Room-temperature hydrosilylation of the C–F bond of vinyl fluoride catalyzed by osmium hydrides

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Dedicated to Prof. J.J. Ziółkowski, on the occasion of his 70th birthday, for the international character he brought to chemistry in Wrocław.

Abstract

The reactions of $OsH(Ph)(CO)L_2$ ($L = P^tBu_2Me$) with $HSiMe_3$, H_2SiPh_2 or H_3SiPh produce benzene and $OsH_3(silyl)(CO)L_2$, which is characterized as a fac-H_3OsP_3 shape capped on the H_3 face by the silyl group. For H_2SiPh_2 and H_3SiPh, these reactions are shown proceed through an intermediate $Os(H)_2(silylene)(CO)L_2$ species. $OsHF(CO)L_2$ reacts with these silanes to give the same OsH_3 product (and silyl-F). These reactions can be combined to effect osmium catalysis of conversion of $Si{-}H + H_2C{=}CHF$ to fluorosilane and $H_2C{=}CH_2$ from $OsH_3(SiMe_3)(CO)L_2$, or from the catalyst precursor $OsHF(CO)L_2$.
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1. Introduction

Defluorination of fluorocarbons [1–12] is an important current challenge. Transition metal complexes have demonstrated activity in catalysis with silanes [13–17]. The conversion of C−F with M−H is one approach, and would form C−H and M−F. If M−F could then be transformed back into M−H, a catalytic cycle could be achieved (Scheme 1) for the overall reaction in Eq. (1). An attractive choice of E is silicon, since the thermodynamic stability of the Si−F bond could provide

$$C–F + E–H \xrightarrow{\text{``M''}} C–H + E–F \qquad (1)$$

the driving force for this reaction [5,18].

We explore here the implementation of this idea for an F−C(sp^2) bond, that of vinyl fluoride. This will include a comparative survey of the utility of several silanes, as well as a study of catalytic intermediates and several catalyst precursors, all based on a catalyst core furnished by the $Os(CO)L_2$ fragment, where $L = P^tBu_2Me$.

2. Results

2.1. Background

In separate work [19], we found that $OsH(Ph)(CO)L_2$ reacted cleanly with vinyl fluoride at 25 °C to give ethylene and $OsF(Ph)(CO)L_2$. Thus, in this molecule, the phenyl functions as a "spectator" and the observed reaction is simply metathesis between C−F and Os−H bonds. This accomplishes step **a** in Scheme 1. What must next be accomplished is the transfer of this abstracted fluoride from osmium to silicon.

2.2. Regeneration of Os−H

The fluorine in $OsF(Ph)(CO)L_2$ ($L = P^tBu_2Me$) is replaced by H upon treatment with 23 equiv. of $HSiMe_3$ (Eq. (2)). Formation of $OsH(Ph)(CO)L_2$ is complete in

$$OsF(Ph)(CO)L_2 + HSiMe_3 \rightarrow OsH(Ph)(CO)L_2 + Me_3SiF \qquad (2)$$

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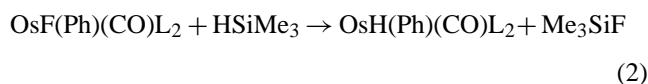
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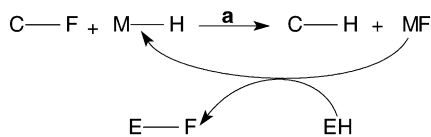
Scheme 1.

3 h at 25 °C in benzene. Because of the excess $HSiMe_3$, the reaction proceeds farther (over a 9.5 h period) to give $OsH_3(SiMe_3)(CO)L_2$ (Eq. (3)). The facility of this reaction is surprising since

$$OsH(Ph)(CO)L_2 + 3HSiMe_3 \rightarrow OsH_3(SiMe_3)(CO)L_2$$
$$+ C_6H_6 + (Me_3Si)_2 \quad (3)$$
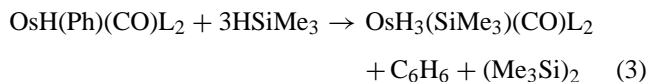
it would appear to require some intermediate with two bulky $SiMe_3$ ligands attached to an osmium which also carries two bulky phosphines [20].

2.3. Catalytic reactivity of $OsH_3(SiMe_3)(CO)L_2$

Fluorine abstraction from vinyl fluoride is possible with $OsH_3(SiMe_3)(CO)L_2$. This *saturated* species is thus a competent catalyst precursor. When excess (36 equiv.) vinyl fluoride is added to a benzene solution of $OsH_3(SiMe_3)(CO)L_2$ and 24 equiv. $HSiMe_3$, catalytic formation of C_2H_4 and Me_3SiF occurs at a rate of 24 turnovers within 0.5 h. Defluorination of $H_2C=CF_2$ is also effected by $OsH_3(SiMe_3)(CO)L_2$ in the presence of excess (35 equiv.) $HSiMe_3$ in benzene at 25 °C. After 1 h, the major product was ethylene, although vinyl fluoride was also detected. For comparison, under these conditions in the absence of the Os complex, $HSiMe_3$ was shown to be unreactive towards either vinyl fluoride or H_2CCF_2 over 24 h.
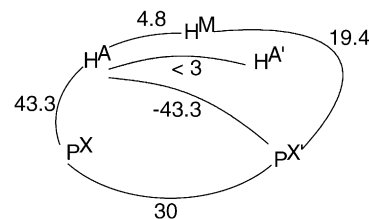
Scheme 2.

