Tungsten(0) Inserts into a Carbon–Fluorine Bond in the Presence of a Carbon–Hydrogen Bond

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The first examples of chelate assisted insertion of a transition metal centre into a C–F bond of mono- and di-fluoro substituted aromatic rings resulting in chelate stabilized aryl fluoride oxidative addition complexes are reported.

The great strength of the carbon–fluorine bond is in part responsible for the useful technological properties and generally low chemical reactivity of fluorinated organic molecules. In contrast to the wealth of information available on carbon–hydrogen bond activation,[1] only recently has progress been made in the high yield activation of carbon–fluorine bonds by transition metal reagents. Early work involving low yields and harsh conditions[2] to cleave C–F bonds as well as the first well defined systems demonstrating oxidative addition of C–F bonds to tungsten(0)[3] and platinum(II)[4] metal centres, involved perfluorinated aromatic rings, which are known to be susceptible to nucleophilic aromatic substitution. Similar reactivity patterns are observed in metal assisted C–F bond functionalization reactions[5] and bimolecular fluoride abstraction reactions with organolanthanide complexes.[6] A conceptually diverse approach to activating aromatic C–F bonds to nucleophilic attack involves π-coordination with low valent metals.[7] In this work we report that chelate assisted oxidative addition of C–F bonds can be extended to substrates containing only 2,6-difluoro and even 2-fluoro substituted aromatic rings of suitably designed Schiff's base ligands. Investigations of the reactivity of fluorinated aromatics with transition metals may lead to new catalysis for C–F bond synthesis and other chemical transformations of fluorinated organic molecules.

As shown in Scheme 1,† warming complex **1** in tetrahydrofuran (THF) results in quantitative spectroscopic conversion after 2 h at 55 °C to the oxidative addition product **2**, which may be isolated by crystallization with Et_2O. The aromatic fluorine resonance in **2** is observed at $\delta - 114.68$ and the tungsten bound fluoride resonance at $\delta - 216.4$ ($\nu_{1/2} = 54$ Hz) relative to internal CCl_3F in $[^2H_6]$acetone. This material is identical to that obtained by stepwise metathesis of **4** with silver trifluoromethanesulphonate (AgOTf) followed by treatment with potassium fluoride dihydrate in THF. In the room temperature synthesis of **4** from **3**, the isomeric product involving C–F bond activation was not detected and the observed regiochemistry has been confirmed by single crystal X-ray diffraction.[8] Thus, consistent with its greater bond strength,[9] C–X bond cleavage is much slower for X = F than for X = Cl.

We have also obtained evidence that C–F bond activation can occur in the monofluoro system **5** to afford a mixture of the C–F oxidative addition product and the inert tetracarbonyl complex **7**. Identification of **6** was achieved by comparison of its spectroscopic properties with an authentic sample prepared by halide metathesis[3] and **7** was easily prepared by reaction of carbon monoxide with **5**. Quantitative IR experiments conducted by heating 2.9–11.5 mmol dm^{-3} solutions of **5** in THF for 2–4 h at 60 °C resulted in 49 ± 5% yield of **6** and 28 ± 5% yield of **7** accounting for 77 ± 2% based on tungsten (89 ± 2% based on CO) of the starting material in four independent trials. Both products are stable to the reaction conditions. The tetracarbonyl is invariably formed even with rigorous exclusion of the atmospheric contaminants, which could lead to partial decomposition of the complex and provide a source of CO. It is possible that C–H bond activation to afford an unstable tungsten hydride complex is competitive with C–F bond activation and decomposition or reactions of the hydride produces CO, which is trapped by **5**. Synthetic attempts to prepare the putative hydride have resulted in the formation of tetracarbonyl complexes such as **7**. The present behaviour is in contrast to Puddephatt's observation of exclusive C–H activa-

