Organometallics **2002,** *21,* 2332−2335

Notes

Hydride−Carbyne to Carbene Transformation in a Cyclopentadienyl−Osmium Complex: An Alternative to the Single Hydride−C_α Migration

Miguel Baya and Miguel A. Esteruelas*

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

Received December 18, 2001

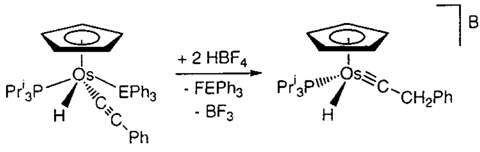
Summary: Complexes $OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)(EPh_3)(P^iPr_3)$ *[E = Si (**1**), Ge (**2**)] react with 2.0 equiv of* $HBF_4{\cdot}OEt_2$ *to give* $[OsH(\eta^5\text{-}C_5H_5)({\equiv}C{-}CH_2Ph)(P^iPr_3)]BF_4$ *(**3**). Treatment of **3** with KOH affords* $OsH(\eta^5\text{-}C_5H_5)({=}C{=}CHPh)(P^iPr_3)$ *(**5**) in equilibrium with the metalated species* $\overline{OsH(\eta^5\text{-}C_5H_5)(o\text{-}C_6H_4CH{=}CH)}(P^iPr_3)$ *(**7**)* ($\Delta H° = -3.6 \pm 0.2$ *kcal* mol^{-1} *and* $\Delta S° = -10.8 \pm 1.9$ *cal* K^{-1} mol^{-1} *for the formation of **7**). The addition of* $P(OMe)_3$ *to the solution of the isomeric mixture leads to* $Os(\eta^5\text{-}C_5H_5)\{(E)\text{-}CH{=}CHPh\}\{P(OMe)_3\}(P^iPr_3)$ *(**8**), which reacts with* $HBF_4{\cdot}OEt_2$ *to give* $[Os(\eta^5\text{-}C_5H_5)({=}CHCH_2Ph)\{P(OMe)_3\}(P^iPr_3)]BF_4$ *(**4**).*

Complexes $OsHCl_2({\equiv}CCH_2R)(PR'_3)_2$ ($PR'_3 = P^iPr_3$,[1] PCy_3[2]), isomers of the osmium counterparts to the Grubbs-type carbene−ruthenium compounds $RuCl_2({=}CHCH_2R)(PR'_3)_2$, are known and can be easily prepared by reaction of the corresponding dihydride−dichloro compounds $OsH_2Cl_2(PR'_3)_2$ with terminal alkynes[1,2] or alternatively with olefins.[3] However, in the solid state and in solution they do not evolve into the carbene isomers, by migration of the hydride ligand to the C_α atom of the carbyne. DFT calculations indicate that, although the isomer energies are similar, the necessary energy for the hydride migration is too large (27.2 kcal mol^{-1}).[3]

Despite this high energy barrier and despite the saturated character of the carbyne compounds, complex $OsHCl_2({\equiv}CEt)(P^iPr_3)_2$ reacts with carbon monoxide to give the carbene derivative $OsCl_2({=}CHEt)(CO)(P^iPr_3)_2$, at convenient rate.[3,4] To rationalize this surprising finding, it has been proposed that the mechanism of the above-mentioned transformation must involve nucleophilic assistance of the hydride-to-carbyne-carbon migration; Os−L bond making will lower the activation energy from its unimolecular value.[3]

In the context of our investigations on the reactivity of the cyclopentadienyl−osmium complex $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$, we have recently reported the preparation of the hydride−alkynyl compounds $OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)(EPh_3)(P^iPr_3)$ [E = Si (**1**), Ge (**2**)].[5] Now we have observed that these complexes are the entry to obtain the hydride−carbyne derivative $[OsH(\eta^5\text{-}C_5H_5)({\equiv}CCH_2Ph)(P^iPr_3)]BF_4$ (**3**). The easy accesibility to **3** prompted us to investigate the hydride−carbyne to carbene transformation promoted by trimethyl phosphite, a π-acidic ligand as carbon monoxide.

Complex **3** was prepared, as a dark brown solid in nearly quantitative yield, by addition of 2.0 equiv of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of **1** or **2** (eq 1). The formation of $FEPh_3$ (E = Si, Ge) was also detected.[6] When the reactions were carried out using 1.0 equiv of $HBF_4{\cdot}OEt_2$, complex **3** was obtained in about 50% yield.