2.4. Structure and dynamics of $OsH_3(SiMe_3)(CO)L_2$ and its relation to catalysis

Since $OsH_3(SiMe_3)(CO)L_2$ is an 18-electron complex, we sought full characterization in order to better understand its reactivity. At 20 °C, the ^1H NMR spectrum of $OsH_3(SiMe_3)(CO)L_2$ shows two hydride signals (2:1 intensity ratio) at −9.5 ppm (broad singlet) and −10.3 ppm (broad triplet). At −70 °C, the singlet decoalesced into a non-first-order five-line pattern and the triplet was resolved into a triplet of triplets ($J_{PH} = 19.5$ Hz; $J_{HH} = 4.5$ Hz), as shown in Fig. 1. At −70 °C, the selectively hydride-coupled ^{31}P NMR spectrum (Fig. 1) showed a 10-line pattern that was essentially a doubling of the five-line ^1H NMR pattern seen at −9.5 ppm. These NMR patterns identify the H_3P_2 part of the molecule as an AA'MXX' spin system, which implies mirror symmetry for the molecule. Among 22 possible line assignments for the observed spectra [21], one was distinctly better than all others, and yielded the coupling constants shown in Scheme 2. These J values are structurally diagnostic. Based on the general trends of J_{PP} and J_{HP} with their mutual angles, we can conclude:

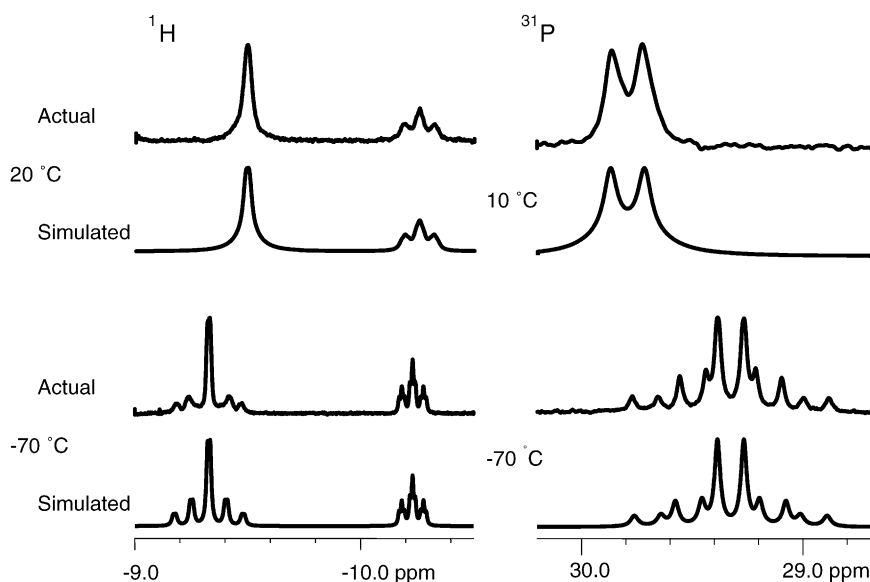(a) the phosphines are mutually *cis* (30 Hz is a very small J_{PP}),

Fig. 1. Observed (upper) and calculated variable-temperature 300 MHz ^1H (left) and selectively hydride-coupled ^{31}P (122 MHz) NMR spectra of $OsH_3(SiMe_3)(CO)(P^tBu_2Me)_2$ in d_8-toluene.

(b) neither H^A nor $H^{A'}$ is approximately *trans* to P^X or $P^{X'}$,

(c) hydrogens A, A' and M are cisoid; no two are mutually *trans*.

We propose two mirror symmetric shapes, **1** and **2**, that can accommodate these conditions. **1** is based on a face-capped octahedron [22,23], and the angle $H^A–Os–H^{A'}$ must deviate much from 90° to avoid A *trans* to X', etc. **2** is a triangular face-capped trigonal prism, and thus


1   **2**
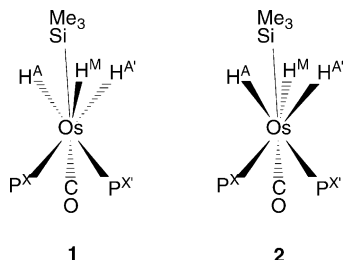
naturally has no *trans* relationships. None of our observations allows any conclusion about incipient Si/H^M bonding [24,25].

The temperature dependence of the coalescence of the A and A' hydrogens from AA'MXX' to A_2MX_2 at five temperatures in the range −70 to −20 °C (Fig. 1) was simulated using the program GNMR. An Eyring plot of $\ln(k/T)$ versus T^{-1} gave $\Delta H^{\ddagger} = 7.6$ kcal/mol and $\Delta S^{\ddagger} = -16.6$ cal/deg mol. This entropy change is inconsistent with a dissociative process [26,27].

