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A Useful Access to the Chemistry of the Indenyl-Osmium-Triisopropylphosphine Moiety

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Summary: Complex $OsH_3Cl(P^iPr_3)_2$ *(**1**) reacts with indenyllithium to give* $OsH(\eta^5\text{-}C_9H_7)(P^iPr_3)_2$ *(**2**), which affords* $[OsH(\eta^5\text{-}C_9H_7)\{CH_2CH(CH_3)P^iPr_2\}(P^iPr_3)]OTf$ *(**3**) by treatment with methyl trifluoromethanesulfonate. In acetonitrile, complex **3** evolves to an equilibrium mixture of the acetonitrile adducts* $[Os(\eta^5\text{-}C_9H_7)(NCCH_3)(P^iPr_3)_2]OTf$ *(**4**) and* $[Os(\eta^5\text{-}C_9H_7)(NCCH_3)_2(P^iPr_3)]OTf$ *(**5**). The addition of 2,5-norbornadiene (NBD) to this mixture leads to* $[Os(\eta^5\text{-}C_9H_7)(\eta^4\text{-}NBD)(P^iPr_3)]OTf$ *(**6**). Complex **2** also reacts with* I_2 *and* HBF_4*, to give* $[OsHI(\eta^5\text{-}C_9H_7)(P^iPr_3)_2]I$ *(**7**) and* $[OsH_2(\eta^5\text{-}C_9H_7)(P^iPr_3)_2]BF_4$ *(**8**), respectively.*

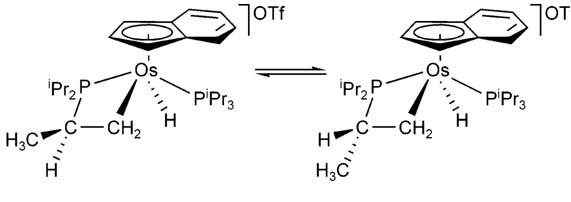
In the search for metallic homogeneous systems that are effective in the synthesis of functionalized organic molecules from basic hydrocarbon units, we are carrying out a wide research program on the chemistry of the cyclopentadienyl-osmium-triisopropylphosphine moiety.[1] Thus, as a part of this program, we have shown that the reactions of the known complex $OsH_2Cl_2(P^iPr_3)_2$[2] with a cyclopentadienyl derivative of an s- or p-block element are a method of general use to obtain cyclopentadienyl-osmium-triisopropylphosphine compounds.[3]

A substantial increase in the rates of associative substitution reactions of electronically saturated complexes has been observed for indenyl derivatives, when compared to their cyclopentadienyl analogues (*indenyl effect*).[4] Since the octahedral osmium(II) complexes showed a marked inertness toward the substitution reactions, the *indenyl effect* prompted us to expand our work to the indenyl-osmium-triisopropylphosphine moiety.

Half-sandwich indenyl-osmium complexes are extremely rare[5] due mainly to the lack of convenient synthetic precursors. Thus, our first objective has been to find an entry to the indenyl-osmium-triisopropylphosphine derivatives. The method employed to prepare cyclopentadienyl derivatives is not useful to obtain an indenyl-osmium-triisopropylphosphine precursor. The treatment of $OsH_2Cl_2(P^iPr_3)_2$ with indenyllithium in toluene leads to a complex mixture of products.

In contrast to the dihydride-dichloro, the related trihydride $OsH_3Cl(P^iPr_3)_2$ (**1**) reacts with indenyllithium, in toluene at room temperature, to afford the monohydride $OsH(\eta^5\text{-}C_9H_7)(P^iPr_3)_2$ (**2**), which is isolated as an orange solid in 69% yield (Scheme 1). The presence of a hydride ligand in this compound is supported by its ^1H NMR spectrum, which shows a triplet at δ −21.48 with a H−P coupling constant of 27.0 Hz.

Complex **2** reacts with CH_3OTf to give methane[6] and the metalated compound $[OsH(\eta^5\text{-}C_9H_7)\{CH_2CH(CH_3)P^iPr_2\}(P^iPr_3)]OTf$ (**3**), which is isolated as a white solid in 83% yield. In solution, complex **3** exists as a 1:1 mixture of the stereoisomers shown in eq 1. The presence of both species is strongly supported by the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **3**. Thus, the ^1H NMR spectrum in acetone-d_6 shows two hydride resonances at δ −14.53 and −14.06, which appear as double doublets. In agreement with the *cisoid* disposition of the hydride to both phosphorus atoms, the values of the H−P coupling constants are 29.1 and 35.4 Hz and 31.2 and 36.9 Hz, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the Os−CH$_2$ and CH signals of the metalated isopropyl group are observed at δ −27.2 and −25.1 and δ 48.9 and 47.2, respectively. These chemical shifts are similar to those previously reported for related cyclopentadienyl compounds.[7] The $^{31}P\{^1H\}$ NMR spectrum shows four doublets at δ 0.1 and −34.5, with a P−P coupling constant of 16 Hz, and at δ 2.9 and −37.4, with a P−P coupling constant of 18 Hz.



