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Reactions of an Osmium-bis(dihydrogen) Complex under Ethylene: Phosphine Addition to a C-C Double Bond and C-H Bond Activation of Fluoroarenes

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The bis(dihydrogen) complex $[OsTp(\eta^2\text{-}H_2)_2(P^iPr_3)]BF_4$ (Tp = hydridotris(pyrazolyl)borate; **1**) reacts with ethylene under 2 atm of the gas to afford $[OsTp(CH_2CH_2P^iPr_3)(\eta^2\text{-}CH_2{=}CH_2)_2]BF_4$ **(2)**, which promotes the CH bond activation of fluorobenzene and 1,3-difluorobenzene to give $OsTp(3\text{-}C_6H_4F)(\eta^2\text{-}CH_2{=}CH_2)_2$ **(3)** and $OsTp(3,5\text{-}C_6H_3F_2)(\eta^2\text{-}CH_2{=}CH_2)_2$ **(4)**, respectively, releasing $[EtP^iPr_3]BF_4$. The formation of **2** takes place via $[OsTp(\eta^2\text{-}CH_2{=}CH_2)_2(P^iPr_3)]BF_4$ **(5)**, which has been isolated and characterized by X-ray diffraction analysis.

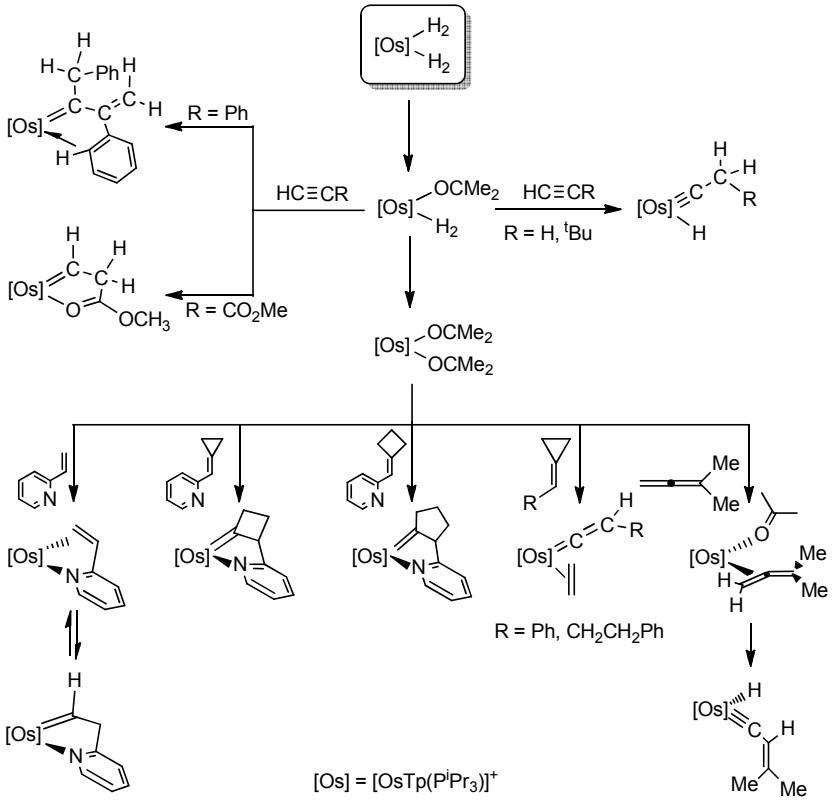
Introduction

The dihydrogen ligand of some compounds can be easily displaced by unsaturated organic molecules. In this way, it stabilizes highly unsaturated metal centers without bothering the coordination of organic molecules.[1] The bis(dihydrogen) derivatives $[MH_2(\eta^2\text{-}H_2)_2(PR_3)_2]^+$ (M = Rh, Ir)[2] and $RuH_2(\eta^2\text{-}H_2)_2(PR_3)_2$[3] are good examples of this behavior.

Few complexes containing two dihydrogen ligands are known. With some notable exception,[4] the majority of the bis(dihydrogen) compounds of late transition metals contain also hydride ligands.[5] The hydridotris(pyrazolyl)borate ligand (Tp) avoids the piano stool structures, typical for the cyclopentadienyl group (Cp), and enforces dispositions allowing N–Os–N angles close to 90º.[4d, 6] These structures favor the nonclassical interactions between the hydrogen atoms bonded to the metal center.[7] Thus, in contrast to the dihydride-dihydrogen Cp-cation $[OsH_2Cp(\eta^2\text{-}H_2)(P^iPr_3)]^+$,[8] the Tp-counterpart $[OsTp(\eta^2\text{-}H_2)_2(P^iPr_3)]BF_4$ (**1**) is a rare example of bis(dihydrogen) derivative that does not contain any hydride co-ligand.[6]

This bis(dihydrogen) compound is the starting point of an interesting novel organometallic OsTp-chemistry with unsaturated organic molecules (Scheme 1), including the transformation of terminal alkynes into carbynes and carbenes,[9] the olefin-alkylidene tautomerization of 2-vinylpyridine,[10] the formation of cyclobutylidene[11] and cyclopentylidene[12] derivatives by ring expansion of pyridyl substituted alkylidenecyclopropanes and alkylidenecyclobutanes, the cleavage of both $C(sp^3)$-$C(sp^2)$ bonds of alkylidenecyclopropanes in the absence of a coordinating substituent,[13] and the double C-H bond activation of *gem*-disubstituted allenes to afford hydride-alkenylcarbyne species.[14] Now, we report the formation of a phosphoniumethyl ligand and the C-H bond activation of fluoroarenes.