The three hydride signals coalesce to a single line ~0.8 ppm broad at 60 °C. While these NMR results help to establish the structure and dynamics of $OsH_3(SiMe_3)(CO)L_2$, they alone fail to reveal whether a 16-electron species reactive towards vinyl fluoride is formed by reductive elimination of H_2 or of $HSiMe_3$. The latter is favored by steric effects, but the former would produce $OsH(SiMe_3)(CO)L_2$, whose ruthenium analog is known: $RuH(SiHPh_2)(CO)L_2$ [28].

To test for Eq. (4) as the source of an unsaturated catalytic reactant, the ^{1}H NMR spectra

$$OsH_3(SiMe_3)(CO)L_2 \rightleftharpoons OsH_2(CO)L_2 + HSiMe_3 \qquad (4)$$
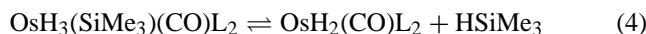
of a 1:3 mixture of $OsH_3(SiMe_3)(CO)L_2$ and $HSiMe_3$ was recorded in the temperature range 20–70 °C. By 60 °C, when the two osmium hydride signals of $OsH_3(SiMe_3)(CO)L_2$ have just *coalesced* (thus, their exchange rate is ~3×10^2 s^{-1}), the line width of the Si*H* signal of free $HSiMe_3$ shows exchange *broadening* with a rate of ~3×10^1 s^{-1}). This suggests that OsH_3 site exchange has a lower barrier (which governs the dynamic NMR behavior of $OsH_3(SiMe_3)(CO)L_2$ in the absence of added $HSiMe_3$), but that the (slower, more energetically demanding) $HSiMe_3$ dynamic process is that of Eq. (4). The intramolecular character of the OsH_3 site exchange is established by the retention of $H_3–Os–P$ coupling above the OsH_3 coalescence temperature for the $SiHPh_2$ and SiH_2Ph analogs (see below). A viable species on a

catalytic cycle is thus $OsH_2(CO)L_2$. This species was also invoked recently based on observations of the PPh_3 analog [29].

2.5. SiH_2Ph_2

The benzene elimination reaction with $HSiMe_3$ in Eq. (3) effectively converts $OsH(Ph)(CO)L_2$ into the synthetic equivalent of "$Os(CO)L_2$". Converting this into a *tri*hydride *mono*silyl product requires three moles of a tertiary silane (cf. Eq. (3)), and so some *intermediate* osmium complex is implicated by this 1:3 stoichiometry. To investigate this point, the secondary silane SiH_2Ph_2 was reacted with $OsH(Ph)(CO)L_2$ in a 1:1 mole ratio in toluene at 20 °C (Eq. (5))

$$OsH(Ph)(CO)L_2 + H_2SiPh_2 \longrightarrow \qquad + HPh \qquad (5)$$

3
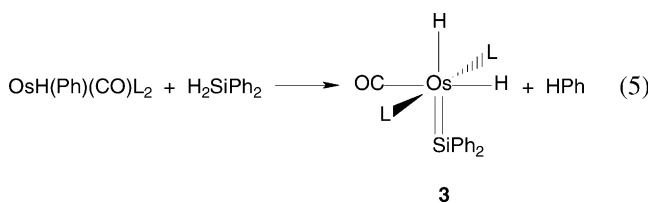
After 1 h, there was 90% conversion to a species identified as **3**. Although hydride (two chemical shifts) and ^{31}P{^{1}H} NMR signals were broad at 20 °C, by −60 °C the ^{31}P{^{1}H} NMR signal was a sharp singlet and the hydride region was resolved into two triplets of doublets; these two showed equal intensity. Both doublet couplings were 3.9 Hz, supporting the intensity conclusion that these hydrides are in the same molecule (i.e. mutually coupled), and mutually *cis*. This was confirmed by observing a selectively hydride coupled ^{31}P NMR spectrum (at −50 °C); the spectrum was a doublet of doublets with *J* values (25 and 19 Hz) which agreed well with the triplet splitting in the hydride signals. The ^{29}Si NMR spectrum at −40 °C is a broadened (due to unresolved coupling) line at 328 ppm, which identifies this as a silylene ligand. For comparison [30], SiR_2 (R = Me or Ph) ligands on Ru or Ir have ^{29}Si chemical shifts in the range 250–350 ppm. A ^{31}P{^{1}H} NMR spectrum collected for high S/N ratio at −40 °C showed satellites revealing $J_{PSi} = 20$ Hz and $J_{POs} = 82$ Hz, thus confirming connectivity and composition consistent with formulation $Os(H)_2(SiPh_2)(CO)L_2$. It is especially diagnostic of the reducing power of osmium in this molecule that the ruthenium analog [28] is the valence isomer $RuH(SiHPh_2)(CO)(P^tBu_2Me)_2$, where the Ph_2Si/H bond has <u>not</u> oxidatively added to the metal. However, the dynamic process evident in **3** by NMR at 20 °C may be H migration from Os to Si.

