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Dihydride versus Elongated Dihydrogen in $[H_2Os(\kappa^2\text{-}O_2CCH_3)L(P^iPr_3)_2]^+$ Complexes: Influence of the L Ligand

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*Summary: The complex $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ (**1**) reacts with aniline, pyridine, and trimethyl phosphite. The reaction with aniline affords the dihydride derivative $[OsH_2(\kappa^2\text{-}O_2CCH_3)(NH_2Ph)(P^iPr_3)_2]BF_4$ (**2**), while in the presence of pyridine a 7:1 equilibrium mixture of the dihydride $[OsH_2(\kappa^2\text{-}O_2CCH_3)(py)(P^iPr_3)_2]BF_4$ (**3a**) and the elongated dihydrogen-containing complex $[Os(\eta^2\text{-}H_2)(\kappa^2\text{-}O_2CCH_3)(py)(P^iPr_3)_2]BF_4$ (**3b**) is obtained. The reaction with trimethyl phosphite leads to the elongated dihydrogen complex $[Os(\eta^2\text{-}H_2)(\kappa^2\text{-}O_2CCH_3)\{P(OMe)_3\}(P^iPr_3)_2]BF_4$ (**4**). The structures of **2** and **4** have been determined by X-ray diffraction analysis.*

The nature of the H_2 moiety of H_2ML_n complexes can be modified by subtle changes in the ML_n fragment. It has been shown for octahedral compounds that the dihydrogen character of the H_2 unit is very dependent on the nature of the ligand *trans* to the hydrogen atoms:[1] strong acceptor ligands weaken the M−H_2 bond and destabilize the oxidative addition of dihydrogen, while weak acceptor ligands increase the MH_2 bond energy and favor the classical dihydride.[2]

The strength of the metal−hydrogen interaction is also dependent on the ligand disposed *cis* to the H_2 unit. The replacement of a hydride ligand in $\overline{OsH_3\{NH{=}C(Ph)C}_6H_4\}(P^iPr_3)_2$ by chloride, bromide, or iodide produces significant disruptions in the interaction between the other hydrogens and the osmium atom, giving rise to elongated dihydrogen derivatives.[3]

The dihydride or elongated dihydrogen nature of the osmium complexes containing two hydrogen atoms bonded to the metal depends not only on the ligands located *cis* or *trans* to the H_2 unit but also on other factors, as revealed by the chemistry of the unsaturated osmium(IV) dihydride $OsH_2Cl_2(P^iPr_3)_2$. Substitution of a chloride ion in this complex by $[ROCS_2]^-$ (R = Me, Et) produces saturated compounds, where a dihydride−elongated dihydrogen transformation has occurred.[4] Similarly, the addition of pyrazole[5] and benzophenone imine[6] also yields elongated dihydrogen species, $OsCl_2(\eta^2\text{-}H_2)L(P^iPr_3)_2$.

These dihydride−elongated dihydrogen transformations involve a formal increase of the coordination number of the osmium atom along with a rearrangement of the coordination polyhedron, which changes from a square antiprism with two missing vertexes in the starting compound[7] to an octahedron in the elongated dihydrogen derivatives.[4−6] However, the increase in the coordination number of the osmium does not appear to be the reason for the change in the coordination polyhedron. The substitution of the chloride anions of $OsCl_2H_2(P^iPr_3)_2$ by acetate affords the saturated seven-coordinate osmium(IV) dihydride $OsH_2(\kappa^1\text{-}OCOCH_3)(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$,[8] which reacts with $HBF_4{\cdot}H_2O$ to give $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$.[9] In the solid state, the structure of these compounds is similar to that of $OsCl_2H_2(P^iPr_3)_2$ and can also be described as a square antiprism, with only one missing vertex.[8,9] Here we provide evidence that the change in the coordination polyhedron that accompanies this dihydride−elongated dihydrogen transformation is promoted by π-acceptor ligands.

The water ligand of $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ (**1**) can be readily displaced by aniline, pyridine, or trimethyl phosphite (Scheme 1). This substitution is facilitated by the weakness of the Os−OH_2 bond.

