# Formation of Azabutadienyl Fragments by Addition of the Isopropenyl Substituent of a Phosphine to Benzonitriles, Promoted by an Osmium Center

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Complex $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**1**) reacts with *p*-tolunitrile, benzonitrile, and *p*-chlorobenzonitrile to give the corresponding iminophosphine derivatives $Os(\eta^5\text{-}C_5H_5)Cl\{NH{=}C(p\text{-}C_6H_4R)CH{=}C(CH_3)P^iPr_2\}$ (R = $CH_3$ (**2**), H (**3**), Cl (**4**)), as a result of the insertion of the carbon−nitrogen triple bond of the nitriles into one of the C($sp^2$)−H bonds of the phosphine of **1**. Treatment of **2**−**4** with $NaBH_4$ and methanol produces the rupture of the P−C($CH_3$) bond of the iminophosphine ligands and the formation of the respective osmapyrrole derivatives $Os(\eta^5\text{-}C_5H_5)\{NH{\cdots}C(p\text{-}C_6H_4R){\cdots}CH{\cdots}C(CH_3)\}(PH^iPr_2)$ (R = $CH_3$ (**5**), H (**6**), Cl (**7**)). The addition of $HBF_4{\cdot}Et_2O$ to the diethyl ether solutions of **5**−**7** leads to the hydride-azabutadienyl-osmium(IV) complexes $[OsH(\eta^5\text{-}C_5H_5)\{NH{=}C(p\text{-}C_6H_4R)CH{=}C(CH_3)\}(PH^iPr_2)]BF_4$ (R = $CH_3$ (**8**), H (**9**), Cl (**10**)), as a consequence of the protonation of the metallic center of **5**−**7**. Complexes **3** and **10** have been characterized by X-ray diffraction analysis.

## Introduction

The formation of carbon−carbon bonds mediated by transition metal compounds has emerged in its own right over the past few years as an important step in organic synthesis.[1] Because the alkanes are among the most abundant molecules, there is great interest in the development of methods for the coupling between alkyl groups and other organic fragments.[2] However, the direct addition of a C($sp^3$)−H bond to unsaturated molecules remains difficult.

In contrast to alkanes, the reactions involving alkenes are promising processes regarding synthetic applications. Thus, for example, those between olefins and nitriles provide convenient routes to useful organonitrogen molecules.[3] So, the alkane dehydrogenation[4] seems to be the most reasonable first step in order to perform alkane functionalization.

In addition, it should be noted that alkanes are very weak Lewis bases and, therefore, blind molecules. They generally need the assistance of a coordination auxiliary to approach the transition metal. In this context, alkylphosphines could play an important role as guiding alkane models. The use of a coordination assistance strategy involves the rupture of the carbon-assistant bond after the coupling, as an additional step within the overall synthetic process.[5]

As a part of our work on the chemistry of the Os-cyclopentadienyl unit,[6] we have recently reported that the triisopropylphosphine complex $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ can be converted into the isopropenyldi(isopropyl)phosphine derivative $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}CH_2{=}C)CH_3)]P^iPr_2\}$ in a three-step procedure (Scheme 1). The process involves the oxidative addition of molecular hydrogen to $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$, the subsequent reaction of the

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(1) See for example: (a) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281. (b) Naota, T.; Takaya, H.; Murahashi, S.-I. *Chem. Rev.* **1998**, *98*, 2599. (c) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *Eur. J. Inorg. Chem.* **1999**, 1047. (d) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741. (e) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067. (f) Esteruelas, M. A.; López, A. M. In *Recent Advances in Hydride Chemistry*; Elsevier: Amsterdam, 2001; Chapter 7, pp 189−248. (g) Guerchais, V. *Eur. J. Inorg. Chem.* **2002**, 783.

(2) See for example: (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180. (b) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995. (c) Jones, W. D. *Science* **2000**, *287*, 1942. (d) Kondo, Y.; García-Cuadrado, D.; Hartwig, J. F.; Boaen, N. K.; Wagner, N. L.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 1164. (e) Periana, R. A.; Mironov, O.; Taube, D.; Bhalla, G.; Jones, C. J. *Science* **2003**, *301*, 814.

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(5) Crochet, P.; Demerseman, B.; Rocaboy, C.; Schleyer, D. *Organometallics* **1996**, *15*, 3048, and references therein.

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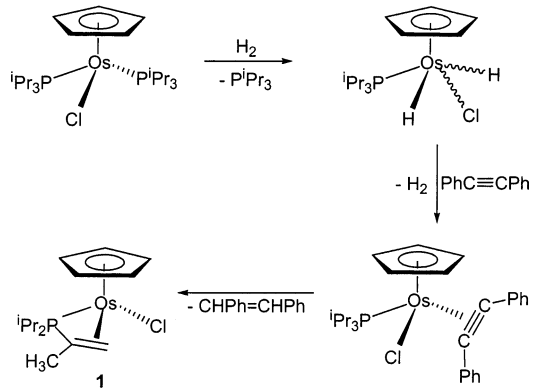
**Scheme 1**

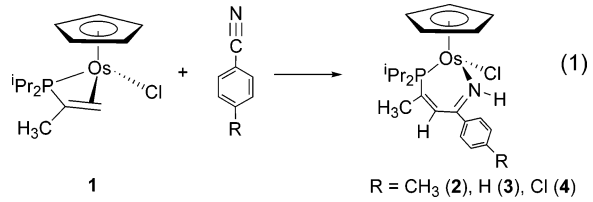



resulting dihydride with diphenylacetylene to afford $Os(\eta^5\text{-}C_5H_5)Cl(\eta^2\text{-}PhC{\equiv}CPh)(P^iPr_3)$, and the reduction of the coordinated alkyne by hydrogen transfer from an isopropyl substituent of the phosphine that is dehydrogenated.[7]

Our interest in developing new carbon−carbon coupling processes,[1f] in particular those leading to organonitrogen fragments,[8] prompted us to investigate the reactions of the isopropenyldi(isopropyl)phosphine complex $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}CH_2{=}C)CH_3)]P^iPr_2\}$ with benzonitriles. In this paper, we show the formation of azabutadienyl fragments by transfer of the isopropenyl group of this compound from the phosphine to benzonitriles.

## Results and Discussion

**Addition of the Isopropenyl Group to Nitriles.** In toluene under reflux, the isopropenyldi(isopropyl)-phosphine complex $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}CH_2{=}C)CH_3)]P^iPr_2\}$ (**1**) reacts with *p*-tolunitrile, benzonitrile, and *p*-chlorobenzonitrile to give the corresponding imino-phosphine derivatives $Os(\eta^5\text{-}C_5H_5)Cl\{NH{=}C(p\text{-}C_6H_4R)\text{-}CH{=}C(CH_3)P^iPr_2\}$ (R = $CH_3$ (**2**), H (**3**), Cl (**4**)), as a result of the addition of one of the C($sp^2$)−H bonds of the isopropenyl substituent of the phosphine of **1** to the carbon−nitrogen triple bond of the nitriles. The coupling is regiospecific and involves the formation of new carbon−carbon and nitrogen−hydrogen bonds (eq 1).




Complexes **2**−**4** were isolated as purple solids in 60−65% yield and characterized by MS, elemental analysis, IR, and $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Complex **3** was further characterized by an X-ray crystallographic study. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. A drawing of one of them is shown in Figure 1. Selected bond distances and angles for both molecules are listed in Table 1.

