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Facile and Reversible Cleavage of C−F Bonds. Contrasting Thermodynamic Selectivity for Ru−CF_2H vs F−Os=CFH

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Abstract: In the presence of a catalytic amount of F^-(CsF), Me_3SiR_f (R_f = CF_3 and C_6F_5) exchanges R_f with fluoride of the 16-electron complexes $MHF(CO)L_2$ (M = Ru, Os; L = P^iPr_3, P^tBu_2Me) to give Me_3Si-F and the unsaturated pentafluorophenyl complexes, $MH(C_6F_5)(CO)L_2$, or (when R_f = CF_3) saturated fluorocarbene complexes, $MHF(CF_2)(CO)L_2$, via α-fluorine migration. X-ray crystal structure and solution ^{19}F NMR studies reveal that, in the ground state, the three atoms of the CF_2 group lie in a plane perpendicular to the P−Ru−P axis so that the π-back-donation is maximized and the carbene substituents are inequivalent. Having hydride trans to the CF_2 ligand, $MHF(CF_2)(CO)L_2$ is a kinetic product, which converts to a thermodynamic isomer. For Ru, the final product is a 16e complex, $RuF(CF_2H)(CO)L_2$, formed by combination of CF_2 and hydride. For Os, the product is an 18e complex, $OsF_2(=CFH)(CO)L_2$, resulting from exchange of one carbene fluoride with the hydride. The distinct difference between Os and Ru demonstrates the principle that third-row transition metals show a pronounced tendency toward a higher oxidation state. The isomerization mechanism involves phosphine dissociation as a slow step. Coordinatively saturated $RuHF(CF_2)(CO)L_2$ reacts with CO within the time of mixing to give the F and CF_2 recombination product, $RuH(CF_3)(CO)_2L_2$. This unexpectedly fast carbonylation reaction, as well as ^{19}F spin saturation transfer experiments, reveals the existence of a fast α-F migration equilibrium between $RuHF(CF_2)(CO)L_2$ and $RuH(CF_3)(CO)L_2$ in solution. In sharp contrast, the Os analogue does not have such a fast equilibrium, and therefore it does not react with CO at room temperature. At higher temperature, reaction occurs forming the hydride and fluoride exchanged product, $Os(CHF_2)(F)(CO)_2L_2$. The contrasting behavior of Ru vs Os regarding stability of fluoroalkyl and fluorocarbene is discussed on the basis of the theoretical calculations, which also provide insight into the isomerization of $RuHF(CF_2)(CO)L_2$. Hydrogenolysis of $Ru(CF_2H)F(CO)L_2$ liberates CH_2F_2, forming $RuHF(CO)L_2$.

Introduction

Transition metal complexes with polyfluoroalkyl ligands are receiving significant attention because they are crucial in the polyfluorocarbon C−F bond activation and functionalization processes, synthesis of fluorocarbon-containing organic compounds with pharmaceutical interest, and development of organometallic catalysts soluble in polyfluorocarbon solvents.[1,2] The chemistry of transition metal perfluoroalkyl complexes was studied about 30 years ago, with the focus on new synthetic methods, mainly by Stone and co-workers.[3] Some pioneering work on metal trifluoromethyl complexes, the simplest perfluoroalkyl, was also carried out at that time.[4] Since then, several methods and reagents have been developed to synthesize this type of complex, such as oxidative addition of CF_3I or CF_3Br to low-valent metals,[5] decarbonylation of trifluoroacetyl complexes,[6] and application of $Cd(CF_3)_2(DME)$ (DME = 1,2-dimethoxyethane)[7] and $Hg(CF_3)_2(DME)$.[8] However, these methods are usually quite specific or involve highly toxic metals. Therefore, more general, milder, and safer synthetic routes are in demand.

A convenient CF_3 transfer reagent, Me_3SiCF_3, has been exploited extensively in organic synthesis for several years.[9] In sharp contrast, its application in organometallic synthesis has not been previously reported. Reported here are the first example of such applications, and, surprisingly, these yield Ru and Os difluoro*carbene* complexes. Constructive transformation of coordinated fluorocarbyl ligands to valuable organic compounds is an important research topic relevant to utilization of perfluorocarbon wastes.[10] It is well documented that the perfluoroalkyl metal−C bond is stronger than that in hydrocarbon analogues and is thus relatively inert toward migratory insertion, an important type of reaction for transition metal alkyl complexes applied in organic synthesis.[11] On the other hand, in many cases the α-fluorine of a perfluoroalkyl group is

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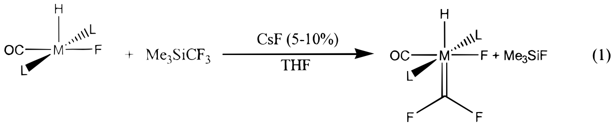
activated and is subject to electrophilic attack. Therefore, the majority of reaction pathways of perfluoroalkyl complexes involve α-F abstraction by Lewis acids to give difluorocarbenes, which are often highly hygroscopic and further react with water to give coordinated carbonyl ligands and release HF.[12] In some cases, coordinated water is sufficiently acidic to protonate the α-fluoride.[13,14] Rarely has an α-fluoro migration of an unsaturated metal perfluoroalkyl complex (which functions as an internal Lewis acid) been reported.[15] Presented here is one such example where a fast reversible α-F migration occurs on an Ru complex and double α-F migration occurs on an analogous Os complex.[16]

Results

Reaction of $MHF(CO)L_2$ (M = Os, Ru; L = P^tBu_2Me, P^iPr_3) with Me_3SiCF_3. In the presence of a catalytic amount (5−10 mol percent) of CsF, Me_3SiCF_3 reacts with $MHF(CO)L_2$[17] to give $MHF(CF_2)(CO)L_2$, **4**, **5**, and **6** (eq 1).[18] The reaction is quite solvent dependent. In a polar solvent such as THF or fluorobenzene, the reaction is complete in 30 min (M = Ru), while in benzene the reaction takes longer (5 h). The solvent dependence is likely to be related to the better solubility of CsF in polar solvents. The osmium analogue, **3**, reacts more sluggishly and requires heating in fluorobenzene (80 °C) in order to complete the reaction in 30 min. While **4** and **5** react instantly with water, **6** reacts slowly (over 3 h), in all cases to produce HF[19] and $MHF(CO)_2L_2$, which has been synthesized independently from **1**−**3** and CO. To completely exclude moisture, surface silylated glassware must be used. Complexes **4**−**6** have been characterized spectroscopically and by an X-ray single-crystal study (for **4**). The most distinctive NMR spectral features are the hydride peak at −2 to −3 ppm as a triplet of triplets of doublets with large coupling constants (45−50 Hz) to CF_2 fluorine atoms and the smaller coupling (12 Hz) to metal-bound fluoride. The $^{31}P\{^1H\}$ signal is a doublet of triplets due to two types of fluorine atoms. The carbene carbon resonance appears at low field (254 ppm for **4**, and 225 ppm for **6**) as a triplet of multiplets with large $^1J(CF)$ values (495 Hz for **4**, and 445 Hz for **6**), in agreement with the presence of a metal-bound CF_2 unit. At room temperature, two broad ^{19}F resonances are detected with a 2:1 ratio, at low and high field (for CF_2 and M−F, respectively). Since the CF_2 is a single-faced π-acid, its orientation becomes an issue. Upon cooling of the sample to −80 °C, the CF_2 peak in **4** decoalesces ($\delta(F^a) - \delta(F^b) = 10$ ppm) to one AMX (X = H) pattern with a large $^2J(FF)$ value (221 Hz). These results reveal that the ground-state geometry of the CF_2 ligand has the p orbital of the carbene carbon parallel to the P−M−P axis. By adopting this orientation, the CF_2 ligand avoids competing for the same d_B electrons with CO. Thus, it maximizes the π-back-donation from the metal. The CF_2 ligand in crystallographically characterized $[CpFe(CO)(PPh_3)(CF_2)]BF_4$ also adopts an orientation for maximum back-donation.[12d]



(1)

1, L = P^tBu_2Me, M = Ru
2, L = P^iPr_3, M = Ru
3, L = P^tBu_2Me, M = Os

4, L = P^tBu_2Me, M = Ru
5, L = P^iPr_3, M = Ru
6, L = P^tBu_2Me, M = Os

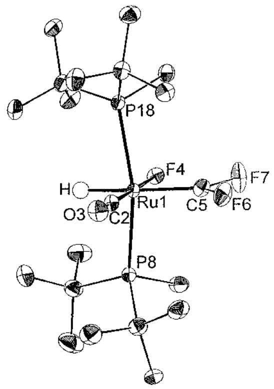


Figure 1. ORTEP diagram of $RuHF(CF_2)(CO)(P^tBu_2Me)_2$, **4**. Hydrogen atoms are omitted except for the one bound to Ru. Selected bond lengths: Ru1−F4, 2.065(1); Ru1−C5, 1.952(3); Ru1−C2, 1.820(2); Ru1−P18, 2.4048(4); Ru1−P8, 2.4105(6); C5−F7, 1.323(2); C5−C6, 1.341(3). Angles: P18−Ru1−P8, 159.23(3); C2−Ru1−F4, 178.38(10); Ru1−C5−F6, 129.77(13); Ru1−C5−F7, 127.10(8); F6−C5−F7, 103.09(23).

The structure of **4** was determined by X-ray single-crystal analysis. The ORTEP diagram is depicted in Figure 1. As in common six-coordinate d^6 complexes, **4** adopts an octahedral geometry with the two sterically demanding phosphines trans to each other and the strong π-donor F trans to the strong π-acceptor CO. Thus, the push−pull stabilization is maximized.[20] The hydride is located trans to the CF_2 ligand, which also, in the solution state, lies in the plane perpendicular to the P−Ru−P plane, as suggested from the low-temperature ^{19}F NMR spectrum. The Ru−F distance is 2.065 Å. This value is comparable to the Ru−F distance (2.011 Å) of $RuF_2(CO)_2(PPh_3)_2$, in which the F is also trans to CO.[21] The Ru−CF_2 distance is 1.952 Å. No comparable value can be found since this complex is the first structurally characterized six-coordinate Ru difluorocarbene complex.[22] A structurally characterized five-coordinate $RuCF_2$ complex, $Ru(CO)_2(CF_2)(PPh_3)_2$, has a shorter Ru−CF_2 bond (1.829 Å).[23] Apparently, the back-donation in

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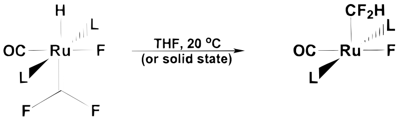
the latter complex is larger due to the lower oxidation state of the metal and the CF_2 carbon is not expected to be as electrophilic as in **4**. A quantum computation (below) reveals this lengthening to also be a result of the carbene being trans to hydride. The Ru−CF_2 distance (1.829 Å) of $Ru(CO)_2(CF_2)(PPh_3)_2$ compares to the Ru−CO distance (1.870−1.915 Å) in the same molecule, showing the multiple bond character of both. Moreover, bending of the P−Ru−P angle (of **4**) away from the carbene effects rehybridization of the filled dB orbital to enhance back-bonding to the carbene.[24]

Isomerization of $RuHF(CF_2)(CO)L_2$. **4** has a long lifetime in a nonpolar solvent such as benzene (1 week) at 20 °C. However, it rearranges within 5 h in THF to $RuF(CF_2H)(CO)L_2$, **7** (eq 2), which is isolated as yellow crystals from pentane. **5** also isomerizes to **8** in THF, but much more slowly (over 48 h) and with formation of unidentified byproducts. In the solid state, however, **4** and **5** are converted to **7** and **8** cleanly in about 6 months. A similar phosphine dependence of the isomerization rate on the phosphine cone angle, i.e., $^iPr_3P$ vs $^tBu_2Me$ in Ru and Os carbene (CH_2) complexes, has been attributed to the different size of the two phosphine ligands, with P^tBu_2Me being larger than P^iPr_3.[25]



(2)

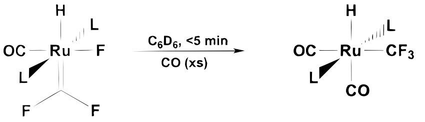
4, L = P^tBu_2Me
5, L = P^iPr_3

7, L = P^tBu_2Me
8, L = P^iPr_3

The most characteristic NMR feature of **7** is the proton resonance of the CF_2H group, a triplet (^2J(HF) = 59 Hz, ^3J(HF) = 5.6 Hz) of doublets at low field (8.2 ppm). Consistent with this, the ^{19}F NMR spectrum has a doublet of triplets of doublets with the largest ^2J(HF) coupling (59 Hz) to the CF_2H proton. The (Ru)−F signal is a broad peak at high field (−236 ppm). The CF_2H carbon resonance is a triplet of triplets of doublets at 140 ppm with a ^1J(FC) value (293 Hz) much smaller than that of CF_2 (495 Hz). Unlike the correlation of ^1J(CH) with the s orbital component of the carbon atom, there is no quantitative relationship between carbon orbital hybridization and the magnitude of ^1J(CF).[26] However, electron deficiency at carbon often increases the ^1J(CF) value, as is also true in this case.[26] The geometry of **7** is derived from the $^{13}C\{^1H\}$ NMR spectrum, which gives a doublet of multiplets at 205 ppm for the carbonyl ligand with a large coupling constant with Ru−F (75 Hz), revealing the mutual trans disposition of the F−Ru−CO unit. Consistent with this, the CO stretching frequency is low (1917 cm^{-1}).

Isomerization Mechanism. **4** is a six-coordinate, saturated complex, which is normally not fluxional. Hydride being trans to the CF_2 blocks rapid 1,2-H migration; this accounts for the metastability of **4**. To isomerize to **7**, ligand dissociation is essential before H and CF_2 can become cis and combine. The possible dissociating ligands are CO, L, and F^-. THF can stabilize one of these five-coordinate intermediates: $RuHF(CF_2)L_2$, $RuH(CF_2)(CO)L$, or $RuH(CF_2)(CO)L_2^+$. We tested all three possibilities individually.

(a) The Effect of Added Co on the Isomerization. To test for the rate suppression in a CO dissociation mechanism, we stirred $RuHF(CF_2)CO)L_2$ with CO (1 atm) in THF at 20 °C. Surprisingly, the saturated complexes **4** and **5** react with CO; within the time of mixing the yellow color of **4** and **5** gave way to a colorless solution. NMR spectral analysis reveals formation of $RuH(CF_3)(CO)_2L_2$, **9** and **10** (eq 3), the product of the combination of CF_2 and F (not hydride) with a CF_3 ligand. **9** and **10** were characterized spectroscopically. The most characteristic feature is the hydride resonance, which is a triplet of quartets with large coupling to the phosphine and small coupling to the CF_3. The existence of a CF_3 group is also supported by the $^{13}C\{^1H\}$ NMR spectrum, which gives a quartet of triplets with a large $^1J_{CF}$ value (358 Hz). This $^1J(C(sp^3)−F)$ coupling constant typically increases with increasing fluorine content.[26] The geometries of **9** and **10** are deduced from the fact that there are two virtual triplets for the methyl protons of ^tBu (**9**) and two doublets of virtual triplets for the methyl protons of ^iPr (**10**) accounting for the trans phosphine geometry. The ^{13}C NMR spectrum also reveals two CO signals, one a triplet of quartets (trans to CF_3) and the other a triplet. At room temperature the NMR signals of **9** are broad due to the hindered rotation around the Ru−P bond.[27] This hindered rotation does not give rise to two isomers for **10**, which has sharp and well-resolved NMR signals over the temperature range from +60 to −80 °C. If ^{13}CO is used in the reaction of eq 3, the ^{13}CO is found exclusively trans to the hydride. The ^1H NMR spectrum of the isotopomer of **10**, $RuH(CF_3)(CO)(^{13}CO)L_2$, **11**, reveals a hydride doublet of triplets of quartets with large coupling constant (^2J(CH) = 29 Hz) to trans ^{13}CO; consistent with this, the proton-coupled ^{13}C NMR spectrum gives a doublet of triplets of quartets at δ 203.8 with the same doublet coupling ($^2J_{CH}$ = 29 Hz).

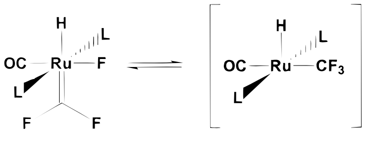


(3)

4, **5**

9, L = P^tBu_2Me
10, L = P^iPr_3

The rapid reaction between six-coordinated **4** (or **5**) and CO led us to suspect that there is a fast equilibrium between six-coordinated $RuHF(CF_2)(CO)L_2$ and the unseen five-coordinated $RuH(CF_3)(CO)L_2$ with CF_3 trans to the CO (eq 4). Thus, we carried out a ^{19}F spin saturation transfer (SST) study of **4** in toluene. At 25 °C, saturation of the CF_2 resonance does not cause an observable intensity change of the Ru−F signal. However, at elevated temperatures (>60 °C), irradiation of the CF_2 group causes a drastic loss of intensity of the fluoride bound to the Ru. This result corroborates the presence of the fast and reversible C−F bond cleavage and argues against CO dissociation being necessary for the **4** → **7** rearrangement.



