. L.; Goldberg, K. I., *Top. Organomet. Chem.* **2011,** *35*, 1. (c) Vigalok, A., *Acc. Chem. Res.* **2015,** *48*, 238.
(6) (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.
(7) (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.
(8) Madison, B. L.; Thyme, S. B.; Keene, S.; Williams, B. S., *J. Am. Chem. Soc.* **2007,** *129*, 9538.
(9) Ariafard, 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.
(10) (a) Racowski, J. M.; Ball, N. D.; Sanford, M. S., *J. Am. Chem. Soc.* **2011,** *133*, 18022. (b) Maleckis, A.; Kampf, J. W.; Sanford, M. S., *J Am Chem Soc* **2013,** *135*, 6618.
(11) Rendina, L. M.; Puddephatt, R. J., *Chem. Rev.* **1997,** *97*, 1735.
(12) Forniés, J.; Martín, A.; Navarro, R.; Sicilia, V.; Villarroya, P., *Organometallics* **1996,** *15*, 1826.
(13) (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.
(14) (a) Newman, C. P.; Deeth, R. J.; Clarkson, G. J.; Rourke, J. P., *Organometallics* **2007,** *26*, 6225. (b) Crosby, S. H.; Clarkson, G. J.; Deeth, R. J.; Rourke, J. P., *Organometallics* **2010,** *29*, 1966.
(15) (a) Lam, S. Y.; Louis, C.; Benoit, R. L., *J. Am. Chem. Soc.* **1976,** *98*, 1156. (b) Slater, J. W.; Lydon, D. P.; Alcock, N. W.; Rourke, J. P., *Organometallics* **2001,** *20*, 4418. (c) Kryachko, E. S.; Zeegers-Huyskens, T., *J. Phys. Chem. A* **2002,** *106*, 6832. (d) Mamtora, J.; Crosby, S. H.; Newman, C. P.; Clarkson, G. J.; Rourke, J. P., *Organometallics* **2008,** *27*, 5559.
(16) Shaw, P. A.; Phillips, J. M.; Newman, C. P.; Clarkson, G. J.; Rourke, J. P., *Chem. Commun.* **2015,** *51*, 8365.
(17) (a) Meriwether, L. S.; Leto, J. R., *J. Am. Chem. Soc.* **1961,** *83*, 3192. (b) Garrou, P. E., *Chem. Rev.* **1981,** *81*, 229.
(18) Albrecht, M.; Dani, P.; Lutz, M.; Spek, A. L.; Koten, G. v., *J. Am. Chem. Soc.* **2000,** *122*, 11822.
(19) (a) Ryabov, A. D.; Yatsimirsky, A. K., *Inorg. Chem.* **1984,** *23*, 789. (b) Ryabov, A. D., *Inorg. Chem.* **1987,** *26*, 1252.
(20) Dijkstra, H. P.; Albrecht, M.; van Koten, G., *Chem. Commun.* **2002**, 126.
(21) Roca, F. X.; Motevalli, M.; Richards, C. J., *J. Am. Chem. Soc.* **2005,** *127*, 2388.
(22) (a) Thomas, H. R.; Deeth, R. J.; Clarkson, G. J.; Rourke, J. P., *Organometallics* **2011,** *30*, 5641. (b) Crosby, S. H.; Clarkson, G. J.; Rourke, J. P., *Organometallics* **2011,** *30*, 3603.
(23) Baerends, E. J. B., A.; Bo, C.; Boerrigter, P. M.; Cavallo, L.; Deng, L.; Dickson, R. M.; Ellis, D. E.; Fan, L.; Fischer, T. H.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Groeneveld, J. A.; Gritsenko, O. V.; Harris, F. E.; van den Hoek, P.; Jacobsen, H.; van Kessel, G.; Kootstra, F.; van Lenthe, E.; Osinga, V. P.; Philipsen, P. H. T.; Post, D.; Pye, C. C.; Ravenek, W.; Ros, P.; Schipper, P. R. T.; Schreckenbach, G.; Snijders, J. G.; Sola, M.; Swerhone, D.; te Velde, G.; Vernooijs, P.; Versluis, L.; Visser, O.; van Wezenbeek, E.; Wiesenekker, G.; Wolff, S. K.; Woo, T. K.; Ziegler, T. *ADF 2008.01*, Scientific Computing and Modelling NV: Free University, Amsterdam, 2008.
(24) Velde, G. t.; Baerends, E. J., *J. Comput. Phys.* **1992,** *99*, 84.

(25) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M., *Phys. Rev. Lett.* **1996,** *77*, 3865. (b) Handy, N. C.; Cohen, A. J., *Mol. Phys.* **2001,** *99*, 403.