α-Substituted Alkenyl and α-Disubstituted Alkylidene Complexes with the $OsCl(CO)(P^iPr_3)_2$ Skeleton

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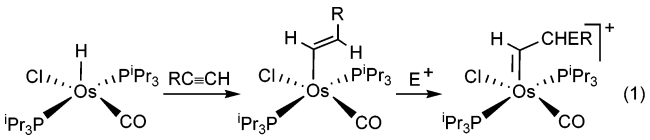
*Summary: Complex Os(η²-PhC≡CPh)(CO)(P^{i}Pr$_3$)$_2$ (**1**) reacts with 1 equiv of HBF$_4$ to give the hydride species [OsH(η²-PhC≡CPh)(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (**2**), which affords the α-substituted alkenyl compound Os{(E)-C(Ph)=CHPh}Cl(CO)(P^{i}Pr$_3$)$_2$ (**3**) by treatment with NaCl. Complex **3** reacts with Brønsted acids to give α-disubstituted alkylidene derivatives. Thus, the reaction with 1 equiv of HBF$_4$ yields the cationic complex [OsCl{=C(Ph)CH$_2$Ph}(CO)(P^{i}Pr$_3$)$_2$][BF$_4$] (**4**). The treatment of **3** with 1 equiv of HCl gives the neutral alkylidene derivative OsCl$_2${=C(Ph)CH$_2$Ph}(CO)(P^{i}Pr$_3$)$_2$ (**5**), while the reaction with an excess of HCl yields the anionic alkylidene complex [HP^{i}Pr$_3$][OsCl$_3${=C(Ph)CH$_2$Ph}(CO)(P^{i}Pr$_3$)] (**6**).*

The five-coordinate complex $OsHCl(CO)(P^iPr_3)_2$[1] is an important homogeneous catalyst for the reduction of unsaturated organic substrates,[2] the addition of silanes to alkynes,[3] the dehalogenation of polychloroarenes,[4] and C−C coupling reactions including the dimerization of terminal alkynes to butatrienes,[5] and the ring-opening metathesis polymerization of norbornene and 2,5-norbornadiene.[6] Furthermore, it has been one of the cornerstones in the development of modern organometallic osmium chemistry.[7]

Among the stoichiometric reactions of this complex, the addition of the Os−H bond across the C≡C bond of alkynes to afford alkenyl derivatives has received particular attention,[8] by its connection with the catalytic processes involving alkynes and as an entry to other interesting organometallic compounds.[7,9] However, it is limited to terminal alkynes. Since the addition of the alkyne to the metal first occurs followed by migration of the hydride from the metal to the carbon atom, it has been argued that steric effects are mainly responsible for this limitation.[8a,9]

The insertion of terminal alkynes into the Os−H bond of $OsHCl(CO)(P^iPr_3)_2$ selectively leads to alkenyl derivatives with *E* stereochemistry around the C−C double bond. These compounds react with electrophiles by addition to the RC(sp²) atom. Thus, the selective formation of alkylidene compounds containing a hydrogen atom at the C_α carbon of the alkylidene ligand takes place (eq 1).[8d,e,10] Because α-substituted alkenyl and α-disubstituted alkylidene complexes with the $OsCl(CO)(P^iPr_3)_2$ skeleton are unknown, while related osmium compounds with triphenylphosphine have been reported,[11] one might think that the lack of reactivity for internal alkynes could be not only a consequence of a restricted coordination but also due to the low stability of the resulting α-substituted alkenyl derivatives; that is, the lack of reactivity for internal alkynes could be not only kinetic but also thermodynamic in origin.



(1)

The problem is certainly kinetic in origin; α-substituted alkenyl (Scheme 1) and α-disubstituted alkylidene (Scheme 2) complexes not only can be prepared but also are stable.

