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Relieving Steric Strain at Octahedral Platinum(IV): Isomerization and Reductive Coupling of Alkyl and Aryl Chlorides

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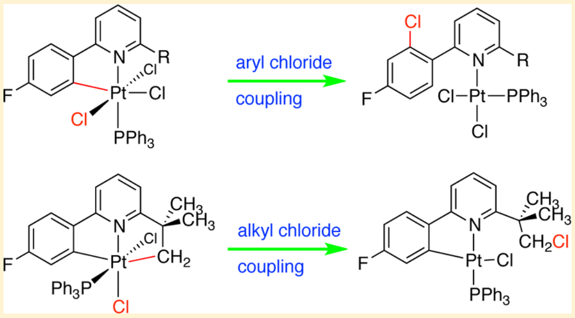
Supporting Information

ABSTRACT: Oxidation of monocyclometalated platinum(II) complexes results in octahedral platinum(IV) complexes. Depending on the substitution, two different reactions occur: either a simple isomerization, resulting in the exchange of ligand positions, or a reductive coupling of aryl chloride. With a doubly cyclometalated complex, stability of the oxidized form is dependent on isomeric form: whereas the *trans* isomer is robust, being manipulable in air at room temperature, the *cis* isomer decomposes at −20 °C and above. Reductive coupling at this *cis* isomer is 100% selective for alkyl chloride over aryl chloride and is suggested to be a concerted process.



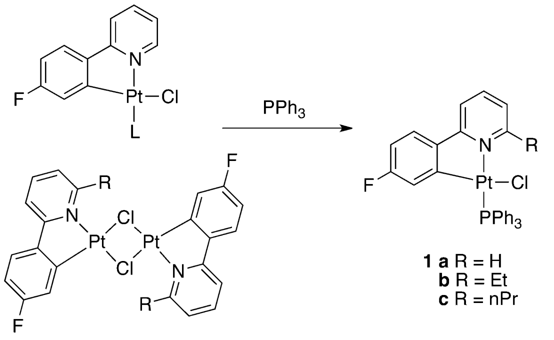
INTRODUCTION

Examples of the reductive elimination of alkyl and aryl halides from metal centers are few and far between. Reports of alkyl halide elimination are particularly rare: examples include a 1969 report on the pyrolysis of a Pt(IV) complex resulting in the elimination of methyl chloride,[1] a 1994 report that discussed the competition between C−C and C−I reductive elimination,[2] a later paper that indicated that the oxidative addition of methyl chloride was actually an equilibrium,[3] some recent examples of alkyl-F elimination,[4] and our own work with alkyl-chloride elimination.[5] Reports of reductive elimination of aryl halides are more prevalent, with some synthetic uses being described,[6] but still the number of examples is only on the order of 10.[7]

We have recently been investigating agostic complexes of,[8] C−H activation by,[8a,9] and the oxidation of[8b,9] a number of platinum(II) complexes and subsequent reactivity.[8c,10] Rarely do we get a product that does not isomerize or react in some way. With DMSO ligands we observed initial formation of sulfur-bound ligands, which isomerized to oxygen-bound ligands,[8b] with other complexes we observed dissociation of ligands to give agostic complexes,[8c,10] and with others we observed reductive elimination.[5] It would seem, therefore, that the initial products of oxidation, the geometry of which is largely determined by the geometry of the starting square-planar platinum(II) complexes, are the kinetic products and not necessarily the most stable. The driving force for isomerization or reductive elimination can nearly always be ascribed to a reduction in steric interactions in the newly formed octahedral platinum(IV) complexes. In this paper we present further results on reductive elimination reactions of both alkyl and aryl chlorides that fit very well with this pattern.

RESULTS

New monomeric cyclometalated phenylpyridine complexes of platinum(II), **1**, with a triphenylphosphine ligand were synthesized, eq 1. The basic complex (**1a**) with no additional



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functionality on the phenyl pyridine was synthesized via ligand substitution from a monomeric precursor (L = phenyl pyridine or DMSO), with the more substituted complexes (**1b** and **1c**) being synthesized via the splitting of chloride-bridged dimers.

In all cases excellent yields were obtained and the complexes were fully characterized. An X-ray study of single crystals of **1a** confirms that the triphenylphosphine group is, as expected,[11] *trans* to the pyridine, Figure 1. The similarity of spectroscopic data and the confirmation of the proximity of the PPh_3 rings to the proton *ortho* to both F and Pt (from NOE measurements) allows us to assign the same geometry to all three complexes.

Oxidation of complexes **1** proceeds smoothly with iodobenzene dichloride at room temperature to give, in all cases, octahedral platinum(IV) complexes **2**, eq 2.

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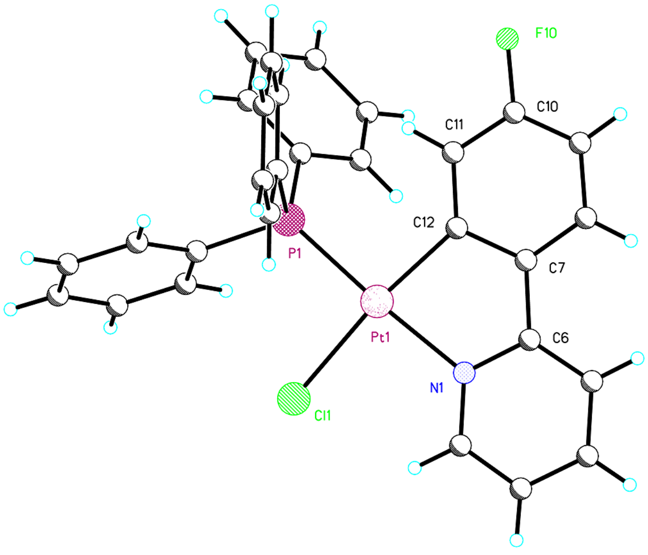
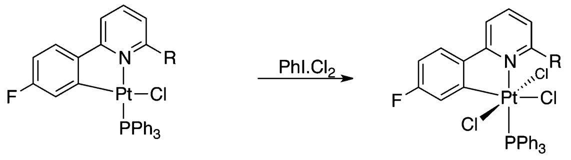
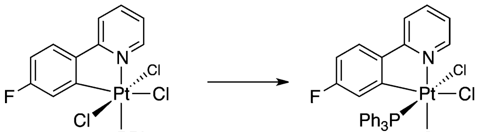


Figure 1. X-ray structure of **1a**. Selected bond lengths (Å) and angles (deg): Pt(1)–C(12) 2.019(3); Pt(1)–N(1) 2.092(2); Pt(1)–P(1) 2.2269(7); Pt(1)–Cl(1) 2.3719(6); C(6)–C(7) 1.463(4); C(12)–Pt(1)–N(1) 80.92(10); C(12)–Pt(1)–P(1) 95.34(8); N(1)–Pt(1)–P(1) 175.60(6); C(12)–Pt(1)–Cl(1) 172.81(8); N(1)–Pt(1)–Cl(1) 92.06(6); P(1)–Pt(1)–Cl(1) 91.61(2); C(2)–N(1)–C(6) 119.7(2); C(2)–N(1)–Pt(1) 125.74(19); C(6)–N(1)–Pt(1) 114.59(18); C(11)–C(12)–C(7) 116.7(2); C(11)–C(12)–Pt(1) 129.8(2); C(7)–C(12)–Pt(1) 113.4(2).



1 **2** (2)

Complexes **2** have, like their precursors **1**, the phosphine *trans* to the pyridine and now have a *mer* arrangement of the three chlorides. This particular isomer can be easily identified from the proton NMRs of the substituted complexes **2b** and **2c**, as the alternative, with a *fac* arrangement of the three chlorides (like **3a**, below), would have each of the protons of each CH$_2$ group of the R chain exhibiting a unique resonance. The sterically crowded alternative *mer* isomer with the phosphine *trans* to the cyclometalated carbon can be ruled out on two grounds: first, NOE experiments confirm the proximity of the triphenyl phosphine to the cyclometalated ring, and second, the observed ^{195}Pt–^{31}P coupling constants are larger than that expected for a P *trans* to a C. For the case of **2a**, the argument that rules out the alternative *mer* isomer is valid, but the first argument cannot be used. However, we observe a slow isomerization of the initially formed product to a new Pt(IV) species that has the same pattern of NMR signals, eq 3. We were able to unequivocally assign the *fac* geometry to this new complex **3a**, as we were able to grow crystals suitable for X-ray analysis, Figure 2. Since the new species is definitely the *fac* isomer, we are able to conclude the initial product was the depicted *mer* isomer, **2a**.



