Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polyhedron 25 (2006) 459–468
POLYHEDRON
www.elsevier.com/locate/poly

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

Dejian Huang, Kenton B. Renkema, Kenneth G. Caulton *

Department of Chemistry, Indiana University, 800 E. Kirkwood, CHEM A250B, Bloomington, IN 47405-4001, USA

Received 12 May 2005; accepted 9 August 2005
Available online 4 October 2005

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-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(η^1-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.

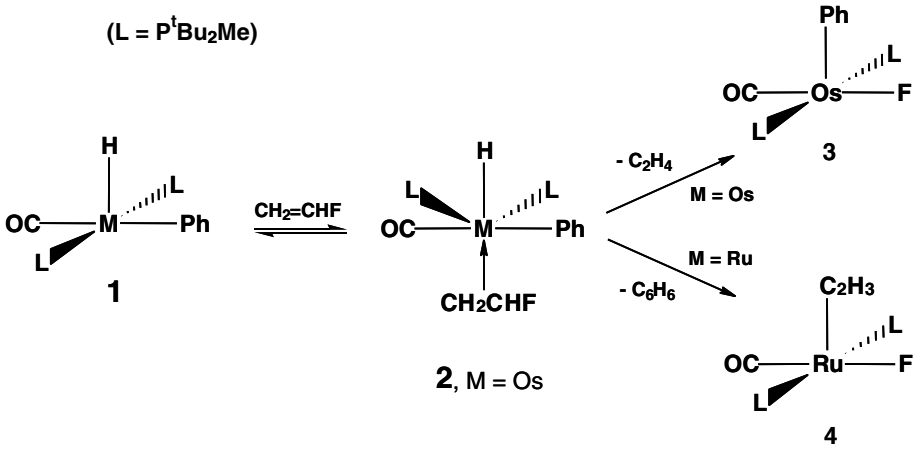
2. Results

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

* Corresponding author. Tel.: +1 812 855 4798; fax: +1 812 855 8300.
E-mail address: caulton@indiana.edu (K.G. Caulton).

0277-5387/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2005.08.012



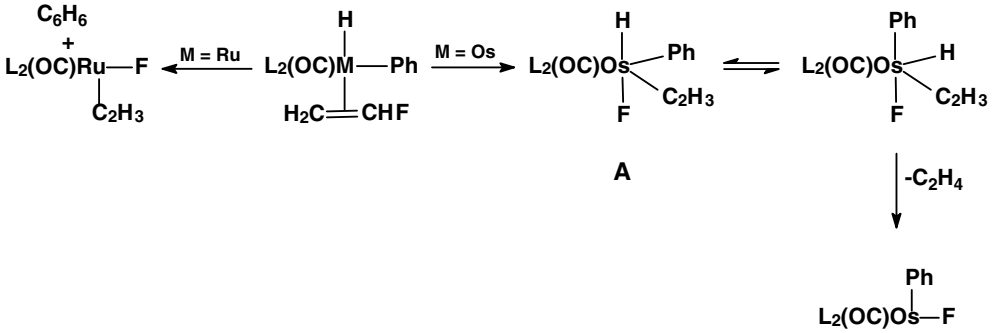
Scheme 1.

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**), $OsH(Ph)(CO)L_2(C_2H_3F)$. The ^1H 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 $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ 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 ν_{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 $^{31}P\{^1H\}$ NMR spectrum shows a doublet with the same J_{PF} value. The ^1H 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_2H_2. Combination of $RuHF(CO)L_2$ and 1 atm C_2H_2 in benzene gives $Ru(C_2H_3)F(CO)L_2$ quantitatively in 30 min at room temperature.

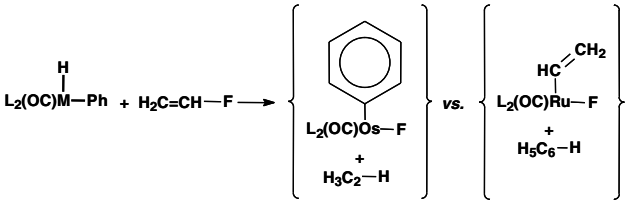
(c) Mechanism. We interpret these results without invoking a wholly different mechanism for the reaction of the Ru and Os species $MH(Ph)(CO)L_2$ with vinyl fluoride. The idea that an oxidant, including even an electron deficient olefin like $(NC)_2C{=}C(CN)_2$, can trigger reductive elimination is termed 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 $H_2C{=}CHF$ triggers rapid reductive elimination of H with C_6H_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

[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 ^1H and ^{31}P NMR spectroscopy.



Scheme 2.

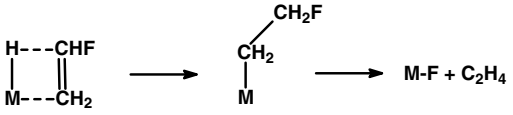
but probably not so for Os. Based on our earlier evidence that M–F bond formation is thermodynamically favored for the reactions of the various five-coordinate species studied here [33], the metal dependent products in Scheme 1 probably involve very small differences in reaction enthalpy (i.e., they differ by vinyl versus phenyl on the metal (Eq. (1)) but share the production of a M–F bond). The different products are thus best explained by being under kinetic control via the distinct accessibility of redox changes at a 4d versus a 5d metal.



(1)

In order to test for possible phosphine dissociation at or prior to the rate determining step in the reaction of $MH(Ph)(CO)L_2$ with vinyl fluoride, a rate comparison was made in the absence and presence of 2–5 equivalents of free phosphine (P^tBu_2Me). For either M = Ru or Os, the half-lives for product appearance were observed to be comparable with and without added L, eliminating phosphine dissociation as a mechanistic component.

Based on the mechanism previously deduced for reaction of $OsHCl(CO)(P^iPr_3)_2$ with RCCH [42], a direct attack of the M–H bond on the olefin must also be considered here (Eq. (2)). Here, no prior η^2-olefin adduct is on the reaction path and the first M/C interaction is concurrent with C/H bond formation.



(2)

Since this is a path to M–F and ethylene, it might explain the results when M = Os, but not for Ru. Because it is not clear *why* this mechanism would have higher $\Delta G^{\ddagger}$ for Ru, we discount it. In contrast, the known redox differences of Ru and Os naturally account for the observed selectivity difference via Scheme 2.