This implied α-H migration of $Os–SiHPh_2$ to $HOs=SiPh_2$ in Eq. (5) is caused by reaction conditions where there is a deficiency of (silane-derived) ligands (e.g., hydride). Indeed, when $OsH(Ph)(CO)L_2$ is reacted with SiH_2Ph_2 in a 1:2.5 mole ratio, the final product, $OsH_3(SiHPh_2)(CO)L_2$ appears within 1 h (Eq. (6)), although $Os(H)_2(SiPh_2)(CO)L_2$ is present at earlier observation times, and is thus an interme-

diate in formation of the trihydride. The resulting

$$Os(H)_2(SiPh_2)(CO)L_2 + 2SiH_2Ph_2$$

$$\rightarrow OsH_3(SiHPh_2)(CO)L_2 + (SiHPh_2)_2 \qquad (6)$$
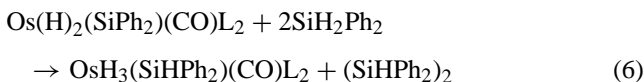
$OsH_3(SiHPh_2)(CO)L_2$ has a lower barrier to hydride site exchange than does the $SiMe_3$ analog, since all three hydrides are coalesced to a sharp triplet at $20\,^\circ C$, and they broaden, but do not decoalesce at $-80\,^\circ C$.
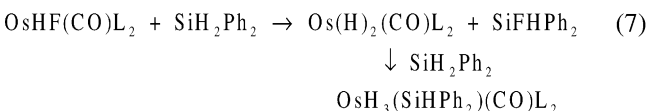
2.6. SiH₃Ph

Reaction of $OsH(Ph)(CO)L_2$ with two moles of SiH_3Ph at $25\,^\circ C$ completely consumes the Os reagent in 1 h to give two products, which are assigned as $Os(H)_2(SiHPh)(CO)L_2$ and $OsH_3(SiH_2Ph)(CO)L_2$. This follows in part from their similar ^{31}P chemical shifts to their analogs from SiH_2Ph_2. The latter compound showed a sharp hydride triplet at $20\,^\circ C$, consistent with rapid intramolecular fluxionality. $Os(H)_2(SiHPh)(CO)L_2$ showed, at $20\,^\circ C$, two broad hydride peaks and one broad ^{31}P NMR signal.

2.7. Alternative synthesis of OsH₃(silyl)(CO)L₂
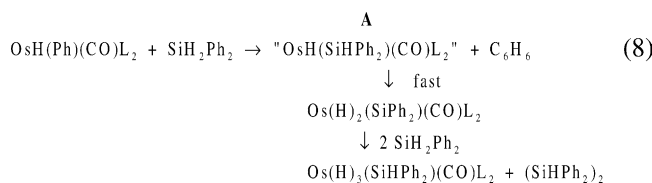
Since the phenyl group of $OsH(Ph)(CO)L_2$ is not integral to the catalysis of Eq. (1), we sought a simpler access to the catalytic cycle. When $OsHF(CO)L_2$ is reacted with the silanes $SiHPh_3$, SiH_2Ph_2 or SiH_3Ph (1:2–8 mole ratio), at $20\,^\circ C$ in benzene, there is rapid (<30 min) conversion to $OsH_3(silyl)(CO)L_2$. The replaced fluoride is established by ^{19}F NMR spectroscopy to be on silicon, and the released primary and secondary fluorosilanes show evidence for F/H redistribution to generate all possible multi-fluoro species (e.g., $SiH_nF_{3-n}Ph$). The reaction applies equally to $OsHF(CO)L_2$ and $HSiMe_3$, and all $OsH_3(silyl)(CO)L_2$ analogs show ^{31}P NMR chemical shifts within a narrow (4 ppm) range, and hydride chemical shifts within a 0.5 ppm range. What differs is the rate of hydride scrambling in $OsH_3(silyl)(CO)L_2$ at $20\,^\circ C$: the $SiPh_3$ and $SiMe_3$ examples show two signals (2:1 intensity) while the $SiHPh_2$ and SiH_2Ph examples show a coalesced spectrum for three H. Because the coalesced spectra show triplet coupling to phosphorus, this process is intramolecular, and involves no ligand loss.

The conversion of $OsHX(CO)L_2$ to $OsH_3(silyl)(CO)L_2$ by an Si–H reagent is faster for X = F than for X = Ph. This acceleration probably involves incipient F/Si bonding in the mechanism. Also consistent with our interpretation is the lack of silylene intermediate for the $OsHF(CO)L_2$ route. There (Eq. (7)) the *needed* intermediate (**A**, Eq. (8)) for silylene formation is absent and final product derives from

$$OsHF(CO)L_2 + SiH_2Ph_2 \rightarrow Os(H)_2(CO)L_2 + SiFHPh_2 \qquad (7)$$
$$\downarrow SiH_2Ph_2$$
$$OsH_3(SiHPh_2)(CO)L_2$$

one more step. The silylene complex can accumulate since the final product in Eq. (8) requires reaction with *two* additional

bulky silane molecules

$$\overset{\mathbf{A}}{OsH(Ph)(CO)L_2 + SiH_2Ph_2 \rightarrow \text{"}OsH(SiHPh_2)(CO)L_2\text{"} + C_6H_6} \qquad (8)$$
$$\downarrow \text{ fast}$$
$$Os(H)_2(SiPh_2)(CO)L_2$$
$$\downarrow 2\,SiH_2Ph_2$$
$$Os(H)_3(SiHPh_2)(CO)L_2 + (SiHPh_2)_2$$

