ChemComm

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

COMMUNICATION

Concerted reductive coupling of an alkyl chloride at Pt(IV) †

Sarah H Crosby, Helen R Thomas, Guy J Clarkson and Jonathan P Rourke*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

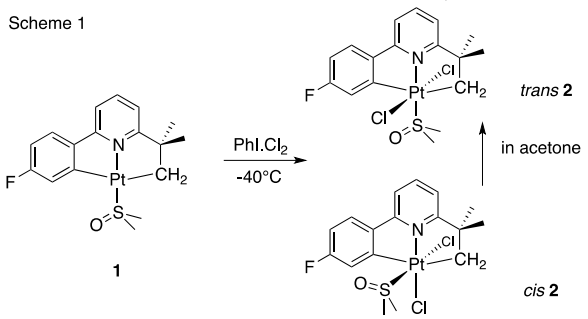
Oxidation of a doubly cyclometallated platinum(II) complex results in two isomeric platinum(IV) complexes. Whereas the *trans* isomer is robust, being manipulable in air at room temperature, the *cis* isomer decomposes at -20°C and above. Reductive coupling of an alkyl chloride at the *cis* isomer gives a new species which can be reoxidised. The independence of this coupling on additional halide rules out the reverse of an S_N2 reaction, leaving a concerted process as the only sensible reaction pathway.

The oxidative addition of alkyl and aryl halides to metal centres is a very commonly observed reaction. The microscopic reverse is rather rare. Though a 1969 report on the pyrolysis of a Pt(IV) complex described the elimination of methyl chloride,[1] and two reports in the mid 1990s discussed the competition between C-C and C-I reductive elimination,[2] and some later work indicating that the oxidative addition of methyl chloride was an equilibrium,[3] there are only a few further examples of alkyl halide elimination in the literature: the first example of C-F elimination at platinum was only reported last year.[4] The reductive elimination of aryl halides is perhaps better documented, with some synthetic uses being described,[5] but still the number of examples is in the order of ten or so,[6] with the first reports of aryl-F reductive elimination at palladium last year.[7]

We have recently been studying some cyclometallated pyridine complexes of platinum(II). Using pyridines containing both aryl and alkyl groups that are in close proximity to a metal, once coordinated, we have been able to study the activation of both sp^2 and sp^3 C-H bonds,[8] and the formation of agostic complexes.[8c,9] Though the activation of sp^2 bonds is favoured, by changing conditions and ligands we were able to activate sp^3 bonds too.[8c,10] Indeed we are able to make doubly cyclometallated complexes where both sp^2 and sp^3 C-H bonds have been activated in the same complex. We now report on the oxidation[8a,8b,9a] of these doubly cyclometallated complexes to platinum(IV).

Oxidation of the doubly cyclometallated complex **1** with iodobenzene dichloride proceeds rapidly at -40°C to yield two new platinum(IV) complexes. The presence of two complexes was immediately apparent from the ^{19}F NMR spectrum of the reaction mixture which showed two peaks with ^{195}Pt satellites – no other signals were seen; their identification as Pt(IV) species came from the reduced couplings seen from the ^{195}Pt to the ^{1}H and ^{19}F signals and the observation of new ^{195}Pt resonances at -2092 and -1926 ppm. The relative proportions of the two new complexes are dependent on the reaction solvent, with reactions carried out in acetone giving product ratios of roughly 20:1, whereas chloroform solutions gave product ratios of roughly 3:1 (in both cases the same product formed the majority). In our previous work on oxidation of platinum complexes we formed isomers in a solvent dependent manner, and were able to rationalise this;[8a,8b,9a] others have made similar observations.[11] We had therefore predicted the formation of the two isomeric forms (*cis* **2** and *trans* **2**) of the oxidation product and were able to confirm their formulations as described below, Scheme 1.

