Organometallics **1996,** *15,* 878−881

Notes

New Cyclopentadienylosmium Derivatives Prepared from the Five-Coordinate Complex $[OsHCl(CO)(PPr^i_3)_2]$

Miguel A. Esteruelas,* Angel V. Gómez, Ana M. López, and Luis A. Oro

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

Received August 8, 1995[⊗]

Summary: The reaction of $[OsHCl(CO)(PPr^i_3)_2]$ (**1**) *with cyclopentadiene in refluxing methanol affords the novel cyclopentadienylosmium(II) complex* $[OsH(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]$ (**2**). *Reaction of* **2** *with* CCl_4 *in pentane gives the chloro complex* $[Os(\eta^5\text{-}C_5H_5)Cl(CO)(PPr^i_3)]$ (**3**). *The protonation of* **2** *with* $HBF_4\cdot Et_2O$ *leads to the trans-dihydridoosmium(IV) complex* $[OsH_2(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]BF$ (**4**). *Treatment of the chloro complex* **3** *with* $AgBF_4$ *followed by the terminal alkyne phenylacetylene or 1-ethynyl-1-cyclohexanol gives the stable vinylidene* $[Os(\eta^5\text{-}C_5H_5)\{{=}C{=}C(H)Ph\}(CO)(PPr^i_3)]BF_4$ (**5**) *or vinylvinylidene* $[Os(\eta^5\text{-}C_5H_5)\{{=}C{=}C(H)\overline{C{=}CH(CH_2)_3CH_2}\}(CO)(PPr^i_3)]BF_4$ (**6**), *respectively.*

Introduction

We have previously reported that the treatment of $OsCl_3\cdot xH_2O$ with triisopropylphosphine in refluxing methanol leads to $[OsHCl(CO)(PPr^i_3)_2]$ in nearly quantitative yield.[1] This complex, which is an active and highly selective catalyst for the reduction of unsaturated organic substrates[2] and for the addition of $HSiEt_3$ to phenylacetylene,[3] has been also the master key for the development of an extensive organometallic chemistry, including mono-[4] and binuclear tetrahydridoborate,[5] vinyl,[6] alkynyl,[7] vinylacetate,[7b] and carbene[7b,8] compounds.

We have now observed that the reaction of the complex $[OsHCl(CO)(PPr^i_3)_2]$ with cyclopentadiene leads to the cyclopentadienyl derivative $[OsH(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]$, which can be the starting point for new half-sandwich osmium complexes.

Although half-sandwich cyclopentadienylruthenium complexes exhibit a particularly rich and interesting chemistry[9] and have formed one of the cornerstones in the development of organometallic chemistry, the chemistry of the corresponding $Os(\eta^5\text{-}C_5R_5)$ complexes has attracted comparatively less attention. This is in part due to the lack of convenient osmium synthetic precursors.[10] Traditional synthetic routes to half-sandwich cyclopentadienyl or (pentamethylpentadienyl)osmium complexes have, in general, relied extensively upon the dicarbonyl compounds $[Os(\eta^5\text{-}C_5R_5)X(CO)_2]$ (X = H, Br, I)[9a,11,12] and the bis(phosphine) derivatives $[Os(\eta^5\text{-}C_5R_5)X(PR_3)_2]$ (X = Cl, Br, I, H)[9a,13] as starting materials. In general, cyclopentadienylosmium complexes are less accessible than the related (pentamethylcyclopentadienyl)osmium derivatives.

In this paper we report a new synthetic route to obtain cyclopentadienylosmium complexes, including hydrido, halide, vinylidene, and vinylvinylidene derivatives.

Results and Discussion

Treatment of a boiling methanol suspension of $[OsHCl(CO)(PPr^i_3)_2]$ (**1**) with freshly distilled cyclopentadiene in a 1:25 molar ratio for 2 days gives, after filtration and solvent removal, a sticky residue. Pentane extraction of the residue and filtration to remove the salt $[HPPr^i_3]Cl$ affords a yellow solution that contains the hydrido cyclopentadienyl complex $[OsH(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]$ (**2**; Scheme 1). Complex **2** was isolated as a white crystalline solid in 52% yield after solvent removal and recrystallization from methanol. If the diolefin is added in one portion, it dimerizes before completion of the reaction. Two successive additions of cyclopentadiene improve the yield: half at the beginning and half after reflux for 1 day.

