

The Cyclopentadienyl-Osmium Moiety as Template for the Formation of a Dihydronaphthylphosphine by Coupling between Phenylacetylene and an α -Alkenylphosphine

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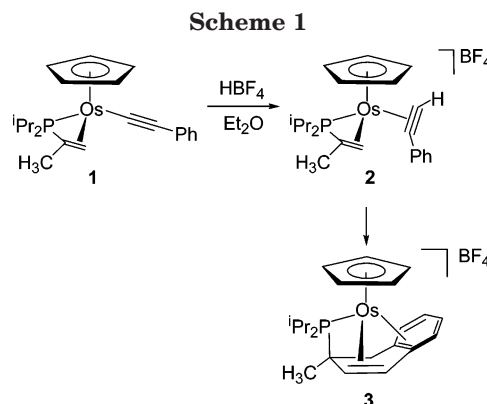
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Summary: Complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CPh})\{\eta^2\text{-CH}_2=\text{C}(\text{CH}_3)\text{P}^i\text{Pr}_2\}$ (**1**) reacts with $\text{HBF}_4\cdot\text{OEt}_2$ to give the π -alkyne derivative $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-HC}\equiv\text{CPh})\{\eta^2\text{-CH}_2=\text{C}(\text{CH}_3)\text{P}^i\text{Pr}_2\}]\text{BF}_4$ (**2**), which is transformed to $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(1,2\text{-dihydro-2-methylnaphth-2-ylideneisopropylphosphine})]\text{BF}_4$ (**3**) as a result of the coupling of the alkyne with the isopropenyl substituent of the starting phosphine. The tridentate coordination mode of the dihydronaphthylphosphine in **3** is proved by X-ray diffraction analysis.

Intermolecular reactions between alkenes and alkynes promoted by transition metal compounds are of pivotal importance for the assembly of unsaturated linear molecules and cyclic products.¹ The linear couplings take place via metallacycle or vinylidene intermediates or, alternatively, involve hydrometalation or C–H bond activation processes.² Most of the cyclization reactions are [2 + 2] additions, which lead to strained carbocycles.³

As a part of our work on the chemistry of the cyclopentadienyl-osmium unit⁴ and within a research program dedicated to the functionalization of trialkylphosphines,⁵ one year ago, we performed the dehydrogenation of one of the phosphines of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$.⁶ Subsequently the resulting isopropenyldiisopropylphosphine of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}\{\eta^2\text{-CH}_2=\text{C}(\text{CH}_3)\text{P}^i\text{Pr}_2\}$ has been transformed into allylphosphines by reaction with diazoalkanes via [2 + 2] cycloaddition processes,⁷ iminophosphines by insertion of the carbon–nitrogen triple bond of benzonitriles into one of the $\text{C}(\text{sp}^2)\text{--H}$ bonds of the isopropenyl group,⁸ and dienyphosphines via enyne reactions between the carbon–carbon double bond



of the α -alkenylphosphine and the carbon–carbon triple bond of alkyne and alkynol substrates.⁹

We now show the transformation of isopropenyldiisopropylphosphine into a novel dihydronaphthylideneisopropylphosphine (Scheme 1). This unprecedented cyclization between the isopropenyl substituent of the phosphine and phenylacetylene takes place via both metallacycle and vinylidene intermediates. Furthermore, it involves vinyl- and aryl-CH bond activation and hydrometalation processes.

In contrast to the known high nucleophilicity of the C_β atom of the alkynyl groups in late-transition-metal alkynyl complexes, the addition of 1.8 equiv of $\text{HBF}_4\cdot\text{OEt}_2$ to a diethyl ether solution of the alkynyl compound $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CPh})\{\eta^2\text{-CH}_2=\text{C}(\text{CH}_3)\text{P}^i\text{Pr}_2\}$ (**1**) leads to the π -phenylacetylene derivative $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-HC}\equiv\text{CPh})\{\eta^2\text{-CH}_2=\text{C}(\text{CH}_3)\text{P}^i\text{Pr}_2\}]\text{BF}_4$ (**2**), which is isolated as an orange solid in 60% yield.