2a **3a** (3)

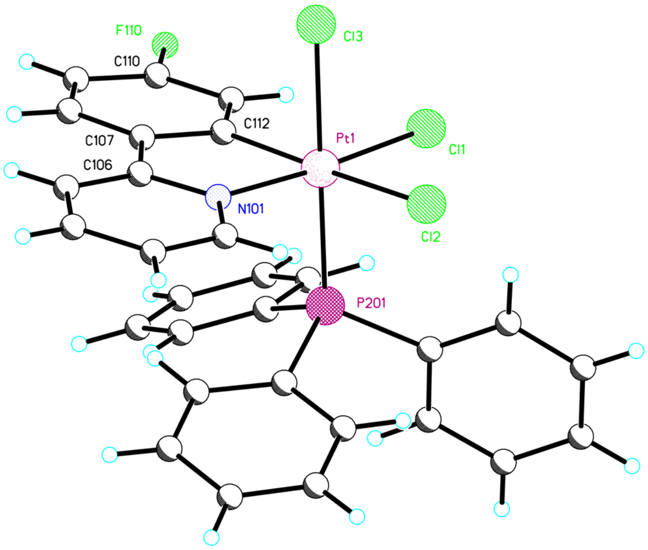
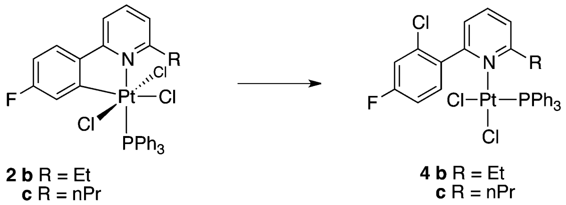


Figure 2. X-ray structure of **3a**. Selected bond lengths (Å) and angles (deg): Pt(1)–C(112) 2.031(3); Pt(1)–N(101) 2.053(3); Pt(1)–P(201) 2.3144(8); Pt(1)–Cl(1) 2.3171(8); Pt(1)–Cl(3) 2.4031(7); Pt(1)–Cl(2) 2.4431(8); N(101)–C(102) 1.343(4); N(101)–C(106) 1.361(4); C(106)–C(107) 1.460(5); C(112)–Pt(1)–N(101) 80.90(12); C(112)–Pt(1)–P(201) 92.79(9); N(101)–Pt(1)–P(201) 92.98(8); C(112)–Pt(1)–Cl(1) 93.48(9); N(101)–Pt(1)–Cl(1) 174.27(8); P(201)–Pt(1)–Cl(1) 88.36(3); C(112)–Pt(1)–Cl(3) 86.50(9); N(101)–Pt(1)–Cl(3) 88.10(8); P(201)–Pt(1)–Cl(3) 178.60(3); Cl(1)–Pt(1)–Cl(3) 90.47(3); C(112)–Pt(1)–Cl(2) 172.53(9); N(101)–Pt(1)–Cl(2) 93.27(8); P(201)–Pt(1)–Cl(2) 92.17(3); Cl(1)–Pt(1)–Cl(2) 92.24(3); Cl(3)–Pt(1)–Cl(2) 88.65(3).

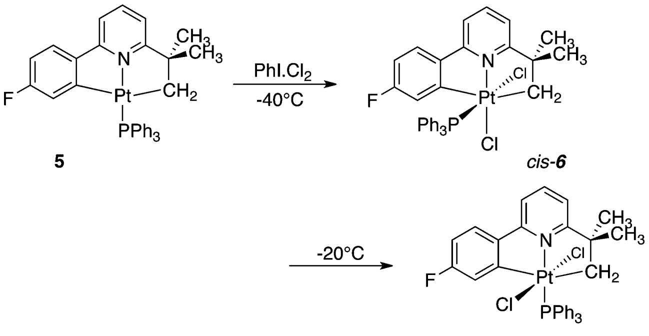
The isomerization of **2a** to **3a** takes about 2 weeks in dilute solution at room temperature with the same product formed in chloroform or acetone; reaction temperature does not affect the product formed. A different isomerization was seen with substituted complexes **2b** and **2c**. In both cases a reductive coupling was seen, accompanied by a color change from yellow to essentially colorless. Evidence for the reduction comes from a dramatic change in the ^{195}Pt chemical shift (e.g., −1661 ppm for **2b** to −3440 for **4b**) and in the ^{195}Pt–^{31}P coupling constant (e.g., form 2619 Hz for **2b** to 3765 for **4b**). Evidence for the cleavage of the Pt–C bond comes from the loss of ^{19}F–^{195}Pt coupling in the reduced species, but the coupling pattern (^{1}H–^{1}H and ^{1}H–^{19}F) of the protons in that ring suggests replacement of Pt by another group. Evidence that this other group is a chloride comes from the mass spectra of complexes **4**: very strong signals that can be assigned to a chlorinated version of the phenyl pyridine are found in the positive ion mass spectrum, with high-resolution spectra confirming the elemental composition. The fact that each of the protons of each CH$_2$ group of the R chain does exhibit a unique resonance in the ^{1}H NMR allows us to assign a *cis* geometry to the new complex, but one in which there is, on the NMR time scale, restricted rotation of the pyridine fragment about the N–Pt bond.[12]

Taken together, this evidence allows us to assign the structures depicted as **4b** and **4c** to the new Pt(II) species, eq 4. The aryl chloride reductive coupling reaction seen here was rather slow, with reaction times being on the order of 4 weeks at room temperature.



(4)

We also investigated the oxidation of the related complex **5**, which is derived from the *tert*-butyl version of the phenyl pyridine present in complexes **1**–**4**.[8a,d,10] Oxidation of **5** in chloroform proceeds cleanly and rapidly at −40 °C to give a single Pt(IV) species, identified as the complex *cis*-**6**, eq 5. The product **6** could easily be identified as the *cis* isomer from the inequivalence of both the CH_2 protons and the Me groups of the cyclometalated alkyl group in the ^{1}H NMR (signals of relative intensity 1:1:3:3) and the NOE interactions of only one of the CH_2 protons and of only one of the Me groups with the triphenylphosphine. Due to its reactivity, we were unable to isolate samples of *cis*-**6** and fully characterize it, but we were able to record complete NMR spectra at low temperature in solution. Complex *cis*-**6** underwent further reactions: it isomerized to *trans*-**6**, which showed single resonances for the CH_2 protons and for the Me groups (relative intensity 2:6), at temperatures above −20 °C, eq 5.



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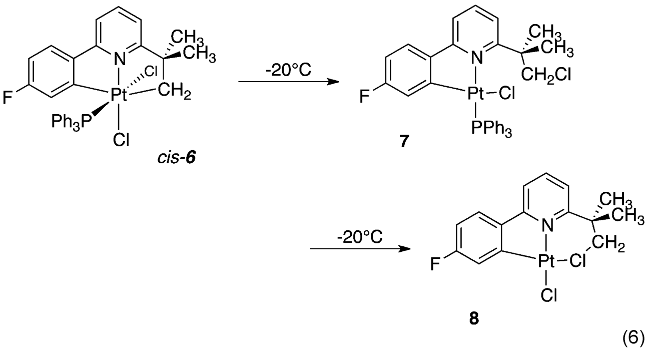
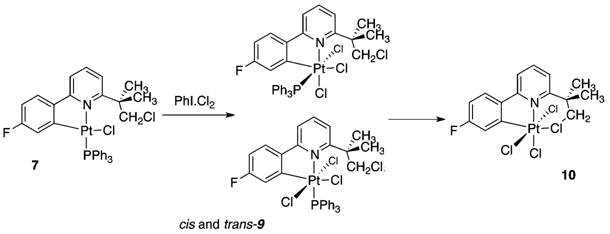
Complex *trans*-**6** can be isolated and manipulated in air at room temperature and was fully characterized. In addition to the isomerization to *trans*-**6**, complex *cis*-**6** also undergoes a reductive coupling, but, unlike complexes **2b** and **2c**, it is an *alkyl* chloride coupling rather than an aryl chloride coupling. The coupling we see takes place much more rapidly than that seen with complexes **2b** and **2c** and takes place at temperatures above −20 °C: it is complete in minutes in any sample taken to 0 °C. The initial product of reduction can be identified as **7**: a single peak in the ^{31}P NMR with a ^{195}Pt–^{31}P coupling constant consistent with a Pt(II) species and a ^{195}Pt chemical shift consistent with Pt(II) and two ^{1}H resonances in the ratio 2:6 (neither with Pt satellites) for the chloroalkyl group. In solution at −20 °C the ratio of **7** to *trans*-**6** produced is roughly 3:1. The production of **7** and *trans*-**6** appears to be via parallel and competing reactions. Using chloroform as the solvent (to minimize the extent of the isomerization), we sought to extricate some of the reaction parameters. However it proved impossible to satisfactorily separate the kinetics of the two reactions. Addition of extra phosphine did not appear to significantly affect the rate of the reductive coupling, but seemed to retard the rate of isomerization. Addition of extra chloride (in the form of Bu_4NCl) did not appear to affect either reaction rate.