1, 2 **3** (**1**)

The formation of a hydride−carbyne species according to eq 1 is strongly supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra of the obtained solid. The ^1H NMR spectrum in chloroform-*d* contains at −12.15 a doublet ($^2J_{HP} = 24$ Hz), due to the hydride ligand, whereas in the $^{13}C\{^1H\}$ NMR spectrum the C_α resonance of the carbyne is observed at 290.9 ppm.

Complex **3** is stable in chloroform-*d* under argon, and the migration of the hydride to the C_α atom of the carbyne is not observed. The addition of trimethyl phosphite to chloroform-*d* solutions of **3** gives a complex mixture of products, which does not contain the carbene derivative $[Os(\eta^5\text{-}C_5H_5)({=}CHCH_2Ph)\{P(OMe)_3\}(P^iPr_3)]BF_4$ (**4**). This complex can be obtained according to Scheme 1.

The CH_2 group of the carbyne ligand of **3** is fairly acidic and can be easily deprotonated. Thus, the

---

[1] Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683.

[2] Werner, H.; Jung, S.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **1999**, 951.

[3] Spivak, G. J.; Coalter, J. N.; Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999.

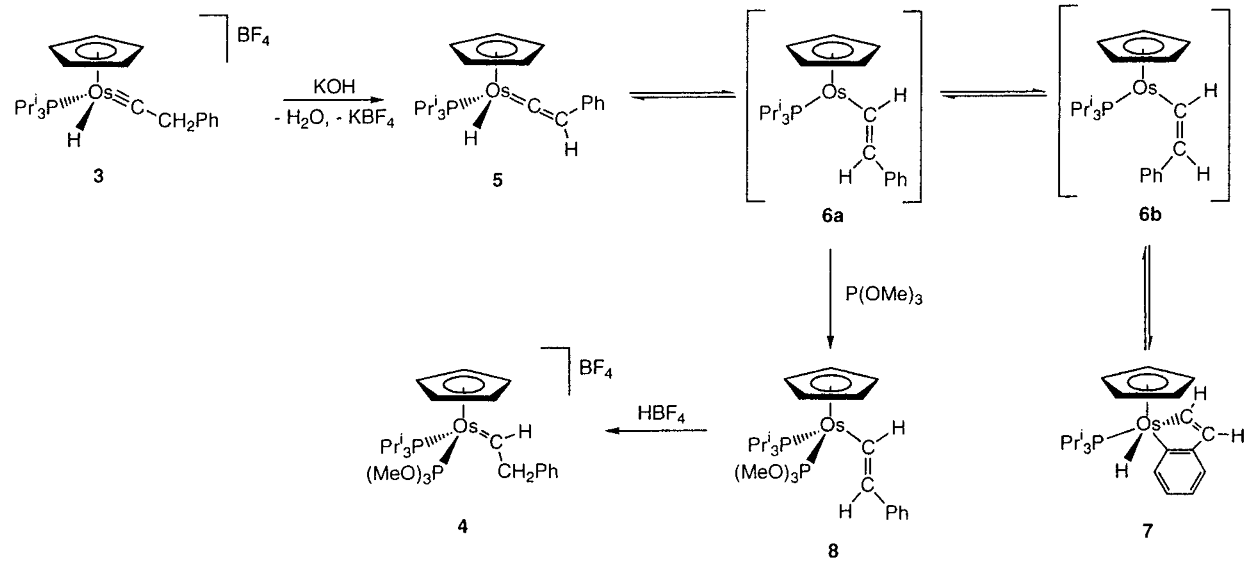
[4] Spivak, G. J.; Caulton, K. G. *Organometallics* **1998**, *17*, 5260.

[5] Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 4875.

[6] (a) MS (FAB^+) of $F{-}GePh_3$: *m/z* 305 ($Ge{-}Ph_3^+$), 247 ($F{-}GePh_2^+$)]. (b) $^{13}C\{^1H\}$ NMR spectrum of $FSiPh_3$ (75.4 MHz, C_6D_6, plus APT): Δ 135.8 (+, d, C_{ortho} Ph, $^3J_{CF} = 1.9$); 133.4 (−, d, C_{ipso} Ph, $^2J_{CF} = 17.1$); 131.4 (+, s, C_{para} Ph); 128.8 (+, s, C_{meta} Ph)].