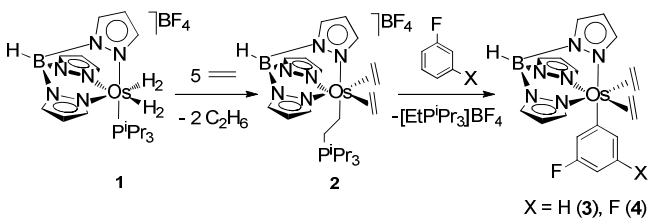
Scheme 1



Results and Discussion

The stirring of fluorobenzene solutions of **1** at 120 ºC, under 2 atm of ethylene, for 90 min, leads to the phosphoniumethyl derivative $[OsTp(CH_2CH_2P^iPr_3)(\eta^2\text{-}CH_2{=}CH_2)_2]BF_4$ (**2**), as a result of the hydrogenation of two ethylene molecules to ethane (δ, 0.85), the coordination of three additional olefins to the osmium atom, and the subsequent migration of the triisopropylphosphine ligand to one of the coordinated olefins (Scheme 2). Complex **2**, was isolated as a white solid in 80% yield and characterized by X-ray diffraction analysis. Figure 1 shows a view of the cation of the salt.

Scheme 2



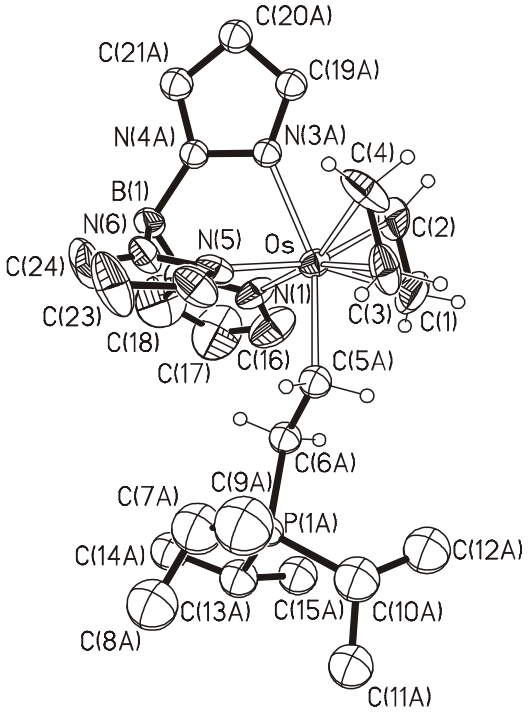


Figure 1. Molecular diagram of the cation of **2**. "A" labeled atoms are disordered (see Supporting Information). Selected bond lengths (Å) and angles (deg): Os–N(1) 2.132(7), Os–N(3A) 2.190(5), Os–N(5) 2.118(7), Os–C(1) 2.156(9), Os–C(2) 2.144(8), Os–C(3) 2.139(8), Os–C(4) 2.136(10), Os–C(5A) 2.200(12), C(1) –C(2) 1.424(14), C(3) –C(4) 1.407(15); N(1)–Os–N(5) 91.0(3), N(1)–Os–N(3A) 84.7(3), N(5)–Os–N(3A) 79.3(3), N(3A)–Os–C(5A) 155.9(5).

The structure proves the formation of the 2-(triisopropylphosphonium)ethyl ligand. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}NMR spectra in dichloromethane-d_2, at room temperature, are consistent with its formation. Characteristic features of this ligand in the ^{1}H NMR spectrum are two resonances at 1.91 and 1.35 ppm due to the CH_2 units. In the ^{13}C{^{1}H}NMR spectrum, the $OsCH_2CH_2P$ resonances appear at –4.8 and 18.0 ppm as triplets with C-P coupling constants of 14 and 32 Hz, respectively. The ^{31}P{^{1}H}NMR spectrum contains a singlet at 37.4 ppm, shifted by about 17 ppm towards lower field with regard to that of **1** (δ, 20.1). The ethylene molecules lie *trans* to the pyrazolyl groups, with the C–C double bonds parallel disposed and Os–C distances between 2.136(10) Å and 2.156(9) Å. They agree well with those found in other osmium-olefin complexes.[12-15] Similarly, the olefinic bond lengths of 1.424(14) Å

(C(1)–C(2)) and 1.407(15) Å (C(3)–C(4)) are within the range reported for transition-metal olefin complexes (between 1.340 and 1.445 Å).[16] The ethylene molecules are chemically equivalent, however the carbon atoms of each molecule are inequivalent. In spite of this, the ^{1}H NMR spectrum of **2** in dichloromethane-d_2, at room temperature, shows an AA'BB' spin system centered at 2.43 ppm for the coordinated ethylene molecules, which indicates a rapid rotation of the olefins around the osmium-ethylene bonds. In agreement with this, the $^{13}C\{^{1}H\}$NMR contains only one ethylene resonance at 52.8 ppm, even at −80 ºC, for the inequivalent carbon atoms.