(6)

Complex **7** could not, however, be fully characterized: it lost triphenylphosphine when attempts were made to isolate it and formed (among other unidentified products) the previously characterized **8**. Further reactivity of complex **7** was observed if it was treated with more oxidant: NMR signals consistent with new complexes **9** were identified before they lost triphenylphosphine to give (among other unidentified products) the previously characterized **10**, eq 7



(7)

■ DISCUSSION

As shown in eq 2, complexes **2** form, upon initial oxidation, with all the previously bound species in the same relative positions as the starting complexes **1**. Such a result can be thought of as arising either from the delivery of the two new chloride ligands to the same face of the platinum(II) square plane, with the existing chloride moving, or from the delivery of the two new chlorides separately to opposite sides of the molecule.[9b,13] The isomerization of **2a** to **3a** depicted in eq 3 can be seen as providing steric relief, as the large phosphine ligand is moved out of the plane of the metalated pyridine to a position in **3a** where it is less encumbered. This isomerization has many similarities to isomerization reactions we have seen before with other Pt(IV) complexes,[8b,9,10] and our observations here add nothing to the lessons learned there.

The presence of the alkyl chains in **2b** and **2c** would not be expected to electronically destabilize the Pt(IV) center in **2b** and **2c** compared with **2a**; if anything, the electron-releasing chains might be expected to help stabilize the high oxidation state. However, we might expect more steric crowding in complexes **2b** and **2c** compared with **2a** and a greater driving force toward isomerization. Though the final products are ones that arise from reductive elimination, presumably an isomerization to unseen **3b** and **3c** is also possible for complexes **2b** and **2c**. Whether the additional steric interactions of the alkyl chain affect their stability adversely and the unseen **3b** and **3c** rapidly reductively eliminate or whether complexes **2b** and **2c** directly reductively eliminate to **4b** and **4c** cannot be determined from our current experiments. Either way, the fact that neither **2a** nor **3a** shows any tendency to reductively eliminate demonstrates how fine the balance between the relative stabilities of the Pt(IV) and Pt(II) centers in the alkyl-substituted complexes really is.

If we consider the mechanism of reductive elimination that operates to give complexes **4b** and **4c**, it is generally accepted that a concerted route for aryl halide reductive eliminations exists. Recent work on aryl oxygen[14] and aryl bromine[15] eliminations and demonstrations of the involvement of dimeric Pd(III) complexes[16] in eliminations all invoke concerted routes: our work here fits in nicely with these results, and we would expect a concerted mechanism to operate for reaction 4. For such a process, we would need with *cis* C and Cl to form the new bond and, further, we might expect the coupling chloride to have its Pt−Cl bond parallel with the p orbitals of the π system of the aryl ring on which the C atom is located.[7b,17] Such an arrangement is present in both complexes **2** and **3** and cannot therefore be used to distinguish between complexes **2b** and **2c** isomerizing first or directly reductively eliminating.

If we consider the oxidation of doubly cyclometalated **5** shown in eq 5, we see the initial formation of only a single isomer of the product, *cis*-**6**, which can be thought of as arising from delivery of both of the new chlorides to the same face of **5**, with the phosphine being moved out of the plane of the phenyl pyridine. In our previous work we had established that the solvent was often noninnocent,[5,9b,10] particularly if acetone or DMSO was used, and for this reason we used chloroform as the reaction solvent. That doubly cyclometalated **5** gives only *cis*-**6** is not unexpected: the equivalent complex with a DMSO ligand in place of the triphenylphosphine gave predominately the *cis* isomer in the equivalent reaction.[5] We see *cis*-**6** isomerize to *trans*-**6** on warming to −20 °C, and all previous work on the isomerization of octahedral d^6 complexes of Pt(IV) indicates a likely dissociative mechanism;[18] our observation of a retarding of the rate with added phosphine is consistent with this mechanism. The isolation of unreactive *trans*-**6** has parallels with our previously reported DMSO complexes, where we also saw an isomerization of *cis* to *trans* and were again able to isolate and characterize the *trans* isomer.

The reductive elimination reaction we observe with *cis*-**6**, the coupling of a chloride with the cyclometalated alkyl group to give **7**, also has precedent in our earlier work: with the DMSO complex we saw the same parallel reaction where the *cis* reductively eliminated an alkyl chloride group. The triphenylphosphine complex *cis*-**6** is more prone to reductive elimination than the DMSO equivalent: whereas the DMSO complex began to react only at temperatures above 0 °C, the triphenylphosphine complex begins to reductively eliminate above −20 °C. Such an observation is entirely consistent with the increase steric bulk of the triphenylphosphine compared with the DMSO.

With the equivalent DMSO complexes, we were intrigued as to why the *cis* complex reductively eliminated, but the *trans* remained stable. There, provisional DFT studies had indicated that there was not a great thermodynamic preference for *trans* over *cis* (∼4 kJ mol^{-1}). With the triphenylphosphine complexes **6** and **7** we see a similarly small preference for the *trans* over the *cis* (∼2 kJ mol^{-1}), with both disfavored by some 10 kJ mol^{-1} over the reductively coupled product **7**. Thus it cannot be that the *trans*-**6** is favored over both the *cis*-**6** and the coupled product, but that there is a low-energy route from *cis*-**6** to **7**, one that is not available to *trans*-**6**.

The S_N2 type of oxidative addition of alkyl halides to late transition metals has been well established,[19] and thus the microscopic reverse reaction would be expected to initiate with the dissociation of halide from the metal, with this liberated halide then combining with the eliminating alkyl group. It is hard to see how the difference in rates of reductive coupling at *cis*- and *trans*-**6** could fit with the microscopic reverse of the S_N2 process, and we were able, with a detailed kinetic analysis (and other reactions), to definitively assign a unimolecular concerted mechanism to the reductive coupling for the DMSO analogue.[5] With the triphenylphosphine complex **6**, we see the same isomeric dependence of the reductive elimination and see no reason not to assign a concerted mechanism to this new example. With a simplistic model of a concerted process, we can see in the *cis* orientation a chloride *trans* to the N can couple easily with the alkyl group, whereas in the *trans* it cannot, Figure 3. Such an isomeric dependence of reaction route would not exist for an S_N2-type process.

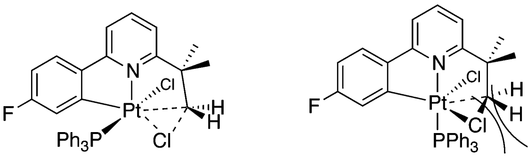


Figure 3. In the *cis* isomer (left) the chloride can couple with the alkyl group with little disruption to the rest of the molecule, whereas in the *trans* isomer (right) an initial steric clash with a hydrogen needs a substantial rearrangement of the cyclometalated ring in order to facilitate the coupling.

Apart from our previous work, there has been no other examples of a concerted mechanism for alkyl chloride reductive elimination. Sterically crowded platinum complexes have been shown to undergo concerted alkyl fluoride reductive elimination when treated with XeF_2 to generate a putative dicationic Pt(IV) center[4a] (earlier work with XeF_2 and platinum showing benzylic-F elimination did not suggest a mechanism[4c]), and another more recent example suggests that a concerted mechanism might be working for an alkyl-F coupling at Pd(IV).[4b] A few other studies on systems related to the work presented here have been conducted, but it is the reductive elimination of alkyl oxygen groups at Pt(IV) that is of most relevance: an S_N2-type process has been demonstrated with unconstrained ligand systems,[20] but a concerted process in a solitary example with chelating groups.[21] Our work here therefore fits in with an emerging pattern of concerted alkyl-X reductive elimination reactions where steric factors force the coupling groups into close proximity.