10.1021/om011077e CCC: $22.00

Scheme 1



treatment of methanol solutions of **3** with 5.5 equiv of KOH affords the hydride–vinylidene $OsH(\eta^5\text{-}C_5H_5)({=}C{=}CHPh)(P^iPr_3)$ (**5**) in equilibrium with its metalated isomer $\overline{OsH(\eta^5\text{-}C_5H_5)(o\text{-}C_6H_4CH{=}CH})(P^iPr_3)$ (**7**).

In the ^{1}H NMR spectrum of the isomeric mixture in benzene-d_6, the =CH proton of the vinylidene of **5** displays at 2.80 ppm a double doublet by spin coupling with the hydride (2.1 Hz) and the phosphorus of the phosphine (2.1 Hz). The spin coupling with the hydride was confirmed by a ^{1}H COSY spectrum. The hydride ligand gives rise to a double doublet with a H–P coupling constant of 29.7 Hz at −14.27 ppm. In the $^{13}C\{^1H\}$ NMR spectrum the C_α resonance of the vinylidene appears at 290.2.

In agreement with a hydride ligand disposed *cisoid* to the phosphine in **7**, the ^{1}H NMR spectrum of the isomeric mixture also contains at −13.65 ppm a doublet with a H–P coupling constant of 44.1 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the orthometalated carbon atom displays at 162.0 ppm a doublet ($^2J_{CP} = 2.7$ Hz). The C_α and C_β vinylic resonances of the metallacycle appear at 135.8 and 148.8 ppm, respectively, as doublets with C–P coupling constants of 19.4 and 3.7 Hz. These spectroscopic data agree well with those obtained for the related complex $\overline{OsH(\eta^5\text{-}C_5H_4SiPh_3)(o\text{-}C_6H_4C(CH_3){=}CH})(P^iPr_3)$, where the distribution of ligands around the osmium atom has been confirmed by X-ray diffraction analysis.[5]

The constants for the equilibrium between the hydride–vinylidene and metalated species were measured in the temperature range from 253 to 343 K. The temperature dependence of the equilibrium gives the values $\Delta H° = -3.6 \pm 0.2$ kcal mol^{-1} and $\Delta S° = -10.8 \pm 1.9$ cal K^{-1} mol^{-1} for the formation of **7**. The negative entropy increment is consistent with the less ordered character of **5**. The value of $\Delta H°$ reveals a small stabilization of the system, probably as a consequence of the formation of the five-membered ring.

The isomerization of **5** to **7** occurs via the spectroscopically undetected *Z*-alkenyl intermediate **6b**, which evolves into **7** by C–H activation of the *ortho* C–H bond of the aryl group. Intermediate **6b** is in equilibrium with its *E*-isomer **6a**. The formation of **6a** and **6b** could be the result of the migration in **5** of the hydride to the C_α atom of the vinylidene, which should be rotating around the osmium–vinylidene axis. Alternatively, the equilibrium **6a**–**6b** could be a consequence of the isomerization of **6b** into **6a** via a zwitterionic carbene form.

The presence, in spectroscopically undetected amounts, of **6a** in the isomeric mixture is strongly supported by the reaction of the latter with trimethyl phosphite. The addition of 2.0 equiv of this ligand to the isomeric mixture in toluene affords the *E*-styryl derivative $Os(\eta^5\text{-}C_5H_5)\{(E)\text{-}CH{=}CHPh)\}\{P(OMe)_3\}(P^iPr_3)$ (**8**), which was isolated as a brown oil in 75% yield. The *E* stereochemistry at the carbon–carbon double bond of the styryl group is supported by the resonances of the vinylic protons, in the ^{1}H NMR spectrum. The value of the coupling constant between them (17.4 Hz) is characteristic for this arrangement.[7] The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the brown oil are also consistent with the formation of **8**. The resonances corresponding to the C_α and C_β atoms of the alkenyl ligand appear in the $^{13}C\{^1H\}$ NMR spectrum at 136.9 and 130.1 ppm, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets ($^2J_{PP} = 32.8$ Hz) at 107.2 ($P(OMe)_3$) and 17.7 (P^iPr_3) ppm.

