Intramolecular transcyclometallation: the exchange of an aryl-Pt bond for an alkyl-Pt bond via an agostic intermediate

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Oxidation of a square-planar platinum complex leads to a five coordinate cationic intermediate that can be stabilized and trapped out via an agostic interaction with the alkyl chain of a ligand. Subsequent reaction of this species leads to the formation of an alkyl-Pt bond at the expense of an aryl-Pt bond: an intramolecular transcyclometallation.

Part of the attraction of cyclometallation, one of the oldest methods by which late transition metals can activate C-H bonds, is that the initial coordination directs a specific C-H bond to the metal centre, facilitating activation and providing selectivity. Cyclometallation also encompasses some less conventional\(^2\) reactions such as rollover\(^3\) reactions, and recent examples where C-H activation is preceded by reductive elimination.\(^4\)

Our recent contributions to the area of cyclometallation include investigating agostic complexes of\(^5\) C-H activation by\(^5,6\) and the oxidation and reduction\(^7\) of a number of cycloplatinated complexes. Some of these results, in particular the reductive coupling that occurs following oxidation, prompted us to revisit some of our earlier work with C\(^2\)N\(^2\)C pincer complexes\(^8\) and attempt to oxidise them. In these symmetrical complexes, where both carbons are formally sp\(^2\) hybridised, the possibility of reductive coupling\(^9\) is there, but as it transpires, something very different happens. The strain of the doubly cyclometallated system is relieved in a novel way, via transcyclometallation.

Transcyclometallation, originally defined\(^9\) as the exchange of one cyclometallated ligand by another, has been known for some time,\(^10\) and has been used to great effect, including its use to induce multiple\(^11\) or chiral\(^12\) cyclometallations. A more recent development has been its use to exchange one metal within the metallacycle with another, for example the exchange of gold with platinum.\(^13\) Here we present another variant: the exchange of one cyclometallated ring for another within the same complex. Furthermore, we show how it is possible to stimulate the formation of the coordinatively unsaturated intermediate that is required for this transcyclometallation reaction.

Starting from the C\(^3\)N\(^3\)C platinum DMSO complex (1a) we synthesised two different phosphine derivatives with the fourth ligand being PMe\(_3\) or PBu\(_3\) (1b and 1c respectively).

The single crystal Xray structures of 1a and 1b are reported here for the first time, Figure 1.

Figure 1: the molecular structures of 1a and 1b. Full details are in the SI.

Oxidation of complexes 1b and 1c with iodobenzene dichloride is rapid, taking place in less than one minute, even at temperatures as...
low as -60°C. In both cases the mechanism of oxidation appears to be the same, that is an S_{2}2 type process, but there are some significant differences in the outcome of the reaction which are directly related to phosphine.

With the trimethylphosphine derivative, 1b, a rapid oxidation at low temperature gives exclusively the octahedral Pt(IV) complex with the added chlorides mutually trans, 2b(t). Upon warming the reaction mixture to room temperature, another compound is observed within 20 minutes, one that we assign as the cis product 2b(c). It would appear that the two isomers are in equilibrium, and it proved impossible to separate them, though we were able to get complete spectroscopic characterisation of the isomers from the ~85:15 (trans:cis) mixture. The PMe_{3} ligand is not sterically demanding, which is presumably why the cis isomer (with the phosphine over the less crowded main plane of the molecule) is not sufficiently favoured over the trans isomer to allow it to be isolated cleanly.

We can account for the initial formation of a trans product on the basis of a two step electrophilic oxidation of the platinum centre: an initial delivery of Cl on one face of the square planar Pt(II) centre is followed by the subsequent delivery of a Cl\(^{−}\) to the opposite face, with no rearrangement of the existing ligands; thus the geometry of the initial product is determined by the geometry of the starting square planar platinum(II) complex. Isomerisation to relieve steric interactions takes place subsequent to the oxidation, and this pattern of behaviour is common to many of our previous studies: with DMSO ligands we observed initial formation of sulfur bound ligands which isomerised to oxygen bound ligands, with other complexes we observed dissociation of ligands to give agostic complexes, and with others we observed reductive elimination.

When the tributylphosphine complex 1c is oxidised in acetone, the reaction also cleanly gives the trans Pt(IV) product 2c(t), which again subsequently isomerises to the cis product 2c(e). Isomerism is substantially slower than for 2b(t) with complete isomerisation taking around a week in solution at room temperature.

However, both isomers could be characterised in solution and in the solid state: it proved possible to grow crystals of both 2c(e) and 2c(t), Figure 2.

![Figure 2: the molecular structures of 2c(e) and 2c(t). Full details are in the SI.](image)

However, when the oxidation is carried out in chloroform, other products form. In the first instance, at -60°C, another species, representing around 25% of the sample, forms; the remaining 75% is 2c(t). The new species is a complex with a symmetrical doubly cyclometallated diphenylpyridine system (one ^{19}F resonance, with Pt satellites), with a ^{31}P shift indicative of chelate ring formation (49.5 ppm compared with 2.3, -13.7 and -0.7 for 1c, 2c(t) and 2c(e), respectively) and a clear interaction of one of the end methyls of the phosphine with the platinum (satellites visible at ~20 Hz, and a strong correlation in the ^{1}H,^{195}Pt spectrum. A platinum shift of -2341 indicates a Pt(IV) species. This complex is, we believe, the agostic species identified as 3 in the scheme below, and arises from the alkyl chain of the phosphine trapping out the five coordinate intermediate in an intramolecular fashion.