The reductive elimination we observe is completely selective for the $C(sp^3)$−Cl coupling over $C(sp^2)$−Cl coupling and can be attributed to the thermodynamics of the weaker M−C bond being cleaved. Once formed, complex **7** can lose triphenylphosphine to form complex **8**, where the last ligand position at platinum is taken up by the chloride attached to the *tert*-butyl group. Presumably the entropic factors associated with the chelating of this group to the central metal, coupled with a reduction in steric crowding, are sufficient to overcome the replacement of the strong Pt−P bond with a weaker Pt−Cl bond. If we compare the situation with our previously reported

DMSO complexes, it is interesting to note that the equivalent of **7** was not seen, and only **8** was observed. Further oxidation of **7** or **8** (or indeed a mixture of **7** and **8**) ultimately gives the same product: the previously characterized **10**, where the additional steric congestion of the alternative products, *cis*- and *trans*-**9**, is relieved.

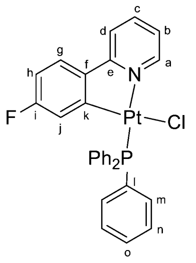
■ CONCLUSIONS

Square-planar platinum(II) complexes evidently experience increased steric strain upon oxidation to octahedral platinum(IV) species. We have demonstrated that the balance between relieving this strain through the simple expedient of ligand rearrangement or through reductive coupling of two of the groups is very fine. In complex *cis*-**6**, steric strain is relieved through a reductive coupling that is totally selective for alkyl chloride over an alternative aryl chloride elimination.

■ EXPERIMENTAL SECTION

General Procedures. All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 400, 500, or 600 MHz spectrometer and are referenced to external TMS, assignments being made with the use of decoupling, NOE, and the 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 were prepared as previously reported.[8a,9]

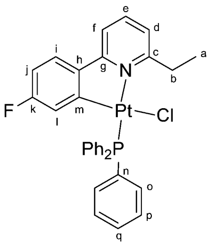
Synthesis of Complex 1a. Pendant phenylpyridine complex (F-PhPy-H)Pt(PhPy)Cl (0.0201 g, 3.49×10^{-5} mol, 1 equiv) and PPh_3 (0.0092 g, 3.49×10^{-5} mol, 1 equiv) were dissolved in acetone (15 mL) and allowed to stir at room temperature for 5 h. The solvent was removed and the residue dissolved in DCM. The solution was washed with 2.5 M HCl (2 × 20 mL) and dried over $MgSO_4$, and the solvent was removed. Yield: 0.018 g, 2.65×10^{-5} mol, 76%. A crystal suitable for X-ray diffraction was grown by slow evaporation of solvent from a chloroform solution. Details are given in Table 1 (SI).



1a

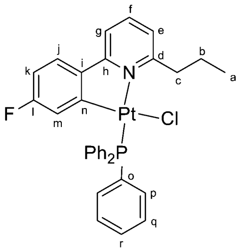
δ_H (400 MHz, 298 K, $CDCl_3$): 9.78 (1H, ddd, ^{3}J = 5.8 Hz, ^{4}J = 1.3 Hz, $^{4}J_{H-P}$ = 4.1 Hz, H_a), 7.80 (1H, td, ^{3}J = 7.8 Hz, ^{4}J = 1.6 Hz, H_c), 7.71−7.75 (6H, m, H_n), 7.62 (1H, d, ^{3}J = 8 Hz, H_d), 7.43 (1H, dd, ^{3}J = 8.5 Hz, $^{4}J_{H-F}$ = 5.8 Hz, H_g), 7.38 (3H, td, ^{3}J = 7.4 Hz, ^{4}J = 2 Hz, H_o), 7.30−7.33 (6H, m, H_m), 7.20−7.23 (1H, m, H_b), 6.59 (1H, td, $^{3}J_{H-H,\ H-F}$ = 8.4 Hz, ^{4}J = 2.5 Hz, H_h), 6.23 (1H, dt, $^{3}J_{H-F}$ = 11.2 Hz, $^{4}J_{H-H,\ H-P}$ = 2.8 Hz, $^{3}J_{H-Pt}$ = 63 Hz, H_j) ppm. δ_C (100 MHz, 298 K, $CDCl_3$): 163.7 (C_e), 161.8 (d, $^{1}J_{C-F}$ = 251 Hz, C_i), 148.3 (d, $^{7}J_{C-F}$ = 4.6 Hz, $^{2}J_{C-Pt}$ = 24 Hz, C_a), 143.6 (d, $^{3}J_{C-F}$ = 6 Hz, C_k), 140.8 (C_f), 138.5 (C_c), 134.3 (C_n), 129.9 (C_o), 129.0 (C_l), 127.0 (C_m), 123.9 (d, $^{3}J_{C-F}$ = 9.2 Hz, $^{3}J_{C-Pt}$ = 52 Hz, C_g), 123.1 (d, $^{2}J_{C-F}$ = 21 Hz, C_j), 120.7 ($^{3}J_{C-Pt}$ = 23 Hz, C_b), 117.2 ($^{3}J_{C-Pt}$ = 29 Hz, C_d), 109.2 (d, $^{2}J_{C-F}$ = 23 Hz, C_h) ppm. δ_F (375 MHz, 298 K, $CDCl_3$): −110.1 ($^{4}J_{F-Pt}$ = 54 Hz) ppm. δ_P (121 MHz, 298 K, $CDCl_3$): 22.9 ($^{1}J_{P-Pt}$ = 4265 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −4160 (d, $^{1}J_{Pt-P}$ = 4283 Hz) ppm. HR-MS (ESI): *m*/*z* 628.1091 calculated for $C_{29}H_{22}FNP^{194}Pt$ = $(M - Cl)^+$ 628.1095. Anal. Found (Expected): C 51.93 (52.38), H 3.54 (3.33), N 1.89 (2.11).

Synthesis of Complexes 1b and 1c. Chloride-bridged dimer ((F-PhPy-R)PtCl)$_2$ (0.0728 g, 8.45×10^{-5} mol, 1 equiv) was dissolved in acetone, and PPh_3 (0.0443 g 1.69×10^{-4} mol, 2 equiv) added. The solution was stirred at room temperature for 1 h. The solvent was removed to give **1b**. Yield: 0.0550 g, 7.94×10^{-5} mol, 94%. Similarly **1c** was produced in 92% yield.



1b

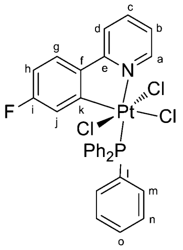
δ_H (400 MHz, 298 K, $CDCl_3$): 7.73 (6H, m, H_o), 7.66 (1H, t, ^{3}J = 7.8 Hz, H_e), 7.46 (1H, d, ^{3}J = 7.9 Hz, H_f), 7.21−7.40 (10H, m, $H_{p,\ q\ and\ i}$), 7.09 (1H, d, ^{3}J = 7.8 Hz, H_d), 6.52 (1H, td, $^{3}J_{H-H,\ H-F}$ = 8.4 Hz, ^{4}J = 2.5 Hz, H_j), 6.16 (1H, ddd, $^{3}J_{H-F}$ = 10.8 Hz, $^{4}J_{H-P}$ = 3.5 Hz, $^{4}J_{H-H}$ = 2.5 Hz, $^{3}J_{H-Pt}$ = 60 Hz, H_l), 3.60 (2H, q, ^{3}J = 7.5 Hz, H_b), 1.33 (3H, t, ^{3}J = 7.5 Hz, H_a) ppm. δ_C (100 MHz, 298 K, $CDCl_3$): 168.0 (C_c), 162.8 (C_g), 160.5 (d, $^{1}J_{C-F}$ = 252 Hz, C_k), 143.6 (d, $^{4}J_{C-F}$ = 6 Hz, C_h), 141.8 (d, $^{3}J_{C-F}$ = 2 Hz, C_m), 138.0 (C_e), 134.2 (d, $^{2}J_{C-P}$ = 11.5 Hz, C_o), 129.7 (d, $^{4}J_{C-P}$ = 3 Hz, C_q), 128.8 (d, $^{1}J_{C-P}$ = 63 Hz, C_n), 127.0 (d, $^{3}J_{C-P}$ = 12.3 Hz, C_p), 124.3 (d, $^{3}J_{C-F}$ = 8.4 Hz, $^{3}J_{C-Pt}$ = 38 Hz, C_i), 122.2 (dd, $^{2}J_{C-F}$ = 20.7 Hz, $^{3}J_{C-P}$ = 7.7 Hz, C_l), 121.1 (d, $^{4}J_{C-P}$ = 4.6 Hz, C_d), 114.2 (C_f), 109.3 (d, $^{2}J_{C-F}$ = 23 Hz, C_j), 31.1 (C_b), 14.1 (C_a) ppm. δ_F (282 MHz, 298 K, $CDCl_3$): −112.0 ($^{4}J_{F-Pt}$ = 64 Hz) ppm. δ_P (121 MHz, 298 K, $CDCl_3$): 21.4 ($^{1}J_{P-Pt}$ = 4449 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −3943 (d, $^{1}J_{Pt-P}$ = 4497 Hz) ppm. HR-MS (ESI): *m*/*z* 656.1425 calculated for $C_{31}H_{26}FNP^{194}Pt$ = $(M - Cl)^+$ 656.1408. Anal. Found (Expected): C 53.67 (53.72); H 3.88 (3.78); N 2.42 (2.02).