(1)

Figure 1 shows a view of the structure of the cation of one of the stereoisomers of **3**. The distribution of ligands around the osmium atom can be described as a

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[1] Esteruelas, M. A.; López, A. M. *Organometallics* **2005**, *24*, 3584.

[2] (a) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288. (b) Castarlenas, R.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Jean, Y.; Lledós, A.; Martín, M.; Oñate, E.; Tomàs, J. *Organometallics* **2000**, *19*, 3100, and references therein.

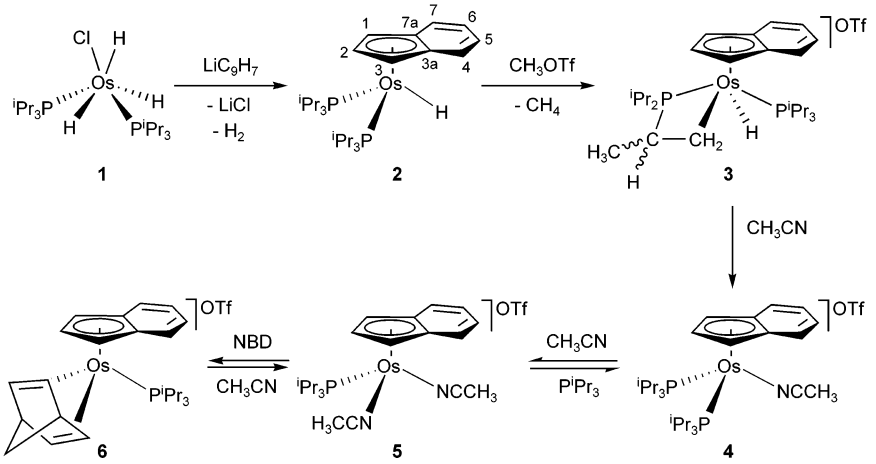
[3] (a) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657. (b) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2004**, *23*, 3021. (c) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2004**, *23*, 5633.

[4] (a) Zargarian, D. *Coord. Chem. Rev.* **2002**, *233−234*, 157, and references therein. (b) Calhorda, M. J.; Romão, C. C.; Veiros, L. F. *Chem. Eur. J.* **2002**, *8*, 868, and references therein.

[5] (a) Gamasa, M. P.; Gimeno, J.; Gonzalez-Cueva, M.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1996**, 2547. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137. (c) Koch, J. L.; Shapley, P. A. *Organometallics* **1997**, *16*, 4071. (d) Gimeno, J.; Gonzalez-Cueva, M.; Lastra, E.; Perez-Carreño, E.; García-Granda, S. *Inorg. Chim. Acta* **2003**, *347*, 99.

10.1021/om050595c CCC: $30.25

Scheme 1



four-legged piano-stool geometry with the phosphorus atoms *transoid* disposed (P(1)−Os−P(2) = 110.04(3)°). The metalated phosphine acts with a bite angle C(2)−Os−P(1) of 64.79(10)°. The Os−C(2) bond length of 2.179(4) Å agrees with the values previously reported for other Os−C(sp^3) bonds.[8]