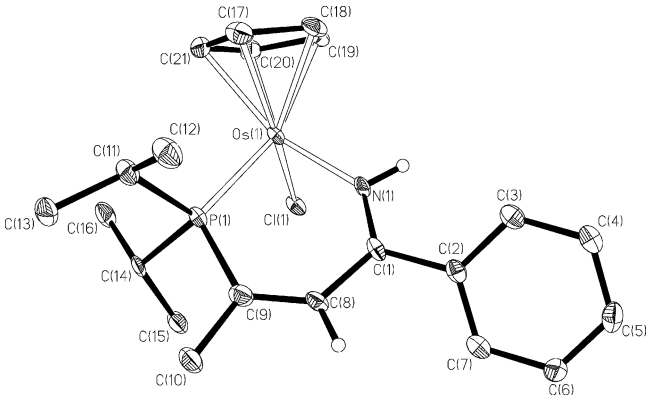



**Figure 1.** Molecular diagram of $Os(\eta^5\text{-}C_5H_5)Cl\{NH{=}C(Ph)CH{=}C(CH_3)P^iPr_2\}$ (**3**).

The molecules are associated by intermolecular Cl···· H−N hydrogen bonds. Thus, the separations between the atoms involved in the interactions (2.55(3) and 2.60(3) Å) are significantly shorter than the sum of the van der Waals radii of hydrogen and chlorine ($r_{vdw}$(H) = 1.20, $r_{vdw}$(Cl) = 1.80 Å).

The geometry around the osmium atom of each molecule can be described as a distorted octahedron, with the cyclopentadienyl ligand occupying the three sites of a face. The formed P,N-chelate ligand acts with a bite angle of 90.34(8)° in both molecules and forms an almost planar six-membered ring with the metal.

The imine group is bonded to the osmium center with Os−N−C angles of 136.9(2)° (molecule **a**) and 137.3(2)° (molecule **b**), which compare well with the M−N−C angles found in the osmium derivatives $OsCl_2(=C{=}CHPh)(NH{=}CH_2)(P^iPr_3)_2$ (142.5(6)°), $[OsCl(=C{=}CHPh)(NH{=}CMe_2)(H_2O)(P^iPr_3)_2][CF_3SO_3]$ (142.7(6)°),[9] and $OsCl_2(=C{=}CHPh)(NH{=}CMe_2)(NH_2CH_2CH{=}CH_2)$-

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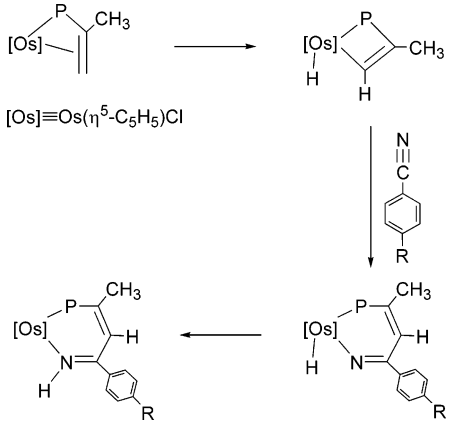
**Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex Os($\eta^5$-$C_5H_5$)Cl{NH=C(Ph)CH=C($CH_3$)P$^i$Pr$_2$} (3)**

| | molecule a | molecule b | | molecule a | molecule b |
|---|---|---|---|---|---|
| Os(1)−Cl(1) | 2.4468(8) | 2.4461(8) | Os(1)−C(21) | 2.208(3) | 2.201(3) |
| Os(1)−P(1) | 2.2686(9) | 2.2687(9) | P(1)−C(9) | 1.818(3) | 1.817(3) |
| Os(1)−N(1) | 2.015(3) | 2.017(3) | N(1)−C(1) | 1.307(4) | 1.304(4) |
| Os(1)−C(17) | 2.174(3) | 2.176(3) | C(1)−C(2) | 1.485(4) | 1.487(4) |
| Os(1)−C(18) | 2.187(3) | 2.181(3) | C(1)−C(8) | 1.457(5) | 1.459(5) |
| Os(1)−C(19) | 2.235(3) | 2.222(3) | C(8)−C(9) | 1.336(5) | 1.344(5) |
| Os(1)−C(20) | 2.207(3) | 2.202(3) | C(9)−C(10) | 1.512(5) | 1.519(5) |
| P(1)−C(11) | 1.864(3) | 1.867(3) | P(1)−C(14) | 1.846(3) | 1.858(3) |
| Cl(1)−Os(1)−P(1) | 94.42(3) | 94.19(3) | Os(1)−P(1)−C(9) | 115.23(12) | 114.99(12) |
| Cl(1)−Os(1)−N(1) | 86.29(8) | 86.54(8) | Os(1)−N(1)−C(1) | 136.9(2) | 137.3(2) |
| Cl(1)−Os(1)−M[a] | 120.1 | 120.1 | P(1)−C(9)-C(8) | 121.5(3) | 121.9(3) |
| P(1)−Os(1)−N(1) | 90.34(8) | 90.34(8) | P(1)−C(9)-C(10) | 120.4(3) | 120.2(3) |
| P(1)−Os(1)−M[a] | 128.1 | 128.2 | N(1)−C(1)-C(2) | 119.6(3) | 119.9(3) |
| N(1)−Os(1)−M[a] | 126.3 | 126.3 | N(1)−C(1)-C(8) | 124.1(3) | 124.0(3) |
| C(8)−C(9)-C(10) | 118.1(3) | 117.9(3) | C(2)−C(1)-C(8) | 116.2(3) | 116.1(3) |

[a] M is the centroid of the C(17)−C(21) Cp ligand.

(P$^i$Pr$_3$) (141.8(6)°)[10] and in the rhenium complex Re($\eta^5$-$C_5H_5$)(NO)(NH=CPh$_2$)(PPh$_3$) (136.2(2)°).[11] The Os(1)−N(1) bond lengths (2.015(3) (**a**) and 2.017(3) (**b**) Å) agree well with those found in the above-mentioned imine-osmium derivatives and support the Os−N single bond formulation. The N(1)−C(1) distances (1.307(4) (**a**) and 1.304(4) (**b**) Å) are also similar to the observed ones in imine derivatives,[9−11] azavinylidene compounds,[12] organic azaallenium cations,[13] and 2-azaallenyl complexes.[14] The C(1)−C(8) (1.457(5) (**a**) and 1.459(5) (**b**) Å) and C(8)−C(9) (1.336(5) (**a**) and 1.344 (**b**) Å) bond lengths are in accordance with the mean values reported for single and double C(sp$^2$)−C(sp$^2$) bonds, 1.48 and 1.34 Å, respectively.[15] The P(1)−C(9) distances (1.818(3) (**a**) and 1.817(3) (**b**) Å) are between 0.03 and 0.05 Å shorter than the P(1)−C(11) (1.864(3) (**a**) and 1.867(3) (**b**) Å) and P(1)−C(14) (1.846(3) (**a**) and 1.858(3) (**b**) Å) bond lengths. A similar fact has been observed for the isopropenyldi(isopropyl)phosphine complex [Os($\eta^5$-$C_5H_5$){$\eta^2$-(*Z*)-PhCH=CHPh}{[$\eta^2$-$CH_2$=C($CH_3$)]P$^i$Pr$_2$}]-$PF_6$, where the P−C(sp$^2$) distance is about 0.06 Å shorter than the P−C(sp$^3$) bond lengths. The Os(1)−P(1) distances of 2.2686(9) (**a**) and 2.2687(9) (**b**) Å are about 0.02 Å shorter than the Os−P distance found in the complex OsH($\eta^5$-$C_5H_4CH_3$){$\eta^2$-(*E*)-PhCH=CHPh}-{P[C($CH_3$)=$CH_2$]$^i$Pr$_2$} (2.2886(11) Å).[7] Since in the latter the phosphorus atom is also bonded to a C(sp$^2$) substituent and two C(sp$^3$) groups, this difference appears to be a consequence of the chelate effect in **3**.