Complex **2** is moderately stable under the reaction conditions. After 24 h, at 120 ºC, and under 2 atm of ethylene, it reacts with a solvent molecule to give $[EtP^{i}Pr_3]BF_4$ and a mixture of compounds from which the aryl derivative $OsTp(3\text{-}C_6H_4F)(\eta^2\text{-}CH_2{=}CH_2)_2$ (**3**) is the major species (> 80% by ^{19}F NMR).[17] After 48 h, under the same conditions, the 1,3-difluorobenzene solutions of **2** afford $OsTp(3,5\text{-}C_6H_3F_2)(\eta^2\text{-}CH_2{=}CH_2)_2$ (**4**) as a major isomer (> 80%). Complexes **3** and **4** were isolated as pale-yellow solids in 56% and 70%, respectively. Complexes **3** and **4** are notable, since they would not be accessible by classical electrophilic aromatic substitution. Thus, in most cases the formation of 2-fluoroaryl and 2,6-difluoroaryl derivatives is thermodynamically favored with regard to the related 3-fluoroaryl and 3,5-difluoroayl species.[18] The preferred formation of **3** and **4** with regard to their respective 2-fluoro and 2,6-difluoroaryl isomers, in addition to steric reasons, may be related to the electronic repulsion experienced by the *p*-orbitals of the fluorine atoms of the aryl ligands and the *p*-orbitals of the pyrazolyl groups *trans*-disposed to the olefins in the latter. The functionalization of the less sterically hindered C-H bond has been also observed in the borylation of 1,3-disubstituted arenes.[19] The $^{13}C\{^{1}H\}$ NMR spectrum of **3** supports the preferred *meta* C-H bond activation of fluorobenzene. In agreement with other 3-fluoroaryl complexes,[20] the spectrum shows six aryl resonances with C-F coupling constants decreasing in the sequence 242 ($J_C{}^{3}{}_{-F}$; δ, 161.3), 21 ($J_C{}^{4}{}_{-F}$; δ, 107.6), 17 ($J_C{}^{2}{}_{-F}$; δ, 125.5), 8 ($J_C{}^{5}{}_{-F}$; δ, 126.2) and 0 ($J_C{}^{1}{}_{-F}$ and $J_C{}^{6}{}_{-F}$; $\delta_C{}^{1}{}_{-Os}$, 153.2; $\delta_C{}^{6}$, 135.3) Hz. As expected for a 3,5-difluoroaryl derivate, the $^{13}C\{^{1}H\}$NMR spectrum of **4** contains four aryl resonances with C-F coupling constants of 245 and

12 ($J_C^{3,5}{}_{-F}$ and $J_C^{3,5}{}_{-F'}$; δ, 160.6), 26 ($J_C^{4}{}_{-F}$; δ, 96.2), 19 ($J_C^{2,6}{}_{-F}$; δ, 121.0) and 4 ($J_C^{1}{}_{-F}$; δ, 154.7) Hz. In agreement with **2**, the ^{1}H NMR spectra of **3** and **4** in dichloromethane-d_2 at room temperature contain AA'BB' spin systems centered at 2.70 and 2.78 ppm, respectively, for the coordinated olefin molecules, whereas the $^{13}C\{^1H\}$ NMR spectra between 25 and −80 ºC show only one ethylene resonance at about 57 ppm.

