Carbon−Carbon Coupling and Carbon−Hydrogen Activation Reactions in Bis(triisopropylphosphine)osmium Complexes†

Miguel A. Esteruelas,* Fernando J. Lahoz, Enrique Oñate, Luis A. Oro, and Eduardo Sola

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

Received July 5, 1995⊗

Abstract: Reaction of the alkenyl complex OsCl(*E*-CH═CHPh)(CO)(P^iPr_3)$_2$ (**1**) with phenyllithium gives OsH{C_6H_4-2-(*E*-CH═CHPh)}(CO)(P^iPr_3)$_2$ (**2**). The structure of **2** (isomer **2a**) has been determined by X-ray diffraction: triclinic, *P*1, $a = 9.230(1)$ Å, $b = 10.092(1)$ Å, $c = 18.525(2)$ Å, $\alpha = 88.667(7)°$, $\beta = 87.172(7)°$, $\gamma = 71.110(6)°$, $V = 1630.6(3)$, $Z = 2$, R (F, $F_o \geq 4\sigma(F_o)$) = 4.01, wR (F^2, all reflections) = 9.94%. The geometry around the osmium can be described as a distorted octahedron with the two triisopropylphosphine ligands occupying two relative *trans* positions. The remaining perpendicular plane is formed by the carbonyl and the 2-(*E*-1′-styryl)-phenyl ligands mutually *trans* disposed, the hydride ligand and one olefinic hydrogen of the 2-(*E*-1′-styryl)phenyl ligand, which shows an agostic interaction with the osmium atom (distance 2.05(7) Å). The solutions of **2** show equilibria between the agostic isomer (**2a**) and a nonagostic isomer (**2b**). The thermodynamic magnitudes involved in the equilibrium as well as the activation parameters for the conversion between the two isomers were determined in toluene-d_8 by ^{1}H NMR spectroscopy. The values obtained were $\Delta H° = -1.6$ (±0.1) Kcal mol^{-1} and $\Delta S° = -9.6$ (±0.6) cal K^{-1} mol^{-1} for the formation of the agostic isomer, whereas the activation parameters for the breaking of the agostic interaction were $\Delta H^‡ = 7.6$ (±0.2) Kcal mol^{-1} and $\Delta S^‡ = -1.0$ (±0.7) cal K^{-1} mol^{-1}. **2** reacts with CO to give the octahedral complex OsH{C_6H_4-2-(*E*-CH═CHPh)}(CO)$_2$(P^iPr_3)$_2$ (**3**). Reactions of **1** with methyllithium and CD_3Li give OsH{C_6H_4-2-(*E*-CH═CHCH$_3$)}(CO)(P^iPr_3)$_2$ (**4**) and OsH{C_6H_4-2-(*E*-CH═CHCD$_3$)}(CO)(P^iPr_3)$_2$ (**4-*d*$_3$**), respectively. The spectra of these complexes indicate that in solution they also show equilibria between agostic and nonagostic isomers. Reactions of **4** with P(OMe)$_3$ and CO afford OsH{C_6H_4-2-(*E*-CH═CHCH$_3$)}(CO){P(OMe)$_3$}(P^iPr_3)$_2$ (**5**) and OsH{C_6H_4-2-(*E*-CH═CHCH$_3$)}(CO)$_2$(P^iPr_3)$_2$ (**6**), respectively, in which the incoming ligands coordinate *trans* to the hydride. **4** and **4-*d*$_3$** isomerize in solution to give OsH(η^3-CH_2CHCHPh)(CO)(P^iPr_3)$_2$ (**11**) and OsD(η^3-CD_2CHCHPh)(CO)(P^iPr_3)$_2$ (**11-*d*$_3$**), respectively. Reaction of **11** with CO leads to OsH(η^1-CH_2CH═CHPh)(CO)$_2$(P^iPr_3)$_2$ (**12**). The first order constants k_{obs} and $k_{obs\text{-}d_3}$ for the isomerization of **4** and **4-*d*$_3$** to **11** and **11-*d*$_3$** were obtained in $CDCl_3$, giving activation parameters of $\Delta H^‡ = 20.8$ (±1.7) Kcal mol^{-1} and $\Delta S^‡ = -2.8$ (±2.0) cal K^{-1} mol^{-1} for the isomerization of **4** to **11** and a relation $k_{obs}/k_{obs\text{-}d_3} = 3.6$ at 303 K.

Introduction

The design of homogeneous systems effective in the synthesis of functionalized organic molecules from basic hydrocarbon units is both challenging and industrially important. In this respect, obtaining systems which consecutively promote carbon−carbon bond formation and C−H activation is significant and of general interest.

The formation of carbon−carbon bonds mediated by transition metal compounds has emerged in its own right over the last few years as an important step in organic synthesis. These reactions can involve migratory *cis*-ligand insertion, the coupling of adjacent carbon−metal bonds, and the attack of a reagent to an unsaturated organic ligand without metal−reagent bond formation.[1]

The oxidative addition of C−H bonds to transition metal compounds also possess a considerable interest in connection with organic synthesis and catalysis,[2] where efforts have been concentrated to develop homogeneous systems adequate to activate C−H bonds. Representative examples of these systems include the complexes: FeH_2(dmpe)$_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane),[3] Os(η^6-arene)(CO)$_2$,[4] RhCl(CO)(PR_3)$_2$[5] and Tp*Ir(C_2H_4)$_2$ (Tp* = HB(3,5-Me_2pz)$_3$),[6] and metallic fragments generated "in situ" such as Cp*ML (M = Rh, Ir; L = CO, PMe_3),[7] M(PMe_3)$_4$ (M = Ru, Os),[8] M{P(OMe)$_3$}$_2$-

† Dedicated to Professor Rafael Usón on the occasion of his 70th birthday.

⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1995.

(1) (a) Stille, J. K. *Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patal, S., Ed.; Wiley: Chichester, 1985; Vol. 2. (b) Hayashi, T.; Kumada, M. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1985; Vol. 5. (c) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition-metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (e) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031. (f) Brookhardt, M.; Volpe, A. F., Jr.; Yoon, J. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, Y., Ed.; Pergamon Press, 1991; Vol 4.

(2) (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Riedel Publishing Co.: Dordrecht, The Netherlands, 1984. (b) Bergman, R. G. *Science* **1984**, *223*, 902. (c) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (d) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (e) Green, M. L.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897. (f) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley and Sons: New York, 1989; Chapter IV, p 111. (g) Ryabov, A. *Chem. Rev.* **1990**, *90*, 403. (h) Chaloner, P. A.; Esteruelas, M. A.; Joo, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994; Chapter 3.

(3) (a) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433. (b) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7436. (c) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1987**, *109*, 2825. (d) Field, L. D.; George, A. V.; Messerle, B. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1339. (e) Whittlesey, M. K.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Field, L. D.; Wilkinson, M. P.; George, M. *J. Am. Chem. Soc.* **1993**, *115*, 8627.

