Phosphine Dissociation Mediates C−H Cleavage of Fluoroarenes by $OsH(C_6H_5)(CO)(P^tBu_2Me)_2$

Kenton B. Renkema,[†] Ramon Bosque,[‡,§] William E. Streib,[†] Feliu Maseras,*[,‡,⊥] Odile Eisenstein,*[,‡] and Kenneth G. Caulton*[,†]

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405-4001, and LSDSMS (UMR 5636), Case Courrier 14, Université de Montpellier 2, 34095, Montpellier Cedex 5, France

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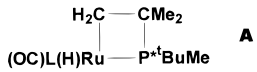
Abstract: $OsH(Ph)(CO)L_2$ ($L = P^tBu_2Me$, $Ph = C_6H_5$) is synthesized and studied by spectroscopic and DFT (B3LYP) calculations. It forms 1:1 adducts with CO or MeCN, but D_2 causes reductive elimination of C_6H_6. Reaction with C_6D_6 gives exclusively $OsD(C_6D_5)(CO)L_2$. Lack of conversion of $OsD(C_6H_5)(CO)L_2$ to $OsH(C_6H_4D)(CO)L_2$ under the same conditions indicates that zerovalent $Os(\eta^2\text{-}C_6H_5D)(CO)L_2$ is not kinetically relevant. DFT calculations confirm that an η^2-arene complex is not accessible and also show that the *dissociative* reductive elimination of arene is a high energy process. Reaction of $OsH(Ph)(CO)L_2$ with fluorinated arenes, HAr_F gives benzene and $OsH(Ar_F)(CO)(P^tBu_2Me)_2$ (i.e., attack on the HAr_F C−H bond), with the fastest attack involving more heavily fluorinated arenes (but C_6F_6 does not react) and the attack occurring preferentially at the C−H bond *ortho* to fluorine. DFT calculations show that the observed isomer is thermodynamically controlled. These results, isotope-labeling results, and rate suppression and exchange involving added free phosphine lead to a mechanism where reagent arene associates with $OsH(Ph)(CO)L_2$, but benzene loss demands preliminary dissociation of phosphine from such an adduct.

Introduction

We have been exploring the ability of ligands containing lone pairs of electrons on their alpha atom to donate such electrons into otherwise empty metal orbitals.[1−4] This subject includes the entire range of molecules traditionally termed unsaturated (16- or 14-valence electrons), such as $IrCl(CO)L_2$, $RhClL_3$, $RuHCl(PPh_3)_3$, $Os(H)_2Cl_2(P^iPr_3)_2$, $RuCl(Ph_2PC_2H_4PPh_2)_2^+$, $Rh(PPh_3)_3^+$, etc. We have studied potential π-donor ligands that extend from halide to amide, alkoxide, siloxide, and thiolate.[5] We are also interested in probing the limits of π-donation by studying hydrocarbyl ligands. We have evaluated this for acetylide as a ligand in the coordination environment $RuHX(CO)L_2$ where $L = P^tBu_2Me$.[2] When X = phenyl, methyl, CH_2SiMe_3, we found that any species $RuHX(CO)L_2$ loses R−H already by −40 °C and oxidatively adds a C−H bond of the ^{t}Bu group of one phosphine.[6] The observed product **A** exists as two diastereomers (both P* and Ru are chiral centers). RuHR-



A

$(CO)L_2$ is thus a transient species which is difficult to characterize by conventional means. In an attempt to more fully study $MHR(CO)L_2$, we now report the properties, stability and subsequent reactivity of $OsH(aryl)(CO)L_2$. With regard to anticipated reaction mechanism, the molecules $OsH(R)(CO)L_2$ might be expected to be reluctant to undergo concerted (i.e., "unassisted") reductive elimination of RH since that process would lead to the 14-electron, three-coordinate, zerovalent molecule $Os(CO)L_2$. Even 16-electron zerovalent species of Fe, Ru, or Os are exceedingly rare.[7−10]

Experimental Section

General. All manipulations were done under an atmosphere of dry, O_2-free Ar employing a Vacuum Atmospheres inert atmosphere glovebox or standard Schlenk-line techniques. The solvents were reagent grade, distilled from the appropriate drying agents under Ar. MeCN and pyridine were distilled from CaH_2 before use. Due to the moisture sensitivity of $OsH(Ph)(CO)(P^tBu_2Me)_2$, glassware from a drying oven was cooled in a glovebox. Celite was heated under vacuum and then cooled under argon. Phenanthrene was sublimed. Phenyllithium in cyclohexane/ether 70:30, monofluorobenzene, 1,4-difluoroben-

[†] Indiana University.

[‡] Université de Montpellier.

[§] Present address: Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Avgda, Diagonal 647, 08028 Barcelona, Catalonia, Spain.

[⊥] Present address: Unitat de Quimica Fisica, Universitat Autonoma de Barcelona, 08193 Bellaterra, Catalonia, Spain.

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zene, 1,3-difluorobenzene, pentafluorobenzene, α,α,α-trifluorotoluene 1,3-bistrifluoromethylbenzene, and 1,4-bistrifluoromethylbenzene were purchased from the Aldrich Chemical Co. and used without further purification. The ^{1}H, ^{31}P, and ^{19}F NMR signals were collected on Varian Gemini 2000 or Inova 400 spectrometers (^{1}H: 300, 400 MHz; ^{31}P: 122, 162 MHz; ^{19}F: 282, 376 MHz). In addition, some ^{1}H NMR were collected on a Varian XL300 operating at 300 MHz and some of the ^{31}P spectra collected on a Nicolet 360 operating at 146 MHz. Proton NMR were referenced to residual solvent peaks as internal standards. ^{31}P NMR was referenced to an external standard of 85% H_3PO_4. ^{19}F NMR was referenced to trifluoroacetic acid in benzene. Infrared spectra were recorded on a Nicolet 510P FT-IR. GC/MS was done on a Hewlett-Packard 5890 Series II instrument.

OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ (1). To OsHCl(CO)(P^{t}Bu$_2$Me)$_2$ (34.0 mg, 0.0591 mmol) partially dissolved in 15 mL of pentane (which facilitates separation of the product from LiCl), was added 1.01 equivalents of 1.75 M PhLi (34 μL, 0.0595 mmol) via a 50-mL syringe. The reaction mixture turned from orange to red-orange within 1 min of addition. The solution was then filtered through Celite under rigorously dry and O_2-free conditions and the solvent removed by vacuum to give a 75% yield of a red-brown powder. Anal. for $C_{25}H_{48}P_2OOs$: Calcd (found) C, 48.68 (47.55); H, 7.84 (7.94). ^{1}H NMR (298 K, C_6D_6) *o*-Ph, 7.58 (d, 1H, [J_{H-H}] = 6 Hz); *m*-Ph, 7.34 (t, 1H, [J_{H-H}] = 6 Hz); *m*-Ph, 7.29 (t, 1H, [J_{H-H}] = 7 Hz); *p*-Ph, 7.07 (t, 1H, [J_{H-H}] = 8 Hz); *o*-Ph, 6.97 (d, 1H, [J_{H-H}] = 6 Hz); PCC*H*$_3$, 1.16 (vt, 18H, [J_{P-H}] = 6 Hz); PCC*H*$_3$, 1.13 (vt, 18H, [J_{P-H}] = 6 Hz); PC*H*$_3$, 0.79 (vt, 6H, [J_{P-H}] = 3 Hz); OsH, −39.3, (t, 1H, [J_{P-H}] = 14 Hz). ^{13}C NMR (C_6D_{12}, 298 K) CO, 197.3 (br s); 142.4 (dt, J_{CH} = 151.9, J_{CH} = 8 Hz); 134.5 (dt, J_{CH} = 146.9, J_{CH} = 9 Hz); *m*-Ph, 128.0 (dd, J_{CH} = 152.5, J_{CH} = 7.6 Hz); *m*-Ph, 126.7 (dd, J_{CH} = 152.0, J_{CH} = 7 Hz); 121.8 (dt, J_{CH} = 154.0, J_{CH} = 8 Hz); P*C*(Me)$_3$, 39.44 (t, J_{CP} = 10.3 Hz); 36.37 (t, J_{CP} = 11.9 Hz); PC(*C*H$_3$)$_3$, 29.03 (s) PC(*C*H$_3$)$_3$, 29.87; P*C*H$_3$, 6.83 (t, J_{PC} = 14.1 Hz). ^{31}P{^{1}H} NMR (298 K, C_6D_6) 37.1 (s). IR (C_6D_6) ν(CO) = 1878 cm^{-1}.

OsH(C$_6$H$_5$)(CO)(P^{t}Bu$_2$Me)$_2$ + C$_6$D$_6$. Into an NMR tube was placed 11.8 mg (0.091 mmol) of **1**. This was dissolved in 800 μL of C_6D_6. The tube was mixed thoroughly and monitored by ^{1}H and ^{31}P NMR for 1.5 d at 20 °C. Gradually, C_6H_6 was produced, while the signals for Os−C_6H_5 disappeared. Hydride on Os also disappeared, but at rate slightly slower than phenyl due to some scrambling of Os-D with ^{t}BuC−H.

OsH(OH)(CO)(P^{t}Bu$_2$Me)$_2$. A solution of OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ (5.3 mg, 0.0086 mmol) in d_8-toluene reacted completely with 1 μL (0.056 mmol) of H_2O. Excess H_2O broadens the OH signal so that coupling to phosphorus was no longer seen. ^{1}H NMR (298 K, C_6D_6) O*H*, 4.09, (t, 1H, [J_{P-H}] = 9 Hz); PCC*H*$_3$, 1.29, (vt, 18H, [J_{P-H}] = 5.7 Hz); PCC*H*$_3$, 1.27, (vt, 18H, [J_{P-H}] = 5.7 Hz); PC*H*$_3$ = 1.37, (vt, 6H, [J_{P-H}] = 2.4 Hz); OsH, −27.42, (t, 1H, [J_{P-H}] = 13.5 Hz). ^{31}P{^{1}H} NMR (298 K, C_6D_6) 37.3, (s). IR (C_6D_6) ν(CO) = 1878 cm^{-1}.

Os(H)$_2$(H$_2$)(CO)(P^{t}Bu$_2$Me)$_2$. One atmosphere of H_2 (excess) was added to a solution of OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$. The mixture turned a pale yellow at the time of mixing. The yield of Os(H)$_2$(H$_2$)(CO)(P^{t}Bu$_2$Me)$_2$ was quantitative by ^{31}P NMR. ^{1}H NMR (298 K, C_6D_6) OsH, −7.95, (t, 4H, [J_{P-H}] = 10.8 Hz); PC*H*$_3$, 1.65, (vt, 6H, [J_{P-H}] = 3 Hz); PCC*H*$_3$, 1.24, (vt, 36H, [J_{P-H}] = 6 Hz). ^{31}P{^{1}H} NMR (298 K, C_6D_6) 41.6 (s). IR (C_6D_6) ν(CO;Os−H) 1950, 1887, 1867 cm^{-1}; (KBr) 2020, 1948, 1908, 1883, 1867 cm^{-1}. IR of OsD$_4$(CO)(P^{t}Bu$_2$Me)$_2$ (C_6D_6) ν(CO) 1910 cm^{-1}.

