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Preparation of Half-Sandwich Osmium Complexes by Deprotonation of Aromatic and Pro-aromatic Acids with a Hexahydride Brønsted Base

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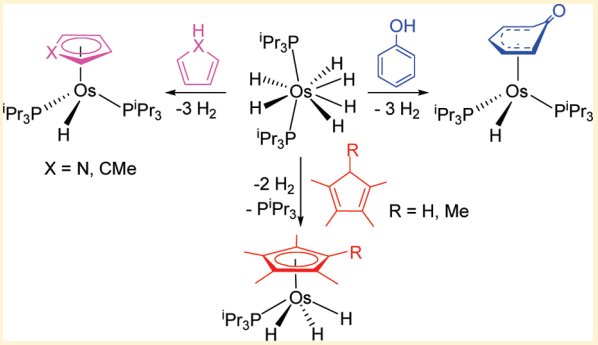
Supporting Information

ABSTRACT: Half-sandwich osmium(II) and osmium(IV) complexes have been prepared by reaction of the hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) with phenol, pyrrole, and methylcyclopentadienes. The reaction with phenol initially leads to $OsH_3(OPh)(P^iPr_3)_2$ (**2**). In toluene, **2** undergoes reductive elimination of phenol, which tautomerizes to give $OsH_2(\eta^4\text{-}2,4\text{-cyclohexadien-1-one})(P^iPr_3)_2$ (**3**). The equilibrium mixture of **2** and **3** evolves into $OsH(\eta^5\text{-}PhO)(P^iPr_3)_2$ (**4**) with loss of molecular hydrogen. The addition of HBF_4 to diethyl ether solutions of **4** leads to $[OsH(\eta^6\text{-}PhOH)(P^iPr_3)_2]BF_4$ (**6**). The reaction of **1** with pyrrole gives $OsH(\eta^5\text{-}C_4H_4N)(P^iPr_3)_2$ (**7**), which by addition of HBF_4 affords $[OsH_2(\eta^5\text{-}C_4H_4N)(P^iPr_3)_2]BF_4$ (**8**). Similarly, treatment of **1** with methylcyclopentadiene leads to $OsH(\eta^5\text{-}C_5H_4Me)(P^iPr_3)_2$ (**9**), which reacts with HBF_4 to give $[OsH_2(\eta^5\text{-}C_5H_4Me)(P^iPr_3)_2]BF_4$ (**10**). Treatment of toluene solutions of **1** with tetramethylcyclopentadiene gives a mixture of the trihydride $OsH_3(\eta^5\text{-}C_5HMe_4)(P^iPr_3)$ (**11**; 56%) and the dihydride-tolyl derivatives $OsH_2(m\text{-tolyl})(\eta^5\text{-}C_5HMe_4)(P^iPr_3)$ (**12**; 14%) and $OsH_2(p\text{-tolyl})(\eta^5\text{-}C_5HMe_4)(P^iPr_3)$ (**13**; 30%). However in *n*-octane the trihydride **11** is formed in 85% yield. In contrast to tetramethylcyclopentadiene, pentamethylcyclopentadiene reacts with **1** in toluene to give selectively the trihydride $OsH_3(\eta^5\text{-}C_5Me_5)(P^iPr_3)$ (**14**). Complexes **2** and **7** have been characterized by X-ray diffraction analysis.



INTRODUCTION

η^5-Half-sandwich complexes are one of the cornerstones of transition-metal chemistry. Those of the iron triad have played a fundamental role in the development of the organometallic area and homogeneous catalysis. A number of half-sandwich ruthenium compounds have been shown to be versatile catalysts or reaction intermediates for relevant organic transformations.[1] In contrast to ruthenium, osmium chemistry is still underdeveloped. However, recent findings have proved that osmium is a promising alternative to ruthenium catalysts,[2] and since stoichiometric osmium chemistry seems to be more rich than that of ruthenium,[3] an increasing interest in η^5-half-sandwich osmium complexes begins to be perceptible.

The methods of general use to prepare η^5-half-sandwich osmium complexes are limited to the synthesis of species with cyclopentadienyl and related five-membered hydrocarbon rings. They are furthermore very scarce. We have reported that the treatment of $OsH_2Cl_2(P^iPr_3)_2$ or $OsH_3Cl(P^iPr_3)_2$ with the corresponding hydrocarbon derivative of an s- or p-block element allows obtaining Os—P^iPr_3 compounds,[3c,4] whereas Jia and co-workers have shown that reactions of $OsH_3Cl(PPh_3)_3$ with cyclopentadienes and monosubstituted fulvenes afford Os-PPh_3 derivatives.[5]

Transition-metal hydride compounds, as η^5-half-sandwich complexes, play a central role in modern organometallic and inorganic chemistries.[6] The hydride ligand is viewed as one of the best anchors to secure unsaturated organic molecules in transition-metal compounds. As a consequence of this property, osmium hydride complexes have generated a wide range of organometallic functional groups,[3d,7] which facilitate some carbon—carbon coupling reactions and the formation of organic fragments with a rich chemistry.[8] Our interest in complexes that promote the functionalization of organic molecules[2,9] prompted us to search for new general methods to prepare half-sandwich osmium hydride complexes, including those containing a heteroaromatic ring.

The saturated d^2 hexahydride complex $OsH_6(P^iPr_3)_2$ activates C—H bonds of a broad number of organic molecules[10] and, by protonation with weak Brønsted acids, releases molecular hydrogen to afford d^4-osmium hydride species, which contain the corresponding conjugated Brønsted base as a ligand.[11] Because phenol, pyrrole, and cyclopentadienes are weak Brønsted acids of conjugated aromatic Brønsted bases, which can be η^5-coordinated, we have investigated the reactivity of $OsH_6(P^iPr_3)_2$ with these

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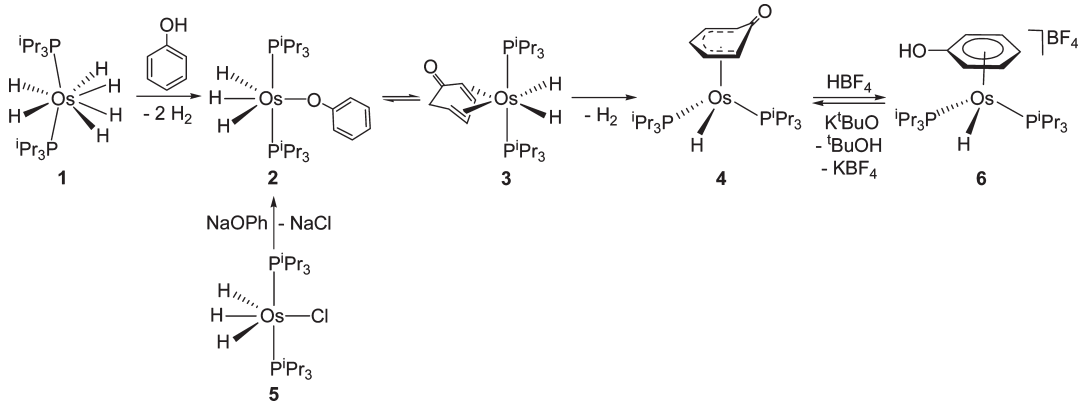
Scheme 1



Brønsted acids, in order to prepare half-sandwich osmium hydride complexes in a general manner.

This paper describes a general method to prepare half-sandwich osmium hydride complexes and shows the influence of the η^5-ligand on the stoichiometry of the formed species and the protonation of the latter.

RESULTS AND DISCUSSION

1. Reactions with Phenol. Treatment of toluene solutions of the hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) with 3.0 equiv of phenol for 5 h, under reflux, leads to a mixture of $OsH_3(OPh)(P^iPr_3)_2$ (**2**), $OsH_2(\eta^4$-2,4-cyclohexadien-1-one$)(P^iPr_3)_2$ (**3**), and $OsH(\eta^5$-PhO$)(P^iPr_3)_2$ (**4**), in a 1.3:1:4.3 molar ratio. The formation of the mixture can be rationalized according to Scheme 1.

Osmium polyhydrides are Brønsted bases that show a marked tendency to deprotonate alcohols to afford alkoxy species, which evolve by β-hydrogen elimination into ketone derivatives[12] or via aldehyde intermediates into carbonyl compounds.[2b,9c,13] Phenol is a particularly acidic alcohol having no geminal hydrogen atoms. Thus, the abstraction of its OH-hydrogen by one of the hydride ligands of **1** generates molecular hydrogen and a phenoxy species, which releases a second hydrogen molecule to give **2**. The latter can be prepared as a brown solid in 96% yield, by stirring of a tetrahydrofuran solution of the trihydride $OsH_3Cl(P^iPr_3)_2$ (**5**) in the presence of 6.0 equiv of sodium phenoxide, for 20 min, at room temperature.

