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# Cleavage of F–C($sp^2$) bonds by MHR(CO)($P^tBu_2Me$)$_2$ (M = Os and Ru; R = H, $CH_3$ or Aryl): Product dependence on M and R

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In celebration of the coming of age of Malcolm Harold Chisholm.

## Abstract

Both $MH(Ph)(CO)L_2$ ($L = P^tBu_2Me$; M = Ru and Os) react with vinyl fluoride to form M–F bonds; however, Ru eliminates benzene, while Os eliminates ethylene. In contrast, $Ru(H)_2(CO)L_2$ and $Os(H)_2(CO)(1\text{-butene})L_2$ both react with vinyl fluoride to give ethylene and $MHF(CO)L_2$. Ethylene production from *both* dihydrides is attributed to β-F migration to M from an $MCH_2CH_2F$ transient, while the unique behavior of $RuH(Ph)(CO)L_2$ (giving the C–F oxidative addition product $Ru(\eta^1\text{-vinyl})F(CO)L_2$) is attributed to the difficulty of achieving $Ru^{IV}$, and the ability of the strongly π-acidic vinyl fluoride to rapidly trigger reductive elimination of benzene. The products of reaction of $RuH(Ar)(CO)L_2$ with vinyl fluoride are redirected more towards ethylene formation when Ar carries fluorine substituents. The reaction products of $OsH(R)(CO)L_2$ with vinyl fluoride revert to R-H elimination when R is methyl. Finally, the more π-acidic $H_2C{=}CF_2$ triggers very rapid $CH_4$ elimination from $OsH(CH_3)(CO)L_2$; cleavage of the second C–F bond yields the vinylidene $OsF_2(CCH_2)(CO)L_2$. All selectivity is rationalized via the fate of the adduct $MH(R)(C_2H_{4-n}F_n)(CO)L_2$.

*Keywords:* Fluorocarbons; Ruthenium; Osmium; Organometallic; Mechanisms

## 1. Introduction

C–F bond cleavage is a goal for accomplishing catalytic transformation of perfluoroalkanes (and arenes) and Freons to valuable or environmentally benign materials [1–5]. This is also a topic of interest in organic synthesis [6–19]. The early transition elements have a strong tendency to cleave F–C($sp^2$) bonds [20–25]. A fundamental problem in C–F activation by soluble transition metal complexes is selective cleavage of the C–F in preference to the C–H bond in partially fluorinated alkanes and arenes since the C–F bond is normally stronger than the C–H bond [26]. That is, kinetic selectivity is required [27–32]. In at least one case, C–F bond cleavage is thermodynamically favored, but kinetically disfavored [33]. However, rarely has there been a report of different selectivity for reaction of a metal complex with vinyl fluoride versus aryl fluoride. Such an example is documented here.

## 2. Results

### 2.1. MH(Ph) Reactivity with $H_2C{=}CHF$

*(a) M = Os.* The molecule $OsH(Ph)(CO)L_2$ ($L = P^tBu_2Me$) (**1**), is reported to be "triggered" by reaction with fluoroarenes ($C_6H_{6-n}F_n$, with $n$ = 1, 2, 5) at 25 °C to eliminate $C_6H_6$ and oxidatively add an arene C–H

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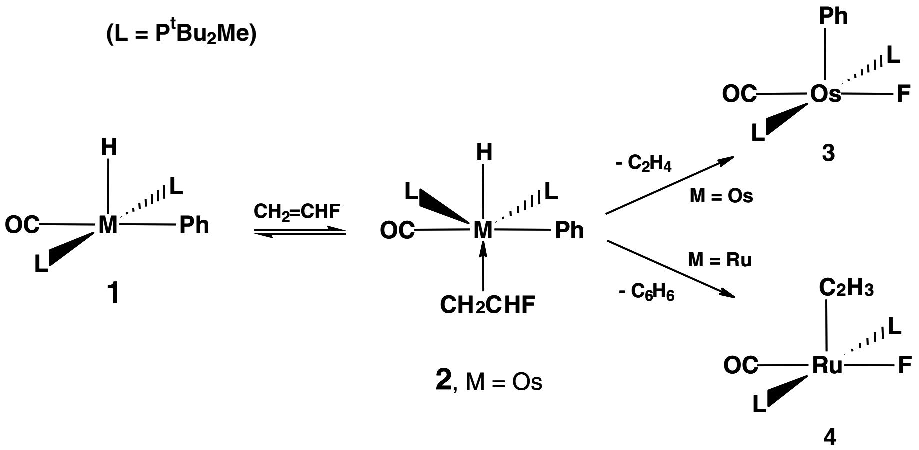

Scheme 1.

