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Oxidative Addition of Aryl-Halogen Bonds to Platinum(II) and the Structure of a Complex formed by Aryl-Fluoride Oxidative Addition

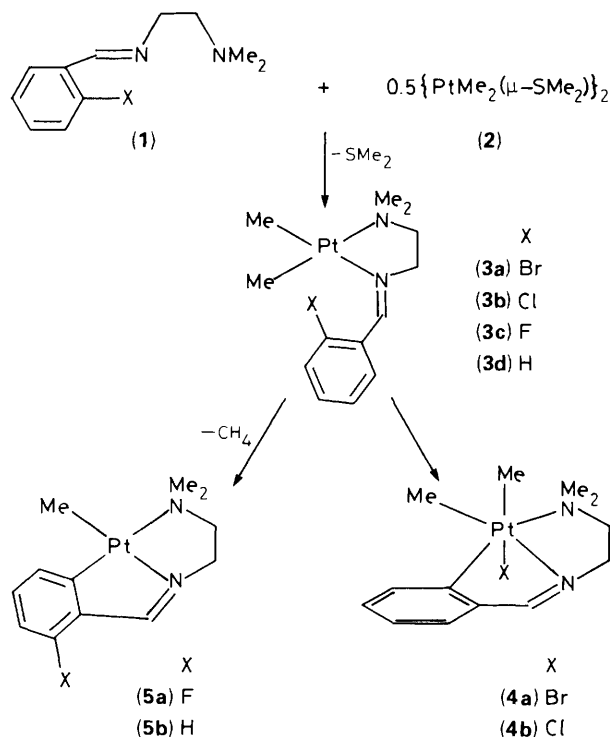
Craig M. Anderson,^a Richard J. Puddephatt,^{*a} George Ferguson,^{*b} and Alan J. Lough^b^a Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7^b Chemistry Department, University of Guelph, Guelph, Ontario, Canada N1G 2W1

The complexes [PtMe₂(Me₂NCH₂CH₂N=CHAr)] react by oxidative addition of the aryl-halogen bond when Ar = 2-BrC₆H₄, 2-ClC₆H₄, or C₆F₅ but by *ortho*-metallation when Ar = 2-FC₆H₄ or C₆H₅, and in the case where Ar = C₆F₅, the oxidative addition product adds acetone across the imine bond and the complex formed has been characterized crystallographically as a hydrogen-bonded dimer; the reactivity to oxidative addition can be correlated with the C-X bond energy.

Oxidative addition of aryl halides to d¹⁰ complexes such as [Ni(PEt₃)₄]¹ and d⁶ complexes such as [W(CO)₃(MeCN)₃]² is known, but few such reactions appear to be known for square planar d⁸ complexes.¹ Indeed, the complex [PtMe₂(2,2'-bi-pyridine)] is one of the most reactive complexes known in oxidative addition of alkyl halides³ but it fails to react with aryl halides. This article reports the first oxidative additions of aryl halides to platinum(II) and the structure of the first product of aryl fluoride oxidative addition to a late transition element.² Thus, even though these elements have a low affinity for the fluoride ligand, activation of C-F bonds is still possible and there are potential applications in catalysis if it can be extended to intermolecular activation.