OsD$_2$(D$_2$)(CO)(P^{t}Bu$_2$Me)$_2$. OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ (8.8 mg, 0.016 mmol) was dissolved in 500 μL of decalin and D_2 (700 Torr, 0.114 mmol) added to it. C_6H_6 was released within two minutes of mixing. All signature spectra are seen by ^{1}H and ^{31}P NMR to be similar to OsH$_2$(H$_2$)(CO)(P^{t}Bu$_2$Me)$_2$ except for the absence of a hydride signal.

OsH(Ph)(CO)$_2$(P^{t}Bu$_2$Me)$_2$. A solution of **1** (7.7 mg, 0.0125 mmol) was freeze−pump−thaw degassed three times. Then excess CO (∼43 mmol) was added via a gas line. Upon mixing, the red solution turned a translucent faint yellow with a very small amount of precipitate. ^{1}H NMR (298 K, C_6D_{12}) OsH, −6.4 (t, 1H, [J_{P-H}] = 24 Hz); PC*H*$_3$, 1.65, (vt, 6H, [J_{P-H}] = 5 Hz); PCC*H*$_3$, 1.25, (vt, 18H); PCC*H*$_3$, 1.30, (vt, 18H). ^{31}P{^{1}H} NMR (298 K, C_6D_{12}) 23.2 (s). IR (C_6D_6) ν(CO) 1966, 1894 cm^{-1}.

OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ + MeCN. Spectra were recorded on a solution of OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ (15.2 mg, 0.025 mmol) in d_8-toluene containing MeCN (0.7 μL, 0.550 mmol). ^{1}H NMR (298 K, C_7D_8) selected arene signals: 8.17, 7.77, 7.59, 7.31, 7.18; CH_3CN, 1.8 (br, s); PC(C*H*$_3$)$_3$, 1.37, (t, 18H, J_{PH} = 6 Hz); PC(C*H*$_3$)$_3$, 1.25, (t, 18H, J_{PH} = 6 Hz); 0.93, PC*H*$_3$, (t, 6H, J_{PH} = 3 Hz); OsH, −13.62, (t, 1H, J_{PH} = 20 Hz). ^{31}P NMR (298 K, C_7D_8) 19.5, (s).

OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ + N$_2$. A solution of OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ (15.1 mg, 0.024 mmol) in d_8-toluene, when placed under 1 atm N_2, shows loss of P−H coupling in the hydride signal. Cooling of this solution caused the decoalescence into signals of OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ and those of the following new species: ^{1}H NMR (238 K, C_7D_8) selected arene signals: 8.05, (br s); 7.93, (d); 7.65, (d); 7.43, (t); 7.02, (d); PC(C*H*$_3$)$_3$; 1.11, (t, 18H); PC(C*H*$_3$)$_3$; 1.10, (t, 18H); PC*H*$_3$, 0.74, (br s, 6H); OsH, −11.41, (t, 1H, J_{PH} = 14.8 Hz). ^{31}P NMR (238 K, C_7D_8) 21.0, (br s).

OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ + phenanthrene. A solution of OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ (11.8 mg, 0.019 mmol) in 500 μL C_6D_{12} was allowed to react with phenanthrene (2.8 mg, 0.016 mmol) for 5 days, after which time, there was 50% conversion to five new products. Four of the new products were the result of C−H activation at four of the five ring positions on phenanthrene as was identified by new hydride triplets at extreme upfield shifts. ^{1}H NMR (C_6D_{12}, 20 °C) OsH, −39.3 (t, J_{PH} = 14.3 Hz); OsH, −39.4 (t, J_{PH} = 14.6 Hz); OsH, −39.47 (t, J_{PH} = 14.6 Hz); OsH, −39.5 (t, J_{PH} = 14.6 Hz). ^{31}P NMR (C_6D_{12}, 20 °C) 37.3 (s); 37.0 (s); 36.7 (s); 36.5 (s). The absence of signals in the range 2−6 ppm indicates the lack of an η^2-arene product.

OsH(2,6-C$_6$H$_3$F$_2$)(CO)(P^{t}Bu$_2$Me)$_2$. To **1** (7.5 mg, 0.012 mmol) dissolved in 500 μL C_6D_{12} was added 1.25 equiv of 1,3-difluorobenzene (1.5 μL, 0.015 mmol). Within 1 h of mixing, the solution had turned from its characteristic red color to a much paler orange color. ^{1}H NMR (298 K, C_6D_6) OsH, −38.5, (tdd, 1H, [J_{P-H}] = 14.5 Hz, [$J_{F(1,2)H}$] = 5.9, 4.3 Hz); PC*H*$_3$, 0.84, (vt, 6H, [J_{P-H}] = 3 Hz); PCC*H*$_3$, 1.18, (vt, 18H, [J_{P-H}] = 6 Hz); PCC*H*$_3$, 1.22, (vt, 18H, [J_{P-H}] = 6 Hz); 6.37, (ddd, 1H); 6.49, (ddd, 1H); 6.76, (multiplet). ^{31}P{^{1}H} NMR (298 K, C_6D_{12}) 36.3 (ppm). ^{19}F NMR (298 K, C_6D_{12}) −83.2 (m, 1F); −91.7, (m, 1F). IR (C_6D_{12}) ν(CO) = 1898 cm^{-1}.

OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ + 1,3-difluorobenzene + P^{i}Pr$_3$. A sealed NMR tube was prepared containing OsH(Ph)(CO)(P^{t}Bu$_2$Me)$_2$ (12.3 mg, 0.0199 mmol), 1,3-difluorobenzene (3.2 μL, 0.0326 mmol), and P^{i}Pr$_3$ (6.50 μL, 0.0365 mmol) dissolved in 500 μL of C_6D_{12}. After 4 days at room temperature, three products were seen. OsH(2,6-C$_6$F$_2$H$_3$)(CO)(P^{t}Bu$_2$Me)$_2$ was

Table 1. Crystallographic Data for OsH($C_6H_3F_2$)(CO)(P^tBu_2Me)$_2$

a, Å	14.331(2)	formula weight	652.81
b, Å	18.409(2)	space group	$P\bar{1}$
c, Å	10.665(1)	*T*, °C	−160
α, Å	97.84(1)	*λ*, Å	0.71069
β, Å	93.44(1)	ρ_{cald}, g/cm^{-3}	1.560
γ, Å	87.19(1)	*μ*(Mo Kα), cm^{-1}	47.282
V, Å^3	2779.89	*R*	0.0425
Z	4	R_w	0.0388

characterized earlier; OsH(2,6-$C_6F_2H_3$)(CO)(P^tBu_2Me)(P^iPr_3) was characterized as follows: ^{1}H NMR (C_6D_{12}, 20 °C) OsH, −37.90 (tdd, J_{PH} = 14.6, J_{HF1} = 9.0, J_{HF2} = 3.9 Hz), ^{31}P NMR (C_6D_{12}, 20 °C) AB quartet centered at 39.4 (J_{PP} = 236 Hz, Δδ 0.8 ppm). ^{19}F NMR (C_6D_{12}, 20 °C) −85.9 (br s), −96.9 (br s). OsH(2,6-$C_6F_2H_3$)(CO)(P^iPr_3)$_2$ was identified with the following signals: ^{1}H NMR (C_6D_{12}, 20 °C) −36.67 (tdd, OsH, J_{PH} = 15.0 Hz, J_{HF} = 15.0 Hz, J_{HF2} = 2.6 Hz), ^{31}P NMR (C_6D_{12}, 20 °C), 40.9 ^{19}F NMR (C_6D_{12}, 20 °C) −87.2 (br s), −103.6 (br s).

X-ray Structure of OsH($C_6H_3F_2$)(CO)(P^tBu_2Me)$_2$. The crystal was mounted using silicone grease and was transferred to a goniostat where it was cooled to −160 °C for characterization and data collection. A preliminary search for peaks followed by analysis using programs DIRAX and TRACER revealed a triclinic cell (Table 1). The choice of space group $P\bar{1}$ was later proven correct by the successful solution of the structure. After an analytical correction for absorption (transmission factors 0.40−0.66), data processing produced a set of 9847 unique intensities ($6° < 2\theta < 50°$) and an R_{av} = 0.035 for the averaging of 4605 of these which had been observed more than once. Four standards (0 0 5, 0 9 0, −2 1 1, and −4 0 0) measured every 300 data showed no significant trends. The structure was solved using system DIRDIF-96.[11] Nearly the entire structure was apparent. The positions of the remaining non-hydrogen atoms were obtained from iterations of a least-squares refinement, followed by a difference Fourier calculation. Hydrogens bonded to carbon were included in fixed calculated positions with thermal parameters fixed at one plus the isotropic parameters of the parent carbons. There are two independent molecules in the asymmetric unit. The anticipated hydride on the osmium was not observed. The final cycles of refinement used 560 variables. The largest peak in the final difference map was 2.1 e/Å^3 located 1.1 Å from Os(32), and the deepest hole was −1.6 e/Å^3.

OsH(2-C_6H_4F)(CO)(P^tBu_2Me)$_2$. To **1** (8.2 mg, 0.013 mmol) dissolved in 500 μL of C_6D_{12} was added 1.2 equiv of monofluorobenzene (1.5 μL, 0.016 mmol). There was a gradual fading of the red color of **1** over 1 day. After 1 h, approximately half of the starting material has been converted to two new products with the major product having the following spectra features: ^{31}P NMR, 38 ppm; ^{1}H NMR, OsH at −38 (td); ^{19}F NMR, −76.5 ppm). After 4 days, a slow conversion from the first major product to the second one, with the corresponding loss of **1** and the first product has occurred. The spectroscopic data for the final product follows: ^{1}H NMR (298 K, C_6D_{12}) OsH, −39.9, (td, 1H, [J_{P-H}] = 14.1 Hz, [J_{Fl-H}] = 5.8 Hz); PCH_3, 0.85, (vt, 6H, [J_{P-H}] = 2 Hz); PCCH_3, 1.21 (vt, 18H, [J_{P-H}] = 3 Hz); PCCH_3, 1.27 (vt, 18H, [J_{P-H}] = 3 Hz); and selected aryl peaks 7.2, 6.56, 6.76, 6.79 (ppm). ^{31}P{^{1}H} NMR (298 K, C_6D_{12}) 36.8 (ppm). ^{19}F NMR (298 K, C_6D_{12}) −85.0, (m, 1F); IR (C_6D_{12}) ν(CO) = 1894 cm^{-1}.

OsH(2,5-$C_6H_3F_2$)(CO)(P^tBu_2Me)$_2$. To **1** (9.1 mg, 0.015 mmol) dissolved in 500 μL of C_6D_{12} was added 1.12 equiv of 1,4-difluorobenzene (1.7 μL, 0.017 mmol). Slight fading occurred over the next 2 days. **1** was initially converted to the kinetic product (^{31}P = 38.0; ^{1}H OsH = −38.25, ^{19}F *o*-F = −75.6, *m*-F = −106.6 ppm) and then to its rotamer. With time, the thermodynamic rotamer emerged with the concurrent disappearance of the less stable one. The final product has the following spectroscopic characteristics: ^{1}H NMR (298 K, C_6D_{12}) OsH, −40.0, (td, 1H, [J_{P-H}] = 14.0 Hz, [J_{F-H}] = 5.7 Hz); PCH_3, 0.90, (vt, 6H, [J_{P-H}] = 2 Hz); PCCH_3, 1.22 (vt, 18H, [J_{P-H}] = 6.4 Hz); PCCH_3, 1.27, (vt, 18H, [J_{P-H}] = 6.4 Hz); selected aryl peaks 6.40, 6.47, 6.91. ^{31}P{^{1}H} NMR (298 K, C_6D_{12}) 36.2 (ppm). ^{19}F NMR (298 K, C_6D_{12}) −87.0, −106.7, (m, 1F); IR (C_6D_{12}): ν(CO) = 1898 cm^{-1}.

