A Novel Method To Prepare Hydride−Phosphinito Complexes

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Summary: *The cyclopentadienyl complex Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ (**1**) reacts with diphenylphosphine to give the mixed-ligand compound Os(η^5-C_5H_5)Cl($PHPh_2$)(P^iPr_3) (**2**). Treatment of **2** with $TlPF_6$ in humid acetone and in methanol affords the cationic dihydride complexes [OsH_2(η^5-C_5H_5){P(OR)Ph_2}(P^iPr_3)]PF_6 (R = H (**3**), CH_3 (**4**)), respectively. Similarly, the treatment of **2** with $TlPF_6$ in $(CD_3)_2CO$ containing D_2O and in CD_3OD gives the deuterated complexes [OsHD(η^5-C_5H_5){P(OR)Ph_2}(P^i-Pr_3)]PF_6 (R = D (**3-d_2**), CD_3 (**4-d_4**)). The reaction of **3** with $NaOCH_3$ produces its deprotonation and the formation of the dihydride−phosphinito derivative OsH_2(η^5-C_5H_5){P(O)Ph_2}(P^iPr_3) (**5**). Under the same conditions, the deprotonation of **4** yields OsH(η^5-C_5H_5)-{P(OMe)Ph_2}(P^iPr_3) (**6**) as a result of the extraction of one of the two hydrides. The treatment of **3-d_2** with NaOMe selectively affords OsHD(η^5-C_5H_5){P(O)Ph_2}(P^i-Pr_3) (**5-*d***).*

The oxidative addition of the P−H bond of diphenylphosphine oxide to platinum(0) and palladium(0) complexes has been previously the method used to prepare hydride−phosphinito derivatives. Although the formation of these compounds is one of the key steps in the stereoselective hydrophosphinylation of alkynes, affording alkenylphosphine oxides,[1] only a few hydride−phosphinito transition-metal compounds have been reported. As far as we know, they are monohydride−platinum(II) and −palladium(II) derivatives, where the phosphinito ligand is stabilized by an electrostatic interaction between the oxygen atom and a Lewis acid.[2] In general, this acid is the hydrogen atom of a diphenylphosphine oxide cis-disposed to the phosphinito group.[2b−d]

We now report a novel method to prepare hydride−phosphinito complexes. The new strategy leds to OsH_2(η^5-C_5H_5){P(O)Ph_2}(P^iPr_3), which is the first hydride−phosphinito compound stabilized by a transition metal different from platinum and palladium, and where the phosphinito ligand is not stabilized by an oxygen−Lewis acid interaction.

Despite the high kinetic stability of the $OsCpL_3$ compounds,[3] we have described overwhelming evidence showing that the complex Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ (**1**) is a labile starting material for the development of new cyclopentadienyl−osmium chemistry.[4] The addition of PPh_3 to pentane solutions of **1** produces the displacement of a triisopropylphosphine group to give Os(η^5-C_5H_5)Cl(PPh_3)(P^iPr_3), which is a suitable compound for studying the selectivity of the competitive alkane−arene intramolecular C−H activation.[5] Although the treatment of **1** with $TlPF_6$ produces the release of the chloro and the methyl C−H activation of a triisopropylphosphine, the treatment of Os(η^5-C_5H_5)Cl(PPh_3)(P^iPr_3) with $TlPF_6$ gives rise to the release of the chloro ligand and the ortho C−H activation of triphenylphosphine.

Similarly to the reaction of **1** with PPh_3, the addition of $PHPh_2$ to pentane solutions of **1** affords Os(η^5-C_5H_5)Cl($PHPh_2$)(P^iPr_3) (**2**). Treatment of **2** with $TlPF_6$ in humid acetone also produces the release of the chlorine ligand; however, the C−H activation of a C_{ortho}−H bond of a phenyl group is not observed. Instead of a C−H activation reaction, the formation of [OsH_2-(η^5-C_5H_5){P(OH)Ph_2}(P^iPr_3)]PF_6 (**3**) takes place. The generality of this reaction is evident in the synthesis of [OsH_2(η^5-C_5H_5){P(OMe)Ph_2}(P^iPr_3)]PF_6 (**4**), which is prepared by treatment of **2** with $TlPF_6$ in methanol (Scheme 1).

