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# Reactions of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ with $NH{=}CPh_2$ and $PPh_3$: The Unit $Os(\eta^5\text{-}C_5H_5)(P^iPr_3)$ as Support for the Study of the Competitive Alkane−Arene Intramolecular C−H Activation

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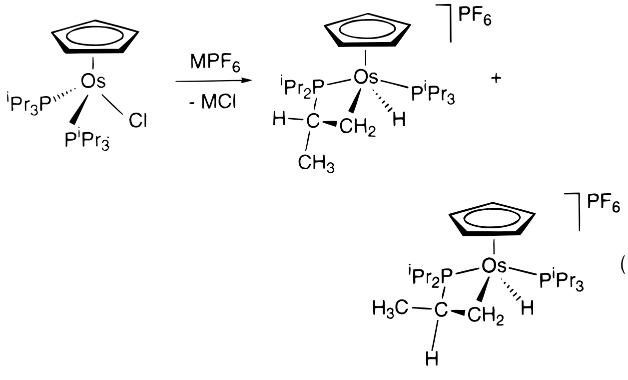
The cyclopentadienyl complex $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) reacts with benzophenone imine to give the cationic orthometalated derivative $[\overline{OsH(\eta^5\text{-}C_5H_5)\{NH{=}C(Ph)C}_6H_4\}(P^iPr_3)]Cl$ (**2a**), containing the hydride ligand and the metalated phenyl group mutually *cisoid* disposed. Treatment of **2a** with $NaOCH_3$ affords the neutral species $\overline{Os(\eta^5\text{-}C_5H_5)\{NH{=}C(Ph)C}_6H_4\}$-$(P^iPr_3)$ (**3**), which by protonation with $HBF_4{\cdot}OEt_2$ gives $[\overline{OsH(\eta^5\text{-}C_5H_5)\{NH{=}C(Ph)C}_6H_4\}$-$(P^iPr_3)]BF_4$ (**4**). The structure of **4** was determined by an X-ray investigation. The geometry around the osmium center can be described as a four-legged piano-stool geometry, with the hydride ligand *transoid* disposed to the metalated phenyl group and *cisoid* to the NH of the imine. The separation between the hydride and the NH hydrogen atom is about 2.5 Å. Complex **1** also reacts with triphenylphosphine. In this case the reaction product is the mixed-ligand compound $Os(\eta^5\text{-}C_5H_5)Cl(PPh_3)(P^iPr_3)$ (**5**). Treatment of **5** with $TlPF_6$ affords the orthometalated triphenylphosphine derivative $[\overline{OsH(\eta^5\text{-}C_5H_5)(PPh_2C}_6H_4\}(P^iPr_3)]PF_6$ (**6**). The structure of **6** was also determined by an X-ray investigation. As for **4**, the geometry around the osmium center can be described as a four-legged piano-stool geometry with the hydride ligand and the metalated phenyl group in *transoid* positions. Treatment of **6** with $NaOCH_3$ produces the extraction of the hydride ligand and the formation of the neutral species $\overline{Os(\eta^5\text{-}C_5H_5)(PPh_2C}_6H_4)(P^iPr_3)$ (**7**), which in methanol under reflux gives $OsH(\eta^5\text{-}C_5H_5)(PPh_3)$-$(P^iPr_3)$ (**8**). Protonation of **8** with $HBF_4{\cdot}OEt_2$ affords the cationic dihydride $[OsH_2(\eta^5\text{-}C_5H_5)(PPh_3)(P^iPr_3)]BF_4$ (**9**).

## Introduction

We have recently reported the synthesis of the half-sandwich compound $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$, which is a labile starting material for the development of new cyclopentadienyl−osmium chemistry.[1] Thus, in pentane and toluene, the splitting of an Os−P bond takes place, and the reactions of this complex with olefins and alkynes afford chloro $\pi$-olefin and $\pi$-alkyne derivatives.[1b,d] On the other hand, in polar solvents such as methanol and acetone, the dissociation of the chlorine ligand occurs, and the resulting fragment is capable of activating a methyl C−H bond of a triisopropylphosphine to give $[\overline{OsH(\eta^5\text{-}C_5H_5)\{CH_2CH(CH_3)P}^iPr_2\}(PiPr_3)]^+$, as a mixture of two pairs of diasteroisomers (eq 1).



(1)

Tilley and co-workers[2] have also observed that the bis(triphenylphosphine) derivative $Os(\eta^5\text{-}C_5H_5)(OTf)(PPh_3)_2$ evolves, in a similar way, into the orthometalated species $[\overline{OsH(\eta^5\text{-}C_5H_5)(PPh_2C}_6H_4)(PPh_3)]OTf$ in dichlo-

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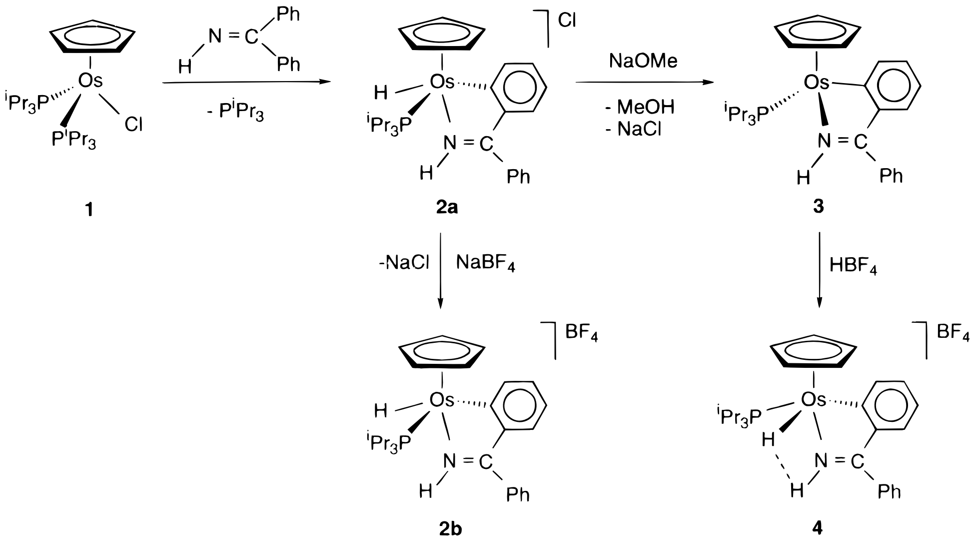
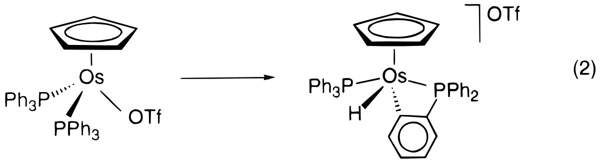
10.1021/om990538h CCC: $19.00

**Scheme 1**



romethane and in the solid state under nitrogen (eq 2).



(2)

The activation of C−H bonds by transition-metal compounds has attracted a great deal of attention in recent years,[3] in particular the selectivity of the competitive alkane−arene intermolecular activation.[4] Although the arene C−H bond is between 14 and 8 kcal·mol$^{-1}$ stronger than the alkane C−H bond, in general, the activation of the first one is kinetically and thermodynamically favored. The kinetic advantange of the arene activation appears to be due to its prior $\pi$-coordination, while the thermodynamic preference has been largely attributed to a metal−carbon bond much stronger for aryl than for alkyl.

The selectivity of the competitive alkane−arene intramolecular C−H activation is much less clear. In examining the numerous examples of cyclometalations,[5] one finds that is not easy to conclude about the arene or alkane preference, because many variables are being changed at the same time.

The lability of an Os−P bond of the complex Os($\eta^5$-$C_5H_5$)Cl(P$^i$Pr$_3$)$_2$ makes this compound a suitable candidate to generate mixed-ligand fragments of the type [Os($\eta^5$-$C_5H_5$)(LPh)(P$^i$Pr$_3$)]$^+$, which have the same metal−ligand system to activate, in a competitive manner, the isopropyl or alternatively the phenyl group of the corresponding P$^i$Pr$_3$ and LPh ligands.

This paper shows the selective arene intramolecular C−H activation in the mixed-ligand fragments [Os($\eta^5$-$C_5H_5$)(NH=CPh$_2$)(P$^i$Pr$_3$)]$^+$ and [Os($\eta^5$-$C_5H_5$)(PPh$_3$)(P$^i$Pr$_3$)]$^+$. In addition, we report a new example of H···H interaction in a four-membered LH···H−M ring. Of great importance in biological and organic chemistry,[6] the hydrogen bonding is presently attracting considerable interest in the chemistry of transition metals.[7]

## Results and Discussion

**1. C−H Activation of a Phenyl Group of Benzophenone Imine.** Treatment at room temperature of pentane suspensions of Os($\eta^5$-$C_5H_5$)Cl(P$^i$Pr$_3$)$_2$ (**1**) with 1 equiv of benzophenone imine affords after 2 h the cationic orthometalated complex [OsH($\eta^5$-$C_5H_5$)-{NH=C(Ph)$C_6H_4$}(P$^i$Pr$_3$)]Cl (**2a**), which was isolated as a yellow solid in 85% yield. The [BF$_4$]$^-$ salt (**2b**) was obtained by addition of sodium tetrafluoroborate to a tetrahydrofurane solution of **2a** (Scheme 1).