OsH(C_6F_5)(CO)(P^tBu_2Me)$_2$. To **1** (4.2 mg, 0.0066 mmol) dissolved in 500 μL of C_6D_{12} was added 1.59 equiv of pentafluorobenzene (1.2 μL, 0.011 mmol). The reaction was complete within 1 h, and no noticeable change was found in the color of the solution. ^{1}H NMR (298 K, C_6D_{12}) OsH, −38.9, (tt, 1H, [J_{P-H}] = 10.5 Hz, [J_{Fl-H}] = 3.0 Hz); PCH_3, 0.96 (vt, 6H, [J_{P-H}] = 2 Hz); PC(CH_3)$_3$, 1.24 (vt, 18H, J_{P-H} = 4.8 Hz); PCCH_3, 1.27 (m), 18H, [J_{P-H}] = 4.8 Hz). ^{31}P{^{1}H} NMR (298 K, C_6D_{12}) 36.6 (ppm). ^{19}F NMR (298 K, C_6D_{12}) *o*-F, −114.5, (dvt, 1F, [J_{FF}] = 32 Hz); *o*-F, −122.9 (dd, 1F, [J_{FF}] = 34 Hz, [J_{F-H}] = 6 Hz); also signals for *meta* and *para* fluorine −164.8, −165.12, −165.4 ppm. IR (C_6D_{12}) ν(CO) = 1908 cm^{-1}.

OsH(Ph)COL_2 + 1,3-$(CF_3)_2C_6H_4$. A solution of **1** (5.5 mg, 0.0089 mmol) in 600 μL of C_6D_{12} was reacted with 1,3-bis-(trifluoromethyl)benzene (6.5 μL, 0.0097 mmol) at 55 °C for 1 h. A single new species was seen by ^{1}H, ^{31}P, and ^{19}F NMR. ^{1}H NMR (298 K, C_6D_{12}) p-ArH, 7.75, (br s, 1H); o-ArH, 7.32, (br s, 2H); $PCCH_3$, 1.23 (vt, 36H, J_{PH} = 6.9 Hz); PCH_3, 0.69, (vt, 6H, J_{PH} = 2.9 Hz), OsH, −39.9, (t, 1H, J_{PH} = 15 Hz). ^{31}P{^{1}H} NMR (298 K, C_6D_{12}) 35.9 (s). ^{19}F NMR (298 K, C_6D_{12}) m CF_3−Ar, −54.45, (s); −54.52, (s). IR (298 K, C_6D_{12}) 1902 cm^{-1}.

OsH(Ph)(CO)L_2 + $CF_3C_6H_5$. A solution of **1** (5.6 mg, 0.0091 mmol) in 600 μL of C_6D_{12} was reacted with (1.5 μL, 0.012 mmol) α,α,α-trifluorotoluene for 6 h at 55 °C. Full consumption of **1** was accompanied by decomposition. Three new products were seen by ^{1}H, ^{31}P, ^{19}F NMR. ^{1}H NMR (298 K, C_6D_{12}) aryl protons, 7.6−6.8 ppm; $PCCH_3$, 1.35−1.16 (vt); PCH_3, 0.8−0.7 (vt); −39.75 (t, 1H, J_{PH} = 14.6 Hz); −39.78 (t, 1H, J_{PH} = 14.5 Hz); −39.86 (t, 1H, J_{PH} = 14.3 Hz). ^{31}P{^{1}H} NMR (298 K, C_6D_{12}) 37.1 (s); 37.82 (s); 36.46 (s). ^{19}F NMR (298 K, C_6D_{12}) 54.17 (s); 54.97 (s); 55.04 (s).

OsH(Ph)(CO)L_2 + 1,3-$C_6F_2H_4$ + P^tBu_2Me. OsHPh(CO)-L_2 (10.4 mg, 0.0168 mmol) was weighed into an NMR tube and 3.0 μL (0.0168 mmol, 1 equiv) of P^tBu_2Me was added. Then 1.09 equiv of 1,3-difluorobenzene (1.81 μL, 0.0184 mmol) was also syringed in followed by 500 μL of C_6D_{12}. The reaction was over 90% complete after 1 day.

Computational Details. Calculations were carried out on the OsH(C_6H_5)(CO)(PH_3)$_2$ and OsH($C_6H_3F_2$)(CO)(PH_3)$_2$ model systems at the B3LYP computational level[12,13] with the Gaussian 94 package.[14] An effective core potential was used to replace the 54 innermost electrons of Os[15] and the 10 innermost

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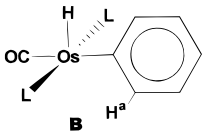
electrons of P,[16] with the LANL2DZ contraction which is valence double-ζ quality.[17] A valence double-ζ quality basis set was also used for the C, H, and F atoms.[18,19] Geometry optimizations were without symmetry restrictions, except where indicated.

Results

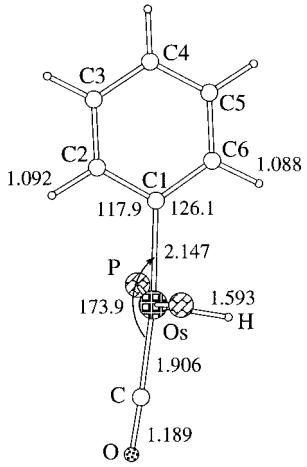
Synthesis and Characterization of $OsH(Ph)(CO)L_2$. Synthesis of $OsH(Ph)(CO)L_2$ (**1**) ($L = P^tBu_2Me$) occurs by addition of equimolar PhLi (in 70:30 cyclohexane/ether) to $OsHCl(CO)L_2$ in pentane, hexane, or benzene at 23 °C. The reaction occurs immediately as judged by the color change from orange to red-orange. The chemical shift of the hydride of $OsH(Ph)(CO)L_2$, (**1**), at a very high field position (−39.3 ppm), suggests that H is *trans* to an empty coordination site, as shown in structure **B**.



B

The aryl region of the ^1H NMR spectrum shows five signals, at both 25 and at 50 °C. The proton-coupled ^{13}C NMR spectrum shows five signals at 25 °C. This is consistent with significantly hindered rotation about the Os−C(*ipso*) bond. Atypical of other $OsHX(CO)(P^tBu_2Me)_2$ molecules, the phosphine CH_3 ^1H NMR chemical shift of $OsH(Ph)(CO)L_2$ lies upfield of the ^{t}Bu signal. This may be attributed to a ring current effect of the phenyl ring, with the PMe groups occupying a position over the phenyl plane. This also requires that the phenyl ring plane be perpendicular to the L−Os−L line.

Optimized Structure of $OsH(C_6H_5)(CO)(PH_3)_2$, 2. The structure of **2** was fully optimized by DFT(B3LYP) calculations in part to learn if there is an agostic interaction between Os and H^a in **B**. The resulting structure (**2**, Figure 1) is a square-pyramid like many d^6 ML_5 species.[20,21] The hydride ligand, being a stronger σ-donor group, occupies the apical site. The angles between the apical bond and the four basal ligands are close to 90°, with a minimum of 87.7° for H−Os−C(carbonyl) and a maximum of 98.4° for H−Os−C(phenyl). The phenyl ring plane eclipses the Os−H bond, in agreement with experiment, and the molecule adopts C_s symmetry. The Os−C(phenyl) distance, computed to be 2.147 Å, is indistinguishable from the experimental value (see below). The computed Os−C(carbonyl) (1.906 Å) and Os−P (2.396 Å) are also in good agreement with experimental average values (1.857 and 2.378 Å, respectively). Although there is a small tilting of the phenyl ring C_2 axis

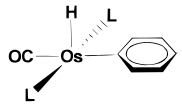


2

Figure 1. B3LYP optimized structure of $Os(H)(Ph)(CO)(PH_3)_2$, **2**, distances in Å, angles in deg.

(Os−C1−C2 = 117.9°, Os−C1−C6 = 126.1°), no agostic interaction of the C−H bond is apparent, as shown by the very small difference in the C−H distances (C2−H = 1.092 Å, C6−H = 1.088 Å). All phenyl C−C distances are approximately equal (1.40−1.42 Å).

The transition state **3** for the rotation around the Os−C(phenyl) bond is computed through a C_s geometry optimization with the phenyl plane perpendicular to the Os−H bond. Structure **3** has an energy 6.2 kcal/mol^{-1} above **2**. Thus, the conformational preference experimentally observed for **1** is supported by the calculations even for PH_3 ligands. However, the calculated energy barrier certainly underestimates the real rotational barrier since the large phosphines should disfavor **3**.



3

The presence of a small but noticeable phenyl rotational barrier even for PH_3 ligands requires some comment. Of the three occupied Os d orbitals *xy*, *xz*, and *yz* (*z* along the Os−H bond), *xy* and *xz*, which are both stabilized by π^*_{CO}, have the proper symmetry to interact with the occupied and empty π orbitals of the rotating phenyl ring. Orbitals *xy* and *xz* are not degenerate; the orbital which is coplanar with the Os−H bond is at higher energy (influence of the negatively charged hydride on the spatially more proximate occupied d orbital). The phenyl ring is a weak π-donor, and the best orientation should thus correspond to the π orbitals of the phenyl ring overlapping with the d orbital of lower energy, *xy*, to minimize the 4-electron repulsion. This leads to the preference for **2**.

Reactivity. (a) General. In CH_2Cl_2 or $CHCl_3$, **1** degrades (within 4 h at 23 °C, as judged by ^{31}P NMR) to a large number of products. In benzene or hexane solution, the molecule remains unchanged for 24 h at 25 °C in the absence of O_2 and water. Water reacts to give $OsH(OH)(CO)L_2$ and benzene. As a solid, the compound is stable at least one month in dry inert atmosphere. The reaction with even substoichiometric O_2, in C_6D_6, is not clean and selective, giving instead $^tBu_2MePO$, free phosphine, free C_6H_6, and one as yet unidentified phosphine complex which shows a hydride triplet.

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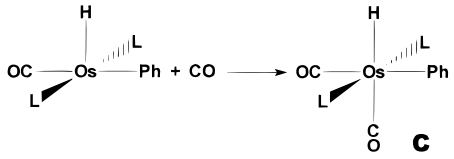
(b) Reactivity with CO. Reaction of OsH(Ph)(CO)L$_2$ with CO (1 atm, 25 °C) immediately yields OsH(Ph)(CO)$_2$L$_2$. The hydride signal has moved far downfield, to −6.4 ppm, indicating that there is now a ligand *trans* to hydride. The ^{t}Bu ^{1}H NMR signals appear as *two* virtual triplets, which uniquely demand *trans*-phosphines and *cis*-carbonyls. Consistent with this, two ν(CO) absorptions, of similar intensity, are observed. This is consistent with simple addition of CO to the empty coordination site of OsH(Ph)(CO)L$_2$ (**C** in eq 1). The PMe ^{1}H chemical shift is again upfield of that of the ^{t}Bu signal, consistent with a ring current influence by the phenyl ligand.