**Scheme 2**




In agreement with the presence of the N−H group in **2**−**4**, the IR spectra in Nujol of these compounds show a $\nu$(N−H) band between 3150 and 3190 cm$^{-1}$. In the $^1$H NMR spectra in benzene-$d_6$ at room temperature, the NH resonance appears at about 11.9 ppm, as a broad signal. In addition, the resonances corresponding to the olefinic CH-hydrogen atom and the PCC$H_3$ protons of the P,N-chelate ligands should be mentioned. The olefinic hydrogen atom of these ligands gives rise to a double multiplet at 6.5 ppm, with a H−P coupling constant of about 27 Hz, whereas the PCC$H_3$ protons display a double doublet at about 1.4 ppm, with H−P and H−H coupling constants of about 7 and 1 Hz, respectively. In the $^{13}$C{$^1$H} NMR spectra the C(sp$^2$) carbon atoms of the diheterometallaring give rise to doublets at about 160 (CN), 140 (CH), and 132 (CP) ppm, with C−P coupling constants of between 10 and 11, about 8, and between 20 and 22 Hz, respectively. The $^{31}$P{$^1$H} NMR spectra contain a singlet at about 24 ppm, shifted about 27 ppm to lower field with regard to that of **1**.

The formation of **2**−**4** can be rationalized according to Scheme 2. Initially, the activation of one of the C(sp$^2$)−H bonds of the $CH_2$ group of the isopropenyl substituent of the phosphine of **1** should afford a

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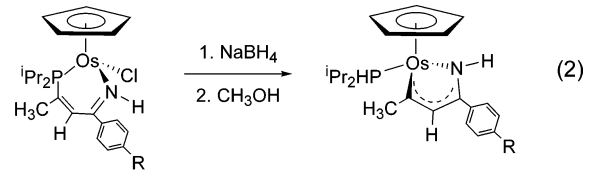
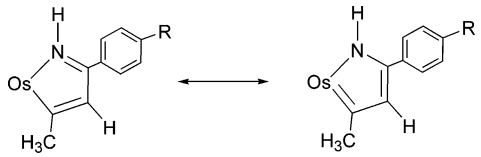
hydride-alkenyl intermediate. Thus, the insertion of the carbon−nitrogen triple bond of the nitriles into the Os−C($sp^2$) bond, followed by the subsequent migration of the hydride from the metallic center to the nitrogen atom, could give the iminophosphine derivatives. Although the insertion of the carbon−nitrogen triple bond of nitriles into a metal−carbon $\sigma$ bond is not a common process, it has been found to occur.[16]

**2. Release of the Isopropenyl-Benzonitrile Units from the $^i$Pr$_2$P Group.** The fragments resulting of the addition of the C($sp^2$)−H bond of the isopropenyl substituent of the phosphine to the carbon−nitrogen triple bond of the nitriles can be removed from the phosphine group by reaction with sodium tetrahydrideborate (eq 2). Treatment at room temperature of toluene solutions of **2**−**4** with approximately 8.0 equiv of sodium tetrahydrideborate and 1.0 mL of methanol produces the cleavage of the P−C($CH_3$) bond of the iminophosphine ligands and the formation of the corresponding osmapyrrole derivatives Os($\eta^5$-$C_5H_5$){NH⋯C(*p*-$C_6H_4$R)⋯CH⋯C($CH_3$)}(PH$^i$Pr$_2$) (R = $CH_3$ (**5**), H (**6**), Cl (**7**)).




Complexes **5**−**7** were isolated as brown oils in high yield (70−90%) and characterized by MS and $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR spectroscopy. In agreement with the presence of a diisopropylphosphine ligand in these compounds, their $^1$H NMR spectra in benzene-$d_6$ at room temperature contain a HP resonance at about 3.5 ppm, which appears as a double triplet with H−P and H−H coupling constants of about 336 and 4 Hz, respectively. The $^1$H NMR spectra are also consistent with the cleavage of the P−C($CH_3$) bond and the formation of osmapyrrole units. Thus, the CH resonance of the five-membered heterometallacycles does not show any H−P coupling and appears as a singlet at about 7.5 ppm. The NH resonance is observed at about 8.8 ppm, shifted about 3 ppm toward higher field with regard to the chemical shifts observed for **2**−**4**. In the $^{13}$C{$^1$H} NMR spectra the CH resonance of the osmapyrrole units also appears as a singlet, between 126 and 129 ppm. The OsC and CN resonances are observed as doublets, between 222 and 224 ppm and between 177 and 180 ppm, with C−P coupling constants of about 7 and 4 Hz, respectively. The $^{31}$P{$^1$H} NMR spectra show a singlet at about 41 ppm.

**Scheme 3**



The $^{13}$C{$^1$H} NMR spectra of **5**−**7** are consistent with the delocalized structure shown in eq 2 and suggest that for an adequate description of the bonding situation in the five-membered heterometallaring of these compounds the resonance forms shown in Scheme 3 should be taken into account. Thus, the OsC resonance in **5**−**7** appears shifted about 70 ppm to higher field in comparison with the shift of a typical Os-carbene[17] and more than 30 ppm to lower field with regard to the chemical shift observed for the $OsC_\alpha$ resonance in six-coordinate osmium-alkenyl complexes.[18] The chemical shifts of the OsC resonance of **5**−**7** are consistent with those corresponding to the OsC resonance of complexes Os{CHCHC(O)Ph}Cl(CO)(P$^i$Pr$_3$)$_2$ (230.13 ppm),[19] OsH{CHCHC(O)$CH_3$}(CO)(P$^i$Pr$_3$)$_2$ (250.8 ppm),[20] and OsH$_3$-{$C_6H_8$C(O)$CH_3$}(P$^i$Pr$_3$)$_2$ (255.9 ppm),[21] where a similar bonding situation has been proposed to exist. On the basis of spectroscopic data, delocalized metalapyrrole structures have been also proposed for W,[22] Fe,[23] and Ir[24] complexes.

The formation of **5**−**7** by reaction of **2**−**4** with sodium tetrahydrideborate and methanol can be rationalized according to Scheme 4. The replacement of chloride by hydride in the starting compounds should afford hydride-iminophosphine derivatives, which should evolve by elimination of [NH=C(*p*-$C_6H_4$R)CH=C($CH_3$)PH$^i$Pr$_2$]$^+$.[25] These cations could stabilize the metallic center by means of the coordination of the nitrogen atom and the carbon−carbon double bond.

(16) See for example: (a) Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 4063. (b) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. (c) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. (d) Dormond, A.; Aaliti, A.; Elbouadili, A.; Moise, C. *J. Organomet. Chem.* **1987**, *329*, 187. (e) Sternal, R. S.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7920. (f) den Haan, K. H.; Luinstra, G. A.; Meetsma, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1509. (g) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041. (h) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *J. Am. Chem. Soc.* **1987**, *109*, 5868. (i) Bochmann, M.; Wilson, L. M.; Husthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148. (j) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. (k) Stack, J. G.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *Organometallics* **1990**, *9*, 453. (l) Alelyunas, Y. W.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406. (m) Klose, A.; Solari, E.; Ferguson, R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 2414.

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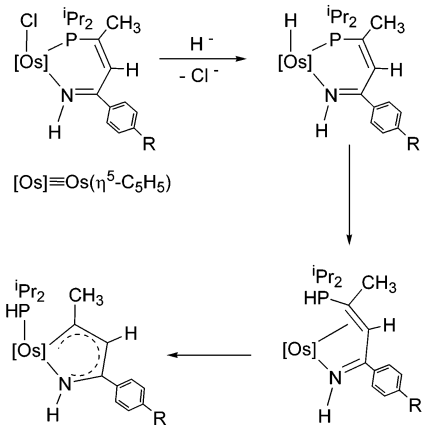
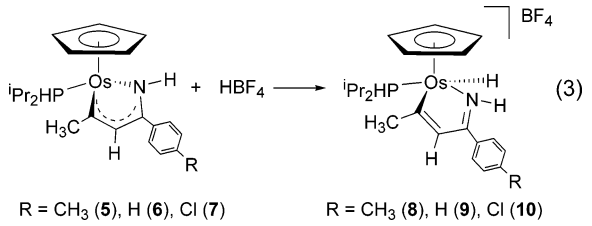
**Scheme 4**




Transition metal complexes containing an $\eta^2$-[$R_3PC(R)$=$CR'_2$]$^+$ ligand are known.[26] Finally, the activation of the P−C($CH_3$) bond of these cations should give **5**−**7**.