### 2.8. Confirmation of catalytic conversion of vinyl fluoride to ethylene with OsHF(CO)L₂ as catalyst precursor

The catalyst is most conveniently prepared within 1 h by reacting $OsHF(CO)L_2$ with excess silane in C_6D_6 at $25\,^\circ C$. The production of $OsH_3(silyl)(CO)L_2$ was in every case confirmed by ^{31}P, ^1H and ^{19}F NMR spectroscopy. Following addition of vinyl fluoride (vinyl fluoride:Os $\geq$ 36:1), the appearance of products and disappearance of reactants (Eq. (9)) was monitored (NMR) over time. The reaction with $HSiMe_3$ converted 24 equiv. silane

$$H_2C{=}CHF + HSi{\equiv} \xrightarrow{\text{[Os]}} H_2CCH_2 + FSi{\equiv} \qquad (9)$$

within 30 min. Consumption of 6 equiv. $HSiPh_3$ required 3 h, while SiH_2Ph_2 and SiH_3Ph were slower still. Heating to $60\,^\circ C$ consumed 9.4 equiv. SiH_2Ph_2 in 30 min. The final osmium-containing product after consumption of all the silane ($HSiMe_3$ or SiH_2Ph_2) was always $OsHF(CO)(\eta^2\text{-}H_2{=}CCHF)L_2$, and this was the only species seen throughout the catalysis using $SiHPh_3$. Catalyst decomposition was insignificant except for the SiH_3Ph example at elevated temperature.

3. Discussion

The structure of $OsH_3(silyl)(CO)(P^tBu_2Me)_2$ deduced here shares only *certain* features with the structure for $OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$ derived from X-ray diffraction and from DFT calculations [31]. Central among these is the pyramidal $Os(CO)P_2$ substructure. The ^1H NMR spectral data presented by Buil et al. show 2:1 intensity for hydride ligands, but incipient ^{31}P NMR decoalescence was detected by $193\,^\circ K$. This contrasts to what we observe for $OsH_3(SiMe_3)(CO)(P^tBu_2Me)_2$. Buil et al. report two inequivalent Si–Os–P angles, and thus *no* mirror symmetry to the structure. While our observations might suffer a yet-undetected (i.e., low barrier) fluxional process, giving the illusion of mirror symmetry, the fact that $OsH_3(SiMe_3)(CO)(P^tBu_2Me)_2$ has a higher barrier for hydride site exchange than $OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$ makes this less probable. The mirror symmetry deduced here for $OsH_3(SiMe_3)(CO)(P^tBu_2Me)_2$ is in full agreement with that reported [29] for the PPh_3 analog as well as for several $RuH_3(SiR_3)(PR_3)_3$ cases [20,22,23]. Thus, we suggest that the lack of mirror symmetry in the X-ray structure of
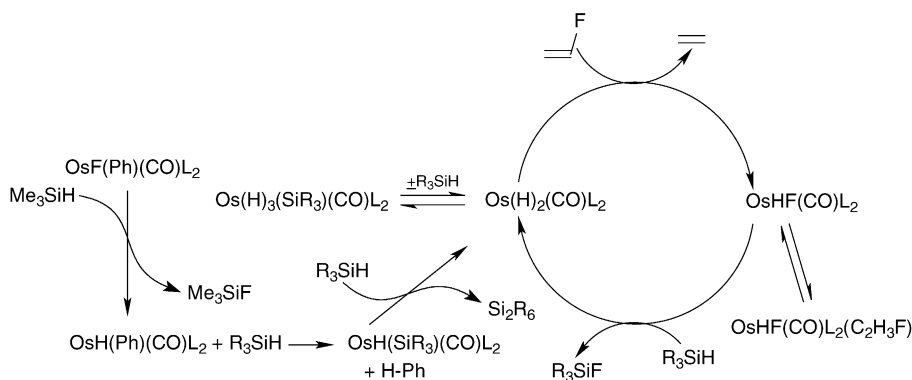
Scheme 3.

$OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$ may be induced by the very different steric demands of the Ph and H substituents on Si. The published ^{1}H NMR data [31] showed no clear evidence for *three* different hydride environments, but are fully consistent with mirror symmetry.

A highly schematic portrayal of the observations reported here appears in Scheme 3, which indicates why there are numerous ways to enter the catalytic cycle. Both the relationship to and the contrast to analogous ruthenium chemistry is evident since $RuH_3(SiHPh_2)(CO)(P^tBu_2Me)_2$ has been shown [32] to exchange with added free SiH_2Ph_2, but also to *lose* H_2 under vacuum, to furnish $RuH(SiHPh_2)(CO)(P^tBu_2Me)_2$.