The π-diphenylacetylene group of the previously reported complex Os(η²-PhC≡CPh)(CO)(P^{i}Pr$_3$)$_2$ (**1**) acts as a four-electron donor ligand.[12] Thus, in spite of the four coordination, its metal center has nucleophilic character, reacting with electrophiles. Treatment at room temperature of dichloromethane solutions of **1** with 1.0 equiv of HBF$_4$·OEt$_2$ leads to the hydride derivative [OsH(η²-PhC≡CPh)(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (**2**), as a result of the addition of the proton of the acid to the metal, which undergoes oxidation. Complex **2** is related to compounds [OsH(=C=CHR)(η²-HC≡CR)(P^{i}Pr$_3$)$_2$]BF$_4$ (R = H, Cy, Ph,[13] C(OH)Ph$_2$, C(OH)Me$_2$[14]) and [OsH(=C=C=CPh$_2$)(η²-HC≡CH)(P^{i}Pr$_3$)$_2$]BF$_4$,[15] which, on the basis of an X-ray diffraction study on [OsH(=C=CH$_2$)(η²-HC≡CH)(P^{i}Pr$_3$)$_2$]BF$_4$,[13] have been de-

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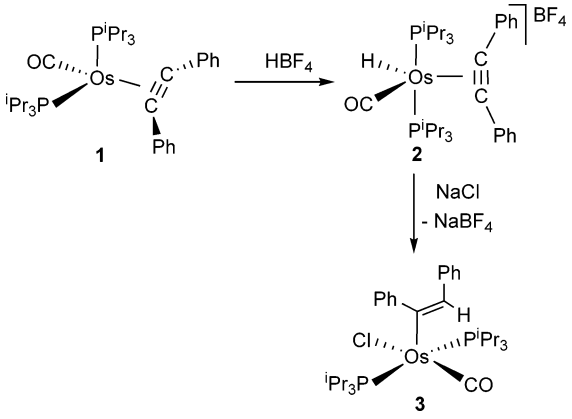
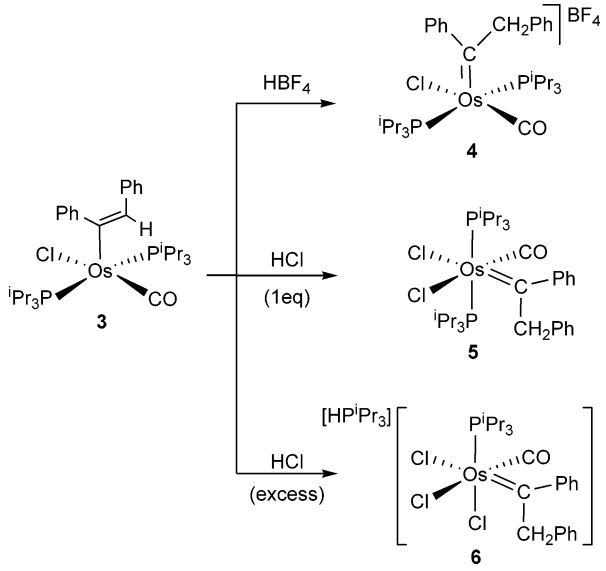
Scheme 1



Scheme 2



scribed as bipyramidal species with apical phosphines and inequivalent angles within the Y-shaped equatorial plane. The π-alkyne group, which also acts in this compound as a four-electron donor ligand, lies in the foot of the Y.[16]

Complex **2** is isolated as a yellow solid in 94% yield. The presence of a hydride ligand in this compound is strongly supported by its ^{1}H NMR spectrum, which at 233 K in dichloromethane shows a triplet at −7.37 ppm with an H−P coupling constant of 25.5 Hz. In accordance with the chemical shifts found for other osmium complexes where the alkynes also act as four-electron donor ligands,[12−15,17] the acetylenic resonance in the ^{13}C{^{1}H} NMR spectrum is observed at 165.4 ppm. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 42.3 ppm.