Complex **2** has been characterized by X-ray diffraction analysis. Figure 1 shows a view of the molecular geometry. The structure has essentially C_{2v} symmetry with *trans* phosphines (P(1)−Os−P(2) = 176.15(5)°) and the oxygen atom of the phenoxy group, the metal center, and the hydride ligands lying in the plane perpendicular to the P−Os−P direction. The most noticeable feature of the complex are the H(01)−Os−H(02) and H(02)−Os−H(03) angles of 58.1(5)° and 62.1(15)°, respectively, which markedly deviate from 90°. It is well known that the octahedral geometry is not favorable for heavy metal d^4 complexes, which prefer to be diamagnetic.[11a,12c,14] These complexes therefore undergo a distortion that destabilizes one orbital from the t_{2g} set and simultaneously stabilizes some occupied orbitals. The distortion is typical for $OsH_3X(PR_3)_2$ complexes and partially cancels the electron deficiency at the metal, which receives additional electron density from the hydrides via stronger σ-bonds and from one lone pair of X via a π-bond.[14e] In agreement with the latter, the Os−O distance of 2.027(3) Å is

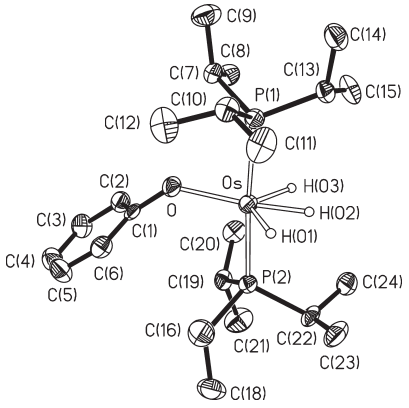


Figure 1. Molecular diagram of complex **2**. Selected bond lengths (Å) and angles (deg): Os−P(1) = 2.3370(14), Os−P(2) = 2.3311(14), Os−O = 2.027(3), H(01)−H(02) = 1.53(1), H(02)−H(03) = 1.63(4); P(1)−Os−P(2) = 176.15(5), Os−O−C(1) = 134.9(3), H(01)−Os−H(02) = 58.1(5), H(02)−Os−H(03) = 62.1(15).

consistent with some multiple character for the Os−O bond.[15] The π-donation from the oxygen atom into the metal is also supported by the Os−O−C(1) angle of 134.9(3)°, which is certainly greater than that expected from a pyramidal oxygen atom.

Fast rotation around the Os−O bond gives rise to a single time-averaged $^{31}P\{^1H\}$ NMR signal at 53.2 ppm, between 298 and 183 K. The hydride ligands display at −18.60 ppm a triplet with a H−P coupling constant of 11.4 Hz in the ^1H NMR spectrum, in toluene-d_8, at room temperature. Lowering the sample temperature produces a broadening of the resonance. However, decoalescence is not observed at 183 K. A variable-temperature 300 MHz T_1 study between 273 and 183 K gave a $T_{1(min)}$ value of 133 ± 1 ms at 203 K, which is consistent with the trihydride character of the complex.

Phenol normally exists in solution as an enol. However, when it is coordinated to a transition metal, its dienone tautomers can become energetically competitive. Thus, several transition-metal cyclohexadien-1-one derivatives have been isolated and characterized.[16] Complex **2** is unstable in solution. At room temperature, it undergoes reductive elimination of phenol, which tautomerizes into 2,4-cyclohexadien-1-one to afford after 48 h a 93:7 mixture of **2** and **3**. Free phenol stabilizes the coordinated dienone form as a consequence of the formation of O···H−O hydrogen bonds between the OH-hydrogen atom and the

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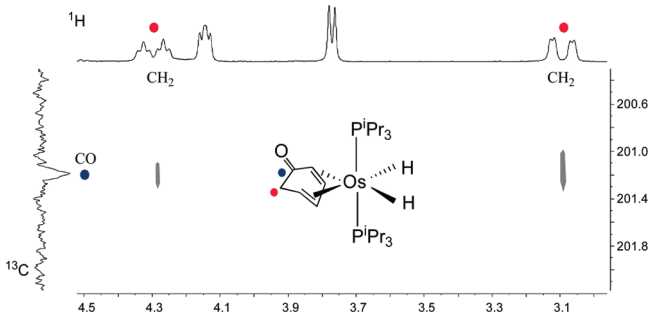


Figure 2. Partial view of the ^{1}H−^{13}C HMBC NMR spectrum of **3**.

carbonyl group. Thus, in the presence of 3.0 equiv of phenol the amount of dienone derivative increases to 67%, whereas in the presence of 6.0 equiv 90% of **3** is formed.

The ^{31}P{^{1}H} and ^{1}H NMR spectra of **3** suggest that the dienone rotates around an Os−dienone axis, in agreement with that previously observed for the related compound $OsH_2(\eta^4$-1,3-cyclohexadiene$)(P^iPr_3)_2$.[17] Thus, at room temperature, the ^{31}P-{^{1}H} NMR spectrum contains a singlet at 31.5 ppm for the inequivalent phosphine groups, whereas the ^{1}H NMR spectrum shows at −13.40 ppm a triplet with a H−P coupling constant of 30.8 Hz, for the inequivalent hydride ligands. As expected for the rigid structure proposed in Scheme 1, at 193 K, the ^{31}P{^{1}H} NMR spectrum contains an AB spin system centered at 33.6 ppm and defined by $\Delta\nu$ = 930 Hz and J_{A-B} = 661.0 Hz, while the ^{1}H NMR spectrum shows two hydride resonances at −12.8 and −15.7 ppm. Assuming an entropy of activation close to 0, a $\Delta H^{\ddagger}$ value of about 9 kcal·mol^{-1} can be estimated as the rotation barrier, on the basis of a coalescence temperature of 203 K. In the low-field region of the ^{1}H NMR spectrum, the inequivalent CH$_2$-hydrogen atoms of the dienone display resonances at 4.30 and 3.09 ppm, which show cross signals with the carbonyl resonance at 201.2 ppm in the ^{1}H−^{13}C HMBC NMR spectrum (Figure 2).

The equilibrium mixtures of **2** and **3** lose molecular hydrogen in toluene to afford the η^5-dienylone derivative **4**, which reacts with $HBF_4\cdot OEt_2$ to give the η^6-phenyl compound $[OsH(\eta^6$-PhOH$)(P^iPr_3)_2]BF_4$ (**6**), as a result of the protonation of the carbonyl group. The protonation is reversible. Treatment of tetrahydrofuran solutions of **6** with 1.1 equiv of K^{t}BuO regenerates **4** in almost quantitative yield. Characteristic spectroscopic data of **4** are a singlet at 15.4 ppm in the ^{31}P{^{1}H} NMR spectrum and a triplet (J_{H-P} = 33.5 Hz) at −14.20 ppm, due to the hydride ligand, in the ^{1}H NMR spectrum.

The solvation of the oxygen atom of the carbonyl group with free phenol significantly improves the stability of **4**. Phenol is less volatile than *tert*-butanol, and its hydrogen bonds with the dienylone ligand are stable under vacuum. Thus, in contrast to the oil resulting from the deprotonation of **6** with K^{t}BuO, which is extremely unstable in benzene-d_6 at room temperature once we obtained accurate spectroscopic data, the oil generated from the deprotonation with NaPhO can be handled without much difficulty. The oxygen atom seems to have the size to form a first solvation sphere with five phenol molecules. Figure 3 shows the ^{1}H NMR resonances of the hydrogen atoms of the η^5-coordinated ligand of the $OsH(\eta^5$-PhO$)(P^iPr_3)_2\cdot x$PhOH adducts, resulting from the sequential addition of phenol to the benzene-d_6 solutions of the oil formed by deprotonation of **6** with NaPhO ($OsH(\eta^5$-PhO$)(P^iPr_3)_2\cdot$PhOH). The resonances corresponding to the protons 2, 6, and 4 move to lower field