4. Experimental

4.1. General

All manipulations were done under an atmosphere of dry, O_2-free Ar employing a vacuum atmospheres inert atmosphere glovebox or standard Schlenk-line techniques. The solvents were reagent grade, and distilled from the appropriate drying agents under Ar. A lecture bottle of $HSiMe_3$ and solid $HSiPh_3$ were obtained from Aldrich and used directly. H_2SiPh_2 and H_3SiPh were also obtained from Aldrich, but were dried and distilled before use. Vinyl fluoride and gem-difluoroethylene were purchased from Lancaster Chemicals. All other reagents were used without further purification. $OsH(Ph)(CO)(P^tBu_2Me)_2$ [33] and $OsHF(CO)(P^tBu_2Me)_2$ [34] were synthesized according to literature. The ^{1}H, ^{31}P, ^{19}F, and ^{29}Si NMR were collected on Varian Gemini 2000 or Inova 400 spectrometers (^{1}H: 300, 400 MHz; ^{13}C: 100 MHz; ^{31}P: 122, 162 MHz; ^{19}F: 282, 376 MHz; ^{29}Si: 79.5 MHz). Proton NMR spectra were referenced to residual solvent peaks as internal standards. ^{31}P NMR was referenced to an external standard of 85% H_3PO_4. ^{19}F NMR was referenced to trifluoroacetic acid in benzene.

4.2. Os(Ph)F(CO)(P^{t}Bu$_2$Me)$_2$ + HSiMe$_3$

When a solution of $Os(Ph)F(CO)(P^tBu_2Me)_2$ (15.8 mg, 2.5×10^{-5} mol) in 500 µL cyclohexane-d_{12} was re-

acted with $HSiMe_3$ (5.8×10^{-4}, 23 equiv.) conversion first to $OsH(Ph)(CO)(P^tBu_2Me)_2$ and then to $OsH_3(SiMe_3)(CO)(P^tBu_2Me)_2$ was accomplished over two days. ^{1}H NMR (C_6D_6, 293 K): 1.28 (overlapping vt, 18H each, PCCH_3, $J_{HP} = 12$ Hz); 1.41 (vt, 6H, PCH_3, $J_{PH} = 2.8$ Hz); 0.59 (s, 9H, SiCH_3); −9.41 (br s, 2H, OsH); −10.17 (br t, 1, OsH, $J_{HP} = 19.9$ Hz). ^{31}P NMR (C_6D_6, 293 K): 29.9 (s). Cooling the sample in d_8-toluene reduced chemical exchange such that more coupling could be seen in ^{1}H and partially coupled ^{31}P NMR. In addition to the parameters given in the text, the signals for PCCH_3 are found at 1.17 and 1.14 as broad singlets and PCH_3 at 1.03, also as a broad singlet.

4.3. OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ + HSiMe$_3$

When $OsH(Ph)(CO)(P^tBu_2Me)_2$ (9.4 mg, 1.52×10^{-5} mol) in 500 µL d_8-toluene was reacted with $HSiMe_3$ (6.2 equiv.) at 20 °C for 12 h, greater than 90% conversion to $OsH_3(SiMe_3)(CO)(P^tBu_2Me)_2$ (vide supra) was observed. ^{31}P NMR did show a small amount of an intermediate species (at 42.8 ppm), which was present from beginning to end; we suggest it is $OsH_2(SiMe_3)_2(CO)(P^tBu_2Me)_2$.

4.4. OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ + HSiPh$_3$

When $OsH(Ph)(CO)(P^tBu_2Me)_2$ (7.1 mg, 1.15×10^{-5} mol) in 500 µL C_6D_6 was reacted with $HSiPh_3$ (6.4 mg, 2.46×10^{-5} mol) at 20 °C for 12 h, greater than 90% conversion to $OsH_3(SiPh_3)(CO)L_2$ (vide supra) was observed. ^{31}P NMR again showed an intermediate present throughout the conversion process (at 30.8 ppm) which is assigned as $OsH_2(SiPh_3)_2(CO)(P^tBu_2Me)_2$.

4.5. Os(H)$_2$(=SiPh$_2$)(CO)(P^{t}Bu$_2$Me)$_2$

When $OsH(Ph)(CO)(P^tBu_2Me)_2$ (8.4 mg, 1.36×10^{-5} mol) dissolved in 500 µL d_8-toluene was reacted with H_2SiPh_2 (6.2 µL, 3.30×10^{-5} mol) at 20 °C for 1 h, two products were formed. The kinetic product constituted about 80% after 1 h and was assigned to the title

compound using the following NMR. ^{1}H NMR (C_7D_8, 233 K): selected aryl peaks (8.05, 7.32, 7.29, 7.25); 1.48 (br s, 6H, PCH_3); 1.21 (vt, 18H, PCCH_3, $J_{HP} = 5.9$ Hz); 1.14 (vt, 18H, PCCH_3, $J_{HP} = 5.9$ Hz); −8.98 (dt, 1H, OsH, $J_{HP} = 19.0$ Hz, $J_{HH} = 3.9$ Hz); −10.07 (dt, 1H, OsH, $J_{HP} = 25.2$ Hz, $J_{HH} = 3.9$ Hz). ^{31}P NMR (C_7D_8, 233 K): 45.5 (s, Os and Si satellites: $J_{OsP} = 82$ Hz; $J_{Si-P} = 19.7$ Hz); ^{31}P{hydride coupled, 223 K} 45.1 (dd, 2P, $J_{PH} = 25.2$ Hz, $J_{PH} = 19.0$ Hz). ^{29}Si NMR (C_7D_8, 233 K): 328 (br).