(1)

C

Similar compounds OsHR(CO)$_2$(L)$_2$ with R = H, Me, or CH$_2$OMe and L = P^{i}Pr$_3$ and P^{t}Bu$_2$Me have been reported.[22] Upon heating, OsHPh(CO)$_2$L$_2$ to 90 °C in toluene for 24 h, unchanged reagent was recovered; Os(CO)$_2$L$_2$ was not produced. In contrast, RuH(CH$_3$)(CO)$_2$L$_2$ at room temperature for 4 h yields Ru(CO)$_2$L$_2$.[6]

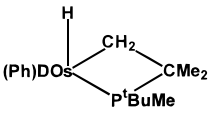
(c) Reactivity with MeCN. OsH(Ph)(CO)L$_2$ reacts with 1 equiv of MeCN in toluene to form an equilibrium mixture. The ^{31}P NMR spectrum showed two broadened signals at 37 and 20 ppm. They are consistent with assignment as OsH(Ph)(CO)L$_2$ and OsH(Ph)(MeCN)(CO)L$_2$. ^{1}H NMR spectra confirmed the existence of two species in solution and suggests, via hydride chemical shifts, that they are five- and six-coordinate.

(d) Reactivity with N$_2$. A similar result was achieved when **1** was reacted with excess N$_2$ in d_8-toluene. At room temperature, ^{31}P NMR shows a broad singlet while ^{1}H NMR shows a broadened hydride signal at −39.1 ppm, near but not identical to the same chemical shift of free **1**. Phenyl signals were also different from free **1**. Lowering the temperature causes the decoalescence of two hydride signals by −20 °C. Two sharp triplets were found by −60 °C at −11.4 and −39.3 ppm, in an approximate 1:1 ratio. At this temperature, ^{31}P{^{1}H} NMR shows two signals, a sharp one due to OsHPh(CO)(P^{t}Bu$_2$Me)$_2$ and a broad ($\Delta\nu_{1/2}$ = 0.5 ppm) one assigned to the N$_2$ adduct. The broadening is attributed to decoalescing rotamers in the more crowded six-coordinate species.[23]

(e) Arene Exchange with Benzene. In C$_6$D$_6$ at 25 °C, OsH(C$_6$H$_5$)(CO)L$_2$ shows the loss of OsH and all five C$_6$H$_5$ ^{1}H NMR signals, due to exchange of C$_6$D$_6$ with the OsH(C$_6$H$_5$) units.

$$\mathrm{OsH(C_6H_5)(CO)L_2 + C_6D_6 \rightarrow OsD(C_6D_5)(CO)L_2 + C_6H_6} \quad (2)$$

this reaction is complete within 2 days. At 70 °C, this process is accompanied by a second, more pervasive isotope exchange: ^{1}H NMR intensity is lost from the ^{t}Bu sites (but not from the PCH$_3$ sites). This implicates a second mechanism in which Os-D and γ C−H bonds are exchanged. Since we have independent evidence for metalation of P^{t}Bu C−H bonds,[6] we suggest a mechanism incorporating a metallacycle with partial structure **D**.



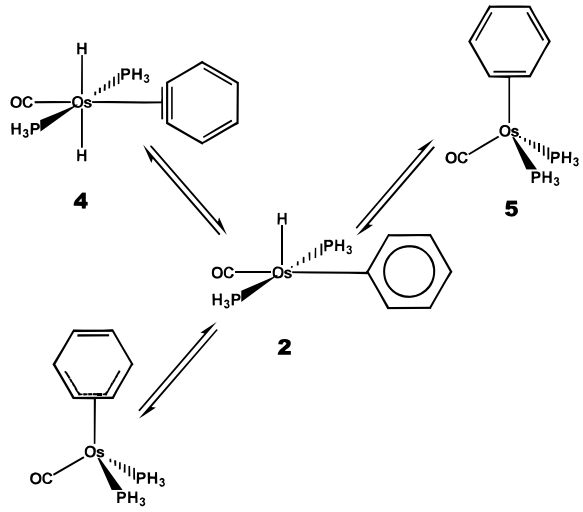
D

(f) Intramolecular Rearrangement. (1) Experiment. Previous work[24−29] on saturated CpRh(PMe$_3$)(H)(aryl) revealed a reversible rearrangement to CpRh(PMe$_3$)(η^2-arene), with migration of Rh to different aryl ring carbons. To test for such a process, OsD(C$_6$H$_5$)(CO)L$_2$, made from OsDCl(CO)L$_2$ and LiC$_6$H$_5$, was monitored by deuterium NMR over 24 h at 25 °C in protio cyclohexane, as well as after heating at 55 °C. Only slow decomposition by loss of C$_6$H$_5$D was observed. There was no growth of any of the five deuterium NMR signals of OsH(C$_6$H$_4$D)(CO)L$_2$ isotopomers.

An attempt was made to trap an η^2-arene complex by reaction with an arene that forms a more stable η^2-adduct. Reaction of **1** with one equivalent of phenanthrene in C$_6$D$_{12}$ at room temperature for 5 days produced partial conversion to multiple products, four of which were phenanthrene C−H activation products as judged by hydride chemical shifts. The ^{1}H NMR spectrum rules out any η^2-arene product.

(2) Computational Studies on Unimolecular Os−H/C−H Hydrogen Exchange in OsH(C$_6$H$_5$)(CO)(PH$_3$)$_2$, 2. The absence of unimolecular scrambling of hydrogen of the C$_6$H$_5$ ligand with the hydride of **1** contrasts with the observed exchange in CpRhH(aryl)L.[24] It was thus of interest to study the mechanism and to understand the factors that may make this exchange difficult in the present Os complex. Several possible pathways are displayed in Scheme 1. The presence of

Scheme 1



an empty orbital (i.e., unsaturation) at Os could favor the formation of a dihydride benzyne complex, **4**. Alternatively, the hydride may shift to the *ipso* carbon to give a benzene Os(0) complex which could be either η^4-bonded, and thus saturated, or η^2-bonded (**5**), and thus remain unsaturated. In the saturated Cp*RhL(arene) system, the H exchange occurs via an equilibrium between an aryl-hydride-Rh(III) and an η^2-arene Rh(I)

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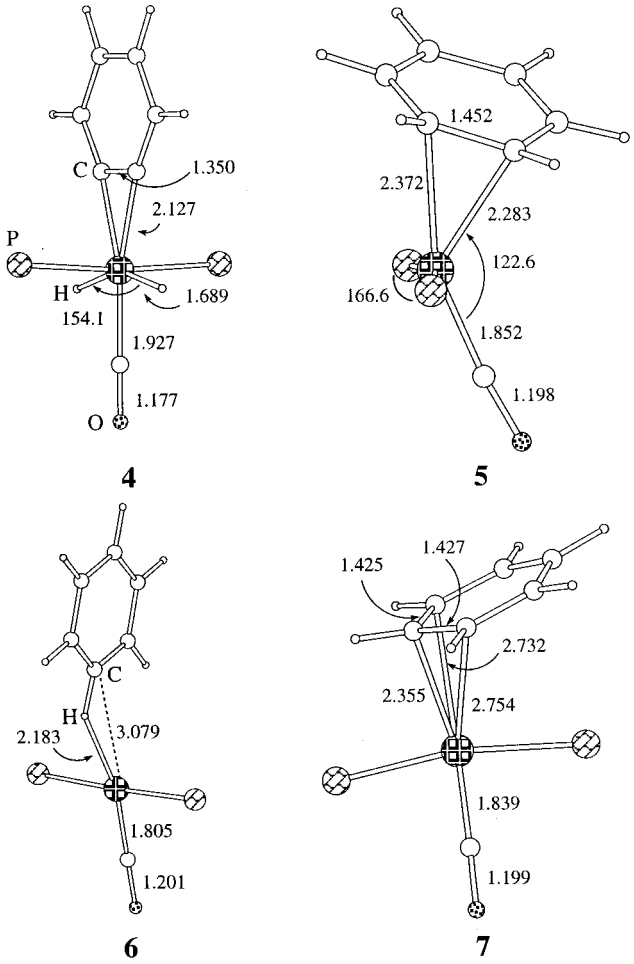


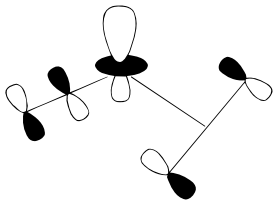
Figure 2. B3LYP optimized structures for H exchange in **2**, distances in Å, angles in deg.

system. On this Rh center, the η^2-coordination is preferred for some arenes and the thermodynamic difference between the two isomers is directly linked[30] to the cost of the loss of aromaticity when incoming arene binds in an η^2 manner. Thus, certain polycyclic aromatics favor η^2 coordination since loss of aromaticity is not so great relative to other smaller arenes. In the present study, however, one polycyclic aromatic which favors η^2 binding (phenanthrene) gave no η^2-complex of $Os(CO)L_2$, but proceeds instead to C−H oxidative addition products. To better understand the high-energy barrier found for $OsH(Ph)(CO)L_2$, we have evaluated intermediates and transition states for the H exchange process.

Dihydrido-Benzyne Mechanism via 4. We optimized two different geometries, with the C≡C bond either parallel to the Os−H or the Os−P bond, with transoid H centers and constrained to C_{2v} symmetry. The lower energy structure of the two, **4**, (C≡C parallel to Os−H) is calculated to be 30.2 kcal mol^{-1} above the minimum **2** (Figure 2). It is furthermore probably only a minimum because of symmetry constraints. This high energy is due to an accumulation of unfavorable effects such as the *trans* arrangement of two hydride ligands, the strain contained in the benzyne ligand, and the presence of a new and potent π-acceptor (benzyne) competing with the CO ligand. A geometry with a *cis* arrangement of the two hydrides was not obtained during a search of the potential energy surface in the absence of any symmetry (see below). It can thus be concluded that such a dihydrido system is at high energy and is not a viable path for H scrambling at 25−50 °C.

Os(0)-benzene Mechanism via 5. A search for a minimum with no symmetry constraints starting from a complex with η^2-benzene led to structure **5** (Figure 2). This same η^2-structure was obtained when the geometry optimization was started from a complex with η^4-coordinated benzene. It is at relatively high energy, 17.6 kcal mol^{-1}, above **2**.

