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Influence of the Solvent in the Synthesis of Osmium Complexes Containing Cyclopentadienyl Ligands with a Pendant Donor Group

Miguel A. Esteruelas,* Ana M. López, Enrique Oñate, and Eva Royo

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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*Summary: The course of the reactions between complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) and the functionalized cyclopentadienyllithium derivatives $Li[C_5H_4(CH_2)_2E]$ ($E = NMe_2$ (**2**), OMe (**3**)) strongly depends on the solvent used. Thus, in the presence of donor solvents such as THF, the salts $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2E\}(P^iPr_3)_2][OsHCl_2(CO)(P^iPr_3)_2]$ ($E = NMe_2$ [**4**][**5**], OMe [**6**][**5**]) with a carbonylated osmium anion are produced, while in hydrocarbon solvents the chloride salts $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2E\}(P^iPr_3)_2]Cl$ ($E = NMe_2$ [**4**]**Cl**, OMe [**6**]**Cl**) are formed.*

The cyclopentadienyl group is one of the most important ligands in organometallic chemistry. In 1991, Janiak and Schumann estimated that at that time more than 80% of all known organometallic complexes of transition metals contained the cyclopentadienyl fragment or a derivative thereof.[1]

Complexes containing cyclopentadienyl ligands with a pendant donor group are attracting increased interest in recent years.[2] As a consequence of the reversible coordination of the pendant group, these ligands stabilize highly reactive fragments, facilitating the study of some reaction mechanisms.[3]

For the iron triad, the chemistry of the osmium-cyclopentadienyl complexes is a field much less studied than the chemistry of related iron and ruthenium compounds.[4] In accordance with this, a significant number of iron and ruthenium complexes containing a cyclopentadienyl ligand with a pendant donor group have been prepared,[2c] while the osmium counterparts were unknown until very recently.

In a previous work,[5] we have shown the preparation and full characterization of the first osmium(IV) and osmium(II) derivatives with the 2-diphenylphosphinoethylcyclopentadienyl ligand, which are also the first osmium complexes containing a cyclopentadienyl ligand with a pendant donor group. We now wish to report that the reaction used at that time is also useful to obtain compounds with the 2-dimethylaminoethylcyclopentadienyl and 2-methoxiethylcyclopentadienyl ligands. Furthermore, we show that although these reactions are a method of general use to obtain osmium complexes containing a cyclopentadienyl ligand with a pendant donor group, the choice of the solvent is critical for the course of the reaction.

The typical procedure to introduce a cyclopentadienyl group into a transition metal involves the reaction between a cyclopentadienyl derivative of an s- or p-block element and a transition metal halide. The method has proved to be efficient in the osmium chemistry. Thus, the six-coordinate dihydride-dichloro complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) reacts with $Tl(C_5H_5)$ to give the cyclopentadienyl derivative $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$,[6] and the reaction of **1** with $Li[C_5H_4(CH_2)_2PPh_2]$ affords the 2-diphenylphosphinoethylcyclopentadienyl compound $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(P^iPr_3)]Cl$.[5] This prompted us to investigate the reactions of **1** with the lithium compounds $Li[C_5H_4(CH_2)_2E]$ ($E = NMe_2$ (**2**), OMe (**3**)), which are prepared by treatment of the corresponding modified cyclopentadienes with *n*-butyllithium in THF. They have the advantage of their high solubility in THF over the potassium counterparts.[7]

Interestingly, the treatment at about 25 °C of the dihydride dichloro complex **1** with the cyclopentadienyl derivatives **2** and **3** in THF leads to the salts $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(P^iPr_3)_2][OsHCl_2(CO)(P^iPr_3)_2]$ ([**4**][**5**]) and $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2OMe\}(P^iPr_3)_2][OsHCl_2(CO)(P^iPr_3)_2]$ ([**6**][**5**]), respectively, which were isolated as white solids in 60–65% yield. It should be noted that the anion present in both salts is the same and that this anion contains a carbonyl group (Scheme 1).