The presence of a P(OH)Ph_2 ligand in **3** is strongly supported by the IR and ^{1}H NMR spectra of this compound. The IR spectrum in Nujol shows a ν(OH) band at 3467 cm^{-1}, whereas the ^{1}H NMR spectrum in CD_2Cl_2 at 193 K contains a broad signal at 4.92 ppm, corresponding to the OH proton. Furthermore, in the high-field region, the spectrum shows a double doublet at −12.97 ppm both having J(HP) values of 28.8 Hz, which agree well with a four-legged piano-stool geometry around the metallic center, with mutually transoid hydrides that are cisoid-disposed to the phosphorus donor ligands.[6] The ^{1}H and ^{31}P{^{1}H} NMR spectra of **4** are also in accordance with the structure proposed for this compound in Scheme 1.

When the treatment of **1** with $TlPF_6$ was carried out in $(CD_3)_2CO$ containing D_2O and in CD_3OD, the deu-

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(4) (a) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oro, L. A. *Organometallics* **1996**, *15*, 878. (b) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657. (c) Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E. *Organometallics* **1998**, *17*, 3141. (d) Crochet, P.; Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1998**, 17, 3479. (e) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Ruiz, N. *Organometallics* **1999**, *18*, 5034.

(5) Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Oñate, E..; Tolosa, J. I. *Organometallics* **2000**, *19*, 275.

(6) The mentioned J(HP) values are typical for this arrangement. See for example refs 4e and 5 and: (a) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267. (b) Wanandi, P. W.; Tilley, T. D. *Organometallics* **1997**, *16*, 4299.

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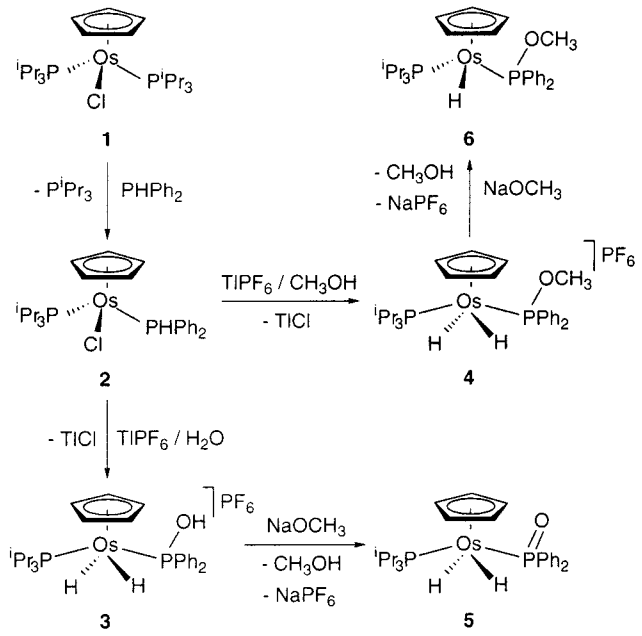
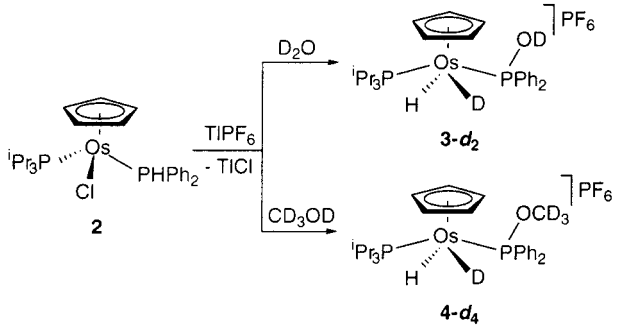
Scheme 1