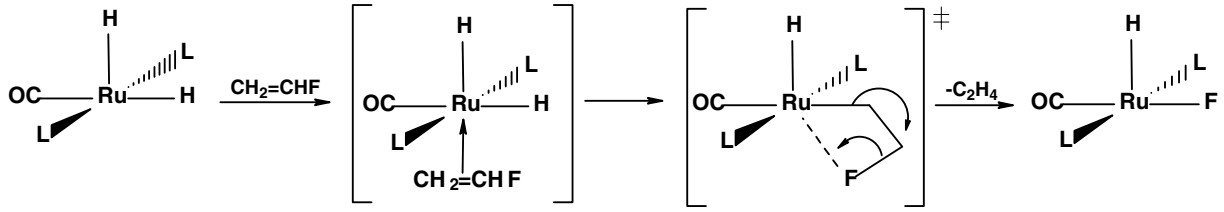
$M(H)_2$ reactivity with H_2C=CHF. A mechanism which incorporates the adduct $MHR(H_2C{=}CHF)(CO)L_2$ also naturally explains the high rate and *similar* products, for M = Ru and Os, when R = H, as will now be described. The feature common to the reactions in Scheme 1 is that the hydride ligand cannot react immediately with a vinyl fluoride ligand *trans* to itself, and thus metal-dependent selectivity develops from within the adduct. To create the contrasting situation of hydride *cis* to the olefin, excess vinyl fluoride was reacted with $Ru(H)_2(CO)L_2$ [36]: immediately at −80 °C ethylene and $RuHF(CO)L_2$ are formed. We propose the reaction proceeds by insertion of vinyl fluoride into the *cis* Ru–H bond, followed by β-F migration (Scheme 3).

To compare this dihydride reactivity of Ru to that for Os, $Os(H)_2$(1-butene)$(CO)L_2$ [43,44] (as a source of the currently unknown $Os(H)_2(CO)L_2$) was prepared from $Os(H)_2(H_2)(CO)L_2$ and 1-butene. This molecule reacts with excess (19 equivalents) vinyl fluoride within 30 min at 25 °C in C_6D_6 to give ethylene and $OsHF(CO)L_2$; since this product molecule shows dynamic NMR effects from binding olefin, identification is simplified by first removing all volatiles, then redissolving in benzene.

Thus, and in contrast to $MH(Ph)(CO)L_2$, unsaturated Ru and Os show analogous reactivity when a hydride is *adjacent* to the empty coordination site.

2.2. Influence of R group identity in $MH(R)(CO)L_2$

The essential feature of species **A** is that C_2H_3 and H are *not* mutually *cis* because H, Ph, C_2H_3, and F are coplanar. Therefore, the different results seen for Ru and Os were argued to occur because the unstable Ru(IV) intermediate analogous to **A** would not allow time for rearrangement, followed by elimination of the most thermodynamically favorable products, $MF(Ar)(CO)L_2$ and olefin. The furthest extension of this mechanism, where a Ru(IV) intermediate never exists, is represented in Scheme 4.



Scheme 3.

In order to understand what role M–R bond strength plays in these reactions, we synthesized $RuH(2\text{-}C_6H_4F)(CO)L_2$ and $RuH(C_6F_5)(CO)L_2$ by reacting $RuH(Ph)(CO)L_2$ with monofluorobenzene and pentafluorobenzene, respectively. We expect that these species will have greater thermal stability against arene elimination with increasing number of fluorines on the aryl ring since $OsH(2,6\text{-}C_6F_2H_3)(CO)L_2$ persists unchanged after 30 h at 70 °C in d_{12}-cyclohexane, but $OsH(C_6H_5)(CO)L_2$ decomposes to free benzene, phosphine and unidentified osmium products under the same conditions. Previous DFT-calculations on $OsH(C_6H_5)(CO)(PH_3)_2$ showed that π donation was partially responsible for restricted rotation about the M–C(*ipso*) bond. The calculated and observed thermodynamic preference for metal–aryl complexes with fluorine *ortho* to the metal suggest that fluorines on the aryl ring increase the amount of π donation from a fluoroaryl ring to a metal.

(a) Ru–Ar^F. When $RuH(2\text{-}C_6H_4F)(CO)L_2$ was reacted with one equivalent of vinyl fluoride for 20 h at 50 °C, the products, $Ru(C_2H_3)F(CO)L_2$ and C_6H_5F, are analogous to those in Eq. (2), i.e., aryl/H reductive elimination. Reaction of the less oxidizable $RuH(C_6F_5)(CO)L_2$ with less than one equivalent C_2H_3F for 7 days at 85 °C yields $Ru(C_2H_3)F(CO)L_2$, C_6F_5H, $Ru(C_6F_5)F(CO)L_2$, and C_2H_4. These last two products therefore indeed indicate that reactions of *both* types in Scheme 2 compete for this more stable ruthenium hydrido-fluoroaryl reagent, consistent with Ru–C bond strength influencing the decay mode of the intermediate.

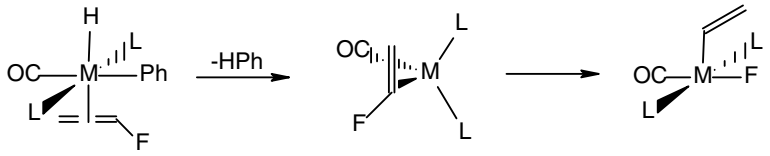
(b) Os–CH$_3$. Continuing this hypothesis, an osmium species with a *weaker* Os–C bond than Os–C_6H_5 should change reaction selectivity. To that end, $OsH(CH_3)(CO)L_2$ (**5**), was synthesized by reaction of $OsHCl(CO)L_2$ with one equivalent of MeLi. Centrifugation of the solution most efficiently removed the LiCl co-product. The NMR signatures of **5** are consistent with other five-coordinate osmium complexes where hydride is in the apical position. The hydride chemical shift is far upfield (−33.2 ppm). The methyl ^{1}H NMR signal (integrated to intensity 3) is a triplet at 0.46 ppm. The *t*-butyl signals are diastereotopic virtual triplets and the ^{31}P NMR spectrum shows one sharp singlet. In benzene at 22 °C, **5** undergoes slow conversion to $OsH(Ph)(CO)L_2$. Species **5** thus has a weaker Os–C bond than $OsH(Ph)(CO)L_2$.