1c

δ_H (400 MHz, 298 K, $CDCl_3$): 7.71−7.76 (6H, m, H_p), 7.62 (1H, t, ^{3}J = 7.8 Hz, H_f), 7.45 (1H, d, ^{3}J = 8 Hz, H_g), 7.28−7.38 (10H, m, $H_{j,\ q\ and\ r}$), 7.06 (1H, d, ^{3}J = 7.5 Hz, H_e), 6.52 (1H, td, $^{3}J_{H-H,\ H-F}$ = 8.3 Hz, ^{4}J = 2.5 Hz, H_k), 6.16 (1H, ddd, $^{3}J_{H-F}$ = 10.8 Hz, $^{4}J_{H-P}$ = 2.7 Hz, $^{4}J_{H-H}$ = 2.5 Hz, $^{3}J_{H-Pt}$ = 62 Hz, H_m), 3.57−3.60 (2H, m, H_c), 1.88 (2H, sextet, ^{3}J = 7.5 Hz, H_b), 0.88 (3H, t, ^{3}J = 7.5 Hz, H_a) ppm. δ_C (100 MHz, 298 K, $CDCl_3$): 166.6 (C_d), 163.0 (d, $^{3}J_{C-P}$ = 3 Hz, C_h), 160.5 (dd, $^{1}J_{C-F}$ = 252 Hz, $^{4}J_{C-P}$ = 3 Hz, C_l), 143.6 (t, $^{4}J_{C-F}$ = 6 Hz, $^{3}J_{C-P}$ = 6 Hz, C_i), 141.7 (d, $^{3}J_{C-F}$ = 2 Hz, C_n), 137.9 (C_f), 134.1 (d, $^{2}J_{C-P}$ = 10 Hz, C_p), 129.7 (d, $^{4}J_{C-P}$ = 2.3 Hz, C_r), 128.9 (d, $^{1}J_{C-P}$ = 61 Hz, C_o), 127.0 (d, $^{3}J_{C-P}$ = 11.5 Hz, C_q), 124.3 (d, $^{3}J_{C-F}$ = 9 Hz, C_j), 122.1 (dd, $^{2}J_{C-F}$ = 20 Hz, $^{3}J_{C-P}$ = 7 Hz, C_m), 121.9 (C_e), 114.3 (C_g), 109.2 (d, $^{2}J_{C-F}$ = 23 Hz, C_k), 39.4 (C_c), 23.5 (C_b), 12.8 (C_a) ppm. δ_F (375 MHz, 298 K, $CDCl_3$): −112.0 ($^{4}J_{F-Pt}$ = 60 Hz) ppm. δ_P (161 MHz, 298 K, $CDCl_3$): 21.1 ($^{1}J_{P-Pt}$ = 4446 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −3923 (d, $^{1}J_{Pt-P}$ = 4466 Hz) ppm. HR-MS (ESI): *m*/*z* 670.1573 calculated for $C_{32}H_{28}FNP^{194}Pt$ = $(M - Cl)^+$ 670.1565. Anal. Found (Expected): C 53.82 (54.36); H 3.45 (3.99); N (1.96 (1.98).

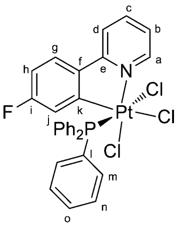
Synthesis of Complexes 2a and 3. Complex **1a** (0.011 g, 1.65×10^{-5} mol, 1 equiv) was dissolved in $CDCl_3$, and (dichloroiodo)benzene (0.0045 g, 1.65×10^{-5} mol, 1 equiv) was added at room temperature. After 10 min the solvent was removed and the product washed with pet ether 40–60 to give pure complex **2a**. Yield: 0.011 g, 1.49 × 10^{-5} mol, 90%.



2a

δ_H (400 MHz, 273 K, $CDCl_3$): 10.00 (1H, td, ^3J = 6 Hz, ^4J = 1 Hz, $^3J_{H-Pt}$ = 30 Hz, H_a), 8.09 (6H, m, H_m), 7.97 (1H, td, ^3J = 7.8 Hz, ^4J = 1.3 Hz, H_c), 7.89 (1H, d, ^3J = 8 Hz, H_d), 7.71 (1H, m, H_g), 7.53 (3H, m, H_o), 7.44–7.48 (7H, m, H_b and H_n), 6.89 (1H, td, $^3J_{H-H,\ H-F}$ = 8 Hz, ^4J = 2.6 Hz, H_h), 6.50 (1H, dt, $^3J_{H-F}$ = 10 Hz, $^4J_{H-H,\ H-P}$ = 2.6 Hz, $^3J_{H-Pt}$ = 32 Hz, H_j) ppm. δ_C (100 MHz, 298 K, $CDCl_3$): 160.0 (C_e), 146.6 (d, $^3J_{C-P}$ = 6 Hz C_a), 139.3 (C_c), 139.1 (d, $^4J_{C-F}$ = 6 Hz, C_f), 137.8 (d, $^3J_{C-F}$ = 2 Hz, C_k), 134.8 (d, $^2J_{C-P}$ = 9 Hz, C_m), 130.9 (d, $^4J_{C-P}$ = 2 Hz, C_o), 126.6 (d, $^3J_{C-P}$ = 12 Hz, C_n), 125.6 (d, $^3J_{C-F}$ = 9 Hz, C_g), 125.4 (d, $^1J_{C-P}$ = 66 Hz, C_l), 122.5 (d, $^4J_{C-P}$ = 5 Hz, C_b), 120.7 (dd, $^2J_{C-F}$ = 24 Hz, $^3J_{C-P}$ = 3 Hz, C_j), 119.4 (d, $^4J_{C-P}$ = 3 Hz, $^3J_{C-Pt}$ = 21 Hz, C_d), 112.2 (d, $^2J_{C-F}$ = 23 Hz, C_h) ppm. δ_F (375 MHz, 273 K, $CDCl_3$): −105.5 ($^4J_{F-Pt}$ = 30 Hz) ppm. δ_P (161 MHz, 273 K, $CDCl_3$): −3.2 ($^1J_{P-Pt}$ = 2494 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −1916 (d, $^1J_{Pt-P}$ = 2494 Hz) ppm.

NMR spectra of the sample were collected over a number of days, showing the disappearance of **2a** and appearance of a new species identified as **3**. Crystals of **3** suitable for single-crystal analysis were grown by slow evaporation of solvent from a chloroform solution. X-ray data are given in Table 1 (SI).

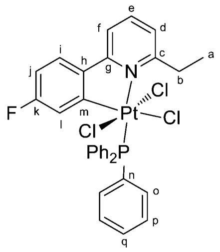


3

δ_H (500 MHz, 298 K, $CDCl_3$): 9.29 (1H, dd, ^3J = 6.3 Hz, ^4J = 1.3 Hz, $^3J_{H-Pt}$ = 30 Hz, H_a), 7.63 (1H, td, ^3J = 7.8 Hz, ^4J = 1.4 Hz, H_c), 7.60 (1H, m, H_j), 7.48–7.51 (6H, m, H_m), 7.46 (1H, dd, ^3J = 8.8 Hz, $^4J_{H-F}$ = 5.4 Hz, H_g), 7.38–7.41 (1H, m, H_d), 7.32–7.35 (3H, m, H_o), 7.14–7.18 (6H, m, H_n), 6.86 (1H, td, ^3J = 7.0 Hz, ^4J = 1.4 Hz, H_b), 6.78 (1H, td, $^3J_{H-H,\ H-F}$ = 8.3 Hz, ^4J = 2.4 Hz, H_h) ppm. δ_F (375 MHz, 298 K, $CDCl_3$): −101.8 ($^4J_{F-Pt}$ = 28 Hz) ppm. δ_P (202 MHz, 298 K, $CDCl_3$): −8.6 ($^1J_{P-Pt}$ = 2303 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −2102 (d, $^1J_{Pt-P}$ = 2354 Hz) ppm. HR-MS (ESI): *m/z* 756.0080 calculated for $C_{29}H_{22}{}^{35}Cl_3FNNaP^{194}Pt$ = $(M + Na)^+$ 756.0058, 698.0490 calculated for $C_{29}H_{22}{}^{35}Cl_2FNP^{194}Pt$ = $(M - Cl)^+$ 698.0472. Anal. Found (Expected): C 46.94 (47.33); H 3.32 (3.01); N 1.72 (1.90).