Scheme 2



terated complexes $[OsHD(\eta^5\text{-}C_5H_5)\{P(OD)Ph_2\}(P^iPr_3)]PF_6$ (**3-*d*$_2$**) and $[OsHD(\eta^5\text{-}C_5H_5)\{P(OCD_3)Ph_2\}(P^iPr_3)]PF_6$ (**4-*d*$_4$**) were obtained, respectively (Scheme 2). The presence of a deuterium atom at the oxygen of **3-*d*$_2$** is supported by the IR spectrum of this compound in Nujol, which shows a ν(OD) band at 2535 cm^{-1}, whereas the presence of a deuterium atom at the metallic center of both **3-*d*$_2$** and **4-*d*$_4$** is supported by the ^2H NMR spectra, which contain a double doublet at −12.78 (**3-*d*$_2$**) and −12.60 (**4-*d*$_4$**) ppm, with J(DP) values of 4.3 (**3-*d*$_2$**) and 4.7 (**4-*d*$_4$**) Hz.

The distribution of deuterium atoms in **3-*d*$_2$** and **4-*d*$_4$** indicates the following.

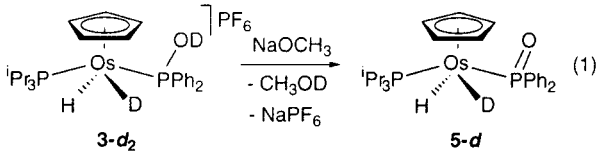
(i) The formation of **3** and **4** takes place via the hydride−phosphido intermediate $[OsH(\eta^5\text{-}C_5H_5)(PPh_2)(P^iPr_3)]^+$. This species is generated by intramolecular P−H oxidative addition of diphenylphosphine in the unsaturated $[Os(\eta^5\text{-}C_5H_5)(PHPh_2)(P^iPr_3)]^+$ metallic fragment.[7] Once the hydride−phosphido species is formed, the RO−H addition to the Os−phosphido bond affords **3** and **4**.[8]

(ii) The P−H oxidative addition in $[Os(\eta^5\text{-}C_5H_5)(PHPh_2)(P^iPr_3)]^+$ is favored with regard to the methyl C−H activation of triisopropylphosphine and the ortho C−H activation of diphenylphosphine. This suggests that, under strictly the same metal ligand system, the M−P−H oxidative addition is favored with regard to the alkyl metalation and aryl ortho metalation.

Treatment of **3** with NaOMe in THF produces its deprotonation and the formation of the dihydride−phosphinito−osmium(IV) derivative $OsH_2(\eta^5\text{-}C_5H_5)\{P(O)Ph_2\}(P^iPr_3)$ (**5**). Under the same conditions, the deprotonation of **4** yields $OsH(\eta^5\text{-}C_5H_5)\{P(OMe)Ph_2\}(P^iPr_3)$ (**6**) as a result of the extraction of one of the two hydrides (Scheme 1).

The most noticeable feature in the IR spectrum of **5** in KBr are the absence of any ν(OH) band and the presence of two absorptions at 1105 and 1047 cm^{-1} due to the P=O bond.[9] In the ^1H NMR spectrum, the hydride ligands give rise to a double doublet with J(HP) values of 26.1 and 29.7 Hz, which are in agreement with the structure proposed for **5** in Scheme 1.

The deprotonation of **4** to give **6** could suggest that the formation of **5** proceeds by extraction of a hydride of **3** and subsequent 1,3-hydrogen migration from the oxygen atom of the OH group to the osmium. However, the treatment of **3-*d*$_2$** with NaOMe selectively affords $OsHD(\eta^5\text{-}C_5H_5)\{P(O)Ph_2\}(P^iPr_3)$ (**5-*d***), indicating that the deprotonation of **3** is a one-step process and occurs at the OH group of the $P(OH)Ph_2$ ligand (eq 1).



The presence of a deuteride ligand in **5-*d*** is supported by the ^2H NMR spectrum of this compound, which contains a broad singlet at −13.07 ppm.

In conclusion, the oxidative addition of the P−H bond of secondary phosphines to unsaturated complexes followed by the addition of water and deprotonation of the resulting $P(OH)Ph_2$ ligand is a useful method to prepare hydride−phosphinito complexes.

