Facile intermolecular aromatic C–F bond activation reactions of $[Ru(dmpe)_2H_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$)

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***cis*-$[Ru(dmpe)_2H_2]$ reacts at −78 °C with hexafluorobenzene to generate the pentafluorophenyl hydride complex, *trans*-$[Ru(dmpe)_2(C_6F_5)H]$; reaction also takes place with C_6F_5H, $C_6F_5CF_3$, $C_6F_5OCH_3$, 1,2,3,4-$C_6F_4H_2$ and 1,2,3-$C_6F_3H_3$ to yield products from C–F insertion exclusively.**

Nucleophilic attack of metal carbonyl anions on fluoroaromatic C–F bonds was demonstrated over 20 years ago.[1] These reactions occur over many hours at reflux temperatures. Much more recently, C–F activation at electron-rich metal centres has been demonstrated under milder conditions.[2] Aizenberg and Milstein have taken a further step and rendered these processes catalytic with the aid of coordinatively unsaturated rhodium complexes.[3] We have reported photochemical C–F activation reactions of hexafluorobenzene at half-sandwich complexes of rhodium and iridium.[4] For $[Rh(\eta^5\text{-}C_5Me_5)(PMe_3)(C_2H_4)]$, the reaction followed an analogous pathway to that established for C–H activation of C_6H_6: formation of an isolable $(\eta^2\text{-}C_6F_6)$ complex followed by the appearance of $[Rh(\eta^5\text{-}C_5Me_5)(PMe_3)(C_6F_5)F]$. We were puzzled to find that photolysis of $[Ir(\eta^5\text{-}C_5H_5)(PMe_3)H_2]$ yielded instead the pentafluorophenyl *hydride* complex $[Ir(\eta^5\text{-}C_5H_5)(PMe_3)(C_6F_5)H]$. Another dihydride complex known for its photochemical C–H activation behaviour is *cis*-$[Ru(dmpe)_2H_2]$ **1** (dmpe = $Me_2PCH_2CH_2PMe_2$). Its photoreactions proceed *via* $[Ru(dmpe)_2]$ and yield *cis*-products: *cis*-$[Ru(dmpe)_2(R)H]$.[5] We now report (*i*) that *cis*-$[Ru(dmpe)_2H_2]$ activates C_6F_6, (*ii*) that the reaction proceeds *without* photoinitiation well below room temperature, (*iii*) that it yields a product with the alternative *trans* stereochemistry in which one hydride ligand is retained and (*iv*) that reactions with partially fluorinated arenes yield products from C–F activation only.

Condensation of a twofold excess of hexafluorobenzene into a thf solution of **1** resulted in an immediate reaction upon thawing the solution to −78 °C. A slight yellowing of the colourless solution was observed along with the precipitation of a small amount of white solid. ^1H, $^{31}P\{^1H\}$ and ^{19}F NMR spectra of the soluble fraction in $[^2H_8]$thf established the formation of the pentafluorophenyl hydride complex, *trans*-$[Ru(dmpe)_2(C_6F_5)H]$ **2** [eqn. (1)].

$$\underset{\mathbf{1}}{cis\text{-}[Ru(dmpe)_2H_2]} \xrightarrow[-78\,^\circ C,\ -HF]{C_6F_6,\ thf} \underset{\mathbf{2}}{trans\text{-}[Ru(dmpe)_2(C_6F_5)H]} \qquad (1)$$

The $^{31}P\{^1H\}$ NMR spectrum of **2** displayed a triplet resonance at δ 47 (*J* 11.7 Hz) for four equivalent phosphorus nuclei coupled to two fluorine nuclei. The ^{19}F NMR spectrum showed the expected three resonances.† The reaction of C_6F_6 with *cis*-$[Ru(dmpe)_2D_2]$ yielded *trans*-$[Ru(dmpe)_2(C_6F_5)D]$. A suitable single crystal of complex **2** was obtained by slow evaporation of a thf solution and its structure determined by X-ray crystallography (Fig. 1). The X-ray structure of **2** showed the expected *trans* disposition of the hydride and C_6F_5 group: the plane of the C_6F_5 group bisects the C–C bonds of the dmpe backbone. The hydride was located on a difference map.‡