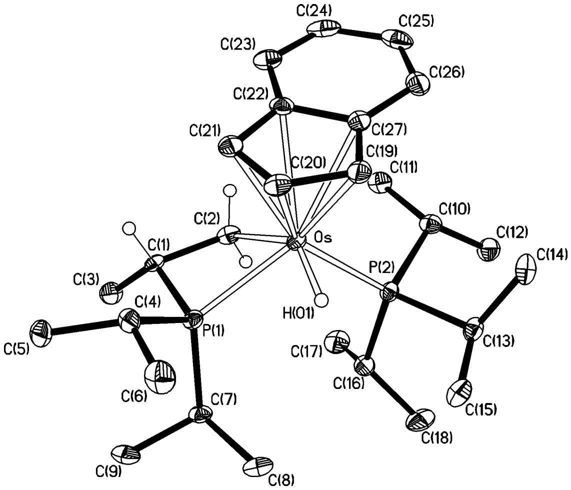


Figure 1. Molecular diagram of the cation of one of the stereoisomers of **3**. Selected bond distances (Å) and angles (deg): Os−C(2) 2.179(4), Os−P(1) 2.3066(10), Os−P(2) 2.3853(10), Os−C(19) 2.248(3), Os−C(20) 2.184(3), Os−C(21) 2.221(3), Os−C(22) 2.402(3), Os−C(27) 2.417(3); C(2)−Os−P(1) 64.79(10), C(2)−Os−P(2) 89.27(10), P(1)−Os−P(2) 110.04(3).

The formation of **3** probably takes place via the unsaturated intermediate [Os(η^5-C$_9$H$_7$)(P^{i}Pr$_3$)$_2$]$^+$, which is trapped with acetonitrile. The addition of this coordinating molecule to **3** affords the osmium(II) derivative [Os(η^5-C$_9$H$_7$)(NCCH$_3$)(P^{i}Pr$_3$)$_2$]OTf (**4**), which is isolated as an orange solid in 77% yield.

Figure 2 shows a view of the structure of the cation of **4**. The geometry around the osmium center can be described as a distorted octahedron with the five-membered ring of the indenyl ligand occupying the three sites of a face. The distortion is mainly caused by the mutual *cis* disposition of the phosphine ligands, which describe a P−Os−P angle larger than 90°. This angle of 102.61(4)° is similar to other P−M−P angles previously found in complexes with two triisopropylphosphine ligands mutually *cis* disposed.[7]

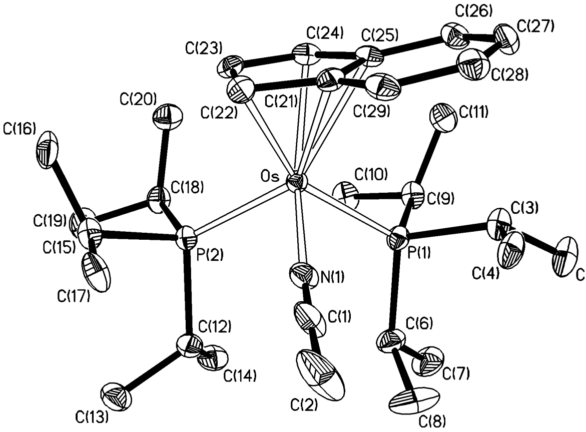


Figure 2. Molecular diagram of the cation of **4**. Selected bond distances (Å) and angles (deg): Os−N(1) 2.023(4), Os−P(1) 2.3789(13), Os−P(2) 2.3185(13), Os−C(21) 2.383(5), Os−C(22) 2.209(5), Os−C(23) 2.189(5), Os−C(24) 2.215(5), Os−C(25) 2.407(5); P(1)−Os−P(2) 102.61(4), P(1)−Os−N(1) 90.98(13), P(2)−Os−N(1) 90.44(12).

In acetonitrile, complex **4** dissociates triisopropylphosphine to reach an equilibrium with [Os(η^5-C$_9$H$_7$)(NCCH$_3$)$_2$(P^{i}Pr$_3$)]OTf (**5**). The addition of 2.0 equiv of 2,5-norbornadiene (NBD) to the mixture leads to the diolefin derivative [Os(η^5-C$_9$H$_7$)(η^4-NBD)(P^{i}Pr$_3$)]OTf (**6**), which is isolated as an orange solid in 84% yield. In the ^{1}H NMR spectrum, the vinylic protons of the diolefin give rise to a complex signal between δ 3.85 and 3.70, whereas in the ^{13}C{^{1}H} NMR spectrum, the C(sp^2) atoms display two doublets at δ 41.6 and 41.4, with a C−P coupling constant of 7 Hz, and two singlets at δ 35.9 and 36.0.

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(6) Similarly, Girolami and co-workers have observed that reductive elimination of methane occurs by protonation of (C$_5$Me$_5$)Os(dmpm)(CH$_3$). See: Gross, C. L.; Girolami, G. S. *J. Am. Chem. Soc.* **1998**, *120*, 6605.

(7) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Inorg. Chem.* **2005**, *44*, 4094, and references therein.