Experimental Section

All reactions were carried out with exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The starting material $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) was prepared by the published method.[4b]

In the NMR spectra, chemical shifts are expressed in ppm downfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P).

Preparation of Os(η^5-C_5H_5)Cl($PHPh_2$)(P^iPr_3) (2). A suspension of **1** (200 mg, 0.33 mmol) in 15 mL of pentane was treated with $PHPh_2$ (56.4 μL, 0.33 mmol). After the mixture

(7) The oxidative addition of the P−H bond of secondary phosphines to unsaturated transition-metal complexes is a well-known process of interest in connection with the catalytic phosphination and hydrophosphination of olefins. See for example: (a) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039. (b) Kourkine, I. V.; Sargent, M. D.; Glueck, D. S. *Organometallics* **1998**, *17*, 125. (c) Wicht, D. K.; Paisner, S. N.; Lew, B. M.; Glueck, D. S.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A.. L.; Haar, C. M.; Nolan, S. P. *Organometallics* **1998**, *17*, 652. (d) Wicht, D. K.; Kovacik, I.; Glueck, D. S.; Liable-Sands, L. M.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5141. (e) Wicht, D. K.; Kourkine, I. V.; Kovacik, I.; Glueck, D. S.; Concolino, T. E.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L.*Organometallics* **1999**, *18*, 5381.

(8) Similar additions of methanol and water across a W=P bond have been reported. See for example: (a) Jörg, K.; Malisch, W.; Reich, W.; Meyer, A.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 92. (b) Malisch, W.; Hirth, U.-A.; Grün, K.; Schmeusser, M.; Fey, O.; Weis, U. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2500.

(9) Malisch, W.; Hindahl, K.; Grün, K.; Adam, W.; Prechtl, F.; Sheldrick, W. S. *J. Organomet. Chem.* **1996**, *509*, 209.

was stirred for 5 h at room temperature, the solvent was partially evaporated until a yellow solid precipitated, which was washed with 3 mL of cold pentane and dried in vacuo. Yield: 180 mg (86%). IR (Nujol): ν(PH) 2292 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.81 (d, J(PH) = 352.2 Hz, 1 H, PH), 7.76 (m, 2 H, Ph), 7.32 (m, 2 H, Ph), 7.09−6.94 (m, 6 H, Ph), 4.58 (s, 5 H, Cp), 2.39 (m, 3 H, PCH), 1.17 (dd, J(HH) = 7.1 Hz, J(PH) = 13.4 Hz, 9 H, $PCCH_3$), 0.83 (dd, J(HH) = 7.1 Hz, J(PH) = 13.4 Hz, 9 H, $PCCH_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 12.1 (d, J(PP) = 22.6 Hz, P^iPr_3), −5.8 (d, J(PP) = 22.6 Hz, $PHPh_2$). Anal. Calcd for $C_{26}H_{37}ClOsP_2$: C, 49.01; H, 5.85. Found: C, 48.86; H, 5.76. MS (FAB$^+$): m/e 638 (M^+).

Preparation of [OsH$_2$(η^5-C$_5$H$_5$){P(OH)Ph$_2$}(P^{i}Pr$_3$)]PF$_6$ (3). A solution of **2** (140 mg, 0.22 mmol) in 15 mL of acetone was treated with $TlPF_6$ (76.7 mg, 0.22 mmol). After the mixture was stirred for 15 min at room temperature, the suspension obtained was filtered through Kieselguhr and the solvent was removed in vacuo. The addition of diethyl ether caused the precipitation of a white solid, which was washed whith diethyl ether and dried in vacuo. Yield: 160 mg (95%). IR (Nujol): ν(OH) 3467, ν(PF_6) 840 cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.62−7.55 (m, 6 H, Ph), 7.47−7.40 (m, 4 H, Ph), 5.22 (s, 5 H, Cp), 1.85 (m, 3 H, PCH), 1.08 (dd, J(HH) = 6.9 Hz, J(PH) = 14.7 Hz, 18 H, $PCCH_3$), −12.97 (dd, J(PH) = 28.8 Hz, J(PH) = 28.8 Hz, 2H, OsH_2). ^{1}H NMR (300 MHz, CD_2Cl_2, 193 K): δ 4.92 (br, P(OH)). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 83.2 (d, J(PP) = 20.4 Hz, $P(OH)Ph_2$), 40.6 (d, J(PP) = 20.4 Hz, P^iPr_3). Anal. Calcd for $C_{26}H_{39}OOsP_3F_6$: C, 40.83; H, 5.14. Found: C, 41.14; H, 5.32. MS (FAB$^+$): m/e 619 (M^+).