The presence of the π -alkyne ligand in **2** is supported by the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of this compound. The carbon–carbon triple bond gives rise, in the IR spectrum, to a $\nu(\text{C}\equiv\text{C})$ band at 1729 cm^{-1} . In the ^1H NMR spectrum in dichloromethane- d_2 , the $\text{HC}(\text{sp})$ -hydrogen atom displays a singlet at 4.09 ppm, whereas the resonances corresponding to $\text{H}_2\text{C}(\text{sp}^2)$ -hydrogen atoms of the phosphine are observed at 4.06 and 2.81 ppm as double doublets with H–P coupling constants of 30.2 and 8.7 Hz, respectively, and a H–H coupling constant of 3.0 Hz. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the $\text{C}(\text{sp})$ resonances of the alkyne appear at 124.5 and 120.8 ppm as singlets, while the $\text{C}(\text{sp}^2)$ resonances of

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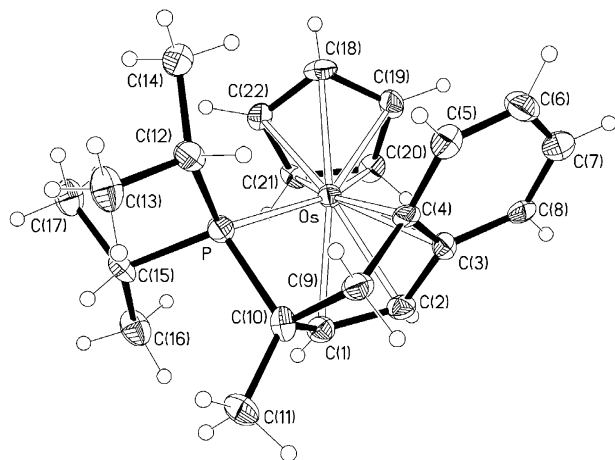


Figure 1. Molecular diagram of the cation of $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{-(1,2-dihydro-2-methylnaphth-2-ylideneisopropylphosphine)}]\text{B-Ph}_4$ (**3**). Selected bond lengths (Å) and angles (deg): Os–C(1) = 2.244(8), Os–C(2) = 2.180(8), Os–C(3) = 2.197(7), Os–C(4) = 2.369(7), Os–P = 2.317(2), C(1)–C(2) = 1.416(10), C(3)–C(4) = 1.392(9), C(2)–C(3) = 1.423(9); C(9)–C(10)–C(1) = 107.0(6), C(2)–C(1)–C(10) = 124.8(7), C(1)–C(2)–C(3) = 117.2(7), C(4)–C(3)–C(2) = 116.9(7); C(3)–C(4)–C(9) = 115.4(6); C(4)–C(9)–C(10) = 109.4(6).

the olefin are observed at 52.7 and 31.4 ppm as doublets with C–P coupling constants of 17.3 and 5.7 Hz, respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 21.9 ppm.

In dichloromethane, complex **2** is converted to the dihydronaphthylideneisopropylphosphine derivative $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{-(1,2-dihydro-2-methylnaphth-2-ylideneisopropylphosphine)}]\text{BF}_4$ (**3**), which is isolated as a brown solid in 60% yield.

The tridentate coordination mode of the phosphine was proved by an X-ray diffraction analysis experiment on a single crystal of the BPh_4 salt of **3**. This salt was prepared by treatment of the BF_4 salt with NaBPh_4 in dichloromethane. Figure 1 shows a view of the structure of the cation.

The geometry around the osmium center can be described as a very distorted octahedron, with the cyclopentadienyl ligand occupying the three sites of a face, whereas the phosphorus atom and the double bonds C(1)–C(2) and C(3)–C(4) of the phosphine are situated in the sites of the opposite face.

The C(1)–C(2)–C(3)–C(4) moiety of the phosphine coordinates to the metal center as expected for a butadiene ligand.¹⁰ Coordination of both double bonds is asymmetrical. The Os–C(terminal) distances (Os–C(1) = 2.244(8) Å and Os–C(4) = 2.3697(7) Å) are significantly longer than the Os–C(central) bond lengths (Os–C(2) = 2.180(8) Å and Os–C(3) = 2.197(7) Å). On the other hand, both C(terminal)–C(central) distances (C(1)–C(2) = 1.416(10) Å and C(3)–C(4) = 1.392(9) Å) are shorter than the C(central)–C(central) bond length (C(2)–C(3) = 1.423(9) Å). These structural parameters strongly support a $\eta^4\text{-}\pi$ -coordination for the diene moiety. In agreement with this coordination mode, the dihedral angle between the C(1)–Os–C(4) and C(1)–C(2)–C(3)–C(4) planes (θ) is 80.5(4)°, and the Δd and

Δl parameters¹¹ have values of 0.12 and -0.02 Å, respectively.