Scheme 1



The major product was the *cis* isomer and was clearly identifiable as such on the basis of its ^{1}H NMR: two signals were present for the CH_2 protons, two separate resonances were observed for the two CH_3 groups and two resonances (of relative integral three) were observed for the DMSO protons. Confirmation that a single molecule was responsible for all these resonances came from a combination of ^{1}H-^{1}H COSY (showing mutual coupling of the CH_2 and the CH_3 signals) and the ^{1}H-^{195}Pt HMBC spectrum (showing correlations to only one Pt from both CH_2 signals, both of the two DMSO signals and one signal in the aromatic region).¶

As will become clear from the discussion, it proved impossible to isolate pure samples of *cis* **2**, but samples of the *trans* isomer could be isolated: the *trans* isomer is sufficiently robust to be manipulated (including column chromatography) at room temperature in air. Thus, analytically pure samples of the *trans* isomer were isolated and it was fully characterised. Though we were unable to grow a crystal of *trans* **2**, all other data confirms the *trans* formulation, with the Xray structure of a closely related structure confirming the stability of the *trans* isomer, Fig 1.

Solutions containing the *cis* isomer at -40°C change in a solvent dependent manner: solutions in chloroform do not change appreciably on a timescale of hours, but solutions in acetone slowly isomerise to the *trans* isomer. Further changes occur on increasing temperature: once the temperature approaches 0°C the

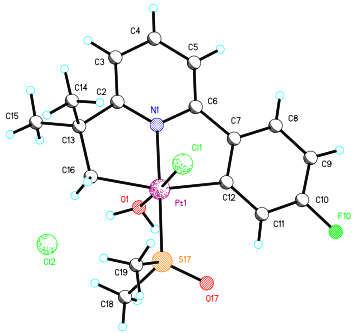
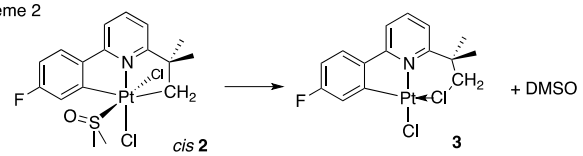


Figure 1, the Xray structure of hydrated *trans* **2**.

cis isomer begins to disappear with all of it being consumed within 30 mins at +5°C. We can identify two reactions of the *cis* isomer: the isomerisation to the *trans* (only seen in acetone), and the formation of new Pt(II) species (seen in both acetone and chloroform, at similar rates). Typically, a solution of 75% *cis*/ 25% *trans* in chloroform transformed to 25% *trans* and 75% Pt(II), whereas solutions of 95% *cis*/ 5% *trans* in acetone transformed to 20% *trans* and 80% Pt(II).‡

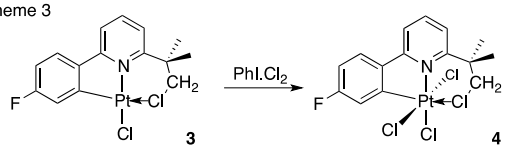
The initial identification of the new product in solution as being a platinum(II) species comes from increased couplings seen from the ^{195}Pt and the observation of a new ^{195}Pt resonance at -3577 ppm. The ^{1}H NMR spectrum also showed no obviously coordinated DMSO ligand on the new material, and a change in the chemical shift of the CH_2 protons from 3.33 and 3.71 (with platinum satellites) to 3.89 ppm (without platinum satellites). The new complex was sufficiently robust that it could be manipulated in air at room temperature and separated from the *trans* **2** by column chromatography. Analysis of the NMR spectra and mass-spectra of pure samples of **3** indicated the formulation shown in Scheme 2, where a reductive coupling of a chlorine atom on the platinum with the CH_2 group has generated a CH_2Cl group which then datively coordinates to the central platinum. The presence of the Cl bonded to a carbon of the organic fragment was suggested from the change in chemical shift of the CH_2 protons and confirmed from the presence of $C_{15}H_{16}{}^{35}ClFN$ and $C_{15}H_{16}{}^{37}ClFN$ fragments in the high resolution mass spectrometer – none of our many complexes containing fluorophenyl, ^{t}butyl derivatised pyridines have ever shown a fragment corresponding to a chlorinated pyridine before. A mass peak at 514.0019 corresponds to the sodiated mass ion $C_{15}H_{14}{}^{35}Cl_2FNNa^{194}Pt$. The coordination of the Cl to the platinum has not been proved, but the alternative of an agostic interaction from either the CH_2, or the remaining two Me groups, can be ruled out from variable temperature NMR experiments which show no significant interactions between these protons and the ^{195}Pt nucleus.

