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Platinum(IV) centres with agostic interactions from either sp² or sp³ C–H bonds[†]

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Agostic complexes of platinum(IV) have been isolated and characterised. A Pt(II) sp³ agostic complex maintains the agostic interaction upon oxidation giving a Pt(IV) sp³ agostic complex; in another Pt(IV) complex the agostic interaction from an sp² C–H bond is sufficient to displace another ligand.

Agostic complexes are widely invoked as intermediates in the activation of C–H bonds in organometallic chemistry,^{1,2} and are much sought after as part of the search for the selective and general transformation of unreactive C–H bonds to other functional groups.^{3,4} Many metals have been investigated in the quest for such transformations: of particular relevance to this paper is the use of platinum.^{3,5} Agostic interactions have considerable precedent in the stabilisation of coordinatively unsaturated metal centres which then ought to be ideally set up for subsequent C–H activation.

Here we report the synthesis and characterisation of complexes containing agostic interactions from either sp² or sp³ hybridised C–H bonds to platinum(IV) centres. Whilst formally 14e T shaped platinum(II) complexes containing agostic interactions have long been known,⁶⁻⁸ with a recent contribution to the area from our own work,⁹ agostic interactions within formally 16e square pyramidal Pt(IV) complexes are very rare, with only one crystallographically characterised example known.¹⁰ The paucity of observed Pt(IV) agostic complexes is perhaps surprising, given that all substitution reactions of these 18e octahedral centres are expected to proceed *via* dissociative processes¹¹ and therefore formally five coordinate centres. It is pertinent to note that a number of five coordinate Pt(IV) complexes have been isolated and characterised;¹²⁻²² none however contain agostic interactions.

During our study into the properties of our⁹ previously characterised Pt(II) sp³ agostic species **1** we decided to test the resilience of the agostic interaction, reasoning that a suitably protected metal centre might maintain an agostic interaction even on oxidation. Oxidation of the platinum(II) species **1** with the iodine(III) reagent iodobenzene dichloride proceeds rapidly at room temperature to yield cleanly a single species. The room temperature ¹H NMR spectrum of the new species exhibits the same coupling pattern as its precursor, with slight changes in chemical shift. Significantly, the ¹⁹⁵Pt satellites on the single sharp resonance for the nine protons of the ¹⁹Bu group now show a reduced coupling constant – down from 16 Hz in 1 to 5 Hz. Such a change is consistent with oxidation to Pt(IV) and is mirrored in the ¹⁹F spectrum where the ⁴*J*_{F-Pt} of 67 Hz reduces to 33 Hz. A platinum chemical shift of –1016 ppm can be determined for the new complex, again consistent with a Pt(IV) species. Thus all spectroscopic evidence suggests that the oxidation proceeded to give a Pt(IV) species that retains the agostic interaction present in **1**, Scheme 1.



Scheme 1

We were able to grow crystals of the new species 2, and the structure is indeed that of a Pt(IV) species with a δ agostic interaction with the 'Bu group, Fig. 1.

The structure shown above represents the second reported example of a crystallographically characterised Pt(IV) agostic interaction. Whilst we23 have reported solution evidence (backed up with calculations) for the presence of Pt(IV) agostic species as reactive intermediates in solution and others have postulated their existence,²⁴ there has previously been only one definitive example.¹⁰ Our crystal structure of **2** clearly identifies the agostic interaction as occurring with a single hydrogen, which was directly located in the difference map: the H-Pt distance is 2.15(3) Å and the corresponding C-Pt distance is 2.721(3) Å. This single interaction is unlike that present in 1 where we identified a bifurcated dual interaction. It is also pertinent to note that whilst the H-Pt distances in 1 and 2 are very similar, the C-Pt distance in 2 is significantly longer than in 1 (2.721(3) versus 2.472(4) Å) suggesting the single C-H agostic interaction in 2 is weaker than the bifurcated one found in 1.

Variable temperature ¹H NMR studies (on a 500 MHz spectrometer) on **2** show the single room temperature resonance of the ¹Bu group noticeably broadening by about -40 °C. Although this broadening had become significant at -95 °C (the lowest temperature we were able to access in solution), this peak was clearly still a single resonance, indicating the agostic interaction is rapidly exchanging across all nine hydrogens. A single ¹³C

Department of Chemistry, University of Warwick, Coventry, UK, CV4 7AL. E-mail: j.rourke@warwick.ac.uk; Fax: 44 2476 524112; Tel: 44 2476 523263 † Electronic supplementary information (ESI) available: Full experimental details. CCDC reference number 790276. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01428a



level. Selected bond lengths (Å) and angles (deg): Pt(1)-H(16A) 2.16(3); Pt(1)-C(16) 2.721(3); C(16)-H(16A) 1.04(3); C(16)-H(16B) 1.03(3); C(16)-H(16C) 0.93(3); Pt(1)-C(12) 1.996(3); Pt(1)-N(1) 2.029(2); Pt(1)-Cl(1) 2.2984(6); Pt(1)-Cl(3) 2.3021(7); Pt(1)-Cl(2) 2.3161(6); C(13)-C(16) 1.533(4); C(12)-Pt(1)-N(1) 83.21(10); C(12)-Pt(1)-Cl(1) 97.41(8); N(1)-Pt(1)-Cl(1) 179.30(7); C(12)-Pt(1)-H(16A) 164.0(9); N(1)-Pt(1)-H(16A) = 87.3(8); Cl(1)-Pt(1)-H(16A) = 92.2(8); Cl(3)-Pt(1)Pt(1)-H(16A) 76.7(9); Cl(2)-Pt(1)-H(16A) 102.1(9); C(2)-N(1)-C(6) 121.7(2).