bond, to yield OsH(Ar$^F$)(CO)L$_2$ [34]. The reactions are thus selective *against* C–F bond scission; indeed, $C_6F_6$ does not react. In contrast, **1** is now reported to react with vinyl fluoride to ultimately produce a C–F bond-cleaved product. Reaction of OsH(Ph)(CO)L$_2$ with excess vinyl fluoride at −90 °C in toluene (Scheme 1) gives a π-adduct (**2**), OsH(Ph)(CO)L$_2$(C$_2$H$_3$F). The $^1$H NMR spectrum of **2** shows a hydride peak at −3.7 ppm as an apparent triplet. The coordinated vinyl protons appear at 2.7, 2.9 and 7.6 ppm and the $^{19}$F NMR signal of the bound vinyl fluoride (−171 ppm) is shifted significantly upfield, compared to that of free vinyl fluoride (−113 ppm) [35]. The $^{31}$P{$^1$H} NMR spectrum of this adduct at −50 °C is an AB quartet and the relatively small $J'_{PP} = 162$ Hz is indicative of two phosphines bent significantly away from a ~180° P–Os–P angle, consistent with strong back donation to this olefin [35]. At 25 °C, **2** reacts further (complete in 4 h) to release ethylene and form **3**, OsPh(F)(CO)L$_2$. The $^{19}$F NMR spectrum shows a triplet ($^2J_{PF} = 28$ Hz) at a chemical shift (−202.1 ppm) consistent with F bonded to osmium (not carbon), and $^{31}$P{$^1$H} NMR shows a doublet with the same splitting. The $^t$Bu groups are diastereotopically inequivalent and they, as well as the PCH$_3$ groups, are virtual triplets consistent with structure **3**. The $\nu_{CO}$ value (1874 cm$^{-1}$) is low enough to be consistent with a push/pull F → COπ* donation when these ligands are mutually *trans*. There are four (one of intensity 2) distinct phenyl proton NMR signals, suggesting slow rotation of the Ph around the Os–C(*ipso*) bond [36].

*(b) M = Ru.* RuH(Ph)(CO)L$_2$ also cleaves the C–F bond of vinyl fluoride but it gives a different product. Combination of RuH(Ph)(CO)L$_2$ with 1 atm CH$_2$=CHF in benzene[1] gives quantitative formation of Ru(CH=CH$_2$)F(CO)L$_2$ (**4**), after 12 h at room temperature (Scheme 1). The $^{19}$F NMR spectrum of **4** shows a broad triplet ($^3J_{PF} = 22$ Hz) and the $^{31}$P{$^1$H} NMR spectrum shows a doublet with the same $J_{PF}$ value. The $^1$H NMR spectrum of **4** features an α-vinyl proton at 8.3 ppm (ddd, $J_{HH} = 14.7$ Hz, $J_{HH} = 7.5$, $J_{FH} = 6.9$ Hz) with the β-protons at higher field (5.4 and 5.1 ppm). The low ν(CO) value (1894 cm$^{-1}$) is consistent with CO *trans* to F. For comparison, **4** can also be synthesized from RuHF(CO)L$_2$ and C$_2$H$_2$. Combination of RuHF(CO)L$_2$ and 1 atm C$_2$H$_2$ in benzene gives Ru(C$_2$H$_3$)F(CO)L$_2$ quantitatively in 30 min at room temperature.

*(c) Mechanism.* We interpret these results without invoking a wholly different mechanism for the reaction of the Ru and Os species MH(Ph)(CO)L$_2$ with vinyl fluoride. The idea that an oxidant, including even an electron deficient olefin like (NC)$_2$C=C(CN)$_2$, can trigger reductive elimination is termed oxidatively induced reductive elimination [37–41]. We suggest that the absence of *detectable* vinyl fluoride adduct for M = Ru is of quantitative (i.e., a few kcal/mol) rather than qualitative significance. Indeed, it serves as a reminder that Os is a more potent π base than Ru, since back-bonding is an important component of binding of the fluorinated olefin. This difference in π-basicity can also be used to interpret the distinct selectivities shown by Ru and Os. In brief (Scheme 2), osmium is more tolerant to high oxidation states, so the C–F oxidation product, containing Os$^{IV}$, can be achieved. This seven-coordinate species will be sufficiently persistent and nonrigid, to permit isomerization of H to a site *cis* to the vinyl group; reductive elimination of ethylene follows. For M = Ru, η$^2$ binding of π-acidic H$_2$C=CHF triggers rapid reductive elimination of H with C$_6$H$_5$ as the lowest energy process, in order to avoid the high (versus Os) energy of Ru$^{IV}$; the prompt character of these two events prohibits establishing any inherent (i.e., thermodynamic) preference for phenyl versus vinyl remaining on ruthenium. That is, selectivity is truly kinetically controlled for Ru

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[1] No detectable amount of adduct is formed from RuH(Ph)(CO)L$_2$ under 1 atm vinyl fluoride in $d_{14}$-methylcyclohexane at −70° by $^1$H and $^{31}$P NMR spectroscopy.