In the presence of NaCl, the methanol solutions of **2** evolve to the α-substituted alkenyl derivative Os{(*E*)-C(Ph)═CHPh}-Cl(CO)(P^{i}Pr$_3$)$_2$ (**3**), as a consequence of the migratory insertion of the C≡C triple bond of the alkyne into the Os−H bond of **2** and of the coordination of the chloride ligand to the osmium atom. We note that the related complex Os{(*E*)-C(Ph)═CHPh}-Cl(CS)(PPh$_3$)$_2$ has been previously prepared by Roper by treatment of Os(η^2-PhC≡CPh)(CS)(PPh$_3$)$_2$ with HCl.[18] Complex **3**, which precipitates in the reaction medium, is isolated as a dark red solid in 70% yield. The presence of the alkenyl ligand in the compound is strongly supported by the ^{13}C{^{1}H} NMR spectrum, which, in agreement with other alkenyl-osmium complexes,[8,11,18,19] shows the C$_\alpha$(sp^2) and C$_\beta$(sp^2) resonances at 140.0 and 134.5 ppm, respectively. In accordance with the *trans* disposition of the phosphine ligands, the ^{31}P{^{1}H} NMR spectrum contains a singlet at 16.3 ppm.

The formation of **3** via **2** allows the rationalization of another observation that demands some explanation. The key step for the selective hydrogenation of alkynes to olefins catalyzed by OsHCl(CO)(P^{i}Pr$_3$)$_2$ is the reaction of chloro-alkenyl intermediates, related to **3**, with molecular hydrogen.[8b] In spite of the fact that **3** cannot be obtained from OsHCl(CO)(P^{i}Pr$_3$)$_2$ and diphenylacetylene, this hydride complex catalyzes the hydrogenation of the alkyne to *Z*-stilbene.[20] Furthermore, interestingly, the reaction rate increases in the solvent sequence benzene < 1,2-dichloroethane < 2-propanol. The formation of **3** according to Scheme 1 suggests that, under the catalytic conditions, the coordination of the alkyne to the metal center of the catalyst produces the dissociation of the chloride ligand to afford **2**, which subsequently evolves to **3**. Polar solvents favor the dissociation and therefore the catalysis.

Complex **3** is the entry key to the preparation of cationic, neutral, and anionic α-disubstituted alkylidene derivatives, which are easily formed from reactions with acids (Scheme 2), in agreement with the expected nucleophilic character of the C$_\beta$ atom of an alkenyl ligand coordinated to osmium.[9,21]

Treatment of dichloromethane solutions of **3** with 1.0 equiv of HBF$_4$•OEt$_2$ leads to the cationic five-coordinate alkylidene compound [OsCl{═C(Ph)CH$_2$Ph}(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (**4**), which is isolated as a yellow solid in 87% yield. This compound has been characterized by elemental analysis, IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy, and an X-ray crystallographic study. A view of the structure of this compound is shown in Figure 1.

The geometry around the osmium atom can be rationalized as a square pyramid with the alkylidene located at the apex. The four atoms, P(1), P(2), Cl, and C(15), forming the base, are approximately in a plane, whereas the osmium atom is located 0.465(1) Å above this plane toward the apical position. The phosphine ligands are *pseudo-trans* disposed with a P(1)−Os−P(2) angle of 155.78(3)°. Similarly, the chloride and carbonyl group lie *pseudo-trans* disposed with a Cl−Os−C(15) angle of 156.41(10)°. The separation of 1.888(3) Å between the osmium atom and the alkylidene supports the Os−C(1) double bond formulation.[10,14,22]

The ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra of **4** are consistent with Figure 1. In the ^{13}C{^{1}H} NMR spectrum in dichloromethane-d_2, the most noticeable resonance is a triplet (J_{C-P} = 6 Hz) at 285.8 ppm due to the C$_\alpha$ atom of the alkylidene. In agreement with the *pseudo-trans* disposition of the phosphine ligands, the ^{31}P{^{1}H} NMR spectrum contains a singlet at 41.2 ppm.

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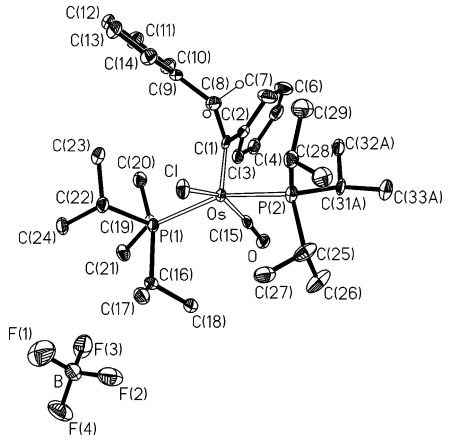