Compound **5** is completely consumed by excess vinyl fluoride at −75 °C in d_8-toluene; *two* new species were observed by ^{19}F NMR. The ^{31}P NMR spectrum of *one* of these showed an AB pattern ($J_{PP} = 161$ Hz). ^{1}H NMR gave two defining signals, a hydride signal at −6.3 ppm (d of d) and signal intensity 3 at −1.1 ppm (assigned to Os–CH_3). These spectroscopic features are consistent with assignment of (Eq. (3)) the most abundant primary product as the simple adduct $OsH(CH_3)(CO)L_2(C_2H_3F)$.

$$\begin{aligned} &OsH(CH_3)(CO)L_2 + H_2C{=}CHF \\ &\quad \rightleftharpoons OsH(CH_3)(CO)L_2(C_2H_3F) \\ &\quad \xrightarrow{RT} OsF(CH_3)(CO)L_2 + H_2C{=}CH_2 \end{aligned} \tag{3}$$

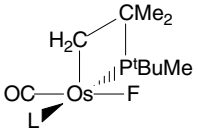
Warming the mixture to −15 °C increased the rate of olefin exchange sufficiently to cause the ^{19}F NMR signals at −169 ppm for bound olefin to broaden nearly into the baseline. Significant conversion of this olefin adduct to the final product did not occur until room temperature, but this is faster than the corresponding reaction of $OsH(Ph)(CO)L_2$. A ^{19}F NMR triplet (−198 ppm, $J_{FP} = 27$ Hz), a $^{31}P\{^1H\}$ NMR doublet (26.0 ppm, $J_{PF} = 27$ Hz), the loss of the hydride signal, and the production of ethylene are all consistent with assignment of the new compound as $OsF(CH_3)(CO)L_2$. This represents reactivity analogous to that of $OsH(Ph)(CO)L_2$ with vinyl fluoride.

The amount and spectral features of the *second* low temperature product change very little upon warming the sample from −45 to 20 °C. Over those temperatures,



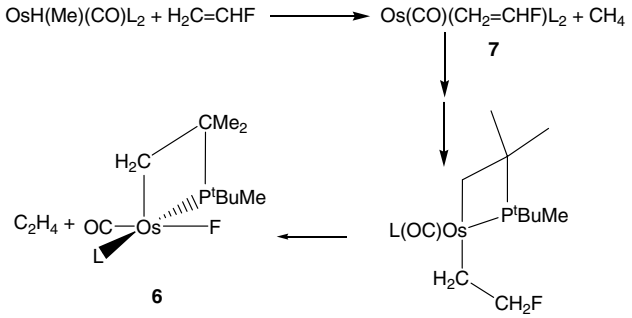
Scheme 4.

the $^{31}P\{^{1}H\}$ NMR spectrum showed an AM pattern ($\Delta\delta = 32$ ppm) with a J_{PP} of 148 Hz. One of the phosphorus nuclei showed coupling to fluorine ($J_{PF} = 15$ Hz) whose magnitude is consistent with F on Os. This fluorine is detected at −195 ppm as a doublet of multiplets. AM patterns with large $\Delta\delta$ are typical for metallated alkyl ligands on phosphines; we propose structure **6**. The presence of this second product where the osmium complex has lost methane, HR, shows the competitive occurrence of a second mechanism, that used by Ru in Scheme 2, prior to activation of a C–F bond. This species declines in intensity as the temperature is raised and ultimately disappears from both ^{31}P and ^{19}F NMR spectra.



6

Detection of this species is especially important because it has the stoichiometry of $Os(CO)L_2$ *minus* one H and *plus* one F. It is thus a plausible product of a second fate for $OsH(Me)(CO)L_2$, following olefin-induced reductive elimination of methane. The primary product would then be zerovalent, unsaturated **7** (Scheme 5), in which oxidative addition of a *t*-Bu C–H bond would permit hydrogen migration to vinyl fluoride, then fluorine migration to Os, with liberation of ethylene.

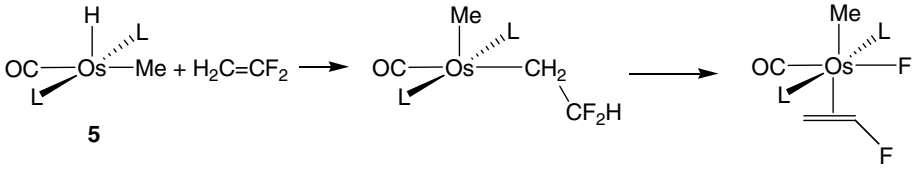


Scheme 5.

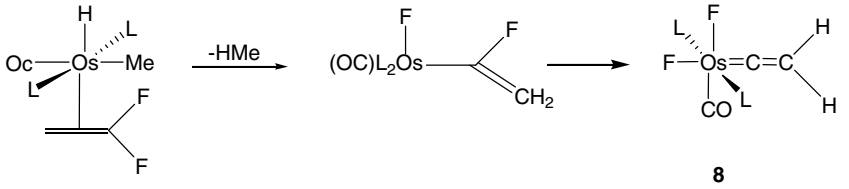
The detection of a second competitive reaction channel for $OsHMe(CO)L_2$ in reacting with vinyl fluoride thus links the ruthenium chemistry ($RuH(Ph)(CO)L_2$) to that of osmium; the more facile elimination of H with an sp^3 carbon (versus sp^2 in $OsH(Ph)(CO)L_2$) makes this oxidatively induced reductive elimination now detectable (but not dominant) for $OsHMe(CO)L_2$.