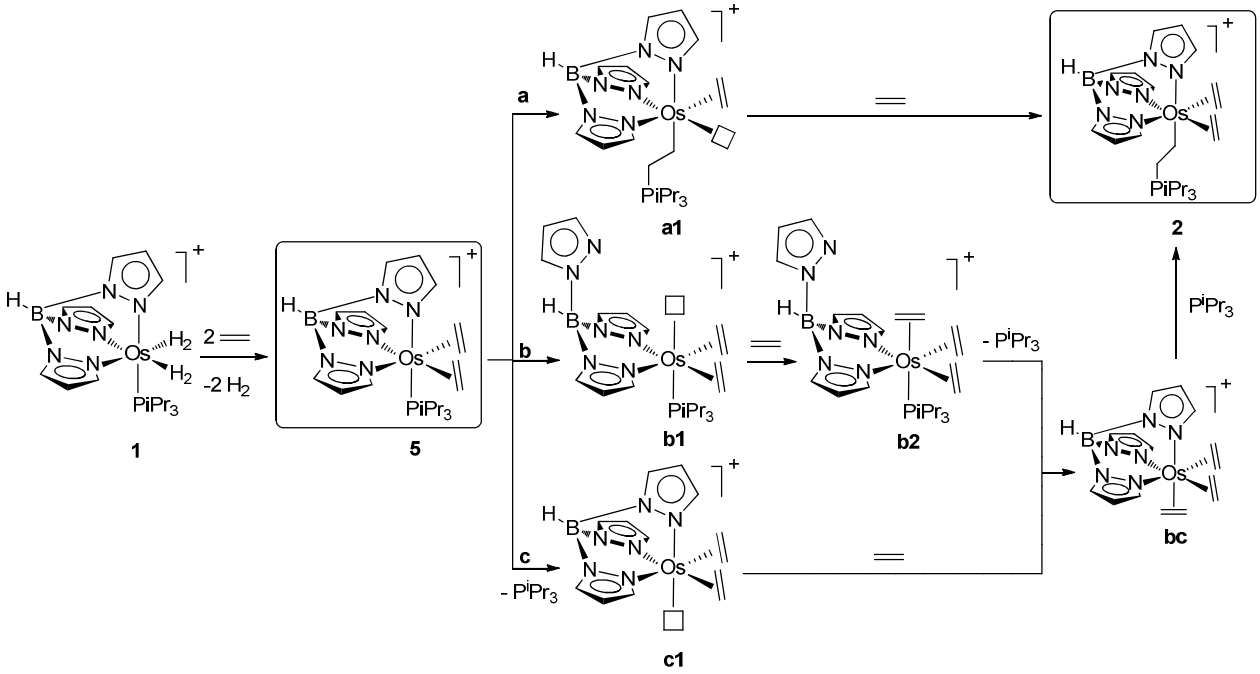
Because the $TpOs^{II}L$ fragment shows a very low tendency to afford Os^{IV} species by oxidative addition,[6,10,12,14] the formation of **3** and **4** most probably involves a σ-bond metathesis reaction between the activated C-H bond of the arene and the Os-C bond in an $Os(CH_2CH_2P^iPr_3)(\eta^2$-CH-arene)-intermediate, which is generated by dissociation of an arm of the Tp ligand. In this context, it should be mentioned that an EXSY experiment under ethylene atmosphere revealed no exchange between coordinated and free ethylene molecules.

Complex **2** is formed via the bis(ethylene) intermediate $[OsTp(\eta^2\text{-}CH_2{=}CH_2)_2(P^iPr_3)]BF_4$ (**5**), which results from the displacement of the dihydrogen ligands of **1** by ethylene molecules (Scheme 3). Intermediate **5** was isolated as a white solid in 90% yield, after stirring **1** in fluorobenzene, at 120 ºC, under 2 atm of ethylene, for 7 min. After 90 min, the stirring of **5** in fluorobenzene at 120 ºC under 2 atm of ethylene leads to **2**. Figure **2** shows a view of the X-ray structure of **5**. Like in **2**, the ethylene molecules lie *trans* to pyrazolyl groups with the C-C doble bonds parallel disposed. The Os–C and C–C bond lengths indicate that the Os-olefin bonds in **5** are weaker than in **2**. Thus, the Os–C distances, which range from 2.175(4) Å to 2.220(4) Å, are between 0.01 and 0.06 Å longer than those in **2** and, as expected for the Dewar-Chatt-Duncanson model, the C(1)–C(2) and C(3)–C(4) bond lengths of 1.388(6) and 1.376(6) Å are between 0.02 and 0.04 Å shorter than the olefinic distances in the latter. As expected for weaker Os-C_2H_4 bonds, in the ^{1}H NMR spectrum of **5** in dichloromethane-d_2, at room temperature, the AA'BB' part of the AA'BB'X spin system (X = ^{31}P) corresponding to the coordinated ethylene molecules appears at 3.19 ppm, shifted by 0.76 ppm towards lower field with regard to that of **2**. Like in the latter, the $^{13}C\{^1H\}$NMR spectrum between 25 and −80 ºC shows only one ethylene

resonance at 54.0 ppm.

At first glance, intermediate **5** could evolve into **2** through three pathways: a, b, and c (Scheme 3).