Intermediate **5** is an η^2-benzene complex with the C−C double bond perpendicular to the P−Os−P direction. The most remarkable structural aspect is the geometry of the four ligands around Os. The metal is in a trigonal bipyramidal geometry with one missing equatorial ligand. The two phosphine ligands occupy the axial sites, and the angle between the two other ligands, (O)C−Os−(C−C) midpoint, is 140.9°, not 180°. This structure is thus closely related to the geometry of $Ru(CO)_2L_2$[27] and $Ru(CO)(NO)L_2^+$,[8] where the absence of planarity has been attributed to the presence of π-acceptor ligands.[31] In the η^2-benzene complex **5**, the best back-donation is obtained when C═C is parallel to Os−CO:



The coordination of benzene in **5** resembles that of C_6F_6 in $Cp^*Rh(\eta^2\text{-}C_6F_6)(PMe_3)$.[32] The benzene carbons in **5** stay planar and only the two H of the coordinated C−C bond are strongly bent away from the plane of the six carbons (dihedral C6−C1−C2−H2 = 24°). The benzene ligand in **5** has thus lost part of its aromaticity, and the four noncoordinated carbons form a butadiene fragment (Figure 2). The dihedral angle Os−(C1−C2-midpoint)−C2−C3 is 106°, which forces the benzene ring to remain close to one phosphine ligand. Significant steric hindrance may thus occur with the bulky phosphines used experimentally and can make this intermediate even less energetically accessible than that calculated with the PH_3 ligand.

We searched for a transition state between **5** and **2**. Starting from several alternate conformations for bound benzene, we could find no transition state from a σ-bound phenyl to **5**. When this search was done for similar complexes but on a different metal, $CpRh(PH_3)(\eta^2\text{-}C_6H_6)$, $CpRh(PH_3)H(C_6H_5)$, and $CpRh(PH_3)H(C_6H_3F_2)$, a transition state between the two structures was found,[33] consistent with experiment. In the attempt to find a starting structure similar to **5** that converted to **2**, the structure with benzene lying in the symmetry plane, equating the two phosphines, was tried. This starting structure led to **6** (Figure 2), with an energy 28.3 kcal mol^{-1} above **2**. The coordination of benzene to the metal seems very weak, the closest carbon being C1 (Os−C1 = 3.076 Å) and the closest hydrogen H1 (Os−H1 = 2.236 Å). There is, however, some interaction of the C1−H1 bond with the metal, because C1−H1 is 1.104 Å, 0.015 Å longer than the 1.089 Å bond length of C2−H2, which are further from osmium (Os−C2 = 3.370 Å, Os−H2 = 2.871 Å). This structure thus has benzene weakly bonded to Os primarily via H, not C. It is by no means clear whether it actually corresponds to the sought (**5** to **2**) transition state. This structure,

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(33) Bosque, R.; Maseras, F.; Eisenstein, O., unpublished.

which has a very small negative eigenvalue in the Hessian, could be the transition state for full dissociation of benzene or a very weak sigma complex. A calculation of the Hessian and a study of the minima that connect to **6** would be necessary for a full understanding of this point. Even though it may not be the transition state between **5** and **2**, the energy of **6** (28.3 kcal mol^{-1}) could be taken as a lower threshold for the barrier between **2** and **5**. Such a process is thus not likely to take place at 25−50 °C. More fundamentally, it shows that reaching **6** is more likely to lead to complete loss of benzene than merely H scrambling.

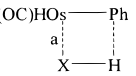
Reaching intermediate **5** and returning to **2** is not sufficient for exchanging the hydride and the H of the phenyl ring in **2** since these are still not equivalent in **5**. Unless some additional fluxional process occurs, only the hydride that was originally on the metal can return to it. The transition state, **7** (Figure 2), for a *hapto*-tropic shift[34] was located. It is only 4.1 kcal mol^{-1} above intermediate **5**. The metal fragment migrates from the C1−C2 bond to the C1−C6 bond; C1 is closer (2.350 Å) to Os than the two exchanging carbons, C2 (2.730 Å) and C6 (2.747 Å), which are approximately equivalent. The bond angle of the carbonyl with respect to the benzene is essentially unchanged from **5**, (O)C−Os−C1 is 146.6° in **7**. Transition state **7** can be viewed as an allylic-bound benzene.

It thus appears that if the η^2-benzene complex could be reached, full exchange of hydrides would occur since the subsequent *hapto*-tropic shift of the Os(CO)L_2 fragment above the benzene is energetically very easy (4.1 kcal mol^{-1}). The energy of the η^2-benzene above the ground state is thus the crucial parameter that controls the facility of the reaction. This result is consistent with the studies on Cp*RhL(arene), where it was found that the difference in energy between the η^2-(arene) and hydride−aryl complexes controls the C−H activation process and thus the exchange between the hydrides.[30] The energy difference between the η^2-arene and the hydrido−aryl species is small in the case of Rh, since the two structures correspond well to the known oxidation state (Rh(I) and Rh(III)). Calculations have confirmed that the transition state connecting these two structures is energetically accessible.[33] In the case of Os, the metal goes from Os(II) to Os(0) in a 16-electron species. While unsaturated Os(II) is a common situation, unsaturated Os(0) is extremely rare and presumably highly energetic. This accounts for the lack of hydride−hydrogen scrambling in **1**. The metal is strongly reducing, and only the accumulation of π acceptors as in Os(CO)$_4$ has permitted *matrix isolation* of such a species.[35] For apparently similar reasons, no 18-electron Os(0) intermediate, (η^4-benzene)Os(CO)L_2 could be located on the potential energy surface. Our studies also show that any intramolecular rearrangement involving unimolecular reductive coupling of C and H is unfavorable. Full reductive elimination of benzene, leaving behind the highly unsaturated (14-electron) Os(CO)L_2, is naturally not favorable.

(g) Reactivity with H_2. Reaction of OsH(Ph)(CO)L_2 with H_2 (1 atm, 25 °C) yields, within time of mixing, exclusively Os(H)$_2$(H_2)(CO)L_2 and benzene. The very different rates of reaction with H_2 and with C_6D_6 suggests that the two reactions do not both proceed through a dissociative mechanism where the departure of PhH will be the common rate-determining step. Therefore, at least one of these involves a second-order (i.e., associative) mechanism.

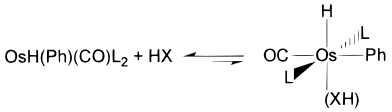
(h) Associative Reductive Eliminations? Reductive eliminations, especially those of the late transition metals (e.g., Ni, Au) are frequently "triggered" by coordination of an additional ligand,[36−38] particularly a strong π acid. Because OsH(Ph)(CO)L_2 is unsaturated, it might eliminate C_6H_6 by a bimolecular mechanism. It is thus surprising that addition of CO to OsH(Ph)(CO)L_2 does *not* stimulate reductive elimination of benzene. Even after 24 h at 90 °C, OsH(Ph)(CO)$_2L_2$ is recovered unchanged. The exchange reaction with benzene or other arenes (see below) thus stands in surprising contrast to the stability of this CO adduct.

The presence of unsaturation also might enable operation of a σ-bond metathesis mechanism for replacement of phenyl by X of HX. This is because the bond formation shown at **a** in **E**



E

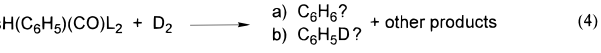
can occur by donation of electron density of X (e.g., a lone pair) into the available LUMO on Os which saturated (late) transition metal complexes lack. It must be recognized at the outset, however, that this concerted four-center mechanism which is typically envisioned for σ-bond metathesis cannot easily be distinguished from a conventional preequilibrium binding of HX to OsH(Ph)(CO)L_2 (eq 3). The binding of HX



(3)

to Os could be η^1 (e.g., H−OR, or the reaction with water) or η^2 (e.g., C_6H_6). We have investigated this question where the HX reagent is H_2. Our goal is thus to discuss the mechanism of benzene loss in the presence of HX. Calculations show that unimolecular dissociation of benzene is a high-energy process. We will attempt to establish experimentally if the mechanism via dissociation of benzene can be excluded, and we will consider both oxidative addition and σ-bond metathesis mechanisms.

Hydrogenolysis of OsH(Ph)(CO)L_2 offers a special opportunity to test the degree of equivalence of the arriving H_2 with the H on Os. We therefore studied the product of reaction with D_2 (eq 4). The central question is whether the departing

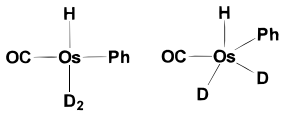


(4)

benzene incorporates only the original hydride (eq 4a), or instead one proton derived from an incoming dihydrogen (eq 4b). That is, we investigate the selectivity of the C−H bond-forming event. Stirring a solution of OsH(C_6H_5)(CO)L_2 in decalin under D_2 gives a rapid color change from red to pale peach. GC/MS analysis of the benzene which was transferred away from the osmium-containing product shows 90% C_6H_6, together with (after subtraction of intensity for $^{12}C_5{}^{13}CH_6^+$) 10% C_6H_5D. A control experiment in which OsD_4(CO)L_2 is contacted with C_6H_6 under the same transfer and analytical conditions shows no significant incorporation of deuterium into C_6H_6. A σ-bond metathesis mechanism, which would predict 100% C_6H_5D, is clearly excluded. The initial adduct in an oxidative addition

(34) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396.
(35) Schreckenbach, G.; Ziegler, T.; Li, J. *Int. J. Quantum Chem.* **1995**, *56*, 477.
(36) Hardy, D. T.; Wilkinson, G.; Young, G. B. *Polyhedron* **1996**, *15*, 1363.
(37) Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466.
(38) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1992**, *114*, 6087.

mechanism will have structure **F1** (phosphines, perpendicular to the plane portrayed, have been omitted), and thus the original hydride of $OsH(Ph)(CO)L_2$ is chemically inequivalent from the added dihydrogen, regardless of whether the latter binds as the intact molecule or it immediately oxidatively adds, to give **F2**.

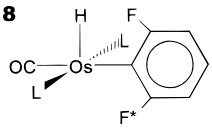


F1 **F2**

If reductive elimination is faster than any site exchange among all 3 Os−H sites, the released benzene could be 100% C_6H_5D or 100% C_6H_6. If fluxionality is faster than benzene reductive elimination, then the benzene will be 67% C_6H_5D; an ordinary primary kinetic isotope effect on reductive elimination will decrease the yield of C−D product. Given the low level of D incorporation in released benzene, we believe our results are in best agreement with either **F1** or **F2** with slow H site exchange, i.e., with a mechanism where π-acidic D_2 (or H_2) "triggers" reductive elimination of the C_6H_5 with the H already present in reagent **1**.

(i) Reactivity with Fluorinated Arenes. We sought to establish the thermodynamics and the selectivity of arene substituent cleavage by $OsH(Ph)(CO)L_2$ by reacting it with 1:1.5 mole ratio fluorinated arene in d_{12}-cyclohexane solvent at 25 °C.

(a) 1,3-$C_6H_4F_2$. This reaction proceeds to completion within 1 h at 25 °C to give a single product. The product shows a $^{31}P\{^1H\}$ NMR singlet and a hydride resonance which is a triplet of doublets of doublets, due to coupling to two equivalent ^{31}P and two inequivalent equal intensity ^{19}F nuclei. The fluorine chemical shifts are characteristic of F on carbon, not osmium, and exclude any significant agostic interaction of F* with Os. Both the hydride and the ^{31}P chemical shifts are within 2 ppm of those of $OsH(Ph)(CO)L_2$. The ^{19}F NMR spectrum shows two chemical shifts, which is consistent with structure **8** under the assumption that rotation around the Os−C(*ipso*) bond is slow and the aryl ring plane is coincident with the H−Os−CO plane.