(4)

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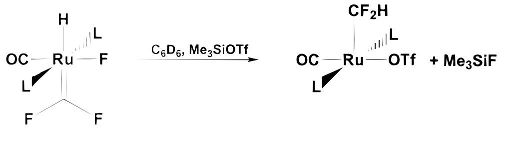
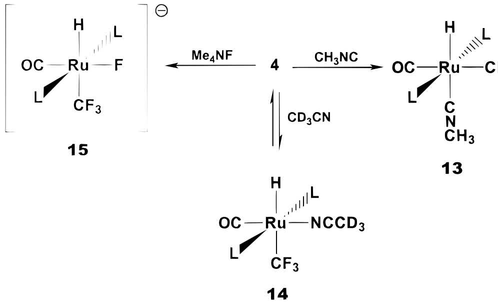
(b) The Effect of Added Phosphine Ligand. Addition of equimolar ${}^{t}Bu_2PMe$ to a THF-d_8 solution of **4** inhibits the isomerization over 24 h at 20 °C. The only species observed by ^{1}H and ^{31}P NMR spectra are the free phosphine and **4**, ruling out possibility of adduct formation of **4** with added phosphine. Therefore, a preliminary step in the isomerization is reversible phosphine dissociation.

(c) Fluoride Dissociation as Another Possible Mechanism. We have proved that phosphine dissociation is sufficient for **4** to isomerize. Will F^- dissociation also trigger the process? Although the SST experiment reveals the rapid cleavage and re-formation of the Ru−F bond, this process does not require the dissociation of F^-; instead, it more likely to be a migratory insertion process, and the F^- does not spontaneously dissociate from Ru. Addition of a hydrogen-bonding donor, indole (catalytic amount),[28] to help F^- dissociation does not accelerate the isomerization in benzene. However, when fluoride is fully abstracted by Me_3SiOTf, the combination of CF_2 with hydride occurs. Addition of 1 equiv of Me_3SiOTf to the benzene solution of **4** generates $Ru(CF_2H)(OTf)(CO)L_2$, **12**, cleanly within the time of mixing at 25 °C (eq 5). The fast combination of CF_2 with H in this reaction is apparently caused by dissociation of the weak ligand triflate instead of phosphine. **12** is fully characterized spectroscopically. The CF_2H proton appears at low field as a triplet of triplets with large ^2J(HF) (58 Hz) and small ^3J(HP) values (3 Hz). Two virtual triplets indicate diastereotopic ^{t}Bu. The $^{31}P\{^1H\}$ signal is a triplet, and the CF_2H fluoride appears as a doublet of triplets. In the $^{13}C\{^1H\}$ NMR spectrum, the CO resonance is a triplet of triplets with a small CF coupling constant (7.6 Hz), which supports the cis disposition of CF_2H and CO. The CO stretching frequency is high (1944 cm^{-1}) compared to that of $RuH(OTf)(CO)L_2$ (1921 cm^{-1}),[29] revealing that CF_2H is a weaker F-donor ligand than hydride. Although the complex can be isolated as orange crystals from toluene at −40 °C, it decomposes in 1 day at room temperature to give HL^+ and other, unknown species.



4 **12** (5)

Scheme 1



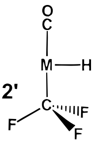
Reaction of 4 with Other Nucleophiles. The CF_2 carbon of **4**, and the Ru of an unobserved isomer of **4**, $[RuH(CF_3)(CO)L_2]$, are two potential positions for a nucleophile to attack. We have demonstrated that CO attacks Ru of $[RuH(CF_3)(CO)L_2]$ irreversibly to give $RuH(CF_3)(CO)_2L_2$. Similarly, CH_3NC binds **4** to give **13** (Scheme 1), which is characterized spectroscopically. The most informative peak is the hydride resonance, which is a triplet of quartets (J(FH) = 6.3 Hz, J(PH) = 26 Hz) at −7.9 ppm. The CF_3 fluoride appears at −13.7 ppm as a doublet of broad triplets (J(FH) = 6 Hz, J(PF) is not well resolved), and the ^{31}P signal is a broad peak at 64 ppm. These values compare well with that of **9**, suggesting that the two have similar geometries. The much weaker donor CD_3CN also attacks Ru but reversibly to give $RuH(CD_3CN)(CF_3)(CO)L_2$, **14**. The hydride of **14** appears at −9.7 ppm as a triplet of quartets (J(PH) = 22 Hz, J(HF) = 19 Hz). The significantly large J_{HF} of **14** (vs **13**) suggests it has a different geometry. The ^{31}P NMR signal is a quartet (J(PF) = 6 Hz). The CF_3 fluoride exhibits a well-resolved doublet of triplets at −7.5 ppm. Removal of all the volatiles regenerates **4** along with a small amount of **7**. Similar to CD_3CN, addition of F^- (as the anhydrous NMe_4^+ salt) rapidly gives an adduct, **15**, with CF_3 trans to hydride (Scheme 1). The hydride of **15** is an apparent sextet of doublets with the same coupling constant with CF_3 fluoride and the phosphine (20 Hz). The smallest coupling constant, that of Ru−F (5.4 Hz), suggests that F is cis to the hydride. The CF_3 fluoride resonance is a doublet of apparent quartets (^3J(FH) = 21 Hz, ^3J(PF) = ^3J(FF) = 6 Hz) at −10 ppm, and the fluoride peak appears as a multiplet at high field (−325 ppm). The $^{31}P\{^1H\}$ NMR spectrum is a doublet of quartets (coupling with Ru−F and CF_3). The CO stretching frequency is lower (1910 cm^{-1}) than that of **4**, in agreement with better π-donation of Ru in **15**. The different geometry of **15** compared to those of **13** and **10** is inconsistent with F^- addition trans to hydride in $RuH(CF_3)(CO)L_2$ and strongly implies that the added fluoride attacks the CF_2 carbon instead. Less nucleophilic CsF does not interact with **4**. To probe the initial reaction site of F^-, anhydrous n-Bu_4NCl was used as cheap "isotope" labeling reagent, but it fails to give any chloride adduct of **4**. Instead, it only accelerates the isomerization of **4** to **7**; no Cl and F exchange is observed.

DFT Calculations. We carried out these calculations to learn the relative energies of various isomeric structures, to learn more about the equilibrium in eq 4 (including structural features of the CF_3 complex), and to compare ruthenium to osmium. Details of the computational method, especially the need to model fluorine adequately, are given in the Experimental Section. We will first summarize aspects of the calculated structures. This will consist of (a) comparison of the various structures for a given metal and (b) comparison of Ru and Os analogues. Among all 10 structures, M−P distances vary insignificantly (2.413−2.445 Å).

Both $MHF(CO)(PH_3)_2$ species (**M1**) are square pyramids, with H apical. Bond lengths for Ru and Os are identical to within 0.02 Å, but the ∠H−M−F is 10° larger for Os.

The species (**M2**) with CF_3 trans to hydride optimize to a stationary point where one F is bonded to both carbon and the metal, interacting with the site trans to CO; we will refer to this as an agostic interaction. There is clearly an alternative isomer, **M2′**, but this is found *not* to have an agostic interaction. Perhaps the trans effect of hydride prevents this agostic donation. It is worth noting that isomer **M2′** cannot easily form the observed next product, **M3**, while **M2** can (the

M2′



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[28] Wessel, J.; Lee, J. C., Jr.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507.

[29] Huang, D.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 7398.

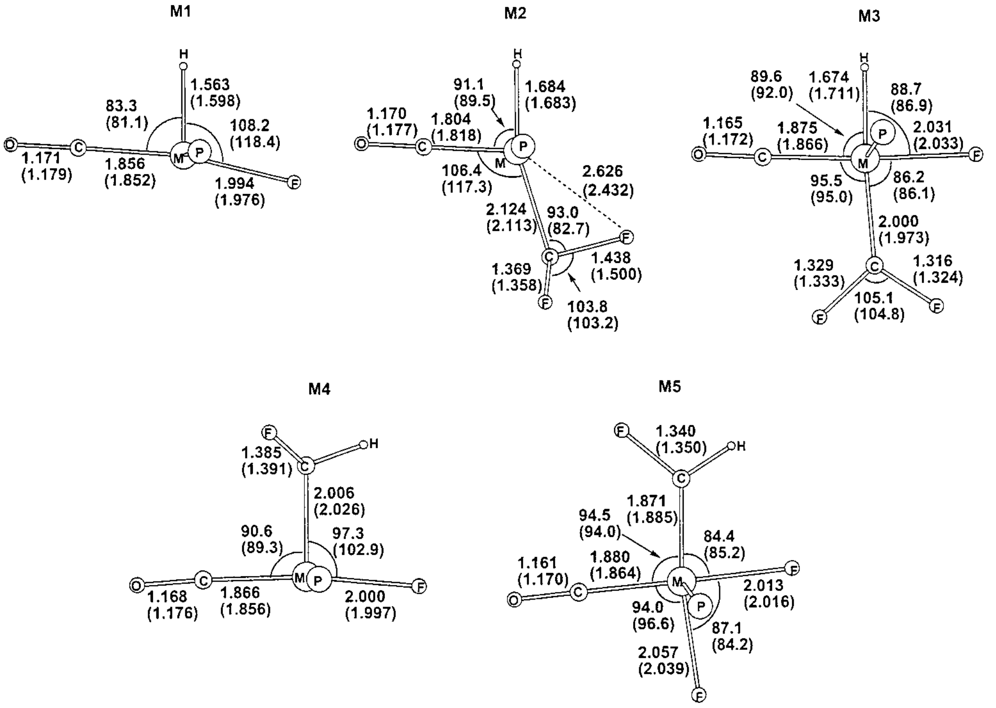
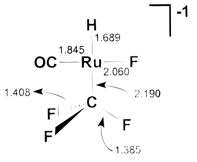
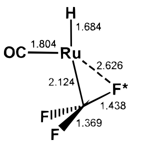


Figure 2. Optimized structures (distances in angstroms, angles in degrees) for $MHF(CO)(PH_3)_2$ and isomers of $MH(CF_3)(CO)(PH_3)_2$, M = Ru (Os in parentheses), projected onto their mirror symmetry plane. Hydrogens of PH_3 have been removed for simplicity. M2 and M4 each have one fluorine on carbon eclipsed by the one shown.

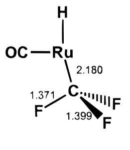
emerging CF_2 is trans to the hydride in **M2**), and also that lone pairs of the agostic F in **M2** can to some extent participate in a push/pull interaction with the carbonyl ligand. Most bond lengths differ insignificantly (0.01 Å) between **Ru2** and **Os2**; the exception is the MCF_3 group, involving the agostic F (denoted F*): the interaction of F* is stronger to Os than to Ru, as judged by a shorter (by 0.19 Å) M−F distance and a longer (by 0.06 Å) C−F* distance. As if to compensate the CF_3 carbon of **M2**, the remaining two C−F bonds in **Os2** are shorter (by 0.01 Å) than they are in **Ru2**. For comparison, in H_3Si-CF_3, the calculated C−F bond length is 1.360 Å. The distance Os−C is shorter by 0.01 Å and ∠M−C−F* is smaller (by 10°). To accommodate the F*/Os interaction, ∠O*C*−Os−CF_3 is *larger* (by 11°). The angle F−C−F here and in the other structures shown in Figure 2 is always ∼103°, so it is not diagnostically useful. The structure of a relevant comparison compound, **X**, shows the most remarkable change to be the rapid development of a shorter Ru−CF_x bond in **Ru2**, as Ru=C (carbene) character develops concurrently with C−F* bond stretching. This is also evident by comparing to the Ru−CF_3 distance in **Y**, a conformer of **Ru2**.



X



Ru2



Y

On isomerizing from **M2** to **M3**, the CF bonds shorten considerably (0.02−0.05 Å) as the C−F* bond is cleaved, the resulting CF_2 group rotates 90° in order to π-accept from the d_π orbital which is not donating to CO, and the M/CF_x bond shortens by up to 0.14 Å. The M/CF_2 bond is *not* as short as the M/CO bond, however. **Os3** differs from **Ru3** mainly by a shorter M=C bond and a correspondingly longer M−H bond. Osmium is thus a stronger π base (i.e., more reducing) than Ru. This is also evident in the M−CO distances, which are shorter to Os in **M1**, **M3**, **M4**, and **M5**. **M4** can be profitably compared to **M1** to evaluate the difference between H and CHF_2 ligands in a square pyramid. The changes are seen to be mainly angular: the apical/basal angles. In the **M3** → **M4** isomerization, the M−F bond shortens by up to 0.04 Å, indicating more F → M π donation in unsaturated **M4**.

The biggest change from **M3** to **M5** is the shortening of the M/CF_x distance (by about 0.1 Å). This explains why the M/CF_x bond does not lengthen as much as expected on going from M=C (**M3**) to M−C (**M4**): the larger trans influence of hydride (vs fluoride) makes the M=C bond long in **M3**. In **M5**, the M−F distance trans to CO is shorter than that trans to CHF. Distances vary by no more than 0.02 Å between **Ru5** and **Os5**.

The calculated energies of the various products (Figure 3) also reveal some insights, with the proviso that, by studying simultaneously two metals from the same periodic group, one learns by *comparison*. At the level of theory employed, we seek *trends* more than absolute agreement; errors of perhaps 5 kcal/mol will not obscure the true, underlying periodic trends.

(1) The reaction of $MHF(CO)(PH_3)_2$ with H_3Si-CF_3 is calculated to be approximately thermoneutral (±4 kcal/mol) for both M = Ru and Os. This shows that, despite the very strong Si−F bond which is formed, the reactants have comparable stabilities. This suggests that the M−F bond, while synthetically very useful, is itself quite strong.

(2) The (experimentally unobserved) $MH(CF_3)(CO)L_2$ species show a structure which presages an unexpected feature of the chemistry reported here: C−F cleavage. The α-agostic F species is a minimum, and its geometry can lead easily only to a product with the CF_2 carbene ligand trans to H, where subsequent combination of these ligands is unfavorable.

(3a) The full cleavage of the C−F bond, to form **M3** from **M2**, is much more favorable for M = Os (−16 kcal/mol) than

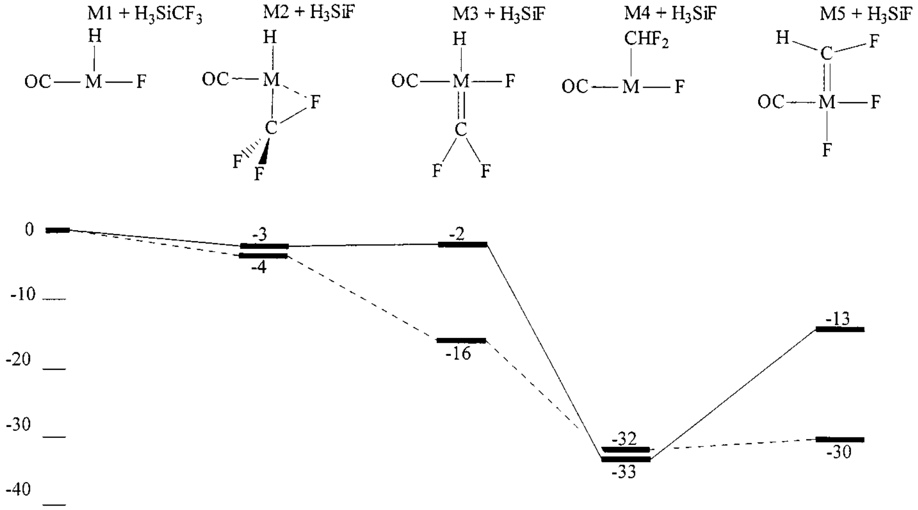
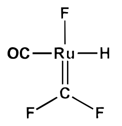


Figure 3. Calculated energies of the speices shown in Figure 2, comparing M = Ru (solid lines) to M = Os (dashed lines). For simplicity, PH_3 ligands are omitted from the drawings.

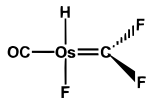
for Ru (thermoneutral). This is in agreement with the experimental fact that **Ru3** is detectably in equilibrium with a CF_3 isomer at 60 °C, while this is not the case for **Os3**. Osmium thus shows a greater preference than ruthenium for being saturated and having more π-acid ligands (i.e., to be more oxidized).

(3b) Isomer **Ru3′**, which may be relevant to finally forming the CHF_2 ligand (H has migrated "toward" the carbene), is only 1 kcal/mol higher in energy than **Ru3**. This shows that H has an energetically comparable effect whether it is trans to CO or to CF_2.



Ru3'

(3c) Isomer **Os3″**, where the carbene has migrated "toward" H, is 6 kcal/mol less stable than **Os3**. This must be attributed to competition between the two π-acid ligands CO and CF_2 for back-bonding and the decreased push/pull interaction between F and CO in **Os3″**.



Os3"

(4) The transformation from **M3** to **M4** is very favorable for both metals, although much more so for Ru than for Os. This metal dependence of ΔE_{3-4} can be attributed to the same effects cited above: a greater preference for saturation, and the greater reducing power of the 5d metal.

(5) Consistent with this logic, the isomerization of **Os4** to **Os5** is thermoneutral, while it is unfavorable by 20 kcal/mol for Ru. Thus, for Ru, any benefit from achieving an 18-valence electron count must be offset by the diminished reducing power of this 4d metal: it is less able than osmium to tolerate the additional π-acid ligand CF_2.

In broad strokes, then, the calculations agree with experiment for ruthenium, and they give a quantitative measure of the stability of isomers, both observed and unobserved. The predicted disparate behavior of these two metals will be revisited below, after further consideration of the reactivity of **4**.