4.6. OsH₃(SiMe₃)(CO)(PᵗBu₂Me)₂

When OsHF(CO)(P^{t}Bu$_2$Me)$_2$ (9.0 mg, 1.61×10^{-5} mol) dissolved in 500 μL C_6D_6 was reacted with HSiMe$_3$ (23.0 equiv.) at 20 °C for 1 h, conversion to the title compound was accomplished.

4.7. OsH(Ph)(CO)(PᵗBu₂Me)₂ + H₃SiPh

When OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ (6.1 mg, 1.09×10^{-5} mol) in 500 μL C_6D_6 was reacted with H$_3$SiPh for 1 h at 20 °C, two new products, OsH$_3$(SiH$_2$Ph)(CO)(P^{t}Bu$_2$Me)$_2$ (vide supra) and OsH$_2$(SiHPh)(CO)(P^{t}Bu$_2$Me)$_2$ ($\delta(^{31}$P) = 42.5 ppm, br s; δ(Os−H) = −9.6 ppm, br), free phosphine, and the complete consumption of OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ were observed. Another hour of stirring caused the conversion of OsH$_2$(SiHPh)(CO)(P^{t}Bu$_2$Me)$_2$ to OsH$_3$(SiH$_2$Ph)(CO)(P^{t}Bu$_2$Me)$_2$.

4.8. OsH₃(SiPh₃)(CO)(PᵗBu₂Me)₂

When OsHF(CO)(P^{t}Bu$_2$Me)$_2$ (7.1 mg, 1.27×10^{-5} mol) dissolved in 500 μL C_6D_6 was reacted with HSiPh$_3$ (5.9 μL, 2.27×10^{-5} mol) at 20 °C for 30 min, conversion to the title compound was accomplished. ^{1}H NMR (C_6D_6, 293 K): 8.06 (d, 6H, $J_{HH} = 6.9$ Hz); 7.6 (d, 3H, $J_{HH} = 6.5$ Hz); 7.3 (t, 6H, $J_{HH} = 6.9$ Hz); 1.24 (vt, 6H, PCH_3, $J_{HP} = 2.9$ Hz); 1.10 (vt, 18H, PCCH_3, $J_{HP} = 6.7$ Hz); 1.00 (vt, 18H, PCCH_3, $J_{HP} = 6.7$ Hz); −8.59 (s, 2H, OsH); −9.7 (br t, 1H, OsH, $J_{HP} = 21$ Hz). ^{31}P NMR (C_6D_6, 293 K): 27.50 (s).

4.9. OsH₃(SiHPh₂)(CO)(PᵗBu₂Me)₂

When OsHF(CO)(P^{t}Bu$_2$Me)$_2$ (6.3 mg, 1.13×10^{-5} mol) dissolved in 500 μL C_6D_6 was reacted with H$_2$SiPh$_2$ (20 μL, 1.07×10^{-4} mol) at 20 °C for 30 min, >95% conversion to the title compound was observed. ^{1}H NMR (C_6D_6, 293 K): selected aryl peaks (8.00, 7.27, 7.08, 7.03); 6.67 (t, 1H, SiH, $J_{HP} = 7.2$ Hz); 1.16 (vt, 18H, PCCH_3, $J_{HP} = 6.6$ Hz); 1.14 (vt, 18H, PCCH_3, $J_{HP} = 6.6$ Hz); 1.06 (vt, 6H, PCH_3, $J_{HP} = 2.7$ Hz); −9.1 (t, 3H, OsH, $J_{HP} = 15.6$ Hz). ^{31}P NMR (C_6D_6, 293 K): 31.0 (s).

4.10. OsH₃(SiH₂Ph)(CO)(PᵗBu₂Me)₂

When OsHF(CO)(P^{t}Bu$_2$Me)$_2$ (5.2 mg, 9.31×10^{-6} mol) dissolved in 500 μL C_6D_6 was reacted with H$_3$SiPh (2.5 μL, 2.02×10^{-5} mol) at 20 °C for 15 min, the title compound was produced in greater than 95% yield. ^{1}H NMR (C_6D_6, 293 K): selected aryl peaks (8.12, 7.50, 7.31, 7.14, 7.08); 5.75 (t, 1H, SiH, $J_{HP} = 4.5$ Hz); 1.17 (vt, 36H, PCCH_3, $J_{HP} = 6.1$ Hz); 1.35 (vt, 6H, PCH_3, $J_{HP} = 3.0$ Hz); −8.9 (t, 3H, OsH, $J_{HP} = 15.8$ Hz). ^{31}P NMR (C_6D_6, 293 K): 29.4 (s).