**3. Protonation of the Osmapyrrole Units.** Complexes **5**−**7** react with $HBF_4$·$Et_2O$. The addition at 0 °C of 1.0 equiv of the acid to diethyl ether solutions of these compounds leads to the corresponding hydride-azabutadienyl-osmium(IV) derivatives [OsH($\eta^5$-$C_5H_5$){NH=C(*p*-$C_6H_4$R)CH=C($CH_3$)}($PH^iPr_2$)]$BF_4$ (R = $CH_3$ (**8**), H (**9**), Cl (**10**)), as a result of the addition of the proton of the acid to the metallic center of **5**−**7**. Complexes **8**−**10** were isolated as yellow solids in high yield (80−82%), according to eq 3.




Complexes **8**−**10** were characterized by MS, elemental analysis, IR, and $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR spectroscopy. Complex **10** was further characterized by an X-ray crystallographic study.[27] Figure 2 shows a view of the structure. Table 2 collects selected bond distances and angles.

The distribution of ligands around the osmium atom can be described as a four-legged piano-stool geometry with the metalated carbon atom (C(3)) of the azabutadienyl fragment *transoid* to the hydride and *cisoid* to the phosphine ligand. The C(3)−Os(1)−H(01) and P(1)−Os(1)−C(3) angles are 139.0(2)° and 79.6(2)°, respectively.

The chelate azabutadienyl ligand acts with a bite angle of 75.4(3)°. The five-membered heterometallacycle is almost planar. The deviations (in Å) from the best plane are 0.004(3) (Os(1)), −0.006(4) (N(1)), 0.004(5) (C(1)), 0.001(5) (C(2)), and −0.004(4) (C(3)). The imine group is bonded to the metallic center with an Os(1)−N(1)−C(1) angle of 120.3(5)°. The Os(1)−N(1) (2.040(5) Å), N(1)−C(1) (1.314(9) Å), C(1)−C(2) (1.419(10) Å), and C(2)−C(3) (1.366(10) Å) bond lengths are statistically identical with the distances Os(1)−N(1), N(1)−C(1), C(1)−C(8), and C(8)−C(9) of **3**. This indicates that the bonding situation in the sequence Os−N−C−C−C of the heterometallacycle of **10** is the same as that in the diheterometallacycle of **3**. Furthermore, it suggests that the contribution of the carbene resonance form to the structure of the five-membered rings of **8**−**10** is not significant. In agreement with this, the Os−C(3) distance of 2.098(7) Å is similar to those found in alkenyl derivatives such as [Os{(*E*)-CH=CHPh}(C≡CPh)(≡$CCH_2$Ph)($P^iPr_3$)$_2$]$BF_4$ (2.036(9) Å),[28] OsH($\eta^5$-{$C_5H_4SiPh_3$}{*o*-$C_6H_4C(CH_3)$=CH}($P^iPr_3$) (2.082(5) Å),[6k] or [Os{CH=CHC(O)$OCH_3$}(=C=CH$CO_2CH_3$)(CO)($P^i$-$Pr_3$)$_2$]$BF_4$ (2.078(5) Å).[29]

The $^{13}$C{$^1$H} NMR spectra of **8**−**10** agree well with the structural parameters of the heterometallacycle of

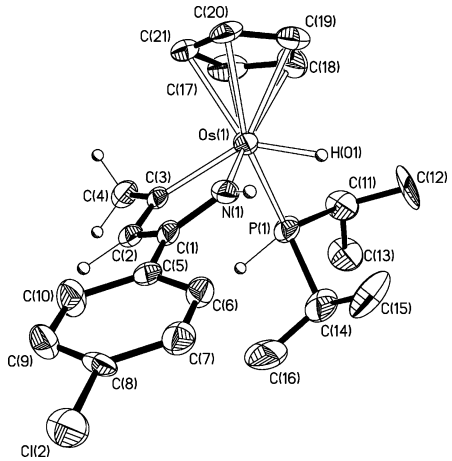



**Figure 2.** Molecular diagram of the cation of [OsH($\eta^5$-$C_5H_5$){NH=C(*p*-$C_6H_4$Cl))CH=C($CH_3$)}($PH^iPr_2$)]$BF_4$ (**10**).

**Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex [OsH($\eta^5$-$C_5H_5$)-{NH=C(*p*-$C_6H_4$Cl))CH=C($CH_3$)}($PH^iPr_2$)]$BF_4$ (10)**

| | | | |
|---|---|---|---|
| Os(1)−P(1) | 2.290(2) | P(1)−C(11) | 1.802(8) |
| Os(1)−N(1) | 2.040(5) | P(1)−C(14) | 1.862(8) |
| Os(1)−C(3) | 2.098(7) | P(1)−H(1B) | 1.480(6) |
| Os(1)−C(17) | 2.202(6) | N(1)−C(1) | 1.314(9) |
| Os(1)−C(18) | 2.188(8) | C(1)−C(2) | 1.419(10) |
| Os(1)−C(19) | 2.264(8) | C(1)−C(5) | 1.467(10) |
| Os(1)−C(20) | 2.274(6) | C(2)−C(3) | 1.366(10) |
| Os(1)−C(21) | 2.244(7) | C(3)−C(4) | 1.509(9) |
| M[a]−Os(1)−H(01) | 103.5 | C(3)−Os(1)−H(01) | 139.0(2) |
| M[a]−Os(1)−N(1) | 129.0 | Os(1)−N(1)−C(1) | 120.3(5) |
| M[a]−Os(1)−C(3) | 117.9 | N(1)−C(1)-C(2) | 113.8(6) |
| M[a]−Os(1)−P(1) | 130.1 | N(1)−C(1)-C(5) | 121.8(6) |
| N(1)−Os(1)−C(3) | 75.4(3) | C(2)−C(1)-C(5) | 124.4(7) |
| N(1)−Os(1)−P(1) | 99.89(18) | C(1)−C(2)-C(3) | 115.2(7) |
| P(1)−Os(1)−C(3) | 79.6(2) | C(2)−C(3)-Os(1) | 115.3(5) |
| N(1)−Os(1)−H(01) | 79.0(2) | C(2)−C(3)-C(4) | 121.5(7) |
| P(1)−Os(1)−H(01) | 74.0(2) | C(4)−C(3)-Os(1) | 123.1(5) |

[a] M represents the midpoint of the Cp ring.

(26) See for example: Esteruelas, M. A.; Lahoz, F. J.; Martín, M.; Martínez, A.; Oro, L. A.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **1999**, *577*, 265.

(27) The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. However, we only discuss one of them because the other one is disordered.

(28) Barrio, P.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2004**, *126*, 1946.

(29) Bohanna, C.; Buil, M. L.; Esteruelas, M. A.; Oñate, E.; Valero, C. *Organometallics* **1999**, *18*, 5176.

**10** and reveal that the contribution of the carbene resonance form to the structure of the five-membered heterometallarings is much less in **8**−**10** than in **5**−**7**. Thus, in the $^{13}C\{^1H\}$ NMR spectra of **8**−**10**, the OsC resonance appears as a doublet, between 194 and 197 ppm, shifted almost 30 ppm toward higher field with regard to the chemical shifts observed for **5**−**7**. The C−P coupling constant (16 Hz for the three compounds) is also sensitive to the protonation of the metallic center, increasing its value more than 100%. The diminution of the contribution of the carbene resonance form to the bonding, as a result of the protonation, is in agreement with the formal oxidation of the metallic center, which decreases the back-bonding Os(d$\pi$) → C(p$\pi$) interaction. The CN resonance is observed between 183 and 185 ppm, as a singlet, whereas the CH resonance of the five-membered rings appears at about 135 ppm as a doublet, with a C−P coupling constant of 3 Hz for the three complexes.