$[Ru(dmpe)_2H_2]$ also underwent C–F activation reactions with partially fluorinated arenes to yield *trans*-fluoroaryl hydride complexes (Scheme 1).§ C_6F_5H reacted under similar conditions to C_6F_6 yielding exclusively *trans*-$[Ru(dmpe)_2(p\text{-}C_6F_4H)H]$.† Activation of 1,2,3,4-$C_6F_4H_2$ and 1,2,3-$C_6F_3H_3$ proceeded more slowly, the latter requiring days at room temperature to go to completion.¶ Neither 1,3,5-trifluorobenzene nor 1,2-difluorobenzene reacted. In no case was there any evidence for aromatic C–H bond activation.

We have considered three mechanisms for these C–F insertion reactions: nucleophilic attack, concerted oxidative addition and electron transfer. A nucleophilic substitution mechanism is excluded by the very mild conditions and the lack of nucleophilicity of $[Ru(dmpe)_2H_2]$. The mechanism cannot involve oxidative addition to $[Ru(dmpe)_2]$, since this type of reaction yields *cis*-products, *cis*-$[Ru(dmpe)_2(R)H]$.[5] Moreover, the thermal generation of $[Ru(dmpe)_2]$ from $[Ru(dmpe)_2(naphthyl)H]$[6] at 70 °C in neat C_6F_6 did not yield the pentafluorophenyl hydride complex **2**. Additionally, we would expect selectivity for C–H bonds in partially fluorinated arenes as was observed in the photoreactions of $Rh(\eta^5\text{-}C_5R_5)$ complexes.[7]

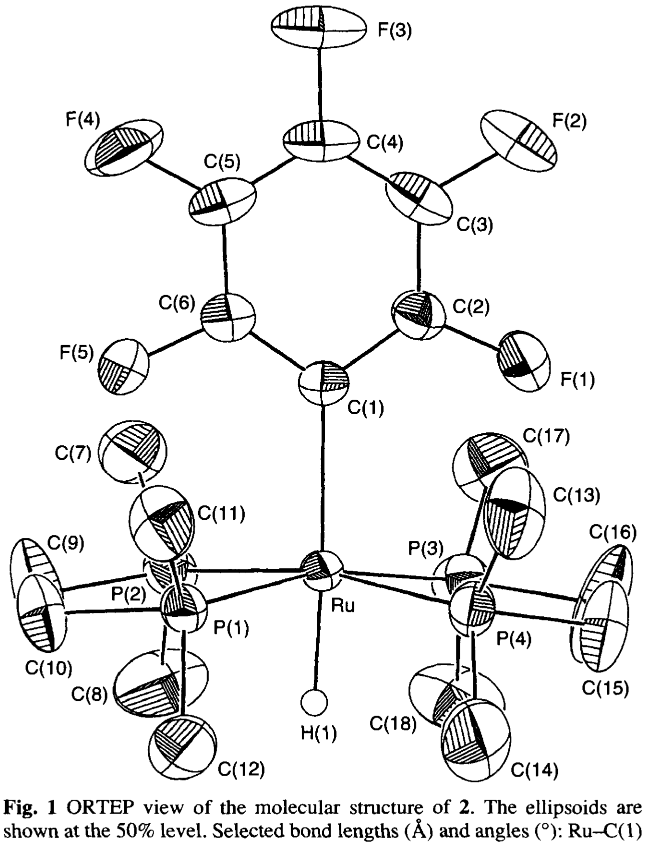
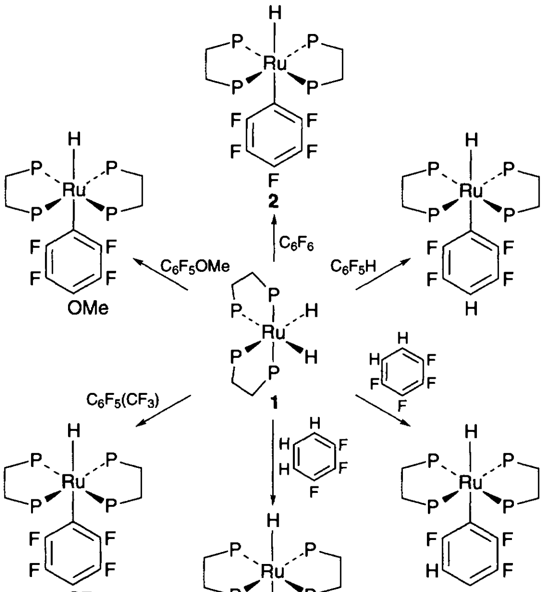