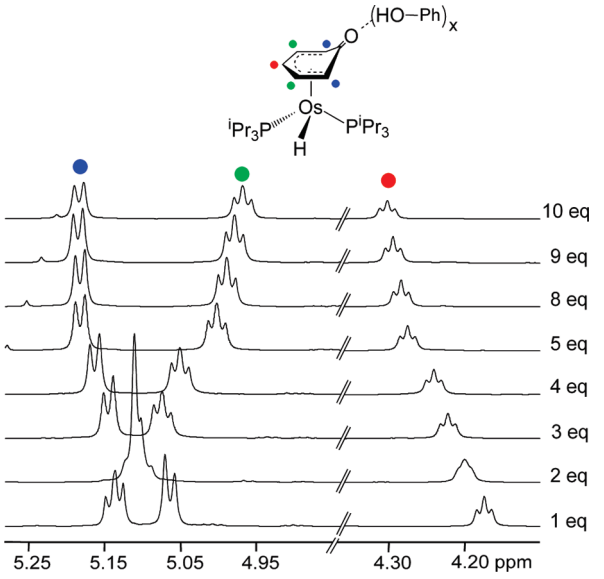
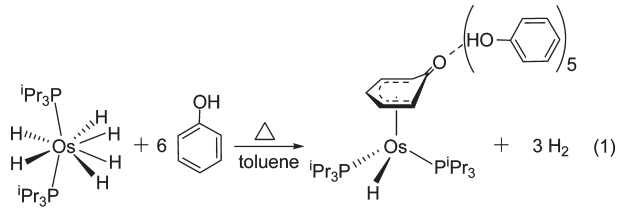


Figure 3. Partial view of the ^{1}H NMR spectra of $OsH(\eta^5$-PhO$)(P^iPr_3)_2\cdot x$PhOH as a function of the amount of phenol in the benzene-d_6 solution.

as the amount of phenol in the solution increases, while the resonance due to protons 3 and 5 is shifted toward higher field. Interestingly, the value of $\Delta\delta$ ($\delta_{3,5} - \delta_{2,6}$) changes from 0.08 to −0.19 as the amount of phenol in the solution increases from 1 to 5 equiv. However, an increase of 5 to 10 in the number of equivalents of phenol only produces a change from −0.19 to −0.21 in the value of $\Delta\delta$. In agreement with the formation of a five-solvated phenol species the treatment of toluene solutions of **1** with 6.0 equiv of phenol for 5 h under reflux leads to $OsH(\eta^5$-PhO$)(P^iPr_3)_2\cdot$5PhOH, which is isolated as a brown oil in 93% yield, according to eq 1. The hydrogen bonds certainly weaken the C−O double bond of the dienylone ligand. In agreement with other η^5-dienylone compounds[18] the CO resonance in the ^{13}C{^{1}H} NMR spectrum appears at 161.4 ppm, shifted by about 50 ppm toward higher field with regard to that of **3**.



The phenol complex **6** was isolated as a white solid in 71% yield. At room temperature the ^{31}P{^{1}H} NMR spectrum in dichloromethane-d_2 shows a singlet at 13.7 ppm, whereas the ^{1}H NMR spectrum contains at −12.95 ppm a triplet with a H−P coupling constant of 36.6 Hz due to the hydride ligand. These spectroscopic data agree well with those reported for the complexes $[OsH(\eta^6$-$C_6H_5R)(P^iPr_3)_2]BF_4$ (R = CH$_3$, H, F).[19] Characteristic features of **6** are also a broad singlet at 8.21 ppm, corresponding to the OH-proton, in the ^{1}H NMR spectrum and a singlet at 137.1 ppm due to the COH-carbon atom in the ^{13}C{^{1}H} NMR spectrum. The latter appears shifted by about 24 ppm toward higher field with regard to the CO resonance of the phenol-solvated dienylone adduct.

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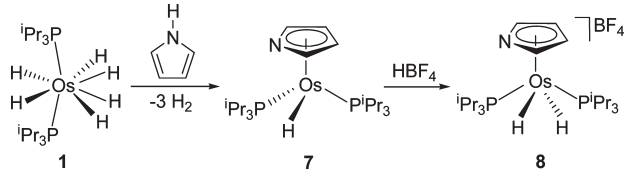
Scheme 2



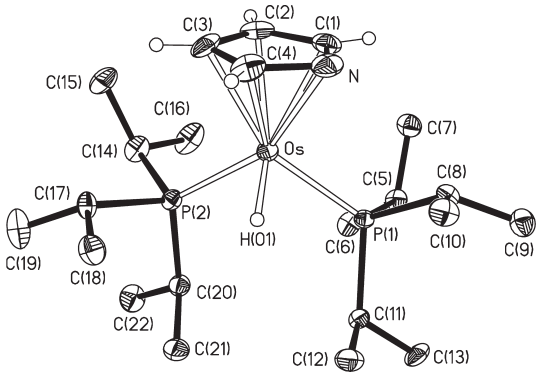


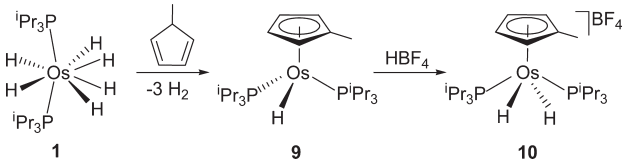
Figure 4. Molecular diagram of complex **7**. Selected bond lengths (Å) and angles (deg): Os−P(1) = 2.2970(17), Os−P(2) = 2.2867(17), C(1)−C(2) = 1.396(11), C(2)−C(3) = 1.412(11), C(3)−C(4) = 1.404(11), N−C(1) = 1.390(10), N−C(4) = 1.384(10); P(1)−Os−P(2) = 106.00(6).

2. Reactions with Pyrrole. Five-membered heterorings containing two C−C double bonds can also have an aromatic sextet if the heteroatom has an unshared pair of electrons. Such is the case of pyrrole. Thus, since the unshared pair is needed for the aromatic sextet, the basicity of the nitrogen atom is much weaker than that of pyridine and the NH-hydrogen has some protic character, although its pK_a value is about five units higher than that of phenol. In agreement with this weak Brønsted acidic nature of the heterocycle and the significant Brønsted basicity of **1**, the treatment of the toluene solutions of the hexahydride with 6.0 equiv of pyrrole for 7 h under reflux produces the release of molecular hydrogen, as a consequence of the abstraction of the NH-hydrogen with the hydride ligands. The resulting unsaturated metal fragment is stabilized by coordination of the generated pyrrolide in a η^5-fashion. The formed half-sandwich derivative, OsH(η^5-C_4H_4N)(P^iPr_3)$_2$ (**7**), is isolated as a beige solid in 55% yield, according to Scheme 2.

Figure 4 shows a view of the structure of **7**. The geometry around the osmium center is close to octahedral, with the aromatic ring occupying three sites of a face. The mutually *cis* disposed phosphine groups experience a large steric hindrance, as a consequence of their cone angle (160°).[20] Thus, the P(1)−Os−P(2) angle of 106.00(6)° strongly deviates from the ideal value of 90°. This angle is similar to other P−M−P angles previously found in complexes with two triisopropylphosphine ligands mutually *cis* disposed.[4d,19,21] The pyrrolide ligand is almost planar, with a maximum deviation of 0.0133(41) Å for C(1), with statistically identical C−C bond lengths of 1.396(11) Å (C(1)−C(2)), 1.412(11) Å (C(2)−C(3)), and 1.404(11) Å (C(3)−C(4)) and C−N distances of 1.390(10) Å (N−C(1)) and 1.384(10) Å (N−C(4)).

The $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectra of **7** in benzene-d_6 at room temperature are consistent with the structure shown in Figure 4. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 27.7 ppm. In the ^1H NMR spectrum, the most noticeable resonances are those corresponding to the hydride and pyrrolide ligands. The first of them gives rise to a triplet (J_{H-P} = 29.8 Hz) at −18.88 ppm, whereas the second one displays two signals at 5.88 and 4.85 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the pyrrolide resonances are observed at 98.7 and 72.5 ppm as triplets with C−P coupling constants of 1.5 and 2.6 Hz, respectively. These spectroscopic date agree well with those reported for the ruthenium complex RuH(η^5-C_4NH_4)(PCy_3)$_2$.[22]

Scheme 3



One should expect that the pyrrolide nitrogen atom of **7**, like the dienylone oxygen atom of **4**, is a strong basic center, since only two of its three unshared electrons are needed for the aromatic sextet. However, in contrast to **4**, the addition of 1.0 equiv of HBF_4 to diethyl ether solutions of **7** produces the protonation of the osmium atom, revealing a strong electron donor power of the η^5-pyrrolide group. The oxidized product [OsH_2(η^5-C_4NH_4)(P^iPr_3)$_2$]BF_4 (**8**) is isolated as a white solid in 83% yield.