The ^1H NMR spectrum shows three unit intensity aryl multiplets. Free benzene is also detected (^1H NMR) following this reaction. This reaction is thus highly selective for a single ring hydrogen of 1,3-$C_6H_4F_2$ (no product of C−F activation is formed), and this product persists unchanged in cyclohexane for at least 7 days. The fluorinated aryl is thus thermodynamically preferred (in comparison to C_6H_5), and the most "perturbed" C−H bond (that between two fluorines) is also the one which reacts. This surely rules out any steric influence on the preferred product, and implies that electronic effects lead to the observed selectivity. Is this selectivity kinetic or thermodynamic?

This product is unchanged after heating for 30 h at 70 °C in C_6D_{12}, suggesting that this is the thermodynamically most stable isomer. We have followed the evolution of the reaction of $OsH(Ph)(CO)L_2$ with 10 equiv of 1,3-$C_6F_2H_4$ from five to 30 min of combining these reagents (the reaction is then complete), and found no evidence of any other product. Thus, we feel that the kinetic product is the thermodynamic product. Note also that the persistence of $OsH(2,6\text{-}C_6F_2H_3)(CO)L_2$ for 30 h at 70 °C in d_{12}-cyclohexane marks this as more durable than $OsH(Ph)(CO)L_2$, which decomposes to free phosphine and benzene under such conditions.

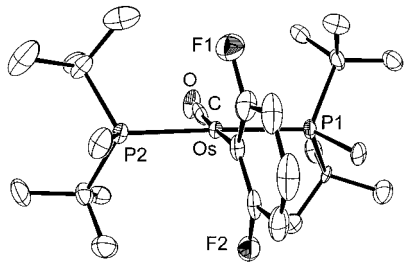
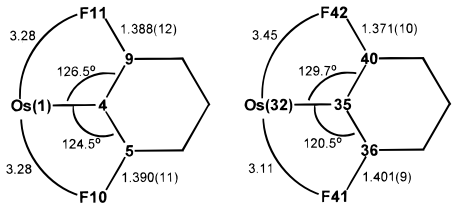


Figure 3. ORTEP drawing of one molecule of **8** showing selective atom labeling. The hydride was not located.

Table 2. Bond Distances and Angles

			molecule A	molecule B
		Distances		
Os(1)	P(12)		2.3644(23)	2.3890(23)
Os(1)	P(22)		2.3841(22)	2.3665(23)
Os(1)	C(2)		1.856(10)	1.859(9)
Os(1)	C(4)		2.132(8)	2.145(8)
F(10)	C(5)		1.390(11)	1.401(9)
F(11)	C(9)		1.388(12)	1.371(10)
O(3)	C(2)		1.176(11)	1.176(10)
		Angles		
P(12)	Os(1)	P(22)	175.82(8)	175.97(7)
P(12)	Os(1)	C(2)	92.39(27)	92.25(26)
P(12)	Os(1)	C(4)	88.69(23)	87.49(23)
P(22)	Os(1)	C(2)	91.68(27)	91.73(26)
P(22)	Os(1)	C(4)	87.26(22)	88.53(23)
C(2)	Os(1)	C(4)	178.1(4)	179.5(3)
Os(1)	P(12)	C(13)	113.8(3)	114.6(3)
Os(1)	P(12)	C(14)	113.6(3)	114.63(27)
Os(1)	P(12)	C(18)	114.4(3)	113.5(3)
Os(32)	P(43)	C(44)	113.7(3)	114.1(3)
Os(32)	P(43)	C(45)	113.0(3)	112.1(3)
Os(32)	P(43)	C(49)	115.1(3)	114.9(3)
Os(1)	C(2)	O(3)	178.9(8)	179.2(8)
Os(1)	C(4)	C(5)	124.5(7)	120.3(6)
Os(1)	C(4)	C(9)	126.5(7)	129.7(6)

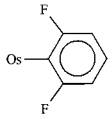
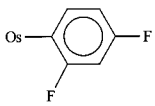
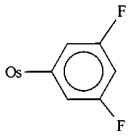
Scheme 2



8A **8B**

A single-crystal X-ray structure determination (Figure 3 and Table 2) confirms all of the conclusions made above from spectroscopic data. The molecule is square-pyramidal with the aryl ring lying nearly in the mirror plane which relates the two phosphines, and the methyl groups lie *syn* to the aryl group. The hydride ligand was not detected in the X-ray study. There are two crystallographically independent molecules in the asymmetric unit, and the two have quite similar structures (Table 2). Both show a curious inequality ($\sim 10\sigma$) of their two Os−P distances of about 0.02 Å. The $OsP_2C(ipso)C(O)$ unit is rigorously planar, but the two molecules differ somewhat in the orientation of the $OsC_6H_3F_2$ unit (Scheme 2; bond lengths are in Å). In molecule **8A**, Os(1) is symmetrically located with respect to the two fluorines. In molecule **8B**, Os does not lie

Table 3. Selected Geometrical Parameters (Å and deg) and Relative Energies E (kcal·mol^{-1}) for the Different B3LYP Optimized Isomers of OsH(x,y-$C_6F_2H_3$)(CO)(PH_3)$_2$

	x,y	E	OsC1C2	OsC1C6	C2H2	C6H6	C2F2	C6F6
	(2,6)	0.0	113.0	134.0			1.430	1.403
	(2,4)	+3.6	111.5	134.3		1.086	1.430	
	(3,5)	+9.5	118.1	125.1	1.088	1.084		

on the C_2 axis of the ring, so that F(41) is closer than F(42) to Os(32), but still not significantly shorter than the sum of van der Waals radii (~3.2 Å).[39] The F closer to Os(32) also has a longer C−F bond. On balance, we conclude that these probably are not incipient *ortho*-agostic interactions. It is also found (Figure 3) that in neither molecule does Os lie rigorously in the aryl plane. The origin of this distortion can be traced to the influence of neighboring molecules: Molecule **8A** shows face-to-face stacking of the aryl ring with that of its centrosymmetrically related partner, and the aryl of Molecule **8B** presents its edge to the face of an aryl of Molecule **8A**. Thus, there are torques acting on each of these molecules in the solid.

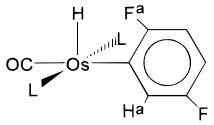
It has been shown that deuterated benzene exchanges with H−Ph from OsH(Ph)(CO)(P^tBu_2Me)$_2$. Our computational study (above), which found a high-energy (28.3 kcal.mol^{-1}) structure with benzene weakly bound to the metal, suggests a preference for an associative mechanism. Interestingly, experiment reveals a strong thermodynamic preference for fluorobenzene to react with OsH(C_6H_5)(CO)(PR_3)$_2$ to replace the phenyl ring by the fluoroaryl. We limited our studies to the thermodynamic aspect of this preference, together with the regioselectivity (position of the F in the ring) of the product. We have thus calculated the isodesmic reaction (eq 5). Several fluorine positional isomers

$$\mathrm{OsHPh(CO)(PH_3)_2} + \text{1,3-}\mathrm{C_6H_4F_2} \rightleftharpoons \mathrm{OsH(C_6H_3F_2)(CO)(PH_3)_2} + \mathrm{C_6H_6} \quad (5)$$

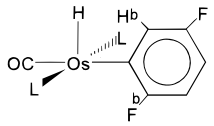
of OsH($C_6F_2H_3$)(CO)(PH_3)$_2$ were considered: (2,6), (2,4), and (3,5). Each of these complexes was fully optimized within the same C_s symmetry orientation of **2**. In the case of the (2,4) isomer, only the isomer with the C−F *ortho* bond *cis* to the empty site was considered, following experimental evidence (vide infra).

None of the isomers of OsH($C_6F_2H_3$)(CO)(PH_3)$_2$ present unusual geometrical features (Table 3). The energetic scheme is in excellent agreement with the experimental results. The isodesmic reaction depicted in eq 5 is shown to be exothermic for any position of F in the ring. The most stable isomer is the (2,6) isomer ($\Delta E = -12.8$ kcal·mol^{-1}), followed by the (2,4) isomer ($\Delta E = -9.2$ kcal·mol^{-1}), and by the (3,5) isomer ($\Delta E = -3.3$ kcal·mol^{-1}). The preference for F substitution on the phenyl ligand with the very specific regioselectivity pattern (*ortho* > *para* > *meta*) is also consistent with phenyl being a π donor in this "unsaturated" species. A similar regioselectivity pattern was also observed in the case of Rh.[40]

(b) 1,4-$C_6H_4F_2$. This substrate has only one type of C−H bond, yet it reacts to give two products **9** and **10**. OsH(Ph)-



9



10

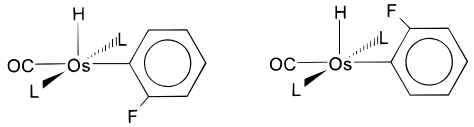
(CO)L_2 is 80% consumed after 2 d at 25 °C, which means it is significantly slower than the reaction with 1,3-$C_6H_4F_2$. The ratio of products, **9** and **10**, varies with time during disappearance of OsH(Ph)(CO)L_2. After 1 d (50% conversion of OsH(Ph)-(CO)L_2), the **9**:**10** ratio was 2.3:1. After a total time of 6 d, the ratio of **9**/**10** becomes 1:8.2, suggesting **9** → **10** conversion at a rate only slightly slower than the rate of formation of **9**. Each product has a hydride triplet (^{31}P) of doublets (coupling to one ^{19}F) and a ^{31}P{^{1}H} NMR singlet; their chemical shifts lie within 2 ppm of those of OsH(Ph)(CO)L_2. The ^{19}F NMR shows two chemical shifts for each product, one value being within 4 ppm of the value of the free 1,4-difluorobenzene, and a second shifted 20−30 ppm to lower field. These latter we assign to F^a and F^b, the fluorines closer to Os in the two *rotamers* which are in only slow exchange (equilibrium). This is compatible with the aryl being perpendicular to the P−Os−P line as in OsH(Ph)(CO)L_2 and with hindered rotation of the aryl for steric and electronic reasons. These structures also explain the hydride NMR multiplet (triplet of doublets) provided the hydride couples only to the *ortho* fluorine. There is *no* evidence for cleavage of C−F bonds in this reaction.

(39) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(40) Semeczy, A. D.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1994**, *13*, 522.

An NOE experiment was carried out on a mixture of the two conformers in an attempt to assign the observed hydrides and *ortho* aryl proton resonances to individual conformers **9** and **10**. We anticipate, upon irradiation of the appropriate hydride resonance, that conformer **9** should show negligible NOE to H^a, while conformer **10** should show enhancement at H^b. In fact, irradiation of the −38.2 ppm hydride (kinetic product) gives virtually no NOE enhancement in the aryl region, while irradiation of the −40.0 ppm hydride (thermodynamic product) gives enhancement of a doublet at +6.88 ppm. The doublet at 6.88 ppm is thus assigned to H^b, and therefore, the thermodynamic isomer has structure **10**. The preference for **10** could be interpreted as indicating a steric repulsion between the hydride and F in **9**. The ^{19}F chemical shifts establish the absence of significant F → Os bonding in **10**. The *meta* fluorine chemical shifts are only 3 ppm (upfield) from those of free p-difluorobenzene (104 ppm), while the *ortho* fluorines are 16 (isomer **10**) and 27 ppm (isomer **9**) downfield from the free arene signal. In comparison to the large shift when a terminal fluoride becomes a μ_2-F ligand, the difference between the two *ortho* chemical shifts (11 ppm) is small and thus permits the conclusion that there is no agostic binding of the F to Os in conformer **10**. Moreover, the ^{19}F δ value for *ortho* fluorine in conformer **10** is *less* shifted from the value in free *para*-$C_6H_4F_2$ than the *ortho*- fluorine in conformer **9**.