The reaction with aniline leads to the dihydride $[OsH_2(\kappa^2\text{-}O_2CCH_3)(NH_2Ph)(P^iPr_3)_2]BF_4$ (**2**), which was isolated as a yellow solid in 90% yield. The structure of **2** is presented in Figure 1. The cation has no symmetry elements other than a C_1 axis, and the geometry around the osmium atom can be described as being derived from a very distorted square antiprism with a missing vertex, in agreement with the structure found for dihydride $OsH_2(\kappa^1\text{-}OCOCH_3)(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$.[8] One of the two square planes is made up of the two phosphorus atoms

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[1] See for example: (a) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946. (b) Bautista, M. T.; Capellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876. (c) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (e) Craw, J. S.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **1994**, *116*, 5937. (f) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes*; Kluwer Academic/Plenum Publishers: New York, 2001.

[2] (a) Dapprich, S.; Frenking, G. *Organometallics* **1996**, *15*, 4547. (b) Michos, D.; Luo, X.-L.; Howard, J. A. K.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 3914.

[3] Barea, G.; Esteruelas, M. A.; Lledós, A.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **1998**, *17*, 4065.

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[5] Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Oñate, E.; Ruiz, N. *Inorg. Chem.* **1994**, *33*, 787.

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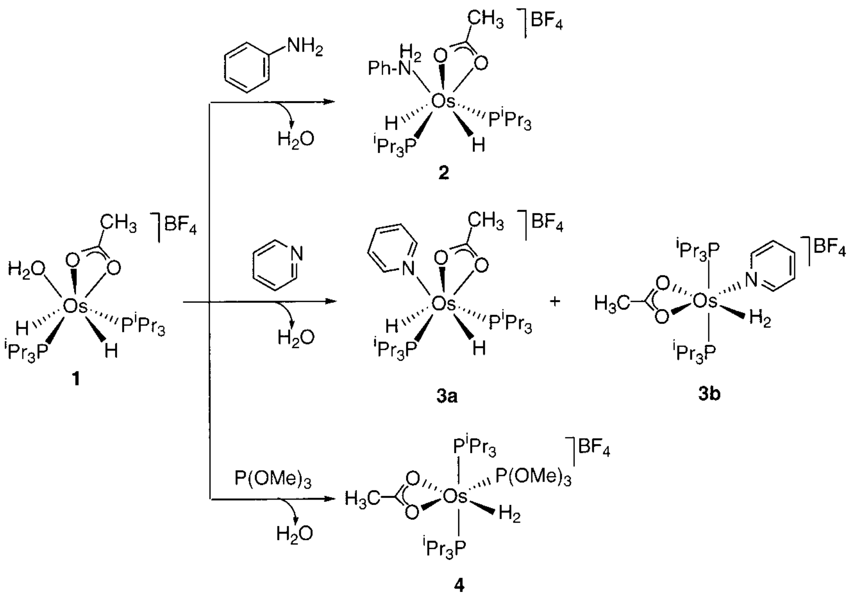
Scheme 1