F(10

resonance for the methyl groups was also observed at both room and low temperature. One further parameter we were able to determine, the ${}^{1}J_{C-H}$ coupling constant of the methyl groups of the 'Bu, showed an insignificant change between uncoordinated ligand (128 Hz) and agostic species 2 (127 Hz), indicating little back-bonding from the Pt(IV) centre.

In parallel to our studies on oxidation of the agostic species 1, we also looked at the oxidation of the sp^3 cyclometalated species 3. Oxidation with iodobenzene dichloride results in the rapid and clean formation of a new species 4 at -40 °C. Spectroscopic evidence points clearly to the formulation depicted in Scheme 2 below: the coupling patterns of the signals in the ¹H NMR spectrum remain similar to those observed in the starting material 3, a single signal is observed in the ¹⁹F spectrum, and a platinum resonance is seen at -1568 ppm. The presence of a single ¹H resonance for the six protons of the DMSO, and likewise a single resonance for the CH₂ group (both with ¹⁹⁵Pt satellites) confirms the DMSO has not moved to a position cis to both the N and the CH₂; we can rule out its unlikely movement to the crowded position trans to the CH₂ group on the basis of NOE measurements: clear NOE enhancements are seen between the signals of the DMSO and the CH₂ group (and vice versa) with none seen between the aromatic signals and the DMSO.



Whilst we were able to clearly identify the new complex 4, we were unable to isolate it: at about 0 °C 4 begins to transform cleanly to another new species 5. The new complex 5 is sufficiently stable to be isolated and manipulated at room temperature in air. At room temperature the ¹H NMR spectrum of 5 resembles

that of 4 with two exceptions: there are no signals corresponding to a coordinated DMSO and the ${}^{2}J_{H-Pt}$ on the CH₂ group has increased from 72 to 87 Hz. Complex 5 has a single ¹⁹⁵Pt resonance at -851 ppm and, in the absence of any other ligating species, we propose a structure with an agostic interaction from the phenyl ring completing the coordination sphere of the platinum centre, Scheme 2.

Whilst platinum satellites are not obvious on the phenyl ring proton ortho to the pyridine (meta to the F) in 5, a ¹H-¹⁹⁵Pt NMR correlation experiment shows a clear interaction - presumably the satellites are lost in sides of the peaks. Satellites at 7 Hz can be seen on the corresponding carbon resonance providing strong evidence for an agostic interaction.^{25,26} As with complex 2, the ${}^{1}J_{C-H}$ coupling constant for the appropriate C-H bond in 5 changes little from the values observed in the uncoordinated ligand (162 Hz). The ¹H spectrum of 5 is sharp at room temperature, but begins to broaden upon cooling until at around -60 °C (on a 500 MHz spectrometer) two separate signals of relative intensity one are seen for the CH₂ group (a single broad signal is still seen for the CH₃ groups) and at least six signals are seen in the aromatic region. Even on further cooling to -95 °C the ¹H signals in the aromatic region remained too broad to be fully resolved, as were the ¹³C signals. It is possible to extract an experimental barrier to equilibration of the resonances of 9.5 ± 1 kcal mol⁻¹ from this data.

Quantum chemical calculations were used to determine a likely minimum energy conformation of 5: this was found to be one in which the phenyl ring is inclined $\sim 50^{\circ}$ with respect to the pyridine ring $(0^{\circ} = \text{coplanar}, 90^{\circ} = \text{perpendicular})$, and this brings one of the hydrogens into close (~2.65 Å) proximity to the platinum centre. Such a conformation would account for the low temperature NMR spectra as it not only renders the four protons of the phenyl ring different, it also makes the two CH₂ protons, and the two methyl groups different. Rotational profiles about the phenyl-pyridine bond were calculated using both B3LYP and MP2 methods (Fig. 2): a definite but small barrier to rotation through the perpendicular arrangement of the phenyl and pyridine rings is predicted (~1.5 kcal mol⁻¹), which at least qualitatively explains the experimental results, Fig. 2.



Fig. 2 The energy profile of 5 as a function of rotation about the phenyl-pyridine bond.

We thus have identified two clear examples of Pt(IV) metal complexes containing agostic interactions: in 2 the agostic interaction comes from an sp³ hybridised C-H bond, whereas in 5 the interaction is from an sp² hybridised C-H bond. In both cases, our evidence points to minimal back-bonding from the electron poor Pt(IV) centre suggesting these interactions might be relatively weak. However, in the case of complex **5**, Scheme 2, the agostic interaction, together with an expected release of steric strain is sufficiently strong to displace a DMSO ligand.²⁷

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