(8) See for example: (a) Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Oro, L. A.; Schlünken, C.; Valero, C.; Werner, H. *Organometallics* **1992**, *11*, 2034. (b) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Zanazzi, P. *Inorg. Chem.* **1993**, *32*, 547. (c) Rickard, C. E. F.; Roper, W. R.; Woodman, T. J.; Wright, L. J. *Chem. Commun.* **1999**, 1101. (d) Mui, H. D.; Brumaghim, J. L.; Gross, C. L.; Girolami, G. S. *Organometallics* **1999**, *18*, 3264. (e) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Valentini, F.; Zucaccia, C.; Foresti, E.; Sabatino, P. *Organometallics* **2000**, *19*, 4320.

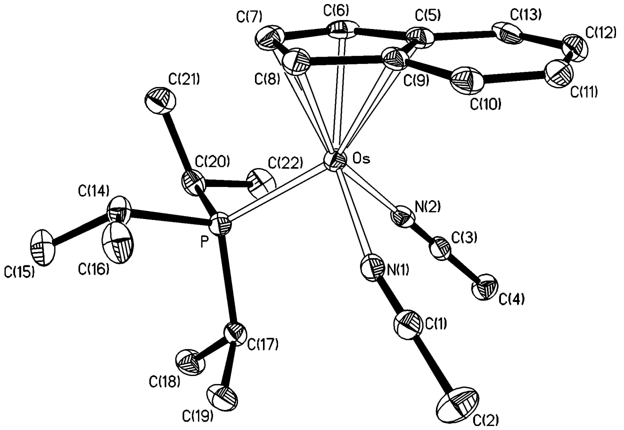
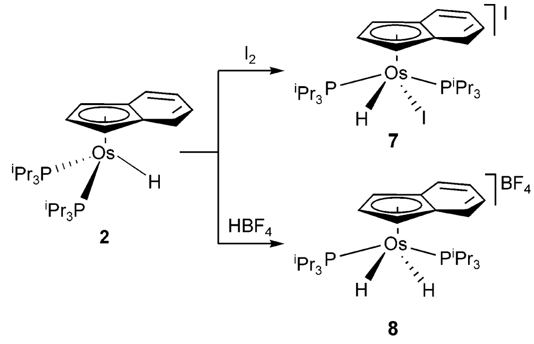


Figure 3. Molecular diagram of the cation of **5**. Selected bond distances (Å) and angles (deg): Os−N(1) 2.039(3), Os−N(2) 2.040(3), Os−P 2.2965(8), Os−C(5) 2.311(3), Os−C(6) 2.171(3), Os−C(7) 2.157(3), Os−C(8) 2.180(3), Os−C(9) 2.300(3); P−Os−N(1) 94.01(7), P−Os−N(2) 89.38(7), N(1)−Os−N(2) 82.93(9).

Scheme 2



At 50 °C, in acetonitrile, complex **6** loses the diolefin and regenerates **5**, which is isolated as a yellow solid in 63% yield. Complex **5** has also been characterized by X-ray diffraction analysis. The geometry around the osmium atom can be described as an octahedron (Figure 3). In contrast to **4**, the angles between the monodentate ligands are close to 90°.

The chemistry of the indenyl-osmium-triisopropylphosphine moiety is also consistent with the intrinsically high basicity of the osmium atom, which is revealed in the reactions of **2** with molecular iodine and HBF_4 (Scheme 2).

Treatment of a pentane solution of **2** with 1.1 equiv of I_2 affords the osmium(IV) derivative $[OsHI(\eta^5\text{-}C_9H_7)(P^iPr_3)_2]I$ (**7**), which is isolated as a red-brown solid in 78% yield. In agreement with the structure proposed for this compound, its ^1H NMR spectrum shows a triplet at δ −15.89, with a H−P coupling constant of 36.6 Hz, corresponding to the hydride ligand, and the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at δ −2.2.

The reaction of **2** with $HBF_4{\cdot}OEt_2$ in diethyl ether leads to the dihydride complex $[OsH_2(\eta^5\text{-}C_9H_7)(P^iPr_3)_2]BF_4$ (**8**), which is isolated as a white solid in 77% yield.[9] Figure 4 shows the structure of the cation of this compound. The distribution of ligands around the osmium atom can be described as a four-legged piano-stool geometry with the five-membered ring of the indenyl ligand occupying the three-membered face while the phosphorus donor atoms lie in the four-membered face mutually *transoid* disposed (P(1)−Os−P(2) = 112.80(4)°). In agreement with the *transoid* disposition of the hydride ligands, the ^1H NMR spectrum of **8** shows a triplet at δ −14.90 with a H−P coupling constant of 30 Hz.