Scheme 3



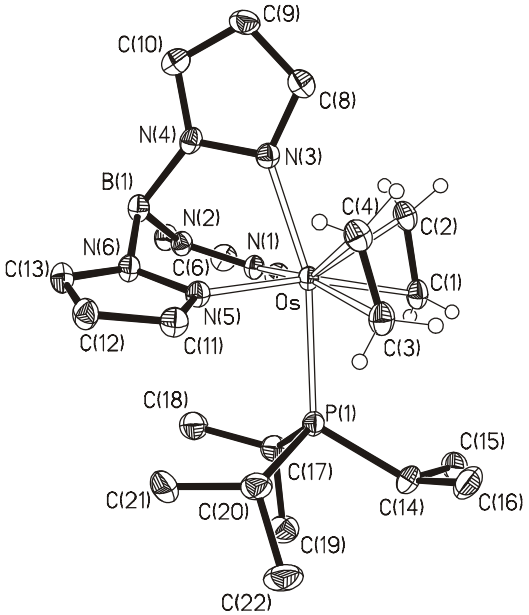


Figure 2. Molecular diagram of the cation of **5**. Selected bond lengths (Å) and angles (deg): Os–N(1) 2.126(3), Os–N(3) 2.172(3), Os–N(5) 2.108(3), Os–C(1) 2.221(4), Os–C(2) 2.175(4), Os–C(3) 2.220(4), Os–C(4) 2.200(4), Os–P(1) 2.4880(10), C(1) –C(2) 1.388(6), C(3) –C(4) 1.376(6);

N(1)–Os–N(5) 93.23(13), N(1)–Os–N(3) 79.10(12), N(3)–Os–N(5) 79.42(12), N(3)–Os–P(1) 163.12(9).

The olefinic carbon atoms are co-planar with the metal and the phosphorus atoms of the phosphine, in particular with C(1) and C(2). The torsion angles between the Os–P bond and the C(1)–C(2) and C(3)–C(4) ethylene bonds are 1.2(3)º and 13.0(3)º, respectively. This should favor the concerted migration of the phosphine from the metal center to C(1), to afford the unsaturated phosphoniumethyl species **a1** (Scheme 3). The latter could yield **2** by coordination of a new ethylene molecule. According to pathway **b**, the dissociation of an arm of the Tp ligand of **5** should lead to the unsaturated species **b1**, which could give a tris(ethylene) intermediated **b2** by coordination of ethylene. The subsequent displacement of the phosphine from the metal center of **b2** by the free pyrazolyl arm should afford **bc**, which could be also formed through pathway **c**. According to the latter, the formation of **bc** involves the direct dissociation of phosphine from the metal center of **5** and the subsequent coordination of ethylene to the osmium atom of the resulting **c1** intermediate. Once **bc** is formed, the nucleophilic attack of the dissociated phosphine to one of the coordinated ethylene molecules should generate the phosphoniumethyl product **2**. The metal promoted nucleophilic additions of phosphines to coordinated olefins are reactions common to a number of transition metals.[21]

The dissociation of triisopropylphosphine from the osmium atom of **5** is favored with regard to the dissociation of a pyrazolyl arm from an entropic point of view. In order to discern between pathways **a** and **c**, we stirred a fluorobezene solution of **1** in the presence of 1.2 equiv of tricyclohexylphosphine, at 120 ºC, under 2 atm of ethylene, for 24 h. Under these conditions, in addition to the aryl complex **3**, a mixture of $[EtP^{i}Pr_3]^+$ and $[EtPCy_3]^+$ was formed in a 2:3 molar ratio. This result is strong evidence in favor of pathway **c** and indicates that the formation of the phosphoniumethyl ligand is a formal insertion. Actually, the process involves the dissociation of the phosphine ligand of **5** and the external nucleophilic attack of the dissociated phosphine to a coordinated ethylene molecule.

Concluding Remarks

This study has revealed that under 2 atm of ethylene, the bis(dihydrogen) complex [OsTp((η^2-CH_2=CH_2)$_2$(P^iPr_3)]BF_4 replaces its monodentate ligands by olefins. The subsequent attack of the free phosphine to a coordinated ethylene molecule generates a phosphoniumethyl derivative, which promotes the C-H bond activation of fluorobenzene and 1,3-difluorobenzene to give 3-fluoroaryl and 3,5-difluoroaryl compounds, respectively, releasing [EtP^iPr_3]BF_4.

Experimental Section

General Methods and Instrumentation. All manipulations were performed with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use or obtained oxygen- and water-free from an MBraun solvent purification apparatus. The starting material [OsTp(η^2-H_2)$_2$(P^iPr_3)]BF_4 (**1**) was prepared according with the published method.[8] NMR spectra were recorded in CD_2Cl_2 at 298 K and chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C), external H_3PO_4 (^{31}P), or $CFCl_3$ (^{19}F). Coupling constants, *J*, are given in hertz. All coupling constants for the pyrazolyl proton resonances were about 2 Hz. Spectral assignments were achieved by ^{1}H-^{1}H COSY, ^{1}H{^{31}P},^{1}H{^{19}F}, ^{13}C APT, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC experiments.