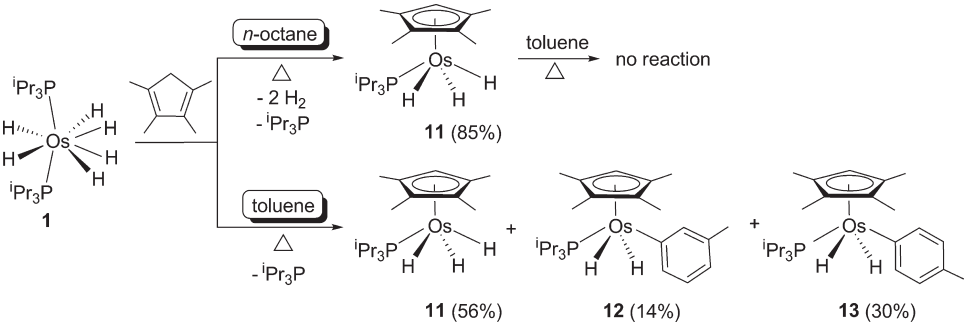
The $^{31}P\{^1H\}$ NMR spectrum of **8** in dichloromethane-d_2 shows a singlet at 33.9 ppm. In the ^1H NMR spectrum, the hydride resonance appears at −14.50 ppm as a triplet with a H−P coupling constant of 28.6 Hz, whereas the pyrrolide signals are observed as singlets at 6.60 and 6.02 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the aromatic carbon atoms display singlets at 104.7 and 90.4 ppm. It should be noted that the oxidation of the metal center produces the displacement of the ^1H and ^{13}C pyrrolide resonances toward lower field.

3. Reactions with Methylcyclopentadienes. Cyclopentadienes have acidic properties, since on loss of a proton, the resulting carbanion is stabilized by a resonance that is greater than in pyrrole. Thus some cyclopentadienyl derivatives have been prepared by displacement of Brønsted base ligands with these dienes.[23] In agreement with the Brønsted basicity of **1**, the hexahydride deprotonates methylcyclopentadienes to afford osmium(II)- and osmium(IV)-methylcyclopentadiene half-sandwich derivatives. The oxidation state of the metal center and the experimental conditions of the synthesis depend upon the number of the methyl substituents of the dienes.

Treatment of the toluene solutions of **1** with 6.0 equiv of methylcyclopentadiene for 24 h under reflux leads to the osmium(II) hydride OsH(η^5-C_5H_4Me)(P^iPr_3)$_2$ (**9**), which is isolated as a pale yellow oil in 74% yield according to Scheme 3. This compound is analogous with **7**, containing a CMe moiety instead of a nitrogen atom. In agreement with the latter, its $^{31}P\{^1H\}$ NMR spectrum in benzene-d_6 at room temperature shows a singlet at 28.9 ppm, whereas in the ^1H NMR spectrum, the hydride resonance appears at −15.66 ppm as a triplet with a H−P coupling constant of 30.2 Hz.

The metal center of **9** undergoes protonation, like that of **7**. The addition of 1.2 equiv of HBF_4 to its diethyl ether solutions produces the instantaneous precipitation of the dihydride derivative [OsH_2(η^5-C_5H_4Me)(P^iPr_3)$_2$]BF_4 (**10**), counterpart of **8**, as a white solid in 75% yield. Characteristic data of **10** are a singlet

Scheme 4



at 32.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum in dichloromethane-d_2 and a triplet (J_{H-P} = 29.2 Hz) at −14.14 ppm in the ^1H NMR spectrum. The spectroscopic data of both **10** and **9** compare well with those of related cyclopentadiene compounds.[4a]

Tetramethylcyclopentadiene, in contrast to methylcyclopentadiene, generates osmium(IV) species, as expected for a stronger electron donor character of the tetramethylcyclopentadienyl group with regard to the methylcyclopentadienyl ligand. Treatment of toluene solutions of **1** with the tetrasubstituted diene for 5 h under reflux leads to a mixture of osmium(IV) compounds, including the trihydride $OsH_3(\eta^5\text{-}C_5HMe_4)(P^iPr_3)$ (**11**; 56%) and the dihydride-tolyl derivatives $OsH_2(m\text{-tolyl})(\eta^5\text{-}C_5HMe_4)(P^iPr_3)$ (**12**; 14%) and $OsH_2(p\text{-tolyl})(\eta^5\text{-}C_5HMe_4)(P^iPr_3)$ (**13**; 30%). The tolyl compounds **12** and **13** are the result of the respective *meta*- and *para*-CH bond activations of toluene promoted by **1** before the deprotonation of the diene. In this context, it should be noted that the hexahydride complex catalyzes the H/D exchange between pyridines and benzene-d_6.[10i] The C−H bond activation processes generate bisphosphine osmium hydride tolyl intermediates,[24] which deprotonate the diene. The subsequent coordination of the resulting cyclopentadienyl group to the metal center stabilizes the osmium(IV)-tolyl complexes. In agreement with this, we have also observed that the treatment of *n*-octane solutions of **1** with 6.0 equiv of tetramethylcyclopentadiene for 4 h under reflux gives **11**, which does not react with toluene under reflux to afford **12** and **13** (Scheme 4).

The trihydride complex **11** is isolated as a pale yellow oil, in 85% yield, from the reaction in *n*-octane. Its $^{31}P\{^1H\}$ NMR spectrum in toluene-d_8 at room temperature shows a singlet at 50.5 ppm, whereas in the ^1H NMR spectrum, the hydride ligands display a singlet at −14.06 ppm and a doublet (J_{H-P} = 32.6 Hz) at −14.85 ppm in a 1:2 intensity ratio. These ^1H resonances are temperature dependent between 373 and 183 K. The spectrum at 373 K contains a broad signal centered at about −14.6 ppm, which is consistent with the operation of a thermally activated site exchange process between the unique hydride and the pair of equivalent hydride ligands. The exchange process proceeds at a sufficient rate to lead to a single hydride resonance. Between 353 and 343 K, decoalescence occurs, and between 343 and 233 K the expected two resonances are observed. Line shape analysis of these spectra yields rate constants at different temperatures. The activation parameters obtained from the Eyring analysis are $\Delta H^{\ddagger} = 16.0 \pm 0.9$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -2.9 \pm 1.6$ cal·mol^{-1}·K^{-1}. The value of the entropy of activation close to zero is in agreement with an intramolecular process, while the value of the enthalpy of activation lies in the range reported for $OsH_3(\eta^5\text{-}C_5H_5)(P^iPr_3)$[25] and $OsH_3(\eta^5\text{-}C_5Me_5)L$ (L = $AsPh_3$, PPh_3, PCy_3, PEt_3).[26] Between 223 and 183 K, the resonance at higher field splits into two signals, suggesting that at temperatures lower than 223 K the rotation of the cyclopentadienyl group around a cyclopentadienyl−osmium axis is stopped. This reduces the symmetry of the molecule, and as a consequence, the *transoid* hydride ligands become inequivalent.

The osmium(IV)-dihydride-tolyl complexes **12** and **13** are rare examples of products resulting from C−H activation reactions with the late transition metal in high oxidation state[27] (d^4 ion). They have been fully characterized by $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **12** in benzene-d_6 at room temperature contains a singlet at 42.4 ppm. In the ^1H NMR spectrum, the hydride ligands display at −12.69 ppm a doublet with a H−P coupling constant of 37 Hz, whereas the tolyl group gives rise to four signals between 7.78 and 6.85 ppm corresponding to its four inequivalent aromatic hydrogen atoms. In agreement with the ^1H NMR spectrum, six aromatic tolyl resonances are observed between 164.1 and 119.9 ppm in the $^{13}C\{^1H\}$ NMR spectrum. Characteristic spectroscopic data of **13** are a singlet at 42.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum, a doublet (J_{H-P} = 37.0 Hz) at −12.65 ppm due to the hydride ligands, and two doublets (J_{H-H} = 7.2 Hz) at 7.79 and 6.77 ppm assigned to the aromatic tolyl hydrogen atoms in the ^1H NMR spectrum and four singlets between 157.8 and 119.6 ppm corresponding to the aromatic tolyl carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum.

The pentamethylcyclopentadienyl group also shows a strong tendency to stabilize osmium(IV) species. The additional methyl group increases the electron richness of the five-membered ring but, however, also augments its steric requirement, which appears to prevent the formation of pentamethylcyclopentadienyl counterparts of **12** and **13**, most probably as a consequence of the steric hindrance experienced between the methyl substituents and the tolyl groups. Thus, the treatment of toluene solutions of **1** with 6.0 equiv of pentamethylcyclopentadiene for 24 h under reflux leads to the selective formation of the trihydride derivative $OsH_3(\eta^5\text{-}C_5Me_5)(P^iPr_3)$ (**14**), which is isolated as a yellow oil in 80% yield, according to eq 2. The $^{31}P\{^1H\}$ and ^1H NMR spectra of **14** are consistent with those of **11**. In toluene at room temperature, the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 47.3 ppm, whereas the hydride resonances in the ^1H NMR spectrum appear as a singlet at −14.47 ppm and a doublet (J_{H-P} = 33.3 Hz) at −14.82 ppm in a 1:2 intensity ratio. At temperatures higher than 273 K, the hydride ligands are also involved in a thermally activated site exchange process. In this

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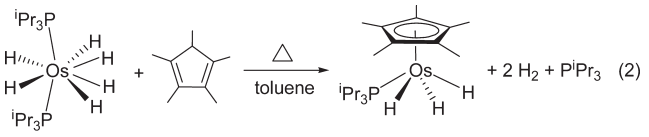
case, the activation parameters for the exchange are $\Delta H^{\ddagger}$ = 15.7 ± 1.2 kcal·mol^{-1} and $\Delta S^{\ddagger}$ = −2.0 ± 2.4 cal·mol^{-1}·K^{-1}.