2.3. A more oxidizing olefin

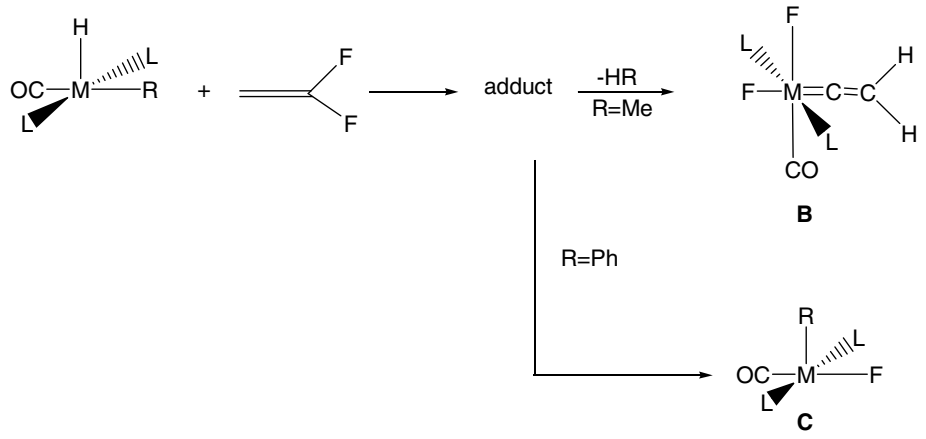
(a) Os–CH₃. The *gem*-difluoro olefin $H_2C{=}CF_2$ provides an additional test of mechanism. An insertion mechanism for reaction of $H_2C{=}CF_2$ with **5** would yield vinyl fluoride (Scheme 6). If, on the other hand, this more π-acidic difluoro olefin promptly triggers methane elimination, then the first C–F oxidative addition to Os(0) could be followed by a second F migration (Scheme 7). Reaction of $OsH(CH_3)(CO)L_2$ with gem-difluoroethylene at 0 °C with subsequent slow warming to room temperature, then removal of excess olefin, gave 75% yield of product **8** with 100% conversion of **5**. The $^{31}P\{^{1}H\}$ NMR spectrum of **8** is a doublet of doublets ($J_{PF} = 41$, 25 Hz). ^{19}F NMR revealed an AB pattern due to inequivalent F on Os. The lower field doublet ($J_{FF} = 143$ Hz) also showed triplet coupling to phosphorus ($J_{FP} = 25$ Hz), while the lines of the higher field doublet were each triplets of triplets, due to two phosphorus ($J_{PF} = 41$ Hz) and two protons ($J_{FH} = 7$ Hz). ^{1}H NMR showed the absence of a hydride chemical shift as well as the appearance of a new signal at 2.0 ppm (vinylidene CH_2), which was a doublet of triplets ($J_{HF} = 7$ Hz,



Scheme 6.



Scheme 7.



Scheme 8.

$J_{HP} = 3$ Hz). $^{13}C\{^1H\}$ NMR showed the β-carbon signal at 94 ppm as a doublet ($J_{CF} = 16$ Hz).

An osmium difluoride product is consistent with an intermediate with fluorine located α to the metal because such species exhibit α-fluoro migration. The "prompt" elimination of H–CH_3 in Scheme 7 contrasts to the reaction of $OsH(Ph)(CO)L_2$ with vinyl fluoride, and may be attributed to the more oxidizing (cf. π-acid) character of $H_2C{=}CF_2$ (versus $H_2C{=}CHF$).

(b) Os–Ph. To test the influence of Os–C(sp^3) versus C(sp^2) on reactivity, the reaction of $OsH(Ph)(CO)L_2$ with excess $H_2C{=}CF_2$ was studied. This yielded primarily $Os(Ph)F(CO)L_2$ on the same time scale as vinyl fluoride; only a trace amount of $OsF_2(CO)(CCH_2)L_2$ forms. This result further illustrates how the energetics of HR elimination from the proposed M(IV) intermediate affects the outcome of the reaction (Scheme 8). When HR elimination is the fastest process from the adduct, then metal difluoride **B** would result. However, if rearrangement (to hydride *cis* to olefin) and elimination of the vinyl species are faster, five-coordinate $OsRF(CO)L_2$ (**C**), forms. Clearly, the latter is favored for osmium: the Os–Ph bond persists through reaction with both $H_2C{=}CHF$ and $H_2C{=}CF_2$.

3. Conclusion

We have demonstrated here several C–F bond cleavage reactions of vinyl fluoride by five-coordinate hydrides $MHR(CO)L_2$ (R = Ph, CH_3, H; M = Os, Ru). The reaction products are highly dependent on the identity of the metal when R = Ph. For Os, Os–H/C–F "exchange" is the dominant pathway, while for Ru and R = Ph, the reaction features reductive elimination of C_6H_6, followed by C–F bond cleavage of vinyl fluoride. The facility for H-Ph formation and the relative stability of (II versus IV) oxidation states are the two factors influencing the metal-dependence. It is also remarkable that benzene loss from $RuH(Ph)(CO)L_2$ is followed by oxidative addition of the C–H bond of partially fluorinated arene [33], but of the C–F bond of vinyl fluoride. It is noteworthy that both metals show kinetic selectivity (C–H cleavage) when reacting with fluorinated arenes to give $MH(Ar^F)(CO)L_2$ but thermodynamic selectivity (M–F bond formation) when reacting with fluorinated olefins.

In a sense, this reaction of $RuH(Ph)(CO)L_2$ as a "$Ru^0(CO)L_2$ equivalent" is analogous to that of elemental magnesium, to generate a Grignard reagent by C–F oxidative addition [45]. In contrast, in *both* dihydride cases reported here, the net reaction is M–H/ C–F exchange, but apparently by a β-F migration mechanism.

This work began by raising the question of the curious selectivity for C–H over C–F scission in reaction of $OsH(Ph)(CO)L_2$ with partially fluorinated arenes. However, vinyl fluoride substrate shows quite the opposite selectivity, and what was discovered here is contrasting *metal* selectivity: Ru versus Os. The question of reversion to "normal" selectivity for C–F scission with fluoro olefins (cf. fluoroarenes) probably relates to the greater ease of binding olefins (versus arenes) to metals, together with the very different ability of metal to attack F–C(H)CH_2 versus F–$C(CH)_2$ (i.e., arene) moieties.

4. Experimental

4.1. General procedures

All manipulations were performed using standard Schlenk techniques or in an argon filled glovebox unless otherwise noted. Solvents were distilled from Na, Na/benzophenone, CaH_2, or 4 Å molecular sieves, degassed

prior to use, and stored in air-tight vessels. OsHCl(CO)(P^tBu_2Me)$_2$ [46], OsH(Ph)(CO)(P^tBu_2Me)$_2$ [34], RuHF(CO)(P^tBu_2Me)$_2$ [47], Ru(H)$_2$(CO)(P^tBu_2Me)$_2$ [36] and RuH(Ph)(CO)(P^tBu_2Me)$_2$ [36] were prepared according to published procedures. All other reagents were purchased from commercial vendors and used as received after drying/degassing when necessary. ^{1}H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents; ^{31}P (always proton-decoupled) and ^{19}F spectra are referenced to external standards of 85% H_3PO_4 and $CFCl_3$, respectively (both at 0 ppm). NMR spectra were recorded with a Varian Gemini 2000 (300 MHz ^{1}H; 121 MHz ^{31}P; 75 MHz ^{13}C, 282 MHz ^{19}F), a Varian Unity Inova instrument (400 MHz ^{1}H; 162 MHz ^{31}P; 101 MHz ^{13}C, 376 MHz ^{19}F), or a Varian Unity Inova instrument (500 MHz ^{1}H, 126 MHz ^{13}C). Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer.