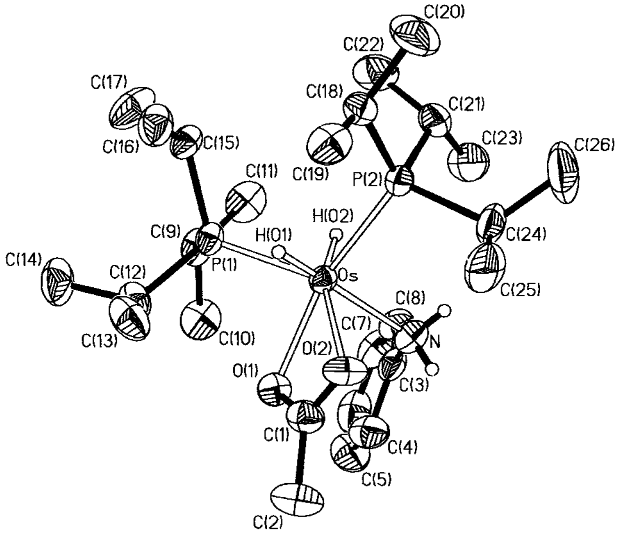


Figure 1. Molecular diagram of the cation of complex **2**. Selected bond distances (Å) and angles (deg): Os−P(1) 2.2824(12), Os−P(2) 2.3081(12), Os−N 2.258(4), Os−O(1) 2.191(3), Os−O(2) 2.187(3); P(1)−Os−P(2) 111.23(4), P(1)−Os−O(1) 84.99(9), P(1)−Os−O(2) 124.54(9), P(1)−Os−N 134.23(12), P(2)−Os−O(1) 161.28(9), P(2)−Os−O(2) 102.82(9), P(2)−Os−N 95.12(13), O(1)−Os−O(2) 59.03(11), O(1)−Os−N 78.65(16), O(2)−Os−N 81.81(16), H(01)−Os−H(02) 119.4(19).

and the two hydride ligands, which occupy alternate positions (P−Os−P = 111.23(4)°). The oxygen atoms of the bidentate acetate (O−Os−O = 59.03(11)°) and the nitrogen atom of the aniline are located in the second plane.

At 183 K, in dichloromethane-d_2, the ^{1}H and ^{31}P{^{1}H} NMR spectra of **2** are consistent with the structure shown in Figure 1. The ^{1}H NMR spectrum contains two hydride resonances at −13.9 and −16.2 ppm, and the ^{31}P{^{1}H} NMR spectrum shows an AB spin system defined by δ_A 44 ppm, δ_B 26 ppm, and $J_{A-B} = 2185$ Hz. At temperatures higher than 183 K, the spectra are temperature dependent, suggesting that **2** has a rigid structure only at very low temperature. At about 233 K, the coalescence of the hydride resonances is observed. At room temperature the hydrides display a triplet centered at −15.15 ppm with an H−P coupling constant of 34.8 Hz. At this temperature the ^{31}P{^{1}H} NMR spectrum shows a singlet at 33.7 ppm.

Pyridine, which is a stronger π-acceptor ligand than aniline, reacts with **1** to give a 7:1 equilibrium mixture of the dihydride $[OsH_2(\kappa^2\text{-}O_2CCH_3)(py)(P^iPr_3)_2]BF_4$ (**3a**) and its elongated dihydrogen tautomer $[Os(\eta^2\text{-}H_2)(\kappa^2\text{-}O_2CCH_3)(py)(P^iPr_3)_2]BF_4$ (**3b**). The ^{1}H and ^{31}P{^{1}H} NMR spectra of **3a** are temperature dependent and consistent with those of **2**. At room temperature in dichloromethane-d_2 the ^{1}H NMR spectrum shows only one hydride resonance, which appears as a triplet at −15.48 ppm with an H−P coupling constant of 36 Hz. Between 213 and 203 K, decoalescence of this resonance is observed. At 173 K, the spectrum contains two broad hydride resonances centered at about −13.7 and −16.6 ppm. At this temperature the ^{31}P{^{1}H} NMR spectrum shows an unresolved AB spin system, while at room temperature a singlet is observed at 34.5 ppm.

In contrast to **3a**, the ^{31}P{^{1}H} NMR spectrum of **3b** is temperature invariant. Between 293 and 173 K, it contains a singlet at 11.7 ppm, indicating the equivalence of the two phosphines and their mutual *trans* disposition. At room temperature the ^{1}H NMR spectrum shows two doublets of virtual triplets at 1.24 and 1.02 ppm for the methyl groups of the triisopropylphosphine ligands. The presence of two signals for these protons, which is a result of the prochirality of the phosphorus atoms, suggests an octahedral disposition of ligands around the osmium atom. In the high-field region, the spectrum contains a broad triplet at −6.56 ppm, with an H−P coupling constant of 9.3 Hz, due to the elongated dihydrogen ligand. A variable-temperature 300 MHz T_1 study of the dihydrogen peak gives a $T_{1(\min)}$ value of 32.6 ± 0.4 ms at 193 K. In agreement with the nonclassical structure, this value corresponds to a hydrogen−hydrogen separation of 1.3 Å,[1b,c] which agrees well with those found in $OsCl_2(\eta^2\text{-}H_2)L(P^iPr_3)_2$ (L = pyrazole, NH=CPh$_2$).[5,6]