The coordination fashion of the diene moiety in **3** agrees well with that found in the 1,4-diphenylbutadiene derivative $[\text{OsH}(\eta^4\text{-C}_4\text{H}_4\text{Ph}_2)\{[\eta^2\text{-CH}_2\text{=C}(\text{CH}_3)]\text{P}^i\text{Pr}_2\}(\text{P}^i\text{Pr}_2\text{Pr}^n\text{Pr})]\text{BF}_4$ ($\theta = 80.0(4)^\circ$, $\Delta d = 0.15$, $\Delta l = -0.05$ Å).^{5c} However, it differs from that observed in the osmium(0) complex $\text{Os}(\eta^4\text{-C}_4\text{H}_5\text{Ph})(\text{CO})(\text{P}^i\text{Pr}_3)_2$, where on the basis of θ (83.0(1)°), Δd (0.064(3) Å), and Δl (0.036(5) Å) parameters, a coordination intermediate between the resonance forms $\eta^4\text{-}\pi$ and $\sigma^2\text{-}\pi$ has been proposed.¹³

Complex **3** is a new example of an η^2 -aromatic compound.¹⁴ The coordination of C(3) and C(4) to the osmium atom produces a slight alteration in the aromatic ring. Thus, the bond lengths C(3)–C(8), C(7)–C(6), and C(5)–C(4) (1.440(9), 1.430(10), and 1.431(9) Å, respectively) are considerably longer than the distances C(8)–C(7) and C(6)–C(5) (1.345(9) and 1.355(10) Å, respectively), which have more double-bond character. A similar phenomenon has been observed for the benzoallyl complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-CHPhC}_6\text{H}_5)\text{-(P}^i\text{Pr}_3)_2$.¹⁵

The Os–P distance of 2.317(2) Å is about 0.01 Å longer than the Os–P bond length in the isopropenylphosphine derivative $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)\{\eta^2\text{-(Z)-PhCH=CHPh}\}[\eta^2\text{-CH}_2\text{=C}(\text{CH}_3)]\text{P}^i\text{Pr}_2]\text{PF}_6$ (2.3093(10) Å),⁶ about 0.02 Å longer than that found in the dienyphosphine compound $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}\{[\eta^2\text{-(E)-PhC=CHCH}_2\text{C(=CH}_2)]\text{P}^i\text{Pr}_2\}$ (2.2990(12) Å),⁹ and about 0.05 Å longer

than those in the complexes iminophosphine $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}\{\text{NH=C(Ph)CH=C(CH}_3\text{)}\text{P}^i\text{Pr}_2\}$ (2.2686(12) Å)⁸ and α -allylphosphine $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\eta^3\text{-CHPhCHC(CH}_3\text{)}\}\text{P}^i\text{Pr}_2]\text{PF}_6$ (2.2634(9) Å).⁷

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **3** are consistent with the structure shown in Figure 1. In the ^1H NMR spectrum in dichloromethane- d_2 , the resonances corresponding to the olefinic protons HC(1) and HC(2) appear at 3.82 and 6.15 ppm, respectively. The $\text{H}_2\text{C(9)}$ group displays two signals, at 1.95 and 1.17 ppm; the latter is masked by a CH_3 resonance. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the ring junction carbon atoms C(3) and C(4) give rise to singlets at 165.1 and 164.16 ppm, while the olefinic C(2) and C(1) atoms display doublets at 66.4 and 49.4 ppm, with C–P coupling constants of 8.5 and 23.1 Hz, respectively. The resonances due to C(9) and C(10) are observed at 33.2 and 52.7 ppm, also as doublets but with C–P coupling constants of 6.1 and 34.8 Hz, respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at -43.2 ppm, shifted 65.1 ppm to higher field in comparison with the resonance of **2**.