Scheme 2



Though we were unable to crystalise samples of **3**, further evidence for its formulation comes from the characterisation of the product of its oxidation. The reaction of pure **3** at -40°C with $PhICl_2$ proceeds directly, rapidly and cleanly to give a single platinum(IV) product (^{195}Pt shift of -1148 ppm) which we were able to identify, isolate and characterise as **4**, Scheme 3.

Scheme 3



Crystals of this new material indicate that it is simply an oxidised form (with two extra chloride ligands) of **3**, Fig 2. The formation of this new platinum(IV) species was also observed when our original doubly cyclometallated **1** was treated with excess oxidant: any *cis* **2** formed was observed to disappear and to be directly replaced by **4** – presumably via the rapid oxidation of any **3** that formed.

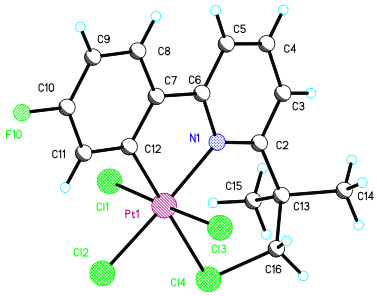


Figure 2, the Xray structure of **4**.

The dependence of the proportion of *cis* and *trans* **2** formed in the initial oxidation, and the rate of isomerism of *cis* to *trans* on solvent is very similar to some of our earlier work and hence need not be discussed any further here.[8b,9a] It is the reductive coupling that takes place in *cis* **2** to give **3** that is of greater interest. Unlike the isomerisation, this reductive coupling takes place at similar rates in both chloroform and acetone, implying that it is taking place in parallel to the isomerisation: the two are independent.

The rate at which *cis* **2** was consumed at +5°C showed first order kinetics (half life 760 s) and was found, within the accuracy of our measurements (±10%), to be unaffected by its concentration, the reaction solvent ($CHCl_3$ or acetone), the presence of additional DMSO or the presence of additional halide (chloride, bromide or iodide, added in the form of the tetrabutyl ammonium salt). The organic part of the product that forms from *cis* **2** was also found to be independent of all the above factors. Even when excess bromide or iodide was present in the reaction mixture, mass spectral analysis of the product showed the ^{t}Bu on the pyridine to be chlorinated (fragments corresponding to $C_{15}H_{16}{}^{35}ClFN$ and $C_{15}H_{16}{}^{37}ClFN$ were observed, with no peaks corresponding to $C_{15}H_{16}BrFN$ or $C_{15}H_{16}FIN$ being seen).

We can attribute a release in steric strain from a crowded octahedral Pt(IV) centre rearranging to a less crowded square planar Pt(II) centre as a major contributor to the driving force for this coupling, with additional relief coming from the dissociation of a DMSO ligand. In our case, there are two alternatives for the reductive coupling: either for the alkyl group to couple with a chloride, or for the aryl group to couple. The elimination of alkyl chloride rather than aryl chloride can be attributed to the thermodynamics of the weaker M-C bond being cleaved. It also seems likely that the flexible $–CMe_2(CH_2Cl)$ group so produced will be able to coordinate to the platinum centre with fewer unfavourable steric interactions than those caused by a more rigid chloro arene. The reductive elimination we observe is completely selective for the C(sp^3)-Cl coupling over C(sp^2)-Cl coupling. Why then does the *cis* **2** isomer reductively couple an alkyl

chloride group, whereas the *trans* does not? Initial DFT calculations indicate very little (~ 4 $kJmol^{-1}$) difference in ground state energies between the two isomers so it cannot simply be that the *trans* isomer is thermodynamically preferred to the reductive product **3**. We can therefore only attribute the difference in behaviour to a kinetic barrier. The oxidative addition of alkyl halides to late transition metals is well known to go via an S_N2 type process with halide anion being released from carbon before binding to the metal. 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.