Figure 1. Molecular diagram of **4**. Selected bond lengths (Å) and angles (deg): Os−C(1) 1.888(3), Os−C(15) 1.835(4), Os−Cl 2.3839(8), Os−P(1) 2.4592(8), Os−P(2) 2.4630(9); C(1)−Os−C(15) 91.79(14), C(1)−Os−Cl 111.79(10), C(1)−Os−P(1) 105.77-(10), C(1)−Os−P(2) 98.46(10), C(15)−Os−Cl 156.41(10), C(15)−Os−P(1) 89.04(10), C(15)−Os−P(2) 89.94(10), Cl−Os−P(1) 84.20(3), Cl−Os−P(2) 87.15(3), P(1)−Os−P(2) 155.78(3), C(2)−C(1)-C(8) 115.0(3), Os−C(1)−C(2) 132.0(2), Os−C(1)−C(8) 112.5(2).

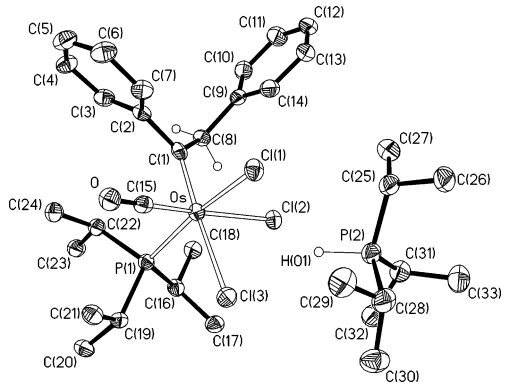

Figure 2. Molecular diagram of **6**. Selected bond lengths (Å) and angles (deg): Os−C(1) 1.929(3), Os−C(15) 1.820(3), Os−Cl(1) 2.4446(7), Os−Cl(2) 2.4813(7), Os−Cl(3) 2.5127(7), Os−P(1) 2.3920(8); C(1)−Os−C(15) 92.76(12), C(1)−Os−Cl(1) 96.12(8), C(1)−Os−Cl(2) 91.51(9), C(1)−Os−Cl(3) 175.13(9), C(1)−Os−P(1) 93.64(8), C(15)−Os−Cl(1) 85.66(9), C(15)−Os−Cl(2) 170.05-(9), C(15)−Os−Cl(3) 92.09(9), C(15)−Os−P(1) 91.70(9), P(1)−Os−Cl(1) 170.00(3), P(1)−Os−Cl(2) 96.99(2), P(1)−Os−Cl(3) 85.91(3), Cl(1)−Os−Cl(2) 84.96(2), Cl(1)−Os−Cl(3) 84.56(3), Cl-(2)−Os−Cl(3) 83.74(3), Os−C(1)−C(2) 125.0(2), Os−C(1)−C(8) 124.0(2).

The addition of 1.0 equiv of HCl in toluene to toluene solutions of **3** affords the dichloro-alkylidene derivative $OsCl_2\{=C(Ph)CH_2Ph\}(CO)(P^iPr_3)_2$ (**5**), as a result of the addition of the proton of the acid to the C_β atom of the alkenyl group of **3** and the coordination of the chloride ligand to the osmium atom. Complex **5** is isolated as an orange solid in 53% yield. In agreement with **4**, in the $^{13}C\{^1H\}$ NMR spectrum in benzene-d_6, the alkylidene OsC resonance appears at 302.1 ppm as a triplet with a C−P coupling constant of 6 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 0.0 ppm.

Bubbling HCl through a toluene solution of **3** for 0.5 h results in the formation of the anionic complex $[HP^iPr_3][OsCl_3\{=C(Ph)CH_2Ph\}(CO)(P^iPr_3)]$ (**6**) via **5**. Complex **6** was isolated as orange crystals suitable for an X-ray diffraction study in 40% yield. Figure 2 shows a view of the structure of this compound.