The $^{31}P\{^1H\}$ NMR spectra of these compounds are also sensitive to the formal oxidation of the metallic center. They show a singlet between 19 and 22 ppm, shifted about 20 ppm to higher field compared with the observed one in the spectra of **5**−**7**.

The IR spectra of **8**−**10** in Nujol are consistent with the presence of the hydride and azabutadienyl ligands in these compounds. Thus, the most noticeable feature of the spectra is the presence of $\nu$(N−H) and $\nu$(Os−H) bands, between 3330 and 3345 $cm^{-1}$ and between 2050 and 2065 $cm^{-1}$, respectively. In the $^1H$ NMR spectra in dichloromethane-$d_2$ at room temperature, the NH resonance is observed between 10.50 and 10.90 ppm, as a broad signal, whereas the CH resonance of the heterometallarings appears at about 7.3 ppm as a singlet. The PH hydrogen atom of the diisopropylphosphine ligand gives rise to a doublet at about 4.5 ppm, with a H−P coupling constant of about 370 Hz. In the high-field region of the spectra the hydride resonance is observed at about −12.4 ppm, as a double doublet by spin coupling with the phosphorus nucleus of the phosphine (about 44 Hz) and the NH hydrogen atom (about 4 Hz). The last coupling was confirmed by the $^1H-^1H$ COSY NMR spectra.

## Concluding Remarks

This paper shows the formation of azabutadienyl fragments, on the coordination sphere of a transition metal, starting from the isopropenyl substituent of a phosphine and benzonitriles.

The insertion of the carbon−nitrogen triple bond of benzonitriles into one of the C($sp^2$)−H bonds of the isopropenyl group of the phosphine of Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=$C(CH_3)$]P$^i$Pr$_2$} affords iminophosphine compounds, Os($\eta^5$-$C_5H_5$)Cl{NH=C(*p*-$C_6H_4$R)CH=$C(CH_3)$P-$^i$Pr$_2$}. Treatment of the latters with sodium tetrahydroborate and methanol produces the rupture of the P−C bond of the iminophosphine ligands and the formation of Os($\eta^5$-$C_5H_5$){NH···C(*p*-$C_6H_4$R)···CH···$C(CH_3)$}(PH-$^i$Pr$_2$), containing an osmapyrrole unit. The protonation of the metallic center of the osmapyrrole complexes leads to the hydride-azabutadienyl-osmium(IV) cations [OsH($\eta^5$-$C_5H_5$){NH=C(*p*-$C_6H_4$R)CH=$C(CH_3)$}(PH$^i$-Pr$_2$)]$^+$.

Although further work needs to be done in order to develop the methodology, in the light of these results it is clear that alkylphosphines, after being dehydrogenated, can be successfully used to add hydrocarbon fragments to unsaturated organic molecules.

## Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use.

$^1H$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian UNITY 300, a Varian Gemini 2000, a Bruker AXR 300, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks ($^1H$, $^{13}C\{^1H\}$) or external $H_3PO_4$ ($^{31}P\{^1H\}$). Coupling constants, *J*, are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer (Nujol mulls on polyethylene sheets). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectra analyses were performed with a VG Austospec instrument. In LSIMS$^+$ mode, ions were produced with the standard $Cs^+$ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used in the matrix.

**Preparation of Os($\eta^5$-$C_5H_5$)Cl{NH=C(*p*-$C_6H_4CH_3$)CH=C($CH_3$)P$^i$Pr$_2$} (2).** A yellow solution of **1** (160 mg, 0.36 mmol) in 8 mL of toluene was treated with *p*-tolunitrile (123 mg, 1.05 mmol) and heated under reflux for 30 h. The resultant deep purple solution was concentrated to dryness, and the product was extracted with diethyl ether (5 × 10 mL). The violet solution was concentrated to dryness, and a purple solid was obtained. The solid was washed with pentane (4 × 3 mL), separated by decantation, and dried in vacuo. Yield: 160 mg (61%). Anal. Calcd for $C_{22}H_{31}ClNOsP$: C, 46.67; H, 5.52; N, 2.47. Found: C, 46.48; H, 5.32; N, 2.40. IR (Nujol, $cm^{-1}$): $\nu$(NH) 3180 (w). $^1H$ NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 11.90 (br, 1H, NH), 7.18 (d, $J_{H-H}$ = 8.1, 2H, *o*-Ph), 6.85 (d, $J_{H-H}$ = 8.1, 2H, *m*-Ph), 6.64 (dm, $J_{H-P}$ = 27.3, 1H, =CH-), 4.69 (s, 5H, $C_5H_5$), 2.60 (m, 1H, PCH), 1.95 (s, 3H, *p*-$CH_3$), 1.61 (dd, $J_{H-P}$ = 14.4, $J_{H-H}$ = 6.9, 3H, PCHC$H_3$), 1.58 (m, 1H, PCH), 1.45 (dd, $J_{H-P}$ = 6.9, $J_{H-H}$ = 1.0, 3H, PC($CH_3$)=), 1.07 (dd, $J_{H-P}$ = 16.2, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), 0.85 (dd, $J_{H-P}$ = 13.2, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), 0.81 (dd, $J_{H-P}$ = 13.5, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 24.5 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $C_6D_6$, 293 K, plus APT): $\delta$ 160.8 (d, $J_{C-P}$ = 11, C=NH), 141.6 (s, $C_{ipso}$Ph), 140.6 (d, $J_{C-P}$ = 8, =CH), 138.2 (s, $C_{ipso}$Ph), 132.6 (d, $J_{C-P}$ = 21, PC=), 129.8 and 124.6 (both s, Ph), 74.2 (s, Cp), 35.0 (d, $J_{C-P}$ = 31, PCH), 27.6 (d, $J_{C-P}$ = 33, PCH), 24.7 (s, *p*-$CH_3$), 21.3 (s, PCH$CH_3$), 21.1 (s, PC($CH_3$)=), 19.3 (d, $J_{C-P}$ = 6, PCH$CH_3$), 18.9 and 18.6 (both s, PCH$CH_3$). MS (LSIMS$^+$): *m/z* 567 ($M^+$); 532 ($M^+$ − Cl).

**Preparation of Os($\eta^5$-$C_5H_5$)Cl{NH=C(Ph)CH=C($CH_3$)P-$^i$Pr$_2$} (3).** A yellow solution of **1** (152 mg, 0.34 mmol) in 12 mL of toluene was treated with benzonitrile (0.13 mL, 1.27 mmol) and heated under reflux for 22 h. The solvent was removed, and the product was extracted with diethyl ether (25 mL). The resultant purple solution was concentrated to dryness, and the purple solid obtained was washed with pentane (4 × 3 mL). The solid was dried in vacuo. Yield: 121 mg (65%). Anal. Calcd for $C_{21}H_{29}ClNOsP$: C, 45.68; H, 5.29; N, 2.54. Found: C, 45.58; H, 5.25; N, 2.60. IR (Nujol, $cm^{-1}$): $\nu$(NH) 3152 (w). $^1H$ NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 11.98 (br, 1H, NH), 7.30−6.90 (m, 5H, Ph), 6.57 (dm, $J_{H-P}$ = 27.0, 1H, =CH), 4.70 (s, 5H, $C_5H_5$), 2.59 (m, 1H, PCH), 1.61 (dd, $J_{H-P}$ = 14.7, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), 1.57 (m, 1H, PCH), 1.43 (dd, $J_{H-P}$ = 7.2, $J_{H-H}$ =

1.5, 3H, PC($CH_3$)═), 1.06 (dd, $J_{H-P}$ = 16.5, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), 0.83 (dd, $J_{H-P}$ = 15.3, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), 0.81 (dd, $J_{H-P}$ = 15.3, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 24.1 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $C_6D_6$, 293 K, plus APT): $\delta$ 160.9 (d, $J_{C-P}$ = 10, C═NH), 144.5 (s, $C_{ipso}$Ph), 140.6 (d, $J_{C-P}$ = 8, ═CH), 132.0 (d, $J_{C-P}$ = 20, PC═), 129.2, 128.8, and 124.5 (all s, Ph), 74.5 (s, Cp), 35.0 (d, $J_{C-P}$ = 31, PCH), 27.6 (d, $J_{C-P}$ = 33, PCH), 24.7, 21.0, 19.3, 18.9, and 18.6 (all s, PCH$CH_3$). MS (LSIMS$^+$): *m/z* 553 ($M^+$); 518 ($M^+$ − Cl).

