Platinum(IV) Complexes: C−H Activation at Low Temperatures

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Received June 24, 2008

The oxidation of square-planar cyclometalated Pt(II) phenylpyridine species using the electrophilic chlorine based oxidant $PhICl_2$ has been studied. Rapid oxidations are observed in chloroform solvent at −40 °C leading to single products. In acetone solvent isomeric forms of the product are formed, and these are observed to isomerize at around −10 °C. The oxidation of a complex with an uncyclometalated pendant arm resulted in the very rapid cyclometalation of that arm by the resulting electrophilic Pt(IV) species.

Introduction

We have recently been studying the synthesis and reactivity of high oxidation state organometallic platinum complexes,[1] with a view to understanding some further details of the cyclometalation reaction.[2] Our interest in the cyclometalation reaction comes about because of its role in the functionalization of C−H bonds[3−7] and the use of the derived complexes,[8−10] which include uses as sensors[11] and as models for the Fischer−Tropsch synthesis.[12] The oxidation of platinum centers is also of fundamental importance to Shilov-type functionalizations of alkanes,[13,14] and the Pt(II)/Pt(IV) redox cycle has been investigated as a model for the activation of C−H bonds.[15,16]

To date, the vast majority of cycloplatination reactions have involved starting with, and ending up, with platinum(II) species, although some examples have platinum(IV) species being synthesized via oxidative addition to platinum(II) complexes.[17−20] However, even though the reductive elimination of hydrocarbons from platinum(IV), which can be seen as analogous to the reverse of a C−H activation, has been widely studied,[21−26] there have been few reports of C−H activation by a platinum(IV) center to date.[1,27−30]

The work we report here builds on our previous work on C−H activation with platinum(II) species, work that leads to the only high-yielding route to CNC triply coordinating complexes[31,32] and to the unusual C−H activation that gave a carbene species, rather than a cyclometalated species.[33] This paper reports and discusses the synthesis of new platinum(IV) species and assesses some of their reactivity in C−H activation.

Results and Discussion

Synthesis and Isomerization of Pt(IV) Complexes. In this paper we describe the oxidation and subsequent reactivity of two related classes of cyclometalated platinum(II) complexes: complexes **1**, which contain an unsubstituted pyridine, and complexes **2**, which contain a pendant phenylpyridine group, Scheme 1. Two variants of the pyridine complexes of 2-(4-

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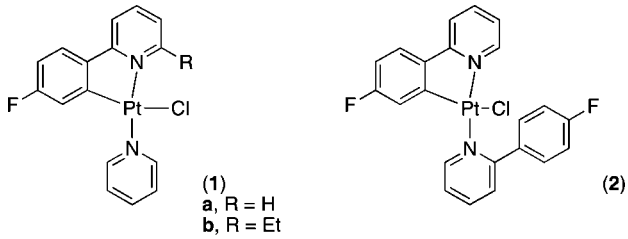
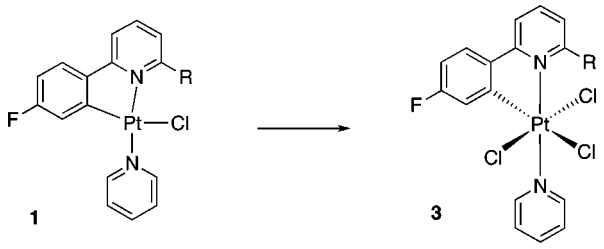
10.1021/om800583c CCC: $40.75
Publication on Web 09/27/2008

Scheme 1



Scheme 2



fluorophenyl)pyridine are discussed: those with a 6-ethyl substituent, complexes **1b**, and those without, complexes **1a**. Attempted synthesis of the 6-ethyl analogues of complexes **2** failed; presumably steric crowding around the platinum center was just too great to allow two of the larger ethyl-substituted ligands to coordinate.

Previously, we have reported the use of hydrogen peroxide as an oxidant for complexes **2**, where a large number of products were formed, some of which could be identified as hydroxide complexes.[1] In order to avoid such confusion, we decided to use the chlorine-based oxidant iodobenzene dichloride to study the oxidation of both complexes **1** and **2**. Thus, reaction of complexes **1** with $PhICl_2$ in chloroform showed a clean and rapid conversion to the platinum(IV) species **3**, Scheme 2.

Solution NMR spectroscopy clearly indicated the new products contained Pt(IV): the ^{195}Pt shift changed dramatically, moving from −3242 for **1a** to −830 ppm for **3a**, and from −3080 for **1b** to −553 ppm for **3b**. In addition, both J_{HPt} and J_{FPt} values dropped considerably compared with the Pt(II) precursor, consistent with the change from Pt(II) to Pt(IV). A geometry whereby the unsubstituted pyridine remains *trans* to the cyclometallated pyridine is suggested by NOE experiments, which clearly show the expected enhancements for that geometry. In general, spectroscopic data for complexes **3a** and **3b** were very similar, indicating equivalent geometries.

Crystals suitable for X-ray crystallography were grown from samples of **3a** from both acetone (Figure 1) and chloroform, both indicating the formulation depicted for **3** in Scheme 2. Redissolution of these crystals confirmed that they did indeed represent the bulk material, and we are therefore confident in assigning an octahedral geometry to complexes **3a**, with both pyridine nitrogens *trans* to each other. The two crystal structures we solved show essentially identical structures, except that the crystals grown from chloroform incorporate a molecule of solvent; these structures are discussed in more detail later. Since the solution spectroscopic data for complexes **3a** and **3b** are so similar, we have assigned them equivalent geometries.