The geometry around the osmium atom can be described as a distorted octahedron with the chloride ligands in a *fac* disposition. The three separations between the latter and the metal are different, 2.4446(7) (Os−Cl(1)), 2.4813(7) (Os−Cl-(2)), and 2.5127(7) (Os−Cl(3)) Å, with that being *trans* to the phosphine ligand the shortest and that *trans* to the alkylidene group the longest one. The Os−C(1) bond length of 1.929(3) Å compares well with the Os−alkylidene separation in **4** and supports the Os−C(1) double bond formulation.

In the $^{13}C\{^1H\}$ NMR spectrum of **6** in dichloromethane-d_2, the alkylidene OsC resonance appears at 297.0 ppm as a doublet with a C−P coupling constant of 7.0 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains two singlets at 24.5 (HP^iPr_3) and 13.2 (P^iPr_3) ppm.

In conclusion, the lack of reaction between $OsHCl(CO)(P^iPr_3)_2$ and nonactivated internal alkynes is kinetic in origin. Although this hydride does not react with diphenylacetylene, the α-substituted alkenyl complex $Os\{(E)\text{-}C(Ph)=CHPh\}Cl(CO)(P^iPr_3)_2$ can be obtained by consecutive reaction of $Os(\eta^2\text{-}PhC\equiv CPh)(CO)(P^iPr_3)_2$ with H^+ and Cl^-. Furthermore, it should be mentioned that the steric hindrance imposed by the substituent at the C_α atom does not play a determinant role on the stability of the system. Thus, the alkenyl complex $Os\{(E)\text{-}C(Ph)=CHPh\}Cl(CO)(P^iPr_3)_2$ proves to be the entry key to cationic, neutral, and anionic α-disubstituted alkylidene derivatives.

Experimental Section

General Methods and Instrumentation. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material $Os(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2$ (**1**) was prepared by the published method.[12] In the NMR spectra, chemical shifts (expresed in ppm) are referenced to residual solvent peaks (^1H and ^{13}C) or external 85% phosphoric acid (^{31}P). Coupling constants, J and N ($N = J_{H-P} + J_{H-P'}$ for ^1H; $N = J_{C-P} + J_{C-P'}$ for ^{13}C), are given in hertz.

Preparation of $[OsH(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2]BF_4$ (2). A red solution of **1** (252 mg, 0.35 mmol) in 3 mL of dichloromethane was treated with a solution of HBF_4 in diethyl ether (54%, 48 μL, 0.35 mmol). The brown solution obtained was stirred at room temperature for 10 min, and the solvent was removed in vacuo. Diethyl ether (6 mL) was added, and the mixture was stirred at 0 °C for 30 min. The yellow solid formed was separated by decantation, washed with cold diethyl ether (2 × 3 mL), and dried in vacuo. Yield: 266 mg (94%). Anal. Calcd for $C_{33}H_{53}BF_4OOsP_2$: C, 49.25; H, 6.64. Found: C, 48.77; H, 6.58. IR (Nujol, cm^{-1}): ν(OsH) 2192 (w), ν(CO) 1930 (vs), ν(C≡C) 1885 (m), ν(BF_4) 1066 (br, vs). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): 7.44 (m, 4H, Ph), 7.35 (m, 2H, Ph), 7.07 (m, 4H, Ph), 2.63 (m, 6H, PCH), 1.36 (dvt, $J_H-H = 7.2$, $N = 15.9$, 18H, $PCHCH_3$), 1.22 (dvt, $J_{H-H} = 7.2$, $N = 15.6$, 18H, $PCHCH_3$), −7.37 (br t, 1H, OsH). ^1H NMR (300 MHz, CD_2Cl_2, 233 K): −7.37 (t, $J_{H-P} = 25.5$, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 233 K): δ 42.3 (s).

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$^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 233 K): δ 177.2 (t, $J_{C-P} = 9$, CO), 165.4 (s, ≡C), 137.2 (s, C_{ipso}Ph), 128.9, 128.7, 125.0 (all s, Ph), 28.8 (vt, $N = 30$, PCH), 21.0, 20.2 (both s, PCH*C*H_3).