**Preparation of Os($\eta^5$-$C_5H_5$)Cl{NH═C(*p*-$C_6H_4$Cl)CH═C($CH_3$)P$^i$Pr$_2$} (4).** A yellow solution of **1** (150 mg, 0.33 mmol) in 8 mL of toluene was treated with 4-chlorobenzonitrile (184 mg, 1.34 mmol) and heated under reflux for 15 h. After that period of time, the solution was cooled to room temperature and the solvent was removed. The product was extracted with diethyl ether (4 × 15 mL). The resultant purple solution was concentrated to dryness, and the purple solid obtained was washed with pentane (5 × 3 mL), separated by decantation, and dried in vacuo. Yield: 117 mg (60%). Anal. Calcd for $C_{21}H_{28}Cl_2NOsP$: C, 43.00; H, 4.81; N, 2.39. Found: C, 43.29; H, 4.88; N, 2.60. IR (Nujol, cm$^{-1}$): $\nu$(NH) 3191 (w). $^1H$ NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 11.88 (br, 1H, NH), 6.97−6.88 (m, 4H, Ph), 6.40 (dm, $J_{H-P}$ = 27.0, 1H, ═CH), 4.72 (s, 5H, $C_5H_5$), 2.59 (m, 1H, PCH), 1.59 (dd, $J_{H-P}$ = 14.7, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), 1.54 (m, 1H, PCH), 1.39 (dd, $J_{H-P}$ = 6.9, $J_{H-H}$ = 1.5, 3H, PC($CH_3$)═), 1.05 (dd, $J_{H-P}$ = 16.5, $J_{H-H}$ = 6.9, 3H, PCHC$H_3$), 0.80 (dd, $J_{H-P}$ = 15.1, $J_{H-H}$ = 7.0, 3H, PCHC$H_3$), 0.79 (dd, $J_{H-P}$ = 12.4, $J_{H-H}$ = 7.3, 3H, PCHC$H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 24.2 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $C_6D_6$, 293 K, plus APT): $\delta$ 159.4 (d, $J_{C-P}$ = 10, C═NH), 142.9 (d, $J_{C-P}$ = 2, $C_{ipso}$Ph), 140.3 (d, $J_{C-P}$ = 8, ═CH), 134.0 ($C_{ipso}$Ph), 132.0 (d, $J_{C-P}$ = 22, PC═), 129.4 and 125.6 (both s, Ph), 74.9 (s, Cp), 35.0 (d, $J_{C-P}$ = 31, PCH), 27.7 (d, $J_{C-P}$ = 33, PCH), 24.8 (s, PC($CH_3$)═), 21.0 (s, PCH$CH_3$), 19.2 (d, $J_{C-P}$ = 6, PCH$CH_3$), 18.9 (d, $J_{C-P}$ = 4, PCH$CH_3$), 18.6 (s, PCH$CH_3$). MS (LSIMS$^+$): *m/z* 587 ($M^+$); 552 ($M^+$ − Cl).

**Preparation of Os($\eta^5$-$C_5H_5$){NH···C(*p*-$C_6H_4CH_3$)···CH···C($CH_3$)}(PH$^i$Pr$_2$) (5).** A purple solution of **2** (216 mg, 0.38 mmol) in 8 mL of toluene was treated with sodium tetrahydrideborate (115 mg, 3.05 mmol), and 1 mL of methanol was added. The slurry was allowed to react at room temperature for 10 min, and then, the solvent was removed. The product was extracted with pentane (20 mL), the resultant dark brown solution was concentrated to dryness, and the product was isolated as a brown oil.[30] Yield: 182 mg (89%). $^1H$ NMR (300 MHz, $C_6D_6$, 293 K, plus COSY): $\delta$ 8.79 (br, 1H, NH), 7.55 (s, 1H, OsC($CH_3$)C*H*), 7.50 (d, $J_{H-H}$ = 8.1, 2H, *o*-Ph), 6.94 (d, $J_{H-H}$ = 8.1, 2H, *m*-Ph), 4.71 (s, 5H, $C_5H_5$), 3.59 (dt, $J_{H-P}$ = 336.6, $J_{H-H}$ = 3.6, 1H, PH), 3.39 (s, 3H, OsC($CH_3$)), 2.06 (s, 3H, *p*-$CH_3$), 1.79 (m, 2H, PCH), 0.95−0.83 (12H, PCHC$H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 41.1 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $C_6D_6$, 293 K, plus APT, plus HSQC, plus HMBC): $\delta$ 222.6 (d, $J_{C-P}$ = 7, OsC), 178.8 (d, $J_{C-P}$ = 4, CNH), 137.9 (s, *p*-Ph), 135.3 (s, $C_{ipso}$Ph), 129.4, 126.5, and 126.3 (all s, Ph + OsC($CH_3$)*C*H), 72.0 (s, Cp), 38.8 (s, OsC($CH_3$)), 26.3 (d, $J_{C-P}$ = 32, PCH), 25.9 (d, $J_{C-P}$ = 29, PCH), 21.5 (s, PCH$CH_3$), 21.1 (s, *p*-$CH_3$), 21.0 and 20.8 (both s, PCH$CH_3$), 20.4 (d, $J_{C-P}$ = 3, PCH$CH_3$). MS (LSIMS$^+$): *m/z* 532 ($M^+$ − H).

**Preparation of Os($\eta^5$-$C_5H_5$){NH···C(Ph)···CH···C($CH_3$)}(PH$^i$Pr$_2$) (6).** The same procedure described for **5** was followed, starting from **3** (91 mg, 0.16 mmol) and sodium tetrahydrideborate (50 mg, 1.40 mmol). The product was isolated as a brown oil.[30] Yield: 62 mg (73%). $^1H$ NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 8.79 (br, 1H, NH), 7.55−6.98 (m, 6H, Ph + OsC($CH_3$)C*H*), 4.70 (s, 5H, $C_5H_5$), 3.58 (dt, $J_{H-P}$ = 336.6, $J_{H-H}$ = 3.6, 1H, PH), 3.37 (s, 3H, OsC($CH_3$)), 1.77 (m, 2H, PCH), 0.93−0.81 (12H, PCHC$H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 41.4 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $C_6D_6$, 293 K, plus APT, plus HSQC): $\delta$ 223.5 (d, $J_{C-P}$ = 7, OsC), 179.2 (d, $J_{C-P}$ = 4, CNH), 138.3 (s, $C_{ipso}$Ph), 129.1, 128.6, 126.9, and 126.8 (all s, Ph + OsC($CH_3$)*C*H), 72.5 (s, Cp), 39.2 (s, OsC($CH_3$)), 26.7 (d, $J_{C-P}$ = 26, PCH), 26.3 (d, $J_{C-P}$ = 23, PCH), 21.9, 21.3, and 21.1 (all s, PCH$CH_3$), 20.7 (d, $J_{C-P}$ = 3, PCH$CH_3$). MS (LSIMS$^+$): *m/z* 518 ($M^+$ − H); 400 ($M^+$ − PH$^i$Pr$_2$).