Fig. 1 ORTEP view of the molecular structure of **2**. The ellipsoids are shown at the 50% level. Selected bond lengths (Å) and angles (°): Ru–C(1) 2.250(4), mean Ru–P 2.3082(5), mean C(1)–Ru–P 96.34(7), P(1)–Ru–P(2) 83.89(5), P(4)–Ru–P(1) 94.60(5), Ru–H 1.56.

An electron-transfer process involving a caged radical pair (Scheme 2) is consistent with the evidence. The proposed mechanism involves initial electron transfer from the electron-rich metal dihydride complex to C_6F_6, which has a positive electron affinity.[8]

The resulting radical anion is known to lose F^- readily.[9] The 17-electron species $[Ru(dmpe)_2H_2]^{\cdot +}$ is expected to be more acidic than the neutral 18-electron precursor.[10] Overall, HF is lost, acting as a thermodynamic sink. Radical recombination within the solvent cage yields $[Ru(dmpe)_2(C_6F_5)H]$. The reaction proceeds less readily as the arene becomes less fluorinated and its electron affinity decreases. The less electron-rich complex, $[Ru(dppe)_2H_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), exhibited no reaction with C_6F_6, even after days at room temperature. The *para* stereoselectivity in the reaction with C_6F_5H can be explained, since the SOMO of $C_6F_5H^{\cdot -}$ has high electron density at the fluorine in the 4-position.[11] When the reaction with hexafluorobenzene was conducted in the presence of a radical trap, 9,10-dihydroanthracene, only trace quantities of anthracene were detected by GC–MS and neither the rate nor the yield of **2** was affected, demonstrating that all of the chemistry does indeed occur in the cage. Electron-transfer reactions of this type have been postulated previously by Milstein and coworkers[12] but the current reactions allow clear distinction from a conventional oxidative addition mechanism on grounds of rate, selectivity and stereochemistry.

We are pleased to acknowledge the support of EPSRC, Johnson Matthey, NATO and the European Commission. We appreciate helpful discussions with Professor W. D. Jones and Drs J. R. Lindsay-Smith and M. G. Partridge. We would also like to thank Mr Bryan Greener for help with the X-ray crystallography.



Scheme 1 Reaction of *cis*-$[Ru(dmpe)_2H_2]$ **1** with fluoroarenes

$$\mathrm{RuH_2 + C_6F_6} \longrightarrow \left\{ [\mathrm{RuH_2}]^{\cdot +}\ [\mathrm{C_6F_6}]^{\cdot -} \right\} \xrightarrow{-\mathrm{HF}} \left\{ \mathrm{RuH^{\cdot} + C_6F_5^{\cdot}} \right\}$$

$$\left\{ \mathrm{RuH^{\cdot} + C_6F_5^{\cdot}} \right\} \longrightarrow \mathrm{RuH(C_6F_5)}$$