As a result of a significant contribution of the zwitterionic carbene form to the structure of alkenyl complexes, the C_β atom of the alkenyl ligands has a marked nucleophilic character.[8] In agreement with this, the addition of 1.0 equiv of $HBF_4 \cdot OEt_2$ to diethyl ether solutions of **8** affords the carbene derivative **4**, which was isolated as an orange solid in 71% yield. This is a rare example of a half-sandwich carbene–osmium complex.[9] As far as we know, cyclopentadienyl–carbene–osmium compounds were unknown until now.

The presence of the carbene ligand in **4** is strongly supported by the ^{1}H and $^{13}C\{^1H\}$ NMR spectrum of this

---

(7) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

(8) Esteruelas, M. A.; Oro, L. A. *Adv. Organomet. Chem.* **2001**, *47*, 1, and references therein.

(9) Weberndörfer, B.; Henig, G.; Werner, H. *Organometallics* **2000**, *19*, 4687.

compound. In the ^{1}H NMR spectrum, the $C_\alpha H$ resonance of the carbene appears at 17.48 ppm, as a multiplet, whereas the $C_\beta H_2$ group gives rise to two double doublets at 3.91 and 3.30 ppm, with a $^2J_{HH}$ coupling constant of 15.6 Hz and $^3J_{HH}$ coupling constants of 9.6 and 6.3 Hz, respectively. In the $^{13}C\{^1H\}$ NMR spectra, the C_α resonance of the carbene is observed at 285.7 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains two doublets ($^2J_{PP} = 33.6$ Hz) at 89.0 ($P(OMe)_3$) and 25.9 (P^iPr_3) ppm.

The sequence of reactions shown in Scheme 1 not only is an elegant manner of obtaining carbene compounds starting from hydride−carbyne complexes but also represents a mechanistic alternative to the single migration, when the barrier to the hydride migration is too high and the carbyne has a $C_\beta HR_2$ group.

An ionic mechanism of this type (dissociation−migration−addition) can explain the formation of $OsCl_2(=CHEt)(CO)(P^iPr_3)_2$, by reaction of $OsHCl_2(\equiv CEt)(P^iPr_3)_2$ with carbon monoxide. It is well known that the CH_2 group of complexes $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$, similarly to **3**, is fairly acidic and can be easily deprotonated by treatment with Brönsted bases, to give $OsHCl(=C=CHR)(P^iPr_3)_2$.[10] It is also well known that six-coordinated hydride−vinylidene complexes of the type $OsHCl(=C=CHR)(CO)(P^iPr_3)_2$ evolve into the corresponding alkenyl derivatives $OsCl\{(E)\text{-}CH=CHR\}(CO)(P^iPr_3)_2$,[11] which react with HCl to afford $OsCl_2(=CCH_2R)(CO)(P^iPr_3)_2$.[11,12]

The examination of these reactions and those shown in Scheme 1 clearly indicates that the function of the Lewis base is to stabilize the alkenyl intermediate with regard to the hydride−vinylidene. In this context, it should be mentioned that for the formation of $OsHCl(=C=CHR)(P^iPr_3)_2$ an alternative pathway to the previously mentioned deprotonation is the insertion of a terminal alkyne into the Os−H bond of a monohydride species, followed by α-elimination in the resulting alkenyl.[13]

In conclusion, in addition to the formation of novel cyclopentadienyl−osmium complexes, this paper shows that when a carbyne ligand has a CHR_2 group, the Lewis base-assisted hydride−carbyne to carbene transformation can take place via a ionic mechanism involving (i) dissociation of a proton from the CHR_2 group of the carbyne, (ii) hydride migration to the C_α atom of the resulting vinylidene, (iii) stabilization of the alkenyl intermediate by coordination of the Lewis base and (iv) protonation of the C_α atom of the alkenyl.

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. The starting materials $OsH(\eta^5\text{-}C_5H_5)(C\equiv CPh)(GePh_3)(P^iPr_3)$ [E = Si (**1**), Ge (**2**)][5] were prepared by the published methods.

NMR spectra were recorded at 293 K and chemical shifts are expressed in ppm downfield from Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, *J*, are given in hertz.

