Intramolecular Activation of a C–F Bond at Platinum(II) in the Presence of Weaker C–X Bonds (X = H, Cl and Br)

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The reaction of [{PtMe$_2$(μ-SMe$_2$)}$_2$] with the bifunctional imines (C$_6$F$_5$)CH=NCH$_2$(2-XC$_6$H$_4$) (X = H, Cl and Br) leads to selective activation of the carbon–fluorine bond even in the presence of the weaker carbon–hydrogen, –chlorine and –bromine bonds.

Intramolecular activation of aromatic C–F bonds by oxidative addition to W^0 and Pt^{II} has recently been established.[1,2] Other reports of the activation of C–F bonds include intermolecular reactions at Rh^I,[3] Ir^I,[4] Yb^{II}[5] and Ti^{IV}.[6] For tungsten(0) the intramolecular activation of the C–F bonds occurs both in perfluorinated and in mono- and di-fluoroaromatic rings.[1] However, for Pt^{II}, activation of the C–F bonds is only achieved for the pentafluorophenyl ring. When both C–H and C–F bonds are present in a position that can, potentially, be activated, exclusive reaction on the C–H bonds takes place.[2] In this communication we report the first C–F bond activation at a Pt^{II} centre taking place in the presence of much weaker C–X bonds (X = H, Cl and Br).
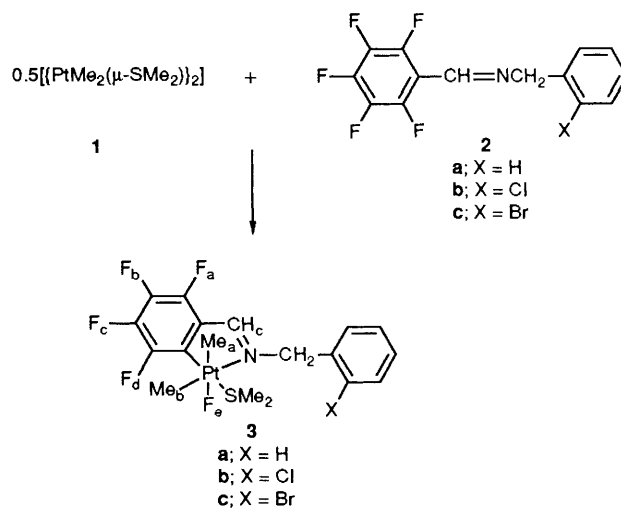
The complex [{PtMe$_2$(μ-SMe$_2$)}$_2$] **1** reacts as shown in Scheme 1 with the bifunctional ligands **2** in acetone solution at room temperature to give **3** both selectively and quantitatively. These compounds were characterized by elemental analysis, and ^{1}H and ^{19}F NMR spectroscopy.† The stereochemistry of these compounds is assigned by analogy with similar species[2,7] and is consistent with the NMR data.

The platinum(IV)-bound fluoride resonance is observed at a higher field and with a larger coupling constant with ^{195}Pt than the corresponding aromatic-fluorine resonances.

The easier formation of five-membered metallocycles containing an endocyclic C=N group rather than an exocyclic double bond has already been found for the similar ligands (C$_6$H$_5$)CH=NCH$_2$(2-XC$_6$H$_4$) (Scheme 2).[7] For X=Cl, activation of a C–H bond to form the endocyclic C=N metallocycle is favoured over oxidative addition at the weaker C–Cl bond to

0.5[{PtMe$_2$(μ-SMe$_2$)}$_2$]   +   F—(C$_6$F$_5$)—CH=NCH$_2$—(2-XC$_6$H$_4$)

1

2

a; X = H
b; X = Cl
c; X = Br

3

a; X = H
b; X = Cl
c; X = Br

Scheme 1

Scheme 2
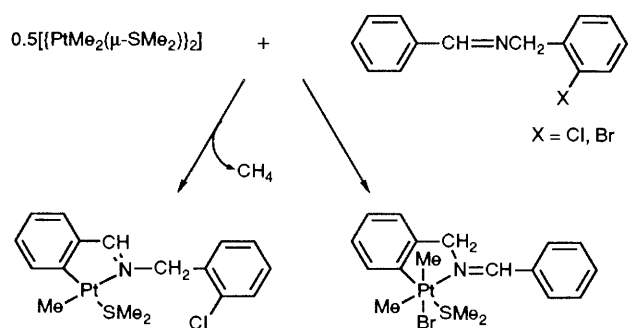
form an *exo*-metallocycle; nevertheless for X=Br the C–Br bond is weak enough to be activated by formation of the metallocycle with exocyclic C=N and C–H activation was not found. With the ligands **2** reported in this communication exclusive activation of C–F bonds in the presence of weaker C–X (X=H, Cl and Br) bonds is observed. Given the fact that the C–F bond is stronger than the corresponding C–X bond, this selective activation even in preference to a C–Br bond cannot be solely related to the formation of an endocyclic *versus* exocyclic C=N. The formation of the strong Pt–F and Pt–C_6F_4 bonds should favour the cleavage of the C–F bond. Besides, the reactivity of the C–F bond should probably be enhanced by the electron-withdrawing effect of the other fluorine atoms in the perfluorinated ligand. In fact for the ligand $(2,6\text{-}F_2C_6H_3)CH=NCH_2(C_6H_5)$ C–F is not activated under the same conditions by **1**.

The kinetics of the reaction shown in Scheme 1 were studied for X=H under the same conditions to those for similar systems already studied.[7] From these experiments, and applying the same rate law, the following activation parameters for the first-order rate constant can be obtained: $\Delta H^\ddagger$ = 30 ± 4 kJ mol^{-1}, $\Delta S^\ddagger$ = −198 ± 14 J K^{-1} mol^{-1}. The activation enthalpy value obtained is small in comparison with

the corresponding values for other C–X bonds[7] and with the values given for C–F activation in other systems.[3a] This result, together with the large and negative activation entropy, indicates that an S_N2 mechanism, or one involving electron transfer from metal to C_6F_5, as suggested for an Ir system,[4] could be more likely than a concerted mechanism as proposed for other C–X activation.

Summarizing, this work demonstrates that for appropriately designed ligands, activation of C–F bonds takes place selectively in the presence of much weaker C–X bonds. Thermodynamic, as well as kinetic, factors may account for this result.

References

1 (*a*) B. L. Lucht, M. J. Poss, M. A. King and T. G. Richmond, *J. Chem. Soc., Chem. Commun.*, 1991, 400; (*b*) T. G. Richmond, C. E. Osterberg and A. M. Arif, *J. Am. Chem. Soc.*, 1987, 109, 8091.

2 (*a*) C. M. Anderson, R. J. Puddephatt, G. Ferguson and A. J. Lough, *J. Chem. Soc., Chem. Commun.*, 1989, 1297; (*b*) C. M. Anderson, M. Crespo, G. Ferguson, A. J. Lough and R. J. Puddephatt, *Organometallics*, 1992, 11, 1177.

3 W. D. Jones, M. G. Partridge and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, 1991, 264.

4 O. Blum, F. Frolow and D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1991, 258.

5 C. J. Burns and R. A. Andersen, *J. Chem. Soc., Chem. Commun.*, 1989, 136.

6 M. J. Burk, D. L. Staley and W. Tumas, *J. Chem. Soc., Chem. Commun.*, 1990, 809.

7 M. Crespo, M. Martinez, J. Sales, X. Solans and M. Font-Bardia, *Organometallics*, 1992, 11, 1288.