Scheme 2

Footnotes

† *Spectroscopic data:* for **2**. NMR {300 MHz, $[^2H_8]$thf, 298 K}: ^1H, δ −15.01 (t qnt), J_{HF} 11.5, J_{HP} 22.0 Hz, 1H, Ru–H), 1.36 (s, 12H, 4 × PCH_3), 1.54 (s, 12H, 4 × PCH_3), 1.69 (m, 4H, 4 × PC*H*H), 2.21 (m, 4H, 4 × PCH*H*); $^{31}P\{^1H\}$, δ 47.3 (t, J_{FP} 11.7 Hz); ^{19}F, δ −92.5 (m, 2F, *ortho*), −163.9 (m, 2F, *meta*), −165.9 (t, J_{FF} 21.0 Hz, 1F, *para*). IR (Nujol): 1834 cm^{-1} ν(Ru–H). EIMS, *m/z* 569 (M^+ − H), 402 (M^+ − C_6F_5H). Satisfactory elemental analysis (C, H) was obtained. For *trans*-$[Ru(dmpe)_2(p\text{-}C_6F_4H)H]$ {300 MHz, $[^2H_8]$thf, 298 K}: ^1H, δ −14.95 (t qnt, J_{HF} 12.0, J_{HP} 22.8 Hz, 1H, Ru–H), 6.46 (tt, J_{HF} 8.7, J_{HF} 5.4 Hz, 1H, C_6F_4H); $^{31}P\{^1H\}$, δ 47.8 (t, J_{FP} 11.7 Hz); ^{19}F, δ −97.1 (m, 2F, *ortho*), −144.1 (m, 2F, *meta*).

‡ *Crystal data for trans*-$[Ru(dmpe)_2(C_6F_5)H]$ **2**: 0.8 × 0.7 × 0.5 mm, $C_{18}H_{33}F_5P_4Ru$, M = 569.39, monoclinic, space group $P2_1/n$, a = 9.064(3), b = 14.425(3), c = 19.288(3) Å, β = 102.97(2)°, U = 2457.4(9) $Å^3$, $F(000)$ = 1160, D_c = 1.539 Mg m^{-3}, Z = 4, λ(Mo-Kα) = 0.71070 Å, μ = 0.938 mm^{-1}, $R_1[I > 2\sigma(I)]$ = 0.037, wR_2 = 0.09, GOF = 1.091, T = 293 K, 4329 unique reflections out of 4824 measured. Data were collected on a Rigaku AFC6S diffractometer for 5 < 2θ < 50°; the structure was solved by direct methods. Full-matrix least-squares refinement was carried out using SHELXL93. All hydrogen atoms were refined with the 'Riding' model. All crystallographic calculations were performed using the TEXSAN software package.[13] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/7.

§ With all of the fluorinated arenes, a second product was also observed in the ^1H NMR spectrum which displayed a hydride resonance at δ −25 and a broad singlet at δ 13.5. Evidence that this product is a bifluoride hydride complex, *trans*-$[Ru(dmpe)_2(HF_2)H]$, will be presented elsewhere. Formation of this species can be suppressed if the reaction is performed in the presence of excess NEt_3. The formation of a precipitate is unique to the C_6F_6 reaction. With a 1 : 1 ratio of **1** : C_6F_6, no white precipitate was observed, but a large excess of hexafluorobenzene yielded this precipitate in larger quantities. This product did not contain any fluoroaromatic group; its full characterization is in progress.

¶ Examination of the volatile products by GC–MS showed that reaction with $C_6F_nH_{6-n}$ (n = 6,5,4,3) yielded some $C_6F_{n-1}H_{7-n}$. Reaction of $[Ru(dmpe)_2D_2]$ with C_6F_6 yielded C_6F_5D. The reaction of **1** with C_6F_6 was followed quantitatively by NMR. The ratio of C_6F_5H: **2** was 1 : 6 and found to be independent of the ratio of C_6F_6: **1**.

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Received, 11th December 1995; Com. 5/08069J