Synthesis of Complexes 2b and 2c. Complex **1b** (0.015 g, 2.16 × 10^{-5} mol, 1 equiv) was dissolved in $CDCl_3$, and (dichloroiodo)benzene (0.0060 g, 2.16 × 10^{-5} mol, 1 equiv) was added at room temperature. After 10 min the solvent was removed and the product washed with pet ether 40–60 to give pure complex **2b**. Yield: 0.0144 g, 1.88 × 10^{-5} mol, 87%.

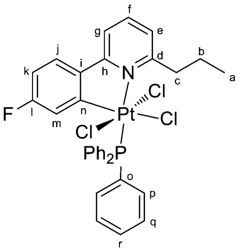
δ_H (400 MHz, 298 K, $CDCl_3$): 7.92 (6H, m, H_o), 7.75 (1H, t, ^3J = 7.6 Hz, H_e), 7.63 (1H, d, ^3J = 8 Hz, H_f), 7.48 (1H, dd, ^3J = 8.5 Hz, $^4J_{H-F}$ = 5.6 Hz, H_i), 7.43 (3H, m, H_q), 7.31 (6H, td, ^3J = 7.6 Hz, ^4J = 3.4 Hz, H_p), 7.13 (1H, br d, ^3J = 7.6 Hz, H_d), 6.74 (1H, td, $^3J_{H-H,\ H-F}$ = 8.2 Hz, ^4J = 2.4 Hz, H_j), 6.32 (1H, ddd, $^3J_{H-F}$ = 9.8 Hz, ^4J = 2.4 Hz, $^4J_{H-P}$ = 3.7 Hz, $^3J_{H-Pt}$ = 39.6 Hz, H_l), 3.87 (2H, q, ^3J = 7.4 Hz, H_b), 1.27 (3H, t, ^3J = 7.4 Hz, H_a) ppm. δ_C (100 MHz, 298 K, $CDCl_3$):



2b

170.0 (C_c), 162.8 (C_g), 160.8 (d, $^1J_{C-F}$ = 253.5 Hz, C_k), 141.1 (d, $^4J_{C-F}$ = 2.2 Hz, C_h), 139.9 (C_m), 139.8 (C_e), 136.1 (d, $^2J_{C-P}$ = 8.5 Hz, $^3J_{C-Pt}$ = 17 Hz, C_o), 131.8 (d, $^4J_{C-P}$ = 2.7 Hz, C_q), 127.8 (d, $^3J_{C-P}$ = 12 Hz, C_p), 126.7 (d, $^3J_{C-F}$ = 8.5 Hz, C_i), 126.5 (d, $^1J_{C-P}$ = 69 Hz, C_n), 123.4 (d, $^4J_{C-P}$ = 6.7 Hz, $^3J_{C-Pt}$ = 19 Hz, C_d), 122.6 (dd, $^2J_{C-F}$ = 24 Hz, $^3J_{C-P}$ = 3 Hz, $^2J_{C-Pt}$ = 51 Hz, C_l), 117.9 (d, $^4J_{C-P}$ = 3.3 Hz, $^3J_{C-Pt}$ = 19 Hz, C_f), 113.2 (d, $^2J_{C-F}$ = 22.5 Hz, C_j), 30.8 (C_b), 15.1 (C_a) ppm. δ_F (375 MHz, 298 K, $CDCl_3$): −108.5 ($^4J_{F-Pt}$ = 34 Hz) ppm. δ_P (161 MHz, 298 K, $CDCl_3$): −1.6 ($^1J_{P-Pt}$ = 2619 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −1661 (d, $^1J_{Pt-P}$ = 2580 Hz) ppm. Anal. Found (Expected): C 48.61 (48.74); H 3.02 (3.43); N 2.21 (1.83).

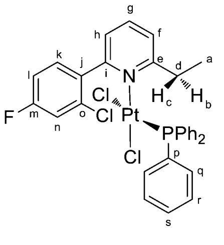
Complex **1c** (0.019 g, 2.69 × 10^{-5} mol, 1 equiv) was dissolved in $CDCl_3$, and (dichloroiodo)benzene (0.0074 g, 2.69 × 10^{-5} mol, 1 equiv) was added at room temperature. After 10 min the solvent as removed and the product washed with pet ether 40–60 to give pure complex **2c**. Yield: 0.0171 g, 2.20 × 10^{-5} mol, 82%.



2c

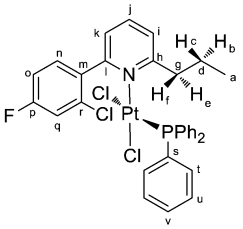
δ_H (300 MHz, 298 K, $CDCl_3$): 7.92–7.98 (6H, m, H_p), 7.78 (1H, t, ^3J = 7.6 Hz, H_f), 7.68 (1H, br d, ^3J = 6.7 Hz, H_g), 7.53 (1H, dd, ^3J = 8.5 Hz, $^4J_{H-F}$ = 5.6 Hz, H_j), 7.45–7.50 (3H, m, H_r), 7.31–7.39 (6H, m, H_q), 7.18 (1H, br d, ^3J = 6.8 Hz, H_e), 6.79 (1H, td, $^3J_{H-H,\ H-F}$ = 8.3 Hz, ^4J = 2.3 Hz, H_k), 6.40 (1H, ddd, $^3J_{H-F}$ = 9.7 Hz, ^4J = 2.5 Hz, $^4J_{H-P}$ = 3.6 Hz, $^3J_{H-Pt}$ = 40 Hz, H_m), 3.81–3.86 (2H, m, H_c), 1.81 (2H, sextet, ^3J = 7.2 Hz, H_b), 0.94 (3H, t, ^3J = 7.2 Hz, H_a) ppm. δ_C (100 MHz, 298 K, $CDCl_3$): 168.8 (C_d), 162.3 (C_h), 160.8 (d, $^1J_{C-F}$ = 254 Hz, C_l), 141.0 (d, $^4J_{C-F}$ = 2.5 Hz, C_i), 139.7 (C_n), 139.5 (C_f), 136.2 (d, $^2J_{C-P}$ = 8.5 Hz, $^3J_{C-Pt}$ = 20 Hz, C_p), 131.8 (d, $^4J_{C-P}$ = 3 Hz, C_r), 129.4 (d, $^1J_{C-P}$ = 63 Hz, C_o), 127.7 (d, $^3J_{C-P}$ = 12 Hz, C_q), 126.8 (d, $^3J_{C-F}$ = 8 Hz, C_j), 124.0 (d, $^4J_{C-P}$ = 7 Hz, $^3J_{C-Pt}$ = 18 Hz, C_e), 122.6 (dd, $^2J_{C-F}$ = 23.5 Hz, $^3J_{C-P}$ = 3 Hz, C_m), 117.9 (d, $^4J_{C-P}$ = 3.3 Hz, C_g), 113.2 (d, $^2J_{C-F}$ = 22 Hz, C_k), 39.1 (C_c), 24.4 (C_b), 13.5 (C_a) ppm. δ_F (282 MHz, 298 K, $CDCl_3$): −109.3 ($^4J_{F-Pt}$ = 32 Hz) ppm. δ_P (121 MHz, 298 K, $CDCl_3$): −1.8 ($^1J_{P-Pt}$ = 2622 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −1661 (d, $^1J_{Pt-P}$ = 2657 Hz) ppm. Anal. Found (Expected): C 49.01 (49.40); H 3.21 (3.63); N 1.61 (1.80).

Synthesis of Complexes 4b and 4c. Chloroform solutions of **2b** and **2c** were monitored via ^1H, ^{19}F, and ^{31}P NMR spectra over a period of one month. Once all the sample had isomerized, the solvent was removed to give analytically pure samples of **4b** or **4c**.