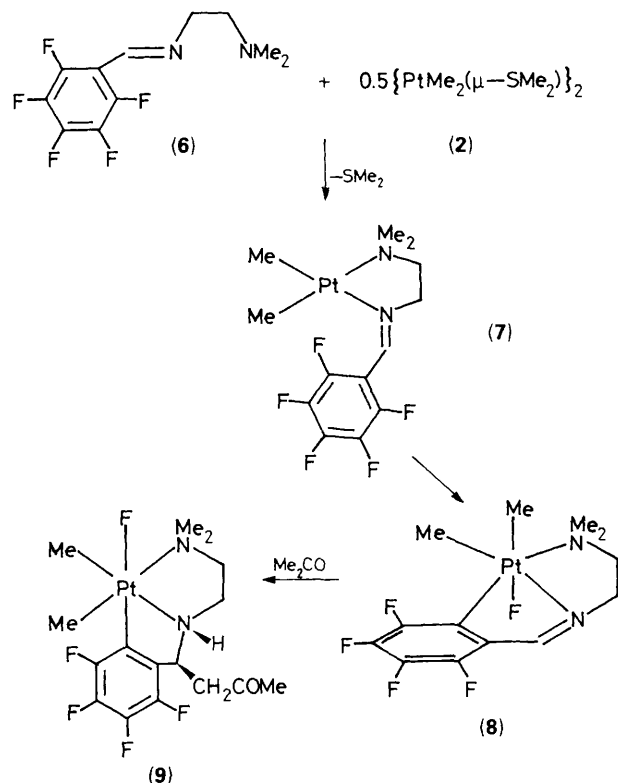
As shown in Scheme 1, the ligands (1) react rapidly with [PtMe₂(μ-SMe₂)₂] (2) to give the platinum(II) complexes (3), which then undergo intramolecular oxidative addition of the aryl-halogen bond to give (4) or *ortho*-metallation⁴ with loss of methane to give (5). The products were readily characterized by elemental analysis and by their ¹H and ¹³C n.m.r. spectra.[†] The first-order rate constants for reaction

of (3) to give (4), at 22 °C in acetone, were $k = 1.6 \times 10^{-4} \text{ s}^{-1}$ when X = Br and $k = 5.2 \times 10^{-5} \text{ s}^{-1}$ when X = Cl. Together with the selectivities given in Scheme 1, and assuming that the *ortho*-metallation involves oxidative addition of an aryl-H bond followed by rapid reductive elimination of methane,



Scheme 1

[†] Typical n.m.r. data (*J* values in Hz): (3a), δ(¹H) 0.12 [s, ²*J*(PtH) 92, *MePt trans* to NMe₂], 0.40 [s, ²*J*(PtH) 84, *MePt trans* to imine]; the ²*J*(PtH) values are characteristic of platinum(II); (4a), δ(¹H) 0.63 [s, ²*J*(PtH) 74, *MePt trans* to Br], 1.00 [s, ²*J*(PtH) 65, *MePt trans* to imine]; the ²*J*(PtH) values are characteristic of platinum(IV); 2.61 [s, ³*J*(PtH) 10, *MeN*], 3.00 [s, ³*J*(PtH) 11, *MeN*], 4.2 [m, CH₂N], 8.12 [s, ³*J*(PtH) 48, CH=N]; δ(¹³C) -4.4 [s, ¹*J*(PtC) 646, *MePt*], 1.4 [s, ¹*J*(PtC) 697, *MePt*], 135.6 [s, ¹*J*(PtC) 943, CPt]; (5a), δ(¹H) 0.80 [s, ²*J*(PtH) 80, *MePt trans* to imine]; δ(¹³C) -11.6 [s, ¹*J*(PtC) 817, *MePt*], 146.8 [s, ¹*J*(PtC) 1200, CPt], 48.8 [s, *MeN*], 52.7 [s, ²*J*(PtC) 31, CH₂N], 68.4 [s, CH₂N], 121.7 [s, CH=N]; (8), δ(¹H) 0.69 [s, ²*J*(PtH) 74, *MePt trans* to F], 1.36 [d, *J*(HF) 5, through-space coupling to aryl-F (confirmed by ¹⁹F n.m.r.)]. ²*J*(PtH) 60, *MePt trans* to imine], 9.12 [s, ³*J*(PtH) 48, CH=N].