The formation of **5** and the presence of the carbonyl group in this complex were confirmed by an X-ray diffraction analysis on a monocrystal of [**4**][**5**]. Figure 1 shows the structure of both the cation and the anion of the salt. The distribution of ligands around the osmium atom of the cation **4** can be described as a four-legged piano stool geometry, with the cyclopentadienyl ring occupying the three-membered face while the phosphine ligands lie in the four-membered face mutually *transoid*

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* To whom correspondence should be addressed. E-mail: maester@posta.unizar.es.

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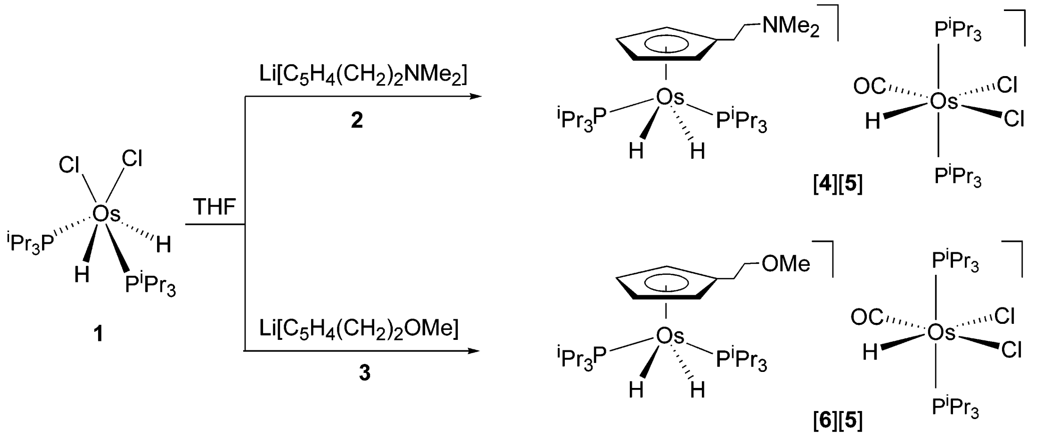
Scheme 1



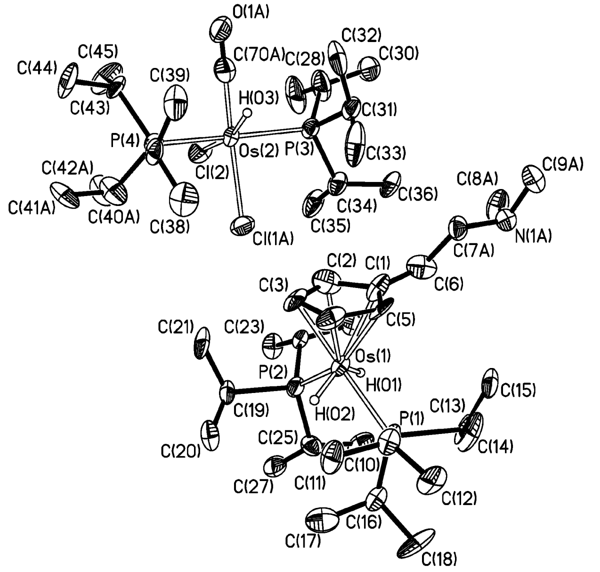
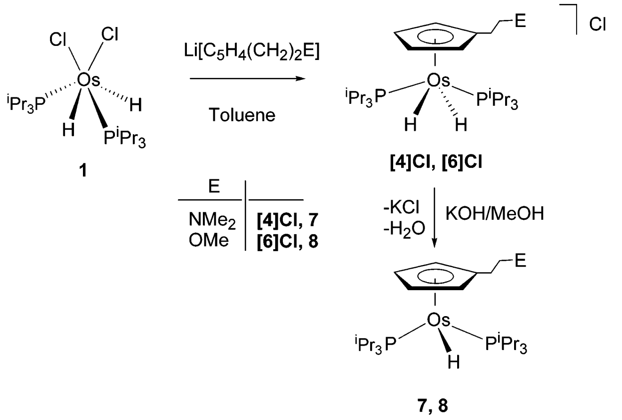
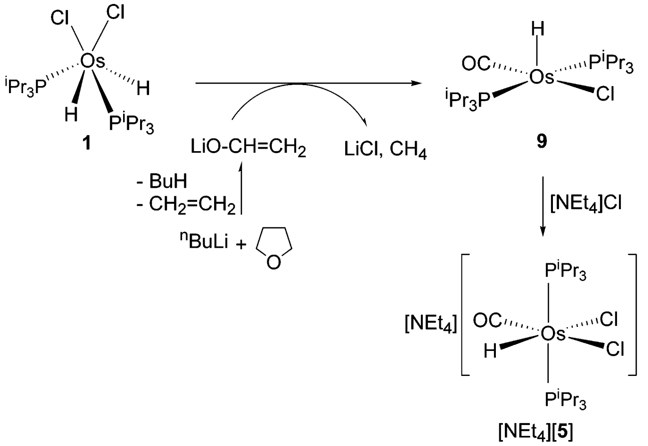