Preparation of [OsHD(η^5-C$_5$H$_5$){P(OD)Ph$_2$}(P^{i}Pr$_3$)]PF$_6$ (3-*d*$_2$). The compound **3-*d*$_2$** was prepared analogously as described for **3**, starting from **2** and a mixture of 15 mL of acetone-d_6 and 0.1 mL of D_2O as solvent. IR (Nujol): ν(OD) 2535, ν(PF_6) 840 cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.62−7.55 (m, 6 H, Ph), 7.47−7.40 (m, 4 H, Ph), 5.22 (s, 5 H, Cp), 1.85 (m, 3 H, PCH), 1.08 (dd, J(HH) = 6.9 Hz, J(PH) = 14.7 Hz, 18 H, $PCCH_3$), −12.97 (dd, J(PH) = 28.8 Hz, J(PH) = 28.8 Hz, 1 H, OsH). ^{2}H NMR (46.07 MHz, CH_2Cl_2, 293 K): −12.78 (dd, J(PD) = 4.3 Hz, J(PD) = 4.3 Hz, OsD).

Preparation of [OsH$_2$(η^5-C$_5$H$_5$){P(OMe)Ph$_2$}(P^{i}Pr$_3$)]PF$_6$ (4). A solution of **2** (140 mg, 0.22 mmol) in 15 mL of methanol was treated with $TlPF_6$ (76.7 mg, 0.22 mmol). After the mixture was stirred for 15 min at room temperature, the suspension obtained was filtered through Kieselguhr and the solvent was removed in vacuo. The addition of diethyl ether caused the precipitation of a white solid, which was washed with diethyl ether and dried in vacuo. Yield: 161.1 mg (94%). IR (Nujol): ν(OsH) 2154, ν(PF_6) 840 cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.62−7.54 (m, 10 H, Ph), 5.20 (s, 5 H, Cp), 3.38 (d, J(PH) = 12.3 Hz, 3 H, OCH_3), 2.08 (m, 3 H, PCH), 1.17 (dd, J(HH) = 7.2 Hz, J(PH) = 15.0 Hz, 18 H, $PCCH_3$), −12.75 (dd, J(PH) = 27.9 Hz, J(PH) = 28.8 Hz, 2 H, OsH_2). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 100.6 (d, J(PP) = 18.2 Hz, $P(OMe)Ph_2$), 41.1 (d, J(PP) = 18.2 Hz, P^iPr_3). Anal. Calcd for $C_{27}H_{41}OOsP_3F_6$: C, 41.64; H, 5.31. Found: C, 42.11; H, 5.39. MS (FAB$^+$): m/e 635 (M^+).

Preparation of [OsHD(η^5-C$_5$H$_5$){P(OCD$_3$)Ph$_2$}(P^{i}Pr$_3$)]PF$_6$ (4-*d*$_4$). The compound **4-*d*$_4$** was prepared analogously as described for **4**, starting from **2** and methanol-d_4 as solvent. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.62−7.54 (m, 10 H, Ph), 5.20 (s, 5 H, Cp), 2.08 (m, 3 H, PCH), 1.17 (dd, J(HH) = 7.2 Hz, J(PH) = 15.0 Hz, 18 H, $PCCH_3$), −12.75 (dd, J(PH) = 27.9 Hz, J(PH) = 28.8 Hz, 1 H, OsH). ^{2}H NMR (46.07 MHz, CH_2Cl_2, 293 K): 3.31 (d, J(PD) = 1.9 Hz, 3 H, OCD_3), −12.60 (dd, J(PD) = 4.7, J(PD) = 4.7, Hz, OsD).