The formation of **2a** is a result of the selective C−H activation of a phenyl group of the imine. The higher

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stability of the five-membered rings with regard to the four-membered rings could explain why the aryl group of the benzophenone imine is selectivily activated in the presence of the isopropyl group of the triisopropylphosphine. The previously mentioned greater strength of the metal−aryl bonds with regard to the metal−alkyl bonds does not seem to be a determinant factor of the process. Thus, it has been previously observed that the reaction of $[Pd(OAc)_2]_3$ with *N*,*N*-dimethyl-*o*-toluidine gives $[Pd(\mu\text{-}OAc)\{CH_2C_6H_4N(CH_3)_2\}]_2$ as a consequence of the metalation of the ortho-methyl group of the amine.[8]

In addition, it should be mentioned that complex **2a** is reminiscent of the intermediates proposed by Murai for the insertion of olefins into aromatic C−H bonds located in ortho position relative to a coordinating group such as ketone, imine, or pyridine.[9]

The $^1$H NMR spectra of **2a** and **2b** are consistent with a four-legged piano-stool structure with the hydride *cisoid* to the triisopropylphosphine ligand. Thus, they show at −12.98 (**2a**) and −12.96 (**2b**) ppm doublets with a H−P coupling constant of 38 Hz, which agrees well with those found in the dihydride−silyl derivative $RuH_2(\eta^5\text{-}C_5Me_5)(SiMePh_2)(P^iPr_3)$ (29 Hz)[10] and in the dihydride cations $[RuH_2(\eta^5\text{-}C_5Me_5)(PMe_3)_2]^+$ (33 Hz),[11] $[RuH_2(\eta^5\text{-}C_5H_5)(PMe_3)_2]^+$ (29 Hz),[12] $[OsH_2(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ (32.2 Hz),[1b] and $[OsH_2(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ (29.0 Hz),[13] where hydride and phosphine ligands mutually *cisoid* have also been proposed. The resonance corresponding to the NH proton appears as a broad singlet at 12.81 ppm in the spectrum of **2a** and at 11.09 ppm in the spectrum of **2b**. The $^{13}C\{^1H\}$ NMR spectra are consistent with the presence of a heterometallacycle in these species. The coordination of the nitrogen atom of the imine is supported by the multiplicity of the resonance due to the C=N carbon atom, which appears as a doublet with a C−P coupling constant of approximately 3 Hz, at about 190 ppm. The resonance of the Os−C carbon atom of the metalated phenyl group is observed at about 165 ppm as a doublet with a C−P coupling constant of about 4 Hz. The chemical shifts of these resonances agree well with those previously observed for related compounds.[14]

Complex **2** can be deprotonated by reaction with sodium methoxide. The addition of this base to tetrahydrofurane solutions of **2a** gives rise to the formation of the neutral compound $Os(\eta^5\text{-}C_5H_5)\{NH{=}C(Ph)C_6H_4\}(P^iPr_3)$ (**3**) (Scheme 1), as a result of the extraction of the hydride ligand. Complex **3**, which is a green, extremely air-sensitive solid, was isolated in 81% yield.

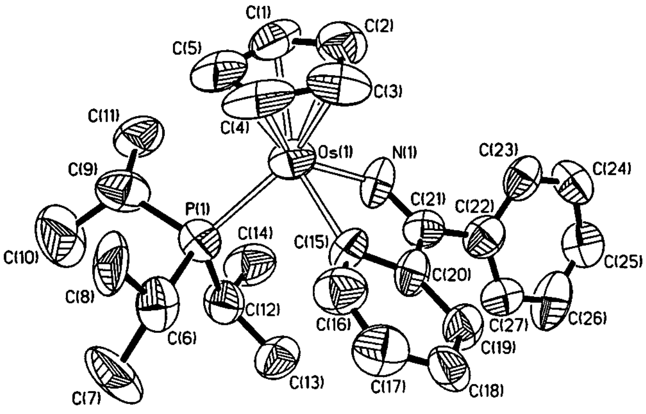

**Figure 1.** Molecular diagram of the cation of **4**, $[OsH(\eta^5\text{-}C_5H_5)\{NH{=}C(Ph)C_6H_4\}(P^iPr_3)]^+$. Thermal ellipsoids are shown at 50% probability.

In the $^1$H NMR spectrum of **3** the most noticeable features are the presence of a broad singlet at 9.96 ppm, corresponding to the NH hydrogen atom, and the absence of any hydride resonance. The $^{13}C\{^1H\}$ NMR spectrum agrees well with those of **2a** and **2b**. The C=N resonance appears at 184.5 ppm, as a doublet with a C−P coupling constant of 2.8 Hz, whereas the Os−C resonance is observed at 186.0 ppm, also as a doublet but with a C−P coupling constant of 7.8 Hz.

Although the protonation of **3** affords a hydride derivative, the deprotonation of **2** is not reversible. The addition of 1 equiv of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of **3** produces **4** (Scheme 1), an isomer of **2b**, which contains the hydride ligand and the nitrogen atom of the imine group in *cisoid* positions instead of *transoid* as in **2b**. Complex **4** was isolated as a brown solid in 92% yield.

The X-ray analysis of a crystal of **4** shows two independent, but chemically equivalent molecules in the asymmetric unit (A and C enatiomers). A view of the molecular geometry of the A enatiomer of **4** is shown in Figure 1. Selected bond distances and angles are listed in Table 1. Although the hydride ligand and the NH hydrogen atom could not be located, the presence of these atoms in the complex is supported by the $^{31}P\{^1H\}$ and $^1$H NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 18.9 ppm, which is split into a doublet under off-resonance conditions, as a result of the coupling with the hydride ligand. In the $^1$H NMR spectrum the NH resonance appears at 11.24 ppm as a broad signal, and the hydride resonance is observed at −11.92 ppm as a double doublet by spin coupling with the phosphorus nucleus of the phoshine ligand [$J$(HP) = 41.7 Hz] and the NH hydrogen atom [$J$(HH) = 4.1 Hz]. The last coupling was confirmed by the $^1$H COSY spectrum.

The distribution of ligands around the osmium atom can be described as a four-legged piano-stool geometry, with the cyclopentadienyl ligand occupying the three-membered face, while the phoshine, hydride, and ortho-metalated benzophenone imine ligands lie in the four-membered face. The phosphine ligand is disposed *transoid* to the N(1) nitrogen atom of the imine group [P(1)−Os−N(1) = 106.5(6)° (molecule **a**) and 103.9(5)° (molecule **b**)], *cisoid* to the metalated C(15) carbon atom [P(1)−Os−C(15) = 87.9(7)° (**a**) and 87.8(6)° (**b**)] and, in

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**Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $[OsH(\eta^5\text{-}C_5H_5)\{NH{=}C(Ph)C_6H_4\}(P^iPr_3)]BF_4$ (4)**

| molecule **a** | | molecule **b** | |
|---|---|---|---|
| | Bond Lengths | | |
| Os(1)−P(1) | 2.335(6) | Os(2)−P(51) | 2.329(6) |
| Os(1)−N(1) | 2.078(18) | Os(2)−N(51) | 2.080(19) |
| Os(1)−C(1) | 2.20(2) | Os(2)−C(51) | 2.25(2) |
| Os(1)−C(2) | 2.28(2) | Os(2)−C(52) | 2.21(2) |
| Os(1)−C(3) | 2.22(2) | Os(2)−C(53) | 2.24(2) |
| Os(1)−C(4) | 2.17(2) | Os(2)−C(54) | 2.21(2) |
| Os(1)−C(5) | 2.19(2) | Os(2)−C(55) | 2.25(2) |
| Os(1)−C(15) | 2.10(2) | Os(2)−C(65) | 2.137(19) |
| N(1)−C(21) | 1.26(3) | N(1)−C(71) | 1.27(2) |
| C(15)−C(16) | 1.42(4) | C(65)−C(66) | 1.35(3) |
| C(15)−C(20) | 1.38(3) | C(65)−C(70) | 1.47(3) |
| C(20)−C(21) | 1.51(3) | C(70)−C(71) | 1.44(3) |
| C(21)−C(22) | 1.49(3) | C(71)−C(72) | 1.48(3) |
| | Bond Angles | | |
| G(1)*−Os(1)−P(1) | 129.2(3) | G(2)*−Os(2)−P(51) | 130.4(4) |
| G(1)*−Os(1)−N(1) | 122.0(6) | G(2)*−Os(2)−N(51) | 123.7(7) |
| G(1)*−Os(1)−C(15) | 117.6(7) | G(2)*−Os(2)−C(65) | 114.7(7) |
| P(1)−Os(1)−N(1) | 106.5(6) | P(51)−Os(2)−N(51) | 103.9(5) |
| P(1)−Os(1)−C(15) | 87.9(7) | P(51)−Os(2)−C(65) | 87.8(6) |
| N(1)−Os(1)−C(15) | 74.0(10) | N(51)−Os(2)−C(65) | 75.7(8) |
| Os(1)−N(1)−C(21) | 123.4(17) | Os(2)−N(51)−C(71) | 121.0(15) |
| Os(1)−C(15)−C(16) | 132(2) | Os(2)−C(65)−C(66) | 130.3(18) |
| Os(1)−C(15)−C(20) | 118(2) | Os(2)−C(65)−C(70) | 113.5(17) |
| C(15)−C(20)−C(21) | 111.9(19) | C(65)−C(70)−C(71) | 112.7(18) |
| N(1)−C(21)−C(20) | 112.6(19) | N(51)−C(71)−C(70) | 117(2) |
| N(1)−C(21)−C(22) | 122(2) | N(51)−C(71)−C(72) | 119.5(19) |

*G(1) and G(2) are the centroids of the C(1)−C(5) and C(51)−C(55) Cp ligands.

agreement with the value of the coupling constant between the hydride and phosphine, *cisoid* to the hydride ligand. The hydride ligand is located *transoid* to the metalated C(15) carbon atom and *cisoid* to the N(1) nitrogen atom. In solution, the *cisoid* disposition of the hydride ligand and the NH group of the imine was confirmed by a NOE experiment. The saturation of the NH resonanace increases the intensity of the hydride signal in 9%. In contrast to **4**, the saturation of the NH resonance of **2b** has no effect on the corresponding hydride signal.