The addition of $\text{DBF}_4\cdot\text{D}_2\text{O}$ to a dichloromethane solution of **1** leads to the instantaneous formation of the monodeuterated π -alkyne derivative $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-DC}\equiv\text{CPh})\{[\eta^2\text{-CH}_2\text{=C}(\text{CH}_3)]\text{P}^i\text{Pr}_2\}]\text{BF}_4$ (**2-d**). Like **2**, in

(11) $\Delta d = \{d[\text{Os}–\text{C}(1)] + d[\text{Os}–\text{C}(4)]\}/2 - \{d[\text{Os}–\text{C}(2)] + d[\text{Os}–\text{C}(3)]\}/2$ and $\Delta l = \{l[\text{C}(1)–\text{C}(2)] + l[\text{C}(3)–\text{C}(4)]\}/2 - l[\text{C}(2)–\text{C}(3)]$. See ref 12.

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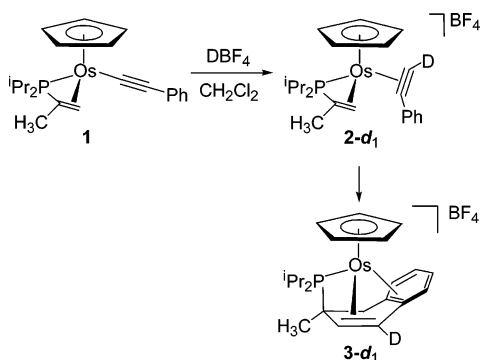
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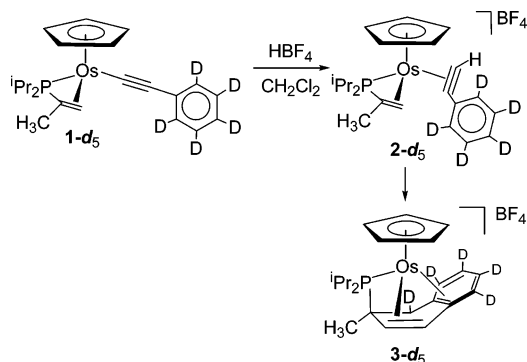
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Scheme 2



Scheme 3

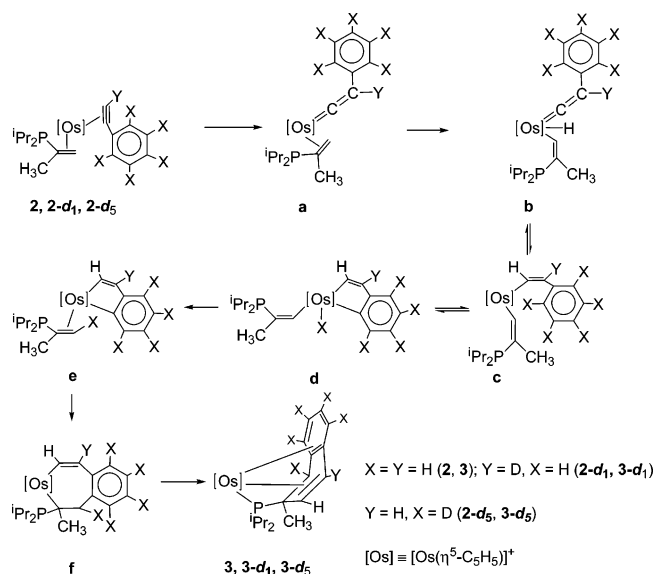


dichloromethane, complex **2-d₁** is converted to the dihydronaphthylphosphine compound **3-d₁**, containing a deuterium atom at C(2) (Scheme 2). The transformation involves a 1,2-deuterium shift in the alkyne of **2-d₁**. This suggests the participation of a vinylidene intermediate in the cyclization process. The positions of the deuterium atoms in **2-d₁** and **3-d₁** are strongly supported by the ^2H NMR spectra, which show broad singlets at 4.1 and 6.2 ppm, respectively.