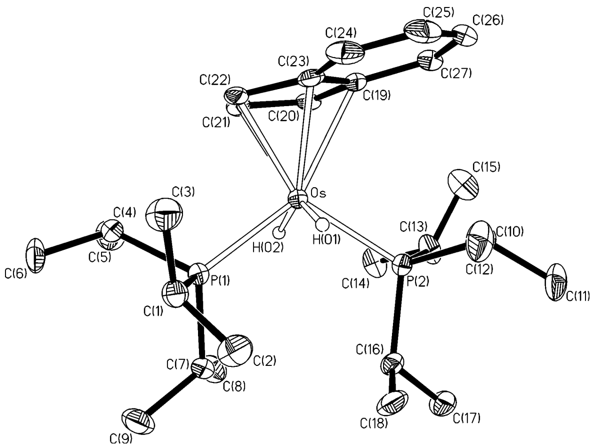


Figure 4. Molecular diagram of the cation of **8**. Selected bond distances (Å) and angles (deg): Os−P(1) 2.3167(12), Os−P(2) 2.3581(10), Os−C(19) 2.384(4), Os−C(20) 2.228(4), Os−C(21) 2.201(4), Os−C(22) 2.228(4), Os−C(23) 2.374(4); P(1)−Os−P(2) 112.80(4).

In conclusion, the reaction of $OsH_3Cl(P^iPr_3)_2$ with indenyllithium leads to the monohydride $OsH(\eta^5\text{-}C_9H_7)(P^iPr_3)_2$, which is a useful starting material to new indenyl-osmium derivatives. Because the osmium center of the indenyl-osmium-triisopropylphosphine skeleton has a marked nucleophilic character, and the solvento complex $[Os(\eta^5\text{-}C_9H_7)(NCCH_3)_2(P^iPr_3)]OTf$ is easily accessible, a promising future can be envisaged for the chemistry of the indenyl-osmium-triisopropylphosphine moiety.

Experimental Section

General Procedures. All reactions were carried out under argon using Schlenk-tube or glovebox techniques. Solvents were dried by known procedures and used freshly distilled. Complex $OsH_3Cl(P^iPr_3)_2$ (**1**) was prepared according to a previous report.[10] NMR spectra were recorded at 293 K. ^1H (300 MHz) and $^{13}C\{^1H\}$ (75.4 MHz), and $^{31}P\{^1H\}$ (121.4 MHz) chemical shifts are reported relative to external tetramethylsilane and H_3PO_4 (85%), respectively. Coupling constants J are given in hertz.

Preparation of $OsH(\eta^5\text{-}C_9H_7)(P^iPr_3)_2$ (2). Toluene (10 mL) was added to a mixture of **1** (1.50 g, 2.73 mmol) and $Li[C_9H_7]$ (0.37 g, 3.0 mmol), and a gas bubbler was connected to the flask system. Stirring of the mixture afforded a suspension, which was filtered, and the residue was extracted with pentane. The filtrate was concentrated to dryness and the residue washed with MeOH and vacuum-dried. Dark orange solid. Yield: 1.18 g (69%). Anal. Calcd for $C_{27}H_{50}OsP_2$: C, 51.73; H, 8.04. Found: C, 52.04; H, 7.95. IR (Nujol, cm^{-1}): ν (Os−H) 2169. MS (FAB$^+$): *m/e* 628 (M$^+$). ^1H NMR (C_6D_6): δ 7.21, 6.91 (m, each 2H, H^{4-7}), 5.30 (m, 1H, H^2), 4.89 (m, 2H, $H^{1,3}$), 1.96 (m, 6H, PCH), 1.08, 1.05 (dd, each 9H, J(HH) = 7.3, J(PH) = 12.0, $PCCH_3$), −21.48 (t, 1H, J(PH) = 27.0,

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[9] Related $[OsH_2(C_5R_5)(PR'_3)_2]^+$ cations are known. See for example: (a) Wilczewski, T. *J. Organomet. Chem.* **1986**, *317*, 307. (b) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267. (c) Jia, G.; Ng, W. S.; Yao, J.; Lau, C.-P.; Chen, Y. *Organometallics* **1996**, *15*, 5039. (d) Jia, G.; Lau, C. P. *J. Organomet. Chem.* **1998**, *565*, 37.

[10] Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.

Os–H). ^{31}P{^{1}H} NMR (C_6D_6): δ 27.6 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 122.2, 122.1 (s, C^{4-7}), 107.2 (s, C^{3a-7a}), 77.1 (s, C^2), 60.6 (d, *J*(PC) = 7, $C^{1,3}$), 32.0 (d, *J*(PC) = 23, PCH), 20.9, 20.8 (s, PC*C*H$_3$).