Reaction of 4 with Me_3SiCCH. The fast equilibrium of **4** and its five-coordinated isomer $RuH(CF_3)(CO)L_2$ indicates that the two species are energetically similar. Logically, by changing the ligand environment, the equilibrium might be induced to favor the unsaturated $Ru-CF_3$ species. One way to alter the ligands is by addition of Ru−H to a CC multiple bond, which converts the Ru−H compound to the Ru−C analogue. Therefore, we tested the reaction of **4** with Me_3SiCCH in an attempt to make the vinyl analogue of **4**. Addition of 2 equiv of Me_3SiCCH to a benzene solution of **4** gives $Me_3SiCH{=}CH_2$ (identified by ^1H NMR) and $Ru(CF_3)(CCSiMe_3)(CO)L_2$, **17**, in 5 h at 20 °C. If only 1 equiv of Me_3SiCCH is added, partial conversion to **17** occurs, and no other intermediate is detected. This observation indicates that $Ru(CH{=}CH(SiMe_3))(CF_3)(CO)L_2$, which is not observed in the reaction, is more reactive toward Me_3SiCCH and gives **17** with release $Me_3SiCH{=}CH_2$. Reactions of transition metal vinyl complexes with terminal alkynes have been reported to give alkenes and alkynyl complexes.[30] **17** is highly soluble in common nonpolar solvents and is isolated as a brown solid from tetramethylsilane. The CF_3 fluorine resonance is a triplet ($J(PF) = 12$ Hz), and correspondingly, the phosphine signal is a quartet. The CO stretching frequency is quite high (1944 cm^{-1}), and the CC triple bond stretching frequency is normal (2019 cm^{-1}). In contrast to the case for **4**, at room temperature there is no evidence for α-F migration of **17** to form $Ru(CCSiMe_3)F(CF_2)(CO)L_2$; **17** is not thermally stable, which excludes a higher temperature search for a possible CF_2 isomer. Apparently, unlike the pure σ-donor hydride, the alkynyl ligand of **17** can donate its π-electrons to Ru and thus stabilize the unsaturated metal center in a way unavailable to the more Lewis acidic $[RuH(CF_3)(CO)L_2]$. This result demonstrates that the equilibrium position for α-F migration is highly dependent on the Lewis acidity of the metal.

Isomerization of $OsH(F)(CF_2)(CO)(P^tBu_2Me)_2$, 6. In marked contrast to its Ru counterpart, **4**, **6** is persistent in THF at room temperature for 1 week, even with heat (65 °C, 12 h). To get an assessment of the *difference* in M−P bond dissociation energies for Ru vs Os, we optimized the structure of the product of eq 6. These reaction energies (after BSSE correction of results

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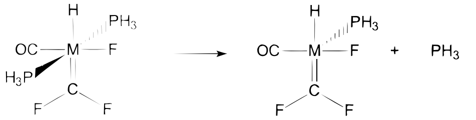
[30] Santos, A.; Lopez, J.; Galan, A.; Gonzalez, J. J.; Tinoco, P.; Echavarren, A. M. *Organometallics* **1997**, *16*, 3482.



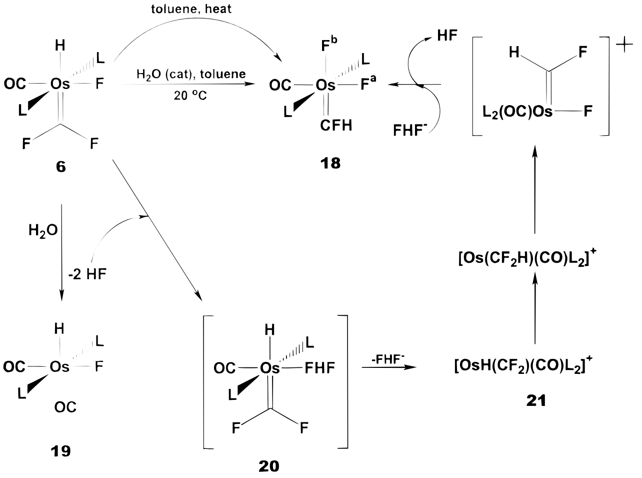
(6)

from an MP2 calculation) are large for both metals—39 kcal/mol for Os and 32 for Ru—but these will certainly be smaller for bulky $\mathrm{P^tBu_2Me}$. Given the nearly identical bond lengths for Ru and Os, due to the lanthanide contraction, this error should be comparable for the two metals. Therefore, a 7 kcal/mol increase in M−P bond dissociation energy on going from Ru to Os is in agreement with the fact that the $\mathrm{H{-}M{=}CF_2 \rightarrow M{-}CF_2H}$ isomerization, which is much slower for Os, involves a dissociative preequilibrium. The higher reaction energy reflects a greater reluctance for a 5d metal to be unsaturated compared to its 4d analogue.

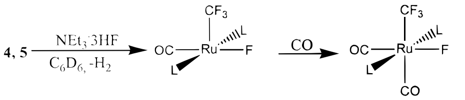
Isomerization can be forced if the solution is heated to higher temperature (110 °C, in a sealed tube) in either THF or toluene to give, instead of $\mathrm{OsF(CF_2H)(CO)L_2}$ (cf. **7**), $\mathrm{OsF_2({=}CFH)(CO)L_2}$, **18** (Scheme 2). The net change from **6** and **18** is the exchange of one $\mathrm{CF_2}$ fluorine with hydride. **18** is characterized spectroscopically. The ^{31}P NMR spectrum is a doublet of doublets with coupling constants with $\mathrm{F^b}$ (45 Hz) twice as large as that with $\mathrm{F^a}$ (see Scheme 2 for definitions of $\mathrm{F^a}$ and $\mathrm{F^b}$). The carbene proton exhibits a signal at low field (15.2 ppm) as a doublet of doublets of doublets due to the coupling with three different fluorines (large ^2J(FH) (80 Hz), medium $J(\mathrm{HF^b})$ (18 Hz), and small $J(\mathrm{HF^a})$ (8 Hz)). The proton-decoupled carbene carbon resonance appears at low field (275 ppm) as a doublet of doublets of multiplets (not well-resolved coupling with phosphine and $\mathrm{F^a}$), with large ^1J(CF) (374 Hz) and small $J(\mathrm{CF^b})$ (99 Hz). Two equivalent phosphine ligands rule out the static geometry with the CFH plane parallel to the P−Os−P axis. The CFH ligand either rotates fast or lies in the plane perpendicular to the P−Os−P axis (which may give rise to two rotamers), with fast rotation being more likely. The CO signal is a doublet of triplets of doublets with large $^2J(\mathrm{CF^a})$ (80 Hz). The ^{19}F NMR spectrum shows some interesting features. The fluorocarbene resonance appears at low field (80.6 ppm) as an apparent triplet due to the same coupling constants with the carbene proton and with $\mathrm{F^b}$. The two metal-bound fluorides are at much higher field (−274 for $\mathrm{F^b}$, −271 for $\mathrm{F^a}$) and strongly coupled with each other ($J(\mathrm{F^aF^b})$ = 121 Hz).

The isomerization of **6** to **18** can also be promoted by water. Addition of 10% (mole) water to **6** in toluene at room temperature slowly forms a small amount of $\mathrm{OsHF(CO)_2L_2}$, **19**, and HF in 3 h. Then **6** is converted to **18** in 24 h, and the HF also disappears (i.e., reacts with the glass walls). **19** is independently synthesized by addition of stoichiometric CO to $\mathrm{OsHF(CO)L_2}$. We propose that the formation of the **18** is catalyzed by acid (HF), which protonates the fluoride of **6** to form the bifluoride adduct $\mathrm{[OsH(FHF)(CF_2)(CO)L_2]}$, **20** (not observed). $\mathrm{FHF^-}$ is a relatively weak ligand[31,32] and dissociates to form a five-coordinated $\mathrm{[OsH(CF_2)(CO)L_2]^+}$, **21**. The hydride and the $\mathrm{CF_2}$ now can combine, followed by α-F abstraction. $\mathrm{FHF^-}$ coordination and dissociation of HF complete the catalytic cycle.

Scheme 2. (L = $\mathrm{P^tBu_2Me}$)



Reaction of $\mathrm{MHF(CF_2)(CO)L_2}$ with $\mathrm{NEt_3{\cdot}3HF}$. To verify that HF can, indeed, catalyze the isomerization of $\mathrm{MHF(CF_2)(CO)L_2}$, we tested the reaction of **4**−**6** in the presence of catalytic amount of $\mathrm{NEt_3{\cdot}3HF}$ as an HF source. This reagent gives some unexpected results, indicating that it does not merely serve as a source of HF. Reaction of $\mathrm{RuHF(CF_2)(CO)(P^tBu_2Me)_2}$ with $\mathrm{NEt_3{\cdot}3HF}$ (Ru:N molar ratio 10:1) in benzene-d_6 for 2 h at room temperature causes partial (30%) conversion of $\mathrm{RuHF(CF_2)(CO)(P^tBu_2Me)_2}$ to free $\mathrm{H_2}$ (as evidenced by a singlet at 4.5 ppm) and $\mathrm{Ru(CF_3)F(CO)(P^tBu_2Me)_2}$ (eq 7), along with a trace amount of $\mathrm{Ru(CF_2H)F(CO)(P^tBu_2Me)_2}$. The reaction is completed by addition of more (1 equiv of HF per Ru in total) $\mathrm{NEt_3{\cdot}3HF}$ to give $\mathrm{Ru(CF_3)F(CO)(P^tBu_2Me)_2}$ as the major product (90%). The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of $\mathrm{Ru(CF_3)F(CO)(P^tBu_2Me)_2}$ is a doublet of quartets ($^2J_{\mathrm{PF}}$ = 23 Hz, $^3J_{\mathrm{PF}}$ = 10 Hz), the $\mathrm{CF_3}$ fluorides appear as doublet of triplets (J_{PF} = 10 Hz, $^3J_{\mathrm{FF}}$ = 13 Hz) at 9.5 ppm, and the Ru-bound fluoride exhibits an overlapping quartet of triplets at −210 ppm, which is close to the chemical shifts of other five-coordinate ruthenium fluorides, $\mathrm{RuR(F)(CO)L_2}$. The small $^3J_{\mathrm{FF}}$ coupling constant indicates a cis arrangement of $\mathrm{CF_3}$ and fluoride. Indeed, in the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum, the CO signal appears as a doublet of multiplets with a large $^2J_{\mathrm{CF}}$ (64 Hz) value, consistent with CO being trans to fluoride. **5** also reacts with equimolar $\mathrm{NEt_3{\cdot}3HF}$ to give $\mathrm{Ru(CF_3)F(CO)(P^iPr_3)_2}$ as the major product (61%), which possesses spectra similar to those of its $\mathrm{P^tBu_2Me}$ counterpart. However, a catalytic (0.05 equiv) amount of $\mathrm{NEt_3{\cdot}3HF}$ does not cause conversion of **6** to $\mathrm{OsF_2(CFH)(CO)(P^tBu_2Me)_2}$, **18**; only **6** is recovered after 24 h at 20 °C.



(7)

$\mathrm{Ru(CF_3)(F)(CO)_2(P^tBu_2Me)_2}$. Addition of excess CO to a benzene solution of $\mathrm{Ru(CF_3)F(CO)(P^tBu_2Me)_2}$ immediately causes a color change from yellow to colorless. ^{1}H NMR analysis of the mixture is consistent with a product $\mathrm{Ru(CF_3)F(CO)_2(P^tBu_2Me)_2}$. Two t-Bu proton resonances reveal that the two CO's are cis to each other. However, the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum exhibits an extremely broad peak at 44 ppm, which sharpens as the temperature is raised to 60 °C. The ^{19}F NMR spectrum behaves similarly, and no ^{19}F signals were detected at room temperature, but at 60 °C two broad peaks are located for $\mathrm{CF_3}$ (−16.3 ppm) and Ru−F (−376 ppm). The broadening of the signals is likely caused by slow rotation of Ru−P bonds in this sterically crowded molecule. Similar NMR signal broadening was also noticed in the spectra of $\mathrm{RuH(CF_3)(CO)_2(P^tBu_2Me)_2}$.

Reaction of 6 with $\mathrm{Me_3SiOTf}$. Replacement of the fluoride by the weaker ligand triflate also causes exchange of the $\mathrm{CF_2}$

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(31) Whittlesey, M. K.; Perutz, R. N.; Greener, B.; Moore, M. H. *Chem. Commun.* **1997**, 187.

(32) Murphy, V. J.; Hascall, T.; Chen, J. Y.; Parkin, G. *J. Am. Chem. Soc.* **1996**, *118*, 7428.

Scheme 3

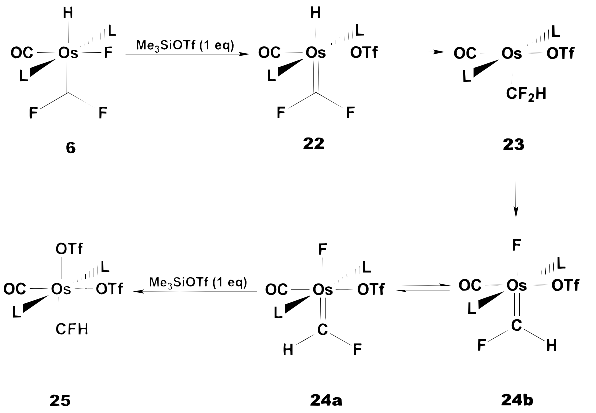
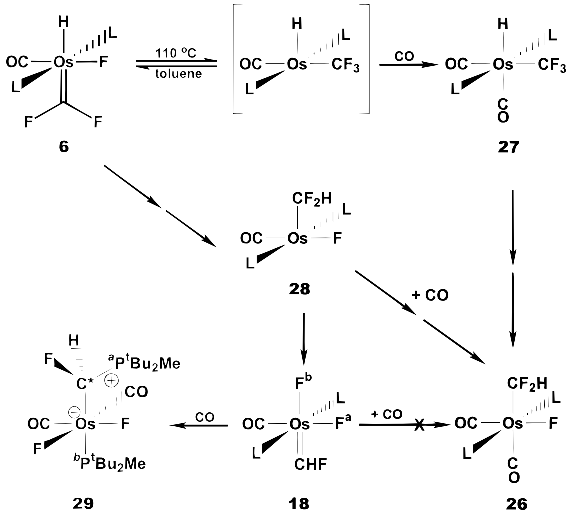


Table 1. Selected NMR Spectral Data for **24a** and **24b**

nuclei	chemical shifts	
	major isomer	minor isomer
Os═CF*H*	14.2, dd, $^2J_{HF} = 80$, $^3J_{HF} = 5.8$	15.9, dd, $J_{HF} = 72$, $^3J_{HF} = 15$
Os═CF*H*	117.8, d, $J_{HF} = 79$, $^3J_{FF}$ not resolved	102.7, dd, $J_{HF} = 72$, $^3J_{FF} = 82$
Os−P^{t}Bu$_2$Me	35.7, d, $J_{PF} = 21$	45.3, d, $J_{PF} = 41$
Os−CO	178.7, t, $J_{CP} = 12$ Hz	178.5, m

fluoride with hydride. The reaction of **6** with Me$_3$SiOTf is slow enough to suggest a mechanism for the analogous reaction for ruthenium (eq 5). Addition of 1 equiv of Me$_3$SiOTf at room temperature gives, in 10 min, four products (Scheme 3): OsH(CF$_2$)(OTf)(CO)L$_2$, **22**, Os(CF$_2$H)(OTf)(CO)L$_2$, **23**, and two isomers of OsF(OTf)(CHF)(CO)L$_2$, **24a** and **24b**. **22** and **23** convert to **24a/b** in 3 h. The most characteristic spectral feature of **22** is the hydride as a virtual triplet of triplets at −2.0 ppm ($J_{FH} = 85$ Hz, $J_{PH} = 27$ Hz). The virtual triplet is caused by coupling between the inequivalent carbene fluorines. The ^{19}F NMR spectrum of **22** has an ABX (X = H) pattern for the carbene fluorides; one peak appears at 107.1 ppm ($J_{FF} = 155$ Hz, $J_{FH} = 33$ Hz) and the other at 104.5 ppm ($J_{FF} = 155$ Hz, $J_{FH} = 52$ Hz). In support of the virtual triplet assignment of the hydride peak, the sum of J_{HF} (33+52) is the same as J_{FH} (85 Hz). The geminal F−F coupling constant of **22** is the same as that of **6** (155 Hz); this strengthens our structural assignment of **22**. The supporting evidence for **23** is the characteristic CF$_2$H proton at 7.24 ppm (cf. 7.72 ppm of **12**) as a triplet of triplets with large $^2J_{FH}$ (62 Hz). The fluorine resonance of the CF$_2$H group is at −54.1 ppm ($J_{FH} = 61$ Hz, $J_{PF} = 16$ Hz). These values are close to that of **12**. Consistent with this, the ^{31}P{^{1}H} NMR spectrum of **23** is a triplet ($J_{PF} = 16$ Hz). **22** and **23** are not long-lived species and convert to **24a/b** over 3 h at 20 °C. The ^{31}P{^{1}H} NMR spectra of **24a** and **24b** coalesce to one broad signal at 20 °C, as do the isomeric CFH protons and fluorines. At low temperature (−60 °C), the signals (^{31}P, ^{19}F of CFH and all ^{1}H signals) decoalesce to two peaks with a 2:1 ratio. The NMR data of **24a** and **24b** are compiled in Table 1. The geometry in each around Os can be deduced from the lack of a large J_{CF} coupling between Os*F* and Os−*C*O, indicative of their cis orientation. In addition, two virtual triplets for the ^{t}Bu protons suggest two trans phosphines in each. The CO stretching frequencies of these two isomers are very close (1967 and 1962 cm^{-1}) and relatively high compared to those of **18** (1939 cm^{-1}), in agreement with CO being trans to a weaker π-donor ligand, triflate. However, **24a** and **24b** have significant, large differences in chemical shifts (10 ppm difference in ^{31}P shifts). The coupling constants among the nuclei are also very different, especially those for $^2J_{PF}$ (21 vs 41 Hz) and $^3J_{FF}$ (<10 vs 82 Hz). Addition of 1 equivalent more of Me$_3$SiOTf replaces the other fluoride of **24** to give clean formation of Os(OTf)$_2$(═CFH)(CO)L$_2$, **25**. The proton-decoupled carbene hydrogen peak is a sharp doublet at room temperature. Even at −70 °C, no rotamers are observed by NMR spectroscopy (^{1}H, ^{19}F, and ^{31}P), indicating much faster rotation around this Os═CFH bond.