The hydrido ligands in complex **2** is readily replaced by a chloro ligand by treatment with CCl_4. Thus, addition of CCl_4 to a pentane solution of **2** in a 1:20

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

(1) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.

(2) (a) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1988**, *45*, 1. (b) Werner, H.; Meyer, U.; Esteruelas, M. A.; Sola, E.; Oro, L. A. *J. Organomet. Chem.* **1989**, *366*, 187. (c) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1989**, *53*, 43. (d) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sánchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (e) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1992**, *11*, 3362.

(3) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1991**, *10*, 462.

(4) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11.

(5) Esteruelas, M. A.; García, M. P.; López, A. M.; Oro, L. A.; Ruiz, N.; Schlünken, C.; Valero, C.; Werner, H. *Inorg. Chem.* **1992**, *31*, 5580.

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

(7) (a) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663. (b) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 1669.

(8) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662.

(9) (a) Albers, M. O.; Robinson, D. J.; Singleton, E. *Coord. Chem. Rev.* **1987**, *79*, 1. (b) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1.

(10) (a) Dev, S.; Selegue, J. P. *J. Organomet. Chem.* **1994**, *469*, 107. (b) Gross, C. L.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1994**, *116*, 10294 and references therein.

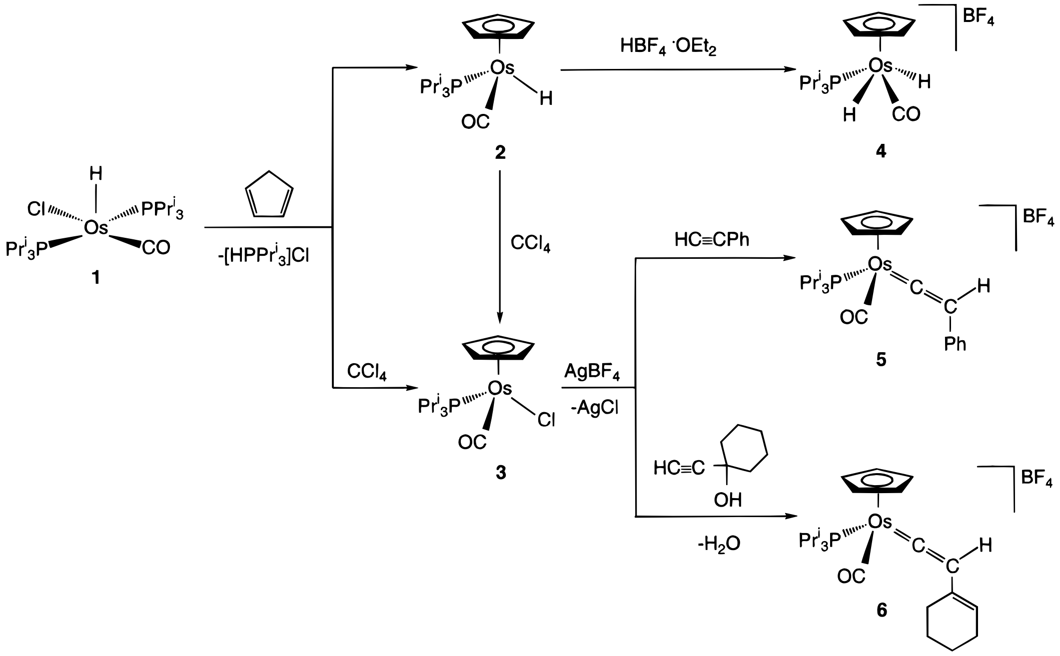
(11) Herrmann, W. A.; Herdtweck, E.; Schäfer, A. *Chem. Ber.* **1988**, *121*, 1907.

(12) Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1986**, *5*, 1337.

(13) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267.

0276-7333/96/2315-0878$12.00/0

Scheme 1



molar ratio leads to the chloro complex [Os(η^5-C_5H_5)-Cl(CO)(PPr^i_3)] (**3**), which is isolated after 3 h as a crystalline yellow solid in 72% yield. However, the most direct route to the chloro complex **3**, which avoids the isolation of the hydride intermediate **2**, is the treatment of the above-mentioned pentane solution, resulting from the filtration of [$HPPr^i_3$]Cl, with CCl_4. This direct route allows the isolation of **3** in higher yield, 66% as opposed to the 36% overall yield of **3** based on the amount of **1** employed to make **2**, probably due to the high solubility of the hydrido complex **2** in most solvents.