Preparation of [OsTp(η^2-CH_2=CH_2)$_2$($CH_2CH_2P^iPr_3$)]BF_4 (2). Method a. A Fischer-Porter bottle was charged with a suspension of **1** (150 mg, 0.23 mmol) in 5 mL of fluorobenzene. The bottle was pressurized to 2 atm of ethylene, and the suspension was stirred for 90 min at 393 K. Then it was allowed to reach room temperature and the white solid was separated by decantation, washed with diethyl ether and dried in vacuo. Yield: 135.6 mg (80%). **Method b**. The same procedure described in method **a** was followed starting from **5** (100 mg, 0.14 mmol). Yield: 89.1 mg (86%). Anal. Calcd for $C_{24}H_{43}B_2F_4N_6OsP$: C, 39.11; H, 5.88; N, 11.41. Found: C, 39.43; H, 5.99; N, 11.54. HRMS (electrospray, *m/z*): calcd. for $C_{24}H_{43}N_6OsBP$ $[M]^+$ 649.2994, found 649.2987; calcd for $C_{22}H_{39}N_6OsBP$

$[M - C_2H_4]^+$ 621.2681, found 621.2663; calcd for $C_{20}H_{35}N_6OsBP$ $[M - 2\ C_2H_4]^+$ 593.2367, found 593.2323. IR (ATR, cm^{-1}): ν(BH) 2495 (s), ν(BF_4) 1030 (s). ^1H NMR (300 MHz): δ 7.96 (d, 1H, Tp), 7.78 (d, 2H, Tp), 7.61 (d, 1H, Tp), 7.40 (d, 2H, Tp), 6.33 (t, 2H, Tp), 6.27 (t, 1H, Tp), 2.43 (AA'BB'spin system, $\delta_A = \delta_{A'} = 2.56$, $\delta_B = \delta_{B'} = 2.29$, $J_{A\text{-}A'} = J_{B\text{-}B'} = 13.0$, $J_{A\text{-}B} = J_{A'\text{-}B'} = -0.9$, $J_{A\text{-}B'} = J_{A'\text{-}B} = 9.0$, 8H, $CH_2{=}CH_2$), 2.53-2.40 (m, 3H, PC*H*CH_3), 1.95-1.86 (complex signal, 2H, OsC*H*$_2$$CH_2P$), 1.40-1.30 (signal overlapped by PCHC*H*$_3$, 2H, $OsCH_2C$*H*$_2$P), 1.20 (dd, $J_{H\text{-}P} = 15.3$, $J_{H\text{-}H} = 7.2$, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.48 MHz): δ 37.4 (s). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 144.7, 137.1, 136.8, 135.5, 107.0, 106.8 (all s, Tp), 52.8 (s, $CH_2{=}CH_2$), 20.4 (d, $J_{C\text{-}P} = 42$, P*C*HCH_3), 18.0 (d, $J_{C\text{-}P} = 32$, $OsCH_2$*C*H_2P), 17.0 (d, $J_{C\text{-}P} = 3$, PCH*C*H_3), −4.80 (d, $J_{C\text{-}P} = 14$, Os*C*H_2CH_2P).

Preparation of OsTp(η^2-$CH_2{=}CH_2$)$_2$(3-C_6H_4F) (3). A Fischer-Porter bottle was charged with a suspension of **2** (150 mg, 0.20 mmol) in 5 mL of fluorobenzene. The bottle was pressurized to 2 atm of ethylene and the suspension was stirred for 24 h at 393 K. During this time a dark solution was formed. It was allowed to reach room temperature and the solvent was removed. Addition of diethyl ether caused the precipitation of a white solid, which was washed with diethyl ether. The solid was identified as $[CH_3CH_2P^iPr_3]BF_4$. Yield: 47.44 mg (86%). The combined diethyl ether solutions were evaporated to dryness to give a yellow oil that was extracted with pentane. The yellow solution was filtered through Celite and the solvent was removed in vacuo to yield a pale-yellow solid, which was characterized as **3**. Yield: 62 mg (56%). Data for **3**: Anal. Calcd for $C_{19}H_{22}BFN_6Os$: C, 41.15; H, 3.97; N, 15.16. Found: C, 41.23; H, 4.02; N, 15.31. HRMS (electrospray, *m/z*): calcd for $C_{19}H_{22}N_6OsBF$ $[M]^+$: 556.1596, found: 556.1602.; calcd for $C_{17}H_{18}N_6OsBF$ $[M - C_2H_4]^+$ 528.1283, found: 528.1279; calcd for $C_{13}H_{18}N_6OsB$ $[M - C_6H_4F]^+$ 461.1398, found: 461.1402. ^1H NMR (400 MHz): δ 8.07 (d, 1H, Tp), 7.78 (d, 2H, Tp), 7.72 (d, 2H, Tp), 6.95 (d, 1H, Tp), 6.62 (ddd, $J_{H\text{-}F} = 14.8$, $J_{H\text{-}H} = J_{H\text{-}H'} = 7.2$, 1H, H^5 C_6H_4F), 6.41 (m, 1H, H^4 C_6H_4F), 6.35 (t, 1H, Tp), 6.24 (m, 1H, H^6 C_6H_4F), 6.15 (t, 2H, Tp), 6.14 (m, 1H, H^2 C_6H_4F), 2.70 (AA'BB'spin system, $\delta_A = \delta_{A'} = 2.84$, $\delta_B = \delta_{B'} = 2.57$, $J_{A\text{-}A'} = J_{B\text{-}B'} = 12.0$, $J_{A\text{-}B} = J_{A'\text{-}B'} = -1.1$, $J_{A\text{-}B'} = J_{A'\text{-}B} = 10.6$, 8H, $CH_2{=}CH_2$). $^{13}C\{^1H\}$ NMR (100.63 MHz): δ 161.3 (d, $J_{C\text{-}F} = 242$, CF), 153.2 (s,