Preparation of OsH$_2$(η^5-C$_5$H$_5$){P(O)Ph$_2$}(P^{i}Pr$_3$) (5). A solution of **3** (100 mg, 0.13 mmol) in 10 mL of THF was treated with NaOMe (10.6 mg, 0.20 mmol). The mixture was stirred for 5 h at room temperature. The yellow solution obtained was concenterated to dryness, and 10 mL of toluene was added. The suspension was filtered through Kieselguhr, and the solvent was removed in vacuo. Addition of pentane caused the precipitation of a yellow solid, which was washed with pentane and dried in vacuo. Yield: 85.6 mg (94%). IR (KBr): ν(OsH) 2129, ν(PO) 1105, 1047 cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.57 (m, 4 H, Ph), 7.26−7.18 (m, 6 H, Ph), 4.94 (s, 5 H, Cp), 2.00 (m, 3 H, PCH), 1.06 (dd, J(HH) = 7.2 Hz, J(PH) = 14.4 Hz, 18 H, $PCCH_3$), −13.31 (dd, J(PH) = 26.1 Hz, J(PH) = 29.7 Hz, 2 H, OsH_2). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 38.9 (d, J(PP) = 20.4 Hz, $P(O)Ph_2$), 34.8 (d, J(PP) = 20.4 Hz, P^iPr_3). Anal. Calcd for $C_{26}H_{38}OOsP_2$: C, 50.47; H, 6.19. Found: C, 50.39; H, 6.00. MS (FAB$^+$): m/e 619 (M^+ + H).

Preparation of OsHD(η^5-C$_5$H$_5$){P(O)Ph$_2$}(P^{i}Pr$_3$) (5-*d*). The compound **5-*d*** was prepared analogously as described for **5**, starting from **3-*d*$_2$**. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.57 (m, 4 H, Ph), 7.26−7.18 (m, 6 H, Ph), 4.94 (s, 5 H, Cp), 2.00 (m, 3 H, PCH), 1.06 (dd, J(HH) = 7.2 Hz, J(PH) = 14.4 Hz, 18 H, $PCCH_3$), −13.31 (dd, J(PH) = 26.1 Hz, J(PH) = 29.7 Hz, 1 H, OsH). ^{2}H NMR (46.07 MHz, CH_2Cl_2, 293 K): −13.07 (br, OsD).

Preparation of OsH(η^5-C$_5$H$_5$){P(OMe)Ph$_2$}(P^{i}Pr$_3$) (6). A solution of **4** (100 mg, 0.13 mmol) in 10 mL of THF was treated with NaOMe (10.6 mg, 0.20 mmol). The mixture was stirred for 5 h at room temperature. The yellow solution obtained was concenterated to dryness, and 10 mL of toluene was added. The suspension was filtered through Kieselguhr, and the solvent was removed in vacuo. Addition of methanol caused the precipitation of a yellow solid, which was washed with methanol and dried in vacuo. Yield: 58 mg (72%). IR (Nujol): ν(OsH) 2083 cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.73−7.65 (m, 4 H, Ph), 7.28−7.09 (m, 6 H, Ph), 4.61 (s, 5 H, Cp), 3.60 (d, J(PH) = 12.9 Hz, 3 H, OCH_3), 1.57 (m, 3 H, PCH), 0.97 (dd, J(HH) = 5.4 Hz, J(PH) = 11.6 Hz, 9 H, $PCCH_3$), 0.95 (dd, J(HH) = 6.6 Hz, J(PH) = 12.3 Hz, 9 H, $PCCH_3$), −15.96 (dd, J(PH) = 27.8 Hz, J(PH) = 27.8 Hz, 1 H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 106.3 (d, J(PP) = 16.8 Hz, $P(OMe)Ph_2$), 38.6 (d, J(PP) = 16.8 Hz, P^iPr_3). Anal. Calcd for $C_{27}H_{40}OOsP_2$: C, 51.25; H, 6.37. Found: C, 51.23; H, 6.28. MS (FAB$^+$): m/e 635 (M^++ H).

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