We note that Geoffroy *et al.* have reported the iodo pentamethylcyclopentadienyl complexes [Os(η^5-C_5Me_5)I-(CO)(PR_3)] (PR_3 = PMe_3, PPh_3). These compounds were readily prepared by photochemical reaction of the precursor [Os(η^5-C_5Me_5)I$(CO)_2$] with PMe_3 or PPh_3 under CO pressure followed by treatment with Me_3NO. However, the related hydrido complex [OsH(η^5-C_5Me_5)-(CO)(PMe_3)] could not be isolated as a pure compound and was characterized by converting it to the bromo derivative [Os(η^5-C_5Me_5)Br(CO)(PMe_3)].[12]

Complexes **2** and **3** have been characterized by elemental analysis and by IR and ^{1}H and ^{31}P NMR spectroscopy. The IR spectrum of **2** in Nujol shows absorptions due to ν(OsH) at 2080 cm^{-1} and ν(CO) at 1900 cm^{-1}. The presence of the hydrido ligand is confirmed by the ^{1}H NMR spectrum, which contains a doublet at −15.32 ppm (J(HP) = 27.2 Hz) together with the expected singlet at 4.71 ppm for the cyclopentadienyl ligand and the characteristic signals for the PPr^i_3 ligand.

The monohydrido complex **2** reacts with HBF_4. The addition of 1 equiv of $HBF_4 \cdot Et_2O$ to a solution of **2** in dichloromethane-d_2 at room temperature, gives quantitative formation of the dihydrido complex [OsH_2(η^5-C_5H_5)(CO)(PPr^i_3)]BF_4 (**4**; Scheme 1), as evidenced by ^{1}H NMR spectroscopy. When the reaction of **2** with HBF_4 is carried out in diethyl ether at room temperature, complex **4** is isolated as a white solid in 70% yield. The IR spectrum in Nujol shows the absorption due to the $[BF_4]^-$ anion with T_d symmetry along with a weak ν-(OsH) absorption at 2140 cm^{-1} and a strong band characteristic of the carbonyl ligand at 2030 cm^{-1}. The *trans* disposition of the hydrido ligands is proposed on the basis of the ^{1}H NMR spectrum in chloroform-*d*, which shows, in the high-field region, a single doublet at −11.41 ppm with a ^2J(HP) coupling constant of 28.8 Hz. An alternative *cisoid* dihydrido structure should give rise to two distinct hydride resonances. Furthermore, a similar ^2J(HP) coupling constant (29.0 Hz) has been observed for the dihydride cation [OsH_2(η^5-C_5H_5)-$(PPh_3)_2$]$^+$, whose *trans* four-legged piano-stool geometry has been determined by X-ray diffraction.[13] The large ^2J(HP) coupling constant together with a T_1(min) value of 457 ms (300 MHz, dichloromethane-d_2, 193 K) support the formulation of **4** as a classical dihydride compound.

The behavior of **2** toward protonation differs markedly from that observed for the related ruthenium complexes [RuH(η^5-C_5H_5)(CO)(PR_3)] (PR_3 = PPh_3, PMe_3, PMe_2Ph, PCy_3), which upon protonation with HBF_4 give the corresponding dihydrogen complexes [Ru(η^5-C_5H_5)(η^2-H_2)(CO)(PR_3)]BF_4[14] and is similar to that shown by the osmium derivatives [OsH(η^5-C_5H_5)$(PR_3)_2$] (PR_3 = PPh_3, $PMePh_2$), which on treatment with CF_3SO_3H afford the dihydrido species [OsH_2(η^5-C_5H_5)(CO)(PR_3)]CF_3SO_3.[13]

Vinylidene compounds are among the most important cyclopentadienyl derivatives of ruthenium.[9,15] However, very few vinylidene analogues of osmium have been reported.[12,16] Treatment of the chloro complex **3** with $AgBF_4$ in the presence of phenylacetylene in dichloromethane gives the vinylidene [Os(η^5-C_5H_5){=C=C(H)-Ph}(CO)(PPr^i_3)]BF_4 (**5**; Scheme 1). Complex **5** is obtained as an orange solid in 82% yield after 3 h. The