Scheme 4



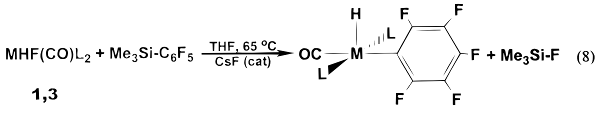
Reaction of OsHF(═CF$_2$)(CO)L$_2$ with CO. In sharp contrast to the case for **4**, carbon monoxide does not react with **6** at room temperature, indicative of no fast equilibrium similar to that between **4** and [RuH(CF$_3$)(CO)L$_2$] (eq 4). With heating to 110 °C over 12 h in toluene-d_8, CO converts **6** cleanly to OsF(CF$_2$H)(CO)$_2$L$_2$, **26** (Scheme 4). The spectroscopic features of **26** include a triplet of triplets of doublets for the CF$_2$H proton at low field (7.7 ppm, near that of **7**), due to coupling with ^{19}F and ^{31}P, with a large (50 Hz) ^2J(HF) value. The ^{13}C{^{1}H} NMR spectrum of the CF$_2$H group is a triplet of doublets of triplets with a large (217 Hz) ^1J(CF). One CO signal appears as a doublet of multiplets with a large ^2J(CF) (70 Hz) splitting, indicative of a trans F−Os−CO arrangement. Similar to the case for **8**, the ^{19}F resonances of CF$_2$H and the ^{31}P resonance of the phosphine of **26** are both broad, and no coupling information can be deduced. The broadening may be caused by hindered rotation around the P−Os bonds, as is often seen in similar six-coordinated Ru(II) complexes.[27]

Mechanism of Reaction of 6 with CO. Based on the reaction of Ru analogue **4**, two possible processes may happen on heating **6** in the presence of CO, as shown in Scheme 4. Combination of CF$_2$ with F could yield five-coordinate OsH(CF$_3$)(CO)L$_2$, which then binds one CO to give OsH(CF$_3$)(CO)$_2$L$_2$, **27**. If the reaction is monitored after 1 h of heating, a small amount of **27** is formed, along with some **26**. The spectroscopic features of **27** are very much like those of its Ru counterpart **9**. Due to the hindered rotation around the Os−P bond, rotamers interconvert slowly at room temperature; the hydride and the fluoride signals are therefore broad. At 60 °C, the signals sharpen. The ^{1}H NMR spectrum signal of the hydride is a triplet of quartets at −6.74 ppm, and the ^{19}F NMR spectrum signal is a broad peak at −2.6 ppm. After longer heating, **27** disappears, and **26** is the only product. **27** can apparently isomerize to form **26.** Alternatively, dissociation of a phosphine from **6**, followed by insertion of CF$_2$ to Os−H and recoordination of lost L, could provide [Os(CF$_2$H)F(CO)L$_2$], **28** (cf. **7**), which would be trapped by CO to form **26**. Or, in the absence of CO, α-F migrates to generate **18**. To test if **18** can be transformed to **26** under CO atmosphere, we heated pure **18** (prepared from thermal isomerization of **6**) in toluene under CO (110 °C). To our surprise, a new product, $OsF_2[(CHF(P^tBu_2Me)](CO)_2L$, **29**, was formed cleanly by a process which *does* implicate phosphine dissociation from **18**. Since the reaction of **6** with CO did not form **29**, it is unlikely that **18** is generated under these reaction conditions.

Characterization of 29. Multinuclear NMR spectroscopy provides sufficient information to establish the geometry of **29**. The formation of a P/C bond is an indication of the electrophilic nature of the CHF ligand of **18**. The presence of several magnetically active nuclei and the lack of symmetry due to a chiral carbon cause a rather complicated NMR spin system. The $^{31}P\{^1H\}$ NMR spectrum has two signals, a doublet of doublets (P^a, $J_{PF} = 58$ and $J_{PP} = 17$ Hz) and a multiplet (P^b). Two ^{t}Bu groups on each phosphine are no longer equivalent, and accordingly four doublets are observed. The ^{19}F resonance of carbon-bound fluorine appears at high field (−209 ppm) as a doublet of doublets with similar $^2J_{FH}$ (51 Hz) and $^2J_{PF}$ (58 Hz) splittings. The assignment of the coupling constants is confirmed by selective ^1H or ^{31}P spin decoupling.[33] The two metal-bound fluorides appear at higher field as broad doublets with $^2J_{FF}$ (141 Hz) (close to 121 Hz of **18**). Large (83 and 88 Hz) $^2J_{FC}$ values for the inequivalent carbonyls support the mutually trans geometry of CO and F. Consistent with this, two CO stretching bands (1989 and 1911 cm^{-1}) with similar intensity (indicating a cis arrangement) were found. The resonance of the chiral carbon appears as a doublet of doublets of multiplets at 91 ppm with large $^1J_{CF}$ (182 Hz) and $^2J_{PC}$ (82 Hz). This large coupling clearly reveals the presence of a trans phosphine ligand.

Phosphine attacking a carbene has been observed before.[34] Roper and co-workers treated $Ru(CH_2)(Cl)(NO)(PPh_3)_2$ with the strong π-acidic ligand $CF_2{=}CF_2$ to form $Ru(\eta^2\text{-}CF_2{=}CF_2)(Cl)(NO)(CH_2PPh_3)PPh_3$, which has a P−C bond.[35] π-Acidic ligands (CO and $CF_2{=}CF_2$) diminish the back-donation to carbene carbon, which then is susceptible to nucleophilic attack. Thus, it appears that addition of the π-acid CO to **18** encourages nucleophilic attack by P^tBu_2Me on the carbene carbon.

Synthesis of $MH(C_6F_5)(CO)L_2$. We attempted to expand the scope of CsF-catalyzed reactions to the transfer of another R_f group. While $Me_3SiC_6F_5$ is not as reactive as Me_3SiCF_3, heating (65 °C) of **1** or **3** and $Me_3SiC_6F_5$ for several hours in THF gives five-coordinate complexes $MH(C_6F_5)(CO)L_2$, **30** (M = Ru) and **31** (M = Os) (eq 8), in good yield. The hydride signal of **30** is a triplet of apparent triplets at high field (−27.6 ppm), in agreement with the hydride being trans to the vacant site. There are five ^{19}F NMR peaks at room temperature, indicating slow rotation around the $Ru-C_6F_5$ bond, and the C_6F_5 lies perpendicular to the P−Ru−P axis. ^1H and ^{19}F NMR spectra are unchanged to −60 °C. This observation rules out the possibility for agostic Ru−F−C bonding from the ortho C−F bond of C_6F_5. Therefore, **30** is a rare example of a persistent 16-electron Ru(II) complexes without a π-donor ligand. The CO stretching frequency (1917 cm^{-1}) of **30** is close to that of $RuH(OTf)(CO)(P^tBu_2Me)_2$ (1921 cm^{-1}), in agreement with C_6F_5 being a very strong electron-withdrawing group. Unlike the phenyl analogue, $RuH(Ph)(CO)L_2$, which reductively eliminates Ph−H readily upon heating in arene solvent, **30** does not eliminate C_6F_5H, even at 100 °C in toluene. The stability of **30** (vs $RuH(Ph)(CO)L_2$) can be attributed to a much stronger $Ru-C_6F_5$ bond.



1,3

30, M = Ru
31, M = Os

Hydrogenolysis of $Ru(CF_2H)F(CO)L_2$: Dependence on Phosphine Ligands. $Ru(CF_2H)F(CO)(P^tBu_2Me)_2$ does not show any reactivity with H_2 at room temperature (or 80 °C) in benzene over 24 h, as the free H_2 peak and the peaks for **7** remain unchanged. The reaction, however, is promoted by addition of CsF (in excess, 80 °C, 5 h) to give only a small amount of CH_2F_2, which is detected by ^{19}F and ^1H NMR spectra. The organometallic products are more complicated and include $RuHF(CO)(P^tBu_2Me)_2$ (47%), $Ru(H)_2(CO)_2(P^tBu_2Me)_2$ (28%), and $RuHF(CO)_2(P^tBu_2Me)_2$ (8%). We attribute the CO source (giving *di*carbonyl products) to some decomposed Ru complexes. In sharp contrast (eq 9), the P^iPr_3 analogue **8** reacts with H_2 at room temperature over 12 h to form CH_2F_2 as a major organic product, along with a 1:2 ratio of $RuHF(CO)(P^iPr_3)_2$ and $RuHF(CO)_2(P^iPr_3)_2$ as the major organometallic products. The reaction also generates an acid (HF), which appears (^1H NMR) as a broad singlet at 12 ppm and a broad peak at −188 ppm in ^{19}F NMR spectrum. HF is responsible for significant broadening of ^{19}F resonances of $RuHF(CO)(P^iPr_3)_2$ and $RuHF(CO)_2(P^iPr_3)_2$ and loss of coupling information (^1H and $^{31}P\{^1H\}$ NMR) of J_{HF} and J_{PF}. These couplings reappear after addition of a small amount of CsF, which removes HF (the peak at 12 ppm disappears in the presence of CsF). The HF source is apparently the reaction of $RuHF(CO)(P^iPr_3)_2$ with excess of H_2, together with the "decomposition" reaction, which liberates CO. Combining this result with eqs 1 and 2, a catalytic hydrogenation of Me_3SiCF_3 to CH_2F_2 can be established in principle (eq 10).

$$\mathbf{8} \xrightarrow{H_2,\ \text{benzene}} CH_2F_2 + RuHF(CO)(P^iPr_3)_2 \qquad (9)$$

$$Me_3SiCF_3 + H_2 \xrightarrow{RuHF(CO)L_2} Me_3SiF + CH_2F_2 \qquad (10)$$

Discussion

Transition metal fluoride complexes have been used as synthetic precursors, in combination with trimethyl silyl reagents Me_3Si-R, for introduction of other functional groups. The driving force of the reaction is the formation of a strong Si−F bond.[7] Our research group has applied this strategy in synthesis of formally 16-electron Ru, Os, and Ir complexes.[36] The reaction often proceeds smoothly and quantitatively. To extend this reaction to a fluorinated R group would open a safe and convenient route to fluoroalkyl complexes. In our earlier communication, the reaction of Me_3SiCF_3 was claimed with $RuHF(CO)L_2$, **1** (L = P^tBu_2Me). We subsequently found that the sample of **1** used in the reaction was contaminated by trace CsF from the synthesis of **1** by salt metathesis of $RuHCl(CO)L_2$ with CsF in acetone. Indeed, pure **1** does not react with Me_3SiCF_3 under the same conditions (THF, 20 °C). If, however, a catalytic amount of CsF is added to the pure sample of $RuHF(CO)L_2$, the reaction proceeds smoothly. This serendipitous

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[33] Irradiation at the frequency of P (or H) of CHFP causes collapse of the fluoride signal (−209 ppm) to a doublet.

[34] Burch, R. R.; Calabrese, J. C.; Ittel, S. D. *Organometallics* **1988**, *7*, 1642.

[35] Burrell, A. K.; Clark, G. R., Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1991**, 609.

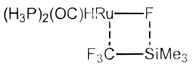
[36] Cooper, A. C.; Huffman, J. C.; Caulton, K. G. *Inorg. Chim. Acta* **1998**, *270*, 261.

discovery seems to make possible a general route to trifluoromethyl complexes (eq 11). We thus screened the reaction with

$$L_nM{-}F + Me_3Si{-}CF_3 \xrightarrow{CsF(cat.)} L_nM{-}CF_3 + Me_3Si{-}F \tag{11}$$

other unsaturated Ru/Os fluorides. However, only OsHF(CO)-L_2 shows a positive result. The fluorides Ru(Ph)(F)(CO)L_2, RuF-(NO)L_2, and RuF(NO)(CO)L_2 are inert to Me_3SiCF_3 even with heating (80 °C). Therefore, reaction 11 is valid only for certain types of fluoride complexes.

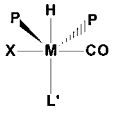
Mechanism of Fluoride Ion Catalysis. It has now been persuasively demonstrated[37,38] that catalytic fluoride reacts with Me_3SiCF_3 to give trigonal bipyramidal $Me_3Si(CF_3)_2^-$ (and Me_3-SiF), and thus this anion is likely to be the CF_3^- transfer reagent functioning under our synthetic conditions. A computational search for a reaction path involving the two unactivated reagents (**M6**) was unsuccessful. The lack of reactivity with other metal fluoride complexes mentioned earlier suggests that the metal centers are not sufficiently Lewis acidic for CF_3^- (not a particularly strong nucleophile) to attack. Indeed, even the much stronger nucleophile MeLi reacts with RuPhF(CO)L_2 only slowly (over 1 week at room temperature). The 16e Ru(0) complex Ru(NO)(F)L_2 adopts a square planar geometry, with the LUMO well protected by the four ligands and not readily accessible for nucleophilic attack. Also, RuF(NO)(CO)L_2 is known to be a weak Lewis acid.[39]



M6

One question arises from this mechanism: which F^- dissociates in eq 1, that from Ru−F, or that from CF_3? It seems more likely that the Ru-bound fluoride is a better leaving group than the carbon-bound one. If the Ru−F bond breaks, the primary product is five-coordinated [RuH(CF_3)(CO)L_2] with CF_3 trans to hydride, in which α-F migration gives the observed isolated product. Dissociation of F^- from CF_3 would form the product directly.

The Origin of Distortion of Six-Coordinate Octahedral Complexes. It is a recurring phenomenon that saturated six-coordinated "octahedral" Ru and Os complexes with the geometry shown below have a remarkable distortion of one trans pair of ligands away from a 180° angle, but the reason is not well understood. Werner and co-workers reported a 141.38(4)° ∠P−Os−P of complex OsHCl(=CH(SiMe$_3$)(CO)(P^{i}Pr$_3$)$_2$ but provided no explanation.[24] Esteruelas and colleagues discovered a case with ∠P−Os−P of 144° in OsH(OH)(η^2-CH$_2$=CH−OC(O)CH$_3$)(CO)(P^{i}Pr$_3$)$_2$.[40] The small angle is retained in solution because $^2J_{PP}$ (165 Hz) is small compared to the normal 250 Hz for a linear P−M−P group. The authors attributed this to steric repulsion of the bulky phosphines and the substituent of the olefin. However, steric repulsion cannot explain the small angle of transient species RuHCl(CH$_2$)(CO)(P^{t}Bu$_2$Me)$_2$ ($^2J_{PP}$ = 166 Hz), where CH$_2$ is not large enough to demand that the phosphines bend away from it.[25] **4** also has an ∠P−Ru−P which deviates significantly from linearity. In contrast, the (O)C−M−X and H−M−L′ angles of all these complexes are close to 180°. On the other hand, when the hydride is replaced by a π-donating ligand halide, the P−M−P angles are much larger and closer to 180°. Thus, in OsCl$_2$(=CHCH=CHPh)(CO)(P^i-Pr$_3$)$_2$, ∠P−M−P is 172°,[41] and that of OsCl$_2$(=CHPh)(CO)-(^{i}Pr$_3$)$_2$ is 167.5°.[24a] Similarly, ∠P−M−P is close to linear in OsCl$_2$(=CCl$_2$)(CO)(PPh$_3$)$_2$[42] and RuCl$_2$[=C(F)(OCH$_2$CMe$_3$)]-(CO)(PPh$_3$)$_2$.[43] The distortion of the hydride complex can be better explained if the electronic rather than steric factors are considered. The common feature of these complexes is the presence of a single-faced π-acceptor L′, which orients its LUMO in-phase with the highest energy metal dπ orbital so that the back-donation is maximized. When L′ is trans to a strong trans-directing ligand such as hydride, the M−L′ σ bond is weakened. This is compensated by bending the P−M−P angle (away from the L′), thus lowering the energy of the metal dπ orbital which affects back-donation. The degree of bending is thus dependent on the π-acidity of the L′. CH$_2$ and CHR are more π-acidic than CF$_2$; thus, a smaller P−M−P angle is expected. The P−M−P bond angle of these carbene complexes is a manifestation of the changing oxidation state of the metal. When the hydride is replaced by a weaker trans-directing and π-donating ligand halide, M−L′ σ bonding is strengthened, and the repulsion between metal dπ and halide p electrons effectively increases π-donation without bending the P−M−P angle. Six-coordinate Ru and Os complexes, MH$_3$XL$_2$ and MH$_2$X$_2$L$_2$, all of which are *unsaturated*, are known to have nonoctahedral geometry, and the electronic origin has studied both theoretically and experimentally.[24b]



α-F Migration: Effects of Metals and Ligands. One well-known reaction of CF$_3$ complexes is that in which, in the presence of Lewis acids as F$^-$ scavenger, the CF$_3$ ligand is transformed to a difluorocarbene. In the compounds discussed here, the unsaturated metal acts as an internal Lewis acid, and the abstracted fluoride becomes coordinated cis to CF$_2$, thus providing a pathway for subsequently re-forming the CF$_3$ group. The thermodynamic preference between MCF$_3$ and F−M=CF$_2$ is highly dependent on the identity of metal and of the ancillary ligands, which directly affect the Lewis acidity of the metal. For example, while RuH(CF$_3$)(CO)L$_2$ spontaneously isomerizes to RuHF(CF$_2$)(CO)L$_2$, the similar compound Ru(CCSiMe$_3$)-(CF$_3$)(CO)L$_2$ is persistent in solution. The π-donor alkynyl ligand in the latter apparently decreases the Lewis acidity of the Ru. Whereas **4** is in fast equilibrium with RuH(CF$_3$)(CO)-L$_2$ at room temperature, the Os analogue **6** is static (based on the fact that there is no observable fast fluoride exchange of Os−F and CF$_2$ by ^{19}F NMR and based on its slow reaction with CO). Nonetheless, at high temperature (100 °C), the reaction of **6** with CO forms OsH(CF$_3$)(CO)$_2$L$_2$, which indicates OsH(CF$_3$)(CO)L$_2$ as a possible intermediate. Both of these observations are consistent with the DFT calculations (Figure 3). Being a 5d metal, Os is a stronger π-donor than Ru, and CF$_2$ is consequently less electrophilic.