In our case, we have a reductive coupling reaction that has a rate that does not depend on either solvent or the presence of added halide. The initial product of reaction is not dependent on the halide present in solution either. An S_N2 process is only compatible with the first of these observations, and then only if dissociation of chloride from the Pt(IV) centre in *cis* **2** was rate determining. However, the absence of any bromide or iodide in the product, when the reaction is carried out in the presence of excess of these halides in solution is not compatible with an S_N2 process. We therefore propose that are results are consistent with the possibility of a unimolecular concerted coupling of chloride bound to the Pt(IV) centre with the bound alkyl group. Such a process would be independent of solvent and the presence of halide, and would also exhibit a strong dependence on the relative arrangement of the groups at the Pt centre. The robustness of *trans* **2** is therefore a result of the Cl and CH_2 groups being arranged in a manner incompatible with a low energy pathway to coupling. Simple modelling shows that, because of the cyclometallated rings, it is very difficult to couple the CH_2 group with a Cl *cis* to the N and maintain sensible bond lengths and angles around the organic fragment. Conversely, *cis* **2** has a Cl *trans* to the N, and these two can easily couple together without undue strain being induced on the rest of the molecule. The observation of a very strong dependence of concerted reductive elimination on isomeric form of platinum complexes has been seen before.[12]

Though a concerted method of reductive elimination has been suggested for the elimination of methyl iodide in a rhodium complex the authors were careful to note that their evidence, based on kinetic data only, rendered an S_N2 process "unlikely",[13] others have clear evidence for the reverse of the S_N2 process at both rhodium and platinum.[2-3] A consensus on the presence of a concerted route for *aryl* eliminations exists, with recent work on aryl oxygen[14] and aryl bromine[15] and demonstrations of the involvement of dimeric Pd(III) complexes[16] all invoking concerted routes. There are few other studies on systems related to the work presented here, but the reductive elimination of alkyl oxygen groups at Pt(IV) is of relevance: it has clearly been demonstrated to be an S_N2 type process with unconstrained ligand systems,[17] but a concerted process in a solitary example with chelating groups.[18] More recently 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) centre.[4]

However, nowhere has there been made an unequivocal case for the involvement of a concerted reaction route for alkyl chloride elimination at a late transition metal. The results in this paper, therefore, offer the first proof for the concerted coupling of an alkyl chloride as part of the reductive elimination process.

Acknowledgements

We thank Warwick University for a WPRS award to SHC and support from Advantage West Midlands (AWM) (part funded by the European Regional Development Fund) for the purchase of a high resolution mass spectrometer and the XRD system that was used to solve the crystal structures of **2** and **4**.

Notes and references

[a] *Department of Chemistry, University of Warwick, Coventry, UK, CV4 7AL; E-mail: j.rourke@warwick.ac.uk*

† Electronic Supplementary Information (ESI) available: Full experimental details and crystal data. See DOI: 10.1039/b000000x/

‡ A solution of 95% *cis*/ 5% *trans* in acetone maintained at -20°C took ~48h for all the *cis* to be consumed, whereupon the material present is the same as that from a solution warmed to +5°C. Note no atempt was made to exclude moisture from this mixture, and we were able to isolate a single crystal of hydrated *trans* isomer, Fig 1.

¶ The possibility that *cis*-**2** is actually the hydrated *trans*-**2**, or a similar solvento complex can be discounted, see SI for an extended discussion.