Preparation of Os{(*E*)-C(Ph)═CHPh}Cl(CO)(P^iPr_3)$_2$ (3). Methanol (5 mL) was added to a mixture of **2** (188 mg, 0.23 mmol) and NaCl (34 mg, 0.58 mmol). A dark red solid began to precipitate immediately. The suspension was stirred at room temperature for 5 h, and the dark red solid was separated by decantation. It was repeatedly washed with methanol (5 × 3 mL) and dried in vacuo. Yield: 124 mg (70%). Anal. Calcd for $C_{33}H_{53}ClOOsP_2$: C, 52.61; H, 7.09. Found: C, 52.23; H, 6.91. IR (Nujol, cm^{-1}): ν(CO) 1900 (vs), ν(C═C) 1589 (w), 1575 (w), 1542 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): 7.69 (m, 2H, Ph), 7.05−6.78 (m, 9H, ═CH + Ph), 2.83 (m, 6H, PCH), 1.19 (dvt, $J_{H-H} = 6.9$, $N = 13.5$, 18H, PCHC*H*$_3$), 1.17 (dvt, $J_{H-H} = 6.9$, $N = 13.5$, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 16.3 (s). $^{13}C\{^1H\}$-APT NMR (75.4 MHz, C_6D_6, 293 K): δ 184.8 (t, $J_{C-P} = 10$, CO), 140.0 (br, Os−C), 140.7 (s, C_{ipso}Ph), 134.5 (br, ═*C*HPh), 130.8, 129.4, 128.6, 128.3, 126.8, 124.6 (all s, Ph), 25.0 (vt, $N = 23$, PCH), 20.3, 20.1 (both s, PCH*C*H_3).

Preparation of [OsCl{═C(Ph)CH_2Ph}(CO)(P^iPr_3)$_2$]BF_4 (4). A solution of **3** (113 mg, 0.15 mmol) in 4 mL of dichloromethane was treated with a solution of HBF_4 in diethyl ether (54%, 21 μL, 0.15 mmol). After 30 min stirring at room temperature, the solution was concentrated to ca. 0.5 mL, and 10 mL of diethyl ether was added. A yellow solid precipitated, which was recrystallized from acetone/diethyl ether. Yield: 110 mg (87%). Anal. Calcd for $C_{33}H_{54}BClF_4OOsP_2$: C, 47.12; H, 6.47. Found: C, 46.96; H, 6.51. IR (Nujol, cm^{-1}): ν(CO) 1961 (vs), ν(C═C) 11587 (w), ν(BF_4) 1058 (br, s). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): 7.75 (m, 3H, Ph), 7.50 (m, 2H, Ph), 7.12 (m, 3H, Ph), 6.78 (m, 2H, Ph), 4.94 (s, 2H, CH_2), 3.00 (m, 6H, PCH), 1.32 (dvt, $J_{H-H} = 7.2$, $N = 14.7$, 18H, PCHC*H*$_3$), 1.27 (dvt, $J_{H-H} = 7.5$, $N = 15.3$, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 41.2 (s). $^{13}C\{^1H\}$-APT NMR (75.4 MHz, CD_2Cl_2, 253 K): δ 285.8 (t, $J_{C-P} = 6$, Os═C), 181.0 (t, $J_{C-P} = 8$, CO), 158.5 (s, C_{ipso}Ph), 134.6, 134.5, 130.2, 129.0, 128.9, 127.6, 127.0 (all s, Ph), 62.8 (s, CH_2), 26.3 (vt, $N = 26$, PCH), 19.8, 19.5 (both s, PCH*C*H_3).