4.11. Catalytic conversions of vinyl fluoride

4.11.1. OsH₃(SiMe₃)(CO)(PᵗBu₂Me)₂ + H₂C=CHF + HSiMe₃

When OsH$_3$(SiMe$_3$)(CO)(P^{t}Bu$_2$Me)$_2$ (9.0 mg, 1.69×10^{-5} mol) in 500 μL C_6D_6 was reacted with H$_2$C=CHF (36 equiv.) in the presence of 24 equiv. of HSiMe$_3$ at 20 °C for 30 min, nearly all HSiMe$_3$ had been consumed. The production of C_2H_4, FSiMe$_3$, and OsHF(CO)(η^2-C_2H_3F)(P^{t}Bu$_2$Me)$_2$ (δ(OsH) = −3.0 (br t, $J = 28$ Hz); $\delta(^{31}$P) = 22.4 (br d); $\delta(^{19}$F) = −171.3 (ddd, $J_{HF} = 73, 19, 21$ Hz) were seen by ^{1}H and ^{19}F NMR spectroscopy.

4.11.2. OsH₃(SiPh₃)(CO)(PᵗBu₂Me)₂ + H₂C=CHF + HSiPh₃

When OsH$_3$(SiPh$_3$)(CO)(P^{t}Bu$_2$Me)$_2$ (7.1 mg, 1.27×10^{-5} mol) in 500 μL C_6D_6 was reacted with HSiPh$_3$ (41.0 mg, 12.4 equiv.) and H$_2$C=CHF (36 equiv.) for 3 h at 20 °C, nearly half of the silane had been consumed. The observation of FSiPh$_3$ and C_2H_4 confirmed the Si−H/C−F metathesis. At all times during the process, the only osmium species that could be seen was OsHF(CO)(η^2-H$_2$C=CHF)(P^{t}Bu$_2$Me)$_2$.

4.11.3. OsH₃(SiHPh₂)(CO)(PᵗBu₂Me)₂ + H₂C=CHF + H₂SiPh₂

When OsH$_3$(SiHPh$_2$)(CO)(P^{t}Bu$_2$Me)$_2$ (6.4 mg, 1.15×10^{-5} mol) in 500 μL C_6D_6 was reacted with C_2H_3F (36 equiv.) and H$_2$SiPh$_2$ (20 μL, 9.4 equiv.) for 30 min at 20 °C, almost no conversion was observed. However, after 1 h at 60 °C, the silane was fully consumed, producing C_2H_4, FSiH$_2$Ph, and (exclusively) OsHF(CO)(η^2-C_2H_3F)(P^{t}Bu$_2$Me)$_2$.

4.11.4. OsH₃(SiH₂Ph)(CO)(PᵗBu₂Me)₂ + H₂C=CHF + H₃SiPh

When OsH$_3$(SiH$_2$Ph)(CO)(P^{t}Bu$_2$Me)$_2$ (6.9 mg, 1.24×10^{-5} mol) in 500 μL C_6D_6 was reacted with C_2H_3F (40 equiv.) and H$_3$SiPh (20 μL, 13.1 equiv.) at 20 °C for 3 h, almost no conversion (less than 5%) took place. When the temperature was raised to 60 °C for 4 h, some of the H$_2$C=CHF was converted to C_2H_4, but ^{31}P NMR showed significant degradation of the complex and ^{19}F NMR showed many signals.

4.11.5. OsH$_3$(SiMe$_3$)(CO)(P^{t}Bu$_2$Me)$_2$ + HSiMe$_3$ + 1, 1-C$_2$H$_2$F$_2$

When a solution of OsH$_3$(SiMe$_3$)(CO)(P^{t}Bu$_2$Me)$_2$ (10 mg, 1.6×10^{-5} mol) in 500 μL benzene-d$_6$ was stirred at room temperature with 35 equiv. of HSiMe$_3$ and C$_2$H$_2$F$_2$, the products, C$_2$H$_4$, C$_2$H$_3$F, FSiMe$_3$, and OsHF(CO)(η^2-C$_2$H$_2$F$_2$)(P^{t}Bu$_2$Me)$_2$ were seen after 1 h. The Os-containing product was identified by a broad signal at 17 ppm in ^{31}P NMR. Conversion slowed with time (4 h).

4.12. Os-free control reactions

4.12.1. HSiMe$_3$ + 1,1-C$_2$H$_2$F$_2$

When a solution of HSiMe$_3$ (3.8×10^{-4} mol) and 1,1-C$_2$H$_2$F$_2$ (3.8×10^{-4} mol) in 500 μL acetone-d$_6$ was stirred for a day at room temperature, H$_2$C=CHF, C$_2$H$_4$, and FSiMe$_3$ were not observed.

4.12.2. HSiMe$_3$ + H$_2$C=CHF

When a solution of HSiMe$_3$ (3.8×10^{-4} mol) and H$_2$C=CHF (3.8×10^{-4} mol) in 500 μL benzene-d$_6$ was stirred for a day at room temperature, no C$_2$H$_4$ or FSiMe$_3$ were observed.

Acknowledgment

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