Figure 1. Molecular diagram of complex $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(P^iPr_3)_2][OsHCl_2(CO)(P^iPr_3)_2]$ ([**4**][**5**]). Thermal ellipsoids are shown at 50% probability.

Scheme 2



Scheme 3



disposed (P(1)−Os(1)−P(2) = 111.90(9)°). The geometry around the osmium atom of the anion **5** can be rationalized as a distorted octahedron with the phosphine groups mutually *trans* disposed (P(3)−Os(2)−P(4) = 170.35(9)°) and chloride ligands mutually *cis* disposed (Cl(1A)−Os(2)−Cl(2) = 87.59(12)°).

The cationic complexes **4** and **6** are the result of the replacement of the chloride ligands in **1** by the modified cyclopentadienyl groups. Since THF contains an oxygen atom and is the only reagent that is present in both reactions shown in Scheme 1, it seems reasonable to think that THF is the source of the carbonyl group of **5**. In agreement with this, we have observed that when the preparations of **2** and **3** are carried out in pentane, and the reactions shown in Scheme 1 are performed in toluene, the corresponding salts [**4**]**Cl** and [**6**]**Cl** are obtained in 82−85% yield (Scheme 2).

The chloride salts of **4** and **6** were isolated as white solids. In the ^1H NMR spectrum of both compounds, the most noticeable resonance is a triplet at −14.2 ppm with a H−P coupling constant of 29.1 Hz. The $^{31}P\{^1H\}$ NMR spectra show singlets at about 32 ppm.

Cations **4** and **6** can be deprotonated by reaction with a methanol solution of KOH. The addition of this base to tetrahydrofuran solutions of both cations produces the extraction of one of the hydride ligands and the formation of the neutral compounds $OsH\{\eta^5\text{-}C_5H_4(CH_2)_2E\}(P^iPr_3)_2$ (E = NMe_2 (**7**), OMe (**8**)), which were isolated as white solids in 92−95% yield. In the ^1H NMR spectra, the hydride ligand of these complexes gives rise to triplets at −15.53 (**7**) and −15.60 (**8**) ppm, with H−P coupling constants of about 31 Hz. The $^{31}P\{^1H\}$ NMR spectra show singlets at about 30 ppm.