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CONCLUDING REMARKS

This study shows that the hexahydride complex $OsH_6(P^iPr_3)_2$ deprotonates phenol, pyrrole, and methylcyclopentadienes to afford half-sandwich osmium(II) hydride or osmium(IV) trihydride derivatives, depending upon the electron richness and the steric requeriment of the conjugated base. These observations reveal a new general method to prepare half-sandwich osmium complexes, including those with a heteroaromatic ligand. The method is a consequence of the existence of transition-metal polyhydride compounds that are Brønsted bases capable of deprotonating weak acids. When the conjugated base of these acids is aromatic, its coordination to the unsaturated metal center resulting from the hydride abstraction generates a half-sandwich complex.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents (except *n*-octane, which was dried over sodium and distilled under argon) were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on Bruker 300 ARX, Bruker Avance 300 MHz, Bruker Avance 400 MHz, and Bruker Avance 500 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or to external 85% H_3PO_4 (^{31}P{^{1}H}). Coupling constants *J* and *N* are given in hertz. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer as neat solids or oils. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). $OsH_6(P^iPr_3)_2$,[12c] $OsH_3Cl(P^iPr_3)_2$,[14b] and NaOPh[18c] were prepared by published methods.

Reaction of $OsH_6(P^iPr_3)_2$ (1) with 3 equiv of PhOH. A colorless solution of **1** (100 mg, 0.19 mmol) in 15 mL of toluene was treated with 3.0 equiv of phenol (54 mg, 0.57 mmol) and heated under reflux for 5 h. The resulting brown solution was filtered through Celite, and the solvent was removed in vacuo. ^{1}H and ^{31}P{^{1}H} NMR spectra show the presence of $OsH_3(OPh)(P^iPr_3)_2$ (**2**), $OsH_2(\eta^4$-2,4-cyclohexadien-1-one$)(P^iPr_3)_2$ (**3**), and $OsH(\eta^5$-PhO$)(P^iPr_3)_2\cdot 2(C_6H_5OH)$ (**4**) in a ratio of 1.3:1:4.3.

Spectroscopic data for $OsH_2(\eta^4$-2,4-cyclohexadien-1-one$)(P^iPr_3)_2$ (**3**): ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 5.13 (dd, J_{H-H} = 3.8, J_{H-H} = 5.1, 1H, C_6H_6O), 4.30 (dt, J_{H-P} = 4.8, J_{H-H} = 17.4, 1H, CH_2 C_6H_6O), 4.14 (dd, J_{H-H} = 3.8, J_{H-H} = 4.2, 1H, C_6H_6O), 3.77 (d, J_{H-H} = 5.1, 1H, $CHCO$ C_6H_6O), 3.09 (dd, J_{H-H} = 3.2, J_{H-H} = 17.4, 1H, CH_2 C_6H_6O), 2.76 (dd, J_{H-H} = 3.2, J_{H-H} = 4.2, 1H, =CHCH$_2$ C_6H_6O), 1.77 (m, 6H, PCH(CH$_3$)$_2$), 1.11 (dvt, J_{H-H} = 6.9, *N* = 13.8, PCH(CH_3)$_2$), 0.93 (dvt, J_{H-H} = 6.9, *N* = 12.6, PCH(CH_3)$_2$), −13.40 (t, J_{H-P} = 30.8, 2H, OsH). ^{1}H NMR (400 MHz, C_7D_8, 193 K, hydride region): δ −12.8 (br, 1H, Os−H), −15.7 (br, 1H, Os−H). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 298 K): δ 31.5 (s). ^{31}P{^{1}H} NMR (161.97 MHz, C_7D_8, 193 K): δ 33.6 (AB spin system, $\Delta\nu$ = 930 Hz, J_{A-B} = 661.0). ^{13}C{^{1}H} NMR plus HSQC and HMBC (75.5 MHz, C_6D_6, 298 K): δ 201.2 (s, *C*=O C_6H_6O), 72.0 (s, *C*H C_6H_6O), 68.6 (s, *C*H C_6H_6O), 56.6 (s, *C*H C_6H_6O), 34.7 (s, CH_2 C_6H_6O), 29.4 (s, *C*H C_6H_6O), 29.4 (vt, *N* = 27, PCH(CH$_3$)$_2$), 28.8 (s, CH, C_6H_6O), 20.7 and 20.4 (both s, PCH(CH_3)$_2$).

Reaction of $OsH_3Cl(P^iPr_3)_2$ (5) with NaOPh: Preparation of $OsH_3(OPh)(P^iPr_3)_2$ (2). A brown solution of **5** (100 mg, 0.18 mmol) in 10 mL of THF was treated with 5 equiv of sodium phenoxide (106 mg, 1.09 mmol) and stirred at room temperature for 20 min. The solvent was evaporated. The brown residue obtained was dissolved in toluene and filtered through Celite. The solution was evaporated to dryness and dissolved in pentane. The solvent was removed in vacuo, and a brown solid was obtained. Yield: 105 mg (96%). IR (cm^{-1}): ν(OsH) 2091 (w), ν(C=C) 1583 (m). ^{1}H NMR (300 MHz, C_7D_8, 298 K): δ 7.25 (m, 3H, *o*- and *p*-OPh), 6.77 (t, J_{H-H} = 7.2, 2H, *m*-OPh), 1.83 (m, 6H, PCH(CH$_3$)$_2$), 1.10 (dvt, J_{H-H} = 7.0, *N* = 13.1, 36H, PCH(CH_3)$_2$), −18.60 (t, J_{P-H} = 11.4, 3H, OsH_3). ^{31}P{^{1}H} NMR (121.48 MHz, C_7D_8, 298 K): δ 53.2 (s). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 298 K): δ 175.6 (s, C_{ipso} Ph), 128.8, 116.9 (both s, *C*H Ph), 27.3 (vt, *N* = 23.4, PCH(CH$_3$)$_2$), 20.7 (s, PCH(CH$_3$)$_2$). $T_{1(min)}$ (ms, OsH_3, 300 MHz, C_7D_8, 203 K): 133 ± 1.

Isomerization of 2 into 3. In a 5 mm NMR tube **2** (20 mg, 0.03 mmol) was dissolved in 0.4 mL of toluene, and the sample was monitored by ^{31}P{^{1}H} NMR periodically. After 48 h at room temperature the ^{31}P{^{1}H} NMR spectrum showed a 93:7 mixture of **2** and **3**.

Isomerization of 2 into 3 in the Presence of 3 equiv of Phenol. In a 5 mm NMR tube **2** (20 mg, 0.03 mmol) and phenol (9.3 mg, 0.098 mmol) were dissolved in 0.4 mL of toluene, and the sample was monitored by ^{31}P{^{1}H} NMR periodically. After 48 h at room temperature the ^{31}P{^{1}H} NMR spectrum showed a 33:67 mixture of **2** and **3**.

Isomerization of 2 into 3 in the Presence of 6 equiv of Phenol. In a 5 mm NMR tube **2** (20 mg, 0.03 mmol) and phenol (18.8 mg, 0.19 mmol) were dissolved in 0.4 mL of toluene, and the sample was monitored by ^{31}P{^{1}H} NMR periodically. After 48 h at room temperature the ^{31}P{^{1}H} NMR spectrum showed a 10:90 mixture of **2** and **3**.