Trimethyl phosphite, which is a stronger π-acceptor ligand than pyridine, reacts with **1** to afford selectively

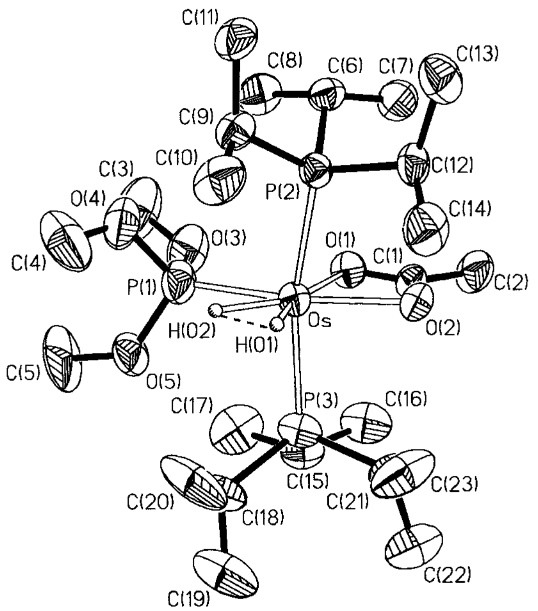


Figure 2. Molecular diagram of the cation of complex **4**. Selected bond distances (Å) and angles (deg): Os−P(1) 2.227(2), Os−P(2) 2.4173(17), Os−P(3) 2.4095(18), Os−O(1) 2.160(4), Os−O(2) 2.165(4), P(1)−Os−P(2) 97.64(7), P(1)−Os−P(3) 96.19(7), P(2)−Os−P(3) 165.15(16), P(1)−Os−O(2) 156.34(13), O(1)−Os−O(2) 59.57(16), H(01)−Os−H(02) 53(3).

the elongated dihydrogen complex $[Os(\eta^2\text{-}H_2)(\kappa^2\text{-}O_2CCH_3)\{P(OMe)_3\}(P^iPr_3)_2]BF_4$ (**4**). The formation of a dihydride tautomer similar to **2** or **3a** was not observed. A view of the molecular geometry of **4** is shown in Figure 2. The geometry around the osmium atom can be rationalized as a distorted octahedron with the two phosphorus atoms of the phosphine ligands occupying opposite positions (P(2)−Os−P(3) = 165.15(16)°). The perpendicular plane is formed by the bidentate acetate group, with a bite angle O(1)−Os−O(2) of 59.57(16)°, and the elongated dihydrogen and the trimethyl phosphite ligands mutually *cis* disposed. The separation between the hydrogen atoms of the elongated dihydrogen is 1.33(7) Å.

The $^{31}P\{^1H\}$ and ^1H NMR spectra of **4** are consistent with the structure shown in Figure 2 and agree well with those of **3b**. Between 293 and 173 K, the $^{31}P\{^1H\}$ NMR spectrum contains a doublet at 20.5 ppm (P^iPr_3) and a triplet at 81.0 ppm ($P(OMe)_3$). The value of the P−P coupling constant is 17 Hz. Similarly to the ^1H NMR spectrum of **3b**, the ^1H NMR spectrum of **4** in dichloromethane-d_2 at room temperature shows two doublets of virtual triplets, at 1.32 and 1.29 ppm, for the methyl groups of the triisopropylphosphine ligands. In the high-field region of the spectrum, the elongated dihydrogen displays a doublet of triplets at −12.11 with $H-P_{P^iPr_3}$ and $H-P_{P(OMe)_3}$ coupling constants of 9.3 Hz. In this case, the variable-temperature 300 MHz T_1 study yields a $T_{1(min)}$ value of 40 ± 1 ms at 183 K, which, in agreement with the X-ray diffraction study, corresponds to a hydrogen−hydrogen separation of 1.3 Å.