In an attempt to identify any intermediates in the oxidation of **1**, we performed the reactions in an NMR tube inside the NMR spectrometer, monitoring both ^{1}H and ^{19}F resonances. In chloroform, at −40 °C both reactants are cleanly consumed, with no visible byproducts, giving **3** and iodobenzene cleanly. The reaction is quite fast and is complete within 5 min at this temperature; there is no appreciable difference in the reaction rates of either derivative of **1**.

The reaction in acetone, however, follows a different course. The first observation is that the reaction is significantly slower than in chloroform. After 1 h at −40 °C, approximately 25% of the starting materials had been consumed, and it was not until the temperature of the sample was raised to around −10 °C that the reaction became reasonably fast (25% of the starting materials being consumed in around 5 min).

The second significant difference is that a further species is clearly observed in the NMR spectra. In addition to the peaks seen for the starting material **1** and the product **3**, another broad peak in the ^{19}F NMR spectrum, likely to be a Pt(IV) species, was observed. The ^{1}H NMR spectra of the reaction showed even more additional features: while one new peak for the protons adjacent to the nitrogen of the unsubstituted pyridine is observed for **3** (and with an integral of twice that of the clearly separate

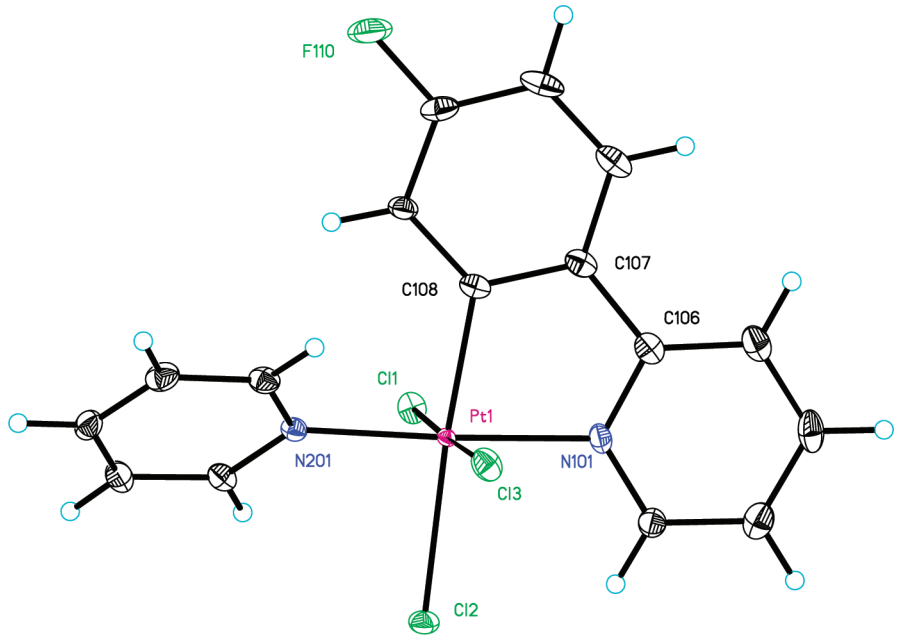


Figure 1. X-ray structure of **3a**.

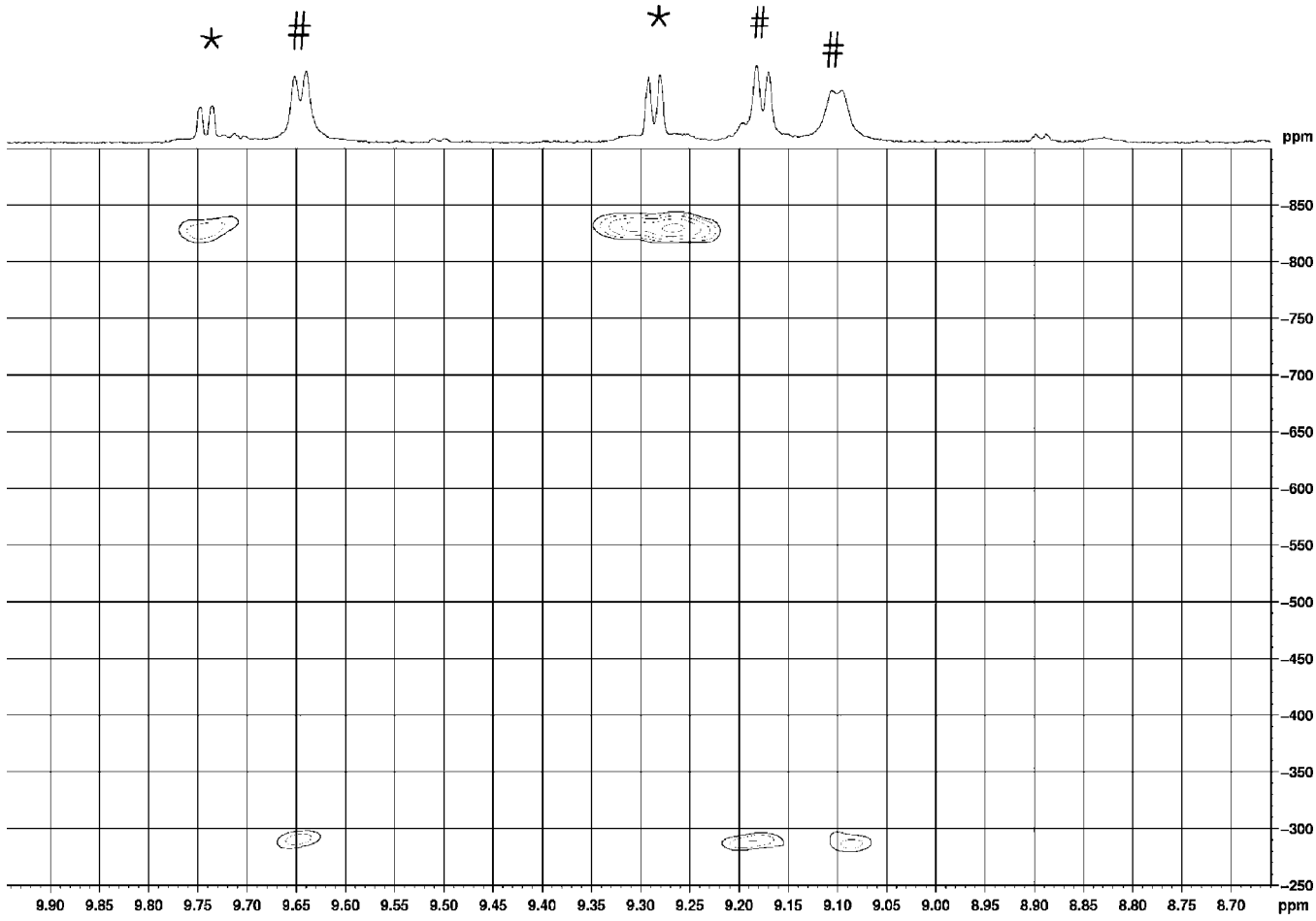
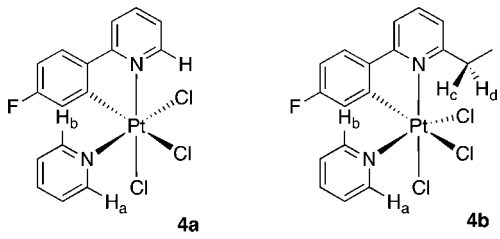