Reaction of $OsH_6(P^iPr_3)_2$ with 6 equiv of PhOH: Preparation of $OsH(\eta^5$-PhO$)(P^iPr_3)_2\cdot 5$(PhOH) (4). A colorless solution of **1** (100 mg, 0.19 mmol) in 15 mL of toluene was treated with 6 equiv of phenol (108 mg, 1.14 mmol) and heated under reflux for 5 h. After this time, the resulting brown solution was filtered through Celite and the solvent was removed in vacuo to obtain a brown oil. Yield: 171 mg (93%). HRMS (electrospray, *m*/*z*): calcd for $C_{24}H_{49}OOsP_2$ $[M + H]^+$ 607.2869; found 607.2900. IR (cm^{-1}): ν(O−H) 3319 (br), ν(Os−H) 2087 (w), ν(C=O) 1593 (s), ν(C−O) 1227 (s). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.68 (br, 5H, PhOH), 7.14−7.05 (m, 20H, *o*- and *m*-PhOH), 6.78 (m, 5H, *p*-PhOH), 5.19 (d, J_{H-H} = 5.5, 2H, *o*-PhO), 5.00 (t, J_{H-H} = 5.5, 2H, *m*-PhO), 4.24 (t, J_{H-H} = 5.5, 1H, *p*-PhO), 1.80 (m, 6H, PCH(CH$_3$)$_2$), 0.96 (dvt, J_{H-H} = 7.0, *N* = 12.3, 18H, PCH(CH_3)$_2$), 0.92 (dvt, J_{H-H} = 7.0, *N* = 12.3, 18H, PCH(CH_3)$_2$), −14.20 (t, J_{P-H} = 33.5, 1H, OsH). ^{31}P{^{1}H} NMR (121.48 MHz, C_6D_6, 298 K): δ 15.4 (s). ^{13}C{^{1}H} NMR plus HSQC (75.5 MHz, C_6D_6, 298 K): δ 161.4 (s, C=O), 157.5 (s, C_{ipso} PhOH), 129.8, 119.9, 116.1 (all s, *C*H PhOH), 85.7 (s, *m*-C_6H_5O), 68.7 (s, *o*-C_6H_5O), 68.2 (s, *p*-C_6H_5O), 29.5 (vt, *N* = 20.2, PCH(CH$_3$)$_2$), 29.2 (vt, *N* = 19.4, PCH(CH$_3$)$_2$), 20.7 and 20.4 (both s, PCH(CH_3)$_2$).

Reaction of $OsH(\eta^5$-PhO$)(P^iPr_3)_2\cdot 5$(PhOH) with HBF_4: Formation of $[OsH(\eta^6$-PhOH$)(P^iPr_3)_2]BF_4$ (6). A dark yellow solution of **4** (100 mg, 0.09 mmol) in diethyl ether (10 mL) was treated with 1 equiv of $HBF_4\cdot OEt_2$ (13 μL, 0.09 mmol) and stirred for 30 min at room temperature. During the course of the reaction a white solid appeared. The solvent was removed, and the solid was washed with diethyl ether (3 × 5 mL) and dried in vacuo. Yield: 95 mg (71%). Anal. Calcd for $C_{24}H_{49}BF_4OOsP_2$: C, 41.62; H, 7.13. Found: C, 41.47; H,

7.24. IR (cm^{-1}): ν(O−H) 3290 (br), ν(Os−H) 2109 (w), $\nu(BF_4)$ 1054 (vs). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.21 (br, 1H, −OH), 5.59 (t, J_{H-H} = 5.5, 2H, *m*-PhOH), 5.56 (d, J_{H-H} = 5.5, 2H, *o*-PhOH), 5.49 (t, J_{H-H} = 5.5, 1H, *p*-PhOH), 2.16 (m, 6H, PC*H*$(CH_3)_2$), 1.28 (dvt, J_{H-H} = 8.1, *N* = 13.1, 18H, PCH(C*H*$_3)_2$), 1.23 (dvt, J_{H-H} = 8.2, *N* = 13.3, 18H, PCH(C*H*$_3)_2$), −12.95 (t, J_{P-H} = 36.6, 1H, OsH). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 298 K): δ 13.7 (s). ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2, 298 K): δ 137.1 (s, *C*OH), 83.4 (s, *C*H *m*-PhOH), 75.5 (s, *C*H *p*-PhOH), 67.4 (t, J_{C-P} = 2.2, *C*H *o*-PhOH), 29.9 (vt, *N* = 24.2, PCH$(CH_3)_2$), 29.6 (vt, *N* = 22.9, PCH$(CH_3)_2$), 20.6 and 20.4 (both s, PCH$(CH_3)_2$).

Reaction of [OsH(η^6-C_6H_5OH)(P^iPr_3)$_2$]BF_4 with K^{t}BuO: Formation of [OsH(η^5-PhO)(P^iPr_3)$_2$]. A solution of [OsH(η^6-C_6H_5OH)(P^iPr_3)$_2$]BF_4 (**6**) (100 mg, 0.14 mmol) in THF (5 mL) was treated with 1.2 equiv of K^{t}BuO (19.6 mg, 0.17 mmol). After stirring for 20 min at room temperature, the resulting suspension was filtered through Celite, and the solution was taken to dryness, affording a brown oil. Yield: 64 mg (73%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 5.12 (t, J_{H-H} = 5.9, 2H, *m*-PhO), 4.93 (d, J_{H-H} = 5.9, 2H, *o*-PhO), 4.09 (t, J_{H-H} = 5.9, 1H, *p*-PhO), 2.03 (m, 6H, PC*H*$(CH_3)_2$), 1.04 (dvt, J_{H-H} = 7.0, *N* = 12.5, 18H, PCH(C*H*$_3)_2$), 0.98 (dvt, J_{H-H} = 7.1, *N* = 12.5, 18H, PCH(C*H*$_3)_2$), −15.13 (t, J_{P-H} = 33.1, 1H, OsH). ^{31}P{^{1}H} NMR (121.48 MHz, C_6D_6, 298 K): δ 17.2 (s).

Reaction of [OsH(η^6-C_6H_5OH)(P^iPr_3)$_2$]BF_4 with NaOPh: Formation of [OsH(η^5-PhO)(P^iPr_3)$_2$]·HOPh. A solution of [OsH(η^6-C_6H_5OH)(P^iPr_3)$_2$]BF_4 (**6**) (100 mg, 0.14 mmol) in THF (5 mL) was treated with 1.1 equiv of PhONa (17.8 mg, 0.15 mmol). After stirring for 20 min at room temperature, the resulting suspension was filtered through Celite and the solution was taken to dryness, affording a brown oil. Yield: 73.4 mg (75%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.31 (d, J_{H-H} = 7.5, 2H, *o*-PhOH), 7.19 (t, J_{H-H} = 7.5, 2H, *m*-PhOH), 6.79 (t, J_{H-H} = 7.5, 1H, *p*-PhOH), 5.11 (t, J_{H-H} = 5.7, 2H, *m*-PhO), 5.03 (d, J_{H-H} = 5.7, 2H, *o*-PhO), 4.14 (t, J_{H-H} = 5.7, 1H, *p*-PhO), 1.98 (m, 6H, PC*H*$(CH_3)_2$), 1.04 (dvt, J_{H-H} = 7.1, *N* = 12.5, 18H, PCH(C*H*$_3)_2$), 0.98 (dvt, J_{H-H} = 7.1, *N* = 12.4, 18H, PCH(C*H*$_3)_2$), −14.82 (t, J_{P-H} = 33.4, 1H, OsH). ^{31}P{^{1}H} NMR (121.48 MHz, C_6D_6, 298 K): δ 15.4 (s).

Addition of Phenol to [OsH(η^5-PhO)(P^iPr_3)$_2$]·HOPh. In a 5 mm NMR tube [OsH(η^5-PhO)(P^iPr_3)$_2$]·HOPh (20 mg, 0.03 mmol) was dissolved in 0.4 mL of benzene-d_6. To this solution were added sequentially up to 10 equiv of PhOH (8.78 M in benzene-d_6), and the ^{1}H NMR spectrum was recorded after the addition of each equivalent.

Reaction of $OsH_6(P^iPr_3)_2$ with Pyrrole: Formation of OsH(η^5-C_4H_4N)(P^iPr_3)$_2$ (7). A colorless solution of **1** (100 mg, 0.193 mmol) in toluene (10 mL) was treated with 6 equiv of pyrrole (80 μL, 1.14 mmol) and heated under reflux for 7 h. The resulting yellow solution was taken to dryness, and the yellow residue was dissolved in pentane (20 mL) and filtered through Celite. Slow evaporation of pentane caused the precipitation of a beige solid, which was washed with pentane (2 × 2 mL) and dried in vacuo. Yield: 61.0 mg (55%). Anal. Calcd for $C_{22}H_{47}NOsP_2$: C, 45.73; H, 8.20; N, 2.42. Found: C, 45.94; H, 7.52; N, 2.22. IR (cm^{-1}): ν(OsH) 2077 (m). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 5.88 (s, 2H, C_4H_4N), 4.85 (s, 2H, C_4H_4N), 1.93 (m, 6H, PC*H*$(CH_3)_2$), 1.16 (dd, J_{H-H} = 7.2, J_{P-H} = 15.8, 18H, PCH(C*H*$_3)_2$), 1.12 (dd, J_{H-H} = 7.2, J_{P-H} = 15.8, 18H, PCH(C*H*$_3)_2$), −18.88 (t, J_{P-H} = 29.8, 1H, OsH). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K): δ 27.7 (s). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 98.7 (t, J_{P-C} = 1.5, C_4H_4N), 72.5 (t, J_{P-C} = 2.6, C_4H_4N), 30.6 (d, J_{P-C} = 25.3, PCH$(CH_3)_2$), 20.8, 20.5 (both s, PCH$(CH_3)_2$).