To know the destination of the hydrogen atom of the ortho-CH bond of the phenyl ring activated during the formation of **3** and **3-d₁**, we have also investigated the reaction of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CC}_6\text{D}_5)\{\eta^2\text{-CH}_2=\text{C}(\text{CH}_3)\text{P}(\text{iPr})_2\}$ (**1-d₅**) with $\text{HBF}_4\cdot\text{OEt}_2$ (Scheme 3). The addition of 1.0 equiv of $\text{HBF}_4\cdot\text{OEt}_2$ to a dichloromethane solution of **1-d₅** gives $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-HC}\equiv\text{CC}_6\text{D}_5)\{\eta^2\text{-CH}_2=\text{C}(\text{CH}_3)\text{P}(\text{iPr})_2\}]\text{BF}_4$ (**2-d₅**). Similarly to **2** and **2-d₁**, complex **2-d₅** leads to **3-d₅**, containing a deuterium atom at C(9). The presence of a deuterium at this carbon atom is strongly supported by the ^2H NMR spectrum of **3-d₅**, which contains a broad singlet at 1.2 ppm.

Scheme 4 shows a sequence of reactions, which rationalizes the presence of deuterium at C(2) of **3-d₁** and at C(9) of **3-d₅**. Previously, we have proved that, in solution, cyclopentadienyl-osmium-hydride-phenylvinylidene species coexist in equilibrium with hydride-osmacyclopentadiene derivatives, resulting from the migratory insertion of the vinylidene into the Os–H bond and subsequent ortho-CH bond activation of the phenyl ring.¹⁶ The π -alkyne-vinylidene tautomerization in **2**, **2-d₁**, or **2-d₅**, followed by a $\text{C}(\text{sp}^2)\text{--H}$ bond activation of the isopropenyl group of the phosphine,

Scheme 4



could afford a hydride-phenylvinylidene intermediate **b**, which, according to our previous observations, should be in equilibrium with the corresponding iPr_2P -alkenyl-hydride-osmacyclopentadiene species **d**. The reductive elimination of isopropenyldiisopropylphosphine in the latter and the subsequent insertion of the isopropenyl group of the phosphine into the Os–aryl bond of the osmacyclopentadiene moiety should lead to an osmacycloheptadiene intermediate **f**. This species could generate the dihydronaphthylphosphine by reductive coupling of the Os– $\text{C}(\text{sp}^2)$ and Os– $\text{C}(\text{sp}^3)$ bonds of the metallacycle.

We note that, in contrast to this osmium system, the indenyl- β -alkenylphosphine-ruthenium(II) $[\text{Ru}(\eta^5\text{-C}_7\text{H}_9)\{\eta^2\text{-CH}_2=\text{CHCH}_2\}\text{PPh}_2]\text{PPh}_3]^+$ reacts with terminal alkynes and alkynols to afford vinylidene and allenylidene intermediates, respectively, which are transformed to bicyclic alkylidene compounds by intramolecular $[2 + 2]$ cycloaddition processes between the olefinic substituent of the phosphine and the $\text{C}_\alpha\text{--C}_\beta$ bonds of the cumulene ligands.¹⁷

In conclusion, the cyclopentadienyl-osmium unit promotes a novel cyclization reaction between phenylacetylene and the isopropenyl group of isopropenyldiisopropylphosphine, which affords a 1,2-dihydro-2-methylnaphth-2-ylideneisopropylphosphine-osmium complex. The new phosphine is generated from two regioselective C–C couplings: the terminal carbon atom of the alkyne with the C_α atom of the isopropenyl group of the starting phosphine, and an ortho carbon atom of the phenyl group of the alkyne with the C_β atom of the olefin substituent of isopropenyldiisopropylphosphine. In addition to these C–C couplings the cyclization involves CH bond activation reactions on the phenyl group of the alkyne and the isopropenyl substituent of the starting phosphine, as intermediate elementary steps of the overall process.

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Experimental Section

General Procedures. 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 $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{-(C}\equiv\text{CPh)}\{[\eta^2\text{-CH}_2\text{=C(CH}_3\text{)}]\text{P}^i\text{Pr}_2\}$ (**1**)⁹ and $\text{DBF}_4\cdot\text{D}_2\text{O}^{16c}$ were prepared by the published methods. Complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CC}_6\text{D}_5)\{[\eta^2\text{-CH}_2\text{=C(CH}_3\text{)}]\text{P}^i\text{Pr}_2\}$ (**1-d**₅) was prepared analogously to **1** using lithium phenylacetylide-*d*₅ instead of $\text{PhC}\equiv\text{CLi}$.