4b

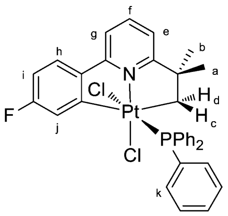
δ_{H} (400 MHz, 298 K, $CDCl_3$): 8.14 (1H, dd, ^3J = 8.6 Hz, $^4J_{\mathrm{H-F}}$ = 6 Hz, H_k), 7.76 (1H, t, ^3J = 7.8 Hz, H_g), 7.38–7.44 (6H, m, H_q), 7.36 (1H, br d, ^3J = 7.8 Hz, H_f), 7.34 (3H, dd, ^3J = 7.4 Hz, ^4J = 2 Hz, H_s), 7.25–7.30 (8H, m, H_h, H_n and H_r), 7.04 (1H, td, $^3J_{\mathrm{H-H,\ H-F}}$ = 8.3 Hz, ^4J = 2.6 Hz, H_l), 4.08 (1H, dq, ^2J = 16 Hz, ^3J = 7.8 Hz, $H_{b/c}$), 3.79 (1H, dq, ^2J = 16 Hz, ^3J = 7.8 Hz, $H_{b/c}$), 1.50 (3H, t, ^3J = 7.6 Hz, H_a) ppm. δ_{C} (100 MHz, 298 K, $CDCl_3$): 165.0 (C_e), 162.7 (d, $^1J_{\mathrm{C-F}}$ = 253 Hz, $^4J_{\mathrm{C-P}}$ = 3 Hz, C_m), 156.9 (C_i), 138.1 (C_g), 136.2 (d, $^3J_{\mathrm{C-F}}$ = 9 Hz, C_k), 134.6 (d, $^2J_{\mathrm{C-P}}$ = 10 Hz, C_q), 130.7 (d, $^4J_{\mathrm{C-P}}$ = 3 Hz, C_s), 128.6 (d, $^1J_{\mathrm{C-P}}$ = 64 Hz, C_p), 127.8 (d, $^3J_{\mathrm{C-P}}$ = 11.5 Hz, C_r), 126.0 (d, $^4J_{\mathrm{C-P}}$ = 3.8 Hz, C_h), 123.9 (d, $^4J_{\mathrm{C-P}}$ = 3.8 Hz, C_f), 116.8 (d, $^2J_{\mathrm{C-F}}$ = 24.5 Hz, C_n), 113.1 (d, $^2J_{\mathrm{C-F}}$ = 19 Hz, C_l), 31.8 (C_d), 13.0 (C_a) ppm. δ_{F} (375 MHz, 298 K, $CDCl_3$): −110.2 ppm. δ_{P} (161 MHz, 298 K, $CDCl_3$): −1.7 ($^1J_{\mathrm{P-Pt}}$ = 3765 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −3440 (d, $^1J_{\mathrm{Pt-P}}$ = 3797 Hz) ppm. HR-MS (ESI): *m/z* 784.0397 calculated for $C_{31}H_{26}{}^{35}Cl_3FNNaP^{194}Pt$ = $(M + Na)^+$ 784.0371, 726.0792 calculated for $C_{31}H_{26}{}^{35}Cl_2FNP^{194}Pt$ = $(M - Cl)^+$ 726.0785, 236.0644 calculated for $C_{13}H_{12}{}^{35}ClFN$ = $(Ligand + H)^+$ 236.0637. Anal. Found (Expected): C 48.55 (48.74); H 3.62 (3.43); N 1.99 (1.83).



4c

δ_{H} (400 MHz, 298 K, $CDCl_3$): 8.14 (1H, dd, ^3J = 8.7 Hz, $^4J_{\mathrm{H-F}}$ = 6.2 Hz, H_n), 7.73 (1H, t, ^3J = 7.8 Hz, H_j), 7.39–7.44 (6H, m, H_t), 7.33–7.37 (4H, m, H_i and H_v), 7.25–7.29 (8H, m, H_k, H_q and H_u), 7.05 (1H, td, $^3J_{\mathrm{H-H,\ H-F}}$ = 8.3 Hz, ^4J = 2.6 Hz, H_o), 4.06–4.14 (1H, m, $H_{e/f}$), 3.55–3.63 (1H, m, $H_{e/f}$), 2.04–2.17 (1H, m, $H_{b/c}$), 1.84–1.97 (1H, m, $H_{b/c}$), 1.13 (3H, t, ^3J = 7.3 Hz, H_a) ppm. δ_{C} (100 MHz, 298 K, $CDCl_3$): 162.9 (C_h), 161.7 (d, $^1J_{\mathrm{C-F}}$ = 252 Hz, C_p), 155.9 (C_l), 136.9 (C_j), 135.1 (d, $^3J_{\mathrm{C-F}}$ = 8.7 Hz, C_n), 133.6 (d, $^2J_{\mathrm{C-P}}$ = 10.6 Hz, C_t), 129.6 (d, $^4J_{\mathrm{C-P}}$ = 2.5 Hz, C_v), 127.6 (d, $^1J_{\mathrm{C-P}}$ = 65.5 Hz, C_s), 126.7 (d, $^3J_{\mathrm{C-P}}$ = 11.3 Hz, C_u), 125.0 (d, $^4J_{\mathrm{C-P}}$ = 4 Hz, C_k), 123.7 (d, $^4J_{\mathrm{C-P}}$ = 4 Hz, C_i), 115.7 (d, $^2J_{\mathrm{C-F}}$ = 25.5 Hz, C_q), 112.0 (d, $^2J_{\mathrm{C-F}}$ = 21.5 Hz, C_o), 40.0 (C_g), 21.4 (C_d), 13.5 (C_a) ppm. δ_{F} (375 MHz, 298 K, $CDCl_3$): −110.2 ppm. δ_{P} (161 MHz, 298 K, $CDCl_3$): −1.9 ($^1J_{\mathrm{P-Pt}}$ = 3758 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −3442 (d, $^1J_{\mathrm{Pt-P}}$ = 3779 Hz) ppm. HR-MS (ESI): *m/z* 740.0956 calculated for $C_{32}H_{28}{}^{35}Cl_2FNP^{194}Pt$ = $(M - Cl)^+$ 740.0942, 250.0795 calculated for $C_{14}H_{14}{}^{35}ClFN$ = $(Ligand + H)^+$ 250.0793. Anal. Found (Expected): C 49.17 (49.40); H 3.52 (3.63); N 1.74 (1.80).

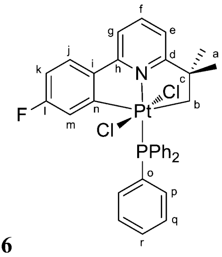
Oxidation of Complex 5: Synthesis of Complexes 6, 8, and 10. Complex **5** was dissolved in $CDCl_3$, the mixture cooled to −40 °C, and one equivalent of iodobenzene dichloride added. By the time any NMR spectra could be recorded, the only platinum-containing species present was the complex identified as *cis*-**6**.



cis-**6**

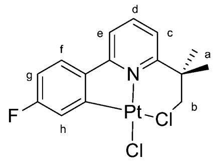
δ_{H} (500 MHz, 233 K, $CDCl_3$): 7.86 (1H, t, ^3J = 7.8 Hz, H_f), 7.79–7.83 (6H, m, H_k), 7.46 (1H, d, ^3J = 7.7 Hz, H_m), 7.38–7.42 (8H, m, H_g, H_h, and H_l), 6.79 (1H, dd, ^3J = 7.7 Hz, ^4J = 1.8 Hz, H_e), 6.70 (1H, td, $^3J_{\mathrm{H-H,\ H-F}}$ = 8.2 Hz, ^4J = 2.2 Hz, H_i), 6.33 (1H, td, $^3J_{\mathrm{H-F,\ H-P}}$ = 9.9 Hz, ^4J = 2.2 Hz, $^3J_{\mathrm{H-Pt}}$ = 42 Hz, H_j), 3.22 (1H, d, ^2J = 8.6 Hz, $^2J_{\mathrm{H-Pt}}$ = 43.5 Hz, H_c), 2.42 (1H, dd, ^2J = 8.6 Hz, $^3J_{\mathrm{H-P}}$ = 3 Hz, $^2J_{\mathrm{H-Pt}}$ = 74 Hz, H_d), 1.88 (3H, s, H_a), 0.84 (3H, s, H_b) ppm. δ_{C} (100 MHz, 233 K, $CDCl_3$): 141.9 (C_f), 135.3 (d, $^2J_{\mathrm{C-P}}$ = 9.2 Hz, C_k), 131.8 (C_m), 128.5 (d, $^3J_{\mathrm{C-P}}$ = 11.5 Hz, C_l), 121.8 (C_j), 118.2 (C_e), 117.8 (C_g), 112.1 (C_i), 44.8 ($C_{a/b}$), 37.6 (C_c), 30.1 (C_d) ppm. δ_{F} (375 MHz, 233 K, $CDCl_3$): −109.6 ($^4J_{\mathrm{F-Pt}}$ = 43 Hz) ppm. δ_{P} (161 MHz, 233 K, $CDCl_3$): 0.5 ($^1J_{\mathrm{P-Pt}}$ = 2993 Hz) ppm. δ_{Pt} (233 K, $CDCl_3$): −2425 (d, $^1J_{\mathrm{P-Pt}}$ = 3026 Hz) ppm.