Figure 2. Part of the $^{1}H-^{195}Pt$ HETCOR NMR spectrum of the reaction mixture of **1a** with $PhICl_2$ in acetone. Peaks in the ^{1}H projection marked * come from the final product **3a**, while those marked # come from the new species.

Scheme 3



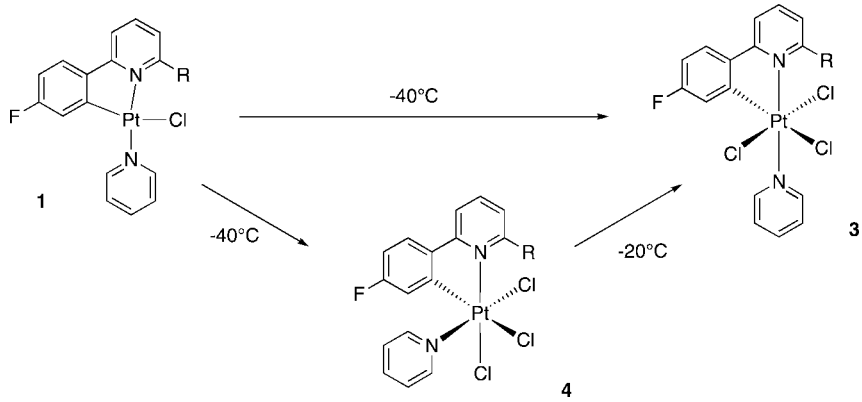
proton adjacent to both F and Pt in the cyclometalated ring), two new pyridine proton peaks were observed for the new compound (each having an integral the same size as the new signal that must represent a new proton adjacent to both F and Pt). In the reaction of **1a**, another clear signal was observed in the ^{1}H NMR: the proton adjacent to the nitrogen of the substituted pyridine (again relative integral one). The peaks for this new species have roughly twice the integrated intensity for the known product **3**. A $^{1}H-^{195}Pt$ correlation experiment on a reaction mixture was used to confirm that all these new signals did indeed correlate to the same platinum nucleus and that this platinum was a Pt(IV) center (a ^{195}Pt signal was observed at −290 ppm for the reaction starting from **1a**), Figure 2.

It is possible to allow the reaction to proceed until all the starting complex **1** is consumed, whereupon no further change is observed if the temperature is maintained at −40 °C. Now, raising the temperature of the mixture to −20 °C results in the new compound disappearing, presumably being transformed into compound **3**, as no other new peaks are observed in the NMR spectra. Thus we would suggest that the new compound is simply an isomer of **3**, as the alternative—that the new compound is an acetone complex—can be ruled out, as we describe in the discussion. There are only two other possible

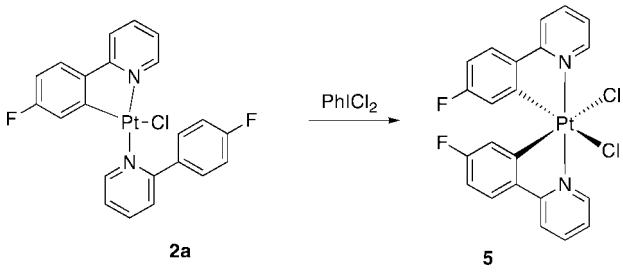
Table 1. Selected Bond Lengths [Å] and Angles [deg] for 3a, 3a·CHCl$_3$, and 1a