4.2. *Os(Ph)F(CO)(P^tBu_2Me)$_2$*

An NMR tube containing OsH(Ph)(CO)(P^tBu_2Me)$_2$ (16.5 mg, 2.68×10^{-5} mol) in 500 μL d_8-toluene had 200 Torr (7.7×10^{-4} mol) of vinyl fluoride condensed into it. At low temperature the η^2-adduct formed: diagnostic ^{1}H NMR (C_7D_8, −90 °C) −3.7, (t, 1H, Os*H*, $J_{PH}=29$ Hz); 2.7, (d, 1H, CCH, $J_{HF}=20.4$ Hz); 2.9 (d, 1H, CCH, $J_{HF}=22$ Hz); 7.54, (d, 1H, CCH, $J_{FH}=72.0$ Hz). ^{31}P NMR (C_7D_8, −90 °C) −2.5, (AB, $J_{PP}=162$ Hz). ^{19}F(C_7D_8, −90 °C) −171.3 (dt, 1F, CCF, $J_{FH}=73$ Hz, $J_{FH}=20$ Hz). Conversion to the final product did not occur until 10 °C and was complete within 4 h at room temperature. The ^{1}H NMR detection of ethylene confirmed product identity. ^{1}H NMR (C_7D_8, 20 °C) 1.00, (vt, 18H, OsPCC*H*$_3$, $J_{PH}=5.8$ Hz); 1.04, (vt, 18H, PCC*H*$_3$, $J_{PH}=5.8$ Hz); 1.29, (broad s, 6H, PC*H*$_3$); 6.39, (t, 1H, Ar-*H*, $J_{PH}=6.0$ Hz); 6.5, (t, 2H, Ar-*H*, $J_{HH}=6$ Hz); 7.32, (d, Ar-*H*, $J_{HH}=6$ Hz); 7.64, (d, Ar-*H*, $J_{HH}=6.0$ Hz). ^{31}P NMR (C_7D_8, 20 °C) 26.5, (d, 2P, $J_{PF}=28$ Hz). ^{19}F(C_7D_8, 20 °C) −202.1 (t, 1F, CCF, $J_{FP}=28$ Hz) ν(CO) = 1874 cm^{-1}.

4.3. *Reaction of OsH(Ph)(CO)(P^tBu_2Me)$_2$ + C_2H_3F in the presence of P^tBu_2Me*

When OsH(Ph)(CO)(P^tBu_2Me)$_2$ (10.5 mg, 1.70×10^{-5} mol) was dissolved in 500 μL C_6D_6 and reacted with two equivalents P^tBu_2Me and C_2H_3F (600 Torr, 5.2 equivalents) the reaction reached completion in 4 h. A similar time scale was observed in the absence of free phosphine.

4.4. *Ru(C_2H_3)F(CO)(P^tBu_2Me)$_2$*

RuHF(CO)L$_2$ (150 mg, 0.32 mmol) was dissolved in diethyl ether (3 mL). The solution was degassed and the headspace was charged with acetylene gas (1 atm). The mixture was stirred at room temperature for 30 min before the volatiles were removed under vacuum. The residue was dissolved in pentane, filtered through a Celite pad and concentrated to ca. 2 mL. After cooling the solution at −40 °C for one day, dark orange crystals were obtained. Yield: 120 mg (76%). ^{1}H NMR (C_6D_6, 20 °C, 300 MHz): 1.20 (vt, N = 12.5, 18H, PC(CH$_3$)$_3$), 1.25 (vt, 18H, N = 12 Hz, PC(CH$_3$)$_3$), 1.21 (vt, 6H, N = 5.9, PCH$_3$), 5.10 (dt, $J_{HH}=14.5$, $J_{PH}=2.0$ Hz, 1H β-H(vinyl)), 5.45 (dt, $J_{HH}=6.4$ Hz, $J_{PH}=2.4$ Hz, 1H, β-vinyl), 8.30 (doublet of apparent triplets, 1H, $J_{HH}=14.5$ Hz, $J_{HH}=7.5$ Hz, $J_{HF}=6.9$ Hz, α-H of vinyl). ^{13}C{^{1}H} NMR (toluene-d_8, 75 MHz, 20 °C): 3.16 (vt, N = 15 Hz, PCH$_3$), 29.7, 29.8 (s, PC(*C*H$_3$)$_3$), 35.4, 35.5 (s, P*C*(CH$_3$)$_3$), 117.5 (s, =CH$_2$), 156.3 (t, J = 20.3 Hz, Ru–CH). ^{31}P{^{1}H} NMR: 41.2 (d, $J_{PF}=22$ Hz). ^{19}F NMR: −214 (t, $J_{PF}=22$ Hz). IR (C_6D_6): 1894 (ν(CO)).

4.5. *Reaction of RuH(Ph)(CO)L$_2$ with vinyl fluoride*

RuH(Ph)(CO)(P^tBu_2Me)$_2$ (10 mg, 0.019 mmol) was dissolved in C_6D_6 (0.5 mL) and degassed by three freeze–pump–thaw cycles. To the tube, C_2H_3F (1 atm) was charged. The mixture was agitated for 12 h. NMR spectroscopies reveal clean formation of Ru(C_2H_3)(F)(CO)L$_2$ by comparison to data in the preceding experiment.

4.6. *Reaction of RuH(Ph)(CO)(P^tBu_2Me)$_2$ with vinyl fluoride in the presence of added phosphine ligand*

In an NMR tube, RuH(Ph)(CO)L$_2$ (10 mg, 0.019 mmol) and P^tBu_2Me (15 mg, 5 eq.) were dissolved in cyclohexane-d_{12}. The solution was degassed and the headspace of the tube was charged with 1 atm vinyl fluoride. After 12 h at room temperature, RuH(Ph)(CO)L$_2$ was completely consumed and Ru(C_2H_3)F(CO)L$_2$ was formed as revealed by its ^{31}P{^{1}H} NMR spectrum.