1. J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. (A)*, 1969, 2969-2970.
2. (a) K. I. Goldberg, J. Y. Yan and E. L. Winter, *J. Am. Chem. Soc.*, 1994**, 116**, 1573-1574. (b) K. I. Goldberg, J. Yan and E. M. Breitung, *J. Am. Chem. Soc.*, 1995**, 117**, 6889-6896.
3. P. W. Vickers, J. M. Pearson, T. Ghaffar, H. Adams and A. Haynes, *J. Phys. Org. Chem.*, 2004**, 17**, 1007-1016.
4. S.-B. Zhao, J. J. Becker and M. R. Gagné, *Organometallics*, 2011**, 30**, 3926-3929.
5. (a) A. Vigalok, *Chem. Eur. J.*, 2008**, 14**, 5102-5108. (b) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010**, 110**, 1147-1169.
6. (a) A. Yahav-Levi, I. Goldberg and A. Vigalok, *J. Am. Chem. Soc.*, 2006**, 128**, 8710-8711. (b) A. Yahav-Levi, I. Goldberg, A. Vigalok and A. N. Vedernikov, *Chem. Commun.*, 2010**, 46**, 3324-3326. (c) J. M. Racowski, N. D. Ball and M. S. Sanford, *J. Am. Chem. Soc.*, 2011**, 133**, 18022-18025.
7. E. Lee, A. S. Kamlet, D. C. Powers, C. N. Neumann, G. B. Boursalian, T. Furuya, D. C. Choi, J. M. Hooker and T. Ritter, *Science*, 2011**, 334**, 639-642.
8. (a) C. P. Newman, K. Casey-Green, G. J. Clarkson, G. W. V. Cave, W. Errington and J. P. Rourke, *Dalton Trans.*, 2007, 3170-3182. (b) J. Mamtora, S. H. Crosby, C. P. Newman, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2008**, 27**, 5559-5565. (c) S. H. Crosby, G. J. Clarkson and J. P. Rourke, *J. Am. Chem. Soc.*, 2009**, 131**, 14142.
9. (a) S. H. Crosby, G. J. Clarkson, R. J. Deeth and J. P. Rourke, *Organometallics*, 2010**, 29**, 1966-1976. (b) S. H. Crosby, G. J. Clarkson, R. J. Deeth and J. P. Rourke, *Dalton Trans.*, 2011**, 40**, 1227-1229. (c) H. R. Thomas, R. J. Deeth, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2011**, 30**, 5641-5648.
10. S. H. Crosby, G. J. Clarkson and J. P. Rourke, *Organometallics*, 2011**, 30**, 3603-3609.
11. S. R. Whitfield and M. S. Sanford, *Organometallics*, 2008**, 27**, 1683.
12. A. Yahav-Levi, I. Goldberg, A. Vigalok and A. N. Vedernikov, *J. Am. Chem. Soc.*, 2008**, 130**, 724-731.
13. C. M. Frech and D. Milstein, *J. Am. Chem. Soc.*, 2006**, 128**, 12434.
14. J. B. Gary and M. S. Sanford, *Organometallics*, 2011**, 30**, 6143-6149.
15. A. L. Renz, L. M. Perez and M. B. Hall, *Organometallics*, 2011**, 30**, 6365-6371.
16. (a) D. C. Powers, D. Benitez, E. Tkatchouk, W. A. Goddard, III and T. Ritter, *J. Am. Chem. Soc.*, 2010**, 132**, 14092-14103. (b) D. C. Powers, M. A. L. Geibel, J. Klein and T. Ritter, *J. Am. Chem. Soc.*, 2009**, 131**, 17050-+. (c) D. C. Powers and T. Ritter, *Nature Chemistry*, 2009**, 1**, 302-309. (d) D. C. Powers, D. Y. Xiao, M. A. L. Geibel and T. Ritter, *J. Am. Chem. Soc.*, 2010**, 132**, 14530-14536.
17. (a) B. S. Williams, A. W. Holland and K. I. Goldberg, *J. Am. Chem. Soc.*, 1998**, 121**, 252-253. (b) B. S. Williams and K. I. Goldberg, *J. Am. Chem. Soc.*, 2001**, 123**, 2576-2587.
18. J. R. Khusnutdinova, L. L. Newman, P. Y. Zavalij, Y. F. Lam and A. N. Vedernikov, *J. Am. Chem. Soc.*, 2008**, 130**, 2174-2175.