The *cisoid* disposition of the hydride ligand and the N(1) nitrogen atom of the imino group leads to a situation where the H−Os−N−H dihedral angle should be about 30°, in agreement with the observed spin coupling between these nuclei. As a result, the distance between the hydride ligand and the NH hydrogen atom should be short. To corroborate this, the $T_1$ values for the resonances corresponding to the hydride ligands of **2b** and **4** were determined over the temperature range 293−203 K, in dichloromethane as solvent. The $T_1$(min) values of the two resonances were found to the same temperature, 213 K. The lower $T_1$(min) value at 300 MHz for the hydride resonance of **4** [285(4) ms] versus the hydride resonance of **2b** [330(5) ms] implies an excess relaxation rate for the hydride resonance of **4** between 0.38 and 0.83 $s^{-1}$. Assuming that the excess relaxation rate for the hydride resonance of **4** is a result of the proximity of the NH hydrogen atom in this compound and that the hydride−NH hydrogen vector rotates with the molecule as a whole, we can estimate a hydride−NH hydrogen separation between 2.6 and 2.3 Å, according to the standard equation.[7k,15] These values lie within the range reported for the hydrogen−hydrogen separation in four-membered rings of the type $LH\cdots H{-}M$, with an electrostatic hydrogen−hydrogen interaction [2.40[7a]−2.90[7k]].

The orthometalated benzophenone imine ligand acts with a bite angle of 74.0(10)° (**a**) and 75.7(8)° (**b**). The five-membered metallacycle is almost planar. The deviations from the best plane are 0.0000(9) (**a**), 0.0001(8) (**b**) [Os], 0.03(2) (**a**), −0.05(2) (**b**) [C(15)], −0.01(2) (**a**), 0.03(2) (**b**) [C(20)], −0.02(2) (**a**), 0.01(2) (**b**) [C(21)], and 0.02(2) (**a**), −0.02(2) (**b**) [N(1)] Å. The Os−N(1) bond lengths of 2.078(18) (**a**) and 2.080(19) (**b**) Å and the Os−C(15) bond distances of 2.10(2) (**a**) and 2.137(19) (**b**) Å are typical for Os−N and Os−C(aryl) single bonds, respectively, and are in agreement with the values previously found for the complexes $OsCl\{NH{=}C(Ph)C_6H_4\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ [2.097(3) and 2.069 Å],[17] $Os(C_2Ph)\{NH{=}C(Ph)C_6H_4\}(CO)(P^iPr_3)_2$ [2.106(7) and 2.089(7) Å],[14] $[Os\{NH{=}C(Ph)C_6H_4\}(\eta^6\text{-}C_6H_3Me_3)(P^iPr_3)]PF_6$ [2.083(4) and 2.072(4) Å],[18] $OsH(C_6H_3\text{-}p\text{Me})(p\text{-tolyl})CNNC(p\text{-tolyl})_2(CO_2)(PPh_3)$ [2.119(5) and 2.100(7) Å],[19] and *fac*-$Os\{C,N\text{-}3\text{-}Me[2\text{-}(MeC_6H_4)NCMe_3]C_6H_3\}(2\text{-}MeC_6H_4)(CN\text{-}^tBu)_3$ [2.193(24) and 2.077(20) Å].[20]

The $^{13}C\{^1H\}$ NMR spectrum of **4** agrees well with the presence of a heterometallacyle in this compound. Similarly to the $^{13}C\{^1H\}$ NMR spectra of **2a**, **2b**, and **3**, the spectrum of **4** shows the resonance due to the C=N carbon atom at 188.3 ppm as a doublet with a C−P coupling constant of 7.8 Hz. The Os−C resonance is observed at 158.0 ppm, as a doublet with a C−P coupling constant of 13.8 Hz.

At first glance, the formation of **4** by protonation of **3** appears to suggest that complex **4**, containing the hydride ligand *cisoid* to the NH group, is thermodynamically favored with regard to **2b**, while the cation of **2b**, which is formed by direct reaction of **1** with benzophenone imine, appears to be the kinetic product of the activation. Scheme 2 shows two possible pathways to the formation of this species.

As a consequence of the large steric hindrance experienced by the triisopropylphosphine groups, which are mutually *cis* disposed, complex **1** shows a high tendency to release a phosphine ligand in pentane as solvent.[1b] So, it seems reasonable to think that the first step for the C−H activation of the phenyl group of the benzophenone imine molecule is the formation of the imine intermediate **A** as a result of the dissociation of a phosphine ligand from **1** and the subsequent coordination of the benzophenone imine group. Although monodentate nitrogen-bonded imine compounds are rare as

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(15) $R = 129.18/r^6$. See ref 16.

(16) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Bautista, M. T.; Earl, K. A.; Maltby, P. A., Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031. (c) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173. (d) Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.

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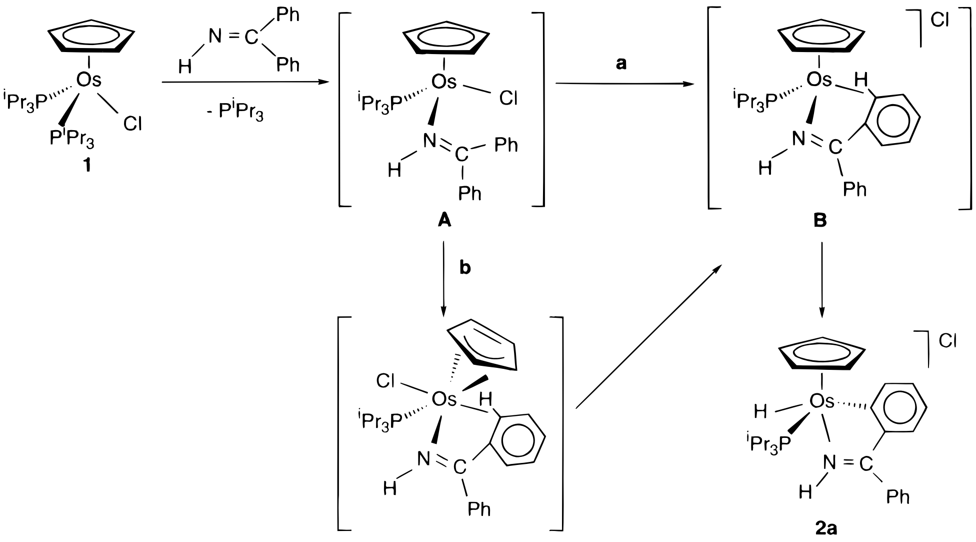
(20) Arnold, J.; Wilkinson, G.; Hussain, B.; Hurthouse, M. B. *Organometallics* **1989**, *8*, 1362.

**Scheme 2**



a consequence of the weak Lewis basicity of the imine nitrogen atom, stable derivatives of ruthenium and osmium have been recently isolated.[21] According to pathway **a**, the dissociation of the chloro ligand could give the intermediate **B** containing the C$_{ortho}$−H bond to be activated parallel to the P−N vector. The oxidative addition of this bond should afford **2a**. Alternatively to the dissociation of chloride from **A**, the intermediate **B** could be formed according to pathway **b**. The $\eta^5$−$\eta^3$ rearrangement of the cyclopentadienyl group in **A** could generate a coordination vacancy disposed *trans* to the chloro ligand. In this way, the subsequent coordination of the C$_{ortho}$−H bond to be activated in this place, followed of the displacement of chloride by, now, an $\eta^3$−$\eta^5$ rearrangement of the cyclopentadienyl group, should afford **B**. Since, the reaction of orthometalation of the imine takes place in pentane as solvent and it is fast, pathway **b** seems to be more reasonable than pathway **a**.

In addition, it should be mentioned that the coordination of the C$_{ortho}$−H bond to the metal center in the [Os($\eta^5$-C$_5$H$_5$)(NH=CPh$_2$)(P$^i$Pr$_3$)]$^+$ fragment can be parallel to the P−N vector as in **B** or, alternatively, perpendicular. In the second case, the oxidative addition of the C−H bond should give **4**. Using a molecular model, it can be observed that, from a geometrical point of view, the parallel coordination is more favored than the perpendicular. This could explain why complex **2a** is the kinetic product.