$[\overline{\mathrm{OsH}(\eta^5\text{-}\mathrm{C_9H_7})\{\mathrm{CH_2CH(CH_3)P}}{}^i\mathrm{Pr_2}\}(\mathrm{P}^i\mathrm{Pr_3})]\mathrm{OTf}$ (3). A solution of **2** (0.30 g, 0.48 mmol) in CH_2Cl_2 was treated with CH_3OTf (56 μL, 0.50 mmol). After 1 h the solvent was removed under reduced pressure and the residue washed with pentane and dried under vacuum. White solid. Yield: 0.31 g (83%). Anal. Calcd for $C_{28}H_{49}F_3O_3OsP_2S$: C, 43.39; H, 6.37; S, 4.14 Found: C, 43.23; H, 6.43; S, 4.27. IR (Nujol, cm^{-1}): ν (Os–H) 2151, ν (SO_3) and ν (CF_3) 1269 (br, s), 1147 (s), 1029 (s). MS (FAB$^+$): *m/e* 627 (M$^+$). ^{1}H NMR (($CD_3)_2CO$): δ 7.80–7.51 (m, 8H, H^{4-7}), 6.37 (d, 1H, *J*(HH) = 2.6, $H^{1,3}$), 6.34 (d, 1H, *J*(HH) = 1.0, $H^{1,3}$), 6.33 (m, 1H, $H^{1,3}$), 6.10 (d, 1H, *J*(HH) = 2.4, $H^{1,3}$), 5.93, 5.61 (m, each 1H, H^2), 3.57, 3.07 (m, each 1H, *H*C–CH_2), 2.93, 2.70 (m, each 1H, PCH), 2.45–1.85 (m, 12H, PCH + $OsCH_2$), 1.70–1.12 (m, 66H, PCC*H*$_3$), −14.06 (dd, 1H, *J*(PH) = 31.2, *J*(P′H) = 36.9, Os–H), −14.53 (dd, 1H, *J*(PH) = 29.1, *J*(P′H) = 35.4, Os–H). ^{31}P{^{1}H} NMR (($CD_3)_2CO$): δ 0.1, −34.5 (d, *J*(PP) = 16), 2.9, −37.4 (d, *J*(PP) = 18). ^{13}C{^{1}H} NMR (($CD_3)_2CO$): δ 132.5, 132.1, 132.0, 126.7, 126.6, 126.4, 125.2, (s, C^{4-7}), 126.5, 121.04, 112.1 (s, $C^{3a,7a}$), 111.5 (d, *J*(PC) = 5, $C^{3a,7a}$), 78.6, 77.6 (s, C^2), 74.5 (d, *J*(PC) = 3, $C^{1,3}$), 73.5 (br, $C^{1,3}$), 73.1, 71.5 (d, *J*(PC) = 7, $C^{1,3}$), 48.9, 47.2 (d, *J*(PC) = 35, CH_2–*C*H), 37.4, 35.6, 35.5 (d, *J*(PC) = 22, PCH), 31.8 (d, *J*(PC) = 27, PCH), 29.2, 28.2 (d, *J*(PC) = 21, PCH), 26.3, 25.6, 23.7, 22.3 (d, *J*(PC) = 6, PC*C*H$_3$), 22.1, 22.0, 21.9, 21.8, (s, PC*C*H$_3$), 21.3 (d, *J*(PC) = 3, PC*C*H$_3$), 21.2 (d, *J*(PC) = 5, PC*C*H$_3$), 21.0 (+, d, *J*(PC) = 3, PC*C*H$_3$), 20.7, 19.6, 18.8 (s, PC*C*H$_3$), −27.2, −25.1 (dd, *J*(PC) = 38, *J*(P′C) = 9, Os–CH_2).