Scheme 2

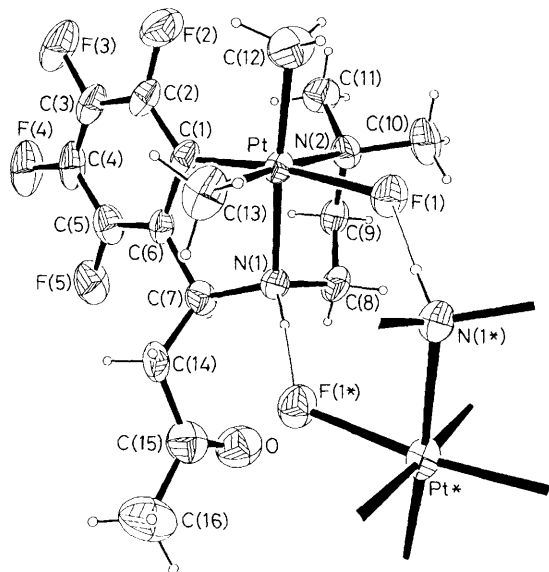


Figure 1. A view of the structure of complex (9). Also shown are the N-H...F hydrogen bond (linking pairs of molecules into centrosymmetric dimers), and some atoms and bonds of the centrosymmetrically related molecule. Typical dimensions are Pt-F(1) 2.070(5); Pt-N(1) 2.173(9); Pt-N(2) 2.242(10); Pt-C(1) 1.978(9); Pt-C(12) 2.060(14); Pt-C(13) 2.038(14) Å; for the NH...F hydrogen bond, N(1)...F(1*) 2.805(10) Å.

these data indicate a reactivity series C-Br > C-Cl > C-H > C-F for oxidative addition of aryl-X bonds to platinum(II). This is the inverse of the order of Ar-X bond energies.⁵ Complex (4a) is also formed by oxidative addition of bromomethane to (5b) (Scheme 1); CD₃Br adds stereospecifically *trans* to (5b), and this is followed by intramolecular

CH₃, CD₃ scrambling within a few minutes at room temperature in the product [²H₃]- (4a).

Oxidative addition of a C-F bond was achieved using a pentafluorophenyl substituted ligand (6), as shown in Scheme 2. Again a platinum(II) intermediate (7), could be detected by ¹H n.m.r. spectroscopy and it rearranged to give (8). Complex (8) reacted with acetone solvent by *cis*-addition of H-CH₂COMe across the imine bond, with a change of stereochemistry at platinum(IV), to give the sparingly soluble complex (9), which was characterized by X-ray crystallography.† The structure of (9) is shown in Figure 1. The Pt-F bond appears to be the longest known⁶ and probably has high ionic character. The low solubility is clearly due to strong intermolecular hydrogen bonding between the NH groups [$\nu(NH)$ 3100 cm⁻¹] and the Pt-F groups of molecules related by centres of symmetry. This arrangement leads to pairs of molecules forming centrosymmetric dimers, as shown in Figure 1.

The above data clearly show that intramolecular oxidative addition of aryl-halogen bonds to square-planar platinum(II) complexes is much easier than intermolecular oxidative addition, which is not yet known. It is not necessary to use a chelate ligand such as (1) or (6), since the ligands PhN=CHAr, Ar = 2-halogenoaryl or pentafluorophenyl, give similar reactions. In terms of the reaction mechanism, the activation parameters for reaction of (3a) to give (4a) are $\Delta H^\ddagger = 97 \pm 2$ kJ mol⁻¹ and $\Delta S^\ddagger = 11 \pm 10$ J K⁻¹ mol⁻¹, and the low value of ΔS^\ddagger precludes an S_N2 mechanism of oxidative addition for which large, negative values of ΔS^\ddagger are characteristic.³ A concerted mechanism, as proposed for C-H oxidative addition,⁷ is consistent with all the experimental data.

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† Crystal data: C₁₆H₂₃F₅N₂O₂Pt, *M* = 549.46, triclinic, space group *P* $\bar{1}$, *a* = 9.463(2), *b* = 12.153(2), *c* = 8.066(2) Å, α = 93.49(2), β = 98.48(2), γ = 104.99(1)°, *V* = 881.5(6) Å³, *Z* = 2, *D*_c = 2.07 g cm⁻³, $\mu(Mo-K\alpha)$ = 81.0 cm⁻¹. Intensity data were measured at 21 °C by using an Enraf-Nonius CAD4 diffractometer; Lorentz, polarization and absorption corrections were applied to the data. The structure was solved by the heavy atom method. Full-matrix least-squares refinement, with hydrogens allowed for as riding atoms, gave *R* = 0.062 and *R*_w = 0.075 for 2811 reflections with *I* ≥ 3σ(*I*). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.