Cleavage of an aryl–CF_3 C–C bond with a transition metal in solution

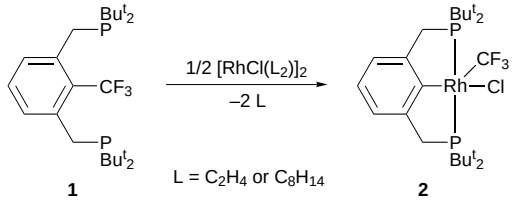
Milko E. van der Boom, Yehoshoa Ben-David and David Milstein*†

The Weizmann Institute of Science, Department of Organic Chemistry, Rehovot 76100, Israel

Unprecedented oxidative addition of a strong, unstrained Ar–CF_3 bond to a metal complex in solution yields the new aryl–Rh^{III}–CF_3 complex 2.

Activation of strong C–C and C–F bonds by soluble metal complexes are topics of much current interest.[1–5] Recently, we reported homogeneous cleavage of a strong C–C bond and catalytic C–F activation by transition metal complexes.[2,5] Here we report the first metal insertion into an unstrained C–C single bond of a fluorocarbon in solution. The Ar–CF_3 bond cleaved is among the strongest known C–C bonds.

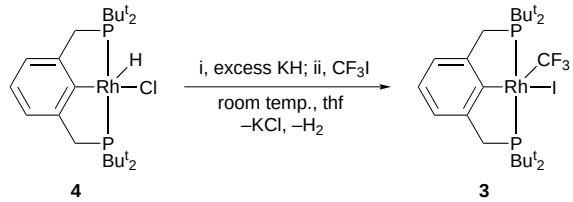
The new phosphine $C_6H_3CF_3$-1-$(CH_2PBu^t)_2$-2,6 **1** was prepared from 2-bromo-*m*-xylene by trifluoromethylation,[6] bromination and phosphination with $HPBu^t_2$.[7a] Compound **1** was obtained as a white powder and fully characterized by various NMR techniques and MS.‡ Reaction of $[RhCl(L)_2]_2$ (L = C_2H_4 or C_8H_{14}) with 2 equiv. of **1** (0.040 mmol) in a dioxane or toluene solution (10 ml) at 180 °C for 9 h in a sealed vessel affords exclusively the new rhodium complex $[Rh(CF_3)Cl\{C_6H_3(CH_2PBu^t)_2$-2,6$\}]$ **2**,§ which was characterized by ^1H, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$ NMR and FDMS (Scheme 1).‡ The reaction can be run at lower temperatures when an excess of **1** is used, leading to quantitative formation of **2** after heating at 120 °C overnight. No other complexes were found. It is noteworthy that the cleaved bond is among the strongest C–C bonds known (compare BDE: Ph–CF_3 = 108.9 kcal mol^{-1}).[8a,b]



Scheme 1

In order to confirm the identity of complex **2**, we prepared the iodide analog $[Rh(CF_3)I\{C_6H_3(CH_2PBu^t)_2$-2,6$\}]$ **3** by dehydrochlorination of the known rhodium complex $[Rh(H)Cl\{C_6H_3(CH_2PBu^t)$-2,6$\}]$[7] (**4**; 0.080 mmol) with excess KH (40 equiv.) in THF (5 ml) followed by oxidative addition of CF_3I (5 psi) in a pressure vessel at room temperature (Scheme 2).¶

Complexes **2** and **3** exhibit similar spectroscopic properties.‡ The $^{31}P\{^1H\}$ NMR spectrum of **2** displayed a doublet of quartets at δ 62.6 ($^1J_{RhP}$ 116.7 Hz, $^3J_{PF}$ 16.3 Hz) for the two magnetically equivalent phosphorus nuclei which are coupled to rhodium and to three fluoride nuclei. The Rh–CF_3 moiety is clearly observed by $^{19}F\{^1H\}$ NMR as a doublet of triplets at δ 9.0 ($^2J_{RhF}$ 21.3 Hz, $^3J_{PF}$ 16.5 Hz). The ^1H NMR shows two 1 : 2 :1 triplets for the inequivalent Bu^t groups at δ 1.42 and 1.05 ($^3J_{PH}$ 7.0, 6.0 Hz), respectively, which collapse to singlets upon phosphorus decoupling. The four benzylic protons (CH_2P) appear as a typical AB pattern at δ 3.10 (ΔABq = 138 Hz, $^2J_{HH}$ 17.0, $^2J_{PH}$ 4.4 Hz), confirming the C_1 symmetry. The FDMS spectrum shows the M^+ (600) and a correct isotope pattern. Recently, two isostructural pentacoordinated rhodium-methyl complexes have been fully characterized by X-ray analysis.[2f,g]

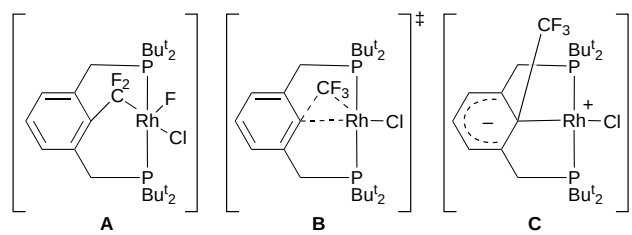


Scheme 2

Mechanistically, coordination of **1** to the metal centre is likely to precede the C–C bond activation step (Scheme 1). Coordination of both phosphine arms to the metal centre was postulated for the Me (instead of CF_3) analog of **1** with rhodium and iridium and was observed for similar substrates with platinum and ruthenium.[2,9] Performing the reaction at room temperature results in the formation of oligomers as indicated by NMR spectroscopy, which probably collapse to monomeric species upon heating. Formation of the oligomeric species is retarded when excess of **1** is used, enabling the C–C activation reaction at lower temperatures.