(4) (a) Werner, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 793. (b) McCamley, A.; Perutz, R. N.; Stahl, S.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1690.

(5) (a) Tanaka, M. *Pure Appl. Chem.* **1990**, *62*, 1147. (b) Sakakura, T.; Sodeyama, T.; Sasaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990**, *112*, 7221, and references therein. (c) Maguire, J. A.; Goldman, A. S. *J. Am. Chem. Soc.* **1991**, *113*, 6706. (d) Rosini, G. P.; Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1994**, *116*, 9498. (e) Boyd, S. E.; Field, L. D.; Partridge, M. G. *J. Am. Chem. Soc.* **1994**, *116*, 9492. (f) Kunin, A.; Eisenberg, R. *Organometallics* **1988**, *7*, 2124.

0002-7863/96/1518-0089$12.00/0 © 1996 American Chemical Society

$(PMe_3)_2$ (M = Ru, Os),[9] or $IrCl(PR_3)_2$.[10] Detailed mechanistic studies have led to a relative understanding of the factors which govern the process. Greater attention has been paid to the kinetic and thermodynamic aspects of C−H activation, and in particular there has been an increased effort to determine the selectivity patterns and the origin of these selectivities.[3e,7f−g,l,m,8b,e,f] However, in many cases the feasibility of the mechanistic studies is restricted by the reaction conditions, which frequently require photochemical or thermal generation of the reactive metallic fragment.

Previously, we have reported the reactions of hydrido−osmium compounds with terminal alkynes which allow the preparation of specific organometallic complexes (vinyl, carbene, hydrido−carbyne, hydrido−vinylidene, and hydrido−dihydrogen−alkynyl), provided that the number of hydrido ligands and the electronic properties of the starting materials are appropriately selected.[11] As a continuation of this work, the reactivity of the above mentioned η^1-organometallic compounds with organic fragments is being studied, in the search for metal-mediated reactions of use in organic synthesis and catalysis. In this paper we report the reactions of the five-coordinate derivative $OsCl(E\text{-}CH{=}CHPh)(CO)(P^iPr_3)_2$ (**1**) with organolithium reagents. The results obtained show the occurrence under mild conditions of C−C coupling reactions followed by C−H activation processes.

Results and Discussion

Reactions of 1 with Phenyllithium and Methyllithium. Reaction of the five-coordinate alkenyl complex $OsCl(E\text{-}CH{=}CHPh)(CO)(P^iPr_3)_2$ (**1**) with a diethyl ether solution of phenyllithium at 60 °C gives a yellow solution from which the complex $OsH\{C_6H_4\text{-}2\text{-}(E\text{-}CH{=}CHPh)\}(CO)(P^iPr_3)_2$ (**2**) was isolated as a yellow solid in 65% yield. Compound **2** was characterized by elemental analysis, IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies, and X-ray diffraction.

Figure 1 shows the molecular diagram of the structure of **2** (isomer **2a**); selected bond distances and angles are listed in Table 1. The most remarkable feature of this structure is the presence of an agostic interaction between the metal atom and one olefinic hydrogen (H(8)) of the 2-(*E*-1′-styryl)phenyl ligand, which is also bonded to the osmium atom by an aromatic carbon atom (C(1)).

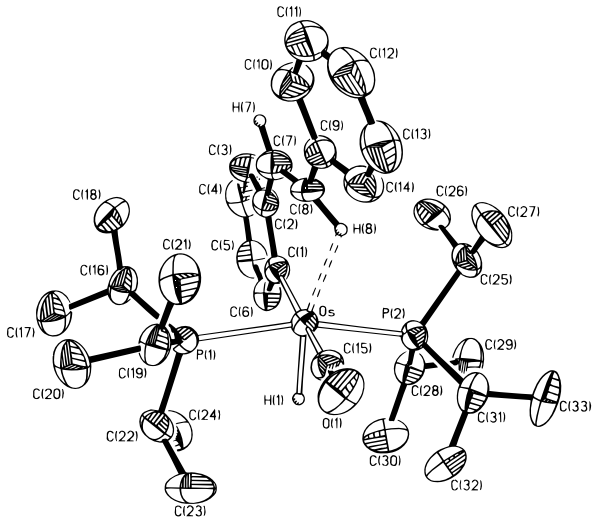


Figure 1. Molecular diagram of the complex $OsH\{C_6H_4\text{-}2\text{-}(E\text{-}CH{=}CHPh)\}(CO)(P^iPr_3)_2$ (**2a**).

The osmium atom is coordinated in a somewhat distorted-octahedral fashion with the two phosphine ligands in *trans* position (P(1)−Os−P(2) = 163.10(6)°). The perpendicular coordination plane is formed by the atoms C(1) and H(8), by the carbonyl group disposed *trans* to C(1) (C(1)−Os−C(15) = 173.3(3)°) and the hydrido ligand disposed *trans* to H(8). The bending of the phosphorus−metal−phosphorus axis points to the direction of the smallest ligand (hydride). The position of this ligand was not determined by the X-ray analysis, but it was included in the location estimated with the HYDEX program.[12] In contrast to the hydrido ligand, the agostic hydrogen H(8) was located in the difference Fourier maps and refined as an isotropic atom together with the rest of the non-hydrogen atoms of the structure, giving a Os−H(8) distance of 2.05(7) Å and a Os···H(8)−C(8) angle of 118(6)°. These distances and angles are similar to those found for other remote agostic interactions in structurally related compounds.[13−15]

The Os−C(1) bond distance of 2.136(7) Å is in agreement with the values previously reported for Os−C(aryl) bond lengths (mean 2.09(3) Å).[16] The C(2)−C(7) (1.486(9) Å), C(7)−C(8) (1.349(11) Å), and C(8)−C(9) bond lengths (1.458(9) Å) compare well with the values found for the carbon−carbon double bond (1.327 Å) and the adjacent carbon−carbon single bonds (1.472 Å) in the free *trans*-stilbene.[17] The relative slight elongation of the olefinic bond and shortening of the saturated

(6) Boutry, O.; Gutierrez, E.; Monge, A.; Nicasio, N. C.; Pérez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288.

(7) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Hoyano, J. K.; Graham, W. A. G.; *J. Am. Chem. Soc.* **1982**, *104*, 3723. (c) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240. (d) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (e) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (f) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620. (g) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732. (h) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91, and references therein. (i) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722. (j) Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *Science* **1992**, *255*, 315. (k) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685. (l) Bell, T. W.; Brough, S.-A.; Partridge, M. G.; Perutz, R. N.; Rooney, A. D. *Organometallics* **1993**, *12*, 2933. (m) Bengali, A. A.; Schultz, R. H.; Moore, B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 9585, and references therein. (n) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

(8) (a) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1346. (b) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 7964. (c) Harper, T. G.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915. (d) Ermer, S. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *Organometallics* **1989**, *8*, 1337. (e) Shinomoto, R. S.; Desrosiers, P. J.; Harper, T. G.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704. (f) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6492.