Preparation of $OsCl_2${═C(Ph)CH_2Ph}(CO)(P^iPr_3)$_2$ (5). A solution of HCl in toluene (0.28 M, 0.43 mL, 0.12 mmol) was added dropwise to a green solution of **3** (91 mg, 0.12 mmol) in 6 mL of toluene at 0 °C. The resulting dark brown solution was stirred for 30 min at room temperature, and then, it was concentrated in vacuo to ca. 0.5 mL. The addition of 4 mL of pentane caused the precipitation of an orange solid, which was separated by decantation, washed with pentane (3 × 2 mL), and dried in vacuo. Yield: 50 mg (53%). Anal. Calcd for $C_{33}H_{54}Cl_2OOsP_2$: C, 50.18; H, 6.89. Found: C, 49.95; H, 6.73. IR (Nujol, cm^{-1}): ν(CO) 1930 (vs), ν(C═C) 1596 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): 7.42 (d, $J_{H-H} = 7.5$, 2H, *o*-Ph), 7.21−6.93 (m, 8H, Ph), 5.28 (s, 2H, CH_2), 2.84 (m, 6H, PCH), 1.28 (dvt, $J_{H-H} = 6.6$, $N = 13.5$, 18H, PCHC*H*$_3$), 1.21 (dvt, $J_{H-H} = 6.9$, $N = 13.5$, 18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 0.0 (s). $^{13}C\{^1H\}$-APT NMR (75.4 MHz, CD_2Cl_2, 243 K): δ 302.1 (t, $J_{C-P} = 6$, Os═C), 178.5 (t, $J_{C-P} = 9$, CO), 165.0, 137.3 (both s, C_{ipso}Ph), 130.0, 129.7, 127.6, 127.2, 125.8, 125.2 (all s, Ph), 65.4 (s, CH_2), 27.0 (vt, $N =$ 23, PCH), 19.9, 19.5 (both s, PCH*C*H_3).

Preparation of [HP^iPr_3][$OsCl_3${═C(Ph)CH_2Ph}(CO)(P^iPr_3)] (6). HCl was bubbled through a solution of **3** (121 mg, 0.16 mmol) in 5 mL of toluene at 0 °C for 30 min. The solution was concentrated in vacuo to ca. 0.5 mL, and the addition of 5 mL of pentane caused the precipitation of an orange solid, which was separated by decantation, washed with pentane (2 × 5 mL), and dried in vacuo. The solid was characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy as a mixture of **5** and **6** in a 1:1.85 molar ratio. Slow crystallization of this solid in toluene/pentane gave complex **6** as orange crystals. Yield: 53 mg (40%). Anal. Calcd for $C_{33}H_{55}Cl_3OOsP_2$: C, 47.97; H, 6.71. Found: C, 47.91; H, 6.86. IR (Nujol, cm^{-1}): ν(PH) 2379 (m), ν(CO) 1932 (vs), ν(C═C) 1600 (w). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): 8.35 (dq, $J_{H-P} = 522$, $J_{H-H} =$ 4.2, 1H, PH), 7.56 (d, $J_{H-H} = 7.2$, 2H, Ph), 7.35 (d, $J_{H-H} = 13.5$, 1H, CH_2), 7.29−7.15 (m, 5H, Ph), 7.00 (m, 3H, Ph), 2.81 (m, 3H, PCH, HP^iPr_3), 2.59 (m, 3H, PCH, P^iPr_3), 2.49 (dd, $J_{H-H} = 13.5$, $J_{H-P} = 3.3$, 1H, CH_2), 1.56 (dd, $J_{H-H} = 7.2$, $J_{H-P} = 16.5$, 18H, PCHC*H*$_3$, HP^iPr_3), 1.46 (dd, $J_{H-H} = 7.2$, $J_{H-P} = 14.0$, 9H, PCHC*H*$_3$, P^iPr_3), 1.25 (dd, $J_{H-H} = 7.4$, $J_{H-P} = 13.7$, 9H, PCHC*H*$_3$, P^iPr_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 24.5 (s, HP^iPr_3), 13.2 (s, P^iPr_3). $^{13}C\{^1H\}$-APT NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 297.0 (d, $J_{C-P} = 7$, Os═C), 177.3 (d, $J_{C-P} = 10$, CO), 168.0, 136.5 (both s, C_{ipso}Ph), 131.0, 128.1, 127.5, 127.1, 125.5, 123.1 (all s, Ph), 67.0 (s, CH_2), 29.9 (br d, $J_{C-P} = 29$, PCH, P^iPr_3), 19.8, (d, $J_{C-P} = 41$, PCH, HP^iPr_3), 19.5 (br, PCH*C*H_3, P^iPr_3), 17.9 (d, $J_{C-P} = 3$, PCH*C*H_3, HP^iPr_3).

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Supporting Information Available: Crystal structure determinations and CIF files giving crystal data for compounds **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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