---

(14) (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

(15) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

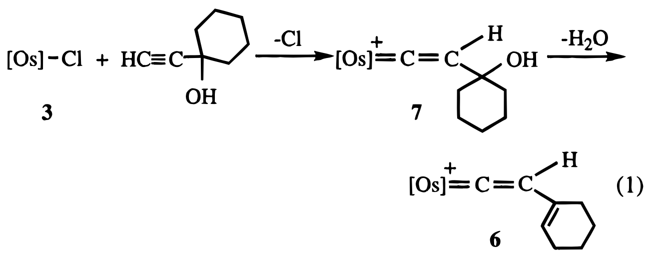
(16) (a) Bruce, M. I.; Humphrey, M. G. *Aust. J. Chem.* **1989**, *42*, 1067. (b) Bruce, M. I.; Humphrey, M. G.; Koutsantonis, G. A.; Liddell, M. J. *J. Organomet. Chem.* **1987**, *326*, 247. (c) Bruce, M. I.; Humphrey, M. G.; Liddell, M. J. *J. Organomet. Chem.* **1987**, *321*, 91. (d) Bruce, M. I.; Koutsantonis, G. A.; Liddell, M. J.; Nicholson, B. K. *J. Organomet. Chem.* **1987**, *320*, 217.

IR spectrum in Nujol of **5** shows the absorptions due to the $[BF_4]^-$ anion at 1080 cm^{-1} along with bands characteristic of the vinylidene and carbonyl ligands at 1670 (ν(C=C)) and 1990 (ν(CO)) cm^{-1}, respectively. The $^{13}C\{^1H\}$ NMR spectrum contains the typical low-field signal for the C_α atom of the vinylidene ligand, which appears as a doublet at 324.78 ppm with a ^2J(CP) coupling constant of 7.9 Hz. The ^1H NMR spectrum shows a singlet at 4.39 ppm corresponding to the proton on the C_β atom.

Although the formation of vinylidene complexes from reactions of 1-alkynes with certain unsaturated or labile transition-metal complexes is now a well-established method,[15] only Geoffroy *et al.* have previously reported a similar route for the synthesis of vinylideneosmium compounds. Treatment of $[Os(\eta^5\text{-}C_5Me_5)I(CO)(PPh_3)]$ with $AgBF_4$ followed by terminal alkynes gave the vinylidene complexes $[Os(\eta^5\text{-}C_5Me_5)\{=C=C(H)R\}(CO)(PPh_3)]BF_4$ (R = Bu^t, Ph).[12] The phenylvinylidene cation rapidly afforded the phenylacetylide complex by deprotonation when filtered through Celite in air; however, the structure of the *tert*-butyl derivative was confirmed by an X-ray diffraction study.

A similar reaction between the chloro derivative **3** and 1-ethynyl-1-cyclohexanol in dichloromethane, in the presence of $AgBF_4$, produced the vinylvinylidene complex $[Os(\eta^5\text{-}C_5H_5)\{=C=C(H)\overline{C=CH(CH_2)_3CH_2}\}(CO)(PPr^i_3)]BF_4$ (**6**; Scheme 1). Complex **6** was isolated as a salmon solid in 78% yield. **6** is formulated as a vinylvinylidene compound on the basis of its spectroscopic data. In particular, the ν(C=C) infrared absorptions at 1656 and 1627 cm^{-1} and the absence of a ν(C=C=C) band at *ca.* 1925 cm1$-^{1}$ [15] indicate that **6** is a vinylvinylidene, rather than an allenylidene, complex. The ^1H NMR spectrum of **6** in chloroform-*d* shows the vinylidene and vinylic protons as a singlet at 4.07 ppm and a broad signal at 5.35 ppm, respectively. The most distinctive features of the $^{13}C\{^1H\}$ NMR spectrum are a doublet at low field (δ 327.68, ^2J(CP) = 7.8 Hz) for the C_α atom of the vinylidene ligand and three singlets at 125.18, 123.21, and 118.80 ppm for the C_β and the vinylic carbon atoms.

From a mechanistic point of view, the vinylvinylidene **6** most probably is the result of the spontaneous dehydration of the hydroxyvinylidene intermediate **7** (eq 1).