(9) (a) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*, C60. (b) Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1983**, *2*, 547. (c) Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73.

(10) (a) Werner, H.; Höhn, A.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1090. (b) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025. (c) Schulz, M.; Werner, H. *Organometallics* **1992**, *11*, 2790. (d) Cundari, T. R. *J. Am. Chem. Soc.* **1994**, *116*, 340.

(11) (a) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295. (b) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sánchez-Delgado, R.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *11*, 7431. (c) Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Oro, L. A.; Schlünken, C.; Valero, C.; Werner, H. *Organometallics* **1992**, *11*, 2034. (d) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663. (e) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Ruiz, N.; Oro, L. A. *J. Am. Chem. Soc.* **1993**, *115*, 4683. (f) Esteruelas, M. A.; Oro, L. A.; Ruiz, N. *Organometallics* **1994**, *13*, 1507. (g) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662.

(12) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

(13) (a) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (c) Crabtree, R. H. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789.

(14) Crabtree, R. H.; Holt, E.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986.

(15) Albéniz, A. C.; Schulte, G.; Crabtree, R. H. *Organometallics* **1992**, *11*, 242.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex OsH{C_6H_4-2-(*E*-CH═CHPh)}(CO)(P^iPr_3)$_2$ (**2a**)

Os−P(1)	2.393(2)	P(1)−Os−P(2)	163.10(6)	Os−C(1)−C(2)	118.1(4)
Os−P(2)	2.377(2)	P(1)−Os−C(1)	89.2(2)	C(1)−C(2)−C(7)	119.4(6)
Os−C(1)	2.136(7)	P(1)−Os−C(15)	88.7(2)	C(2)−C(7)−C(8)	123.9(7)
Os−C(15)	1.871(8)	P(2)−Os−C(1)	90.3(2)	C(7)−C(8)−C(9)	126.2(7)
Os···H(8)	2.05(7)	P(2)−Os−C(15)	93.5(2)	C(7)−C(8)−H(8)	126(4)
C(1)−C(2)	1.421(10)	C(1)−Os−C(15)	173.3(3)	Os−C(15)−O(1)	176.7(6)
C(1)−C(6)	1.408(8)	P(1)−Os···H(8)	113(2)	Os···H(8)−C(8)	118(6)
C(2)−C(3)	1.402(12)	P(2)−Os···H(8)	84(2)		
C(3)−C(4)	1.376(10)	C(1)−Os···H(8)	85(3)		
C(4)−C(5)	1.388(14)	C(15)−Os···H(8)	90(2)		
C(5)−C(6)	1.365(12)				
C(2)−C(7)	1.486(9)				
C(7)−C(8)	1.350(11)				
C(8)−C(9)	1.458(9)				
C(8)−H(8)	1.02(9)				
C(15)−O(1)	1.166(10)				

[a] Esd's are given in parentheses.

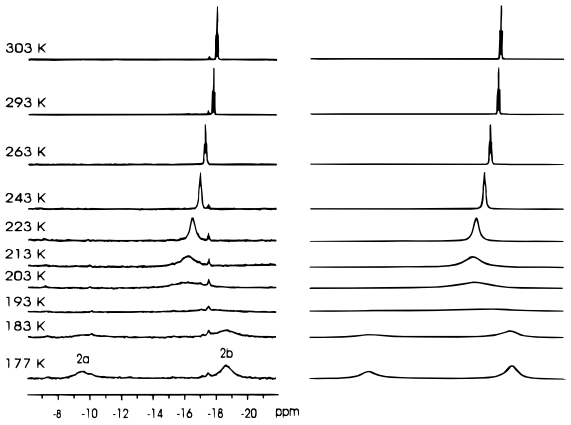
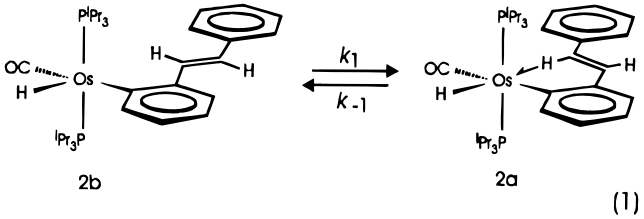


Figure 2. Hydrido region of the ^{1}H NMR spectrum of **2** at different temperatures: experimental in toluene-d_8 (left) and calculated (right).

C(2)−C(7) and C(8)−C(9) bonds reflect the greater electronic delocalization of the coordinated ligand. The Os−P, Os−CO, and C≡O distances are clearly in the expected range and deserve no further comments.

The spectroscopic data obtained for solutions of **2** are in agreement with the presence of the 2-(*E*-1′-styryl)phenyl ligand. The ^{13}C{^{1}H} NMR spectrum at room temperature shows a triplet at 177.3 ppm (J_{CP} = 10.6 Hz) assignable to the aromatic carbon bonded to the osmium. The rest of carbon atoms of the metalated phenyl ring give resonances at 155.4 (t, J_{CP} = 2.3 Hz, quaternary carbon), 142.9, 139.7, 129.8 (broad triplets with J_{CP} < 1 Hz), and 126.5 (s) ppm. A singlet at 121.8 ppm and a broad singlet at 106.2 ppm are assigned to the olefinic carbons. The ^{31}P{^{1}H} spectrum contains a singlet at 22.7 ppm. The ^{1}H NMR spectrum of **2** at room temperature shows a triplet at −17.83 (J_{HP} = 21.0 Hz) for the hydrido ligand. The expected resonances for the metalated and nonmetalated phenyl ring protons are observed in the range 6.7−7.6 ppm, together with a doublet at 7.56 (J_{HH} = 13.6 Hz) which corresponds to one of the two hydrogens atoms of the olefinic bond. This spectrum does not show any resonance attributable to the other olefinic proton, although the ^{1}H COSY spectrum indicates that the signal lies at 1.05 ppm, hidden by the phosphine methyl groups. The chemical shift of this resonance, at higher field than that expected for an olefinic proton, suggests that some agostic interaction is also present in solution.

The spectra of solutions of **2** are temperature-dependent. Figure 2 shows the hydrido region of the ^{1}H NMR spectra in toluene-d_8, between 177 and 303 K. At 177 K, the spectrum contains two broad hydrido resonances at −9.5 and −18.6 ppm. On raising the temperature they coalesce, and the resulting averaged signal finally sharpens to give a triplet, the chemical shift of this triplet being temperature-dependent. This behavior can be understood as the result of the equilibrium shown in eq 1, which involves the cleavage of the agostic interaction present in **2a** to give the nonagostic isomer **2b**. The higher field hydrido resonance at −18.6 ppm is assignable to the unsaturated species **2b**, in the view of the *trans* disposition of the hydrido ligand and the coordination vacancy.