	3a	**3a·CHCl$_3$**	**1a**
Pt(1)−C(108)	2.013(3)	2.017(8)	1.977(6)
Pt(1)−N(101)	2.039(3)	2.049(7)	2.025(5)
Pt(1)−N(201)	2.049(3)	2.062(7)	2.022(5)
Pt(1)−Cl(2)	2.4382(8)	2.432(2)	2.397(2)
Pt(1)−Cl(3)	2.3108(9)	2.311(2)	
Pt(1)−Cl(1)	2.3306(8)	2.331(2)	
C(108)−Pt(1)−N(101)	80.98(14)	81.5(3)	81.1(2)
C(108)−Pt(1)−N(201)	95.94(13)	96.4(3)	94.0(2)
N(101)−Pt(1)−N(201)	175.57(11)	177.5(3)	174.7(2)
C(112)−Pt(1)−Cl(3)	90.42(10)	89.6(2)	
N(101)−Pt(1)−Cl(3)	87.26(9)	87.2(2)	
N(201)−Pt(1)−Cl(3)	89.59(9)	91.5(2)	
C(112)−Pt(1)−Cl(1)	88.60(10)	88.8(2)	
N(101)−Pt(1)−Cl(1)	90.77(9)	90.0(2)	
N(201)−Pt(1)−Cl(1)	92.34(9)	91.3(2)	
Cl(3)−Pt(1)−Cl(1)	177.91(3)	176.95(7)	
C(108)−Pt(1)−Cl(2)	176.21(11)	175.4(3)	178.22(18)
N(101)−Pt(1)−Cl(2)	95.23(9)	94.4(2)	97.66(17)
N(201)−Pt(1)−Cl(2)	87.83(8)	87.80(19)	87.30(15)
Cl(3)−Pt(1)−Cl(2)	89.18(3)	89.27(8)	
Cl(1)−Pt(1)−Cl(2)	91.68(3)	92.15(8)	
C(102)−N(101)−C(106)	121.8(3)	121.2(8)	119.4(6)
C(102)−N(101)−Pt(1)	123.3(2)	124.6(6)	125.4(5)
C(106)−N(101)−Pt(1)	114.8(2)	114.2(6)	115.1(5)
C(107)−C(108)−Pt(1)	126.9(3)	128.5(6)	127.3(5)

Scheme 4



Scheme 5



isomers of **3**: one where the unsubstituted pyridine is *trans* to the cyclometalated carbon and one where it is *cis* to both the cyclometalated carbon and the other pyridine nitrogen. Only in this second isomer is it possible to rationalize the ^{1}H NMR that we see, and even now we have to postulate restricted rotation of the unsubstituted pyridine preventing protons H_a and H_b of **4** in Scheme 3 from becoming equivalent. Further evidence regarding the structure of the new species comes from the NMR of the ethyl derivative that arises from the oxidation of **1b**: the two CH_2 protons (labeled H_c and H_d in Scheme 3) also become inequivalent in the ^{1}H NMR (they are 0.113 ppm apart and couple with a ^2J of 15 Hz). For H_c and H_d to become inequivalent, we need an isomer where the two sides of the phenylpyridine are different, i.e., the unsubstituted pyridine is *cis* to the phenylpyridine, **4b**. The inequivalence of H_c and H_d is not a function of restricted rotation, and we would not expect these signals to change significantly with temperature. The signals for H_a and H_b, however, ought to change with temperature, and we do observe them to coalesce to a single signal at around −10 °C (on a 400 MHz spectrometer). It is difficult to be precise about this coalescence temperature, as compound **4** rapidly transforms to what must be the thermodynamic product of this reaction, **3**, at these sorts of temperatures, but even so, we can do a standard analysis[34] and extract a barrier to the rotation of the pyridine group of 54 ± 5 kJ mol^{-1}, a value very much in line with similar reported barriers.[35,36]

While it is clear that our new compound **4** isomerizes directly to **3**, we are also certain that both **3** and **4** are formed in parallel and that **4** is not necessarily an intermediate in the synthesis of **3**. Our evidence for this assertion comes from the fact that both **3** and **4** are formed at a temperature (−40 °C) where we know isomerization does not take place. As we have already noted, reactions held at this temperature will proceed to the complete consumption of starting compound **1** and then remain as a mixture of **3** and **4** until the temperature is raised to around −20 °C, Scheme 4. Since compound **4** was only ever seen in reaction mixtures and we made no attempt to isolate it, we were not able to fully characterize it, although certain characteristic items of spectroscopic data have been recorded in the Experimental Section.

Two further experiments were performed: first the reaction was followed in a 50/50 mixture of acetone/chloroform at −40 °C. In this mixture, the reaction resembled that in pure chloroform: starting materials were consumed rapidly and **3** was the dominant product, with only a trace of **4** being seen. Second, addition of chloroform to an acetone solution of **3** and **4**, so that the resulting solution was approximately 25% chloroform, did not result in the isomerization of **4** to **3**; after 45 min at −30 °C there was no measurable difference in the integrals of any of the peaks in either the ^{1}H or ^{19}F NMR spectra.

The reaction of the pendant phenylpyridine complex **2a** with iodobenzene dichloride was studied too. In an attempt to identify any intermediates again we performed the reactions in an NMR tube inside the NMR spectrometer, monitoring both ^{1}H and ^{19}F resonances. At −40 °C, in both chloroform and acetone, both reactants are consumed, with no visible byproducts, giving previously characterized **5** and iodobenzene cleanly, Scheme 5. The reaction in chloroform is fast and is complete by the time the first spectra can be obtained at this temperature (within 3 min), whereas in acetone the reaction requires at least 2 h at this temperature.