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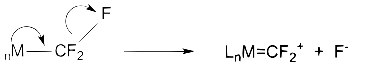
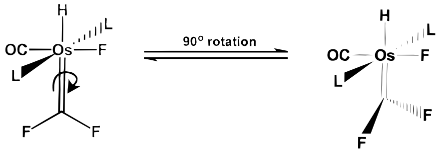
Any general statement that C−F bonds are "strong" and unreactive certainly requires modification for F geminal with a transition metal, and this need not be an unsaturated metal. Heterolytic C−F splitting[44,45] is facilitated both kinetically and thermodynamically because of product stabilization by C/M double bond formation. It follows that this should be promoted most by L_nM moieties which are good π bases (eq 12), and this is certainly true of the octahedral d^6 species studied here. The fact that our *unsaturated* target molecules $MH(CF_3)(CO)L_2$ (M = Ru, Os) need not pay the energetic price of full charge separation in eq 12 (i.e., F^- remains coordinated to M) is only an added benefit of an already attractive rearrangement.



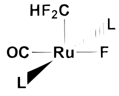
$$L_nM{-}CF_2{-}F \longrightarrow L_nM{=}CF_2^+ + F^- \qquad (12)$$

Rotation of the Fluorocarbene. The orientation of fluorocarbene, a single-face π-acceptor, is determined by the several highest occupied metal d_π orbitals. In all fluorocarbene complexes reported here, the ground state has the carbene p_π orbital perpendicular to the P−M−P axis, with rotation rates highly dependent on the other ligands. For example, in **6**, two carbene fluoride signals have coalesced at 20 °C. When the Os−F is replaced by triflate (**22**, Scheme 3), two relatively sharp carbene fluoride resonances are observed at room temperature. The observation of two different fluoride peaks for **22** is not due to the larger difference in the chemical shifts. In fact, the chemical shift difference of the two fluorides of **22** is smaller (4 ppm) than that observed for **6** (10 ppm). There is no significant steric difference between **6** and **22**. Although CF_3SO_3 is much larger than fluoride, it lies away from the CF_2 group. However, there is a large difference in the electronic influence of these two ligands. Fluoride, being a good π-donor ligand, has filled−filled repulsion between the p electron lone pairs and d_π electrons (the lower two d_π orbitals) of Os, which increases the energy level of the d_π. As a consequence, the higher energy geometry (with the CF_2 plane rotated 90° as shown in eq 13) gains more stabilization from π-back-donation. This leads to a lower rotation barrier for the carbene ligand. The much weaker ligand triflate does not have significant filled−filled repulsion between oxygen lone pairs and the Os d_π electrons, and so the CF_2 rotation barrier is higher. A similar explanation also accounts for the rotation of the Os═CFH bonds of **24** and **25**. **24** has fluorine trans to carbene, while the carbene of **25** is trans to triflate. The energy gap is larger between the high-energy d_π-orbital and the lower energy ones in **24**. An extreme situation for the large rotation barrier for single-faced π-acid ligand occurs when it is bound to a d^2 metal.[46]



(13)

Contrasting 4d/5d Behavior. Comparative studies of analogous reactions for ruthenium and osmium species $MHF(CO)L_2$ have revealed results which, we feel, are quite surprising: redox isomeric forms are preferred for Ru and Os. While unsaturated **7** is the favored form for Ru, saturated **18** is the more stable form for Os. An analogous contrasting thermodynamic preference has been rationalized[47] for the analogous pairs **A** and **B** on the basis of the 5d metal preferring (1) a higher oxidation number, (2) an 18-valence electron count, and (3) more metal ligand bonds. Similar reasoning applies to **7** vs **18**. The preference for **18** over **6** differs in the substructure **C** vs **D**, which may result from the unfavorable trans influence in **C** and the favorable push/pull influence in **D**. Metal/ligand interactions must dominate the thermodynamics here since all evidence suggests C−F bonds are stronger than C−H bonds, which, taken alone, should favor **C**, in contrast to our observations. The CHF carbene should be less of a π-acid than CF_2 due to greater F → C π-donation in the latter.



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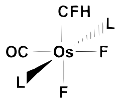
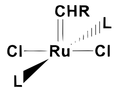
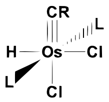


18



A



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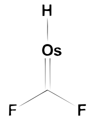
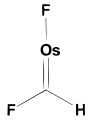


C (6)



D (18)

α-F abstraction occurs not only in unsaturated transition metal CF_3 complexes; it is a rather general phenomenon reported for several main group fluoromethyl complexes. The difference for the late transition metal complexes is that the carbene is stabilized by coordination to the metal. In the case of a metal that has no π-donation ability but is Lewis acidic, the resulting carbene fragment subsequently undergoes oligomerization. Earlier attempts to synthesize CF_3Li and CF_3MgI produced only LiF and MgF_2 by F abstraction.[48] Eujen and Hoge demonstrated that solvent-free $Cd(CF_3)_2$ (more acidic than $Cd(CF_3)_2(DME)$) readily decomposes above −50 °C to give CdF_2 and $(CF_2)_n$ (n = 2, 3).[49] Also related is the unsuccessful earlier attempt to synthesize $(R_f)_3B$ (R_f = perfluoroalkyl). The products are BF_3 and uncharacterized polymers.[50] FCH_2BF_2 also decomposes at room temperature to give BF_3.[51] While the thermodynamic driving force for F abstraction for these main group elements result from the high M−F bond energies, for the late transition metals the driving force could be that the metal gains more electrons (from 16 to 18) and the carbene is stabilized by the π-basic metal.

^{19}F Chemical Shifts of Ru and Os Complexes. ^{19}F NMR spectra have been the most informative tool in characterizing the complexes. The one advantage of this tool comes from the high sensitivity of the ^{19}F chemical shift, which spanned a wide range from +550 (XeF_6) to −500 ppm.[52] While the chemical shift moves downfield as the F content increases (−271.9 (CH_3F), −143.6 (CH_2F_2), −78.6 (CHF_3), and −62.3 ppm (CF_4)), Figure 4 depicts the range of ligand chemical shifts, which shows the following: (1) M═CF_2 fluoride appears at low field, Os═CFH moves to a little higher field, and they are both shifted

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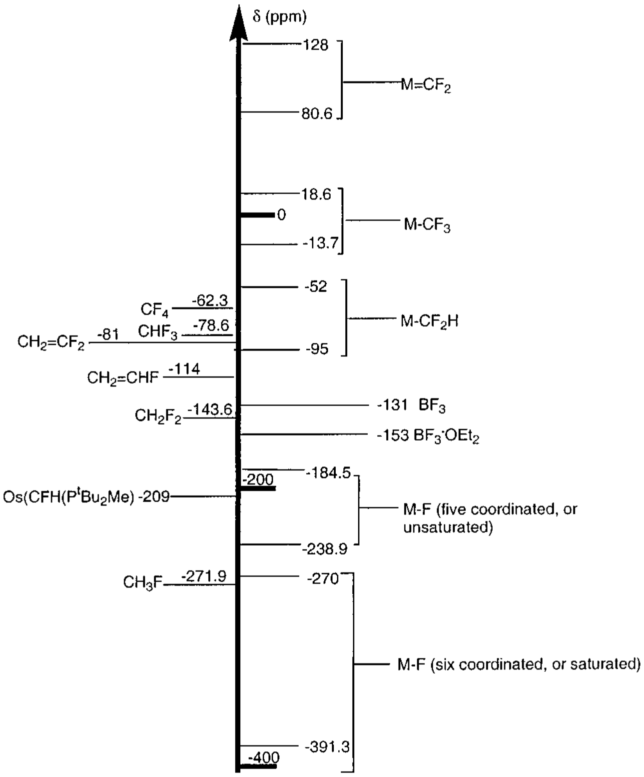


Figure 4. ^{19}F chemical shift of M(=Ru/Os) fluorocarbyl and fluoride. The chemical shifts are referenced to $CFCl_3$ (0 ppm) as an external standard.

downfield in comparison to vinylic CF_2 and CHF units. This trend is comparable to that of the low-field shift of carbene protons, which move from a normal value of 5−6 ppm to around 20 ppm. (2) Chemical shifts of $M-CF_3$ are in a relatively narrow range from 18.6 to −13.7 ppm, and those of $M-CF_2H$ move to higher field (−52 to −95 ppm). They are also downfield in comparison to HCF_3 and CH_2F_2. (3) Five-coordinate Ru/Os complexes of $MRF(CO)L_2$ have lower chemical shifts (−184.5 to −238.9 ppm) than the six-coordinate ones (−270 to −391.3 ppm), each of which falls in a broad (>100 ppm) range. The upfield shift for saturated (six-coordinate) M−F relative to that of five-coordinate ones suggests that the former have a more electron-rich fluoride. This is further supported by the fact that $(C_2H_5)_2O{\cdot}BF_3$ also has a higher ^{19}F chemical shift (−153 ppm) than that of BF_3 (−131 ppm).[52]

Conclusions

We have demonstrated that, in the presence of fluoride as catalyst, Me_3SiCF_3 reacts with the unsaturated Ru(II)/Os(II) fluoride, $MHF(CO)L_2$, to form difluorocarbenes, which are kinetic products. These isomerize to give different thermodynamic products, unsaturated $RuF(CF_2H)(CO)L_2$ or saturated $OsF_2(CFH)(CO)L_2$. These are the first examples of reversible α-F and (irreversible) double α-F migration. Addition of a Brønsted acid has been shown to trigger the conversion of $HMCF_3$ to MCF_2H on Rh and on Ru.[53]

The work reported here also permits some additional conclusions:

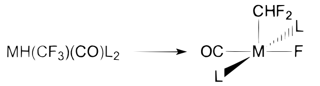
(1) Replacing F on Ru and Os in **4** and **6** speeds the conversion to the thermodynamic product (eq 5 and Scheme 3), even though these are not analogous products (an unsaturated $F-Ru-CF_2H$ species vs a saturated $F_2Os(CHF)$ species).

(2) Replacing H on Ru by a weak π-donor ligand $CCSiMe_3$ speeds the conversion to a unsaturated CF_3 complex (eq 6).

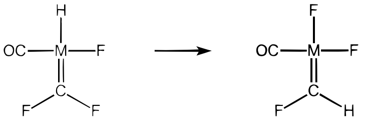
(3) The reagents CO, Me_3NC, MeCN, and perhaps Me_3SiCCH supplement spin saturation transfer in proving eq 4: α-F migration wherein saturated $F-Ru{=}CF_2$ is in equilibrium with an unsaturated, but less stable $Ru-CF_3$ isomer.

(4) Reaction of **6** with CO to give CF_2H species suggests that α-F and/or α-H migration to the carbene does occur for Os, but more slowly than for Ru. However, in contrast to the case for Ru, the Os−CO bond energy is necessary to make such a reaction exergonic.

One perhaps surprising result of these studies is that the conversion of eq 14 is very favorable. How can this be rationalized? This can be analyzed as the conversion of M−H to M−F and of C−F to C−H. While the C−F bond dissociation energy *can* be 40 kcal/mol stronger than that of a C−H bond, this is probably not true of F on a carbon attached to a metal. Moreover, in general, M−F is stronger than M−H, especially in an unsaturated molecule, and especially when CO is present to create a push/pull stabilization. The transformation of eq 15 is perhaps equally surprising, but the above several factors apply equally well here, and agree with the observed exothermicity.



$$MH(CF_3)(CO)L_2 \longrightarrow OC-M(CHF_2)(L)_2-F \qquad (14)$$



$$OC-M(H)(=CF_2)-F \longrightarrow OC-M(F)(=CFH)-F \qquad (15)$$

Experimental Section

All reactions and manipulations were conducted using standard Schlenk and glovebox techniques. Solvents were dried and distilled under argon and stored in airtight solvent bulbs with Teflon closures. Most reagents are commercially available except for NMe_4F, which was obtained by dehydration of NMe_4F hydrate.[54] $RuHF(CO)(P^tBu_2Me)_2$,[55] $RuHCl(CO)(P^iPr_3)_2$,[56] and $OsHCl(CO)(P^tBu_2Me)_2$ were prepared according to the literature. All NMR solvents were dried, vacuum-transferred, and stored in an argon-filled glovebox. ^1H, ^{31}P, ^{19}F, and ^{13}C NMR spectra were recorded on a Varian Gem XL300 or a Unity I400 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent peaks (^1H, ^{13}C), external H_3PO_4 (^{31}P), or external $CFCl_3$ (^{19}F). Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Elemental analyses was performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer at Indiana University.

$RuHF(CF_2)(CO)(P^tBu_2Me)_2$. $RuHF(CO)(P^tBu_2Me)_2$ (2.0 g, 4.2 mmol) was dissolved in THF (20 mL). Me_3SiCF_3 (0.63 mL, 4.6 mmol) and CsF (30 mg, 0.2 mmol) were then added. The color changed from orange to yellow in 30 min. The volatiles were removed, and the residue was dissolved in diethyl ether (10 mL) and cooled to −40 °C for 1 h. Pale yellow crystals formed which were filtered, washed with cold diethyl ether, and dried. Yield: 1.2 g (54%). Anal. Calcd for $C_{20}H_{43}F_3OP_2Ru$: C, 46.23; H, 8.34. Found: C, 46.77; H, 8.23. ^1H NMR (C_6D_6, 20 °C): 1.38 (vt, $N = 7$ Hz, 6H, PCH_3), 1.24 (vt, $N = 13.2$ Hz, 18H, $PC(CH_3)_3$), 1.17 (vt, $N = 13.5$ Hz, 18H, $PC(CH_3)_3$), −3.04 (ttd, $^3J_{HF} = 51$ Hz, $^2J_{HP} = 23$ Hz, $^2J_{HF} = 7.5$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): 68.9 (dt, $^3J_{PF} = 13$ Hz, $^2J_{PF} = 18$ Hz). ^{19}F NMR (C_6D_6, 20 °C): −354

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Table 2. Crystallographic Parameters of RuHF(CF$_2$)(CO)(P^{t}Bu$_2$Me)$_2$ (**4**)

formula	C$_{20}$H$_{43}$F$_3$OP$_2$Ru	fw	519.57
color	pale yellow	space group	*Pbca*
a	15.662(2) Å	T	−172 °C
b	22.825(3) Å	λ	0.71069 Å
c	14.085(1) Å	ρ_{calc}	1.371 g cm^{-1}
V	5035.29 Å^3	μ	7.7 cm^{-1}
Z	8	R (F_o)	0.039
R_w (F_o)	0.046		

($\nu_{1/2}$ = 50 Hz, Ru−F), 122 ($\nu_{1/2}$ = 300 Hz, CF$_2$). The CF$_2$ signal decoalesces to an AMX (X = H) pattern at −80 °C. At this temperature, two rotamers with a ratio of 9:1 can be seen in ^{19}F NMR: for the major rotamer, 128 ($^3J_{HF}$ = 37 Hz, $^2J_{FF}$ = 221 Hz), 114.8 ($^3J_{HF}$ = 46 Hz, $^2J_{FF}$ = 221 Hz); for the minor rotamer, 131.0 ($^3J_{HF}$ = 44 Hz, $^2J_{FF}$ = 216 Hz), 119.4 ($^3J_{HF}$ = 54 Hz, $^2J_{FF}$ = 216 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 20 °C): 254.4 (tm, $^1J_{CF}$ = 498 Hz, CF$_2$), 204.2 (dt, $^2J_{FC}$ = 70 Hz, $^2J_{PC}$ = 12 Hz, CO), 36.5 (vt, N = 18 Hz, P*C*(CH$_3$)$_3$), 36.3 (vt, N = 21.6 Hz, P*C*(CH$_3$)$_3$), 29.81 (m, PC(*C*H$_3$)$_3$), 29.06 (m, PC(*C*H$_3$)$_3$), 5.75 (dvt, $^3J_{FC}$ = 10 Hz, N = 22 Hz, PCH$_3$). IR (C$_6$D$_6$): ν_{CO} = 1937 cm^{-1}. X-ray crystallographic parameters are given in Table 2.