Preparation of $[\mathrm{Os}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{NCMe})(\mathrm{P}^i\mathrm{Pr_3})_2]\mathrm{OTf}$ (4). A solution of **3** (0.12 g, 0.19 mmol) in MeCN (2 mL) was stirred for 12 h. The resulting solution was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 (1 mL). P^{i}Pr$_3$ (0.11 mL, 0.57 mmol) was then added, and the mixture was stirred for 1 h. The solvent was removed under vacuum, and the solid residue was washed with Et_2O and pentane and vacuum-dried. Orange solid. Yield: 0.12 g (77%). Anal. Calcd for $C_{30}H_{52}F_3NO_3OsP_2S$: C, 44.16; H, 6.42; N, 1.72; S, 3.93. Found: C, 44.08; H, 6.75; N, 2.01; S, 4.01. IR (Nujol, cm^{-1}): ν (C≡N) 2260, ν (SO_3) and ν (CF_3) 1270 (br, s), 1146 (s), 1029 (s). MS (FAB$^+$): *m/e* 667 (M$^+$), 626 (M$^+$ − CH_3CN). ^{1}H NMR (CD_2Cl_2): δ 7.39, 7.31 (m, each 2H, H^{4-7}), 5.72 (t, 1H, *J*(HH) = 3.2, H^2), 5.63 (d, 2H, *J*(HH) = 3.2, $H^{1,3}$), 2.70 (t, 3H, *J*(PH) = 1.2, CH_3CN), 2.39 (m, 6H, PCH), 1.24 (dd, 18H, *J*(HH) = 7.2, *J*(PH) = 12.8, PCC*H*$_3$), 1.07 (dd, 18H, *J*(HH) = 7.2, *J*(PH) = 13.6, PCC*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 0.3 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 130.2, 125.0 (s, C^{4-7}), 124.1 (s, $C^{3a,7a}$), 108.4 (t, *J*(PC) = 2, N*C*CH$_3$), 77.3 (s, C^2), 59.6 (s, $C^{1,3}$), 32.6 (d, *J*(PC) = 26, PCH), 22.1, 21.7 (s, PC*C*H$_3$), 6.4 (s, NC*C*H$_3$).

Preparation of $[\mathrm{Os}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{NCMe})_2(\mathrm{P}^i\mathrm{Pr_3})]\mathrm{OTf}$ (5). A solution of **6** (0.45 g, 0.64 mmol) in MeCN (3 mL) was stirred for 48 h at 50 °C. The mixture was filtered through Celite and evaporated to dryness. The residue was washed with Et_2O and vacuum-dried. Yellow solid. Yield: 0.28 g (63%). Anal. Calcd for $C_{23}H_{34}F_3N_2O_3OsPS$: C, 39.65; H, 4.92; N, 4.02; S, 4.59. Found: C, 39.44; H, 4.67; N, 3.98; S, 4.60. IR (Nujol, cm^{-1}): ν (C≡N) 2260, ν (SO_3) and ν (CF_3) 1270 (br, s), 11467 (s), 1029 (s). MS (FAB$^+$): *m/e* 548 (M$^+$), 507 (M$^+$ − CH_3CN), *m/e* 466 (M$^+$ − 2 CH_3CN). ^{1}H NMR (CD_2Cl_2): δ 7.41, 7.31 (m, each 2H, H^{4-7}), 5.10 (m, 3H, H^{1-3}), 2.55 (s, 6H, CH_3CN), 2.39 (m, 3H, PCH), 1.17 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 13.6, PCC*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 20.1 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 129.5, 125.2 (s, C^{4-7}), 123.3 (s, $C^{3a,7a}$), 106.5 (d, *J*(PC) = 5, N*C*CH$_3$), 81.1 (s, C^2), 53.4 (s, $C^{1,3}$), 29.3 (d, *J*(PC) = 29.1, PCH), 20.8 (s, PC*C*H$_3$), 5.6 (s, NC*C*H$_3$).

Preparation of $[\mathrm{Os}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{NBD})(\mathrm{P}^i\mathrm{Pr_3})]\mathrm{OTf}$ (6). A solution of **3** (0.50 g, 0.64 mmol) in MeCN (1 mL) was stirred for 12 h. The resulting suspension was filtered through Celite and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (5 mL) and treated with NBD (0.15 mL, 1.30 mmol) for 12 h. The resulting solution was filtered through Celite and evaporated to dryness. The solid residue was washed with Et_2O and pentane and dried under vacuum. Orange powder. Yield: 0.38 g (84%). Anal. Calcd for $C_{26}H_{36}F_3O_3OsPS$: C, 44.18; H, 5.13; S, 4.54. Found: C, 44.14; H, 5.47; S, 4.47. IR (Nujol, cm^{-1}): ν (SO_3) and ν (CF_3) 1269 (br, s), 1147 (s), 1029 (s). MS (FAB$^+$): *m/e* 558 (M$^+$). ^{1}H NMR (CD_2Cl_2): δ 7.51 (m, 4H, H^{4-7}), 5.95 (d, 2H, *J*(HH) = 2.7, $H^{1,3}$), 5.38 (dt, 1H, *J*(HH) = *J*(PH) = 2.7, H^2), 3.85–3.70 (m, 6H, NBD: −CH + =CH), 2.92 (m, 3H, PCH), 1.35 (dd, 18H, *J*(HH) = 7.2, *J*(PH) = 13.8, PCC*H*$_3$), 0.85 (m, 2H, NBD: −CH_2−). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 7.1 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 130.5, 124.8 (s, C^{4-7}), 105.9 (s, $C^{3a,7a}$), 83.6 (s, C^2), 67.3 (d, *J*(PC) = 18, $C^{1,3}$), 67.2 (s, NBD: −CH_2−), 48.3, 47.6 (s, NBD: −CH), 41.6, 41.4 (d, *J*(PC) = 7, NBD: =CH), 36.0, 35.9 (s, NBD: =CH), 32.3 (d, *J*(PC) = 34, PCH), 21.0 (s, PC*C*H$_3$).