Discussion

Why then do we observe **4** in the oxidation of **1** in acetone, but not in chloroform? The possibility that the isomerization of **4** to **3** is very rapid in chloroform, but not in acetone, can be ruled out, since the addition of chloroform to an acetone solution of **3** and **4** does not result in the immediate isomerization of **4** to **3**. Thus it must be something about the course of the oxidation reaction that is different in the two solvents. Potentially, the oxidation of the platinum centers could have occurred via a concerted homolytic cleavage process, like that seen with hydrogen peroxide,[37] or via the radical one-electron oxidation seen with *N*-chlorosuccinimide.[38] However, precedent would

(34) With an estimated coalescence temperature of 263 K, and a low-temperature peak separation of 53 Hz, use of the formula $\Delta G^{\ddagger} = RT\{23.759-\ln(k/T)\}$, where $k = \pi(|\nu_A\nu_B|)/\sqrt{2}$ gives $\Delta G^{\ddagger} = 53.7$ kJ mol^{-1}.

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Table 2. X-ray Data for Complex 3a

crystal form	yellow block	yellow block
dimensions/mm	0.41 × 0.26 × 0.20	0.28 × 0.18 × 0.10
emp formula	$C_{16}H_{12}Cl_3FN_2Pt$	$C_{17}H_{13}Cl_6FN_2Pt$
M_w	552.72	672.08
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$
a/Å	7.80790(10)	7.3913(14)
b/Å	8.60620(10)	28.633(5)
c/Å	12.1958(2)	10.588(2)
α/deg	82.3340(10)	90
β/deg	87.0520	108.775(5)
γ/deg	85.5150(10)	90
U/Å^3	809.005(19)	2121.6(7)
T/K	120(2)	180(2)
Z	2	4
D_{calc}/Mg m^{-3}	2.269	2.104
$F(000)$	520	1272
μ(Mo Kα)/mm^{-1}	9.176	7.383
θ max/deg	27.52	28.88
reflns measd	17 256	13 159
unique data	3697	5127
R_1 [$I > 2\sigma(I)$]	0.0206	0.0489
wR_2	0.0502	0.0991
data/rest/params	3697/18/208	5127/0/244

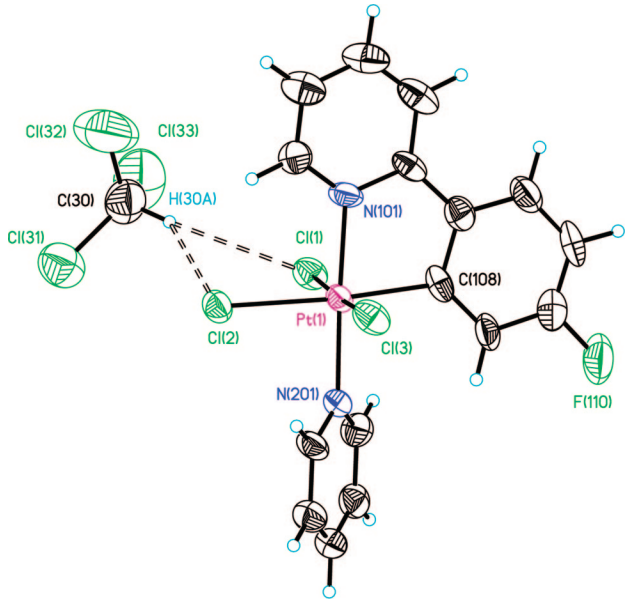

Figure 3. H-Bonding interactions between the chloroform solvate and the platinum chlorides in the X-ray structure of **3a**.

suggest[17,39] that the oxidation is taking place though an S_N2-type attack on the $PhICl_2$, and we would therefore expect a five-coordinate cationic intermediate of the type **6**, Scheme 6. If, in addition, we postulate that **6** exists as a tight ion-pair in acetone, we can see why two products might be formed: when the liberated chloride combines with the platinum center, it will approach from the same side as the initial attack, and thus it will force one of the existing ligands to move to the vacant coordination site, rather than fill it directly.

By contrast with acetone, chloroform is known to be able to solubilize chloride anions via a hydrogen bond type of interaction.[40−42] This would allow the liberated chloride to move more freely in solution, resulting in it being able to come around to the other side of the platinum center and bond directly in the vacant site. Thus only the thermodynamic product **3** is formed. Of course, this type of pathway is possible in acetone too, and might be responsible for the formation of some **3**, but we have no way of distinguishing **3** that arises from this route from **3** that arises from the route depicted in Scheme 6.

This hydrogen-bonding type of stabilization of the chloride ion can also be invoked to explain the more rapid reaction in chloroform compared with acetone. One of the chlorines of the iodobenzene dichloride in the transition state must be somewhere along the reaction pathway toward free chloride, and the chloroform solvent would be able to hydrogen bond to it, providing additional stabilization, thus lowering the activation energy and hence increasing the rate of reaction.

We can discount the possibility that the new compound **4** is simply an intermediate with a coordinated acetone ligand primarily on the grounds that the reaction in a 50/50 acetone/chloroform mixture produces only a trace of **4**, whereas we might expect substantially more if it were an acetone complex. In addition, we,[1] and others,[38] have previously isolated isomers of complexes like **4**, and we are thus confident in postulating their existence here.