In conclusion, the water ligand of $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ can be displaced by neutral Lewis bases to give dihydrides (aniline), dihydride−elongated dihydrogen equilibrium mixtures (pyridine), and elongated dihydrogens (trimethyl phosphite). The dihydrides have a rigid structure only in solution at very low temperatures, which could be described as a square antiprism with a missing vertex. In contrast, the elongated dihydrogens have an octahedral structure, which is rigid in solution. These results clearly indicate that in complexes of formula $[H_2Os(\kappa^2\text{-}O_2CCH_3)L(P^iPr_3)_2]^+$ the π-acceptor power of L determines the coordination polyhedron around the osmium atom and the nature of the $Os-H_2$ interaction.

Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The starting material $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ (**1**) was prepared by a published method.[9] Infrared spectra were recorded on a Perkin-Elmer 883 spectrometer as solids (Nujol mull). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on either a Varian Gemini 2000 or a Bruker AXR 300 instrument. Chemical shifts are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) or external H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants J and N ($N = J_{P-H} + J_{P'-H}$ for ^1H; $N = J_{P-C} + J_{P'-C}$ for $^{13}C\{^1H\}$) are given in hertz. C, H, and N analyses were measured on a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of $[OsH_2(\kappa^2\text{-}O_2CCH_3)(NH_2Ph)(P^iPr_3)_2]BF_4$ (2). A solution of **1** (100 mg, 0.15 mmol) in 10 mL of dichloromethane was treated with aniline (27 μL, 0.30 mmol). After stirring for 75 min at room temperature the solvent was removed to dryness. Addition of diethyl ether caused the precipitation of a pale yellow solid, which was washed with diethyl ether and dried in vacuo. Yield: 100 mg (90%). Anal. Calcd for $C_{26}H_{54}BF_4NO_2OsP_2$: C, 41.55; H, 7.24; N, 1.86. Found: C, 41.07; H, 7.08; N, 1.95. IR (Nujol, cm^{-1}): ν(NH) 3339, 3235, 3157 (s), ν(OsH) 2179 (m), ν(C=C) 1601, ν_{asym}(OCO) 1520 (s), ν_{sym}(OCO) 1350 (s), $\nu(BF_4)$ 1121−1002. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.21 (t, $J_{H-H} = 7.0$, 2H, Ph), 7.08 (t, $J_{H-H} = 7.0$, 1H, Ph), 6.97 (d, $J_{H-H} = 7$, 2H, Ph), 5.92 (br s, 2H, $PhNH_2$), 2.20 (m, 6H, PC*H*), 1.33 (s, 3H, $OCOCH_3$), 1.28 (dd, $J_{H-H} = 7.2$, $J_{P-H} = 14.4$, 36H, $PCH(CH_3)_2$), −15.15 (t, $J_{P-H} = 34.8$, 2H, OsH). ^1H NMR (300 MHz, CD_2Cl_2, 183 K, high-field region): δ −13.9 (t, $J_{P-H} = 35.1$, 1H, OsH), −16.2 (t, $J_{P-H} = 35.1$, 1H, OsH). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 192.8 (s, $OCOCH_3$), 139.0 (br, C_{ipso} Ph), 129.1 (s, C_{meta} Ph), 125.5 (br, C_{para} Ph), 123.2 (br, C_{ortho} Ph), 28.5 (d, $J_{P-C} = 33.5$, PCH), 26.1 (s, $OCOCH_3$), 18.9 (s, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 33.7 (s, triplet under off resonance conditions). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 183 K): AB spin system (δ_A 44 ppm, δ_B 26 ppm, J_{A-B} = 2185).