**Preparation of Os($\eta^5$-$C_5H_5$){NH···C(*p*-$C_6H_4$Cl)···CH···C($CH_3$)}(PH$^i$Pr$_2$) (7).** The same procedure described for **5** was followed, starting from **4** (150 mg, 0.26 mmol) and sodium tetrahydrideborate (77 mg, 2.04 mmol). The product was isolated as a brown oil.[30] Yield: 115 mg (81%). $^1H$ NMR (300 MHz, $C_6D_6$, 293 K, plus COSY): $\delta$ 8.66 (br, 1H, NH), 7.37 (s, 1H, OsC($CH_3$)C*H*), 7.22 (d, $J_{H-H}$ = 8.1, 2H, *o*-Ph), 7.04 (d, $J_{H-H}$ = 8.1, 2H, *m*-Ph), 4.70 (s, 5H, $C_5H_5$), 3.47 (dt, $J_{H-P}$ = 336.9, $J_{H-H}$ = 3.6, 1H, PH), 3.34 (s, 3H, OsC($CH_3$)), 1.75 (m, 2H, PCH), 0.92−0.78 (12H, PCHC$H_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 41.0 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $C_6D_6$, 293 K, plus APT, plus HMQC, plus HMBC): $\delta$ 223.7 (d, $J_{C-P}$ = 7, OsC), 177.0 (d, $J_{C-P}$ = 4, CNH), 136.1 (d, $J_{C-P}$ = 3, $C_{ipso}$Ph), 133.9 (s, $C_{ipso}$Ph), 128.9, and 127.7 (both s, Ph), 126.2 (s, OsC($CH_3$)*C*H), 72.3 (s, Cp), 38.8 (s, OsC($CH_3$)), 26.4 (d, $J_{C-P}$ = 30, PCH), 25.9 (d, $J_{C-P}$ = 27, PCH), 21.5, 20.9, and 20.7 (all s, PCH$CH_3$), 20.3 (d, $J_{C-P}$ = 3, PCH$CH_3$). MS (LSIMS$^+$): *m/z* 552 ($M^+$ − H); 434 ($M^+$ − PH$^i$Pr$_2$).

**Preparation of [OsH($\eta^5$-$C_5H_5$){NH═C(*p*-$C_6H_4CH_3$)-CH═C($CH_3$)}(PH$^i$Pr$_2$)]$BF_4$ (8).** A dark brown solution of **5** (182 mg, 0.34 mmol) in 7 mL of diethyl ether was treated with $HBF_4$·$Et_2O$ (47 $\mu$L, 0.34 mmol) at 0 °C. Immediately, a yellow solid appeared, and the mixture was allowed to react for 10 min. The product was washed with diethyl ether (2 × 2 mL), separated by decantation, and dried in vacuo. Yield: 174 mg (82%). Anal. Calcd for $C_{22}H_{33}BF_4NOsP$: C, 42.65; H, 5.37; N, 2.26. Found: C, 42.69; H, 5.28; N, 2.27. IR (Nujol, cm$^{-1}$): $\nu$(NH) 3335 (m), $\nu$(PH) 2344 (w), $\nu$(OsH) 2061 (w), $\nu$(C═N) 1560, $\nu$($BF_4$) 1051 (vs). $^1H$ NMR (300 MHz, $CD_2Cl_2$, 293 K, plus COSY): $\delta$ 10.54 (br, 1H, NH), 7.58 (d, $J_{H-H}$ = 8.1, 2H, *o*-Ph), 7.28 (m, 3H, *m*-Ph + OsC($CH_3$)C*H*), 5.55 (s, 5H, $C_5H_5$), 4.46 (d, $J_{H-P}$ = 369.9, 1H, PH), 2.99 (s, 3H, OsC($CH_3$)), 2.40 (s, 3H, *p*-$CH_3$), 2.36 (m, 1H, PCH), 1.78 (m, 1H, PCH), 1.20 (dd, $J_{H-P}$ = 17.1, $J_{H-H}$ = 6.9, 3H, PCHC$H_3$), 1.13 (dd, $J_{H-P}$ = 17.7, $J_{H-H}$ = 6.9, 3H, PCHC$H_3$), 1.06 (dd, $J_{H-P}$ = 17.4, $J_{H-H}$ = 6.9, 3H, PCHC$H_3$), 0.80 (dd, $J_{H-P}$ = 17.4, $J_{H-H}$ = 7.3, 3H, PCHC$H_3$), −12.44 (dd, $J_{H-P}$ = 43.5, $J_{H-H}$ = 3.6, 1H, Os−H). $^{31}P\{^1H\}$ NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 21.0 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $C_6D_6$, 293 K, plus APT, plus HSQC): $\delta$ 194.7 (d, $J_{C-P}$ = 16, OsC), 184.6 (s, CNH), 142.1 (s, $C_{ipso}$Ph), 134.9 (d, $J_{C-P}$ = 3, OsC($CH_3$)*C*H), 131.0 (s, $C_{ipso}$Ph), 129.9 and 127.4 (both s, Ph), 84.6 (s, Cp), 34.1 (d, $J_{C-P}$ = 5, OsC($CH_3$)), 26.1 (d, $J_{C-P}$ = 37, PCH), 23.3 (d, $J_{C-P}$ = 40, PCH), 21.2 (s, *p*-$CH_3$), 20.9, 20.6, 19.7, and 18.4 (all s, PCH$CH_3$). MS (LSIMS$^+$): *m/z* 532 ($M^+$ − 2H); 414 ($M^+$ − H − PH$^i$Pr$_2$).

**Preparation of [OsH($\eta^5$-$C_5H_5$){NH═C(Ph)CH═C($CH_3$)}(PH$^i$Pr$_2$)]$BF_4$ (9).** The same procedure described for **8** was followed starting from **6** (90 mg, 0.17 mmol) and $HBF_4$·$Et_2O$ (24 $\mu$L, 0.17 mmol). The product was isolated as a yellow solid. Yield: 84 mg (80%). Anal. Calcd for $C_{21}H_{31}BF_4NOsP$: C, 41.66; H, 5.16; N, 2.31. Found: C, 41.50; H, 5.30; N, 2.21. IR (Nujol, cm$^{-1}$): $\nu$(NH) 3343 (m), $\nu$(OsH) 2055 (w), $\nu$(C═N) 1556 (m), $\nu$($BF_4$) 1051 (vs). $^1H$ NMR (300 MHz, $CD_2Cl_2$, 293 K, plus COSY): $\delta$ 10.66 (br, 1H, NH), 7.71−7.49 (m, 5H, Ph), 7.32 (s, 1H, OsC($CH_3$)C*H*), 5.58 (s, 5H, $C_5H_5$), 4.47 (d, $J_{H-P}$ = 369.6, 1H, PH), 3.00 (s, 3H, OsC($CH_3$)), 2.35 (m, 1H, PCH), 1.78 (m, 1H, PCH), 1.21 (dd, $J_{H-P}$ = 16.8, $J_{H-H}$ = 7.0, 3H, PCHC$H_3$),

(30) All our attempts to achieve a valid elemental analysis determination for this complex were unsuccessful due to the presence of impurity traces (including solvents) in the sample.