![Scheme](image)

The agostic species is not very stable and rapidly converts to another species at above -40°C; the new complex is reasonably stable at room temperature and indeed in air. Spectroscopic data now suggest an unsymmetrical diphenylpyridine system (two ^{19}F resonances, one with satellites, one without), the phosphine still in a ring, though of a different size than before (^{31}P chemical shift of 39.3), the platinum still in oxidation state +4 (^{195}Pt shift of -2570) and a direct platinum bond to one of the alkyl groups of the phosphine. The coupling pattern on this cyclated alkyl chain indicates a five membered ring (one multiplet at 2.45ppm in the ^{1}H NMR, relative integral 1 with platinum coupling of ~100 Hz, coupling to a doublet, relative integral 3 with a ^{1}H shift of 0.42 ppm and platinum satellites of 38 Hz). The presence of coupling from phosphorus to the protons in the remaining cyclometallated aryl ring suggests the P is still trans to the N and an nOe interaction suggests the Me group of the alkylated chain is positioned towards this same aryl ring. We were further able to identify the presence of an uncyclometallated phenyl ring which contains four hydrogens (two sets of two, one set of which has an agostic type interaction with the Pt) and we believe it to be 4 in the scheme above. In contrast to 2c(e), 2c(t) and 5 (below), recording an ESI mass spectrum on 4 gave very intense peaks that correspond to 4 as drawn, providing further evidence for the suggestion that it is an agostically stabilised cation.

Complex 4 converts to another species when we attempted to purify it by column chromatography, if it is treated with NaCl (see below), or if it is simply left in solution for more than a few hours at room temperature and we were unable to completely characterise it. We were, however, able to purify by chromatography and fully characterise this new species that 4 transforms to and the identity of this final species helps to confirm our suggestions above. All the salient features of the structure of this final complex can be deduced from the NMR data (a Pt chemical shift of -2721 indicating Pt(IV); a ^{31}P chemical shift of 40.0 indicating one of the butyl chains is part of a cyclometallated ring, no visible coupling of this P to the protons in the cyclometallated aryl ring, suggesting the P is cis to the pyridine;
two $^{19}$F resonances, one with Pt satellites, one without; an alkyl proton resonance, integral one, coupling to a methyl group and to further protons, together with a large Pt coupling; a methyl group with smaller Pt coupling; an NOE interaction indicating the close proximity in space of the single alkyl proton to the proton adjacent to Pt and F on the cyclometallated fluorophenyl ring) but it is the single crystal X-ray structure (Fig 3) that removes any ambiguity about the connectivity of atoms. This product contains a five membered cyclometallated ring from one of the butyl chains of the phosphine, and the P donor is now cis to the N of the pyridine. Complex 5 is not cationic or agnostic and has the sixth site of its octahedral geometry occupied by a further chloride. The orientation of the groups on the platinated alkyl carbon is not disordered in the crystal structure, and the molecule as a whole is chiral; the asymmetric unit contains equal numbers of both enantiomers.

We thus sought an alternative strategy, and attempted oxidations in the presence of silver salts, rationalising that, if we could (at least temporarily) restrict access to chloride, we could encourage the formation of the agostic species, leading to the alkyl activated species and so on. This strategy proved successful: initiating an oxidation reaction in chloroform at $-40^\circ$C in an NMR tube in the presence of excess AgBF$_4$ gave greater than 50% conversion of 1c to 4. It proved necessary to destroy excess silver salt with sodium chloride to prevent extensive degradation at temperatures above 20$^\circ$C. Gratifyingly, it proved possible to completely suppress the formation of 2e(t) when the oxidation was undertaken in a conventional reaction vessel in the presence of AgBF$_4$ with good stirring; the use of NaCl resulted in the formation of 5 only. Silver has been observed to enhance C-H activation, but there is no evidence here to suggest its presence is altering the reaction course.

As another alternative synthetic route to 5, we also treated 2c(t) with AgBF$_4$. While this reaction did not give high yields of isolable complexes, after quenching with NaCl, complex 5 could clearly be seen to be present in solution. Thus the principle of generating the 5 coordinate complex via halide abstraction from the octahedral Pt(IV) complex is valid, though we did not find it to be a practical alternative to the synthetic routes directly from 1c.

Formally five coordinate 16 electron species of platinum(IV) are frequently invoked as reaction intermediates, but rarely detected. Here we have demonstrated that by preventing such a species from combining with a simple chloride ligand (via the additional stabilisation that an agostic interaction offers) further avenues of reactivity are opened up. In our particular case an intramolecular transcyclometallation reaction occurs and results in the formation of an alkyl-Pt bond at the expense of an alkyl-Pt bond.

Notes and references

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Electronic Supplementary Information (ESI) available: Full experimental details including X-ray structures and CIF files for 1a, 1b, 2e(t), 2e(c) and 5. See DOI: 10.1039/c000000x/

Figure 3: the molecular structure of 5. Full details are in the SI.
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