Crystal Structure of RuHF(CF$_2$)(CO)(P^{t}Bu$_2$Me)$_2$. One of the crystals, grown from diethyl ether solution layered with pentane at −40 °C, was attached to a glass fiber with silicone grease and transferred to the goniostat, where it was cooled to −172 °C for characterization and data collection. Systematic extinctions uniquely identified the space group as *Pbca* (No.61). No correction for absorption was carried out (μ(Mo $K\alpha$) = 7.79 cm^{-1}). The structure was solved by a combination of direct methods (MULTAN-78) and Fourier techniques. When all of the non-hydrogen atoms had been refined using anisotropic thermal parameters, the largest peak in the difference map was 0.90e/A^3 in a position that was suitable for the expected hydride atom, H*. The peak was introduced as H*, and the coordinates and thermal parameters were allowed to vary. The final difference map was essentially featureless, the largest peak being 0.58 e/A^3 and the deepest hole 0.57 e/A^3. The crystallographic parameters are available as Supporting Information.

RuHF(CO)(P^{i}Pr$_3$)$_2$. RuHCl(CO)(P^{i}Pr$_3$)$_2$ (1.0 g, 2.0 mmol) and CsF (1.0 g, 6.5 mmol) were mixed in acetone (30 mL) and stirred at room temperature for 12 h. After evaporation of all the volatiles, the residue was extracted with pentane and filtered through a Celite pad. The filtrate was concentrated to ca. 10 mL and cooled to −40 °C, for 12 h. The orange precipitate was filtered, washed with pentane, and dried. Yield: 0.8 g, 85%. Anal. Calcd for C$_{19}$H$_{43}$FOP$_2$Ru: C, 48.58; H, 9.23. Found: C, 48.96; H, 9.53. ^{1}H NMR (C$_6$D$_6$, 20 °C): 2.30 (m, 6H, C*H*(Me)$_2$), 1.25(dvt, $^3J_{HH}$ = 4.8 Hz, N_{PH} = 13.8 Hz, 18H, PCH(C*H$_3$*), 1.20(dvt, J_{HH} = 4.8 Hz, N = 13.8 Hz, 18H, PCH(CH$_3$)., −23.7(td, J_{HF} = 3 Hz, J_{PH} = 14.1 Hz, 1H Ru−*H*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C): 59.1 (d, J_{PF} = 16 Hz).

RuHF(CF$_2$)(CO)(P^{i}Pr$_3$)$_2$. The same procedure as for the synthesis of RuHF(CF$_2$)(CO)(P^{t}Bu$_2$Me)$_2$ was used. Yield: 60%. ^{1}H NMR (C$_6$D$_6$, 20 °C, 300 MHz): 2.34 (m, 6H, PCH$_3$), 1.20 (dvt, J_{HF} = 6.8 Hz, N = 12.4 Hz, 18H, PCH(CH$_3$)), 1.17 (dvt, J_{HH} = 7.2 Hz, N = 12.4 Hz, 18H, PCH(C*H$_3$*), −3.22 (ttd, $^3J_{HF}$ = 49.2 Hz, J_{PH} = 20.4 Hz, $^2J_{HF}$ = 8 Hz, Ru−H). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C): 69.9 (dt, $^2J_{PF}$ = 21.9 Hz, $^3J_{PF}$ = 10.9 Hz). ^{19}F NMR (C$_6$D$_6$, 20 °C): 119.7 (br, $\upsilon_{1/2}$ = 175.3 Hz, 2F, CF$_2$), −391.7 (br, $\upsilon_{1/2}$ = 49 Hz, 1F, Ru−F).

Ru(CF$_2$H)(F)(CO)(P^{t}Bu$_2$Me)$_2$. RuHF(CF$_2$)(CO)(P^{t}Bu$_2$Me)$_2$ **(**500 mg, 1 mmol) was dissolved in THF (5 mL), and the solution was kept at room temperature for 6 h. Evaporation of THF left a yellow solid which was recrystallized from diethyl ether to afford 370 mg of yellow crystals (74%). Anal. Calcd for C$_{20}$H$_{43}$F$_3$OP$_2$Ru: C, 46.23; H, 8.34. Found: C, 46.56; H, 8.17. ^{1}H NMR (THF-*d*$_8$, 20 °C, 300 MHz): 8.21 (td, $^2J_{HF}$ = 59 Hz, $^3J_{FH}$ = 5 Hz, 1H, CF$_2$H), 1.38 (vt, N = 13.2 Hz, 18H, PC(CH$_3$)$_3$), 1.33 (vt, N = 12.3 Hz, PC(CH$_3$)$_3$), 1.34 (overlapping with the signal of PC(CH$_3$)$_3$, PCH$_3$). ^{31}P{^{1}H} NMR (THF-*d*$_8$, 121 MHz): 44.5 (overlapping doublet of virtual triplets, N = 40 Hz, $^2J_{PF}$ = 20 Hz). ^{19}F NMR (THF-*d*$_8$, 20 °C, 282 MHz): −236 (tm, $^2J_{PF}$ = 20 Hz, Ru−F), −52 (dtd, $^2J_{FH}$ = 59 Hz, $^3J_{PF}$ = 17 Hz, $^3J_{FF}$ = 6.3 Hz, CF$_2$H). ^{13}C{^{1}H} NMR (THF-*d*$_8$, 20 °C): 205.1 (dm, $^2J_{CF}$ = 75 Hz, CO), 140.3 (ttd, $^1J_{CF}$ = 293 Hz, $^2J_{PC}$ = 7.5 Hz, $^2J_{CF}$ = 1 Hz, CF$_2$H), 35.5 (vt, N = 17 Hz, P*C*(CH$_3$)$_3$), 35.3 (vt, N = 16 Hz, P*C*(CH$_3$)$_3$), 30.3 (vt, N = 4.9 Hz, PC(*C*H$_3$)$_3$), 29.5 (vt, N = 5 Hz, PC(*C*H$_3$)$_3$), 6.5 (vtt, N = 10.4 Hz, $^4J_{FC}$ = 3 Hz, PCH$_3$) ppm. IR (C$_6$D$_6$): ν_{CO} = 1917 cm^{-1}.

RuF(CF$_2$H)(CO)(P^{i}Pr$_3$)$_2$. Solid RuHF(CF$_2$)(CO)(P^{i}Pr$_3$)$_2$ was transformed to RuF(CF$_2$H)(CO)(P^{i}Pr$_3$)$_2$ on standing at room temperature for 6 months. ^{1}H NMR (THF-*d*$_8$, 20 °C): 8.05 (td, J_{FH} = 60 Hz, J_{HF} = 5 Hz, 1H RuCF$_2$H), 2.52 (m, 6H, PCH(CH$_3$)$_2$), 1.32 (18H, PH(CH$_3$)$_2$), 1.28 (m, 18H, PCH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (THF-*d*$_8$, 20 °C): 46.2 (dvt, N = 40 Hz). ^{19}F NMR (THF-*d*$_8$, 20 °C): −52.0 (dvt, J_{HF} = 60 Hz, N = 40 Hz, CF$_2$H), −238.9 (br, $w_{1/2}$ = 77 Hz, Ru−F). IR (THF): ν(CO) = 1917 cm^{-1}.

Ru(CF$_2$H)(OTf)(CO)(P^{t}Bu$_2$Me)$_2$. To RuHF(CF$_2$)(CO)(P^{t}Bu$_2$Me)$_2$ (200 mg, 0.38 mmol) dissolved in toluene (5 mL) and cooled to −78 °C was added Me$_3$SiOTf (74.5 μL, 0.38 mmol). After the solution was stirred for 15 min and warmed to room temperature, the volatiles were removed in vacuo, and the residue was recrystallized from toluene layered with pentane at −40 °C. Yield: 130 mg (55%). Anal. Calcd for C$_{21}$H$_{43}$F$_5$O$_4$P$_2$Ru: C, 40.84; H, 7.02. Found: C, 40.53; H, 6.60. ^{1}H NMR (C$_6$D$_6$, 20 °C, 300 MHz): 7.72 (tt, $^2J_{FH}$ = 60 Hz, $^3J_{PH}$ = 3.3 Hz, 1H, CF$_2$H), 1.56 (vt, N = 5.7 Hz, 6H, PCH$_3$), 1.05 (vt, N = 13.5 Hz, 18H, PC(CH$_3$)$_3$), 0.89 (vt, N = 12.9 Hz, 18H, PC(CH$_3$)$_3$). ^{19}F NMR (C$_6$D$_6$, 20 °C, 282 MHz): −54.9 (dt, $^2J_{HF}$ = 60 Hz, $^3J_{PF}$ = 17.5 Hz, CF$_2$H), −79.4 (s, O$_3$SCF$_3$).^{13}C{^{1}H} NMR (toluene-*d*$_8$, −20 °C, 75 MHz): 204.6 (tt, $^2J_{PC}$ = 16 Hz, $^3J_{CF}$ = 7.6 Hz, CO), 129 (tt, $^1J_{CF}$ = 309 Hz, $^3J_{PC}$ = 6.3 Hz, CF$_2$H). 120.7 (quartet, $^1J_{PF}$ = 318 Hz, O$_3$-SCF$_3$), 36.6 (vt, N = 19 Hz, P*C*(CH$_3$)$_3$), 36.0 (vt, N = 19 Hz, P*C*(CH$_3$)$_3$), 29.4 (s, PC(*C*H$_3$)$_3$), 28.9 (s, PC(*C*H$_3$)$_3$), 4.78 (vt, N = 18 Hz, PCH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 20 °C, 121 MHz): 47.3 (vt, N = 34 Hz). IR (C$_6$D$_6$): ν_{CO} = 1944 cm^{-1}.

RuH(CF$_3$)(CO)$_2$(P^{t}Bu$_2$Me)$_2$. RuHF(CF$_2$)(CO)(P^{t}Bu$_2$Me)$_2$ (100 mg, 0.19 mmol) was dissolved in diethyl ether (5 mL). The solution was freeze−pump−thaw degassed and then stirred under 1 atm of CO gas. The solution color changed immediately to pale yellow. After the solution was cooled to −40 °C for several hours, white crystals formed. These were filtered, washed with diethyl ether, and dried in vacuo. Yield: 85 mg (82%). Anal. Calcd for C$_{21}$H$_{43}$F$_3$O$_2$P$_2$Ru: C, 46.06; H, 7.91. Found: C, 46.26; H, 7.87. ^{1}H NMR (toluene-*d*$_8$, 60 °C, 300 MHz): 1.40 (vt, N = 5.7 Hz, 6H, PCH$_3$), 1.23 (vt, N = 12.9 Hz, 18H, PC(CH$_3$)$_3$), 1.22 (vt, N = 13.2 Hz, 18H, PC(CH$_3$)$_3$), −6.51 (tq, $^2J_{PH}$ = 23.4 Hz, $^3J_{FH}$ = 6.6 Hz, 1H, Ru−H). ^{19}F NMR (toluene-*d*$_8$, 60 °C, 300 MHz): −1.39 (broad, CF$_3$). ^{31}P{^{1}H} NMR (toluene-*d*$_8$, 60 °C, 121 MHz): 63.5. ^{13}C{^{1}H} NMR (toluene-*d*$_8$, 60 °C, 75 MHz): 10.65 (br, s P*C*H$_3$), 30.2, 30.4 (s, P^{t}Bu), 36.9, 37.1 (vt, N = 15 Hz, P*C*(CH$_3$)$_3$), 148.0 (qt, $^1J_{CF}$ = 358.6 Hz, $^3J_{PC}$ = 12 Hz, CF$_3$), 203.7 (t, $^2J_{PC}$ = 6 Hz, CO cis to CF$_3$), 205.8 (tq, $^2J_{PC}$ = 14 Hz, $^3J_{CF}$ = 15 Hz, CO trans to CF$_3$). IR (C$_6$D$_6$): 2029, 1927 (ν(CO)).

RuH(CF$_3$)(CO)(^{13}CO)(P^{t}Bu$_2$Me)$_2$. When ^{13}CO was used in the above experiment, RuH(CF$_3$)(CO)(^{13}CO)(P^{t}Bu$_2$Me)$_2$ was obtained. ^{1}H NMR(toluene-*d*$_8$, 60 °C, 300 MHz): 1.39 (vt, N = 6 Hz, 6H, PCH$_3$), 1.22 (vt, N = 12.9 Hz, 18H, P^{t}Bu), 1.21 (vt, N = 13.2 Hz, 18H, P^{t}Bu), −6.51(dtq, $^2J_{CH}$ = 29 Hz, $^2J_{PH}$ = 25 Hz, $^3J_{FH}$ = 6.6 Hz, 1H, Ru−*H*). ^{13}C NMR (toluene-*d*$_8$, 60 °C, 75 MHz): 203.8 (doublet of apparent sextet, $^2J_{CH}$ = 29 Hz, $^3J_{FC}$ = $^2J_{PC}$ = 6 Hz, Ru−^{13}CO). The ^{13}C{^{1}H} NMR resonance for the *C*O carbon showed only an apparent sextet. This proves that the 29 Hz coupling constant is from the trans hydride. There are two rotamers[27] of this product due to the hindered rotation of the Ru−P bond; at room temperature they interconvert slowly, causing broadening of the NMR signals and loss of spin coupling. At higher temperatures (>60 °C), the rotation is faster and the two isomers coalesce; therefore, the NMR signals become sharper. This problem can be avoided if P^{i}Pr$_3$ is used in place of P^{t}Bu$_2$Me. Thus, the NMR spectrum of RuH(CF$_3$)(CO)(^{13}CO)(P^{i}Pr$_3$)$_2$ (prepared by the same method as the P^{t}Bu$_2$Me analogue) at 25 °C in C$_6$D$_6$ shows sharp signals. ^{13}C NMR (C$_6$D$_6$, 75 MHz, 20 °C): 204 (dtq, $^2J_{CH}$ = 28 Hz, $^2J_{PC}$ = $^3J_{FC}$ = 6.4 Hz, Ru−CO). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 20 °C): −6.1 (dtq, $^2J_{CH}$ = 28 Hz, $^2J_{PH}$ = 21 Hz, $^3J_{FH}$ = 7 Hz). Again, the large coupling constant (28 Hz) of hydride to the ^{13}CO supports the trans disposition of the these ligands.

Ru(CF$_3$)(CCSiMe$_3$)(CO)(P^{t}Bu$_2$Me)$_2$. RuH(F)(CF$_2$)(CO)(P^{t}Bu$_2$Me)$_2$ (0.30 g, 0.58 mmol) was dissolved in C$_6$H$_6$ (5 mL). To the yellow solution was added Me$_3$SiCCH (160 μL, 1.2 mmol). The solution color changed immediately to orange. After the solution was stirred for 30 min, the volatiles were removed, and the residue was dissolved in tetramethylsilane and filtered through a Celite pad. The filtrate was concentrated to ca. 2 mL and cooled at −40 °C. Orange crystals were obtained after 2 days. ^{1}H NMR (C_6D_6, 20 °C, δ): 0.37 (s, 9H, $SiMe_3$), 1.08 (vt, $N = 12.6$ Hz, 18H, P^tBu), 1.15 (vt, $N = 12.6$ Hz, 18H, P^tBu), 1.70 (vt, $N = 6.3$ Hz, 6H, PMe). ^{19}F NMR (C_6D_6, 20 °C, δ): 18.6 (t, $J_{PF} = 11.8$ Hz, CF_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C, δ): 45.75 (q, $J_{PF} =$ 11.8 Hz, P^tBu_2Me).

$RuH(CF_3)(CNCH_3)(CO)(P^tBu_2Me)_2$. $RuHF(CF_2)(CO)(P^tBu_2Me)_2$ (10 mg, 0.019 mmol) was dissolved in C_6D_6 (0.5 mL), and $CNCH_3$ (1 μL) was added to the solution. The yellow color of the solution faded immediately. Spectroscopic analysis revealed clean formation of $RuH(CF_3)(CNCH_3)(CO)(P^tBu_2Me)_2$. ^{1}H NMR (400 MHz, 20 °C): 2.34 (s, 3H, $CNCH_3$), 1.54 (vt, $N = 5.3$ Hz, 6H, PCH_3), 1.34 (vt, $N = 12.3$ Hz, $PC(CH_3)_3$), 1.31 (vt, $N = 12.3$ Hz, $PC(CH_3)_3$), −7.90 (tq, $J_{PH} = 26$ Hz, $J_{FH} = 6.3$ Hz, 1H, Ru−H). $^{31}P\{^1H\}$ NMR (162 MHz, 20 °C): 64.3 (br). ^{19}F NMR (376 MHz, 20 °C): −13.7 (doublet of broad triplets, J(FH) = 6H, Ru−CF_3).

$RuH(CF_3)(NCCD_3)(CO)(P^tBu_2Me)_2$. $RuHF(CF_2)(CO)(P^tBu_2Me)_2$ was dissolved in CD_3CN (0.5 mL). NMR spectroscopic data revealed clean formation of $RuH(CF_3)(NCCD_3)(CO)(P^tBu_2Me)_2$. ^{1}H NMR (300 MHz, 20 °C): 1.35 ($N = 12.4$ Hz, $PC(CH_3)_3$), 1.32 (vt, $N = 12.5$ Hz, $PC(CH_3)_3$), −9.73 (tq, $J_{PH} = 22$ Hz, $J_{FH} = 19$ Hz, Ru−H). $^{31}P\{^1H\}$ (121 MHz, 20 °C): 58.7 (q, $J_{PF} = 6$ Hz, Ru−P). ^{19}F NMR (282 MHz, 20 °C): (dq, $J_{FH} = 19$ Hz, $J_{PF} = 6$ Hz, Ru−CF_3).