Scheme 3 shows a sequence of reactions that allows us to rationalize the formation of **5**. It is well known that organolithium compounds produce the fragmentation of donor solvents. The decomposition products of THF are ethylene and the lithium enolate of acetaldehyde.[8] Thus, in the presence of **2** and **3** some amount of THF decomposes to give this lithium enolate. The reaction of the latter with **1** would afford the previously reported five-coordinate carbonyl derivative $OsHCl(CO)(P^iPr_3)_2$ (**9**),[9] which should coordinate a chloride ligand from the salt [**4**]**Cl** or [**6**]**Cl**, to give the anion species **5**. Similar chloride coordination was recently observed for the five-coordinate ruthenium analogue $RuHCl(CO)(P^iPr_2Ph)_2$.[10]

In support of this proposal, we have observed that the addition of *n*-butyllithium to THF solutions of **1** leads to **9** and that the treatment of **9** with $[Et_4N]Cl$ affords the tetraethylamonium salt of **5** as a white solid in 94% yield. Analogously, the treatment of **9** with the chloride salts of **4** and **6** leads to corresponding salts of anion **5**, [**4**][**5**] and [**6**][**5**]. The formation of **9** from **1** is a process similar to that of decarbonylation of aldehydes to afford metal carbonyl derivatives and hydrocarbons. The reaction involves a hydride-acyl intermediate which evolves by deinsertion of methyl and subsequent reductive elimination of methane.[11]

In agreement with the presence of the carbonyl and hydride ligands in **5**, the IR spectrum in Nujol of the tetraethylammonium salt shows $\nu(C\equiv O)$ and $\nu(Os-H)$ bands at 1867 and 2135 cm^{-1}, respectively. In the ^1H NMR spectrum in dichloromethane-d_2 at 223 K, the hydride ligand gives rise to a triplet at −17.43 ppm, with a H−P coupling constant of 18 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 22.1 ppm.

In conclusion, osmium complexes containing a cyclopentadienyl group with a pendant N-, P-,[5] or O-donor group can be prepared by reaction of the known dihydride-dichloro complex $OsH_2Cl_2(P^iPr_3)_2$[12] with the corresponding functionalized cyclopentadienyllithium compound. The reactions and the preparation of the modified cyclopentadienyllithium derivatives must be carried out in hydrocarbon solvents, and the use of donor solvents, in particular THF, should be avoided. They can react with the cyclopentadienyllithium systems to give organic fragments, which promote undesired secondary reactions of the osmium precursor.

Experimental Section

General Information. All manipulations were performed at an argon/vacuum manifold using standard Schlenk techniques. Solvents were dried by known procedures and used freshly distilled. $OsH_2Cl_2(P^iPr_3)_2$ (**1**)[12] and $C_5H_5(CH_2)_2E$ (E = NMe_2, OMe)[13] were prepared according to previous reports. Corresponding lithium salts of the cyclopentadienyl ligands, $Li[C_5H_5(CH_2)_2E]$ (E = NMe_2 **2**, OMe **3**), were prepared by addition of n-BuLi to pentane solutions of the cyclopentadiene systems, according to a modified procedure of previously reported synthesis.[7] In the NMR spectra, ^1H and $^{13}C\{^1H\}$ chemical shifts are reported relative to tetramethylsilane and the $^{31}P\{^1H\}$ ones relative to H_3PO_4 (85%). Coupling constants *J* are given in hertz.