4.7. *Os(H)$_2$(η^2-1-butene)(CO)(P^tBu_2Me)$_2$*

Reaction of OsH$_2$(H$_2$)(CO)(P^tBu_2Me)$_2$ (5.6 mg, 1.04×10^{-5} mol) with 1-butene (100 Torr, 6.95×10^{-5} mol) in C_6D_6 at room temperature gives the title compound within 5 min. The room temperature NMR signals are broadened by dynamic equilibrium. ^{1}H NMR (C_6D_6, 293 K) −11.2 (t, OsH, 1H, $J_{PH}=23$ Hz); −8.66 (t, OsH, 1H, $J_{PH}=33.5$ Hz); 0.86 (t, CH$_2$C*H*$_3$, 3H, $J_{HH}=4$ Hz); 1.26 (vt, PCCH$_3$, 18H, $J_{PH}=6.3$ Hz); 1.28 (vt, PCCH$_3$, 18H, $J_{PH}=6.3$ Hz); 1.62 (m, C*H*$_2$CH$_3$); 2.2 (br s, vinyl CH, 1H); 2.6 (br s, vinyl CH, 1H); 3.2 (br s, vinyl CH, 1H). ^{31}P NMR (C_6D_6, 293 K) 29.6, 29.9 (AB, $J_{PP}=148$ Hz).

4.8. Reaction of $OsH_2(\eta^2\text{-1-butene})(CO)(P^tBu_2Me)_2$ with C_2H_3F

To $OsH_2(\eta^2$-1-butene)(CO)$(P^tBu_2Me)_2$ (1.83×10^{-5} mol) was added C_2H_3F (150 Torr, 19 equivalents); $OsHF(\eta^2\text{-}C_2H_3F)(CO)(P^tBu_2Me)_2$ was formed within 30 min. The signals for this species were broad due to exchange of olefin. The species was identified by ^{1}H NMR (C_6D_6, 293 K); 2.8, (br s, C_2H_3F); −3.1 (br s, Os*H*) and ^{31}P NMR (C_6D_6, 293 K): 24.5 (br s). Evacuation of the excess olefin left $OsHF(CO)(P^tBu_2Me)_2$. ^{1}H NMR (C_6D_6, 293 K) −32.2 (td, OsH, 1H, $J_{PH}=13$ Hz, $J_{HF}=8.7$ Hz); 1.20 (vt, $PCCH_3$, 18H, $J_{PH}=6.9$ Hz); 1.22 (vt, $PCCH_3$, 18H, $J_{PH}=6.9$ Hz). ^{31}P NMR (C_6D_6, 293 K) 44.78 (d, $J_{PF}=26$ Hz). ^{19}F NMR (C_6D_6, 293 K): −184.6 (t, $J_{FP}=26$ Hz).

4.9. Reaction of $Ru(H)_2(CO)(P^tBu_2Me)_2$ with vinyl fluoride

$Ru(H)_2(CO)(P^tBu_2Me)_2$ (10 mg) in toluene-d_8 (0.5 mL) in an NMR tube was freeze–pump–thaw degassed, and the headspace of the NMR tube was charged with vinyl fluoride (1 atm) at −80 °C. The tube was transferred to a precooled NMR probe for observation. At −80 °C, no $Ru(H)_2(CO)L_2$ but only $RuHF(CO)L_2$ was detected by its $^{31}P\{^1H\}$ NMR spectrum (52.5 ppm, doublet $J_{PF}=20$ Hz). The volatiles of the reaction mixture were vacuum transferred to another NMR tube where the ^{1}H NMR spectrum revealed ethylene (5.34, singlet).

4.10. Reaction of $RuH(2\text{-}C_6FH_4)(CO)(P^tBu_2Me)_2$

$RuH(Ph)(CO)(P^tBu_2Me)_2$ (200 mg, 0.38 mmol), cyclohexane (10 mL), and fluorobenzene (1 mL) were stirred together for 18 h. After removal of the volatiles, the residue was extracted with pentane. The pentane solution was filtered through a Celite pad, concentrated to ca. 3 mL, and cooled to −78 °C for 2 h to give yellow crystals after 12 h. The crystals were filtered, washed with pentane and dried in vacuo to yield 125 mg (70%) of the title compound. Newly prepared product contains two rotamers about the Ru–Aryl bond, with 10:6 ratio based on NMR integration of the PCH_3 peaks. Spectroscopic data for the major isomer: ^{1}H NMR (C_6D_6, 20 °C) −28.7 (td, $J_{PH}=19.2$, $J_{FH}=7.6$ Hz, 1H, RuH); 0.70 (vt, 5.5 Hz, 6H, PCH_3); 1.13 (vt, 13 Hz, 18H, $PCCH_3$); 1.20 (vt, 12.7 Hz, 18H, $PCCH_3$); 6.9, 7.1, 7.6 (m, 4H, ArH). ^{31}P NMR (C_6D_6, 20 °C) 57.0 (s). ^{19}F (C_6D_6, 20 °C) −96.7(s). Minor isomer: ^{1}H NMR: −27.2 (td, $J_{PH}=20$ Hz, $J_{HF}=5.2$ Hz, 1H, Ru–H), 0.66 (vt, 5.5 Hz, PCH_3), 1.09 (vt, 12 Hz, 18H, $PC(CH_3)_3$), 1.19 (vt, 13 Hz, 18H, $PC(CH_3)_3$), 6.87, 7.03, 7.55 (4H, Ar). $^{31}P\{^1H\}$ NMR: 57.1 (s). ^{19}F NMR: −84.5 (s).

4.11. Reaction of $RuH(2\text{-}C_6FH_4)(CO)(P^tBu_2Me)_2$ with vinyl fluoride

$RuH(2\text{-}C_6FH_4)(CO)(P^tBu_2Me)_2$ (10 mg, 1.8×10^{-5} mol) was dissolved in C_6D_6 (0.5 mL) and degassed by three freeze–pump–thaw cycles. To the NMR tube, 400 Torr vinyl fluoride was charged. The resulting mixture was heated at 50 °C for 20 h to give $Ru(C_2H_3)F(CO)(P^tBu_2Me)_2$ and fluorobenzene.

4.12. Reaction of $RuH(C_6F_5)(CO)(P^tBu_2Me)_2$

The same procedure as $RuH(2\text{-}C_6FH_4)(CO)(P^tBu_2Me)_2$ was followed except C_6F_5H was used instead of C_6H_5F. Alternatively, it can be prepared from reaction of $RuHF(CO)(P^tBu_2Me)_2$ with $Me_3SiC_6F_5$ in the presence of a catalytic amount of CsF.