¹H, ³¹P{¹H}, and ¹³C{¹H} NMR spectra were recorded on either a Bruker Avance 300 MHz or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (¹H, ¹³C{¹H}) or external H_3PO_4 (³¹P{¹H}). Coupling constants, *J*, are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer (Nujol mulls on polyethylene sheets). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectral analyses were performed with a VG Autospec instrument. In LSIMS⁺ mode, ions were produced with the standard Cs⁺ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used in the matrix.

Preparation of $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-HC}\equiv\text{CPh})\{[\eta^2\text{-CH}_2\text{=C(CH}_3\text{)}]\text{P}^i\text{Pr}_2\}]\text{BF}_4$ (2**).** A solution of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CPh})\{[\eta^2\text{-CH}_2\text{=C(CH}_3\text{)}]\text{P}^i\text{Pr}_2\}$ (**1**) (155 mg, 0.29 mmol) in 6 mL of diethyl ether was treated with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (74 μL , 0.53 mmol). An orange solid was formed immediately. The mixture was stirred for 10 min, and the solution was decanted. The solid was washed with diethyl ether (2 $\times$ 2 mL) and dried in vacuo. Yield: 105 mg (60%). Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{BF}_4\text{OsP}$: C, 41.36; H, 4.89. Found: C, 41.84; H, 5.19. IR (Nujol, cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 1729; $\nu(\text{BF}_4)$ 1064. ¹H NMR (300 MHz, CD_2Cl_2 , 293 K): δ 7.33–7.07 (5H, Ph); 5.92 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 4.09 (s, 1H, HC $\equiv$); 4.06 (dd, 1H, $J_{\text{H-P}} = 30.2$, $J_{\text{H-H}} = 3.0$, PC=CH_{trans} to P); 2.81 (dd, 1H, $J_{\text{H-P}} = 8.7$, $J_{\text{H-H}} = 3.0$, PC=CH_{cis} to P); 2.61 (m, 1H, one of the PCH); 2.32 (d, 3H, $J_{\text{HP}} = 8.2$, PC(CH₃)=); 2.02 (m, 1H, one of the PCH); 1.73–1.43 (12H, PCHCH₃). ¹³C{¹H} NMR (75.4 MHz, CD_2Cl_2 , 293 K, plus APT, plus HSQC): δ 142.0 (s, C_{ipso} Ph); 129.4, 127.5, and 126.8 (all s, Ph); 124.5 (s, $\equiv\text{CPh}$); 120.8 (s, HC $\equiv$); 90.5 (s, $\eta^5\text{-C}_5\text{H}_5$); 52.7 (d, $J_{\text{C-P}} = 17.3$, PC=); 31.4 (d, $J_{\text{C-P}} = 5.7$, CH₂); 30.7 (d, $J_{\text{C-P}} = 31.6$, one of the PCH); 22.6 (d, $J_{\text{C-P}} = 31.0$, one of the PCH); 21.5 (d, $J_{\text{C-P}} = 6.0$, CH₃); 19.9 and 17.7 (both s, CH₃). ³¹P{¹H} NMR (121.4 MHz, CD_2Cl_2 , 293 K): δ 21.9 (br). MS (LSIMS⁺): *m/z* 517 (M⁺); 413 (M⁺ – PhC $\equiv$ CH).

Complex **2-d**₁ was prepared similarly by using $\text{DBF}_4\cdot\text{D}_2\text{O}$ instead of $\text{HBF}_4\cdot\text{OEt}_2$, whereas **2-d**₅ was obtained from **1-d**₅ and $\text{HBF}_4\cdot\text{OEt}_2$.

Preparation of $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(1,2\text{-dihydro-2-methylnaphth-2-ylideneisopropylphosphine})]\text{BF}_4$ (3**).** A solution of $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-HC}\equiv\text{CPh})\{[\eta^2\text{-CH}_2\text{=C(CH}_3\text{)}]\text{P}^i\text{Pr}_2\}]\text{BF}_4$ (**2**) (200