Preparation of $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(P^iPr_3)_2][OsHCl_2(CO)(P^iPr_3)_2]$ ([4][5]). THF (20 mL) was added to a mixture of **1** (1.0 g, 1.71 mmol) and $Li[C_5H_4(CH_2)_2NMe_2]$ (0.30 g, 2.10 mmol). Stirring the reaction mixture for 12 h at about 25 °C gave an orange suspension. The solvent was removed under vacuum, and dichloromethane (3 × 5 mL) was then added to the solid residue. The resulting suspension was filtered to separate the LiCl precipitate and the filtrate concentrated under reduced pressure, washed with toluene (1 × 5 mL) and pentane (1 × 5 mL), and dried under vacuum to give a white powder solid. Yield: 0.70 g (65%). Anal. Calcd for $C_{46}Cl_2H_{101}NOOs_2P_4$: C, 43.86; H, 8.08; N, 1.11. Found: C, 43.88; H, 7.85; N, 1.04. IR (Nujol): ν(CO) 1853, ν(Os−H) 2138 cm^{-1}. MS (FAB$^+$): *m/z* 651, (M^+), 577 ($M^- - Cl + H)^+$. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 5.42, 5.22 (both m, each 2H, C_5H_4), 2.68 (m, 6H, PCH anion), 2.60, 2.44 (both m, each 2H, CH_2CH_2N), 2.20 (s, 6H, $N(CH_3)_2$), 2.06 (m, 6H, PCH cation), 1.31−1.21 (m, 72H, $PCCH_3$/cation+anion), −14.18 (t, 2H, *J*(PH) = 29.4, Os−H), −17.30 (very br, 1H, Os−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 32.3 (s, P^iPr_3 cation), 22.5 (very br, P^iPr_3 anion). ^1H NMR (300 MHz, CD_2Cl_2, 223 K): δ 5.33, 5.15 (both br, each 2H, C_5H_4), 2.75−2.50 (br, 6H, PCH), 2.55, 2.38 (both m, each 2H, CH_2CH_2N), 2.16 (s, 6H, $N(CH_3)_2$), 2.10−1.70 (br, 6H, PCH), 1.20 (br, 72H, $PCCH_3$), −14.18 (t, 2H, *J*(PH) = 29.4, Os−H), −17.31 (t, 1H, *J*(PH) = 18.0, Os−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 223 K): δ 32.4 (s, P^iPr_3 cation), 21.6 (s, P^iPr_3 anion). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K, plus APT): 110.7 (−, s, ipso C_5H_4), 85.0, 77.3 (+, s, C_5H_4), 61.5 (−, s, $CH_2\mathit{C}H_2N$), 45.4 (+, s, $N(CH_3)_2$), 30.6 (+, m, PCH cation), 27.6 (−, s, $\mathit{C}H_2CH_2N$), 25.3 (+, m, PCH anion), 19.8, 19.7 (+, both s, $PC\mathit{C}H_3$).

Preparation of $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2OMe\}(P^iPr_3)_2][OsHCl_2(CO)(P^iPr_3)_2]$ ([6][5]). Treatment of **1** (1.10 g, 1.89 mmol) with $Li[C_5H_4(CH_2)_2OMe]$ (0.27 g, 2.08 mmol) in 20 mL of THF under a protocol analogous to that described for [**4**][**5**] affords a white solid. Yield: 0.71 g (60%). Anal. Calcd for $C_{45}Cl_2H_{98}O_2Os_2P_4$: C, 43.36; H, 7.92. Found: C, 43.39; H, 7.81. IR (Nujol): ν(CO) 1852, ν(Os−H) 2138 cm^{-1}. MS (FAB$^+$): *m/z* 638 (M^+), 577 ($M^- - Cl + H)^+$. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 5.47, 5.22 (both m, each 2H, C_5H_4), 3.49 (m, 2H, $CH_2C\mathit{H}_2O$), 3.30 (s, 3H, OCH_3), 2.71 (m, 2H, $C\mathit{H}_2CH_2O$), 2.68 (m, 6H, PCH/anion), 2.10 (m, 6H, PCH/cation), 1.32−1.10 (m, 72H, $PCCH_3$ cation+anion), −14.19 (t, 2H, *J*(PH) = 29.4, Os−H), −17.30 (very br, 1H, Os−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 32.9 (s, P^iPr_3 cation), 22.5 (very br, P^iPr_3 anion). ^1H NMR (300 MHz, CD_2Cl_2, 223 K): δ 5.33, 5.31 (both br, each 2H, C_5H_4), 3.43 (m, 2H, $CH_2C\mathit{H}_2O$), 3.30 (s, 3H, OCH_3), 2.60 (m, 2H, $C\mathit{H}_2CH_2O$), 2.50−2.40 (br, 12H, PCH), 1.21 (br, 72H, $PCCH_3$), −14.23 (t, 2H, *J*(PH) = 29.4, Os−H), −17.33 (t, 1H, *J*(PH) = 18.0, Os−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 223 K): δ 32.9 (s, P^iPr_3 cation), 20.4 (s, P^iPr_3 anion). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): 182.6 (br, $C\equiv O$), 109.5 (s, ipso-C_5H_4), 85.4 (m, C_5H_4), 77.5 (s, C_5H_4), 73.1 (s, $CH_2\mathit{C}H_2O$), 58.9 (s, CH_3O), 30.6 (m, PCH), 30.4 (m, PCH), 29.8 (s, $\mathit{C}H_2CH_2O$), 25.3 (m, PCH), 19.8, 19.7 (both s, $PC\mathit{C}H_3$).