Although thermodynamically complex **4** seems to be more stable than **2b**, isomerization from **2b** into **4** is not observed. This could be due to the high stability of the five-membered heterometallacycle, which imposes a high activation barrier for the isomerization. The higher stability of **4** with regard to **2b** should not be related with the presence of the H···H interaction in **4** but with the *transoid* disposition of the hydride ligand and the orthometalated phenyl group (vide infra). Previous studies on complexes containing LH···H−M rings indicate that the H···H interaction favors the formation of determined conformers and reduces the dynamic properties of the ligands supporting the interaction. However, it does not impose the stereochemistry of a particular derivative.[7k]

**2. C−H Activation of a Phenyl Group of Triphenylphosphine.** We have previously shown that the addition of 1 equiv of benzophenone imine to pentane suspensions of **1** produces the displacement of both a triisopropylphosphine group and the chloro ligand from the coordination sphere of the osmium atom and the C−H activation of a phenyl group of the imine. The reaction of **1** with triphenylphosphine is different from that mentioned above. The treatment of **1**, in pentane or toluene, with 1 equiv of triphenylphosphine produces only the displacement of a triisopropylphosphine group. As a result, the mixed-ligand complex Os($\eta^5$-C$_5$H$_5$)Cl(PPh$_3$)(P$^i$Pr$_3$) (**5**) was isolated as a yellow solid in 94% yield (Scheme 3). The displacement of the chloro ligand and the subsequent C−H activation does not occur even under refluxing toluene.

The release of the chloro from the coordination sphere of **5** requires the addition of thallium hexafluorophosphate. Thus, the addition of 1 equiv of this salt to acetone solutions of **5** gives rise to the precipitation of thallium chloride and the formation of [OsH($\eta^5$-C$_5$H$_5$)(PPh$_2$C$_6$H$_4$}(P$^i$Pr$_3$)]PF$_6$ (**6**), as a consequence of the activation of a C$_{ortho}$−H bond of a phenyl group of the triphenylphosphine ligand. The selective activation of the phenyl group in the presence of the isopropyl groups of the triisopropylphosphine ligand can be related with the previously mentioned kinetic and thermodynamic preference for the arene C−H activation, in comparison with the alkane C−H activation.

Not only are the activation processes of the phenyl groups of benzophenone imine and triphenylphosphine produced in a different manner but also the stereochemistries of the activated products are different. As it has been previously mentioned, the activation of the phenyl group of the imine appears to take place by approach of the C−H bond in a parallel direction to the P−N vector, and the resulting product, complex **2a**,

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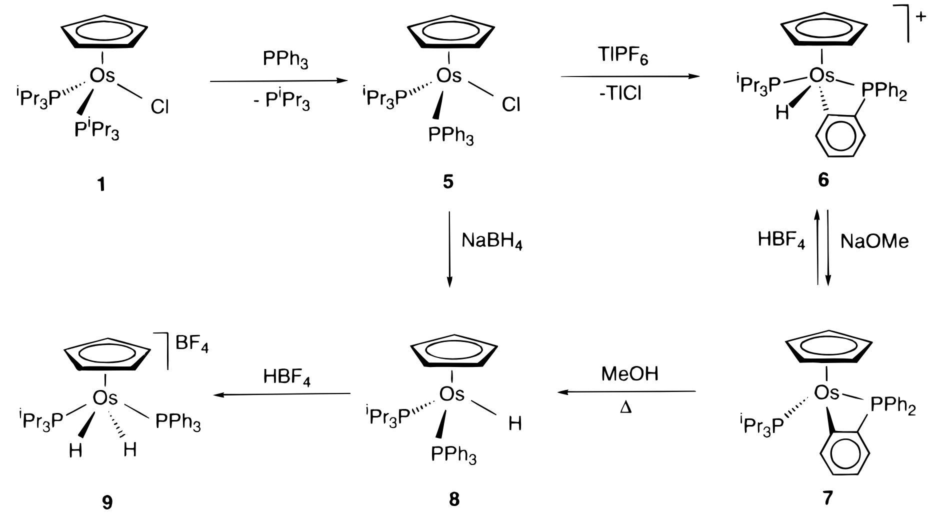
[21] (a) Bohanna, C.; Esteruelas, M. A.; López, A. M.; Oro, L. A. *J. Organomet. Chem.* **1996**, *526*, 73. (b) Albéniz, M. J.; Buil, M. L.; Esteruelas, M. A.; López, A. M. *J. Organomet. Chem.* **1997**, *545−546*, 495.

**Scheme 3**



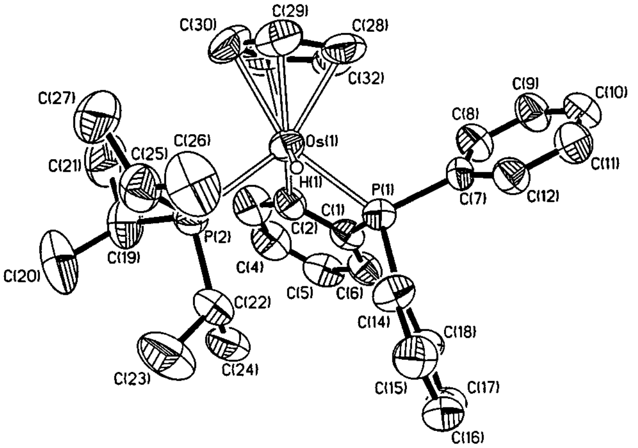


**Figure 2.** Molecular diagram of the cation of **6**, $[\mathrm{OsH}(\eta^5\text{-}C_5H_5)(PPh_2C_6H_4)(P^iPr_3)]^+$. Thermal ellipsoids are shown at 50% probability.

**Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex $[\mathrm{OsH}(\eta^5\text{-}C_5H_5)(PPh_2C_6H_4)(P^iPr_3)]PF_6$ (6)**

| molecule **a** | | molecule **b** | |
|---|---|---|---|
| | Bond Lengths | | |
| Os(1)−P(1) | 2.328(2) | Os(2)−P(3) | 2.319(2) |
| Os(1)−P(2) | 2.395(3) | Os(2)−P(4) | 2.388(2) |
| Os(1)−C(2) | 2.180(9) | Os(2)−C(52) | 2.136(9) |
| Os(1)−C(28) | 2.219(9) | Os(2)−C(78) | 2.202(12) |
| Os(1)−C(29) | 2.264(10) | Os(2)−C(79) | 2.231(11) |
| Os(1)−C(30) | 2.315(10) | Os(2)−C(80) | 2.267(11) |
| Os(1)−C(31) | 2.281(9) | Os(2)−C(81) | 2.339(11) |
| Os(1)−C(32) | 2.224(9) | Os(2)−C(82) | 2.292(11) |
| Os(1)−H(1) | 1.50(6) | Os(2)−H(2) | 1.49(7) |
| P(1)−C(1) | 1.791(8) | P(3)−C(51) | 1.800(9) |
| C(1)−C(2) | 1.387(12) | C(51)−C(52) | 1.412(12) |
| C(2)−C(3) | 1.400(13) | C(52)−C(53) | 1.400(13) |
| | Bond Angles | | |
| G(1)[a]−Os(1)−P(1) | 124.25(15) | G(2)[a]−Os(2)−P(3) | 126.77(16) |
| G(1)[a]−Os(1)−P(2) | 128.39(14) | G(2)[a]−Os(2)−P(4) | 129.65(15) |
| G(1)[a]−Os(1)−C(15) | 117.2(3) | G(2)[a]−Os(2)−C(52) | 123.7(7) |
| G(1)[a]−Os(1)−H(1) | 113(2) | G(2)[a]−Os(2)−H(2) | 114.7(7) |
| P(1)−Os(1)−P(2) | 107.15(8) | P(3)−Os(2)−P(4) | 103.07(8) |
| P(1)−Os(1)−C(2) | 64.9(2) | P(3)−Os(2)−C(52) | 65.3(3) |
| P(1)−Os(1)−H(1) | 79(2) | P(3)−Os(2)−H(2) | 77(3) |
| P(2)−Os(1)−C(2) | 86.7(2) | P(4)−Os(2)−C(52) | 84.5(2) |
| P(2)−Os(1)−H(1) | 70(2) | P(4)−Os(2)−H(2) | 70(3) |
| C(2)−Os(1)−H(1) | 129(2) | C(52)−Os(2)−H(2) | 128(3) |
| Os(1)−P(1)−C(1) | 88.9(3) | Os(2)−P(3)−C(51) | 89.1(3) |
| P(1)−C(1)−C(2) | 98.5(6) | P(3)−C(51)−C(52) | 96.5(6) |
| P(1)−C(1)−C(6) | 138.0(7) | P(3)−C(51)−C(56) | 138.9(8) |
| C(1)−C(2)−C(3) | 118.6(9) | C(51)−C(52)−C(53) | 115.8(9) |
| C(2)−C(1)−C(6) | 123.4(8) | C(52)−C(51)−C(56) | 124.4(9) |

[a] G(1) and G(2) are the centroids of the C(28)−C(32) and C(68)−C(82) Cp ligands.

contains the added fragments in mutually *cisoid* positions. In contrast to the activation of the imine, the approach of the C−H bond of the activated phenyl group of the triphenylphosphine occurs in the direction perpendicular to the P−P vector, and in the resulting product, complex **6**, the hydride ligand and the orthometalated phenyl group lie in mutually *transoid* positions.