Preparation of $[OsH(\eta^5\text{-}C_5H_5)(\equiv CCH_2Ph)(P^iPr_3)]BF_4$ (3). Route a. $HBF_4\cdot OEt_2$ (49 μL, 0.36 mmol) was added to a solution of $OsH(\eta^5\text{-}C_5H_5)(C\equiv CPh)(GePh_3)(P^iPr_3)$ (141 mg, 0.17 mmol) in 10 mL of diethyl ether. An oily precipitate was formed. The resulting solution was decanted, and the residue was washed twice with diethyl ether (2 × 4 mL). A dark brown solid was obtained. Yield: 95 mg (92%).

Route b. The reaction was made by the same method, but using $OsH(\eta^5\text{-}C_5H_5)(C\equiv CPh)(SiPh_3)(P^iPr_3)$ (164 mg, 0.21 mmol) as starting material. A brown solid was obtained. Yield: 115 mg (90%). Anal. Calcd for $C_{22}H_{34}BF_4OsP$: C, 43.57; H, 5.65. Found: C, 43.72; H, 5.80. IR (Nujol, cm^{-1}): ν(Os−H) 2023; ν(BF_4) 1075. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70−7.10 (5 H, −Ph); 5.75 (5 H, s, $\eta^5\text{-}C_5H_5$); 3.05 (AB system, 2 H, $Os\equiv CCH_2-$, $\Delta\nu = 79.0$, $^2J_{HH} = 19.2$); 2.04 (m, 3 H, PCH); 1.20 (dd, 9 H, $PCHCH_3$, $^3J_{HP} = 11.7$, $^3J_{HH} = 7.2$); 1.16 (dd, 9 H, $PCHCH_3$, $^3J_{HP} = 11.7$, $^3J_{HH} = 7.2$); −12.15 (d, 1 H, Os−H, $^2J_{HP} = 24$). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, plus APT): δ 290.9 (−, d, $Os\equiv C$, $^2J_{CP} = 13.2$); 134.3, 131.1, 129.7, 129.4, 129.0, 128.6 (all s, Ph); 88.6 (+, s, $\eta^5\text{-}C_5H_5$); 58.7 (−, s, CH_2); 30.2 (+, d, PCH, $^1J_{CP} = 31.8$); 19.9, 19.3 (+, s, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 47.9 (s, d in off-resonance). MS (FAB$^+$): *m/z* 521 (M$^+$).

Obtention of the Equilibrium Mixture $OsH(\eta^5\text{-}C_5H_5)\{=C=C(H)Ph\}(P^iPr_3)$ (5)−$OsH(\eta^5\text{-}C_5H_5)(o\text{-}C_6H_4CH=CH)(P^iPr_3)$ (7). KOH in pellets (96 mg, 1.45 mmol) was added to a solution of $[OsH(\eta^5\text{-}C_5H_5)(\equiv CCH_2Ph)(P^iPr_3)]BF_4$ (156 mg, 0.26 mmol) in 10 mL of methanol, and the mixture was left to stir for 2 h. The resulting solution was vacuum-dried, and the residue was extracted with toluene (10 mL). The filtrate was vacuum-dried and washed with cold methanol (2 × 2 mL). A pale brown solid was obtained, which resulted to be a 1:2 mixture of the isomers $OsH(\eta^5\text{-}C_5H_5)\{=C=C(H)Ph\}(P^iPr_3)$ (**5**) and $OsH(\eta^5\text{-}C_5H_5)(o\text{-}C_6H_4CH=CH)(P^iPr_3)$ (**7**). Yield: 81 mg (61%). Anal. Calcd for $C_{22}H_{33}OsP$: C, 50.94; H, 6.41. Found: C, 50.65; H, 6.01. IR (Nujol, cm^{-1}): ν(Os−H) 2139, 2110 (w); ν(Os=C=C) 1620 (m).