We can assume the reaction of the pendant compound **2a** with $PhICl_2$ follows a similar course, i.e., an initial oxidation followed by subsequent rearrangement. We can invoke the same arguments regarding relative rate as we used when discussing the oxidation of compounds **1**, and thus this example provides some additional evidence for our proposed mechanism. The absence of any observed intermediates or isomeric products would be expected, as the oxidation reaction would give a very electrophilic five-coordinate cationic Pt(IV) center **7**, which is set up to attack the pendant phenyl ring, giving the doubly cyclometalated product **5**. We would expect this step to be very fast.[2] The geometry of **7** that would arise from the addition of Cl^+ to one face of the square-planar Pt(II) center maintains nitrogen *trans* to nitrogen, and subsequent cyclometalation gives product **5** with *cis* carbons and chlorines. This geometry is known to be the thermodynamically preferred geometry of complexes of this formulation,[1] and hence the question of isomerization does not arise in either chloroform or acetone.

Solid State Structure of Complex 3a. In the course of our studies we solved the X-ray structure of **3a** twice, in two different crystal forms. Crystals grown from acetone gave crystals that contained only **3a**, whereas those grown from chloroform included a molecule of solvent for each molecule of **3a**. Selected bond lengths and angles for both structures are recorded in Table 1. It is obvious that there are only very minor differences between the two structures in terms of the geometry of **3a**.

There are, however, some differences in the intermolecular interactions between the two structures. In the solvated structure hydrogen bonds exist between the chloroform solvate and the chlorides attached to the platinum with H to Cl distances of 2.66 and 3.03 Å, Figure 3.

Additional π-stacking interactions exist in both structures, with a pyridine ring to pyridine ring distance of 3.28 Å, Figure 4.

For comparison, the bond lengths and angles of the starting **1a**, previously reported by us,[1] are included in Table 1. Bond lengths of the ligands to the platinum are marginally larger in the Pt(IV) complexes, presumably due to the greater steric

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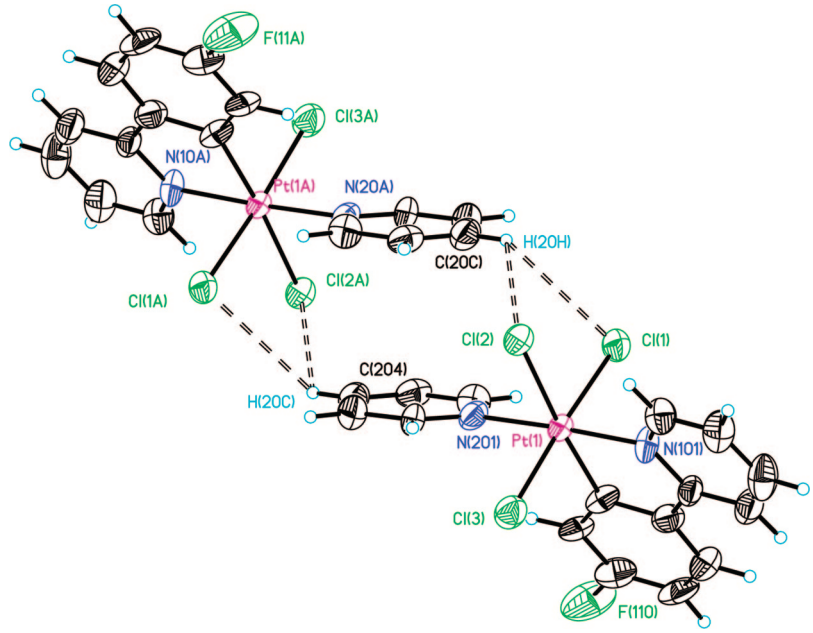
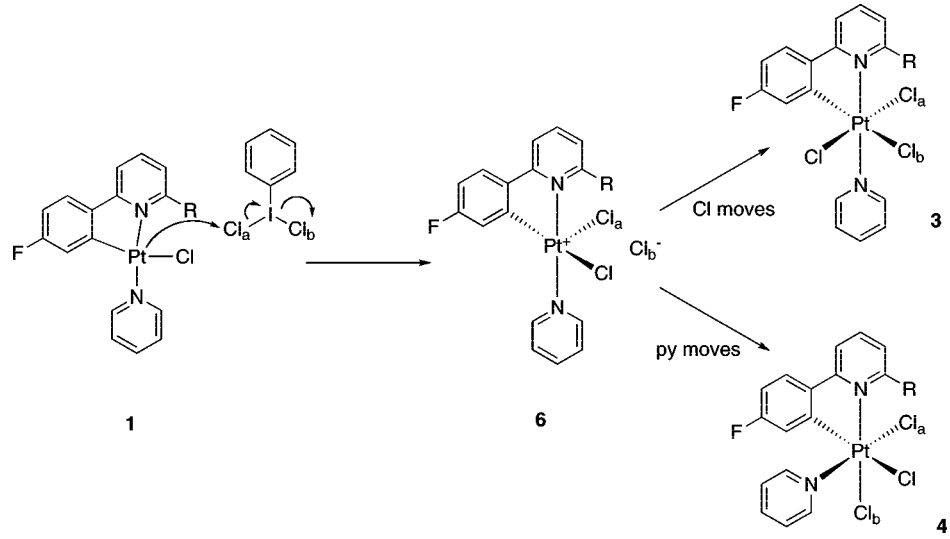
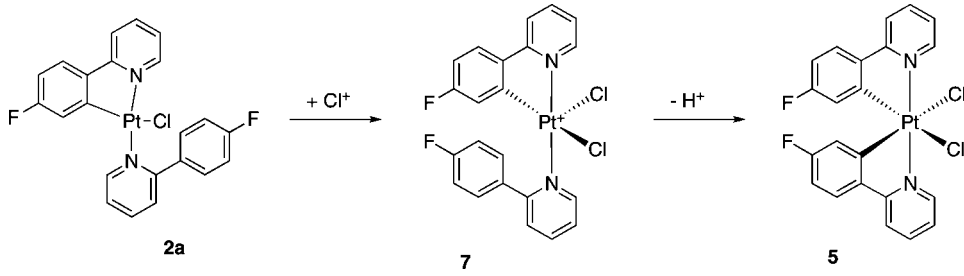


Figure 4. π-Stacking interactions present in the X-ray structure of **3a**.