OsC), 144.6, 139.4, 136.0, 135.2, 106.9, 106.6 (all s, Tp), 135.3 (s, C^6 C_6H_4F), 126.2 (d, J_{C-F} = 8, C^5 C_6H_4F), 125.5 (d, J_{C-F} = 17, C^2 C_6H_4F), 107.6 (d, J_{C-F} = 21, C^4 C_6H_4F), 56.5 (s, CH_2=CH_2). $^{19}F\{^1H\}$ (376.5 MHz): δ −119.3. Data for **$[CH_3CH_2P^iPr_3]BF_4$**: HRMS (electrospray, *m/z*): calcd for $C_{11}H_{26}P$ $[M]^+$ 189.1767, found: 189.1772. IR (ATR, cm^{-1}): ν 1045(BF_4) (s). ^1H NMR (300 MHz): 2.76-2.63 (m, 3H, PC*H*CH_3), 2.31-2.20 (m, 2H, CH_3C*H*$_2$P), 1.41 (dd, J_{H-P} = 15.9, J_{H-H} = 7.9, 18H, PCHC*H*$_3$), 1.37-1.27 (m, 3H, C*H*$_3CH_2P$). $^{31}P\{^1H\}$ NMR (121.48 MHz): δ 43.4 (s). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 20.7 (d, J_{C-P} = 42, P*C*HCH_3), 17.4 (d, J_{C-P} = 3, PCH*C*H_3), 9.8 (d, J_{C-P} = 45, CH_3*C*H_2P), 7.1 (d, J_{C-P} = 6, *C*H_3CH_2P). $^{19}F\{^1H\}$ (282.38 MHz): δ −152.7.

Preparation of OsTp(η^2-CH_2=CH_2)$_2$(3,5-$C_6H_3F_2$) (4). This complex was prepared as described for **3** starting from **2** (150 mg, 0.20 mmol), using 1,3-difluorobenzene as solvent, and maintaining the heating for 48 h. Pale-yellow solid. Yield: 80.15 mg (70%). Anal. Calcd for $C_{19}H_{21}BF_2N_6Os$: C, 39.71; H, 3.68; N, 14.63. Found: C, 40.07; H, 3.75; N, 14.83. HRMS (electrospray, *m/z*): calcd for $C_{17}H_{17}N_6OsBF_2Na$ $[M + Na - C_2H_4]^+$ 569.2348, found: 569.2350. ^1H NMR (300 MHz): δ 8.07 (d, 1H, Tp), 7.80 (d, 2H, Tp), 7.74 (d, 1H, Tp), 6.99 (d, 2H, Tp), 6.36 (t, 1H, Tp), 6.22 (tt, J_{H-F} = 9.5, J_{H-H} = 2.3, 1H, H^4 $C_6H_3F_2$), 6.18 (t, 2H, Tp), 6.02 (dd, J_{H-F} = 12.8, J_{H-H} = 2.3, 2H, H^2 and H^6 $C_6H_3F_2$), 2.78 (AA'BB'spin system, δ_A = $\delta_{A'}$ = 2.93, δ_B = $\delta_{B'}$ = 2.64, $J_{A-A'}$ = $J_{B-B'}$ = 12.0, J_{A-B} = $J_{A'-B'}$ = −0.6, $J_{A-B'}$ = $J_{A'-B}$ = 8.8, 8H, CH_2=CH_2). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 160.6 (dd, J_{C-F} = 245, $J_{C-F'}$ = 12, CF), 154.7 (t, J_{C-F} = 4, OsC), 144.4, 139.3, 136.0, 135.3, 106.8, 106.5 (all s, Tp), 121.0 (d, J_{C-F} = 19, C^2 and C^6 $C_6H_3F_2$), 96.2 (t, J_{C-F} = 26, C^4 $C_6H_3F_2$), 57.0 (s, CH_2=CH_2). $^{19}F\{^1H\}$ (282.4 MHz): δ −118.0. ^{19}F (282.4 MHz): δ −118.0 (dd, J_{F-H} = 12.8, $J_{F-H'}$ = 9.5).