(1)

The equilibrium constants K (= k_1/k_{-1}) were measured in the range from 177 to 303 K (Table 2). The temperature dependence of the equilibrium (Figure 3) gives the values $\Delta H°$ = −1.6 (±0.1) Kcal mol^{-1} and $\Delta S°$ = −9.6 (±0.6) cal K^{-1} mol^{-1} for the formation of **2a**. The negative entropy increment is consistent with the less ordered character of **2b**, which is always the mayor species in the temperature range studied. The value of $\Delta H°$ reveals the small stabilization achieved by means of the agostic interaction. This small value could be justified to be not only due to the weakness of the agostic bond but also to the destabilization due to steric repulsion between the phenyl ring and the bulky phosphines in **2a**. The strength of this agostic interaction in comparison with other systems can be estimated using the r_{bp} parameter defined by Crabtree et al.[14] From the structural data of **2a** the resulting value of r_{bp} is 0.82, which lies in the range of *relatively strong* interactions.

Line shape analysis of the spectra of Figure 2 allow the calculation of the rate constants for the agostic bond cleavage (k_{-1}) at different temperatures. The activation parameters obtained from the Eyring analysis (Figure 4) are $\Delta H^‡$ = 7.6 (±0.2) Kcal mol^{-1} and $\Delta S^‡$ = −1.0 (±0.7) cal K^{-1} mol^{-1}. The activation entropy is nearly zero, as expected for an intramolecular process. The activation enthalpy lies in the range of other reported exchange processes in which agostic interactions are breaking and reforming.[18] No evidence has been found for

(16) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

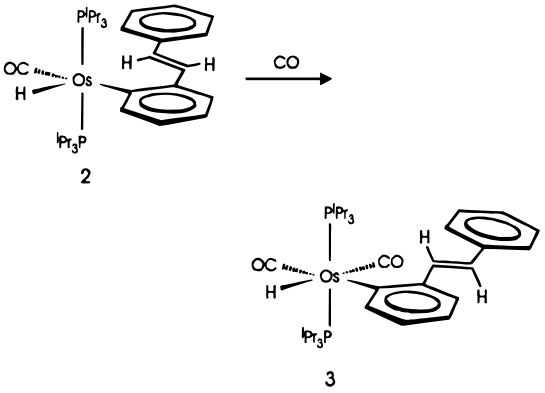
(17) Bouwstra, J. A.; Schouten, A.; Kroon, J. *Acta Crystallogr., Sect C* **1984**, *40*, 428.

Table 2. Equilibrium Constants of Agostic Bond Formation and Rates of Agostic Bond Cleavage for the Complex $OsH\{C_6H_4\text{-}2\text{-}(E\text{-}CH{=}CHPh)\}(CO)(P^iPr_3)_2$ (**2**) in Toluene-d_8

temp (K)	K	k_{-1} (s^{-1})
177	0.742	1.1×10^3
183	0.639	1.9×10^3
193		8.0×10^3
203		1.8×10^4
213	0.367	3.7×10^4
223	0.309	1.2×10^5
243	0.227	6.0×10^6
253	0.199	
263	0.167	1.5×10^7
293	0.128	
303	0.108	

the occurrence of hydrogen exchange between the hydrido ligand and the agostic proton in complex **2**. This agrees with the behavior of the compound *mer*-$[(Me_3P)_3IrH\{Z\text{-}1\text{-}(2'\text{-furyl})\text{-}3,3\text{-dimethyl-1-butyl}\}]$, in which the hydride and the agostic bond are also in *trans* relative positions.[19] Nevertheless, such an exchange has been observed in complexes containing both agostic C−H bonds and hydrido ligands in *cis* relative positions.[20]

As expected from the lability of the agostic bond, the reaction of **2** with CO gives the *cis*-dicarbonyl complex $OsH\{C_6H_4\text{-}2\text{-}(E\text{-}CH{=}CHPh)\}(CO)_2(P^iPr_3)_2$ (**3**), in which the incoming ligand coordinates *trans* to the hydrido position, releasing the C−H bond from the metal coordination sphere (eq 2).



(2)

The spectroscopic data obtained for complex **3** support the proposed octahedral structure. The *cis* relative position of the carbonyl ligands was inferred from the IR spectrum, which shows, together with a ν(Os−H) band at 2032 cm^{-1}, two strong ν(CO) absorptions at 1966 and 1894 cm^{-1}, a typical pattern for mononuclear *cis*-dicarbonyl complexes. The $^{13}C\{^1H\}$ NMR spectrum also supports this proposal, showing two triplets at 190.4 ppm (J_{CP} = 5.5 Hz) and at 185.2 ppm (J_{CP} = 8.3 Hz) attributable to the carbonyl ligands. This spectrum also contains the expected resonances for the 2-(*E*-1′-styryl)phenyl ligand. The two olefinic carbon atoms were assigned to singlets at 141.7 and 156.9 ppm, shifted about 35 ppm toward lower field with regard to the olefinic carbons of **2**. The CH groups of the phosphine ligands give a virtual triplet at 26.5 ppm (N = 27.0 Hz), which is characteristic of two equivalent phosphine ligands in *trans* relative position. This is in agreement with the singlet at 19.1 ppm found in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H spectrum of **3** shows the hydrido resonance at −6.09 ppm as a triplet (J_{HP} = 21.3 Hz). The olefinic protons of the 2-(*E*-1′-styryl)phenyl ligand display two doublets at 8.37 and 6.97 ppm with a H−H coupling constant of 16.2 Hz, in agreement with their *trans* relative position at the carbon−carbon double bond.

Reaction of **1** with CH_3Li in hexane gives a yellow solution from which the complex $OsH\{C_6H_4\text{-}2\text{-}(E\text{-}CH{=}CHCH_3)\}(CO)(P^iPr_3)_2$ (**4**) was isolated as a yellow solid in 89% yield. The presence of a 2-(*E*-1′-propenyl)phenyl ligand in **4** is supported by the $^{13}C\{^1H\}$ and ^1H NMR spectra.

The $^{13}C\{^1H\}$ NMR spectrum of a $CDCl_3$ solution of **4** (Figure 5) exhibits six different resonances for the aromatic carbon atoms of the η^1-carbon ligand: a triplet at 151.5 ppm (J_{CP} = 10.4 Hz) due to the metalated carbon, triplets at 152.3, 137.7, 125.1, and 119.8 ppm with coupling constants J_{CP} in the range of 1 to 2.5 Hz and a singlet at 123.8 ppm. The olefinic carbon

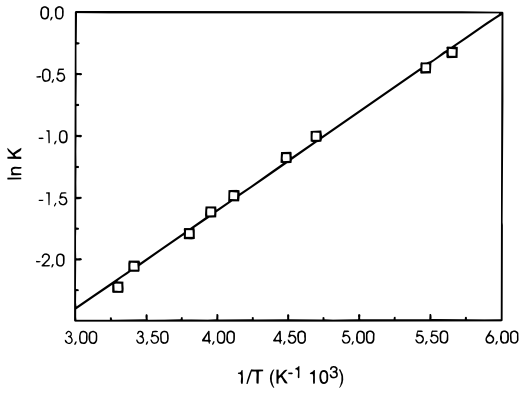


Figure 3. Arrhenius plot of the equilibrium constants for agostic Os···H bond formation in **2**.