(1)

$[Os] = [Os(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]$

The dehydration of hydroxyvinylidene intermediates, containing hydrogen atoms adjacent to the hydroxy group, can occur in two different directions to give either vinylvinylidene or allenylidene derivatives, depending on the electronic and steric properties of the metal. Selegue *et al.* have reported that the electron-rich hydroxyvinylidenes $[Ru(\eta^5\text{-}C_5H_5)\{=C=CHC(OH)RR'\}(PMe_3)_2]^+$ dehydrate to give vinylvinylidenes,[17] while Dixneuf and co-workers have proposed that dehydration of the isoelectronic arene systems $[RuCl(\eta^6\text{-}C_6H_6)\{=C=CHC(OH)RR'\}(PMe_3)]^+$ gives allenylidene intermediates that add methanol to afford methoxyvinylcarbenes.[18] Kolobova and co-workers have observed that the action of SiO_2 or Al_2O_3 on manganese hydroxyvinylidene compounds causes their dehydration to allenylidenes.[19] Very recently, Werner *et al.* have shown that the abstraction of water from the rhodium hydroxyvinylidenes $[RhCl\{=C=CHC(OH)RR'\}(PPr^i_3)_2]$ leads preferentially to rhodium vinylvinylidenes.[20]

In conclusion, the versatile catalyst $[OsHCl(CO)(PPr^i_3)_2]$ is a useful starting material not only for the synthesis of mono- and binuclear tetrahydridoborate, vinyl, alkynyl, vinylacetate, and carbene compounds but also for the preparation of cyclopentadienylosmium complexes, including hydrido, halide, vinylidene, and vinylvinylidene compounds.

Experimental Section

All reactions were carried out with rigorous exclusion of air by using Schlenk tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material $[OsHCl(CO)(PPr^i_3)_2]$ was prepared by published methods.[1]

NMR spectra were recorded on either a Varian UNITY 300 or a Bruker 300 AXR spectrophotometer. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, J, are given in Hz. The T_1 experiments were performed on a Varian UNITY 300 spectrophotometer with a standard 180°$-\tau-$90° pulse sequence. T_1 values are given in milliseconds (ms). IR spectra were run on a Perkin-Elmer 783 spectrophotometer (Nujol mulls on polyethylene sheets). C and H analyses were carried out on a Perkin-Elmer 240C microanalyzer.

Preparation of $[OsH(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]$ (2). To a solution of **1** (1.0 g, 1.74 mmol) in 20 mL of methanol was added an excess of freshly distilled cyclopentadiene (1.5 mL, 22.24 mmol). The mixture was stirred at reflux temperature for 24 h, and then another fraction of 1.5 mL of freshly distilled cyclopentadiene was added and the mixture was refluxed for a further 24 h. The color of the solution changed from red to yellow, and then the solution was filtered and evaporated to dryness. The residue was treated with 20 mL of hexane, and the mixture was filtered to eliminate the $[HPPr^i_3]Cl$. The yellow solution was concentrated to about 3 mL and cooled to −78 °C. A cream-colored solid precipitated, which was separated by decantation, washed with cold hexane, and dried in vacuo. The solid was recrystallized from methanol to give white crystals which were separated by decantation, washed with cold methanol, and dried in vacuo. Yield: 402 mg (52%). Anal. Calcd for $C_{15}H_{27}OPOs$: C, 40.53; H, 6.12. Found: C, 40.70; H, 5.98. IR (Nujol, cm^{-1}): ν(OsH) 2080 m; ν(CO) 1900 vs, br. ^1H NMR (300 MHz, C_6D_6): δ 4.71 (s, 5H, Cp), 1.72 (m, 3H, PC*H*CH$_3$), 0.94 (dd, 9H, J(HH) = 7.1, J(PH) = 13.7, PCHC*H*$_3$), 0.89 (dd, 9H, J(HH) = 7.1, J(PH) = 14.0, PCHC*H*$_3$),

---

(17) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972.

(18) (a) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1989**, 219. (b) Le Bozec, H.; Ouzzine; K.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *29*, 163. (c) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809.

(19) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Derunov, V. V.; Chechulina, I. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1982**, *31*, 2328; *Chem. Abstr.* **1983**, *98*, 126312v.

(20) (a) Rappert, T.; Nürnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156. (b) Werner, H.; Rappert, T. *Chem. Ber.* **1993**, *126*, 669. (c) Werner, H.; Rappert, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994**, *13*, 2721.