The stereochemistry of **6** is strongly supported by the $^1$H, $^{31}$P{$^1$H}, and $^{13}$C{$^1$H} NMR spectra and was confirmed by an X-ray diffraction study on a single crystal of the complex. Similarly to **4**, **6** shows two independent, but chemically equivalent molecules in the asymmetric unit (in this case the same enantiomer). A view of the molecular geometry of one of the molecules of **6** is shown in Figure 2. Selected bond distances and angles are listed in Table 2. In contrast to **4**, the hydride ligand H(1) was located in the difference Fourier maps and refined as an isotropic atom together with the rest of the non-hydrogen atoms of the structure, giving an Os−H(1) distance of 1.50(6) (molecule **a**) and 1.49(7) Å (molecule **b**).

The distribution of ligands around the osmium atom of **6** can be described as a four-legged piano-stool geometry with the hydride ligand *transoid* to the metalated phenyl group and *cisoid* to both phosphorus atoms, which are mutually *transoid* [P(1)−Os−P(2) = 107.15(8)° (**a**) and 103.07(8)° (**b**)]. In agreement with this disposition, the $^1$H NMR spectrum shows at −12.10 ppm a double doublet with H−P coupling constants of 35.7 and 26.4 Hz, for the hydride ligand, and the $^{31}$P{$^1$H} NMR contains two doublets at 16.8 and −74.8 ppm with a P−P coupling constant of 18.1 Hz, which correspond to the triisopropylphosphine and orthometalated triphenylphosphine ligands, respectively.

The orthometalated triphenylphosphine acts with a bite angle of 64.9(2)° (**a**) and 65.3(3)° (**b**). The four-membered heterometallacycle is almost planar. The deviations from the best plane are 0.0001(4) (**a**) and 0.0001(4) (**b**) [Os(1)], −0.059(9) (**a**) and −0.055(9) (**b**)

[C(2)], 0.057(8) (**a**) and 0.055(9) (**b**) [C(1)], and −0.003(2) (**a**) and −0.002(2) Å (**b**) [P(1)]. The Os(1)−C(2) distance [2.180(9) (**a**) and 2.136(9) Å (**b**)] agrees well with the values reported for related compounds.[16−19] The Os(1)−P(1) distance [2.328(2) (**a**) and 2.319(2) Å (**b**)] is about 0.06 Å shorter than the separation between the osmium atom and the triisopropylphosphine ligand. However, it is about 0.02 Å longer than the Os−P bond length in the metalated osmium(IV) compound $[OsH(\eta^5\text{-}C_5H_5)\{CH(SiMe_3)C_6H_4PPh_2\}(PPh_3)]OTf$.[22]

In agreement with the presence of an orthometalated phenyl group in **6**, the $^{13}C\{^1H\}$ NMR spectrum of this compound contains at 116.4 ppm a double doublet with C−P coupling constants of 29.9 and 15.2 Hz.

Similarly to **2b**, the treatment of tetrahydrofuran solutions of **6** with sodium methoxide produces the extraction of the hydride ligand and the formation of the neutral complex $Os(\eta^5\text{-}C_5H_5)(PPh_2C_6H_4)(P^iPr_3)]Cl$ (**7**), which was isolated as a yellow solid in 85% yield. The reaction is reversible. Thus, the addition of 1 equiv of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of **7** affords the $BF_4$ salt of **6**. This suggests that for the hydride ligand and the metalated group the *transoid* disposition is favored not only kinetically but also thermodynamically. A similar situation has also been observed in the complexes $[OsH(\eta^5\text{-}C_5H_5)(PPh_2C_6H_4)(PPh_3)]OTf$,[2] $[OsH(\eta^5\text{-}C_5H_5)\{CH_2CH(CH_3)P^iPr_2\}(P^iPr_3)]^+$,[1b] and $[OsH(\eta^5\text{-}C_5H_5)\{CH(SiMe_3)C_6H_4PPh_2\}(PPh_3)]OTf$.[22]

Characteristic spectroscopic features of **7** are two doublets at 20.9 and −71.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum, with a P−P coupling constant of 18.6 Hz, and in the $^{13}C\{^1H\}$ NMR spectrum a double doublet at 143.1 ppm, with C−P coupling constants of 17.0 and 11.9 Hz, assigned to the Os−C carbon atom.

In the solid state, complex **7** is stable for 1 week if kept under argon at −20 °C. In solution at room temperature it is stable in toluene, benzene, and methanol. However, under refluxing methanol, it evolves in quantitative yield into the monohydride $OsH(\eta^5\text{-}C_5H_5)(PPh_3)(P^iPr_3)$ (**8**) after 24 h. Complex **8**, which is a yellow air-sensitive solid, can also be prepared by reaction of **5** with $NaBH_4$. By this procedure it was isolated in 85% yield. The presence of a hydride ligand in **8** is strongly supported by the $^1H$ NMR spectrum, which contains at −15.27 ppm a double doublet with both H−P coupling constants of 29.7 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows at 33.6 and 21.2 ppm doublets, with a P−P coupling constant of 9.8 Hz, which were assigned to the triisopropylphosphine and triphenylphosphine ligands, respectively.

In contrast to **7**, complex **6** is stable in methanol under reflux and does not evolve into the corresponding dihydride $[OsH_2(\eta^5\text{-}C_5H_5)(PPh_3)(P^iPr_3)]^+$. However, the $BF_4$ salt of this cation (**9** in Scheme 3) can be prepared by addition of 1 equiv of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of **8**.

Complex **9** was isolated as a white solid in 92% yield and characterized by MS, elemental analysis, and IR and $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopies. In the $^1H$ NMR spectrum the most noticeable feature is a double doublet at −13.09 ppm, with both H−P coupling constants of 28.9 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains at 35.4 and 9.7 ppm doublets with a P−P coupling constant of 26.6 Hz. The multiplicity of these signals and the values of the spin coupling constants strongly support the stereochemisty proposed for **9** in Scheme 3.

## Concluding Remarks

This study has revealed that despite the high kinetic stability of the $CpOsL_3$ compounds,[23] the derivative $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) reacts with benzophenone imine and triphenylphosphine to give hydride-metalated complexes, which are the result of the C−H activation of one phenyl group.

Although in both cases the reactions lead to the same type of derivatives, the C−H activations proceed in a different manner. Thus, while the cation $[OsH(\eta^5\text{-}C_5H_5)\{NH{=}C(Ph)C_6H_4\}(P^iPr_3)]Cl$ (**2**) is obtained in an one-pot synthesis starting from **1** and benzophenone imine, the formation of the related cation $[OsH(\eta^5\text{-}C_5H_5)(PPh_2C_6H_4)(P^iPr_3)]PF_6$ (**6**) occurs in a two-step procedure. Initially, the reaction of **1** with triphenylphosphine gives rise to the replacement of a triisopropylphosphine group by the triphenylphosphine ligand. The release of the chloride from the coordination sphere of the osmium atom requires the addition of $TlPF_6$.

The stereochemistries of the cations **2** and **6** are also different. The distribution of ligands around the osmium atom of both cations can be described as a four-legged piano-stool geometry. However, while in the cation **2** the hydride ligand and the metalated phenyl group lie in a *cisoid* disposition, in the cation **6** the hydride ligand and the metalated phenyl group are mutually *transoid* disposed. The different stereochemistry of these species can be related to the different approach to the metallic center of the added bonds. Thus, the approach in the case of the benzophenone imine appears to take place along the direction parallel to the vector P−N of an unsaturated triisopropylphosphine−benzophenone imine−osmium fragment, while in the case of the triphenylphosphine the approach appears to take place along the direction perpendicular to the P−P vector in an unsaturated triisopropylphosphine−triphenylphosphine−osmium fragment.

In the case of the benzophenone imine, the oxidative addition leads to the isomer kinetically favored. Although a spontaneous isomerization of **2** is not observed, its deprotonation and subsequent protonation afford a new isomer, containing the hydride and the metalated phenyl group mutually *transoid* disposed. Furthermore, in this isomer the hydride and NH group of the imine are mutually *cisoid*. As a result, the separation between the hydride and NH hydrogen atom is short (about 2.5 Å), lying in the range previously reported for H···H interactions in four-membered rings of the type LH···H−M. In contrast to benzophenone imine, the

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(22) Koch, J. L.; Shapley, P. A. *Organometallics* **1999**, *18*, 814.

(23) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; VCH Publishers, Inc.: New York, 1997; Chapter 3.

oxidative addition in the case of triphenylphosphine leads to the isomer kinetically and thermodynamically favored.

In addition, it should also be mentioned that this study proves that under, strictly, the same metal ligand system the competitive alkane–arene intramolecular C–H activation shows kinetic and thermodynamic arene preference when, in the resulting product, the formed heterocycle has the same number of members or the reaction gives rise to a more stable heterocycle than the hypothetic product resulting from the alkane activation.