(c) C_6FH_5. This reaction is slower than the above two, requiring 7 d to proceed to completion at 25 °C. Two products (**11** and **12**) are observed by ^{31}P and ^1H NMR spectroscopy,



11 **12**

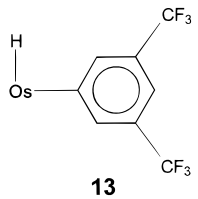
with all chemical shifts being within 1 ppm of those of OsH(Ph)(CO)L_2. The hydride signal of each product is a triplet (^{31}P) of doublets (^{19}F), consistent with structures **11** and **12**. Over the course of the 7 d, the ratio of **11** and **12** changes, indicative of (only) slow equilibration between these two conformers. The final **11**:**12** ratio was 6.7:1. We reject the idea that the two observed products involve Os−aryl products with *meta* and *para* fluorine because these should have significantly reduced hydride/F coupling constants in comparison to what we observe.

(d) C_6F_5H. The reaction of **1** and pentafluorobenzene is the quickest of all the fluorinated arenes, taking just 30 min at 25 °C to fully consume **1**. The single product as observed by ^{31}P and ^1H NMR is consistent with the hydrido−aryl, square-pyramidal products seen for the other arenes. The hydride signal is a broad triplet (^{31}P) of triplets (^{19}F), the two H/F coupling constants being accidentally degenerate. The ^{19}F NMR spectrum showed five signals, demonstrating the slow rotation of the arene in this species. The carbonyl stretching frequency of this product is 10 cm^{-1} higher (1908 cm^{-1}) than that of the difluoro aryl species, OsH(2,6-$C_6F_2H_3$)(CO)(P^tBu_2Me)$_2$, which is in turn 20 cm^{-1} higher than that of the C_6H_5 analogue. This illustrates the cumulative effect of the fluorine substituent diminishing the overall donor power of an aryl group. This is *opposite* to the effect of fluorine directly attached to the metal, and opposite to the π-donor effect of fluorine on the phenyl π-system (which would act to make the fluorinated aryl a stronger π-donor), and thus apparently reflects reduced sigma donation as a phenyl ligand is progressively substituted by fluorines. Such lower sigma donation may explain the greater thermodynamic stability of OsH(Aryl)(CO)L_2 when "Aryl" is fluorinated (eq 5) due to diminished sigma competition with the CO ligand *trans* to "Aryl".

(e) C_6F_6. This arene shows no reaction with **1** under the standard reaction conditions. NMR spectra at −80 °C showed no evidence for arene binding to Os.

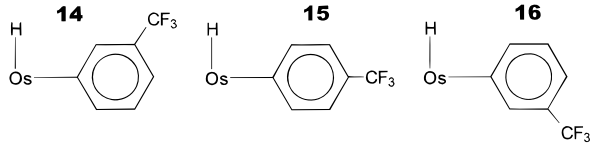
The Effect of F on Rate and Regioselectivity. Each of the above reactions is faster than the reaction of OsH(Ph)(CO)L_2 with neat toluene or benzene, and the above reactions are moreover accelerated as the number of fluorines *ortho* to the cleaved C−H bond is increased. The observed products (both their preference over C_6H_5 itself, and their regioselectivity) are thus favored by *ortho* fluorine substituents. While this must be argued in terms of product stability, we wish to emphasize that back-donation is greater to fluorinated *olefins* than to hydrocarbon olefins, and that this may influence the regiochemistry of binding of Os to the fluoroarene π-cloud *during* the reaction; Os may prefer to interact with the π-cloud *ortho* to the fluorinated carbon, making the kinetic preference also the thermodynamic one. Note also that many reductive elimination reactions of R with H on a single metal are triggered by approach of an electron-deficient olefin or alkyne.[41−44]

Reactivity with CF_3-Substituted Arenes. Since F is a σ-withdrawing but a π-donating arene substituent, we looked at the reactions of arenes bearing the σ-withdrawing but less π-donating CF_3 substituent. All reactions are generally slower than those of fluoroarenes and were studied with 1.5 equiv arene at 55 °C in C_6D_{12}. Reaction (1 h) of 1,3-$C_6H_4(CF_3)_2$ gives only one product, which is assigned structure **13** based on a single



13

new hydride signal (triplet at −39.9 ppm) and a new phosphine resonance. Reaction (24 h) with 1,4-$C_6H_4(CF_3)_2$ gives only gross decomposition to a variety of products (^{31}P NMR evidence); this we attribute to excessive steric hindrance with an *ortho* CF_3 group in any product. Reaction (6 h) with $CF_3C_6H_5$ gives (^{31}P and ^1H NMR evidence) equal amounts of three products, assigned as **14**, **15**, and **16**.



Influence of Added Phosphines. In seeking the reaction pathway for arene exchange, the work with D_2 and OsHPh(CO)(P^tBu_2Me)$_2$, (**1**), suggested that a π acid ligand encourages reductive elimination (note, however, that the π-acid CO does *not* promote reductive elimination here). The experiments with OsD(Ph)(CO)(P^tBu_2Me)$_2$ and the calculation for hydrogen exchange showed that η^2-benzene intermediates have an energy

(41) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.
(42) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350.
(43) Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262.
(44) Pedersen, A.; Tilset, M.; Folting, K.; Caulton, K. G. *Organometallics* **1995**, *14*, 875.

too high to be easily accessed. The observed dependence of rate of arene exchange on type of fluorinated arene suggests that a second arene is present during the rate-determining step.

To test for C−H oxidative addition of reagent arene prior to benzene elimination, OsD(Ph)(CO)(P^tBu_2Me)$_2$ was reacted with 1,3-difluorobenzene in protio cyclohexane at room temperature. The deuterium NMR signal of OsD(Ph)(CO)(P^tBu_2Me)$_2$ decreased over 40 min, while the signal for free C_6H_5D increased over the same time period. There was no evidence (^{2}H NMR) of formation of OsD($C_6H_3F_2$)(CO)(P^tBu_2Me)$_2$. This excludes any dihydride mechanism with two equivalent hydrides.

Addition or loss of Lewis bases triggers certain reductive eliminations.[38] We therefore studied the influence of 1.0 equiv of added P^tBu_2Me on the reaction of OsH(Ph)(CO)L_2 (**1**) with 1,3-difluorobenzene. The reaction took 1 d to reach completion, while in the absence of free phosphine, this reaction was over within 1 h. The simplest explanations of this effect would be a mechanism with preequilibrium phosphine loss (eq 6)

$$\mathrm{OsH(Ph)(CO)(P^tBu_2Me)_2} \overset{C_6D_{12}}{\rightleftharpoons} \underset{\text{reactive}}{\mathrm{OsH(Ph)(CO)(P^tBu_2Me)}} + \mathrm{P^tBu_2Me} \quad (6)$$

or with rate suppression by coordination of the added phosphine (eq 7).

$$\underset{\text{reactive}}{\mathrm{OsH(Ph)(CO)(P^tBu_2Me)_2}} + \mathrm{P^tBu_2Me} \overset{C_6D_{12}}{\rightleftharpoons} \underset{\text{unreactive}}{\mathrm{OsH(Ph)(CO)(P^tBu_2Me)_3}} \quad (7)$$

If there was significant occurrence of equilibrium 6, then there must also be incorporation of free phosphine into **1** in the absence of $C_6H_4F_2$. In fact, combining **1** and 6 equiv of P^iPr_3 (an isomer of P^tBu_2Me) in C_6D_{12} at 25 °C showed no growth of OsHPh(CO)(P^tBu_2Me)(P^iPr_3) on the time scale of the reaction with $C_6H_4F_2$. It is of interest that both OsHX(CO)(P^tBu_2Me)$_2$ (X = Cl, OH) *do* incorporate P^iPr_3 (in place of P^tBu_2Me) under these conditions. Equation 6 is thus excluded.

If eq 7 were operative, then to account for added P^tBu_2Me decreasing the reaction half-life of **1** with $C_6H_4F_2$ by a factor of over 20, there must be detectable amount of this tris-phosphine complex. Since no OsH(Ph)(CO)$(L)_2L'$ complexes are formed on the time scale of exchange in the above experiment, this also rules out rate suppression by eq 7. The mechanism must therefore be more complicated than the simple proposals outlined in eqs 6 and 7.

To test whether the presence of arene facilitated the release or addition of coordinated phosphines (i.e., eq 6 or 7), **1** was combined with 1.5 equiv of P^iPr_3 in C_6H_6. Since the resulting $^{31}P\{^1H\}$ NMR spectrum showed only two sharp signals, indicative of only **1** and free P^iPr_3, arene does not enhance any phosphine substitution or addition. On the time scale of reaction with $C_6H_4F_2$, neither new products nor line broadening of **1** or of free P^iPr_3 were seen.

Next, **1** was reacted at room temperature with 1,3-difluorobenzene in the presence of 1 equiv of triisopropylphosphine. It was found that P^iPr_3 also retarded the rate of arene exchange, as did added P^tBu_2Me. After 2 d, in addition to the previously seen product, OsH(2,6-$C_6H_3F_2$)(CO)(P^tBu_2Me)$_2$, ^{31}P, ^{1}H, and ^{19}F NMR showed two new products whose spectra were consistent with the formulas OsH(2,6-$C_6H_3F_2$)(CO)(P^tBu_2Me)(P^iPr_3) and OsH(2,6-$C_6H_3F_2$)(CO)(P^iPr_3)$_2$. Each has an Os−H triplet of doublets of doublets. Each has two ^{19}F signals. One has a $^{31}P\{^1H\}$ NMR AB quartet, and the other is a singlet. This was the clearest evidence that exchange of phosphine was not a preequilibrium, but occurs later, after $C_6H_4F_2$ is involved in the mechanism. Using 2 equiv of triisopropylphosphine and a longer reaction time of 4 d (25 °C), the same three products are observed, but with an increase of amount of both P^iPr_3-containing species. The gradual downfield displacement of the ^{31}P chemical shift with progressive replacement of P^tBu_2Me by P^iPr_3 was consistent with the comparative chemical shifts of the two free phosphines.

Discussion

The arene exchange reactivity reported here (eq 8) differs

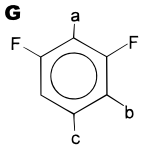
$$\mathrm{OsH(Ph)(CO)(P^tBu_2Me)_2} + \mathrm{*HAr} \rightarrow \mathrm{Os*H(Ar)(CO)(P^tBu_2Me)_2} + \mathrm{HPh} \quad (8)$$

qualitatively from that of the transient Cp*Rh(PMe_3) in that the Rh fragment is such a reactive and sterically unencumbered 16-electron species that it readily bonds arene η^2, which then rearranges to the C−H oxidative addition product. Moreover, CpRh(PMe_3)(η^2-C_6H_5D) undergoes unimolecular migration of CpRh(PMe_3) around the arene ring more rapidly than arene loss. Thus ΔE from $L_nM(H)(C_6H_5)$ to $L_nM(\eta^2\text{-}C_6H_6)$ is larger for the 14-electron fragment Os(CO)(P^tBu_2Me)$_2$ than for the 16-electron fragment, CpRh(PMe_3).