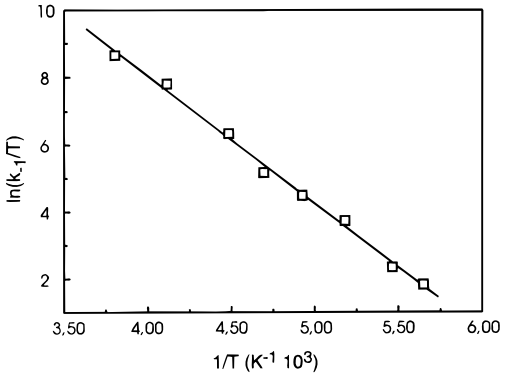


Figure 4. Eyring plot of the rate constants for agostic Os···H bond cleavage in **2**.

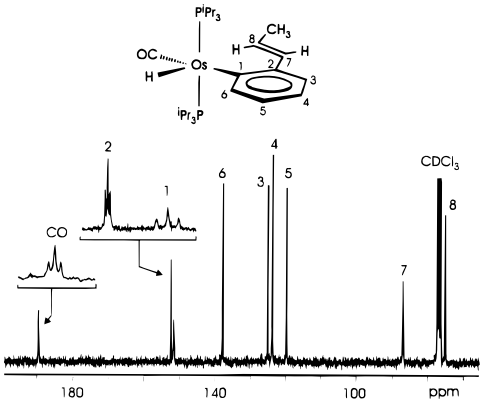


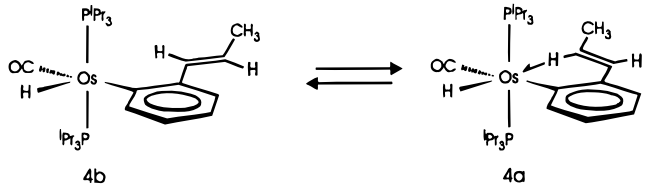
Figure 5. Low field region of the $^{13}C\{^1H\}$ NMR spectrum of **4** ($CDCl_3$, 263 K), and proposed assignment.

(18) Morse, P. M.; Spencer, M. O.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646, and references therein.
(19) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 3800.
(20) (a) Ogasawara, M.; Saburi, M. *Organometallics* **1994**, *13*, 1911. (b) Ogasawara, M.; Aoyagi, K.; Saburi, M. *Organometallics* **1993**, *12*, 3393. (c) McLoughlin, M. A.; Flesher, R. J.; Kaska, W. C.; Mayer, H. A. *Organometallics* **1994**, *13*, 3816.

atoms appear as broad signals at 87.1 and 75.3 ppm, whereas the methyl group gives a singlet at 16.2 ppm. The virtual triplet at 26.6 ppm (N = 25.7 Hz) displayed by the CH groups of the phosphines indicates the equivalence and mutual *trans* disposition of these ligands. This is confirmed by the singlet at 18.8 ppm found in the $^{31}P\{^1H\}$ NMR spectrum. At room temperature, the ^1H NMR spectrum shows a triplet at −13.33 ppm (J_{HP} = 24.0 Hz) for the hydrido ligand. The aromatic region consists of four different resonances at 7.54 (d), 7.05 (t), 6.97 (t), and 6.81 (d), whereas the olefinic protons appear as a multiplet at 2.67 ppm and a doublet at 5.82 (J_{HH} = 10.8 Hz). This large J_{HH} coupling constant strongly supports the mutual *trans* disposition of the hydrogen atoms at the carbon−carbon double bond. The methyl substituent of the olefinic group gives a doublet at 2.14 ppm (J_{HH} = 5.7 Hz).

Reaction of the alkenyl complex **1** with CD_3Li, under the same conditions as those employed for the synthesis of **4,** gives the hydrido-complex $OsH\{C_6H_4\text{-}2\text{-}(E\text{-}CH{=}CHCD_3)\}(CO)(P^iPr_3)_2$ (**4-*d*$_3$**) as unique product, in 84% yield. The presence of a deuterated methyl group in **4-*d*$_3$** was inferred from its ^2H NMR spectrum in benzene which shows a singlet at 2.0 ppm as a unique signal. In agreement with this, the ^1H NMR spectrum does not contain any resonance in the region 2.14 ppm, and the multiplet at 2.67 ppm is simplified into a broad doublet with a H−H coupling constant of about 10 Hz.

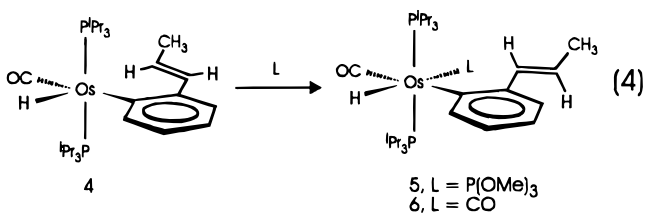
The unusual chemical shifts obtained for the carbons and protons of the 1-propenyl moiety suggest that the substituted phenyl ligands of **4** and **4-*d*$_3$** are involved in agostic interactions similar to that found in **2** (eq 3). In fact, the ^1H NMR spectra of the complexes **4** and **4-*d*$_3$** are also temperature-dependent, as illustrated for **4-*d*$_3$** in Figure 6. On lowering the temperature a remarkable shift of the hydrido resonance is observed, along with a significant broadening of the signal. Simultaneously, the olefinic resonances also shift and broaden.



(3)

In contrast to that found for **2**, at the lowest temperature attained the conversion rate between **4a** and **4b** is still fast in the NMR time scale, and thus the observed hydrido resonance is a result of an average of the two signals. As found for **2**, the lowering of the temperature might favor the agostic complex, hence the hydrido resonance shifts to lower fields. Replacement of the CD_3 substituent by CH_3 has no detectable effect in the position of the equilibrium, as the hydrido chemical shifts observed for **4** and **4-*d*$_3$** are nearly the same at any temperature.

Similarly to **2**, complex **4** reacts with Lewis bases such as $P(OMe)_3$ and CO to give the corresponding adducts $OsH\{C_6H_4\text{-}2\text{-}(E\text{-}CH{=}CHCH_3)\}(CO)\{P(OMe)_3\}(P^iPr_3)_2$ (**5**) and $OsH\{C_6H_4\text{-}2\text{-}(E\text{-}CH{=}CHCH_3)\}(CO)_2(P^iPr_3)_2$ (**6**) (eq 4).