## Experimental Section

**Physical Measurements.** Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Nicolet 550 spectrometer. NMR spectra were recorded on a Varian UNITY 300, Varian GEMINI 2000 (300 MHz), or a Bruker ARX 300. The probe temperature of the NMR spectrometers was calibrated against a methanol standard. For the $T_1$ measurements the 180° pulses were calibrated at each temperature. $^{1}$H and $^{13}$C{$^{1}$H} chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. $^{31}$P{$^{1}$H} chemical shifts are reported relative to $H_3PO_4$ (85%). Coupling constants $J$ are given in hertz. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectra analyses were performed with a VG Auto Spec instrument. The ions were produced, FAB$^+$ mode, with the standard Cs$^+$ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

**Synthesis.** 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 complex Os($\eta^5$-$C_5H_5$)Cl(P$^i$Pr$_3$)$_2$ (**1**) was prepared according to the literature method.[1b]

**Preparation of [OsH($\eta^5$-$C_5H_5$){NH=C(Ph)$C_6H_4$}(P$^i$Pr$_3$)]Cl (2a).** A suspension of **1** (150 mg, 0.24 mmol) in 10 mL of pentane was treated with 48.9 mg (0.27 mmol) of benzophenone imine. After the mixture was stirred for 2 h at room temperature, a yellow solid was formed, which was separated by decantation, washed with pentane, and dried in vacuo. Yield: 130 mg (85%). IR (Nujol): $\nu$(NH) 3386 cm$^{-1}$. $^{1}$H NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 12.81 (br, 1 H, NH), 8.22 (m, 1 H, Ph), 7.72–7.52 (m, 6 H, Ph), 7.06–6.98 (m, 2 H, Ph), 5.77 (s, 5 H, Cp), 2.43 (m, 3 H, PCH), 1.18 (dd, $J$(HH) = 6.9 Hz, $J$(PH) = 14.7 Hz, 9 H, PCCH$_3$), 0.94 (dd, $J$(HH) = 7.2 Hz, $J$(PH) = 13.8 Hz, 9 H, PCCH$_3$), −12.98 (d, $J$(PH) = 38.2 Hz, 1 H, OsH). $^{31}$P{$^{1}$H} NMR (121.42 MHz, $CD_2Cl_2$, 293 K): $\delta$ 20.9. $^{13}$C{$^{1}$H} NMR (75.42 MHz, $CD_2Cl_2$, 293 K, plus APT): $\delta$ 190.1 (−, d, $J$(PC) = 2.8 Hz, N=C), 165.3 (−, d, $J$(PC) = 3.7 Hz, Os–C), 147.5 (−, s, *ipso*-Ph), 146.2 (+, s, Ph), 134.6 (−, s, *ipso*-Ph), 132.3, 131.0, 130.2, 130.2, 129.9, 1292, 128.7, 122.7 (+, all s, Ph), 85.9 (+, s, Cp), 28.2 (+, d, $J$(PC) = 29.9 Hz, PCH), 20.4 (+, s, PC*C*H$_3$), 18.7 (+, d, $J$(PC) = 2.3 Hz, PC*C*H$_3$). Anal. Calcd for $C_{27}H_{37}ClNOsP$: C, 51.29; H, 5.89; N, 2.21. Found: C, 50.86; H, 6.43; N, 2.21. MS (FAB$^+$): *m/e* 598 (M$^+$).

**Preparation of [OsH($\eta^5$-$C_5H_5$){NH=C(Ph)$C_6H_4$}(P$^i$Pr$_3$)]BF$_4$ (2b).** A solution of **2a** (100 mg, 0.16 mmol) in 10 mL of THF was treated with sodium tetrafluoroborate (19.1 mg, 0.17 mmol). After stirring for 20 min at room temperature the brown solution obtained was concentrated to dryness. The product was extracted with 8 mL of dichloromethane. The suspension was filtered through Kieselguhr and concentrated to dryness. Addition of diethyl ether caused the precipitation of a brown solid, which was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 101.5 mg (94%). IR (Nujol): $\nu$(NH) 3286 cm$^{-1}$, $\nu$(BF$_4$) 1073 cm$^{-1}$. $^{1}$H NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 11.09 (br, 1 H, NH), 8.24–8.21 (m, 1 H, Ph), 7.68–7.56 (m, 6 H, Ph), 7.11–7.03 (m, 2 H, Ph), 5.68 (s, 5 H, Cp), 2.40 (m, 3 H, PCH), 1.18 (dd, $J$(HH) = 7.2 Hz, $J$(PH) = 15.0 Hz, 9 H, PCCH$_3$), 0.94 (dd, $J$(HH) = 6.9 Hz, $J$(PH) = 14.4 Hz, 9 H, PCCH$_3$), −12.96 (d, $J$(PH) = 38.5 Hz, 1 H, OsH). $^{31}$P{$^{1}$H} NMR (121.42 MHz, $CD_2Cl_2$, 293 K): $\delta$ 23.7. $^{13}$C{$^{1}$H} NMR (75.42 MHz, $CD_2Cl_2$, 293 K, plus APT): $\delta$ 190.9 (−, d, $J$(PC) = 2.7 Hz, N=C), 165.5 (−, d, $J$(PC) = 4.1 Hz, Os–C), 146.7 (−, s, *ipso*-Ph), 146.2 (+, s, Ph), 134.8 (−, s, *ipso*-Ph), 132.7, 131.3, 130.3, 129.7, 129.0, 123.0 (+, all s, Ph), 86.1 (+, d, $J$(PC) < 1 Hz, Cp), 28.2 (+, d, $J$(PC) = 30.4 Hz, PCH), 20.3 (+, s, PC*C*H$_3$), 18.6 (+, d, $J$(PC) = 2.3 Hz, PC*C*H$_3$). Anal. Calcd for $C_{27}H_{37}BF_4NOsP$: C, 47.44; H, 5.45; N, 2.05. Found: C, 47.89; H, 5.39; N, 2.09. MS (FAB$^+$): *m/e* 598 (M$^+$).

**Preparation of [OsH($\eta^5$-$C_5H_5$){NH=C(Ph)$C_6H_4$}(P$^i$Pr$_3$)] (3).** A yellow solution of **2a** (185 mg, 0.31 mmol) in 10 mL of THF was treated with sodium methoxide (25.1 mg, 0.47 mmol). The mixture was stirred for 17 h at room temperature. The green solution obtained was evaporated to dryness, and 10 mL of toluene was added. The suspension was filtered through Kieselguhr and concentrated to dryness. Addition of methanol caused the precipitation of an extremely air-sensituve green solid, which was separated by decantation and dried in vacuo. Yield: 104 mg (81%). $^{1}$H NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 9.96 (br, 1 H, NH), 8.62 (d, $J$(HH) = 7.8 Hz, 1 H, Ph), 7.77 (d, $J$(HH) = 7.8 Hz, 1 H, Ph), 7.33 (d, $J$(HH) = 7.2 Hz, 2 H, Ph), 7.11 (m, 3 H, Ph), 6.96 (m, 2 H, Ph), 4.62 (s, 5 H, Cp), 1.73 (m, 3 H, PCH), 0.94 (dd, $J$(HH) = 7.5 Hz, $J$(PH) = 13.2 Hz, 9 H, PCCH$_3$), 0.70 (dd, $J$(HH) = 7.2 Hz, $J$(PH) = 12.3 Hz, 9 H, PCCH$_3$). $^{31}$P{$^{1}$H} NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 16.4. $^{13}$C{$^{1}$H} NMR (75.42 MHz, $C_6D_6$, 293 K, plus APT): $\delta$ 186.0 (−, d, $J$(PC) = 7.8 Hz, Os–C), 184.5 (−, d, $J$(PC) = 2.8 Hz, N=C), 144.7 (−, s, *ipso*-Ph), 143.3 (+, s, Ph), 139.2 (−, s, *ipso*-Ph), 130.9, 128.7, 128.4, 127.8, 117.6 (+, all s, Ph), 26.1 (+, d, $J$(PC) = 25.3 Hz, PCH), 20.4, 18.7 (+, both s, PC*C*H$_3$). MS (FAB$^+$): *m/e* 598 (M$^+$ + H).