Interestingly, the expected product of $ArCF_2$–F bond cleavage **A** was not observed during the reactions, indicating a significantly lower activation barrier of the C–C *vs.* C–F oxidative addition. While the C–F bond is slightly stronger than C–CF_3 (BDE: $PhCF_2$–F = 112 kcal mol^{-1}),[8c] three C–F bonds are accessible for activation *vs.* one C–C bond. The formation of two strong aryl– and fluoroalkyl–M σ bonds and two five-membered rings at the expense of an unstrained sp^2–sp^3 C–C bond provides a substantial thermodynamic driving force for the oxidative addition process. There is an increased thermodynamic stability of M–C σ bonds with increasing fluorination of the alkyl group.[10]

This unique bond activation process may proceed *via* a concerted three-centered transition state **B** as recently elucidated for oxidative addition of rhodium and iridium to an Ar–CH_3 bond,[2f] which can be thermodynamically and even kinetically more favorable than the competing C–H activation process. However, the strongly electron withdrawing nature of the CF_3 group may make a nucleophilic attack on the arene by the electron-rich metal centre possible. Formation of an intermediate hexadienyl anion **C** followed by a 1,2-migration of the trifluoroalkyl group would give complex **2**. Further studies are required in order to clarify the mechanism of this unique oxidative addition process.



In conclusion, an unprecedented activation of a strong C–C single bond of a fluorinated organic substrate was achieved using a soluble transition metal complex. No $ArCF_2$–F bond cleavage was observed in parallel to the Ar–CF_3 oxidative addition process, although low-valent metal complexes are capable of activating C–F bonds,[3–5] indicating that nucleophilic rhodium complexes might be designed to selectively activate C–C bonds of fluorocarbons.

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Notes and References

† E-mail: comilst@wiccmail.weizmann.ac.il

‡ *Spectral data*: for **1** ^{1}H NMR ($CDCl_3$) δ 7.61 (d, 2 H, $^3J_{HH}$ 7.8 Hz, ArH), 7.20 (t, 1 H, $^3J_{HH}$ 7.8 Hz, ArH), 3.01 (s, 4 H, CH_2P), 1.02 [d, 36 H, $^3J_{PH}$ 10.9 Hz, $C(CH_3)_3$]. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 38.9 (q, $^5J_{PF}$ 7.3 Hz). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −49.8 (t, $^5J_{PF}$ 7.4 Hz, $ArCF_3$). MS: 463 (M^+ + 1).

For **2**: ^{1}H NMR (C_6D_6) δ 7.0 (m, 3 H, ArH), 3.37 (dvt, 2 H left part of ABq, $^2J_{HH}$ 17.0, $^2J_{PH}$ 4.2 Hz, CH_2P), 2.82 (dvt, 2 H right part of ABq, $^2J_{HH}$ 17.0, $^2J_{PH}$ 4.4 Hz, CH_2P), 1.42 [vt, 18 H, $^3J_{PH}$ 7.0 Hz, $C(CH_3)_3$], 1.05 [vt, 18 H, $^3J_{PH}$ 6.0 Hz, $C(CH_3)_3$]. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 62.6 (dq, $^1J_{RhP}$ 116.7, $^3J_{PF}$ 16.3 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6) δ 9.0 (dt, $^2J_{RhF}$ 21.3, $^3J_{PF}$ 16.5 Hz, $RhCF_3$). FDMS: M^+ 600 (correct isotope pattern).

For **3**: ^{1}H NMR (C_6D_6) δ 7.0 (m, 3 H, ArH), 3.42 (dvt, 2 H left part of ABq, $^2J_{HH}$ 17.0, $^2J_{PH}$ 4.8 Hz, CH_2P), 2.99 (dvt, 2 H right part of ABq, $^2J_{HH}$ 17.0, $^2J_{PH}$ 4.4 Hz, CH_2P), 1.49 [vt, 18 H, $^3J_{PH}$ 6.9 Hz, $C(CH_3)_3$], 1.03 [vt, 18 H, $^3J_{PH}$ 6.1 Hz, $C(CH_3)_3$]. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 62.4 (dq, $^1J_{RhP}$ 115.6, $^3J_{PF}$ 15.7 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6) δ 10.9 (dt, $^2J_{RhF}$ 21.5, $^3J_{PF}$ 15.6 Hz, $RhCF_3$).

§ Reaction of [{$IrCl(C_8H_{14})_2$}$_2$] with 2 equiv. of **1**, applying similar reaction conditions, resulted in a mixture of unidentified products. No C–C or C–F activation was indicated by NMR spectroscopy.

¶ 80% yield by $^{31}P\{^1H\}$ NMR, the other only product formed was the iodide analog of complex **4**.

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