−15.32 (d, 1H, *J*(PH) = 27.2, OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): *δ* 46.54 (s).

Preparation of [OsCl(η^5-C_5H_5)(CO)(PPr^i_3)] (3). Route a. To a solution of **2** (235 mg, 0.53 mmol) in 10 mL of hexane was added an excess of CCl_4 (1 mL, 10.34 mmol). The mixture was stirred for 3 h at room temperature, and a yellow solid precipitated. The solid was separated by decantation, washed with hexane, dried in vacuo, and recrystallized from methanol to give yellow crystals. The crystals were separated by decantation, washed with cold methanol, and dried in vacuo. Yield: 182 mg (72%).

Route b. To a solution of **1** (1.0 g, 1.74 mmol) in 20 mL of methanol was added an excess of freshly distilled cyclopentadiene (1.5 mL, 22.24 mmol). The mixture was stirred at reflux temperature for 24 h, and then another fraction of 1.5 mL of freshly distilled cyclopentadiene was added and the mixture was refluxed for a further 24 h. The solution was filtered and evaporated to dryness. The residue was treated with 20 mL of hexane, and the mixture was filtered to eliminate the [$HPPr^i_3$]Cl. The yellow solution was concentrated to about 10 mL, and an excess of CCl_4 (1.5 mL, 15.51 mmol) was added. The resulting solution was worked up as in route a. Yield: 552 mg (66%). Anal. Calcd for $C_{15}H_{26}ClOPOs$: C, 37.61; H, 5.26. Found: C, 37.79; H, 5.05. IR (Nujol, cm^{-1}): *ν*(CO) 1906 vs, br. ^1H NMR (300 MHz, C_6D_6): *δ* 5.21 (s, 5H, Cp), 2.53 (m, 3H, $PC\mathit{H}CH_3$), 1.25 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 14.5, $PCHC\mathit{H}_3$), 1.19 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 13.4, $PCHC\mathit{H}_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): *δ* 24.16 (s).

Preparation of [OsH_2(η^5-C_5H_5)(CO)(PPr^i_3)]BF_4 (4). Route a. A solution of **2** (85 mg, 0.18 mmol) in 5 mL of diethyl ether at room temperature was treated with HBF_4 (25 *μ*L, 0.18 mmol, 54% in diethyl ether). Immediately a white solid precipitated. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 67 mg (70%). Anal. Calcd for $C_{15}H_{28}BF_4OPOs$: C, 33.84; H, 5.30. Found: C, 33.61; H, 5.35. IR (Nujol, cm^{-1}): *ν*(OsH) 2140 w; *ν*(CO) 2030 vs; *ν*(BF_4) 1050 br. ^1H NMR (300 MHz, $CDCl_3$): *δ* 5.94 (s, 5H, Cp), 2.32 (m, 3H, $PC\mathit{H}CH_3$), 1.27 (dd, 18H, *J*(HH) = 7.1, *J*(PH) = 15.9, $PCHC\mathit{H}_3$), −11.41 (d, 2H, *J*(PH) = 28.8, OsH_2). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): *δ* 43.91 (s).

Route b. A solution of **2** (4.9 mg, 0.011 mmol) in 0.5 mL of CD_2Cl_2 in an NMR tube was treated with a stoichiometric amount of HBF_4 (1.5 *μ*L, 0.011 mmol, 54% in diethyl ether). The NMR tube was sealed under argon, and measurements were made immediately. ^1H NMR (300 MHz, CD_2Cl_2): *δ* 5.84 (s, 5H, Cp), 2.26 (m, 3H, $PC\mathit{H}CH_3$), 1.23 (dd, 18H, *J*(HH) = 7.1, *J*(PH) = 16.1, $PCHC\mathit{H}_3$), −11.45 (d, 2H, *J*(PH) = 29.1, OsH_2). T_1 (OsH_2, 300 MHz, CD_2Cl_2): 845 ms (213 K), 457 ms (193 K).