**Preparation of [OsH($\eta^5$-$C_5H_5$){NH=C(Ph)$C_6H_4$}(P$^i$Pr$_3$)]BF$_4$ (4).** A solution of **3** (103 mg, 0.17 mmol) in 6 mL of diethyl ether was treated with 22.7 $\mu$L (0.17 mmol) of HBF$_4$·OEt$_2$. The brown solid formed was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 109 mg (92%). IR (Nujol): $\nu$(NH) 3304 cm$^{-1}$, $\nu$(BF$_4$) 1047 cm$^{-1}$. $^{1}$H NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 11.24 (br, 1 H, NH), 8.00 (m, 1 H, Ph), 7.66 (m, 1 H, Ph), 7.57 (m, 5 H, Ph), 7.24 (m, 2 H, Ph), 5.52 (s, 5 H, Cp), 2.43 (m, 3 H, PCH), 1.09 (dd, $J$(HH) = 6.9 Hz, $J$(PH) = 15.6 Hz, 9 H, PCCH$_3$), 0.83 (dd, $J$(HH) = 6.9 Hz, $J$(PH) = 13.5 Hz, 9 H, PCCH$_3$), −11.92 (dd, $J$(PH) = 41.7 Hz, $J$(HH) = 4.1 Hz, 1 H, OsH). $^{31}$P{$^{1}$H} NMR (121.42 MHz, $CD_2Cl_2$, 293 K): $\delta$ 18.9. $^{13}$C{$^{1}$H} NMR (75.42 MHz, $CD_2Cl_2$, 293 K, plus APT): $\delta$ 188.3 (−, d, $J$(PC) = 7.8 Hz, N=C), 158.0 (−, d, $J$(PC) = 13.8 Hz, Os–C), 146.6 (−, s, *ipso*-Ph), 143.3 (+, d, $J$(PC) = 1.9 Hz, Ph), 135.2 (−, s, *ipso*-Ph), 131.8, 131.4, 130.1, 129.4, 128.9 (+, all s, Ph), 84.9 (+, d, $J$(PC) = 1.8 Hz, Cp), 26.9 (+, d, $J$(PC) = 32.2 Hz, PCH), 20.4 (+, s, PC*C*H$_3$), 18.5 (+, d, $J$(PC) = 3.7 Hz, PC*C*H$_3$). Anal. Calcd for $C_{27}H_{37}BF_4NOsP$: C, 47.44; H, 5.45; N, 2.05. Found: C, 47.47; H, 5.37; N, 1.88. MS (FAB$^+$): *m/e* 598 (M$^+$).

**Preparation of Os($\eta^5$-$C_5H_5$)Cl(PPh$_3$)(P$^i$Pr$_3$) (5).** A solution of **1** (260 mg, 0.43 mmol) in 8 mL of toluene was treated with 111.5 mg (0.43 mmol) of triphenylphosphine. After stirring for 5 h at room temperature, the yellow solution obtained was filtered through Kieselguhr and concentrated to dryness. Addition of pentane caused the precipitation of a yellow solid, which was separated by decantation, washed with pentane, and dried in vacuo. Yield: 285 mg (94%). $^{1}$H NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 7.91 (dd, $J$(HH) = 8.1 Hz, $J$(HH) = 8.7 Hz, 6 H, *m*-Ph), 7.09–6.96 (m, 9 H, Ph), 4.53 (s, 5 H, Cp), 2.31 (m, 3 H, PCH), 1.05, (dd, $J$(HH) = 7.2 Hz, $J$(PH) = 12.6 Hz, 9 H, PCCH$_3$), 0.87 (dd, $J$(HH) = 7.2 Hz, $J$(PH) = 12.6 Hz, 9 H, PCCH$_3$). $^{31}$P{$^{1}$H} NMR (121.42 MHz, $C_6D_6$, 293 K):

$\delta$ 3.5 (d, $J$(PP) = 16.8 Hz, $P^iPr_3$), −5.7 (d, $J$(PP) = 16.8 Hz, $PPh_3$). Anal. Calcd for $C_{32}H_{41}ClOsP_2$: C, 53.88; H, 5.79. Found: C, 54.34; H, 5.88. MS (FAB$^+$): *m/e* 714 ($M^+$), 679 ($M^+$ − Cl).

**Preparation of $[OsH(\eta^5\text{-}C_5H_5)(PPh_2C_6H_4)(P^iPr_3)]PF_6$ (6).** A solution of **5** (285 mg, 0.40 mmol) in 10 mL of acetone was treated with 140 mg (0.40 mmol) of thallium hexafluorophosphate. After stirring for 15 min at room temperature the colorless solution obtained was filtered through Kieselguhr and concentrated to dryness. The addition of diethyl ether caused the precipitation of a white solid, which was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 302 mg (91%). $^1$H NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 8.06 (m, 2 H, Ph), 7.60 (m, 2 H, Ph), 7.48−7.31 (m, 10 H, Ph), 5.28 (s, 5 H, Cp), 2.02 (m, 3 H, PCH), 0.96 (dd, $J$(HH) = 6.9 Hz, $J$(PH) = 13.2 Hz, 9 H, PCC$H_3$), 0.71 (dd, $J$(HH) = 7.5 Hz, $J$(PH) = 15.3 Hz, 9 H, PCC$H_3$), −12.10 (dd, $J$(PH) = 35.7 Hz, $J$(PH) = 26.4 Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CD_2Cl_2$, 293 K): $\delta$ 16.8 (d, $J$(PP) = 18.1 Hz, $P^iPr_3$), −74.8 (d, $J$(PP) = 18.1 Hz, $(C_6H_4)PPh_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, $CD_2Cl_2$, 293 K, plus APT): $\delta$ 154.4 (−, d, $J$(PC) = 59.9 Hz, *ipso* Ph), 139.7 (+, d, $J$(PC) = 16.1 Hz, Ph), 133.9 (+, d, $J$(PC) = 2.8 Hz, Ph), 132.6 (+, d, $J$(PC) = 2.8 Hz, Ph), 132.3 (+, d, $J$(PC) = 10.1 Hz, Ph), 132.2 (−, d, $J$(PC) = 54.7 Hz, *ipso* Ph), 131.7 (+, d, $J$(PC) = 2.7 Hz, Ph), 131.2 (+, s, Ph), 130.5 (+, d, $J$(PC) = 10.1 Hz, Ph), 129.8 (+, d, $J$(PC) = 11.5 Hz, Ph), 129.7 (+, d, $J$(PC) = 11.0 Hz, Ph), 129.0 (−, d, $J$(PC) = 55.3 Hz, *ipso* Ph), 125.7 (+, d, $J$(PC) = 10.6 Hz, Ph), 116.4 (−, dd, $J$(PC) = 29.9 Hz, $J$(PC) = 15.2 Hz, Os−C), 85.5 (+, s, Cp), 26.5 (+, d, $J$(PC) = 29.9 Hz, PCH), 20.0 (+, s, $PCCH_3$), 19.9 (+, d, $J$(PC) = 4.1 Hz, $PCCH_3$). Anal. Calcd for $C_{32}H_{41}OsP_3F_6$: C, 46.72; H, 5.02. Found: C, 46.95; H, 5.10. MS (FAB$^+$): *m/e* 679 ($M^+$).

**Preparation of $Os(\eta^5\text{-}C_5H_5)(PPh_2C_6H_4)(P^iPr_3)$ (7).** A solution of **6** (150 mg, 0.18 mmol) in 10 mL of THF was treated with sodium methoxide (14.6 mg, 0.27 mmol). The mixture was stirred for 6 h at room temperature. The yellow solution obtained was evaporated to dryness, and 10 mL of toluene was added. The suspension was filtered through Kieselguhr and concentrated to dryness. Addition of methanol caused the precipitation of a yellow solid, which was separated by decantation and dried in vacuo. Yield: 104 mg (85%). $^1$H NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 7.82 (dd, $J$(HH) = 7.8 Hz, $J$(HH) = 8.7 Hz, 2 H, *m*-Ph), 7.60 (m, 1 H, Ph), 7.45 (dd, $J$(HH) = 9.6 Hz, $J$(HH) = 8.4 Hz, 2 H, *m*-Ph), 7.19 (dd, $J$(HH) = 7.5 Hz, $J$(HH) = 7.5 Hz, 1 H, Ph), 7.07−6.88 (m, 8 H, Ph), 4.50 (s, 5 H, Cp), 1.97 (m, 3 H, PCH), 0.88 (dd, $J$(HH) = 7.2 Hz, $J$(PH) = 12.3 Hz, 9 H, PCC$H_3$), 0.81 (dd, $J$(HH) = 7.2 Hz, $J$(PH) = 12.3 Hz, 9 H, PCC$H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 20.9 (d, $J$(PP) = 18.6 Hz, $P^iPr_3$), −71.0 (d, $J$(PP) = 18.6 Hz, $(C_6H_4)PPh_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, $C_6D_6$, 293 K, plus APT): $\delta$ 161.7 (−, d, $J$(PC) = 50.7 Hz, *ipso* Ph), 143.1 (−, dd, $J$(PC) = 17.0 Hz, $J$(PC) = 11.9 Hz, Os−C), 140.4 (−, d, $J$(PC) = 45.2 Hz, *ipso* Ph), 132.6 (+, d, $J$(PC) = 10.1 Hz, Ph), 130.8 (+, d, $J$(PC) = 9.4 Hz, Ph), 129.2 (+, d, $J$(PC) = 4.1 Hz, Ph), 128.7 (+, d, $J$(PC) = 1.8 Hz, Ph), 127.8 (+, d, $J$(PC) = 2.8 Hz, Ph), 127.7 (+, s, Ph), 119.6 (+, d, $J$(PC) = 8.3 Hz, Ph), 73.6 (+, dd, $J$(PC) = 2.3 Hz, $J$(PC) = 2.3 Hz, Cp), 28.6 (+, dd, $J$(PC) = 24.8 Hz, $J$(PC) = 2.3 Hz, PCH), 20.9, 19.8 (+, both s, $PCCH_3$). Anal. Calcd for $C_{32}H_{40}OsP_2$: C, 56.78; H, 5.95. Found: C, 56.29; H, 5.79. MS (FAB$^+$): *m/e* 678 ($M^+$ + H).