Reaction of OsH(η^5-C_4H_4N)(P^iPr_3)$_2$ with HBF_4: Formation of [OsH_2(η^5-C_4H_4N)(P^iPr_3)$_2$]BF_4 (8). A colorless solution of **7** (100 mg, 0.173 mmol) in diethyl ether (10 mL) was treated with 1 equiv of HBF_4·OEt_2 (23.5 μL, 0.173 mmol) and stirred for 30 min at room temperature. During the course of the reaction a white solid formed. The solvent was removed, and the solid was washed with further portions of diethyl ether and dried in vacuo. Yield: 95.6 mg (83%). Anal. Calcd for $C_{22}H_{48}BF_4NOsP_2$: C, 39.69; H, 7.27; N, 2.10. Found: C, 39.42; H, 7.33; N, 1.72. IR (cm^{-1}): ν(OsH) 2152 (w); $\nu(BF_4)$ 1052−1030 (vs). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 6.60 (s, 2H, C_4H_4N), 6.02 (s, 2H, C_4H_4N), 2.12 (m, 6H, PC*H*$(CH_3)_2$), 1.27 (dvt, J_{H-H} = 7.2, *N* = 14, 36 H, PCH(C*H*$_3)_2$), −14.50 (t, J_{P-H} = 28.6, 2H, OsH_2). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 33.9 (s). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 298 K): δ 104.7 (s, C_4H_4N), 90.4 (s, C_4H_4N), 30.3 (vt, *N* = 30.3, PCH$(CH_3)_2$), 19.6 (s, PCH$(CH_3)_2$). $T_{1(min)}$ (ms, OsH_2, 400 MHz, CD_2Cl_2, 223 K): 325 ± 1.

Reaction of $OsH_6(P^iPr_3)_2$ with Methylcyclopentadiene: Formation of OsH(η^5-C_5H_4Me)(P^iPr_3)$_2$ (9). A solution of **1** (100 mg, 0.19 mmol) in toluene (10 mL) was treated with 6 equiv of freshly distilled methylcyclopentadiene (198 μL, 1.14 mmol) and heated under reflux for 2 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo, obtaining a pale yellow oil. Yield: 83 mg (74%). HRMS (electrospray, *m*/*z*): calcd for $C_{24}H_{51}OsP_2$ $[M + H]^+$ 593.3076; found 593.3047. IR (cm^{-1}): ν(Os−H) 2069 (m). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 4.76 (s, 2H, C_5H_4Me), 4.08 (s, 2H, C_5H_4Me), 2.35 (s, 3H, CH_3), 1.98 (m, 6H, PC*H*$(CH_3)_2$), 1.18 (dvt, J_{H-H} = 7, *N* = 15, 18H, PCH(C*H*$_3)_2$), 1.15 (dvt, J_{H-H} = 7, *N* = 15, 18H, PCH(C*H*$_3)_2$), −15.66 (t, J_{P-H} = 30.2, 1H, Os−H). ^{31}P{^{1}H} NMR (121.48 MHz, C_6D_6, 298 K): δ 28.9 (s). ^{13}C{^{1}H} (75.4 MHz, C_6D_6, 298 K): δ 90.7 (s, *C*Me C_5H_4Me), 72.4 (s, *C*H C_5H_4Me), 70.1 (m, *C*H C_5H_4Me), 31.3 (d, J_{C-P} = 24.5, PCH), 20.9 and 20.8 (both s, PCH$(CH_3)_2$), 16.1 (s, CH_3).

Reaction of OsH(η^5-C_5H_4Me)(P^iPr_3)$_2$ with HBF_4: Formation of [OsH_2(η^5-C_5H_4Me)(P^iPr_3)$_2$]BF_4 (10). A solution of **9** (112 mg, 0.19 mmol) in diethyl ether (10 mL) was treated with 1.2 equiv of HBF_4·OEt_2 (32 μL, 0.23 mmol). Immediately a white solid appeared. The mixture was stirred at room temperature for 15 min; the solid was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 97 mg (75%). Anal. Calcd for $C_{24}H_{51}BF_4OsP_2$: C, 42.48; H, 7.57. Found: C, 42.62; H, 7.79. HRMS (electrospray, *m*/*z*): calcd for $C_{24}H_{51}OsP_2$ $[M]^+$ 593.3076, found 593.3109. IR (cm^{-1}): ν(Os−H) 2150, 2105 (m); $\nu(BF_4)$ 1059−1029 (vs). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 5.35 (s, 2H, C_5H_4Me), 5.19 (s, 2H, C_5H_4Me), 2.37 (s, 3H, C_5H_4Me), 2.10 (m, 6H, PC*H*$(CH_3)_2$), 1.28 (dvt, J_{H-H} = 7.1, *N* = 13.9, PCH(C*H*$_3)_2$), −14.14 (t, J_{P-H} = 29.2, 2H, Os−H). ^{31}P{^{1}H} NMR (121.48 MHz, C_6D_6, 298 K): δ 32.1 (s). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 298 K): δ 108.2 (s, *C*Me C_5H_4Me), 85.5 (t, J_{P-C} = 1.8, *C*H C_5H_4Me), 77.0 (s, *C*H C_5H_4Me), 30.7 (vt, *N* = 31.7, PCH$(CH_3)_2$), 30.33 (vt, *N* = 30.9, PCH$(CH_3)_2$), 19.7 (s, PCH$(CH_3)_2$), 14.3 (s, C_5H_4Me). T_1 (ms, 300 MHz, CD_2Cl_2, OsH_2): 662 ± 1 (253 K), 609 ± 1 (243 K), 526 ± 1 (233 K), 440 ± 1 (223 K), 370 ± 1 (213 K), 297 ± 1 (203 K), 246 ± 1 (193 K), 221 ± 1 (183 K).

Reaction of $OsH_6(P^iPr_3)_2$ with Tetramethylcyclopentadiene in Toluene: Formation of OsH_3(η^5-C_5HMe_4)(P^iPr_3) (11), OsH_2(*m*-tolyl)(η^5-C_5HMe_4)(P^iPr_3) (12), and OsH_2(*p*-tolyl)(η^5-C_5HMe_4)(P^iPr_3) (13). A solution of **1** (100 mg, 0.19 mmol) in 10 mL of toluene was treated with 6 equiv of tetramethylcyclopentadiene (206 μL, 1.14 mmol) and heated under reflux for 5 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo, obtaining a pale yellow oil. ^{1}H and ^{31}P{^{1}H} NMR spectra recorded in C_6D_6 show a mixture of OsH_3(η^5-C_5HMe_4)(P^iPr_3) (**11**), OsH_2(*m*-tolyl)(η^5-C_5HMe_4)(P^iPr_3) (**12**), and OsH_2(*p*-tolyl)(η^5-C_5HMe_4)(P^iPr_3) (**13**) in a ratio of 56:14:30.

Spectroscopic data for OsH_2(*m*-tolyl)(η^5-C_5HMe_4)(P^iPr_3) (**12**): ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.78 (s, 1H, *m*-tolyl), 7.71 (d, J_{H-H} = 7.5, 1H, *m*-tolyl), 6.93 (t, J_{H-H} = 7.5, 1H, *m*-tolyl), 6.85 (d, J_{H-H} = 7.5, 1H, *m*-tolyl), 4.49 (s, 1H, C_5HMe_4), 2.34 (s, 3H, CH_3 *m*-tolyl), 1.88 (s, 6H, C_5HMe_4), 1.72 (s, 6H, C_5HMe_4), 1.81 (m, 3H, PC*H*$(CH_3)_2$), 1.06 (dd, J_{H-P} = 13.8, J_{H-H} = 7.3, 18H, PCH(C*H*$_3)_2$), −12.69 (d, J_{H-P} = 37,

2H, Os−H). $^{31}P\{^1H\}$ NMR (121.48 MHz, C_6D_6, 298 K): δ 42.4 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 298 K): δ 164.1 (s, C_{ipso} *m*-tolyl), 151.1 (s, C_{ortho} *m*-tolyl), 147.5 (s, C_{ortho} *m*-tolyl), 128.3 (s, C_{para} *m*-tolyl), 127.2 (s, C_{meta} *m*-tolyl), 119.9 (s, C_{meta} *m*-tolyl), 94.8 (d, J_{P-C} = 4.4, *C*Me C_5HMe_4), 91.1 (d, J_{P-C} = 0.7, *C*Me C_5HMe_4), 77.4 (s, *C*H C_5HMe_4), 29.1 (d, J_{C-P} = 30.6, P*C*H$(CH_3)_2$), 23.4 (s, *C*H$_3$, *m*-tolyl), 19.6 (s, PCH(*C*H$_3)_2$), 13.0 and 10.2 (both s, C_5HMe_4).