4.13. Reaction of $RuH(C_6F_5)(CO)(P^tBu_2Me)_2$ with vinyl fluoride

In an NMR tube, $RuH(C_6F_5)(CO)(P^tBu_2Me)_2$ (10 mg, 0.016 mmol) was dissolved in C_6D_6 (0.5 mL) and degassed by three freeze–pump–thaw cycles. To the tube, vinyl fluoride (400 mm Hg) was added. The mixture was heated at 85 °C for three days to give (based on $^{31}P\{^1H\}$ NMR integration) conversion to $RuF(C_6F_5)(CO)(P^tBu_2Me)_2$ (85%) and $Ru(C_2H_3)(F)(CO)(P^tBu_2Me)_2$ (15%). Addition of CsF to the NMR tube was necessary to resolve all couplings. Spectroscopic data for $RuF(C_6F_5)(CO)(P^tBu_2Me)_2$: ^{1}H NMR (400 MHz, C_6D_6, 20 °C) 0.92 (vt, 13 Hz, 18H, PCH_3,); 0.99 (vt, 6.5 Hz,18H, $PCCH_3$,); 1.22 (broad, 6H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): 42.7 (d, 2P, $J_{PF}=24.6$Hz). ^{19}F NMR (376.3 MHz): −111.5 (dd, $J_{FRuF}=53.3$ Hz, $J_{FF}=28.8$ Hz, 1F, *o*-ArF); −113.7 (d, $J_{FF}=26.5$ Hz, 1F, *o*-ArF,); −162.3 (dt, $J_{FF}=53$ Hz, $J_{PF}=25$ Hz, Ru–F), −164.4 (dd, $J_{FF}=J_{FF}=21$ Hz, *para*-F), −164.9 (dddd, $J_{FF}=26.2$, 21, 5, 5 Hz, *meta*-F); −167.4 (dddd, $J_{FF}=28$, 23, 5, 5 Hz, *meta*-F). The volatiles of the reaction mixture were vacuum transferred to another NMR tube and ^{1}H and ^{19}F NMR spectra showed C_2H_4 and C_6F_5H.

4.14. Reaction of $OsH(CH_3)(CO)(P^tBu_2Me)_2$

A solution containing 40.5 mg (7.04×10^{-5} mol) $OsHCl(CO)(P^tBu_2Me)_2$ in 3 mL of pentane was prepared in a centrifuge tube. Dropwise addition of 49.0 μL (7.11×10^{-5} mol) MeLi solution caused a gradual darkening of the solution concurrent with the appearance of a white suspension. The solution was centrifuged and the supernate was pipetted to a Schlenk flask. The solvent was then removed to leave an orange-red solid. ^{1}H NMR (C_6D_{12}, 20 °C) −33.3, (t, 1H, Os*H*, $J_{PH}=15.1$ Hz); 0.46 (t, 3H, $OsCH_3$, $J_{PH}=7.2$ Hz); 1.18 (vt, 18H, $PCCH_3$,

$J_{PH} = 6.0$ Hz); 1.21 (vt, 18H, PCCH_3, $J_{PH} = 6.0$ Hz); 1.49 (t, 6H, PCH_3, $J_{PH} = 2.8$ Hz). ^{31}P NMR (C_6D_{12}, 20 °C) 36.5, IR(C_6D_6): 1864(ν_{CO}).

4.15. $Os(CH_3)F(CO)(P^tBu_2Me)_2$

The reaction was run in a sealed NMR tube containing 9.2 mg $OsH(CH_3)(CO)(P^tBu_2Me)_2$ (1.658×10^{-5} mol) with 100 Torr vinyl fluoride (6.786×10^{-5} mol) in d_8-toluene. At −75 °C, the adduct $OsH(Me)(\eta^2\text{-}C_2H_3F)(CO)(P^tBu_2Me)_2$ was formed. Its diagnostic spectral features were: ^{1}H NMR (C_7D_8, −75 °C) −6.3 (1H, OsH); −1.1 (3H, OsCH_3); 2.9 (d, 1H, C=CH, $J_{PH} = 22.0$ Hz); 3.2 (m, 1H, C=CH); 6.3 (1H, C=CH). ^{31}P NMR (C_7D_8, −75 °C): 15.2, 12.7 (AB, 2P, $J_{PP} = 161$Hz). ^{19}F(C_7D_8, −75 °C) −170.0 (dt, 1F, CCF, $J_{FH} = 73$Hz, $J_{FH} =$ 20 Hz). Conversion to the final product (the title compound) occurred at 20 °C; its spectroscopic features were: ^{1}H NMR (C_7D_8, 20 °C) −1.1 (3H, OsCH_3); 1.28 (vt, 18H, OsPCCH_3, $J_{PH} = 6$Hz); 1.30 (vt, 18H, PCCH_3, $J_{PH} = 6$Hz); 1.86 (6H, PCH_3). ^{31}P NMR (C_7D_8, 20 °C) 26.0, (d, 2P, $J_{PF} = 27$ Hz). ^{19}F (C_7D_8, 20 °C) −198.0 (t, 1F, OsF, $J_{FP} = 27$Hz).

4.16. $OsF_2(CCH_2)(CO)(P^tBu_2Me)_2$

When 8.5 mg (1.53×10^{-5} mol) of $OsHMe(CO)(P^tBu_2Me)_2$ was warmed slowly with 25 equivalents (3.83×10^{-4}) of *gem*-difluoroethylene, $OsF_2(CCH_2)(CO)(P^tBu_2Me)_2$ formed in 60% yield. Following vacuum removal of excess $C_2H_2F_2$, and other volatiles, the diagnostic spectroscopic signals of the major product were: ^{1}H NMR (C_6D_6, 20 °C) 1.31 (vt, 36H, PCCH_3, $J_{PH} = 7.0$ Hz); 1.44 (vt, 6H, OsPCH_3, $J_{PH} = 4.1$ Hz); 2.01 (dt, 2H, CCH_2, $J_{FH} = 7$ Hz, $J_{PH} = 3$ Hz). ^{13}C NMR (C_6D_6, 20 °C) 3.6 (t, 2C, PCH_3, $J_{CP} = 5$ Hz); 29.7 (s, 6C, PCCH$_3$): 29.5 (s, 6C, PCCH$_3$); 36.2 (t, 2C, PCCH$_3$, $J_{PC} = 10.4$); 36.4 (t, 2C, PCCH$_3$, $J_{PC} = 10.4$); 94.8 (d, 1C, OsCC, $J_{CF} = 16$). ^{31}P NMR (C_6D_6, 20 °C) 34.65 (dd, 2P, $J_{PF} = 41.9$ Hz, $J_{PF'} = 25.1$ Hz). ^{19}F (C_6D_6, 20 °C) −277.45 (dt, 1F, OsF, $J_{FF} = 143$, $J_{FP} = 25$ Hz); −278.6 (dtt, 1F, OsF, $J_{FF} = 143$, $J_{FP} = 41$, $J_{HF} = 7$ Hz).