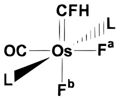
NMR Monitoring of the Reaction of NMe_4F with $RuHF(CF_2)(CO)(P^tBu_2Me)_2$. $RuHF(CF_2)(CO)(P^tBu_2Me)_2$ (10 mg, 0.019 mmol) and anhydrous NMe_4F (7.0 mg, 0.086 mmol) were mixed in THF-d_8 (0.5 mL) in an NMR tube. Fifteen minutes later, the light yellow heterogeneous solution was analyzed, revealing ca. 85% formation of $[RuH(CF_3)(F)(CO)(P^tBu_2Me)_2]NMe_4$. ^{1}H NMR (300 MHz, 20 °C): −8.5 (apparent sextet of doublets, $^3J_{PH} = {}^3J_{FH} = 20$ Hz, $^2J_{FH} = 5.4$ Hz, 1H, Ru−H), 1.33 (vt, $N = 14.4$ Hz, $PC(CH_3)_3$, 1.38 (vt, $N = 14.4$ Hz, $PC(CH_3)_3$) (PCH_3 peak is covered by the ^{t}Bu proton resonances), 3.31 (s, 12H, NMe_4). $^{31}P\{^1H\}$ NMR (121 MHz): 21 (dq, $^2J_{PF} = 16$ Hz, $^3J_{PF} = 6$H, Ru−P). ^{19}F NMR (282 MHz, 20 °C): −325 (m, Ru−F), −10.5 (doublet of apparent quartets, $J_{HF} = 21$ Hz, $J_{PF} = J_{FF} = 6$ Hz, Ru−CF_3). IR (THF-d_8): 1910 (ν(CO)).

$OsHF(CO)(P^tBu_2Me)_2$. $OsHCl(CO)(P^tBu_2Me)_2$ (300 mg, 0.52 mmol) and CsF (240 mg, 1.6 mmol) were mixed in acetone (20 mL) and stirred at room temperature for 2 h. The solution was filtered, and the solid on the frit was washed with acetone. The combined filtrate and washings were evaporated in vacuo, and the residue was dissolved in pentane and filtered to remove a small amount of insoluble white solid. The filtrate was cooled at −40 °C for 3 h before orange crystals were grown. Yield: 0.21 g (69%). Anal. Calcd for $C_{19}H_{43}FOP_2Os$: C, 40.86; H, 7.76. Found: C, 40.90; H, 7.75. ^{1}H NMR (C_6D_6, 20 °C, 300 MHz): 1.34 (vt, $N = 5$ Hz, 6H, PCH_3), 1.24 (vt, $N = 12.6$ Hz, 18H, $PC(CH_3)_3$), 1.241 (vt, $N = 14$ Hz, 18H, $PC(CH_3)_3$), −32.32 (dt, $J_{HF} = 9.3$ Hz, $J_{PH} = 14$ Hz, 1H, Os−H). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C, 121 MHz): 44.5 (d, $J_{PF} = 26$ Hz). ^{19}F NMR: −184.5 (dt, $J_{HF} = 9$ Hz, $J_{PF} = 26$ Hz). IR (C_6D_6, cm^{-1}): 1877 (νCO).

$OsHF(CO)_2(P^tBu_2Me)_2$. $OsHF(CO)(P^tBu_2Me)_2$ (30 mg, 0.059 mmol) was dissolved in toluene-d_8 (0.5 mL) and degassed. The solution was charged with CO (1 atm). Within the time of mixing, the color faded. NMR analysis revealed clean formation of $OsHF(CO)(P^tBu_2Me)_2$. ^{1}H NMR (C_7D_8, 20 °C, 400 MHz): 1.50 (vt, $N = 6.6$ Hz, 6H, PCH_3), 1.30 (vt, $N = 13.5$ Hz, 18H, $PC(CH_3)_3$), 1.26 (vt, $N = 12.8$ Hz, 18H, $PC(CH_3)_3$), −2.36 (dt, $J_{HF} = 13$ Hz, $J_{HP} = 21$ Hz, Os−H). $^{31}P\{^1H\}$ NMR (C_7D_8, 162 MHz, 20 °C): 35.7 (d, $J_{PF} = 30$ Hz). ^{19}F NMR (C_7D_8, 376 MHz, 20 °C): −391.3 ($J_{FH} = 12$ Hz, $J_{PF} = 30$ Hz). $^{13}C\{^1H\}$ NMR (C_7D_8, 75 MHz, 20 °C): 189.7 (dt, $J_{CF} = 11.5$ Hz, $J_{PC} = 5.7$ Hz, CO, cis to F), 183.6 (dt, $J_{FC} = 68$ Hz, $J_{PC} = 7$ Hz, CO, trans to F), 35.6 (vtd, $N = 23$ Hz, $J_{CF} = 6.7$ Hz, $PC(CH_3)_3$), 29.7 (s, $PC(CH_3)_3$), 29.4 (s, $PC(CH_3)_3$), 5.4 (vtd, $J_{CF} = 7.4$ Hz, $N = 27$ Hz, PCH_3). IR (C_7D_8): 1969.6, 1896.3 (ν(CO)).

$OsHF(CF_2)(CO)(P^tBu_2Me)_2$. $OsHF(CO)(P^tBu_2Me)_2$ (150 mg, 0.27 mmol) was dissolved in fluorobenzene (5 mL). To the mixture was added CsF (2.8 mg, 0.018 mmol), followed by Me_3SiCF_3 (42 μL, 0.27 mmol). The mixture was stirred at 80 °C for 30 min. The solution color changed from bright orange to pale yellow. The volatiles were stripped off, and the residue was extracted with diethyl ether and filtered. The filtrate was concentrated to ca. 2 mL and cooled to −40 °C for 4 days. White crystals formed. These were separated, washed with cold diethyl ether, and dried (100 mg (60%)). Anal. Calcd for $C_{20}H_{43}F_3OP_2Os$: C, 39.51; 7.13. Found: C, 39.55; H, 7.56. ^{1}H NMR (toluene-d_8, 20 °C, 300 MHz): 1.46 (vt, $N = 7.5$ Hz, 6H, PCH_3), 1.23 (vt, $N = 13.5$ Hz, 18H, $PC(CH_3)_3$), 1.19 (vt, $N = 13.5$ Hz, 18H, $PC(CH_3)_3$), −2.46 (ttd, $^3J_{HF} = 44.7$ Hz, $^2J_{PH} = 26.4$ Hz, $^2J_{HF} = 12$ Hz, 1H, Os−H). $^{31}P\{^1H\}$ NMR (toluene-d_8, 20 °C): 41.0 (dt, $^2J_{PF} = 26$ Hz, $^3J_{PF} = 2.4$ Hz). ^{19}F NMR (toluene-d_8, 20 °C, 282 MHz): −361.0 ($\upsilon_{1/2} = 113.8$ Hz); CF_2 resonances are coalesced to baseline. At 50 °C, a broad peak is seen at 94.7 ($\upsilon_{1/2} = 759$ Hz). At −60 °C, the peak decoalesces to two AX peaks: one, at δ 104.9, is a doublet of doublets ($^2J_{FF} = 155$ Hz, $^3J_{HF} = 35$ Hz), and the other is a doublet of doublets of doublets ($^2J_{FF} = 155$ Hz, $^3J_{FH} = 51$ Hz, $^3J_{FF} = 28$ Hz) centered at δ 85.3. Although no definitive assignment of these two peaks is possible, the latter peak shows coupling with (Os)−F, while the former does not. It is therefore likely that the coupling is through space and that (C)−F, which shows the coupling with (Os)−F, is proximal. $^{13}C\{^1H\}$ NMR (toluene-d_8, 20 °C, 100 MHz): 235.3 (tdt, $^1J_{CF} = 447$ Hz, $^2J_{CF} = 13$ Hz, $^2J_{PC} = 4.5$ Hz. CF_2), 182.2 (dt, $^2J_{FC} = 72$ Hz, $^2J_{PC} = 7.5$ Hz, CO), 36.6 (vt, $N = 20$ Hz, $PCMe_3$) 36.3 (vt, $N = 20$ Hz, $PCMe_3$), 29.8 (s, $PC(CH_3)_3$, 29.6 s, $PC(CH_3)_3$), 5.75 (dvt, $J_{CF} = 8.4$ Hz, $N = 29$ Hz, PCH_3).

$OsF_2({=}CHF)(CO)(P^tBu_2Me)_2$. In a sealed NMR tube, $OsHF(CF_2)(CO)(P^tBu_2Me)_2$ (10 mg, 0.018 mmol) was dissolved in toluene-d_8 and heated at 100 °C for 8 h to cleanly give $OsF_2({=}CHF)(CO)(P^tBu_2Me)_2$ (see **18** for F labeling). ^{1}H NMR (toluene-d_8, 20 °C, 300 MHz): 15.2 (dd, $^2J_{FH} = 80$ Hz, $^3J_{FbH} = 18.4$ Hz, $^3J_{FaH} = 8.3$ Hz, 1H, (Os)=C*H*F), 1.41 (vt, $N = 7.7$ Hz, PCH_3), 1.22 (vt, $N = 13.5$ Hz, 18H, $PC(CH_3)_3$), 1.19 (vt, $N = 13.5$ Hz, 18H, $PC(CH_3)_3$). $^{31}P\{^1H\}$ NMR (toluene-d_8, 20 °C): 31.4 (dd, $J_{FbP} = 43$ Hz, $J(F^aP) = 20$ Hz). $^{13}C\{^1H\}$ NMR (toluene-d_8, 20 °C): 275.5 (ddtd, $^1J_{FC} = 364$ Hz, $J(F^bC) = 81$ Hz, $^3J_{PC} = 17$ Hz, $^2J_{FaC} = 9$ Hz, Os=*C*HF), 181.7 (dtd, $J(F^aC) = 80$ Hz, J(PC) = 7.5 Hz, $J(F^bC) = 2.8$ Hz, Os−CO), 37.0 (vt, $N = 11$ Hz, P*C*Me_3), 36.0 (vt, $N = 11$ Hz, P*C*Me_3), 29.8 (s, $PC(CH_3)_3$), 29.4 (s, $PC(CH_3)_3$), 3.54 (vt of dd, $N = 27$ Hz, $^2J_{CF} = 5.8$ Hz, $^2J_{CF} = 3.6$ Hz, P*C*H_3). $^{19}F\{^1H\}$ NMR (toluene-d_8, 20 °C): 80.6 (dm, $J(FF^b) = 80$ Hz, (Os)=CH*F*), −274.2(ddt, $J(F^bF^a) = 121$ Hz, $J(PF^a) = 20$ Hz), $J(FF^a) = 12$ Hz,Os−F^b), −270.7(ddt, $J(F^aF^b) = 121$ Hz, $J(FF^b) = 79$ Hz, $J(PF^b) = 45$ Hz, Os−F^b) IR (C_6D_6): 1937 (ν(CO)). The $^{31}P\{^1H\}$ NMR spectrum broadens only slightly at −70 °C, and so does the carbene proton signal (with loss of spin coupling to F^a and F^b), indicative of fast rotation around the Os=CFH bond even at low temperature.



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Reaction of $OsHF(CF_2)(CO)(P^tBu_2Me)_2$ with Water. $OsHF(CF_2)(CO)(P^tBu_2Me)_2$ (30 mg, 0.049 mmol) was dissolved in C_6D_6 (0.5 mL) in an NMR tube. Water (0.1 μL) was added. Ten minutes after the addition, there was not much change in the NMR signals of $OsHF(CF_2)(CO)(P^tBu_2Me)_2$, and the water appeared at 1.45 ppm as a broad singlet. Three hours later, the water was consumed, and $OsHF(CO)_2(P^tBu_2Me)_2$ was formed along with HF. ^{1}H NMR (300 MHz, 20 °C) of HF: 10.8 (d, $J_{HF} = 445$ Hz). ^{19}F NMR of HF: −187.4 (d, $J_{FH} = 445$ Hz).[57] At this moment, starting material dominates, although a small amount of $OsF_2(CFH)(CO)(P^tBu_2Me)_2$ is also formed. After 24 h at room temperature, $OsF_2(CFH)(CO)(P^tBu_2Me)_2$ and $OsHF(CO)_2(P^tBu_2Me)_2$ are the only phosphine-containing products.

$OsF_2(CFH(P^tBu_2Me))(CO)_2(P^tBu_2Me)$. $OsF_2(CFH)(CO)(P^tBu_2Me)_2$ (30 mg, 0.047 mmol) was dissolved in toluene-d_8 (0.5 mL). The solution was freeze−pump−thawed three times and charged with 1 atm of CO. The mixture was heated in a 110 °C oil bath for 24 h. NMR spectroscopic analysis revealed clean formation of $OsF_2(CFH(P^tBu_2$-

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(57) The scalar coupling constant for HF in the gas phase is measured as 529 Hz: Muenter, J. S.; Klemperer, W. *J. Chem. Phys.* **1970**, *52*, 6033.

Me))$(CO)_2(P^tBu_2Me)$. The solvent was removed, and the residue was washed with pentane and dried to give a white powder. Anal. Calcd for $C_{21}H_{43}F_3O_2P_2Os$: C, 39.60; H, 6.81. Found: C, 40.00; H, 6.47. ^{1}H NMR (toluene-d_8, 20 °C, 300 MHz): 7.21 (dm, $^2J_{FH}$ = 47 Hz, 1H, $CHF(P^tBu_2Me)$), 1.68 (d, J = 13.8 Hz, 3H, PCH_3), 1.48 (d, J = 8.1 Hz, 3H, PCH_3), 1.38 (d, J = 12.6 Hz, 9H, $PC(CH_3)_3$), 1.34 (d, J = 12.6 Hz, 9H, $PC(CH^3)_3$), 1.24 (d, J = 14.4 Hz, 9H, $PC(CH_3)_3$), 0.80 (d, J = 13.2 Hz, 9H, $PC(CH_3)_3$). $^{31}P\{^1H\}$ NMR (toluene-d_8, 20 °C, 121 MHz): 49.9 (dd, $^2J_{PF}$ = 58 Hz, J_{PP} = 17 Hz, $CHF(P^tBu_2Me)$, 24.3 (m, Os-P^tBu_2Me). ^{19}F NMR (toluene-d_8, 376 MHz, 20 °C): −209.2 (dd, $^2J_{HF}$ = 48 Hz, $^2J_{PF}$ = 58 Hz, $CHF(P^tBu_2Me)$), −274.0 (dm, $^2J_{FF}$ = 142 Hz, Os−F), −279 (dm, $^2J_{FF}$ = 134 Hz, Os−F). $^{13}C\{^1H\}$ NMR (toluene-d_8, 20 °C, 100.6 MHz): 185.0 (d, $^2J_{CF}$ = 83 Hz, Os−CO), 182.8 (d, $^2J_{CF}$ = 88 Hz, Os−CO), 94.0 (ddm, $^1J_{CF}$ = 184 Hz, J_{PC} = 112 Hz, Os−$CHF(^tBu_2Me)$), 36.2 (d, $^1J_{PC}$ = 17 Hz, $PC(CH_3)_3$), 34.7 (d, $^1J_{PC}$ = 32 Hz, $PC(CH_3)_3$), 34.3 (d, J_{PC} = 36 Hz, $PC(CH_3)_3$), 4.51 (d, J_{PC} = 25.8 Hz), 4.51 (m, PCH_3). IR (toluene-d_8, cm^{-1}): 1990, 1912 (ν(CO)).

$OsF(CF_2H)(CO)_2(P^tBu_2Me)_2$. $OsHF(CF_2)(CO)(P^tBu_2Me)_2$ (20 mg, 0.036 mmol) was dissolved in toluene-d_8 (0.5 mL), and the solution was degassed, charged with CO (1 atm), and heated for 12 h. NMR spectroscopic analysis revealed clean formation of $OsF(CF_2H)(CO)_2(P^tBu_2Me)_2$. ^{1}H NMR (20 °C): 7.70 (ttd, $^2J_{FH}$ = 50 Hz, J_{PH} = 5.3 Hz, $^3J_{FH}$ = 3.3 Hz, Os−CF_2H), 1.47, (vt, N = 6.3 Hz, PCH_3), 1.27, vt, N = 13.2 Hz, $PC(CH_3)_3$), 1.19 (N = 13 Hz, $PC(CH_3)_3$). ^{19}F NMR (20 °C): −95.0 (br, $\upsilon_{1/2}$ = 336 Hz, 2F, CF_2H), −361.5 (t, J_{PF} = 22 Hz, Os−F). $^{13}C\{^1H\}$ NMR (20 °C): 187.7 (m, CO^b), 183.0 (dm, J_{CF} = 70 Hz, CO^a), 133.3 (tdt, $^1J_{CF}$ = 271 Hz, $^2J_{FC}$ = 16.3 Hz, J_{PC} = 7.7 Hz, Os−CF_2H), 37.7 (vt, N = 22 Hz, $PCMe_3$), 37.6 (vt, N = 22 Hz, $PCMe_3$), 30.2 (s, $PC(CH_3)_3$), 30.1 (s, $PC(CH_3)_3$), 6.09 (vt, N = 26 Hz, PCH_3). $^{31}P\{^1H\}$ NMR (20 °C): 16.0 (br).