1.14 (dd, $J_{H-P}$ = 16.8, $J_{H-H}$ = 7.5, 3H, PCHC$H_3$), 1.08 (dd, $J_{H-P}$ = 16.8, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), 0.82 (dd, $J_{H-P}$ = 17.4, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), −12.40 (dd, $J_{H-P}$ = 43.8, $J_{H-H}$ = 3.9, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 20.5 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $C_6D_6$, 293 K, plus APT, plus HSQC): $\delta$ 195.7 (d, $J_{C-P}$ = 16, OsC), 185.0 (s, CNH), 135.2 (d, $J_{C-P}$ = 3, OsC($CH_3$)*C*H), 133.9 (s, $C_{ipso}$Ph), 131.6, 129.4, and 127.6 (all s, Ph), 84.8 (s, Cp), 34.4 (d, $J_{C-P}$ = 5, OsC($CH_3$)), 26.2 (d, $J_{C-P}$ = 37, PCH), 23.5 (d, $J_{C-P}$ = 40, PCH), 21.1 (s, PCH*C*$H_3$), 20.8 (d, $J_{C-P}$ = 2, PCH*C*$H_3$), 20.0 and 18.6 (both s, PCH*C*$H_3$). MS (LSIMS$^+$): *m/z* 520 ($M^+$); 400 ($M^+$ − H − $PH^iPr_2$).

**Preparation of [OsH($\eta^5$-$C_5H_5$){NH=C(*p*-$C_6H_4$Cl)CH=C(**$CH_3$**)}($PH^iPr_2$)]$BF_4$ (10).** The same procedure described for **8** was followed starting from **7** (159 mg, 0.29 mmol) and $HBF_4$·$Et_2O$ (39 $\mu$L, 0.29 mmol). The product was isolated as a yellow solid. Yield: 151 mg (82%). Anal. Calcd for $C_{21}H_{30}BClF_4NOsP$: C, 39.41; H, 4.72; N, 2.19. Found: C, 39.70; H, 4.98; N, 2.14. IR (Nujol, $cm^{-1}$): $\nu$(NH) 3332 (w), $\nu$(PH) 2345 (w), $\nu$(OsH) 2062 (w), $\nu$(C=N) 1557 (m), $\nu(BF_4)$ 1010 (vs). $^1H$ NMR (300 MHz, $CD_2Cl_2$, 293 K, plus COSY): $\delta$ 10.81 (br, 1H, NH), 7.67 (d, $J_{H-H}$ = 8.7, 2H, *o*-Ph), 7.48 (d, $J_{H-H}$ = 8.7, 2H, *m*-Ph), 7.29 (s, 1H, OsC($CH_3$)C*H*), 5.58 (s, 5H, $C_5H_5$), 4.46 (d, $J_{H-P}$ = 369.0, 1H, PH), 3.00 (s, 3H, OsC($CH_3$)), 2.35 (m, 1H, PCH), 1.78 (m, 1H, PCH), 1.21 (dd, $J_{H-P}$ = 17.1, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), 1.14 (dd, $J_{H-P}$ = 17.7, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), 1.08 (dd, $J_{H-P}$ = 17.4, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), 0.81 (dd, $J_{H-P}$ = 17.4, $J_{H-H}$ = 7.2, 3H, PCHC$H_3$), −12.34 (dd, $J_{H-P}$ = 43.8, $J_{H-H}$ = 3.9, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $C_6D_6$, 293 K): $\delta$ 19.9 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $C_6D_6$, 293 K, plus APT, plus HMQC, plus HMBC): $\delta$ 196.4 (d, $J_{C-P}$ = 16, OsC), 183.3 (s, CNH), 137.3 (s, $C_{ipso}$Ph), 134.8 (d, $J_{C-P}$ = 3, OsC($CH_3$)*C*H), 132.1 (s, $C_{ipso}$Ph), 129.4 and 128.9 (both s, Ph), 84.7 (s, Cp), 34.2 (d, $J_{C-P}$ = 5, OsC(*C*$H_3$)), 26.2 (d, $J_{C-P}$ = 36, PCH), 23.4 (d, $J_{C-P}$ = 39, PCH), 20.9, 20.5, 19.7, and 18.4 (all s, PCH*C*$H_3$). MS (LSIMS$^+$): *m/z* 554 ($M^+$); 434 ($M^+$ − H − $PH^iPr_2$).

**X-ray Analysis of Complexes 3 and 10.** Crystals suitable for the X-ray diffraction were obtained by cooling at 4 °C a solution of **3** in diethyl ether and by slow diffusion of diethyl ether into a concentrated solution of **10** in dichloromethane. Two irregular crystals of size 0.30 × 0.28 × 0.10 mm (**3**) and 0.20 × 0.16 × 0.12 mm (**10**) were mounted on a Bruker Smart APEX CCD diffractometer at 100.0(2) K equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, $\lambda$ = 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 $\omega$. The cell parameters were determined and refined by least-squares fit of 5104 (**3**) or 8759 (**10**) collected reflections. The first 100 frames were collected at the end of the data collection to monitor crystal decay. Absorption correction was performed with the SADABS program.[31] Lorentz and polarization corrections were also performed. The structures were solved by Patterson and Fourier methods and refined by full matrix least-squares using the Bruker SHELXTL program package[32] minimizing $w(F_o^2 - F_c^2)^2$. A molecule of pentane was observed in **3** in the last cycles of refinement. On the basis of the systematic absences two space groups were possible for **10**, $P2_1$ and $P2_1/m$. The structure was only correctly resolved on the asymmetric one, and the phosphine ligand of one of the two molecules of the asymmetric unit was observed severely disordered. The hydride ligand of **10** was observed in the nondisordered molecule but did not refine properly, because of that finally was refined with restrained Os−H distance and thermal parameter. Weighted *R* factors ($R_w$) and goodness of fit (*S*) are based on $F^2$; conventional *R* factors are based on *F*.

A summary of crystal data and data collection and refinement details is reported in Table 3.

**Table 3. Crystal Data and Data Collection and Refinement for 3 and 10**

| | **3** | **10** |
|---|---|---|
| | Crystal Data | |
| formula | $C_{21}H_{29}ClNOsP_1$ 0.5$C_5H_{10}$ | $C_{21}H_{30}BClF_4NOsP$ |
| molecular wt | 588.15 | 639.89 |
| color and habit | purple, irregular block | light yellow, block |
| symmetry, space group | triclinic, $P\bar{1}$ | monoclinic, $P2_1$ |
| *a*, Å | 9.4980(6) | 9.6107(5) |
| *b*, Å | 11.9856(8) | 18.7787(10) |
| *c*, Å | 21.0781(14) | 13.2032(7) |
| α, deg | 78.2910(10) | |
| $\beta$, deg | 82.5210(10) | 99.6800(10) |
| $\gamma$, deg | 83.4590(10) | |
| *V*, Å$^3$ | 2320.1(3) | 2915.1(10) |
| *Z* | 4 | 4 |
| $D_{calc}$, g cm$^{-3}$ | 1.620 | 1.809 |
| | Data Collection and Refinement | |
| diffractometer | Bruker Smart APEX | |
| $\lambda$(Mo Kα), Å | 0.71073 | |
| monochromator | graphite oriented | |
| scan type | $\omega$ scans | |
| $\mu$, mm$^{-1}$ | 5.689 | 5.650 |
| $2\theta$, range, deg | 3, 57 | 3, 57 |
| temp, K | 100 | 100 |
| no. of data colld | 28 470 | 29 806 |
| no. of unique data | 10 772 ($R_{int}$ = 0.0311) | 11 396 ($R_{int}$ = 0.0313) |
| no. of params/ restraints | 520/0 | 561/31 |
| $R_1$[a][$F^2 > 2\sigma(F^2)$] | 0.0242 | 0.0389 |
| $wR_2$[b][all data] | 0.0453 | 0.0704 |
| *S*[c][all data] | 0.863 | 0.970 |

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof = $S = \{\sum[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections, and *p* is the number of refined parameters.

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**Supporting Information Available:** $^1H$, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^1H-^{13}C$ HSQC NMR spectra for **5**, **6**, and **7**, and tables of crystallographic data and bond lengths and angles for **3** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049178A

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