Preparation of $[\mathrm{OsH}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{I}(\mathrm{P}^i\mathrm{Pr_3})_2]\mathrm{I}$ (7). I_2 (0.08 g, 0.31 mmol) was added to a solution of **2** (0.22 g, 0.34 mmol) in pentane (20 mL). After 18 h the solid formed was filtered off, washed with cold acetone and pentane, and dried under vacuum. Red-brown powder. Yield: 0.22 g (78%). Anal. Calcd for $C_{27}H_{50}I_2OsP_2$: C, 36.82; H, 5.77. Found: C, 36.59; H, 5.44. MS (FAB$^+$): *m/e* 754 (M$^+$). ^{1}H NMR ($CDCl_3$): δ 7.64, 7.50 (m, each 2H, H^{4-7}), 6.54 (m, 2H, $H^{1,3}$), 6.34 (m, 1H, H^2), 2.64 (m, 6H, PCH), 1.23 (dd, 18H, *J*(HH) = 6.9, *J*(PH) = 13.8, PCCH$_3$), 1.34 (dd, 18H, *J*(HH) = 7.2, *J*(PH) = 14.1, PCCH$_3$), −15.89 (t, 1H, *J*(PH) = 36.6, Os–H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ − 2.2 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 134.3, 127.2 (s, C^{4-7}), 117.2 (s, $C^{3a,7a}$), 73.2 (s, C^2), 69.2 (s, $C^{1,3}$), 32.6 (m, PCH), 21.8, 21.7 (s, PC*CH*$_3$).

Preparation of $[\mathrm{OsH_2}(\eta^5\text{-}\mathrm{C_9H_7})(\mathrm{P}^i\mathrm{Pr_3})_2]\mathrm{BF_4}$ (8). A suspension of **3** (1.10 g, 1.75 mmol) in Et_2O (10 mL) was treated with a 54% solution of HBF_4 in Et_2O (0.26 mL, 1.93 mmol). After stirring the mixture for 5 h, the suspension was filtered off, washed with Et_2O and pentane, and dried under vacuum. White powder. Yield: 0.97 g (77%). Anal. Calcd for $C_{27}H_{51}BF_4OsP_2$: C, 45.37; H, 7.19. Found: C, 45.43; H, 7.26. IR (Nujol, cm^{-1}): ν (Os–H) 2162, 2095. MS (FAB$^+$): *m/e* 628 (M$^+$). ^{1}H NMR (CD_2Cl_2): δ 7.42 (m, 4H, H^{4-7}), 6.15 (d, 2H, *J*(HH) = 2.6, $H^{1,3}$), 5.02 (t, 1H, *J*(HH) = 2.6, H^2), 1.95 (m, 6H, PCH), 1.15 (dd, 36H, *J*(HH) = 7.2, *J*(PH) = 14.2, PCCH$_3$), −14.90 (t, 2H, *J*(PH) = 30, Os–H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 29.5 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 129.7, 124.7 (s, C^{4-7}), 107.2 (s, $C^{3a,7a}$), 79.5 (s, C^2), 71.9 (s, $C^{1,3}$), 28.9 (m, PCH), 19.2 (s, PC*CH*$_3$).

X-ray Analysis of Complexes 3, 4, 5, and 8. Suitable crystals were mounted on a Bruker Smart APEX CCD diffractometer at 100.0(2) K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using ω scans. The structures were solved by Patterson and Fourier methods and refined by full matrix least-squares with all non-hydrogen atoms anisotropically refined.

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

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