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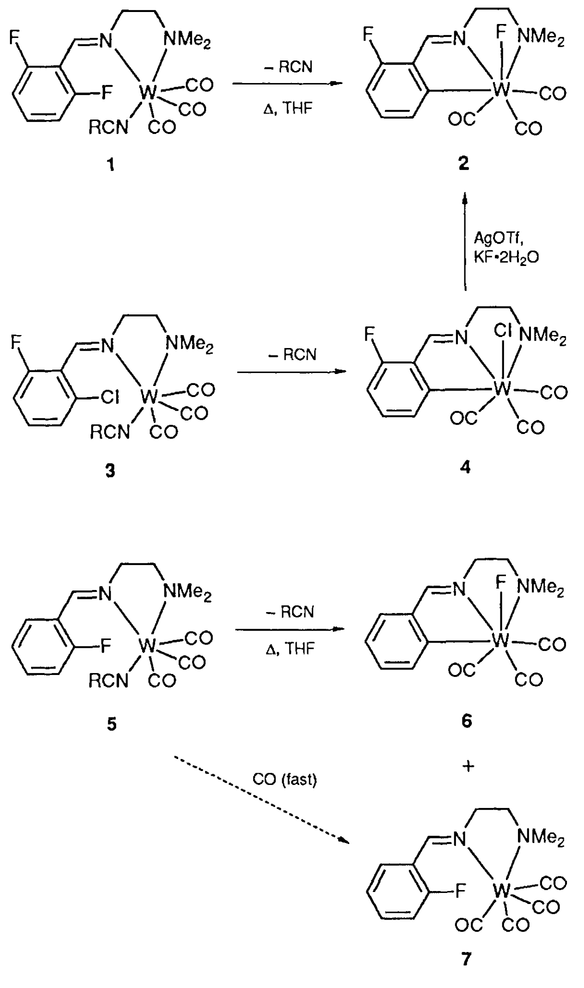
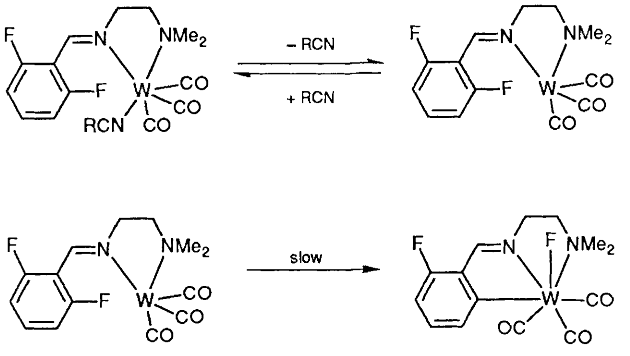
† All new compounds have been characterized by IR, ^1H, ^{19}F and ^{13}C NMR spectroscopic methods and satisfactory elemental analyses (C,H,N) were obtained.



Tf = CF_3SO_2

Scheme 1



Scheme 2

tion in reaction of this ligand at a dimethyl Pt^{II} metal centre, where reductive elimination of methane traps the *ortho*-metallation product and C–F activation is not detected.[4]

A preliminary kinetics investigation of the transformation of **1** to **2** was carried out in THF solution as a function of acetonitrile concentration and temperature (Scheme 2; Fig. 1). The results are consistent with a two step mechanism involving a preequilibrium dissociation of the nitrile ligand, which is rapid and reversible, followed by rate determining insertion of the tungsten into the C–F bond. The activation parameters derived from these data are $\Delta H^‡ = 124 \pm 3$ kJ mol^{-1} and $\Delta S^‡ = 54 \pm 2$ J K^{-1} mol^{-1}. The surprisingly large, positive entropy is inconsistent with an ordered transition state expected for an S_NAr type mechanism and thus a more concerted process seems likely. This work demonstrates that C–F oxidative addition is a viable reaction for simple aromatic substrates under mild conditions even in the presence of weaker C–H bonds.

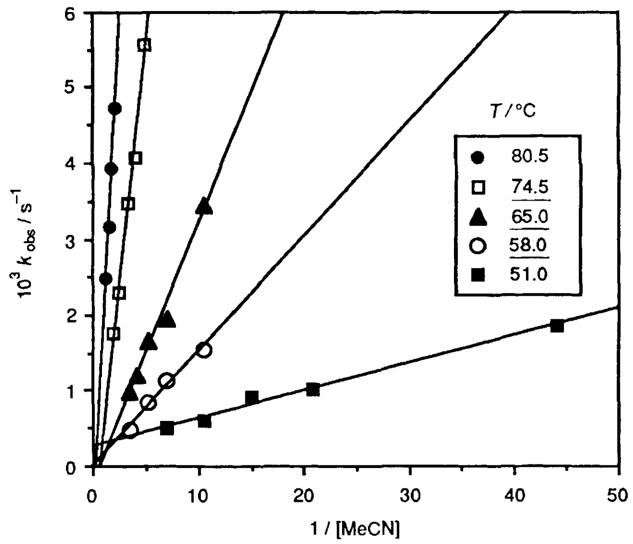


Fig. 1 Kinetics of the transformation of **1** to **2**

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