

A Delicate Balance between sp^2 and sp^3 C–H Bond Activation: A Pt(II) Complex with a Dual Agostic Interaction

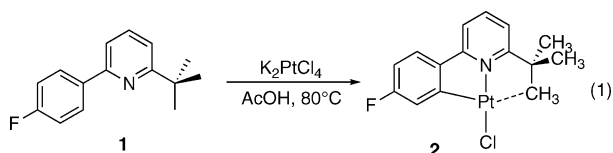
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The selective and general transformation of unreactive C–H bonds to other functional groups is of tremendous worldwide interest and significance;^{1,2} many metals have been utilized to activate C–H bonds, with platinum^{1,3} complexes showing particular promise and palladium⁴ and iridium^{5,6} complexes being utilized catalytically. Cyclometalation reactions,⁷ such as those of phenylpyridines,⁸ are seen as analogues of intermolecular C–H activations, and such complexes have uses in their own right.⁹ Agostic complexes are widely invoked as intermediates in the activation of C–H bonds in organometallic chemistry^{10,11} and have considerable precedent in the stabilization of coordinatively unsaturated metal centers; of particular relevance to the work reported herein are the formally 14e T shaped Pt(II) complexes.^{12–14} Such electrophilic 14e platinum centers ought to be ideally set up for subsequent C–H activation, where it is generally recognized that a preference exists for the activation of sp^2 over sp^3 C–H bonds.³ Here we report the synthesis and characterization of an sp^2 cyclometalated complex containing an agostic interaction that exchanges the sp^2 ring for an sp^3 cyclometalated ring, before eventually activating both C–H bonds to give a doubly cyclometalated species.

Direct reaction of potassium tetrachloroplatinate with 2-*tert*-butyl-6-(4-fluorophenyl)pyridine, **1**, in ethanoic acid slowly, but cleanly, activates one of the C–H bonds of the fluorinated phenyl ring (with the elimination of 1 equiv of HCl and 2 equiv of KCl) to give a cyclometalated product, as evidenced by the ¹H NMR coupling pattern on the phenyl ring and by the presence of platinum satellites on the only ¹⁹F NMR resonance. Normally one would expect the product of this type of reaction either to complete a square-planar coordination geometry with an additional equivalent of pyridine or to become a chloride bridged dimer.^{15–17} In the past we have established that larger ligands such as 2-ethyl-6-(4-fluorophenyl)pyridine are too large to complex to the cyclometalated product, leaving the chloride bridged dimer as the expected product.¹⁸ However, we designed the ligand **1** with the express intention of preventing, through unfavorable steric interactions, even the formation of chloride bridged dimers. Additional platinum satellites of 16 Hz are present on the singlet (relative integral 9) at 1.67 ppm in the ¹H NMR spectrum which comes from the ^tBu group. Platinum satellites are also visible on the ¹³C resonance of the corresponding carbon atom.¹⁹ It is apparent that this coupling is too large to have been transmitted through the bonding to the platinum via the pyridine structure. In the absence of any other potentially ligating species we tentatively assigned an agostic structure **2** to this product (eq 1). Further support for a formally 14e species comes from the high resolution mass spectrum which shows the presence of ions of mass (M+H)⁺ and (M+Na)⁺.



Definitive confirmation of the structure came from an X-ray structure (Figure 1), where the notionally T-shaped geometry of the complex is clear. Interestingly, agostic interactions are present from two of the hydrogens on one of the methyl groups (Pt–H distances of 2.15(3) and 2.14(4) Å and a Pt–C distance of 2.472(4) Å), with these hydrogens being directly located in the X-ray diffraction study. This type of bifurcated agostic interaction has only rarely been observed with late transition metals,^{20–22} and never before with platinum. A variable temperature ¹H NMR study was undertaken to try and establish whether this agostic interaction could be frozen out sufficiently for separate resonances to be observed for any of the hydrogens of the ^tBu, but even at –95 °C in CD₂Cl₂ only one sharp peak was observed for the ^tBu group, indicating a rapid exchange of the agostic interaction across all nine hydrogens. Other features of note in the solid-state structure of **2** include an infinite Pt–Pt stacking interaction of 3.5734(1) Å with a Pt–Pt angle of 156° along the chain.

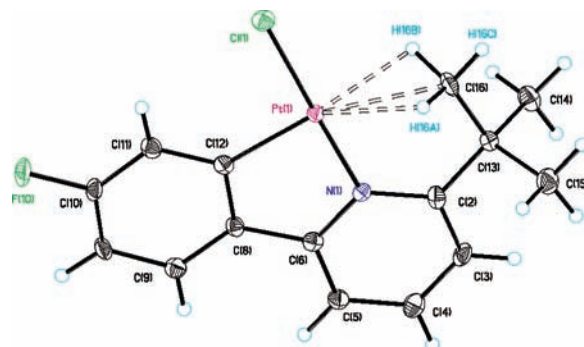
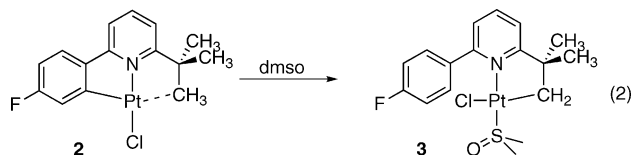