The H/aryl exchange of Cp*Rh(PR_3)H(C_6H_5) with other arenes, as well as the intramolecular exchange of RhH with C(aryl)-H bonds occur through an Cp*Rh(PR_3)(η^2-arene) intermediate. The fundamental difference between that system and ours is that comparable species (i.e., $L_nM(H)$(aryl), $L_nM(\eta^2$-arene), or L_nM) are 18- and 16-valence electron species for M = Rh while they are 16- and 14-electron species for M = Os. This raises the possibility of associative mechanisms for M = Os, especially if the 14-electron count for Os(0) is accepted to be energetically inaccessible in a fully dissociative mechanism as indicated by the calculations. However, the highly crowded nature of OsH(Ph)(CO)(P^tBu_2Me)$_2$ may put severe steric constraints on any associative mechanism.

Regarding an associative mechanism, we have argued that a strong sigma donor (e.g., hydride) *trans* to an empty coordination site diminishes Lewis acidity by raising the energy of the LUMO. In practice, this is confirmed since **1** and its fluoroaryl analogue show no NMR evidence for agostic interactions either with ^{t}Bu groups or with *ortho* aryl H or F, and we detect no adduct with a fluoroarene. However, OsH(Ph)(CO)(P^tBu_2Me)$_2$ does bind N_2 weakly, and thus it does have sufficient Lewis acidity to bind the weak nucleophile N_2.

It has been reported that the transient Cp*Rh(PMe_3), generated from either Cp*Rh(PMe_3)H(Ph) or Cp*Rh(PMe_3)$(H)_2$, shows thermodynamic preference for C−H oxidative addition to the fluoroarene carbon *ortho* to one or two C−F bonds. There, as here, rotamers were observed to give distinct (low temperature) NMR signals. Reaction conditions were more demanding than with OsH(Ph)(CO)L_2 (higher temperature, or photolysis, and use of pure fluoroarene as solvent), due to the high activation energy for production of Cp*Rh(PMe_3). As a result, it was not possible to detect the higher rates of reaction with the more heavily fluorinated arenes which we find here. On the other hand, Cp*Rh(PMe_3) reveals kinetic selectivity, which is in fact surprisingly low; for example, the kinetic product distribution shows similar amounts of σ-aryl products with Rh at sites **a**, **b**, and **c** in **G**. Moreover, the rate of migration of Rh



from **c** to **b** is significantly faster than that from **b** to **a**; migration (via an η^2-arene species) *past* fluorine involves a higher activation energy.

Any mechanism for the arene exchange reaction reported here must account for the following observations:

(1) Rate of exchange is dependent on type of arene, i.e., reagent arene is present at the rate-determining step.

(2) Deuterium of OsD(Ph)(CO)(P^tBu_2Me)$_2$ does not exchange significantly with incoming arene.

(3) Free phosphine inhibits the arene exchange reaction.

(4) A simple Lewis base adduct, OsH(Ph)(CO)(P^tBu_2Me)$_{3-n}$(P^iPr_3)$_n$, was not seen.

(5) Exchange of coordinated P^tBu_2Me with free P^iPr_3 was not found for **1** or the 2,6-difluorobenzene analogue (in arene solvents).

6) Detectable phosphine exchange occurs during the reaction of **1** and 1,3-difluorobenzene and P^iPr_3.

Phosphine inhibition (item 3) was shown not to arise by the direct influence of free phosphine on **1** or any species in thermal equilibrium with **1**. This also excludes CO dissociation (eq 9), because we know that lost CO should rapidly form OsH(Ph)(CO)$_2$(P^tBu_2Me)$_2$, yet this was not observed.

$$\mathrm{OsH(Ph)(CO)(P^tBu_2Me)_2} \not\rightleftharpoons \mathrm{OsH(Ph)(P^tBu_2Me)_2 + CO} \qquad (9)$$

$$\mathrm{OsH(Ph)(CO)(P^tBu_2Me)_2 + CO} \xrightarrow{\text{fast}} \mathrm{OsH(Ph)(CO)_2(P^tBu_2Me)_2}$$

The collective observations summarized above can be accommodated by the mechanism in eq 10, which involves arene association followed by a phosphine dissociation step.

$$\mathrm{OsH(Ph)(CO)(P^tBu_2Me)_2} \underset{-\mathrm{HAr}}{\overset{+\mathrm{HAr}}{\rightleftharpoons}} \mathrm{(HAr)OsH(Ph)(CO)(P^tBu_2Me)_2} \qquad (10)$$

$$\mathrm{(HAr)OsH(Ph)(CO)(P^tBu_2Me)_2} \xrightarrow[k_1]{-\mathrm{P^tBu_2Me}} \mathbf{H}$$

$$\mathrm{OsH(Ar)(CO)(P^tBu_2Me)_{2-n}(L')_n} \xleftarrow[-\mathrm{HPh};\ k_2]{+\mathrm{L'}} \mathrm{Os(\text{"}HArHPh\text{"})(CO)(P^tBu_2Me)} \quad \mathbf{I}$$

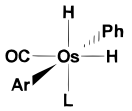
This mechanism accomplishes the arene exchange with the postulate that **I** will eliminate benzene, but that **H** will not; fewer electron-donating phosphine ligands in **I** leaves the metal less reducing, so that C−H reductive coupling has occurred in **I**. This mechanism also obviously involves incoming arene and can therefore explain the dependence of rate on reagent arene. While it places both arenes on the metal at once, there are never two equivalent hydrides (see below), so that it is consistent with the observed lack of isotope exchange. The nature of the association of HAr with Os in **H** and **I** can vary widely, and we purposely leave it unspecified. It is clear that all rate constants will depend on the identity of Ar. In particular, the comparative rate of forward (k_2) and back (k_1) rate constants involving **I** will favor HAr cleavage for electronegative (i.e., "oxidizing") Ar. This is one place where regiochemistry on the HAr ring will be determined.

The observations place some constraints on adduct **H** and species **I**:

(1) Adduct **H** could have HAr bound to the empty coordination site of OsH(Ph)(CO)L$_2$ *trans* to hydride, either by the C−H bond or more likely by the arene π-system (e.g., η^2). It could also involve a π-stacking interaction between the phenyl and the arriving aryl; this is especially attractive for the more highly fluorinated arenes, where some charge transfer would increase binding *and* give rise to the observed acceleration as F content grows. It is also consistent with the π-stacking observed in the crystal structure reported here.

(2) Adduct **H**, being crowded, has a reason to lose a bulky phosphine, which then accounts for rate suppression by added phosphine, and phosphine (L′) incorporation in product, but not in recovered reactant complex.

(3) The structure of **I** must keep the Os−H distinct from the H of the arriving arene. This could be because there is no scission of this C−H bond in **H** and/or **I** (i.e., HAr is bound by a C−H bond or by the arene π-system) or because of an oxidative addition structure with inequivalent hydrides (**J**). In this way, the lack of mixing in our (C_6H_5)Os-D + H−Ar experiments is accommodated.



J

Adduct formation must be endergonic since there is no observational evidence for this species being directly populated; spectroscopic data are essentially identical in cyclohexane and in benzene solvent. An attempt to detect an "adduct" by using the most electron-withdrawing fluoroarene, C_6F_6 (chosen because it does not react further) showed no significant change in either ^{1}H (Os−H) or ^{31}P chemical shift or multiplicity down to −85 °C in a solvent mixture of C_6F_6 and perfluorotoluene; only solvent shifts typical of those seen for 18-electron solutes are observed.

Conclusions

This work has revealed that an OsHR(CO)L$_2$ species can be metastable and that any reactions involving reductive eliminations of benzene from OsH(Ph)(CO)(P^tBu_2Me)$_2$ are initiated by an attacking reagent. Carbon monoxide, MeCN, and N_2 addition is *not* followed by reductive eliminations, but H_2 additions are. Fluorinated benzenes trigger reductive elimination (benzene very slowly and C_6F_5H very fast), but hexafluorobenzene does not react. The only detected products involve scission of C−H bonds of the fluoroarenes. The different oxidation states, different valence electron counts, and different steric encumbrances combine to make the mechanism of reaction with fluoroarenes very different for CpRh(PMe_3)H(Ph) and OsH(Ph)(CO)(P^tBu_2-Me)$_2$. Most noteworthy is that, despite the unsaturation (compensated by significant π donation to Os) of OsH(Ph)(CO)(P^tBu_2Me)$_2$, these C−H reductive eliminations occur by a mechanism where one phosphine dissociates from Os. Until recently, this would have been most unusual. However, it is now known[45] that phosphine loss is a mechanistic requirement for conversion of OsHCl(CO)(P^tBu_2Me)$_2$ to Os(CH_3)Cl(CO)(P^tBu_2Me)$_2$ using CH_2N_2. Certainly among phosphines, the bulky ones are optimal for dissociation with minimum energy cost.

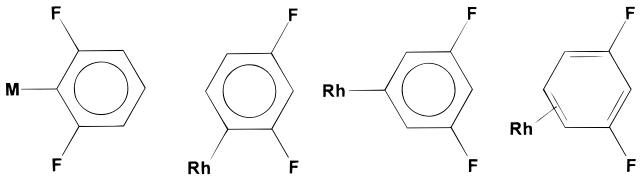
It is broadly true that introduction of a carbonyl ligand into a polyhydride complex can change the redox balance of hydride toward dihydrogen and can also lead to H_2 elimination (thus,

(45) Huang, D.; Spivak, G. J.; Caulton, K. G. *New. J. Chem.* **1998**, *22*, 1023.

to trigger reductive elimination). This is attributed to the metal being less reducing as it accumulates carbonyl ligands (thus, there are *no* polyhydride carbonyls, $MH_m(CO)_n$). This is accomplished in eq 10, where the proportion of CO among ligands increases by dissociation of one phosphine ligand.

Note also that the sequence of two steps in eq 10 is vaguely comparable to an associative interchange mechanism for ligand substitution. In summary, the mechanism deduced here for arene C−H activation has distinct differences from that reported for electron-rich 16-electron transients such as CpRh(PMe_3) and M(dmpe)$_2$ with M = Ru or Fe. There, the initial higher oxidation state (III and II, respectively) is transformed by a 2-electron reductive elimination, and only subsequently does the C−H substrate (new arene) bind. For OsH(Ph)(CO)L_2, because it is already unsaturated, preassociation of the two reagents occurs, but phosphine loss from the saturated aggregate is necessary to trigger C−H bond formation (C_6H_6) and cleavage (H−Ar_F).

In drawing this contrast, it bears mention that the reaction product of 1,3-$C_6H_4F_2$ with OsH(Ph)(CO)L_2, under mild conditions which might be expected to reveal the kinetic product, gives isomer **K**. The transient CpRhPMe_3, however, gives **L** and **M** as kinetic products before isomerizing to the thermodynamic product **K**; both **L** and **M** can be seen as derived from η^2-complex **N**, consistent with different selectivity for the Rh and Os species, and thus from quite distinct *mechanisms* (**N** is never formed for Os) for these two reagent complexes.



K **L** **M** **N**

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

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