(4)

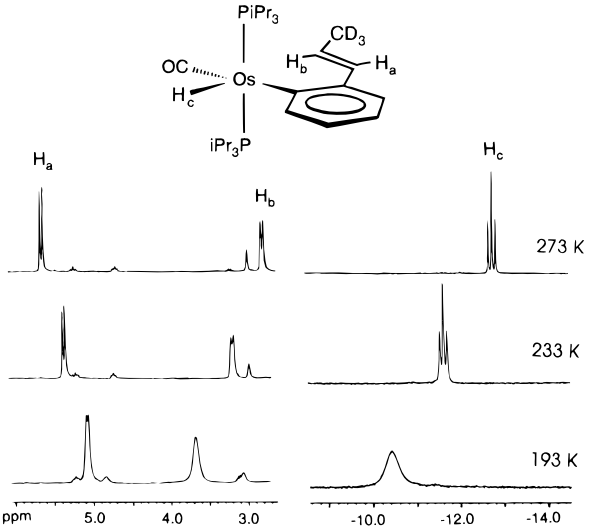


Figure 6. Hydrido and olefinic region of the ^1H NMR spectra of **4-*d*$_3$** at different temperatures in toluene-d_8.

The spectroscopic data obtained for these complexes support the proposed octahedral structures. The $^{31}P\{^1H\}$ NMR spectrum of **5** consists of a triplet at 95.3 ppm and a doublet at 12.5 ppm (J_{PP} = 20.3 Hz), in agreement with a phosphite ligand *cis* to two equivalent P^iPr_3 ligands. The proposed *trans* disposition of hydrido and phosphite ligands is supported by the ^1H spectrum, which contains at −8.34 ppm a doublet (J_{HP} = 143.4 Hz) of triplets (J_{HP} = 29.1 Hz). In the low field region, the spectrum exhibits the expected resonances for the phosphorus donor ligands and for the four aromatic protons, along with a doublet of quartets at 5.94 ppm (J_{HH} = 6.6 and 15.6 Hz), a doublet at 8.06 ppm (J_{HH} = 15.6 Hz), and a doublet at 1.98 (J_{HH} = 6.6 Hz) assigned to the 1-propenyl fragment. The striking difference in the olefinic proton chemical shifts with regard to those observed in complex **4** indicates the nonagostic nature of the 1-propenyl moiety in complex **5**. The $^{13}C\{^1H\}$ spectrum shows two apparent quartets at 188.5 ppm (J_{CP} = 9.5 Hz) and 155.6 ppm (J_{CP} = 12.0 Hz) corresponding to the carbonyl ligand and the metalated carbon atom of the phenyl group respectively. The multiplicity and the values of coupling constants confirm the *cis* disposition of these groups with respect to the three phosphorous donor ligands.

The mutual *cis* disposition of the carbonyl ligands in **6** is supported by the $^{13}C\{^1H\}$ NMR spectrum which shows two separate resonances at 190.3 ppm (J_{CP} = 6.0 Hz) and 185.3 ppm (J_{CP} = 8.3 Hz) and by the IR spectrum, which contains in the terminal carbonyl region two very strong absorptions at 1965 and 1980 cm^{-1}. A singlet at 18.4 ppm in the $^{31}P\{^1H\}$ spectrum confirms the equivalence of the phosphines. In addition, the high field signal of the ^1H NMR spectrum, a triplet at −6.23 ppm (J_{HP} = 21.7 Hz), is in agreement with a hydride *cis* disposed to both triisopropylphosphine ligands.

The exclusive formation of **4-*d*$_3$** and the *trans* position of the two substituents—the metalated phenyl and the R group—at the carbon−carbon double bond of **2** (R = Ph), **4** (R = CH_3), and **4-*d*$_3$** (R = CD_3) suggest that the reactions of **1** with phenyllithium and methyllithium follow the steps shown in Scheme 1. The reactions could initially involve the replacement of the Cl^- anion by the R group to give *R*-styrylosmium(II) species (**7**, **8**, and **8-*d*$_3$**). Subsequently, the carbon−carbon reductive coupling should afford osmium(0) intermediates (**9**, **10**, and **10-*d*$_3$**), containing a coordinated olefin ligand. Because the reductive carbon−carbon coupling is a concerted process, the stereochemistry at the carbon−carbon double bond is retained, thus, the phenyl and the R groups are mutually *trans*

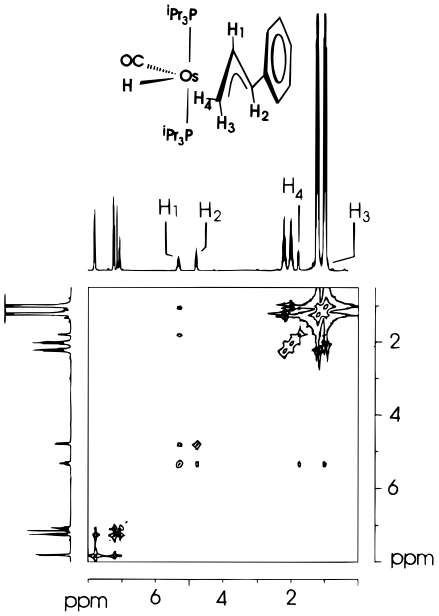
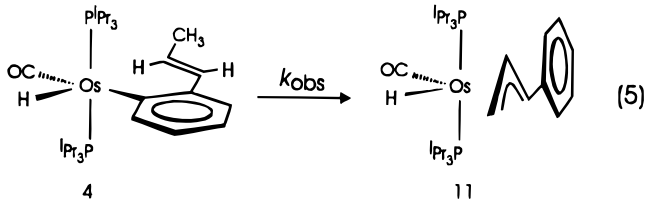


Figure 7. Low field region of the ^{1}H COSY spectrum of **11** in C_6D_6.

disposed. According to this proposal we have recently found that the reactions of complex **1** and its ruthenium analogue with vinylmagnesium bromide afford 1-phenylbutadieneosmium(0) and -ruthenium(0) derivatives. The reactions proceed via bis-vinyl intermediates, which can be detected in the case of ruthenium.[21] Finally the C−H activation of the *ortho*-CH bond of the phenyl group should lead to the reaction products.

Isomerization of 4. In solution, after ca. 20 min. at room temperature, complex **4** transforms into the complex OsH(η^3-$CH_2CHCHPh$)(CO)(P^iPr_3)$_2$ (**11**) (eq 5), which can be isolated in 85% yield by precipitation in methanol.