Scheme 6



Scheme 7



crowding in the octahedral Pt(IV) center compared with the square-planar Pt(II) center, but otherwise there are no gross differences.

Conclusions

The oxidations of the square-planar Pt(II) species discussed in this paper are readily and cleanly achieved using the electrophilic chlorine-based oxidant $PhICl_2$. While isomeric products may be formed in certain solvents, we can account for this on the basis of the presence or absence of hydrogen-bonding interactions with chloride anions. The cleanness of our oxidations is in contrast to other reported oxidations with hydrogen peroxide[43−45] or molecular oxygen,[46,47] whereupon reactions kinetics were reported to be complex and difficult to

reproduce, with radicals implicated in some instances, although not detected in others. The oxidation of our complexes that had an uncyclometalated pendant arm resulted in the very rapid cyclometalation of that arm by the resulting electrophilic Pt(IV) species.

Experimental Section

General Procedures. All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 400 or 500 MHz spectrometer and are referenced to external TMS, assignments being made with the use of decoupling, NOE, and DEPT and COSY pulse sequences. $^{1}H-^{19}F$ and $^{1}H-^{195}Pt$ correlation spectra were recorded using a variant of the HMBC pulse sequence. ^{19}F chemical shifts are quoted from the directly observed signals (referenced to external $CFCl_3$), whereas the ^{195}Pt chemical shifts quoted are taken from the 2D HETCOR spectra (referenced to external Na_2PtCl_6). All elemental analyses were performed by Warwick Analytical Service. Starting platinum complexes **1** and **2** were prepared as previously reported.[1]

Synthesis of Compounds 3 via Oxidation of 1. Full details are provided for **3a**; **3b** was synthesized in the same manner.

A solution of the pyridine complex **1a** (100 mg, 0.274 mmol, 1 equiv) in acetone (10 mL) was treated with $PhICl_2$ (7 mg, 0.274 mmol, 1 equiv) and the mixture left at ambient temperature for 1 h. The resulting yellow precipitate collected was analytically pure and required no further purification. Yield: 109 mg (78%). Crystals suitable for X-ray analysis were grown from concentrated solutions of acetone and chloroform.

3a: ^{1}H NMR (DMSO-d_6, 298 K): δ 9.71 (1H, dd, $^{3}J_{HH}$ 6.2 Hz, $^{4}J_{HH}$ 1.3 Hz, $^{3}J_{PtH}$ 33 Hz), 9.26 (2H, dd, $^{3}J_{HH}$ 7 Hz, $^{4}J_{HH}$ 1.5 Hz, $^{3}J_{PtH}$ 36 Hz), 8.43 (1H, dd, $^{3}J_{HH}$ 8.4 Hz, $^{4}J_{HH}$ 1 Hz), 8.37 (1H, t, $^{3}J_{HH}$ 7.8 Hz), 8.30 (1H, ddd, $^{3}J_{HH}$ 8.2 Hz, $^{3}J_{HH}$ 7 Hz, $^{4}J_{HH}$ 2 Hz), 8.22 (1H, dd, $^{3}J_{HH}$ 8.4 Hz, $^{4}J_{HF}$ 6.2), 7.9 (2H, t, $^{3}J_{HH}$ 7.7 Hz), 7.73 (1H, ddd, $^{3}J_{HH}$ 7.6 Hz, $^{3}J_{HH}$ 5 Hz, $^{4}J_{HH}$ 1.2 Hz), 7.27 (1H, ddd, $^{3}J_{HH}$ 8.7 Hz, $^{4}J_{HF}$ 8.7 Hz, $^{4}J_{HH}$ 2.5 Hz), 6.40 (1H, dd, $^{3}J_{HF}$ 8.8 Hz, $^{4}J_{HH}$ 2.3 Hz, $^{3}J_{PtH}$ 32 Hz). ^{13}C NMR (DMSO-d_6, 298 K): δ 162 (d, $^{1}J_{CF}$ 253 Hz); 162.2; 152.7; 149.9; 142.2; 141.6; 140.4 (d, $^{3}J_{CF}$ 7 Hz); 137.8; 128.3 (d, $^{3}J_{CF}$ 9 Hz); 126.6 (s, $^{3}J_{CPt}$ 28 Hz), 124.7 (s, $^{3}J_{CPt}$ 27 Hz), 119.5 (s, $^{3}J_{CPt}$ 26 Hz), 115.3 (d, $^{2}J_{CF}$ 25 Hz), 113.9 (d, $^{2}J_{CF}$ 25 Hz). ^{19}F NMR (acetone-d_6, 298 K): δ −109.58 (s, $^{4}J_{FPT}$ 24 Hz) ppm. ^{195}Pt NMR (acetone-d_6, 223 K): δ −830 ppm. Anal. Found (expected for $C_{16}H_{12}Cl_3FN_2Pt$): C 34.89 (34.77); H 2.09 (2.19); N 5.01 (5.07).