Preparation of [OsTp(η^2-CH_2=CH_2)$_2$(P^iPr_3)]BF_4 (5). A Fischer-Porter bottle was charged with a suspension of **1** (150 mg, 0.23 mmol) in 5 mL of fluorobenzene. The bottle was pressurized to 2 atm of ethylene, and the suspension was stirred for 7 min at 393 K. After this time, it was allowed to reach room temperature and the white solid was separated by decantation, washed with diethyl ether and dried in vacuo. Yield: 147 mg (90%). Anal. Calcd for $C_{22}H_{39}B_2F_4N_6OsP$: C, 37.27; H, 5.55; N, 11.86. Found:

C, 37.41; H, 5.59; N, 11.94. HRMS (electrospray, *m/z*): calcd for $C_{20}H_{35}N_6OsBP$ $[M - C_2H_4]^+$ 593.2367, found 593.2377; calcd for $C_{22}H_{38}N_7OsBP$ $[M - C_2H_4 + CH_3CN]^+$ 634.2600, found 634.2633; calcd for $C_{20}H_{34}N_7OsBP$ $[M - 2\ C_2H_4 + CH_3CN]^+$ 606.2320, found 606.2344. IR (ATR, cm^{-1}): ν(BH) 2495 (s), $\nu(BF_4)$ 1049 (s). ^1H NMR (300 MHz): δ 7.99 (d, 1H, Tp), 7.90 (d, 2H, Tp), 7.53 (d, 1H, Tp), 7.37 (d, 2H, Tp), 6.42 (t, 2H, Tp), 6.25 (t, 1H, Tp), 3.19 (AA'BB'X spin system (X = ^{31}P), $\delta_A = \delta_{A'} =$ 3.40, $\delta_B = \delta_{B'} = 2.99$, $J_{A\text{-}A'} = J_{B\text{-}B'} = 13.0$, $J_{A\text{-}B} = J_{A'\text{-}B'} = -0.9$, $J_{A\text{-}B'} = J_{A'\text{-}B} = 9.5$, $J_{A\text{-}X} = J_{A'\text{-}X} = 3.6$, $J_{B\text{-}X}$ $= J_{B'\text{-}X} = 2.0$, 8H, $CH_2{=}CH_2$), 2.86 (m, 3H, PC*H*CH_3), 1.06 (dd, $J_{H\text{-}P} = 11.8$, $J_{H\text{-}H} = 7.1$, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.48 MHz): δ – 34.3 (s). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 145.1 (d, $J_{C\text{-}P} = 2$, Tp), 140.5, 139.8, 135.9, 109.2 (all s, Tp), 107.4 (d, $J_{C\text{-}P} = 2.1$, Tp), 54.0 (s, $CH_2{=}CH_2$), 27.4 (d, $J_{C\text{-}P} = 24$, P*C*HCH_3), 20.8 (d, $J_{C\text{-}P} = 3$, PCH*C*H_3).

Reaction of 1 with Ethylene in the Presence of Tricyclohexylphosphine. A Fischer-Porter bottle was charged with a suspension of **1** (150 mg, 0.23 mmol) and PCy_3 (78.5 mg, 0.28 mmol) in 5 mL of fluorobenzene. The bottle was pressurized to 2 atm of ethylene and the suspension was stirred for 24 h at 393 K. After this time, it was allowed to reach room temperature and the solvent was removed. Addition of diethyl ether caused the precipitation of a white solid, which was washed with diethyl ether. The solid was identified as a mixture of $[CH_3CH_2P^iPr_3]BF_4$ and $[CH_3CH_2PCy_3]BF_4$ in a 2:3 molar ratio. The combined diethyl ether solutions were evaporated to dryness to give a yellow oil that was extracted with pentane. The yellow solution was filtered through Celite and the solvent was removed in vacuo to yield a pale-yellow solid, which was characterized as **3**. Data for **$[CH_3CH_2PCy_3]BF_4$**: ^1H NMR (300 MHz): 2.34 (dt, $J_{H\text{-}P} = 23.8$, $J_{H\text{-}H} = 12.1$, 3H, Cy), 2.19 (dq, $J_{H\text{-}P} = 20.1$, $J_{H\text{-}H} = 7.6$, 2H, CH_3CH_2P), 1.93-1.81 (m, 18H, Cy), 1.54-1.42 (m, 12H, Cy), 1.34-1.29 (m, 3H, CH_3CH_2P). $^{31}P\{^1H\}$ NMR (121.48 MHz): δ 32.9 (s). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 30.1 (d, $J_{C\text{-}P} = 41$, PCH Cy), 27.3 (d, $J_{C\text{-}P} = 4$, Cy), 26.9 (d, $J_{C\text{-}P} = 12$, Cy), 25.7 (d, $J_{C\text{-}P} = 1$, Cy), 9.3 (d, $J_{C\text{-}P} = 45$, CH_3CH_2P), 7.1 (d, $J_{C\text{-}P} = 6$, CH_3CH_2P).

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Supporting Information Available. X-ray analysis and crystal structures determination, including a CIF file for **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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FOR TABLE OF CONTENTS USE ONLY

Reactions of an Osmium-bis(dihydrogen) Complex under Ethylene: Phosphine Addition to a C-C Double Bond and Selective *meta*-CH Bond Activation of Fluoroarenes

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