Preparation of $[NEt_4][OsHCl_2(CO)(P^iPr_3)_2]$ ([NEt$_4$][5]). Toluene (10 mL) was added to a mixture of $OsHCl(CO)(P^iPr_3)_2$ (0.30 g, 0.49 mmol) and $[NEt_4][Cl]$ (0.11 g, 0.64 mmol). The initial red solution change to pale yellow, and a white precipitate was formed. After stirring the reaction mixture for 2 h at about 25 °C, the solution was separated by filtration and the solid residue washed with diethyl ether (2 × 2 mL) and pentane (1 × 5 mL) and dried under vacuum to give a white powder. Yield: 0.34 g (94%). Anal. Calcd for $C_{27}Cl_2H_{63}NOOs_2P_2$: C, 43.77; H, 8.57; N, 1.89. Found: C, 44.01; H, 8.90; N, 2.03. IR (Nujol): ν(CO) 1867, ν(Os−H) 2135 cm^{-1}. MS (FAB$^+$): *m/z* 576 ($M^- - Cl)^+$. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 3.36 (q, 8H, *J*(HH) = 7.3, $N-C\mathit{H}_2CH_3$), 2.68 (m, 6H, PCH), 1.34−1.24 (m, 48H, $NCH_2C\mathit{H}_3$ + $PCHC\mathit{H}_3$). $^{31}P\{^1H\}$

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NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 22.5 (very br). ^1H NMR (300 MHz, CD_2Cl_2, 223 K): δ 3.21 (m, 8H, NCH_2CH_3), 2.55 (br, 6H, PCH), 1.27 (m, 48H, NCH_2CH_3 + $PCHCH_3$), −17.43 (t, *J*(PH) = 18.0, Os−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 223 K): δ 22.1 (s).

Preparation of $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(P^iPr_3)_2][Cl]$ ([4]Cl). Toluene (20 mL) was added to a mixture of **1** (1.10 g, 1.89 mmol) and $Li[C_5H_4(CH_2)_2NMe_2]$ (0.29 g, 2.07 mmol). Stirring the reaction mixture for 12 h at about 25 °C gave a yellow suspension. The solvent was removed under vacuum, and dichloromethane (3 × 5 mL) was then added to the solid residue. The resulting suspension was filtered to separate the LiCl precipitate, and the combined filtrate was concentrated under reduced pressure, washed with toluene (1 × 5 mL) and pentane (1 × 5 mL), and dried under vacuum to give a white powder. Yield: 1.06 g (82%). Anal. Calcd for $C_{27}ClH_{58}NOsP_2$: C, 47.38; H, 8.54; N, 2.05. Found: C, 47.26; H, 8.48; N, 2.00. IR (Nujol): ν(Os−H) 2123 cm^{-1}. MS (FAB^+): *m/z* 651 (M^+). ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 5.49, 5.26 (both m, each 2H, C_5H_4), 2.58, 2.43 (both m, each 2H, CH_2CH_2N), 2.18 (s, 6H, $N(CH_3)_2$), 2.08 (m, 6H, PCH), 1.20 (dd, 36H, *J*(HH) = 7.2, *J*(PH) = 14.1, $PCCH_3$), −14.24 (t, 2H, *J*(PH) = 29.1, Os−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 32.9 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K plus APT): δ 110.6 (−, s, ipso-C_5H_4), 84.9, 77.2 (+, both s, C_5H_4), 61.2 (−, s, CH_2CH_2N), 45.2 (+, s, $N(CH_3)_2$), 30.1, 30.5 (+, second-order system, PCH), 27.2 (−, s, CH_2CH_2N), 19.5 (+, s, $PCCH_3$).