Reaction of $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ with Pyridine. A solution of **1** (200 mg, 0.30 mmol) in 10 mL of dichloromethane was treated with pyridine (30 μL, 0.37 mmol). After stirring for 45 min at room temperature the solvent was removed to dryness. Addition of diethyl ether afforded a yellow solid, which was washed with diethyl ether and dried in vacuo. Yield: 148 mg (68%). Anal. Calcd for $C_{26}H_{52}BF_4NO_2OsP_2$: C, 40.73; H, 8.06; N, 1.66. Found: C, 40.70; H, 7.10; N, 1.90. IR (Nujol, cm^{-1}): ν(OsH) 2176 (m), ν(C=C, py) 1604 (s), ν_{asym}(OCO) 1512 (s), ν_{sym} (OCO) 1370 (s), $\nu(BF_4)$ 1000−1100. The ^1H and $^{31}P\{^1H\}$ NMR spectra show the presence of $[OsH_2(\kappa^2\text{-}O_2CCH_3)(py)(P^iPr_3)_2]BF_4$ (**3a**) together with variable amounts (10−20%) of its dihydrogen tautomer $[Os(\eta^2\text{-}H_2)(\kappa^2\text{-}O_2CCH_3)(py)(P^iPr_3)_2]BF_4$ (**3b**). **3b** could be isolated pure by crystallization of the mixture from dichloromethane/diethyl ether at −30 °C.

Spectroscopic Data of 3a. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.75 (d, $J_{H-H} = 7.0$, 2H, H_{ortho} py), 8.63 (t, $J_{H-H} = 7.0$, 1H, H_{para} py), 7.62 (t, $J_{H-H} = 7.0$, 2H, H_{meta} py), 2.16 (m, 6H, PC*H*), 1.66 (s, 3H, $OCOCH_3$), 1.29 (dd, $J_{H-H} = 7.0$, $J_{P-H} =$

14.3, 36 H, PCH(CH_3)$_2$), −15.48 (t, J_{P-H} = 36, 2H, OsH). ^{1}H NMR (300 MHz, CD_2Cl_2, 173K, high-field region): δ −13.7 (br, 1H, OsH), −16.6 (br, 1H, OsH). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 253 K): δ 192.9 (s, O*C*OCH$_3$), 151.5 (s, py), 140.1 (s, py), 126.7 (s, py), 28.1 (d, J_{P-C} = 33, P*C*H), 26.7 (s, OCO*C*H$_3$), 18.7 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 34.5 (s). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 173 K): an unresolved AB spin system centered at 35.5 ppm.

Spectroscopic Data of 3b. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 9.14 (d, J_{H-H} = 5.1, 1H, H_{ortho} py), 8.73 (d, J_{H-H} = 4.8, 1H, H_{ortho} py), 7.77 (t, J_{H-H} = 7.6, 1H, H_{para} py), 7.50 (m, 1H, H_{meta} py), 7.42 (m, 1H, H_{meta} py), 2.09 (m, 6H, PC*H*), 2.03 (s, 3H, OCOCH$_3$), 1.24 (dvt, J_{H-H} = 6.9, *N* = 13.2, 18 H, PCHC*H*$_3$), 1.02 (dvt, J_{H-H} = 7.2, *N* = 13.5, 18H, PCHC*H*$_3$), −6.56 (t, J_{H-H} = 9.3, 2H, Os(η^2-H$_2$)). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 253 K): δ 185.8 (s, O*C*OCH$_3$), 161.6 (s, py), 147.3 (s, py), 137.4 (s, py), 129.2 (s, py), 125.0 (s, py), 24.3 (vt, *N* = 24.8, P*C*H), 24.2 (s, OCO*C*H$_3$), 19.1, 18.6 (both s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 11.7 (s). T_1 (ms, Os(η^2-H$_2$), 300 MHz, CD_2Cl_2): 71.7 ± 0.7 (253 K), 51.2 ± 0.6 (233 K), 38.3 ± 0.3 (213 K), 34.4 ± 0.3 (203 K), 32.6 ± 0.4 (193 K), 37.4 ± 0.6 (183 K), 50.1 ± 0.9 (173 K).