As the temperature of the reaction mixture was increased, three new species were observed with a multiple set of peaks in the ^1H, ^{19}F, ^{31}P, and ^{195}Pt NMR spectra. Column chromatography, loading, and eluting with chloroform resulted in the isolation of complex **8** as fraction 1 (48% based on starting Pt complex) and *trans*-**6** as fraction 2 (17% based on starting Pt complex). No other products could be isolated and fully characterized.



trans-**6**

δ_{H} (500 MHz, 298 K, $CDCl_3$): 7.83–7.87 (7H, m, H_j and H_p), 7.80 (1H, t, ^3J = 8 Hz, H_f), 7.67 (1H, dd, ^3J = 7.8 Hz, ^4J = 2.4 Hz, H_g), 7.49–7.51 (3H, m, H_r), 7.43–7.47 (6H, m, H_q), 7.35 (1H, dd, $^3J_{\mathrm{H-F}}$ = 8.8 Hz, ^4J = 2.7 Hz, $^3J_{\mathrm{H-Pt}}$ = 28.5 Hz, H_m), 7.01 (1H, dd, ^3J = 7.8 Hz, ^4J = 2.5 Hz, H_e), 6.87 (1H, td, $^3J_{\mathrm{H-H,\ H-F}}$ = 8.7 Hz, ^4J = 2.7 Hz, H_k), 2.36 (2H, s, $^2J_{\mathrm{H-Pt}}$ = 47.6 Hz, H_b), 1.44 (6H, s, H_a) ppm. δ_{C} (125 MHz, 298 K, $CDCl_3$): 177.6 (C_d), 167.5 (d, $^3J_{\mathrm{C-F}}$ = 5.7 Hz, C_n), 163.3 (d, $^1J_{\mathrm{C-F}}$ = 255 Hz, C_l), 161.5 (C_h), 144.6 (C_i), 139.1 (C_f), 135.4 (d, $^2J_{\mathrm{C-P}}$ = 9.4 Hz, C_p), 131.4 (d, $^4J_{\mathrm{C-P}}$ = 2.4 Hz, C_r), 127.9 (d, $^3J_{\mathrm{C-P}}$ = 11.5 Hz, C_q), 127.4 (d, $^3J_{\mathrm{C-F}}$ = 8.1 Hz, C_j), 126.5 (d, $^1J_{\mathrm{C-P}}$ = 63.3 Hz, C_o), 124.8 (d, $^2J_{\mathrm{C-F}}$ = 18 Hz, C_m), 121.5 (d, $^4J_{\mathrm{C-P}}$ = 4.2 Hz, C_e), 117.5 (d, $^4J_{\mathrm{C-P}}$ = 4.6 Hz, C_g), 111.5 (d, $^2J_{\mathrm{C-F}}$ = 23.2 Hz, C_k), 52.9 (d, $^3J_{\mathrm{C-P}}$ = 4.5 Hz, C_c), 45.0 ($^1J_{\mathrm{C-Pt}}$ = 311 Hz, C_b) 35.0 (C_a) ppm. δ_{F} (375 MHz, 298 K, $CDCl_3$): −109.4 ($^4J_{\mathrm{F-Pt}}$ = 17.5 Hz) ppm. δ_{P} (202 MHz, 298 K, $CDCl_3$): −5.7 ($^1J_{\mathrm{P-Pt}}$ = 2502 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −2411 (d, $^1J_{\mathrm{P-Pt}}$ = 2550 Hz) ppm. HR-MS (ESI): *m/z* 776.0941 calculated for $C_{33}H_{29}{}^{35}Cl_2FNNaP^{194}Pt$ = $(M + Na)^+$ 776.0917.

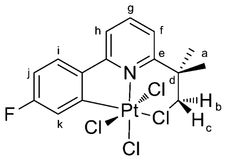


8

δ_{H} (600 MHz, 298 K, $CDCl_3$): 7.79 (1H, t, ^3J = 8 Hz, H_d), 7.54 (1H, dd, $^3J_{\mathrm{H-F}}$ = 9.8 Hz, ^4J = 2.6 Hz, H_h), 7.57 (1H, dd, ^3J = 8 Hz, ^4J = 1.1 Hz, H_e), 7.30 (1H, dd, ^3J = 8.6 Hz, $^4J_{\mathrm{H-F}}$ = 5.5 Hz, H_f), 7.24 (1H, dd, ^3J = 8 Hz, ^4J = 1.3 Hz, H_c), 6.78 (1H, td, $^3J_{\mathrm{H-H,\ H-F}}$ = 8.5 Hz, ^4J = 2.6 Hz, H_g), 3.89 (2H, s, H_b), 1.75 (6H, s, H_a) ppm. δ_{C} (150 MHz, 298 K, $CDCl_3$): 139.2 (C_d), 125.8 (d, $^3J_{\mathrm{C-F}}$ = 9.3 Hz, C_f), 119.6 (d, $^2J_{\mathrm{C-F}}$ = 21.6 Hz, C_h) 118.8 (C_c), 117.9 (C_e), 112.0 (d, $^2J_{\mathrm{C-F}}$ = 23.3 Hz, C_g), 52.7 (C_b), 27.8 (C_a) ppm. δ_{F} (375 MHz, 298 K, $CDCl_3$): −106.9 ($^4J_{\mathrm{F-Pt}}$ = 62 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −3577 ppm. HR-MS (ESI): *m/z* 514.0019 calculated for $C_{15}H_{14}{}^{35}Cl_2FNNa^{194}Pt$ = $(M + Na)^+$ 514.0006.

If the reaction mixture was treated with additional iodobenzene dichloride, a number of other new species were observed, including complex **10**, which was the only species that could be isolated via column chromatography (eluting as the first fraction in chloroform on silica).

δ_{H} (400 MHz, 233 K, $CDCl_3$): 7.97 (1H, t, ^3J = 8 Hz, H_g), 7.87 (1H, dd, ^3J = 8 Hz, ^4J = 1.1 Hz, H_h), 7.70 (1H, dd, ^3J = 8 Hz, ^4J = 1.3 Hz, H_f), 7.65 (1H, dd, $^3J_{\mathrm{H-F}}$ = 9 Hz, ^4J = 2.5 Hz, H_k), 7.57 (1H, dd, ^3J = 8.8 Hz, $^4J_{\mathrm{H-F}}$ = 5.5 Hz, H_i), 7.02 (1H, td, $^3J_{\mathrm{H-H,\ H-F}}$ = 8.4 Hz, ^4J = 2.5 Hz, H_j), 4.96 (1H, br, $H_{b/c}$), 4.01 (1H, br, $H_{b/c}$), 1.81 (6H, s, H_a)



10

ppm. At RT the CH_2 peak appears broad at 4.43 ppm. δ_C (125 MHz, 298 K, $CDCl_3$): 164.2 (C_e), 141.5 (C_g), 127.0 (d, $^3J_{C-F}$ = 9.2 Hz, C_i), 123.0 (C_f) 120.6 (C_h), 118.6 (d, $^2J_{C-F}$ = 25 Hz, C_k), 115.2 (d, $^2J_{C-F}$ = 23 Hz, C_j), 55.3 (C_b), 44.9 (C_d), 30.3 (C_a) ppm. δ_F (375 MHz, 253 K, $CDCl_3$): −101.2 ($^4J_{F-Pt}$ = 31 Hz) ppm. δ_{Pt} (298 K, $CDCl_3$): −1148 ppm. HR-MS (ESI): m/z 583.9381 calculated for $C_{15}H_{14}{}^{35}Cl_4FNNa^{194}Pt$ = $(M + Na)^+$ 583.9389.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full details of the X-ray structures and CIF files for **1a** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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