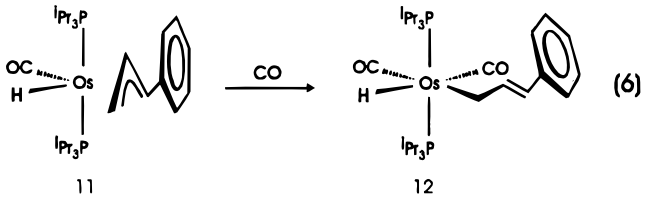


The spectroscopic data of **11**, an isomer of **4**, agree with the presence of the 1-phenylallyl ligand coordinated in a π mode. The ^{1}H NMR spectrum shows at high field a doublet of doublets (−11.52 ppm, J_{HP} = 31.5, 23.5 Hz), attributable to a hydrido ligand disposed *cis* to two chemically inequivalent phosphine ligands. In the low field region the spectrum exhibits the resonances due to the phosphine ligands and the phenyl group, along with three multiplets at 5.32, 4.79, and.1.78 ppm, each one corresponding to one proton. The ^{1}H NMR COSY spectrum shows a fourth multiplet corresponding to the 1-phenylallyl ligand buried under the phosphine methyl groups resonances (Figure 7). The different coupling constants mixed up in these multiplets have been deduced by means of the ^{1}H-{^{31}P} spectrum and selective homonuclear irradiation in the ^{1}H spectrum and are reported in the Experimental Section. The J_{HH} coupling constant between the C*H*Ph and *meso*-CH protons (8.7 Hz) suggests a *syn* conformation for the 1-phenylallyl ligand.[22] This *syn* conformation seems to be sterically more favored, being the only form observed in previously reported complexes containing this ligand structurally characterized by X-ray diffraction.[23]

(21) Bohanna, C.; Esteruelas, M. A.; Lahoz, F.; Oñate, E.; Oro, L. A.; Sola, E. *Organometallics* **1995**, *14*, 4825.

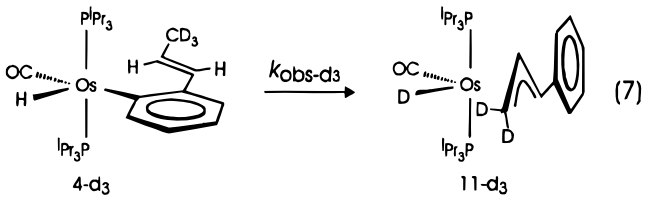
The ^{31}P{^{1}H}spectrum of **11** shows an AB pattern centered at 21.9 ppm with a P−P coupling constant of 208.9 Hz, which requires a *trans* disposition of the phosphine ligands. The η^3 coordination of the 1-phenylallyl ligand is also suggested by the ^{13}C{^{1}H} spectrum, in which the allylic carbons signals consist of a doublet of doublets at 16.3 ppm (J_{CP} = 6.0, 3.2 Hz) for the terminal CH_2, a doublet at 49.7 ppm (J_{CP} = 1.0 Hz) for the phenyl-substituted terminal carbon, and a singlet at 79.8 ppm for the *meso*-CH. The carbonyl ligand gives a doublet of doublets at 192.9 ppm (J_{CP} = 10.8, 8.5 Hz) in agreement with its *cis* location relative to the two phosphine ligands.

In the structure proposed for **11**, shown in eq 5, the hydrido ligand occupies one position *cisoid* to the terminal CH_2 group of the allyl ligand. This postulation bares relation to the structure of complex **12**, which was prepared by reaction of **11** with carbon monoxide (eq 6).



The IR spectrum of **12** contains the absorption attributable to the ν(Os−H) vibration at 2015 cm^{-1} and two ν(CO) bands at 1950 and 1885 cm^{-1}, in agreement with a *cis* arrangement of the carbonyl groups. The ^{13}C{^{1}H} spectrum is consistent with a η^1 coordination of the phenylallyl ligand, showing a triplet at −4.5 ppm (J_{CP} = 6.9 Hz) for the α methylenic carbon atom and singlets at 120.9 and 147.8 ppm for the carbon atoms in β and γ positions, respectively. In the ^{1}H spectrum, the protons in β and γ positions give rise to a doublet of triplets at 7.10 ppm (J_{HH} = 15.3 and 9.0 Hz) and a doublet at 6.14 ppm (J_{HH} = 15.3 Hz), respectively. The large J_{HH} constant confirms their relative *trans* position at the double bond, in agreement with the *syn* conformation proposed for the η^3-allyl ligand of **11**. Both α hydrogens appear as a sole doublet of triplets at 1.82 ppm (J_{HH} = 9.0 Hz, J_{HP} = 8.2 Hz). The ^{31}P{^{1}H} NMR spectrum shows a singlet at 22.8 ppm.

The deuterated complex **4-*d*$_3$** also isomerizes in solution to give the complex OsD(η^3-$CD_2CHCHPh$)(CO)(P^iPr_3)$_2$ (**11-*d*$_3$**), as is illustrated in eq 7. In this case the reaction requires several hours for completion.



The ^{2}H NMR spectrum of **11-*d*$_3$** shows a broad doublet of doublets at −11.5 ppm, together with two broad signals centered at 1.0 and 1.7 ppm, revealing that the compound is deuterated at the hydride and the methylenic allyl carbon. Consequently,

(22) For examples, see: (a) Clark, H. C.; Hampden-Smith, M. J.; Ruegger, H. *Organometallics* **1988**, *7*, 2085. (b) Krivykh, V. V.; Gusev, O. V.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *366*, 109.

(23) (a) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201. (b) Murrall, N. W.; Welch, A. J. *J. Organomet. Chem.* **1986**, *301*, 109. (c) Cotton, F. A.; Luck, R. L. *Acta Crystallogr., C (Cr.yst Struct. Commun.)* **1990**, *46*, 138. (d) Faller, J. W.; Lambert, C.; Mazzieri, M. R. *J. Organomet. Chem.* **1990**, *383*, 161. (e) Henly, T. J.; Wilson, S. R.; Shapley, J. R *Inorg. Chem.* **1988**, *27*, 2551.

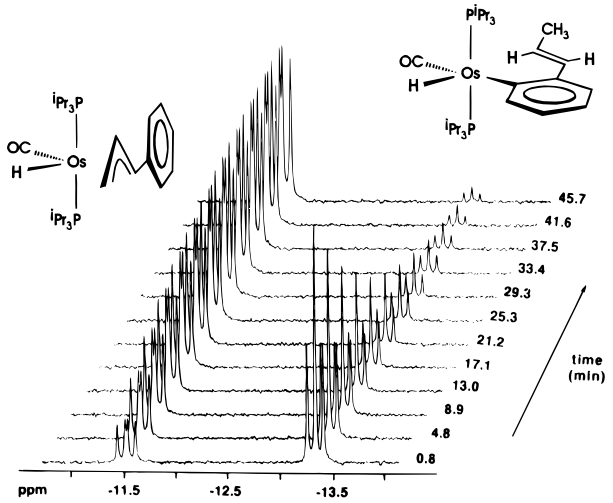


Figure 8. Stacked spectra illustrating the isomerization of complex **4** to **11** in $CDCl_3$ at 303 K.