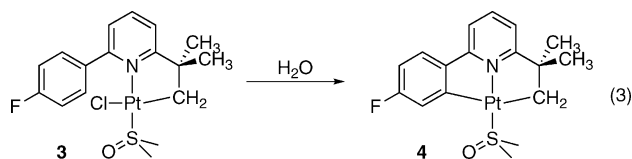
Figure 1. Molecular structure of **2**; thermal ellipsoids at 50% probability level. Selected bond lengths (Å) and angles (deg): Pt(1)–C(16) 2.472(4), Pt(1)–H(16A) 2.15(3), Pt(1)–H(16B) 2.14(4), C(16)–H(16A) 1.00(4), C(16)–H(16B) 1.08(4), C(16)–H(16C) 0.92(4), Pt(1)–C(12) 1.951(4), Pt(1)–N(1) 1.997(3), Pt(1)–Cl(1) 2.3086(8), C(12)–Pt(1)–N(1) 83.0(1), C(12)–Pt(1)–Cl(1) 97.9(1), N(1)–Pt(1)–Cl(1) 178.67(8), C(12)–Pt(1)–C(16) 160.2(1), N(1)–Pt(1)–C(16) 77.3(1).

When an excess of dmsO (~5 equiv) was added to a deuterated chloroform solution of agostic **2**, a clean, albeit slow (~3 days for completion at room temperature), reaction occurred to give a different cyclometalated product. Now it is apparent that one of the C–H bonds of the ^tBu group has been activated (in the ¹H NMR spectrum, there is a signal of relative integral 2 at 2.43 ppm with Pt satellites at 59 Hz, together with a singlet of relative integral 6 at 1.61 ppm), that there is a sulfur coordinated dmsO ligand (¹H NMR signal of relative integral 6 at 3.37 ppm with Pt satellites at 27 Hz), and that the previously cyclometalated phenyl ring is now only connected to the platinum via the pyridine (two sets of protons each of relative integral 2, and no platinum coupling to the ¹⁹F signal) (eq 2).



High resolution mass spectra confirm the formulation as depicted, and NOE measurements strongly suggest that the dmsO is coordinated *trans* to the pyridine.¹⁹ Presumably there is insufficient space around the central platinum for an additional ligand to coordinate directly to **2**, and only by swapping the site of cyclometalation can the weak agostic interactions be replaced by a strong dmsO–Pt bond. The observations that no deuterium is incorporated in the product **3** when the reaction is carried out in deuterated solvent and that reaction of a 50/50 mixture of **2** and a deuterated version of **2** results in only fully protiated **3** and deuterated **3** with no scrambling of isotopes¹⁹ strongly suggest an intramolecular trans-cyclometalation reaction. We can thus see that the balance between the two possible cyclometalations of the pyridine **1** is rather fine and depends on the availability of additional ligating species. In an attempt to gauge the relative ease of cyclometalation of the two sites, the reaction to synthesize **2** was undertaken in CH₃COOD. After a reaction time of 5 days (80 °C) we see extensive deuteration of both the ¹Bu group and the hydrogen *meta* to the fluorine atom in the product **2** but not in any unreacted **1**. An additional study of complex **2** in CD₃COOD at 80 °C showed similarly slow deuterium incorporation in both sites with apparent first-order kinetics and a half-life of ~58 h.¹⁹ These results suggest that (i) the cyclometalation of the phenyl ring is reversible under these conditions, (ii) the butyl group is sufficiently activated to exchange H/D with solvent, and (iii) the barriers to activation of the sp² and sp³ C–H bonds in **1** are very similar.

Finally, treatment of solutions of **3** with water results in the slow elimination of 1 equiv of HCl and the clean regeneration of the cyclometalated phenyl ring to give the doubly cyclometalated complex **4** (eq 3); this reaction can be speeded up with the addition of base (e.g., K₂CO₃). The doubly cyclometalated nature of **4** is apparent from the coupling pattern on the phenyl ring, the presence of platinum satellites on the only ¹⁹F NMR resonance, and the two signals in the aliphatic region of the ¹H NMR spectrum, one of relative integral 2 at 1.64 ppm with Pt satellites at 42 Hz and one of relative integral 6 at 1.32 ppm; there is also a sulfur coordinated dmsO ligand (¹H NMR signal of relative integral 6 at 3.35 ppm with Pt satellites at 28 Hz).¹⁹



We have previously synthesized doubly cyclometalated species where both cyclometalated rings are aryl, where again we found

the addition of water to be crucial in assisting the second cyclometalation step (DFT calculations suggested the hydration and ionization of the liberated HCl was the driving force for the reaction).¹⁶

In summary, reactions of pyridine **1** allow the study of the competitive activation of both sp² and sp³ C–H bonds and provide additional insight into this mechanistically rich area of Pt(II) chemistry.¹

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Supporting Information Available: Full experimental procedures for the synthesis of all complexes, together with all spectroscopic data, the details of the X-ray crystallographic study, the data for the analysis of deuteration of **2**, and the CIF file for **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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