Preparation of $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2OMe\}(P^iPr_3)_2][Cl]$ ([6]Cl). Treatment of **1** (1.16 g, 1.99 mmol) with $Li[C_5H_4(CH_2)_2OMe]$ (0.28 g, 2.16 mmol) in 20 mL of toluene under a protocol analogous to that described for [**4**]Cl afforded a white powder. Yield: 1.13 g (85%). Anal. Calcd for $C_{26}ClH_{55}OOsP_2$: C, 46.51; H, 8.26. Found: C, 46.37; H, 8.41. IR (Nujol): ν(Os−H) 2141, 2116 cm^{-1}. MS (FAB^+): *m/z* 638 (M^+). ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 5.52, 5.20 (both m, each 2H, C_5H_4), 3.45 (m, 2H, CH_2CH_2O), 3.24 (s, 3H, OCH_3), 2.66 (m, 2H, CH_2CH_2O), 2.04 (m, 6H, PCH), 1.17 (dd, 36H, *J*(HH) = 7.2, *J*(PH) = 13.8, $PCCH_3$), −14.22 (t, 2H, *J*(HP) = 29.1, Os−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 31.9 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 293 K, plus APT): δ 108.9 (−, s, ipso-C_5H_4), 85.2, 77.1 (+, both s, C_5H_4), 72.7 (−, s, CH_2CH_2O), 58.6 (+, s, OCH_3), 29.9 (+, second-order system, PCH), 29.1 (−, s, CH_2CH_2O), 19.3 (+, s, $PCCH_3$).

Preparation of $OsH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(P^iPr_3)_2$ (7). A 0.19 M solution of KOH in methanol (9.2 mL, 1.75 mmol) was added to a solution of [**4**]Cl (1.0 g, 1.46 mmol) in 20 mL of THF. The initial colorless solution changed to a yellow suspension during the stirring of the mixture for 12 h at about 25 °C. The solvent was removed under reduced pressure and the residue extracted with pentane (3 × 10 mL). The combined filtrate was concentrated to dryness and the resulting foamy white solid washed with cold ^{i}PrOH and dried under vacuum. Yield: 0.90 g (95%). Anal. Calcd for $C_{27}H_{57}NOsP_2$: C, 50.05; H, 8.87; N, 2.16. Found: C, 50.19; H, 8.59; N, 2.03. IR (Nujol): ν(Os−H) 2062 cm^{-1}. MS (FAB^+): *m/z* 649 (M^+). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 4.78, 4.11 (both m, each 2H, C_5H_4), 2.68 (m, 4H, CH_2CH_2N), 2.19 (s, 6H, $N(CH_3)_2$), 1.91 (m, 6H, PCH), 1.16, 1.15 (both dd, each 18H, *J*(HH) = 10.2, *J*(PH) = 17.4, $PCCH_3$), −15.53 (t, 1H, *J*(PH) = 30.6, Os−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 29.6 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 94.9 (−, s, ipso-C_5H_4), 72.8 (+, s, C_5H_4), 69.2 (+, m, C_5H_4), 63.9 (−, s, CH_2CH_2N), 45.9 (+, s, $N(CH_3)_2$), 31.6 (+, second-order system, PCH), 28.7 (−, s CH_2CH_2N), 21.0, 20.9 (+, both s, $PCCH_3$).