mg, 0.37 mmol) in 0.6 mL of dichloromethane was heated at 40 °C for 16 h. After that period of time, the solvent was concentrated to dryness. Addition of diethyl ether (7 mL) caused the formation of a brown solid. The solution was decanted and the solid washed with diethyl ether (2 $\times$ 3 mL) and dried in vacuo. Yield: 134 mg (60%). Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{BF}_4\text{OsP}$: C, 41.36; H, 4.89. Found: C, 41.11; H, 4.38. IR (Nujol, cm^{-1}): $\nu(\text{BF}_4)$ 1060. ¹H NMR (400 MHz, CD_2Cl_2 , 293 K): δ 7.77–6.80 (m, 4H, Ph); 6.15 (dd, 1H, $J_{\text{H-H}} = 6.0$, $J_{\text{H-P}} = 2.0$, H₂); 4.92 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$); 3.82 (ddd, 1H, $J_{\text{H-H}} = 6.0$, $J_{\text{H-P}} = J_{\text{H-H}} = 2.0$, H₁); 3.03 (m, 1H, one of the PCH); 2.55 (m, 1H, one of the PCH); 1.95 (ddd, 1H, $J_{\text{H-P}} = 5.6$, $J_{\text{H-H}} = 4.4$, $J_{\text{H-H}} = 2.0$, one of the H in CH₂); 1.55 (dd, 3H, $J_{\text{H-P}} = 16.0$, $J_{\text{H-H}} = 7.2$, one of the PCHCH₃); 1.49 (dd, 3H, $J_{\text{H-P}} = 15.6$, $J_{\text{H-H}} = 8.0$, one of the PCHCH₃); 1.47 (dd, 3H, $J_{\text{H-P}} = 16.8$, $J_{\text{H-H}} = 7.6$, one of the PCHCH₃); 1.46 (dd, 3H, $J_{\text{H-P}} = 13.8$, $J_{\text{H-H}} = 7.4$, one of the PCHCH₃); 1.17 (d, 4H, $J_{\text{H-P}} = 14.0$, CH₃ + 1H of the CH₂). ¹³C{¹H} NMR (100.5 MHz, CD_2Cl_2 , 293 K, plus APT, plus HSQC, plus HMBC): δ 165.1 and 164.6 (both s, C₃ and C₄); 139.8, 129.2, 127.0, and 121.6 (all s, C₅, C₆, C₇, and C₈); 80.0 (s, $\eta^5\text{-C}_5\text{H}_5$); 66.4 (d, $J_{\text{C-P}} = 8.5$, C₂); 52.7 (d, $J_{\text{C-P}} = 34.8$, C₁₀); 49.4 (d, $J_{\text{C-P}} = 23.1$, C₁); 33.2 (d, $J_{\text{C-P}} = 6.1$, C₉); 30.2 (d, $J_{\text{C-P}} = 14.0$, one of the PCH); 25.9 (d, $J_{\text{C-P}} = 31.7$, one of the PCH); 23.6 (d, $J_{\text{C-P}} = 3.6$, C₁₁); 21.7; 19.2, 19.1, and 18.5 (all s, CH₃). ³¹P{¹H} NMR (161.4 MHz, CD_2Cl_2 , 293 K): δ –43.2 (s). MS (LSIMS⁺): *m/z* 517 (M⁺).

Complexes **3-d**₁ and **3-d**₅ were prepared similarly starting from **2-d**₁ and **2-d**₅, respectively.

Crystal data for **3:** $\text{C}_{46}\text{H}_{50}\text{BOsP}$, *M*_w 834.84, yellow, irregular block (0.06 $\times$ 0.06 $\times$ 0.02 mm), triclinic, space group *P*1, *a* = 10.1242(17) Å, *b* = 12.635(2) Å, *c* = 14.459(2) Å, α = 88.271(4)°, β = 80.540(3)°, γ = 89.024(3)°, *V* = 1823.4(5) Å³, *Z* = 2, *D*_{calc} = 1.521 g cm^{–3}, *F*(000) = 844, *T* = 100.0(2) K; μ = 3.573 mm^{–1}. 13 118 measured reflections ($2\theta = 3\text{--}57^\circ$, ω scans 0.3°), 8380 unique (*R*_{int} = 0.0541); min./max. trans factors = 0.801/0.882. Final agreement factors were *R*₁ = 0.0581 (6231 observed reflections, *I* > 2σ(*I*)) and *wR*₂ = 0.0977; data/restraints/parameters = 8380/0/459; GoF = 0.831. Largest peak and hole = 1.762 and –1.733 e/Å³.

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Supporting Information Available: Crystallographic data and bond lengths and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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