Acknowledgment

This work was supported by the US National Science Foundation.

References

[1] J.L. Kiplinger, T.G. Richmond, C.E. Osterberg, Chem. Soc. Rev. 94 (1994) 373.
[2] M. Aizenberg, D. Milstein, Science 265 (1994) 359.
[3] M. Aizenberg, D. Milstein, J. Am. Chem. Soc. 117 (1995) 8674.
[4] J. Burdeniuc, R.H. Crabtree, Science 271 (1996) 340.
[5] P.L. Timms, J. Chem. Soc., Dalton Trans. (1999) 815.
[6] B.L. Pagenkopf, E.M. Carreira, Chemistry A 5 (1999) 3437.
[7] K. Fagnou, M. Lautens, Ange. Chem. Int. Ed. 41 (2002) 26.
[8] P. Barthazy, R.M. Stoop, M. Woerle, A. Togni, A. Mezzetti, Organometallics 19 (2000) 2844.
[9] P. Barthazy, A. Togni, A. Mezzetti, Organometallics 20 (2001) 3472.
[10] P. Barthazy, D. Broggini, A. Mezzetti, Can. J. Chem. 79 (2001) 904.
[11] C. Becker, I. Kieltsch, D. Broggini, A. Mezzetti, Inorg. Chem. 42 (2003) 8417.
[12] A. Mezzetti, C. Becker, Helv. Chim. Acta 85 (2002) 2686.
[13] V.V. Grushin, Organometallics 19 (2000) 1888.
[14] V.V. Grushin, W.J. Marshall, Angew. Chem. Int. Ed. 41 (2002) 4476.
[15] V.V. Grushin, Chemistry A 8 (2002) 1006.
[16] V.V. Grushin, W.J. Marshall, J. Am. Chem. Soc. 126 (2004) 3068.
[17] R.J. Young Jr., V.V. Grushin, Organometallics 18 (1999) 294.
[18] T.G. Richmond, Angew. Chem. Int. Ed. 39 (2000) 3241.
[19] C.E. Osterberg, T.G. Richmond, ACS Symp. Ser. 555 (1994) 392.
[20] S.A. Strazisar, P.T. Wolczanski, J. Am. Chem. Soc. 123 (2001) 4728.
[21] E. Clot, C. Megret, B.M. Kraft, O. Eisenstein, W.D. Jones, J. Am. Chem. Soc. 126 (2004) 5647.
[22] W.D. Jones, Dalton Trans. (2003) 3991.
[23] B.M. Kraft, W.D. Jones, J. Am. Chem. Soc. 124 (2002) 8681.
[24] B.M. Kraft, R.J. Lachicotte, J. Rene, W.D. Jones, Organometallics 21 (2002) 727.
[25] T.G. Richmond, Top. Organomet. Chem. 3 (1999) 243.
[26] B.E. Smart, in: M. Audlicky, A.Z. Pavlath (Eds.), Chemistry of Organic Fluorine Compounds. A Critical Review, ACS Monograph 187, American Chemical Society, Washington, DC, 1995.
[27] N.A. Jasim, R.N. Perutz, A.C. Whitwood, T. Braun, J. Izundu, B. Neumann, S. Rothfeld, H.-G. Stammler, Organometallics 23 (2004) 6140.
[28] M. Reinhold, J.E. McGrady, R.N. Perutz, J. Am. Chem. Soc. 126 (2004) 5268.
[29] E. Clot, B. Oelckers, A.H. Klahn, O. Eisenstein, R.N. Perutz, Dalton Trans. 21 (2003) 4065.
[30] E. Clot, M. Besora, F. Maseras, C. Megret, O. Eisenstein, B. Oelckers, R.N. Perutz, Chem. Commun. (Cambridge) 4 (2003) 490.
[31] T. Braun, S. Rothfeld, V. Schorlemer, H.-G. Stammler, Inorg. Chem. Commun. 6 (2003) 752.
[32] D. Noveski, T. Braun, M. Schulte, B. Neumann, H.-G. Stammler, Dalton Trans. (2003) 4075.
[33] R. Bosque, E. Clot, S. Fantacci, F. Maseras, O. Eisenstein, R.N. Perutz, K.R. Renkema, K.G. Caulton, J. Am. Chem. Soc. 120 (1998) 12634.
[34] K.B. Renkema, R. Bosque, W.E. Streib, F. Maseras, O. Eisenstein, K.G. Caulton, J. Am. Chem. Soc. 121 (1999) 10895.
[35] A.J. Edwards, S. Elipe, M.A. Esteruelas, F.J. Lahoz, L.A. Oro, C. Valero, Organometallics 16 (1997) 3828.
[36] R.H. Heyn, S.A. Macgregor, T.T. Nadasdi, M. Ogasawara, O. Eisenstein, K.G. Caulton, Inorg. Chim. Acta 259 (1997) 5.
[37] J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978.
[38] T. Yamamoto, A. Yamamoto, S. Ikeda, J. Am. Chem. Soc. 93 (1971) 3350.
[39] D.G. Morrell, J.K. Kochi, J. Am. Chem. Soc. 97 (1975) 7262.
[40] A. Pedersen, M. Tilset, K. Folting, K.G. Caulton, Organometallics 14 (1995) 875.
[41] A. Ceccanti, P. Diversi, G. Ingrosso, F. Laschi, A. Lucherini, S. Magagna, P. Zanello, J. Organomet. Chem. 526 (1996) 251.
[42] A.V. Marchenko, H. Gerard, O. Eisenstein, K.G. Caulton, New J. Chem. 25 (2001) 1244.

[43] J.N. Coalter III, K.G. Caulton, New J. Chem. 24 (2000) 9.
[44] M.J. Albèniz, M.L. Buil, M.A. Esteruelas, A.M. Lopez, L.A. Oro, B. Zeier, Organometallics 13 (1994) 3746.
[45] R.E. Banks, Fluorocarbons and Their Derivatives, American Elsevier, New York, 1970.
[46] A. Andriollo, M.A. Esteruelas, U. Meyer, L.A. Oro, R.A. Sanchez-Delgado, E. Sola, C. Valero, H. Werner, J. Am. Chem. Soc. 111 (1989) 7431.
[47] J.T. Poulton, M.P. Sigalas, K. Folting, W.E. Streib, O. Eisenstein, K.G. Caulton, Inorg. Chem. 33 (1994) 1476.