Preparation of $OsH\{\eta^5\text{-}C_5H_4(CH_2)_2OMe\}(P^iPr_3)_2$ (8). A solution of [**6**]Cl (1.5 g, 2.23 mmol) in 20 mL of THF was treated with a 0.19 M solution of KOH in methanol (14 mL, 2.70 mmol) under a protocol analogous to that described for **7** to yield 1.30 g (92%). Anal. Calcd for $C_{26}H_{54}OOsP_2$: C, 49.19; H, 8.57. Found: C, 49.41; H, 8.35. IR (Nujol): ν(Os−H) 2065 cm^{-1}. MS (FAB^+): *m/z* 636 (M^+). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 4.75, 4.13 (both m, each 2H, C_5H_4), 3.66 (m, 2H, CH_2CH_2O), 3.17 (s, 3H, OCH_3), 2.77 (m, 2H, CH_2CH_2O), 1.90 (m, 6H, PCH), 1.16, 1.13 (both dd, each 18H, *J*(HH) = 8.7, *J*(PH) = 16.2, $PCCH_3$), −15.60 (t, 1H, *J*(PH) = 30.9, Os−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 29.5 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 93.5 (−, s, ipso-C_5H_4), 76.5 (−, s, CH_2CH_2O), 72.8 (+, s, C_5H_4), 69.5 (+, m, C_5H_4), 58.6 (+, s, OCH_3), 31.6 (+, second-order system, PCH), 30.8 (−, s, CH_2CH_2O), 21.0 (+, s, $PCCH_3$).

X-ray Analysis of [4][5]. A crystal was mounted on a Bruker Smart APEX CCD diffractometer at 100.0(2) K equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering 0.3° in ω. The cell parameters were determined and refined by least-squares fit of 2238 collected reflections. The first 100 frames were collected at the end of the data collection to monitor crystal decay. Absorption correction was performed with the SADABS program.[14] Lorentz and polarization corrections were also performed. The structure was solved by Patterson and Fourier methods and refined by full matrix least-squares using the Bruker SHELXTL program package[15] minimizing $w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were anisotropically refined. The hydrogen atoms were calculated and refined riding on bonded carbon atoms. The hydride ligands were observed in the difference Fourier maps and refined freely with a common thermal parameter or refined riding on bonded Os atoms. In the last cycles of refinement a chloride and a CO ligand situated in *trans* positions were observed disordered about the osmium atom and were refined using two moieties with restrained geometry and restrained anisotropic thermal parameters (occupancy: 0.75 and 0.25, respectively). Two isopropyl groups (anion and cation) and the NMe_2 group were also disordered and refined with two moieties, respectively, complementary occupancy factors, restrained geometry, and restrained anisotropic thermal parameters. Finally, 1.5 molecules of toluene were observed as solvent of crystallization.

Crystal data: $C_{27}H_{58}NOsP_2$, $C_{19}H_{43}Cl_2OP_2Os$, 1.5 × C_7H_8, M_w 1397.66, colorless, prism (0.12 × 0.10 × 0.04 mm), triclinic, space group $P\bar{1}$, a = 12.9411(17) Å, b = 13.9892(18) Å, c = 19.645(3) Å, α = 70.554(2)°, β = 79.482(2)°, γ = 69.884(2)°, V = 3139.7(7) Å^3, Z = 2, D_{calc} = 1.478 g cm^{-3}, $F(000)$ = 1426, T = 100.0(2) K; μ = 4.266 mm^{-1}. A total of 28 533 measured reflections (2θ = 3−57°, ϖ scans 0.3°), 14 170 unique (R_{int} = 0.0801); min./max. transmn factors 0.762/0.598. Final agreement factors were R_1 = 0.0499 (6072 observed reflections, $I > 2\sigma(I)$) and wR_2 = 0.0859; data/restraints/parameters 14 170/468/753; GoF = 0.707. Largest peak and hole = 1.519 and −1.336 e/Å^3. All the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense.

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Supporting Information Available: Tables of 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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