**Reaction of 7 with $HBF_4$.** A solution of **7** (23.6 mg, 0.034 mmol) in 0.5 mL of $CD_2Cl_2$ was treated with 4.8 $\mu$L (0.034 mmol) of $HBF_4\cdot OEt_2$. After 2 min at room temperature, the NMR spectra showed only the presence of the compound $[OsH(\eta^5\text{-}C_5H_5)(PPh_2C_6H_4)(P^iPr_3)]^+$.

**Preparation of $OsH(\eta^5\text{-}C_5H_5)(PPh_3)(P^iPr_3)$ (8).** A solution of **5** (100 mg, 0.14 mmol) in 10 mL of toluene was treated with 33 mg (0.70 mmol) of $NaBH_4$ and, after 3 min, dropwise with 1.0 mL of methanol. After the mixture was stirred for 15 min at room temperature, the solution was filtered through Kieselguhr. The solvent was removed to dryness, and 5 mL of pentane was added. The yellow solid obtained was separated by decantation and dried in vacuo. Yield: 80.8 mg (85%). IR (Nujol): 2052 cm$^{-1}$ (OsH). $^1$H NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 7.91 (m, 6 H, Ph), 7.07 (m, 6 H, Ph), 6.98 (m, 3 H, Ph), 4.46 (s, 5 H, Cp), 1.44 (m, 3 H, PCH), 1.04 (dd, $J$(HH) = 7.2 Hz, $J$(PH) = 12.6 Hz, 9 H, $PCCH_3$), 0.87 (dd, $J$(HH) = 7.2 Hz, $J$(PH) = 12.6 Hz, 9 H, $PCCH_3$), −15.27 (dd, $J$(PH) = 29.7 Hz, $J$(PH) = 29.7 Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 33.6 (d, $J$(PP) = 9.8 Hz, $P^iPr_3$), 21.2 (d, $J$(PP) = 9.8 Hz, $PPh_3$). Anal. Calcd for $C_{32}H_{42}OsP_2$: C, 56.62; H, 6.24. Found: C, 56.34; H, 6.61. MS (FAB$^+$): *m/e* 681 ($M^+$ + H).

**Preparation of $[OsH_2(\eta^5\text{-}C_5H_5)(PPh_3)(P^iPr_3)]BF_4$ (9).** A solution of **8** (70.6 mg, 0.10 mmol) in 6 mL of diethyl ether was treated with 14.2 $\mu$L (0.10 mmol) of $HBF_4\cdot OEt_2$. The white solid formed was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 70 mg (92%). IR (Nujol): $\nu(BF_4)$ 1065 cm$^{-1}$. $^1$H NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 7.60−7.53 (m, 6 H, Ph), 7.51−7.46 (m, 9 H, Ph), 5.18 (s, 5 H, Cp), 1.57 (m, 3 H, PCH), 1.03 (dd, $J$(HH) = 7.2 Hz, $J$(PH) = 15.0 Hz, 18 H, $PCCH_3$), −13.09 (dd, $J$(PH) = 28.9 Hz, $J$(PH) = 28.9 Hz, 2 H, $OsH_2$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CD_2Cl_2$, 293 K): $\delta$ 35.4 (d, $J$(PP) = 26.6 Hz, $P^iPr_3$), 9.7 (d, $J$(PP) = 26.6 Hz, $PPh_3$). Anal. Calcd for $C_{32}H_{43}BF_4OsP_2$: C, 50.13; H, 5.65. Found: C, 49.69; H, 5.26. MS (FAB$^+$): *m/e* 681 ($M^+$).

**X-ray Structure Analysis of Complex $[OsH(\eta^5\text{-}C_5H_5)\{NH{=}C(Ph)C_6H_4\}(P^iPr_3)]BF_4$ (4).** The poor quality of the crystals caused the repetition of the data collection and refinement with different crystals. Finally, a brown, prismatic crystal glued on a glass fiber and mounted on a Siemens-CCD diffractometer (sealed tube 2.4 kW, $\lambda$ = 0.71073, $T$ = 153.0(2) K) gave data good enough to properly solve the structure. A summary of crystal data and refinement parameters is reported in Table 3. A total of 11 782 reflections were collected via runs of $\omega$ scans at different $\varphi$ values, over a $\theta$ range of 1.7−23.5°. All data were corrected for absorption using a semiempirical method.[24] The structure was solved by Patterson (Os atoms, SHELXL97[25]) and conventional Fourier techniques and refined by full-matrix least-squares on $F^2$ (SHELXL97[25]). Two independent molecules (the A and C enantiomers) were observed in the asymmetric unit. Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms (except the hydride and N−H atoms) were included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms. Atomic scattering factors, corrected for anomalous dispersion, were implemented by the program. The refinement converged to R1($F$) = 0.0747 [$F^2 > 2\sigma(F^2)$], and wR2($F^2$) = 0.1914 [all data], with weighting parameters $x$ = 0.1188 and $y$ = 7.0299.

**X-ray Structure Analysis of Complex $[OsH(\eta^5\text{-}C_5H_5)(PPh_2C_6H_4)(P^iPr_3)]PF_6$ (6).** A crystal suitable for X-ray diffraction analysis was mounted onto a glass fibber and transferred to a Siemens-P4 automatic diffractometer ($T$ = 296.0(2) K, Mo K$\alpha$ radiation, graphite monocromator, $\lambda$ = 0.71073 Å). Accurate unit cell parameters and an orientation matrix were determined by least-squares fitting from the settings of 62 high-angle reflections. Crystal data and details on data collection and refinements are given in Table 3. Data were collected by the $\omega$ scan method over a $\theta$ range of 1.5−25°. Decay was monitored by measuring three standard

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[24] *SADABS*, Area-Detector Absorption Correction; Siemens Industrial Automation, Inc.: Madison, WI, 1996.

[25] Sheldrick, G. M. *SHELX Suite of Programs for Crystal Structure Analysis* (Release 97-2); Institüt für Anorganische Chemie der Universität: Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

**Table 3. Crystal Data and Data Collection and Refinement for [$OsH(\eta^5\text{-}C_5H_5)\{NH{=}C(Ph)C_6H_4\}(P^iPr_3)]BF_4$ (4) and [$OsH(\eta^5\text{-}C_5H_5)(PPh_2C_6H_4)(P^iPr_3)]PF_6$ (6)**

| | 4 | 6 |
|---|---|---|
| Crystal Data | | |
| formula | $C_{27}H_{37}BF_4NOsP$ | $C_{32}H_{41}F_6OsP_3$ |
| molecular wt | 683.56 | 822.76 |
| color and habit | brown, prismatic block | orange, prismatic block |
| symmetry, space group | orthorhombic, $Pca2_1$ | monoclinic, $P2_1/c$ |
| $a$, Å | 29.689(2) | 16.516(2) |
| $b$, Å | 10.5522(8) | 21.221(3) |
| $c$, Å | 16.9856(13) | 19.470(2) |
| $\beta$, deg | | 101.059(6) |
| $V$ Å$^3$ | 5321.2(7) | 6697.2(14) |
| $Z$ | 8 | 8 |
| $D_{calc}$, g cm$^{-3}$ | 1.706 | 1.632 |
| Data Collection and Refinement | | |
| diffractometer | Siemens-CCD | Siemens-P4 |
| $\lambda$(Mo K$\alpha$), Å | 0.71073 | 0.71073 |
| monochromator | graphite oriented | graphite oriented |
| $\mu$, mm$^{-1}$ | 4.897 | 4.006 |
| scan type | $\omega$ scans at different $\varphi$ values | $\omega$ |
| $2\theta$ range, deg | $3° \leq 2\theta \leq 46.5°$ | $3° \leq 2\theta \leq 50°$ |
| temp, K | 153.0(2) | 296.0(2) |
| no. of data collect | 11 782 ($h$: −33, 8; $k$: −5, 11; $l$: −18, 18) | 15 033 ($h$: 0, 19; $k$: −25, 25; $l$: −23, 22) |
| no. of unique data | 6767 (merging $R$ factor 0.0398) | 11 710 (merging $R$ factor 0.0515) |
| no. of params refined | 581 | 778 |
| R1[a] [$F^2 > 2\sigma(F^2)$] | 0.0747 | 0.0508 |
| wR2[b] [all data] | 0.1914 | 0.1409 |
| $S$[c] [all data] | 1.054 | 1.011 |

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof $= S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where $n$ is the number of reflections and $p$ is the number of refined parameters.

reflections every 100 measurements. Corrections for decay and absoption (semiempirical method[26]) were applied. The structure was solved by Patterson (Os atoms, SHELXL97[25]) and conventional Fourier techniques and refined by full-matrix least-squares on $F^2$ (SHELXL97[25]). Two independent molecules (both the A enantiomers) were observed in the asymmetric unit. Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms. Atomic scattering factors, corrected for anomalous dispersion, were implemented by the program. The refinement converged to $R1(F) = 0.0508$ [$F^2 > 2\sigma(F^2)$], and $wR2(F^2) = 0.1409$ [all data], with weighting parameters $x = 0.0799$ and $y = 3.877$.

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**Supporting Information Available:** Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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