Preparation of [Os(η^5-C_5H_5){=C=C(H)Ph}(CO)(PPr^i_3)]BF_4 (5). A solution of **2** (85 mg, 0.18 mmol) in 10 mL of dichloromethane was treated with $AgBF_4$ (34.5 mg, 0.18 mmol) and phenylacetylene (21.5 *μ*L, 0.19 mmol). The mixture was stirred at room temperature for 3 h and filtered to eliminate the AgCl. The solvent was removed in vacuo, and the residue was washed with diethyl ether to give an orange solid, which was separated by decantation and dried in vacuo. Yield: 92 mg (82%). Anal. Calcd for $C_{23}H_{32}BF_4OPOs$: C, 43.68; H, 5.10. Found: C, 43.70; H, 4.74. IR (Nujol, cm^{-1}): *ν*(CO) 1990 vs; *ν*(C=C) 1670 s; *ν*(Ph) 1595 w; *ν*(BF_4) 1080 br. ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.15 (m, 5H, Ph), 6.11 (s, 5H, Cp), 4.39 (s, 1H, =CH), 2.50 (m, 3H, $PC\mathit{H}CH_3$), 1.28 (dd, 9H, *J*(HH) = 7.8, *J*(PH) = 15.8, $PCHC\mathit{H}_3$), 1.25 (dd, 9H, *J*(HH) = 7.8, *J*(PH) = 15.8, $PCHC\mathit{H}_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): *δ* 40.10 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): *δ* 324.78 (d, *J*(CP) = 7.9 Hz, Os=C), 176.86 (d, *J*(CP) = 10.9 Hz, CO), 129.23, 127.94, 126.16, 122.56, 120.42 (all s, Ph and =*C*H), 91.21 (s, Cp), 29.32 (d, *J*(CP) = 30.9 Hz, $P\mathit{C}HCH_3$), 19.84 (d, *J*(CP) = 1.9 Hz, $PCH\mathit{C}H_3$), 19.61 (d, *J*(CP) = 1.9 Hz, $PCH\mathit{C}H_3$).

Preparation of [Os(η^5-C_5H_5){=C=C(H)C=CH-(CH_2)$_3$CH$_2$}(CO)(PPr^i_3)]BF_4 (6). A solution of **2** (85 mg, 0.18 mmol) in 10 mL of dichloromethane was treated with $AgBF_4$ (34.5 mg, 0.18 mmol) and an excess of 1-ethynyl-1-cyclohexanol (44.97 mg, 0.36 mmol). The mixture was stirred at room temperature for 3 h and filtered to eliminate the AgCl. The solvent was removed in vacuo, and the residue was washed with diethyl ether to give a salmon solid, which was separated by decantation and dried in vacuo. Yield: 88 mg (78%). Anal. Calcd for $C_{23}H_{36}BF_4OPOs$: C, 43.40; H, 5.70. Found: C, 43.07; H, 5.03. IR (Nujol, cm^{-1}): *ν*(CO) 1981 vs; *ν*(C=C) 1656 s, 1627 m; *ν*(BF_4) 1050 br. ^1H NMR (300 MHz, $CDCl_3$): *δ* 6.11 (s, 5H, Cp), 5.35 (br s, 1H, $CH_2(CH_2)_3C{=}C\mathit{H}$), 4.07 (s, 1H, =C=CH), 2.51 (m, 3H, $PC\mathit{H}CH_3$), 2.41 (m, 2H, Cy), 2.00−1.56 (br, 6H, Cy), 1.31 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 16.2, $PCHC\mathit{H}_3$), 1.28 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 15.9, $PCHC\mathit{H}_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): *δ* 38.45 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): *δ* 327.68 (d, *J*(CP) = 7.8 Hz, Os=C), 177.41 (d, *J*(CP) = 10.6 Hz, CO), 125.18, 123.21 (both s, $CH_2(CH_2)_3C{=}\mathit{C}H$ and =C=*C*H, confirmed by DEPT), 118.80 (s, $CH_2(CH_2)_3\mathit{C}{=}CH$), 91.12 (s, Cp), 29.25 (d, *J*(CP) = 31.1 Hz, $P\mathit{C}HCH_3$), 28.09, 25.54, 22.48, 21.83 (all s, Cy), 19.83 (d, *J*(CP) = 1.7 Hz, $PCH\mathit{C}H_3$), 19.55 (d, *J*(CP) = 2.0 Hz, $PCH\mathit{C}H_3$).

Acknowledgment. We thank the DGICYT (Project PB-92-0092, Programa de Promoción General del Conocimiento) and the EU (European Union) (Project: Selective Processes and Catalysis Involving Small Molecules) for financial support.

OM950620M