Spectroscopic Data for Isomer $OsH(\eta^5\text{-}C_5H_5)\{=C=C(H)Ph\}(P^iPr_3)$ (5). ^{1}H NMR (300 MHz, C_6D_6): δ 7.52 (dd, 2 H, H_{ortho} in Ph, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.5$); 7.26 (t, 2 H, H_{meta} in Ph, $^3J_{HH} = 7.5$, $^3J_{HH} = 7.5$); 6.87 (tt, 1 H, H_{para} in Ph, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.5$); 5.07 (5 H, s, $\eta^5\text{-}C_5H_5$); 2.80 (dd, 1 H, Os=C=CH; $^4J_{HH} = 2.1$, $^4J_{HP} = 2.1$); 1.99 (m, 3 H, PCH); 0.98 (dd, 9 H, $PCHCH_3$, $^3J_{HP} = 13.8$, $^3J_{HH} = 6.9$); 0.97 (dd, 9 H, $PCHCH_3$, $^3J_{HP} = 13.8$, $^3J_{HH} = 6.9$); −14.27 (d, 1 H, Os−H, $^2J_{HP} = 29.7$, $^4J_{HH} = 2.1$). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, plus HETCOR): δ 290.2 (d, Os=*C*=C, $^2J_{CP} = 11.5$); 151.0 (d, C_{ipso} in Ph, $^4J_{CP} = 3.7$); 128.6 (s, C_{meta} in Ph); 124.2 (s, C_{ortho} in Ph); 123.3 (s, C_{para} in Ph); 112.1 (s, Os=C=*C*(H)Ph); 83.4 (d, $\eta^5\text{-}C_5H_5$; $^2J_{CP} = 7.5$); 28.1 (d, PCH, $^1J_{CP} = 30.9$); 20.5, 20.0 (s, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 43.6 (s, d in off-resonance). MS (FAB$^+$): *m/z* 520 (M$^+$).

Spectroscopic Data for Isomer $OsH(\eta^5\text{-}C_5H_5)(o\text{-}C_6H_4\text{-}CH=CH)(P^iPr_3)$ (7). ^{1}H NMR (300 MHz, C_6D_6): δ 8.33 (dd, 1 H, OsC(*H*)=C, $^3J_{HH} = 6.9$, $^3J_{HP} = 5.4$); 8.21, 7.61 (both dd, 1 H each, CH in OsC_6H_4, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.2$); 7.70−7.60 (1 H, OsC(H)=C(*H*)); 7.21, 6.94 (both td, 1 H each, CH in OsC_6H_4, $^3J_{HH} = 7.5$, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.2$); 4.71 (5 H, s, $\eta^5\text{-}C_5H_5$); 2.09 (m, 3 H, PCH); 0.86 (dd, 9 H, $PCHCH_3$, $^3J_{HP} = 14.1$, $^3J_{HH} = 6.9$); 0.75 (dd, 9 H, $PCHCH_3$, $^3J_{HP} = 14.1$, $^3J_{HH} = 6.9$); −13.65 (d, 1 H, OsH, $^2J_{HP} = 44.1$). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, plus HETCOR): δ 162.0 (d, *C*CH= of aryl group, $^3J_{CP} = 2.7$); 148.8 (d, OsC(H)=*C*(H), $^3J_{CP} = 3.7$); 146.5, 122.8 (both s, tertiary C in OsC_6H_4); 135.8 (d, Os*C*(H)=C, $^2J_{CP} = 19.4$); 129.1, 122.3 (both s, tertiary C in OsC_6H_4); 128.1 (OsC of aryl group);

---

[10] Bourgault, M.; Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *Organometallics* **1997**, *16*, 6. 636.

[11] (a) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3596. (b) Buil, M. L.; Esteruelas, M. A. *Organometallics* **1999**, *18*, 1798.

[12] Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935.

[13] (a) Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1997**, *16*, 2227. (b) Oliván, M.; Clot, E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 3091.

83.3 (d, η^5-C_5H_5, $^3J_{CP}$ = 7.5); 28.7 (d, PCH, $^1J_{CP}$ = 30.9); 20.9, 19.0 (s, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 25.8 (s, d in off-resonance).