$OsH(CF_3)(CO)_2(P^tBu_2Me)_2$. When the reaction of $OsHF(CF_2)(CO)(P^tBu_2Me)_2$ and CO was monitored after 1 h of heating, a small amount of $OsH(CF_3)(CO)_2(P^tBu_2Me)_2$ was observed, along with some $OsF(CF_2H)(CO)_2(P^tBu_2Me)_2$. After longer heating, the CF_3 complex disappeared, and only $OsF(CF_2H)(CO)_2(P^tBu_2Me)_2$ remained. ^{1}H NMR (toluene-d_8, 300 MHz, 60 °C): −6.73 (tq, J_{PH} = 24 Hz, J_{FH} = 7.5 Hz, Os−H), 1.51 (vt, N = 6.6 Hz, PCH_3). The *tert*-butyl protons are overlapping with those of $OsHF(CF_2)(CO)(P^tBu_2Me)_2$ and are not assigned. $^{31}P\{^1H\}$ NMR (60 °C, 121 MHz): 26 (br). ^{19}F NMR (60 °C): −2.88 (br). The spectral features are similar to those of the Ru analogue, $RuH(CF_3)(CO)_2(P^tBu_2Me)_2$.

$Os(CFH)(F)(OTf)(CO)(P^tBu_2Me)_2$. In an NMR tube, $OsHF(CF_2)(CO)(P^tBu_2Me)_2$ (20 mg, 0.036 mmol) was dissolved in toluene-d_8 (0.5 mL). To the solution was added Me_3SiOTf (6.4 μL 0.036 mmol). After 30 min, the $^{31}P\{^1H\}$NMR spectra revealed three products: $OsH(OTf)(CF_2)(CO)(P^tBu_2Me)_2$, $Os(CF_2H)(OTf)(CO)(P^tBu_2Me)_2$, and $OsF(CHF)(OTf){-}(CO)(P^tBu_2Me)_2$. After 3 h at room temperature, $OsF(CHF)(OTf)(CO)(P^tBu_2Me)_2$ was the only product.

Spectroscopic data for $OsH(OTf)(CF_2)(CO)(P^tBu_2Me)_2$ follow. ^{1}H NMR: −1.96 (virtual triplet of triplets, N = 84 Hz, J_{PH} = 27 Hz, Os−H). $^{13}P\{^1H\}$ NMR: 46.1 (s). ^{19}F NMR: 107.1 (dd, J_{FF} = 155 Hz, J_{HF} = 33 Hz, Os═CF_2), 104.4 (dd, J_{FF} = 155 Hz, J_{FH} = 52 Hz, Os═CF_2), −76.8 (s, CF_3SO_3).

Spectroscopic data for $Os(CF_2H)(OTf)(CO)(P^tBu_2Me)_2$ follow. ^{1}H NMR: 7.26 (tt, J_{HF} = 62.4 Hz, J_{PH} = 3 Hz, Os−CF_2H). ^{19}F NMR: −54.1 (dt, J_{FH} = 61 Hz, J_{PF} = 16 Hz, Os−CF_2H), −76.6 (s, CF_3SO_3). $^{31}P\{^1H\}$ NMR: 32.7 (t, J_{PF} = 16 Hz).

Spectroscopic data for $OsF(CHF)(OTf)(CO)(P^tBu_2Me)_2$ follow. ^{1}H NMR (20 °C): 15.2 (brd, J_{FH} = 87 Hz, 1H, Os═CFH), 1.60 (vt, N = 7.7 Hz, 6H, PCH_3), 1.11 (vt, N = 13 Hz, 18H, $PC(CH_3)_3$), 1.04 (vt, N = 13 Hz, 18H, $PC(CH_3)_3$). $^{31}P\{^1H\}$ NMR (20 °C): 41.8 (br, $\upsilon_{1/2}$ = 436 Hz, Os−P).

NMR data of the major isomer follow. ^{1}H NMR (−60 °C): 14.2 (dd, $^2J_{FH}$ = 80 Hz, $^3J_{FH}$ = 5.8 Hz, Os═CF*H*), 1.60 (br, 6H, PCH_3), 1.15 (br, 18H, $PC(CH_3)_3$), 0.72 (br, 18H, $PCCH_3)_3$). $^{31}P\{^1H\}$ NMR (−60 °C): 37.2 (d, J_{PF} = 19 Hz, Os−P^tBu_2Me). ^{19}F NMR (376 MHz, −60 °C): 101.4 (d, J_{FH} = 79 Hz, Os═C*F*H), −75.8 (s, CF_3SO_3), −285.6 (br, Os−F).

Spectroscopic data for the minor isomer follow. ^{1}H NMR (−60 °C): 15.9 (dd, $^2J_{FH}$ = 72 Hz, $^3J_{FH}$ = 15 Hz, Os═CF*H*), 1.41 (vt, N = 8.2 Hz, 6H, PCH_3), 1.03 (vt, N = 12 Hz, $PC(CH_3)_3$), 0.86 (vt, N = 13 Hz, $PC(CH_3)_3$). $^{31}P\{^1H\}$ NMR (−60 °C): 47.2 (d, J_{PF} = 44 Hz). ^{19}F NMR (376 MHz, −60 °C): 86.3 (dd, J_{FH} = 72 Hz, J_{FF} = 75 Hz, Os═C*F*H), −285.6 (m, overlapping with that of the major isomer, Os−F).

$Os({=}CFH)(OTf)_2(CO)(P^tBu_2Me)_2$. In an NMR tube, $OsHF(CF_2)(CO)(P^tBu_2Me)_2$ (20 mg, 0.036 mmol) was dissolved in C_6D_6 (0.5 mL). To the solution was added Me_3SiOTf (12.8 μL, 0.072 mmol), and the mixture was kept at room temperature for 3 h. NMR spectroscopic analysis revealed clean formation of $Os({=}CFH)(OTf)_2(CO)(P^tBu_2Me)_2$. ^{1}H NMR (20 °C, 300 MHz): 15.6 (d, J_{FH} = 76 Hz, 1H, Os═CFH), 1.83 (vt, N =7.9 Hz, 6H, PCH_3), 1.13 (vt, N = 14.3 Hz, 18H, $PC(CH_3)_3$), 0.97 (vt, N = 14.3 Hz, 18H, $PC(CH_3)_3$). $^{31}P\{^1H\}$ NMR (20 °C): 45.4 (s). ^{19}F NMR (20 °C): −79.0 ($\upsilon_{1/2}$ = 15 Hz, s).

$RuH(C_6F_5)(CO)(P^tBu_2Me)_2$. $RuHF(CO)(P^tBu_2Me)_2$ (0.30 g, 0.64 mmol), $Me_3SiC_6F_5$ (134 μL, 0.70 mmol), and CsF (5 mg, 0.032 mmol) were mixed in THF (10 mL) and refluxed for 12 h. The solvent was removed in vacuo and the residue extracted with toluene and filtered. The filtrate was concentrated to 3 mL and cooled to −40 °C for 3 days. Bright yellow needles formed, which were filtered, washed with cooled pentane, and dried. Yield: 230 mg (58%). Anal. Calcd for $C_{25}H_{43}F_5OP_2Ru$: C, 48.61; H, 7.02. Found: C, 48.99; H, 6.90. ^{1}H NMR (C_6D_6, 20 °C, 300 MHz): 1.06 (vt, N = 13 Hz, 36H, $PC(CH_3)_3$), 0.538 (vt, N = 6 Hz, 6H, PCH_3), −27.6 (tt, J_{PH} = 19 Hz, J_{FH} = 5.4 Hz, 1H, Ru−H). $^{31}P\{^1H\}$ NMR: 55.2 (s). ^{19}F NMR: −111.1 (dm, J = 33 Hz, *ortho* F), −120.8 (dm, J = 35 Hz, *ortho* F), −163.2 (m, *meta* F), −163.4 (t, J = 20 Hz, *para* F), −165.3 (m, *meta* F). IR (C_7D_8): 1917 (ν(CO)).

$OsH(C_6F_5)(CO)(P^tBu_2Me)_2$. The same procedure as above was used, but the reaction required 24 h for completion. The complex has been synthesized from $OsH(Ph)(CO)L_2$ and C_6F_5H, and the spectroscopic data are published.[58]

Reaction of $RuHF(CF_2)(CO)(P^tBu_2Me)_2$ with $NEt_3{\cdot}3HF$. In an NMR tube, $RuHF(CF_2)(CO)L_2$ (10 mg, 0.020 mmol) was dissolved in toluene-d_8 (0.5 mL). To the solution was added $NEt_3{\cdot}3HF$ (1.0 μL, 0.02 mmol) via syringe. The color changed gradually from colorless to yellow over a period of 2 h at room temperature. NMR spectral analysis reveals consumption of starting material and formation of free H_2 (4.50 ppm, s), $Ru(CHF_2)F(CO)L_2$ (10%), and $RuF(CF_3)(CO)L_2$ (90%).

NMR data for $RuF(CF_3)(CO)L_2$ follow. ^{1}H NMR (300 MHz): 1.27 (vt, N = 12.9 Hz, P^tBu), 1.19 (vt, N = 4.8 Hz), 6H PCH_3), 1.13 (vt, N = 12.6 Hz, 18H, P^tBu). $^{31}P\{^1H\}$ NMR (121 MHz): 39.3 (q, J_{PF} = 9 Hz). ^{19}F NMR (282 MHz): 9.50 (t, J_{PF} = 10 Hz). However, the metal-bound fluoride is not observed. To gain information on the missing fluoride, we added CsF (ca. 10 mg) to the mixture, and the mixture was stirred at room temperature for 2 h. NMR spectral analysis of the solution shows the presence of coordinated fluorides. $^{31}P\{^1H\}$ NMR: 40.9 (dq, $^2J_{PF}$ = 23 Hz, $^3J_{PF}$ = 10 Hz), ^{19}F NMR: 9.50 (dt, $^3J_{FF}$ = 13 Hz, $^3J_{PF}$ = 10 Hz), −210 (tq, J_{FP} = 23 Hz, J_{FF} = 13 Hz, Ru−F). No significant change in the ^{1}H NMR spectrum is observed. $^{13}C\{^1H\}$ NMR (100 MHz): 205.0 (dm, J_{CF} = 65 Hz, Ru−*C*O), 137.5 (qt, $^1J_{CF}$ = 354 Hz, $^2J_{PC}$ = 9.5 Hz, CF_3), 35.8 (vt, N = 16 Hz, $PC(CH_3)_3$), 35.0 (vt, N = 17 Hz, $PC(CH_3)_3$, 29.8 (vt, N = 4 Hz, $PC(CH_3)_3$), 29.5 (brt, $PC(CH_3)_3$), 5.93 (vtd, N = 21 Hz, $^3J_{CF}$ = 1.5 Hz, PCH_3).

$RuF(CF_3)(CO)_2(P^tBu_2Me)_2$. The above solution was charged with CO (1 atm), and the color changed from yellow to colorless immediately. ^{1}H NMR (400 MHz, 60 °C): 1.47 (vt, N = 6 Hz, 6H, PCH_3), 1.32 (vt, N = 14 Hz, 18H), 1.24 (vt, N = 12 Hz, 18H, $PC(CH_3)_3$). ^{19}F NMR (376 MHz, 60 °C): −16.3 (br, $w_{1/2}$ = 158 Hz, CF_3), −376 (br, $w_{1/2}$ = 59 Hz, Ru−F). $^{31}P\{^1H\}$ NMR (162 MHz, 60 °C): 44.0 (br, $w_{1/2}$ = 93.5 Hz).

Reaction of $RuHF(CF_2)(CO)(P^iPr_3)_2$ with $NEt_3{\cdot}3HF$. To a benzene solution of $RuHF(CF_2)(CO)(P^iPr_3)_2$ (10 mg, 0.02 mmol) was added $NEt_3{\cdot}3HF$ (1 μL). After 2 h at room temperature, $^{31}P\{^1H\}$ and ^{1}H NMR spectra of the solution reveal formation of $Ru(CF_2H)F(CO)(P^iPr_3)_2$ (10%) and $Ru(CF_3)F(CO)(P^iPr_3)_2$ (61%) and a small amount of unknown products that contain phosphine ligands.

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[58] Renkema, K. B.; Bosque, R.; Streib, W. E.; Maseras, F.; Eisenstein, O. *J. Am. Chem. Soc.* **1999**, *121*, 10895.

Spectral data for $Ru(CF_3)F(CO)(P^iPr_3)_2$ follow. $^{31}P\{^1H\}$ NMR (162 MHz): 45.0 (q, J_{PF} = 10.5 Hz). ^{19}F NMR (376 MHz): 9.0 (t, J_{PF} = 10.5 Hz). ^1H NMR (400 MHz): 2.43 (m, 6H, PC*H*), 1.14 (m, 36H, $PCH(CH_3)_2$).

Reaction of $Ru(CF_2H)(F)(CO)(P^tBu_2Me)_2$ with H_2 in the Presence of CsF. $Ru(CF_2H)F(CO)(P^tBu_2Me)_2$ (10 mg, 0.02 mmol) was dissolved in benzene-d_6. The solution was degassed, charged with H_2 (1 atm), and stirred at room temperature for 24 h. The ^1H NMR spectrum of the mixture reveals unchanged starting material and a sharp free H_2 peak. The solution was then heated for 4 h in 80 °C oil bath. ^1H NMR assay reveals no observable reaction. To the tube was added ca. 10 mg of CsF, and the heterogeneous mixture was heated for 5 h. ^1H, ^{31}P, and ^{19}F NMR spectra show consumption of $Ru(CF_2H)F(CO)(P^tBu_2Me)_2$ and formation of CH_2F_2, $RuHF(CO)L_2$ (47%), $Ru(H)_2(CO)_2L_2$ (28%), and $RuHF(CO)_2(P^tBu_2Me)_2$ (8%). ^{19}F NMR (282 MHz): −143 ($^2J_{HF}$ = 50 Hz, CH_2F_2).

Reaction of $Ru(CF_2H)F(CO)(P^iPr_3)_2$ with H_2. In an NMR tube, $Ru(CF_2H)F(CO)(P^iPr_3)_2$ (10 mg, 0.02 mmol) was dissolved in benzene-d_6 and the solution was freeze−pump−thawed three times before H_2 (1 atm) was introduced. After 10 min the ^1H NMR spectrum of the mixture does not show any reaction, as the H_2 remains free (4.5 ppm). The tube was tumbled for 24 h at room temperature; $^{31}P\{^1H\}$ NMR spectral analysis shows the disappearance of $Ru(CF_2H)F(CO)(P^iPr_3)_2$ and formation, mainly, of $RuHF(CO)_2(P^iPr_3)_2$ and $RuHF(CO)(P^iPr_3)_2$. The $^{31}P\{^1H\}$ NMR spectrum of the latter, however, shows only a singlet at 59 ppm in the reaction mixture as there is HF formed in the reaction. The ^1H NMR (400 MHz): 12 (br, HF), 4.7 (t, J_{HF} = 50 Hz, CH_2F_2), 4.04 (td, J_{PH} = 19 Hz, J_{HF} = 6 Hz, RuH of $RuHF(CO)_2(P^iPr_3)_2$), −23.4 (t, J_{PF} = 18 Hz, Ru−H of $RuHF(CO)(P^iPr_3)_2$). ^{19}F NMR (376 MHz): −143.0 (t, J_{HF} = 50 Hz, CH_2F_2), −188 (br, HF). ^{19}F peaks for $RuHF(CO)_2(P^iPr_3)_2$ and $RuHF(CO)(P^iPr_3)_2$ are very broad but were sharpened by addition of CsF (ca. 5 mg) to the reaction mixture.

Computational Details. All calculations were performed with the Gaussian 98 package.[59] The level of theory used was B3LYP,[60] which is a hybrid functional consisting of Becke's exchange,[61] Slater's exchange,[62] exact Hartree−Fock exchange, VWN correlation,[63] and the nonlocal (gradient) part of the LYP correlation[64] functionals. The basis set used was a generalized basis consisting of LANL2DZ on Ru and P and D95*[65] on everything else, plus an f-type polarization function with an exponent of 0.400 on the Ru. The basis set LANL2DZ is Los Alamos ECP plus double-ζ valence on Ru and P.[66] The ECP covers the 1s, 2s, and 2p electrons, while all others are treated explicitly. To make the calculations feasible, the P^tBu_2Me groups were replaced with PH_3, and the methyl groups in the silicon species were replaced with H. All calculations were performed with C_s symmetry. It was necessary to change the integration grid from its default size to minimize the grid noise so that geometry optimizations could converge. The new grid has 99 radial points and 434 angular Lebedev points.

It was found to be absolutely necessary to include polarization functions on each center to get the bond lengths and energetics correct. The most profound effect is on the fluorines. Without polarization functions, the bond length is overestimated by several hundredths of an angstrom. In a separate study of diatomic CF, the same trend was observed. A plot of the difference of the B3LYP density between the basis set with polarization functions and the basis set without them clearly shows that inclusion of polarization functions leads to a significant buildup of electron density between the centers leading to stronger bonding characteristics and shorter bond length. The inclusion of polarization functions yields a bond length and D_c much closer to the experimental value:

	D_c (kcal/mol)	bond length (Å)
without pol. (D95)	110.2	1.3597
with pol. (D95*)	128.8	1.2932
experimental[67]	132.6	1.2718

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Supporting Information Available: Full crystallographic details, positional and thermal parameters, and bond distances and angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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