Spectroscopic data for OsH_2(*p*-tolyl)(η^5-C_5HMe_4)(P^iPr_3) (**13**): ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.79 (d, J_{H-H} = 7.2, 2H, *p*-tolyl), 6.77 (d, J_{H-H} = 7.2, 2H, *p*-tolyl), 4.51 (s, 1H, C_5HMe_4), 2.35 (s, 3H, CH$_3$ *p*-tolyl), 1.88 (s, 6H, C_5HMe_4), 1.72 (s, 6H, C_5HMe_4), 1.81 (m, 3H, PC*H*$(CH_3)_2$), 1.11 (dd, J_{H-P} = 13.2, J_{H-H} = 7.1, 18H, PCH$(CH_3)_2$), −12.65 (d, J_{H-P} = 37, 2H, Os−H). $^{31}P\{^1H\}$ NMR (121.48 MHz, C_6D_6, 298 K): δ 42.3 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 298 K): δ 157.8 (s, C_{ipso} *p*-tolyl), 150.0 (s, C_{orto} *p*-tolyl), 121.4 (s, C_{meta} *p*-tolyl), 119.6 (s, C_{para} *p*-tolyl), 94.9 (d, J_{P-C} = 4.5, *C*Me C_5HMe_4), 91.1 (d, J_{P-C} = 0.7, *C*Me C_5HMe_4), 77.4 (s, *C*H C_5HMe_4), 29.1 (d, J_{C-P} = 30.6, P*C*H$(CH_3)_2$), 23.1 (s, *C*H$_3$, *m*-tolyl), 19.6 (s, PCH(*C*H$_3)_2$), 13.0 and 10.2 (both s, C_5HMe_4)

Reaction of $OsH_6(P^iPr_3)_2$ with Tetramethylcyclopentadiene in *n*-Octane: Formation of $OsH_3(\eta^5$-$C_5HMe_4)(P^iPr_3)$ (11). A solution of **1** (100 mg, 0.19 mmol) in 10 mL of *n*-octane was treated with 6 equiv of tetramethylcyclopentadiene (206 μL, 1.14 mmol) and heated under reflux for 4 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo, resulting in a pale yellow oil. Yield: 78 mg (85%). HRMS (electrospray, *m*/*z*): calcd for $C_{18}H_{34}OsP$ $[M - 3H]^+$ 473.2008; found 473.2070. IR (cm^{-1}): ν(Os−H) 2075 (m). ^1H NMR (300 MHz, C_6D_6, 298 K): δ 4.80 (s, 1H, C_5HMe_4), 2.14 (s, 6H, C_5HMe_4), 2.10 (s, 6H, C_5HMe_4), 1.71 (m, 3H, PC*H*$(CH_3)_2$), 1.01 (dd, J_{H-H} = 6.9, J_{H-P} = 13.1, 18H, PCH(*C*H$_3)_2$), −14.06 (br, 1H, Os−$H_{trans\ to\ P}$), −14.85 (d, J_{H-P} = 32.6, 2H, Os−$H_{cis\ to\ P}$). $^1H\{^{31}P\}$ NMR (300 MHz, C_7D_8, 183 K, hydride region): δ −14.01 (br, 1H, OsH), −14.85 (br, 1H, OsH), −14.87 (br, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.48 MHz, C_6D_6, 298 K): δ 50.5 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 298 K): δ 92.4 (d, J_{P-C} = 4, *C*Me C_5HMe_4), 90.7 (d, J_{P-C} = 1, *C*Me C_5HMe_4), 77.8 (s, *C*H C_5HMe_4), 29.3 (d, J_{C-P} = 29.4, PCH$(CH_3)_2$), 20.4 (s, PCH(*C*H$_3)_2$), 14.2 and 12.7 (both s, C_5HMe_4). $T_{1(min)}$ (ms, 300 MHz, tol-d_8): 203 ± 1 (193 K).

Reaction of $OsH_6(P^iPr_3)_2$ with Pentamethylcyclopentadiene: Formation of $OsH_3(\eta^5$-$C_5Me_5)(P^iPr_3)$ (14). A colorless solution of **1** (100 mg, 0.19 mmol) in toluene (10 mL) was treated with 6 equiv of pentamethylcyclopentadiene (181 μL, 1.16 mmol) and heated under reflux during 24 h. The resulting dark yellow solution was filtered through Celite, and the solvent was removed *in vacuo*, producing a pale yellow oil. Yield: 75 mg (80%). HRMS (electrospray, *m*/*z*): calcd for $C_{19}H_{36}OsP$ [M − 3H] 487.2164; found 487.2225. IR (cm^{-1}): ν(OH) 2085 (m). ^1H NMR (300 MHz, C_6D_6, 298 K): δ 2.11 (s, 15H, C_5Me_5), 1.70 (m, 3H, PC*H*$(CH_3)_2$), 1.01 (dd, J_{H-H} = 7.0, J_{P-H} = 13, 18H, PCH(*C*H$_3)_2$), −14.47 (br, 1H, Os−$H_{trans\ to\ P}$), −14.82 (d, J_{H-P} = 33.3, 2H, Os−$H_{cis\ to\ P}$). $^{31}P\{^1H\}$ NMR (121.48 MHz, C_6D_6, 298 K): δ 47.3 (s). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 298 K): δ 90.6 (d, J_{C-P} = 2.2, C_5Me_5), 29.3 (d, J_{C-P} = 28.6, PCH$(CH_3)_2$), 20.3 (s, PCH(*C*H$_3)_2$), 12.8 (s, C_5Me_5). $T_{1(min)}$ (ms, 500 MHz, tol-d_8): 230 ± 1 (208 K).

Structural Analysis of Complexes 2 and 7. Crystals suitable for X-ray diffraction were obtained by cooling (−30 °C) a solution of pentane (**2**) and by slow diffusion of methanol into concentrated solutions of the complex in toluene (**7**). X-ray data were collected on a Bruker Smart APEX CCD diffractometer 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. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[28] The structures were solved by the Patterson (Os atom of **2** and **7**) method and conventional Fourier techniques and refined by full-matrix least-squares on F^2 with SHELXL97.[29] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model. Hydride ligands were observed in the difference Fourier maps but refined with a restrained Os−H bond length (1.59(1) Å, CSD). For all structures the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense.

Crystal data for **2**: $C_{24}H_{50}OOsP_2$, MW 606.78, brown, prism (0.10 × 0.04 × 0.02), monoclinic, space group *P*2(1)/*c*, *a*: 8.965(3) Å, *b*: 40.469(11) Å, *c*: 8.409(2) Å, α: 90.00°, β: 115.301(4)°, γ: 90.00°, *V* = 2758.2(13) Å^3, *Z* = 4, D_{calc}: 1.461 g cm^{-3}, *F*(000): 1232, *T* = 120(2) K, μ 4.751 mm^{-1}; 33 823 measured reflections (2θ: 2−58°, ω scans 0.3°), 6738 unique (R_{int} = 0.0894); minimum/maximum transmission factors 0.631/0.829. Final agreement factors were R_1 = 0.0356 (3968 observed reflections, $I > 2\sigma(I)$) and wR_2 = 0.0482; data/restraints/parameters 6738/4/275; GoF = 0.675. Largest peak and hole 0.880 and −1.445 e/Å^3.

Crystal data for **7**: $C_{22}H_{47}NOsP_2$, MW 577.75, colorless, prism (0.08 × 0.08 × 0.06), monoclinic, space group *P*2(1)/*c*, *a*: 12.589(4) Å, *b*: 11.559(4) Å, *c*: 16.492(6) Å, α: 90.00°, β: 96.380(6)°, γ: 90.00°, *V* = 2385.1(14) Å^3, *Z* = 4, D_{calc}: 1.609 g cm^{-3}, *F*(000): 1168, *T* = 120(2) K, μ 5.488 mm^{-1}; 28 346 measured reflections (2θ: 3−58°, ω scans 0.3°), 5974 unique (R_{int} = 0.0628); minimum/maximum transmission factors 0.565/0.688. Final agreement factors were R_1 = 0.0500 (5094 observed reflections, $I > 2\sigma(I)$) and wR_2 = 0.1067; data/restraints/parameters 5974/1/266; GoF = 1.133. Largest peak and hole 7.519 and −2.453 e/Å^3

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **2** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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