3b: ^{1}H NMR (acetone-d_6, 298 K): δ 9.26 (2H, dd,$^{3}J_{HH}$ 7 Hz, $^{4}J_{HH}$ 1 Hz, $^{3}J_{HPt}$ 34 Hz), 8.22 (1H, tt, $^{3}J_{HH}$ 7.6 Hz, $^{4}J_{HH}$ 1.5 Hz), 7.97−8.02 (2H, m), 7.87 (1H, dd, $^{3}J_{HH}$ 8.2 Hz, $^{4}J_{HF}$ = 5.5 Hz), 7.69 (2H, br t, $^{3}J_{HH}$ 7 Hz), 7.39 (1H, dd, $^{3}J_{HH}$ Hz, $^{4}J_{HH}$ 2.4 Hz), 6.98 (1H, td, $^{3}J_{HH}$ = $^{3}J_{HF}$ 8.8 Hz, $^{4}J_{HH}$ 2.4 Hz), 5.93 (1H, dd, $^{3}J_{HF}$ 8.8 Hz, $^{4}J_{HH}$ 2.4 Hz, $^{3}J_{HPt}$ 33 Hz), 3.99 (2H, q, $^{3}J_{HH}$ 7.3 Hz), 1.29 (3H, t, $^{3}J_{HH}$ 7.3 Hz). ^{19}F NMR (acetone-d_6, 298 K): δ −107.7 ($^{4}J_{FPt}$ 24 Hz). ^{195}Pt NMR ($CDCl_3$, 298 K): δ −553. ESI MS: m/z 545.0 $(M - Cl)^+$, 509.1 $(M - 2Cl)^+$.

Characteristic Spectroscopic Data of Complexes 4. 4a: ^{1}H NMR (acetone-d_6, 233 K): δ 9.50 (1H, br d, $^{3}J_{HH}$ 8 Hz), 9.18 (1H, br d, $^{3}J_{HH}$ 6 Hz), 9.12 (1H, br d, $^{3}J_{HH}$ 7 Hz), 6.46 (1H, br d, $^{3}J_{HF}$ 8 Hz). ^{19}F NMR (acetone-d_6, 233 K): δ −105.6. 31P NMR (acetone-d_6, 233 K): δ −290.

4b: ^{1}H NMR (acetone-d_6, 233 K): δ 9.50 (1H, br d, $^{3}J_{HH}$ 8 Hz, $^{3}J_{HPt}$ 30 Hz), 9.01 (1H, br d, $^{3}J_{HH}$ 8 Hz, $^{3}J_{HPt}$ 30 Hz), 6.00 (1H, dd, $^{3}J_{HF}$ 9 Hz, $^{4}J_{HH}$ 2.5 Hz, $^{3}J_{HPt}$ 32 Hz), 4.03 (1H, dq, $^{2}J_{HH}$ 15 Hz, $^{3}J_{HH}$ 8 Hz), 3.92 (1H, dq, $^{2}J_{HH}$ 15 Hz, $^{3}J_{HH}$ 8 Hz), 1.35 (3H, t, $^{3}J_{HH}$ 8 Hz). ^{19}F NMR (acetone-d_6, 233 K): δ −108.6.

Synthesis of Doubly Cyclometalated Complex 5. A solution of the pendant complex **2** (50 mg, 0.087 mmol, 1 equiv) in acetone (6 mL) was treated with $PhICl_2$ (24 mg, 0.087 mmol, 1 equiv), and the mixture stirred for 1 h. The resulting yellow precipitate was then collected. Yield: 44 mg (0.073 mmol), 84%. ^{1}H NMR (DMSO-d_6, 298 K): δ 9.73 (2H, dd, $^{3}J_{HH}$ 6 Hz, $^{4}J_{HH}$ 1 Hz, $^{3}J_{HPt}$ 22 Hz), 8.55 (2H, t, $^{3}J_{HH}$ 8.5 Hz), 8.48 (2H, dt, $^{3}J_{HH}$ 8.5 Hz, $^{4}J_{HH}$ 1.5 Hz), 8.2 (2H, dd, $^{3}J_{HH}$ 8.9 Hz, $^{4}J_{HF}$ 5.6 Hz), 7.9 (2H, dt, $^{3}J_{HH}$ 6.7 Hz, $^{4}J_{HH}$ 1.32 Hz), 7.18 (2H, ddd, $^{3}J_{HH}$ 7.5 Hz, $^{3}J_{HF}$ 6.7 Hz, $^{4}J_{HH}$ 1.5 Hz), 5.7 (2H, dd, $^{3}J_{HF}$ 8.6 Hz, $^{4}J_{HH}$ 2.5 Hz, $^{3}J_{HPt}$ = 28 Hz). ^{19}F NMR ($CDCl_3$, 298 K): δ −107.52 (s, $^{4}J_{FPt}$ 34 Hz). ^{195}Pt NMR ($CDCl_3$, 298 K): δ −1806. MS (ESI): m/z 610 (M^+). Anal. Found (expected for $C_{14}Cl_2F_2H_{22}N$): C 42.89 (43.29); H 2.24 (2.31); N 4.30 (4.59).

Acknowledgment. We would like to thank the EPSRC UK National Crystallographic Service for collecting the diffraction data for the unsolvated crystal of **3a**.

OM800583C

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