Preparation of [Os(η^2-H$_2$)(κ^2-O$_2$CCH$_3$){P(OMe)$_3$}(P^{i}Pr$_3$)$_2$]BF$_4$ (4). A solution of **1** (100 mg, 0.15 mmol) in 10 mL of dichloromethane was treated with trimethyl phosphite (9.36 μL, 0.16 mmol). After stirring for 45 min at room temperature the solvent was removed to dryness. Addition of diethyl ether caused the precipitation of a gray solid, which was washed with diethyl ether and dried in vacuo. Yield: 65 mg (56%). Anal. Calcd for $C_{23}H_{56}BF_4O_5OsP_3$: C, 35.30; H, 7.21. Found: C, 35.60; H, 7.21. IR (Nujol, cm^{-1}): ν(OsH) 2170, 2148 (m), ν_{asym}(OCO) 1550 (s), ν_{sym}(OCO) 1377 (s), ν(BF$_4$) 1092−1057. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 3.80 (d, J_{P-H} = 11.4, 9H, P(OMe)$_3$), 2.48 (m, 6H, PC*H*), 1.84 (s, 3H, OCOCH$_3$), 1.32 (dvt, J_{H-H} = 6.9, *N* = 13.5, 18H, PCH(C*H*$_3$)$_2$), 1.29 (dvt, J_{H-H} = 6.9, *N* = 13.5, 18H, PCH(C*H*$_3$)$_2$), −12.11 (dt, J_{P-H} = J_{P-H} = 9.3, 2H, Os(η^2-H$_2$)). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 189.2 (s, O*C*OCH$_3$), 54.8 (d, J_{P-C} = 9.66, P(OMe)$_3$), 26.3 (s, OCO*C*H$_3$), 25.2 (vt, *N* = 25.4, P*C*H), 19.5 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 81.0 (t, J_{P-P} = 17, *P*(OMe)$_3$), 20.5 (d, J_{P-P} = 17, P^{i}Pr$_3$). T_1 (ms, Os(η^2-H$_2$), 300 MHz, CD_2Cl_2): 98 ± 2 (243 K), 79 ± 1 (233 K), 64 ± 1 (223 K), 53 ± 1 (213 K), 45 ± 1 (203 K), 41 ± 1 (193 K), 40 ± 1 (183 K), 43 ± 1 (178 K).

X-ray Structure Determination of 2 and 4. Crystal data for **2**: $C_{26}H_{54}BF_4NO_2OsP_2$ (MW = 751.65); triclinic space group, $P\bar{1}$, *a* = 10.5133(10) Å, *b* = 11.3440(10) Å, *c* = 15.0795(14) Å, α = 94.795(2)°, β = 99.201(2)°, γ = 114.106(1)° at 173.0(2) K, *V* = 1598.2(3) Å^3; *Z* = 2. Crystal data for **4**: $C_{23}H_{56}BF_4O_5OsP_3$ (MW = 782.60); monoclinic space group, $P2_1/n$, *a* = 13.3503(13) Å, *b* = 21.666(3) Å, *c* = 13.7786(16) Å, β = 102.541(2)° at 173.0(2) K. Refinement of **2** and **4**: a needle crystal of **2** (0.20 × 0.03 × 0.02 mm) and an irregular block crystal of **4** (0.16 × 0.08 × 0.08 mm) were mounted on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kV sealed tube X-ray source (molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. Data were collected over the entire sphere by a combination of four sets for **2** and **4**. The cell parameters were refined by least-squares fit of 5373 collected reflections for **2** and 4043 for **4**. Each frame exposure time was 30 s covering 0.3° in ω ($3° \leq 2\theta \leq 60°$, 19 665 reflections, 7533 unique, merging *R* factor 0.0599 (**2**) and 30 560 reflections, 7959 unique, merging *R* factor 0.0824 (**4**)). The first 100 frames were re-collected at the end of the data collection to monitor crystal decay. The absorption correction was made using SADABS.[10] The structure was solved by Patterson and Fourier methods using SHELXS.[10] Full-matrix least-squares refinement was carried out using SHELXL97 minimizing $w(F_o^2 - F_c^2)^2$. Weighted *R* factors (*wR*) and goodness of fit (*S*) are based on F^2; conventional *R* factors are based on *F*. Final $R_1[F^2 > 2\sigma(F^2)]$ = 0.0359 (**2**) and 0.0445 (**4**), and wR_2 [all data] = 0.0796 (**2**) and 0.0860 (**4**).

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Supporting Information Available: Tables of positional and displacement parameters, 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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[10] *SAINTPLUS* and *SHELXTL* v.6.1 software packages; Bruker Analytical X-ray Systems: Madison, WI, 2000.