Preparation of Os(η^5-C_5H_5){(E)-CH═CHPh}{P(OMe$_3$)$_3$}(P^{i}Pr$_3$) (8). P(OMe$_3$)$_3$ (100 μL, 0.84 mmol) was added to a solution of the equilibrium mixture of **5** and **7** (220 mg, 0.42 mmol) in 15 mL of toluene. The mixture was heated to reflux during 48 h, then filtered and vacuum-dried. The residue was chromatographed on an alumina column. Diethyl ether eluted a brown fraction. The resulting solution was vacuum-dried. A brown oil was obtained. Yield: 204 mg (75%). ^1H NMR (300 MHz, C_6D_6): δ 9.73 (ddd, 1 H, OsCH═, $^3J_{HH}$ = 17.4, $^3J_{HP}$ = 8.7, $^3J_{HP}$ = 3.0); 7.70−6.90 (6 H, signals of ═CHPh); 4.82 (5 H, s, η^5-C_5H_5); 3.25 (d, 9 H, P(OCH$_3$)$_3$, $^3J_{HP}$ = 11.4); 2.29 (m, 3 H, PCH); 1.06 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 12.9, $^3J_{HH}$ = 7.2); 1.01 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 12.9, $^3J_{HH}$ = 7.2). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, plus APT): δ 145.0 (−, s, C_{ipso} in Ph); 136.9 (+, s, OsC); 135.3, 129.0, 124.3, 123.2 (+, all s, tertiary C's in Ph); 130.1 (+, s, OsCH═CH); 79.7 (+, s, η^5-C_5H_5); 51.1 (+, d, OCH$_3$, $^2J_{CP}$ = 6.0); 28.9 (+, d, PCH, $^1J_{CP}$ = 25.3); 20.5, 20.4 (+, s, PCHCH$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 107.2 (d, P(OCH$_3$)$_3$, $^2J_{PP}$ = 32.8), 17.7 (d, P^{i}Pr$_3$, $^2J_{PP}$ = 32.8). MS (FAB$^+$): m/z 644 (M$^+$), 541 (M$^+$ − CH═CHPh).

Preparation of [Os(η^5-C_5H_5)(═CHCH$_2$Ph){P(OMe$_3$)$_3$}(P^{i}Pr$_3$)]BF$_4$ (4). HBF$_4$·OEt$_2$ (45 μL, 0.33 mmol) was added to a solution of Os(η^5-C_5H_5){(E)-CH═CHPh}{P(OCH$_3$)$_3$}(P^{i}Pr$_3$) (204 mg, 0.32 mmol) in 12 mL of diethyl ether. The subsequent precipitate was decanted and washed with diethyl ether (3 × 6 mL). An orange solid was obtained. Yield: 164 mg (71%). Anal. Calcd for $C_{25}H_{43}BF_4OsP_2$: C, 41.10; H, 5.93. Found: C, 40.76; H, 5.69. ^1H NMR (300 MHz, CDCl$_3$): δ 17.48 (dddd, 1 H, Os═CH, $^3J_{HP}$ = 10.8, $^3J_{HH}$ = 9.6, $^3J_{HH}$ = 6.3, $^3J_{HP}$ = 2.7); 7.40−7.10 (5 H, −Ph); 5.82 (5 H, s, η^5-C_5H_5); 3.91 (dd, 1 H, one H of the CH$_2$ group, $^2J_{HH}$ = 15.6, $^3J_{HH}$ = 9.6); 3.36 (d, 9 H, P(OCH$_3$)$_3$, $^3J_{HP}$ = 11.7); 3.30 (dd, 1 H, one H of the CH$_2$ group, $^2J_{HH}$ = 15.6, $^3J_{HH}$ = 6.3); 2.36 (m, 3 H, PCH); 1.15 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 14.7, $^3J_{HH}$ = 7.2); 0.97 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 14.7, $^3J_{HH}$ = 7.2). $^{13}C\{^1H\}$ NMR (75.4 MHz, CDCl$_3$, plus APT): δ 285.7 (+, br, Os═CH); 135.9 (−, s, C_{ipso} in Ph); 128.8, 128.2 (+, both s, C_{ortho} and C_{meta} in Ph); 126.7 (+, s, C_{para} in Ph); 88.9 (+, s, η^5-C_5H_5); 73.3 (−, s, CH$_2$); 53.0 (+, d, OCH$_3$, $^2J_{CP}$ = 8.3); 29.3 (+, d, PCH, $^1J_{CP}$ = 29.5); 19.3, 19.1 (+, s, PCHCH$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CDCl$_3$): δ 89.0 (d, P(OCH$_3$)$_3$, $^2J_{PP}$ = 33.6), 25.9 (d, P^{i}Pr$_3$, $^2J_{PP}$ = 33.6). MS (FAB$^+$): m/z 645 (M$^+$), 541 (M$^+$ − CHCH$_2$Ph).

Acknowledgment. We thank the DGES (Project PB98-1591, Programa de Promoción General del Conocimiento), for financial support. M.B. thanks the DGA (Diputación General de Aragón) for a grant.

OM011077E