Table 3. Rates of Isomerization of Complex **4** to **11** in $CDCl_3$

complex	temp (K)	k_{obs} (s^{-1} 10^4)
4	308	25.9 ± 0.9
	303	15.2 ± 0.5
	301	12.3 ± 0.4
	295	5.9 ± 0.2
	290	2.9 ± 0.1
4-d_3	313	14.1 ± 0.4
	303	4.2 ± 0.1
	299	2.7 ± 0.1

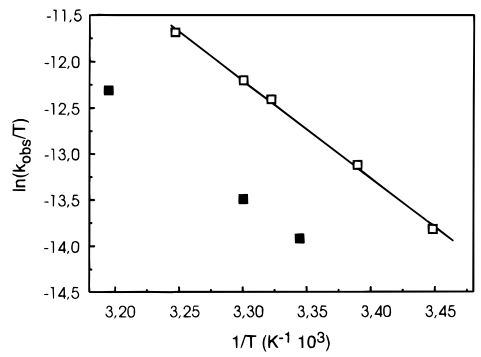
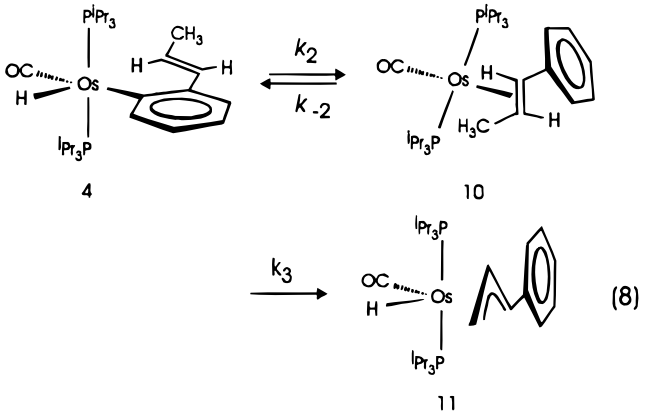


Figure 9. Eyring plot of the first order rate constants (k_{obs}) for the isomerization of **4** to **11** (white), and for the isomerization of **4**-d_3 to **11**-d_3 (black) in $CDCl_3$.

these resonances are absent in the ^1H spectrum of **11**-d_3. The $^{31}P\{^1H\}$ NMR spectrum also suggests the deuteration at the hydrido position, showing a small P−D coupling of 3.6 Hz.

The isomerization reaction[24] depicted in eq 5 was followed by ^1H NMR spectroscopy by measuring the disappearance of the hydrido signal of **4** as a function of time. As shown in Figure 8, the decrease of **4** (with the corresponding increase of **11**) in $CDCl_3$ is an exponential function of time, in agreement with a first order process. The values obtained for the first order rate constant k_{obs} in the temperature range studied are reported in Table 3. The activation parameters of the reaction were obtained from the Eyring analysis shown in Figure 9, giving values of $\Delta H^{\ddagger} = 20.8$ (±1.7) Kcal mol^{-1} and $\Delta S^{\ddagger} = -2.8$ (±2.0) cal K^{-1} mol^{-1}. The near zero activation entropy is consistent with an intramolecular process. Table 3 also includes the values of the first order rate constant $k_{obs\text{-}d_3}$ obtained for the isomerization of the deuterated complex **4**-d_3 (eq 6). A primary isotope effect[25] is evidenced by the value $k_{obs}/k_{obs\text{-}d_3} = 3.6$ at 303 K. This indicates that the rate-determining step of the isomerization reaction involves the cleavage of one C−H bond of the methyl group.

In the view of the *trans* relative position at the C═C bond of the metalated phenyl ring and the methyl substituent, the methyl group C−H activation step seems unlikely to occur in **4**. Thus, the isomerization reaction might involve an initial step consisting of the reductive elimination of 1-phenylpropene from **4** to give the unsaturated osmium(0) intermediate **10**, as shown in eq 8. This intermediate[26] is consistent with the observation that no H/D scrambling occurs between the *ortho* phenyl position and the methyl group during the isomerization of **4**-d_3. The second and slow step of the reaction would consist in the C−H activation of the methyl group of the 1-phenylpropene in **10** to give **11**.[27]



Despite of the fact that the C−H activation of the methyl group in **10** (k_3) is the slow step of the isomerization, no signal corresponding to **10** can be spectroscopically detected in the course of the reaction. Moreover, the only signals observable during the reaction are those corresponding to **4** and **11**. The fact that **10** does not accumulate in solution suggests that a C−H activation process in **10** to reform **4** (k_{-2}) is faster than conversion of **10** to **11**. This is also in agreement with the formation of **4** via the Scheme 1.

The reactions shown in eq 8 may be considered as two competitive C−H activation processes in a undetected osmium-(0) complex. One of these processes, kinetically favored and reversible at room temperature, consists of the activation of the *ortho* C−H bond of the phenyl ring to give the product of kinetic control **4**. The other, which requires a larger activation enthalpy, leads to the isomer **11**. Because the η^3-allyl coordination is expected to give a more stable complex than the η^1-phenyl coordination, complex **11** is the product of thermodynamic control. This is in agreement with the proposal of Jones and Feher, who have suggested that for competitive intramolecular

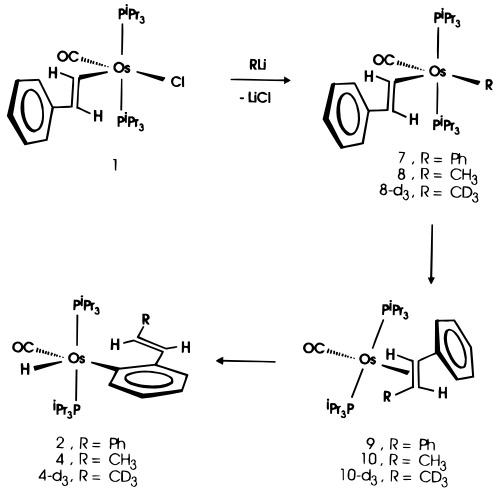
(24) An example of an isomerization reaction similar to that of **4** to **11** has been previously reported. The complex Cp*IrH{η^1,η^2-C_6H_4-2-(CH_2-CH═CH_2)}, which contains an isomeric ligand of the 2-(*E*-1′-propenyl)-phenyl ligand of **4,** partially isomerizes on heating to the species Cp*IrH(η^3-1-phenylallyl). See: McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.

(25) Connors, K. A. *Chemical Kinetics, The Study of Reaction Rates in Solution*; VCH Publishers, Inc.: 1990.

(26) Unsaturated osmium(0) species have been proposed as intermediates in some C−H activation reactions (refs 8 and 9c). In addition some stable 16 electron osmium(0) complexes have been reported: (a) Werner, H.; Flügel, R.; Windmüller, B.; Michenfelder, A.; Wolf, J. *Organometallics* **1995**, *14*, 61. (b) Werner, H.; Michenfelder, A.; Schulz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 596.

(27) For examples on the activation of propene or substituted propenes to give hydrido allyl complexes, see: (a) Heyn, R. H.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 3354. (b) Zhuang, J.-M.; Sutton, D. *Organometallics* **1991**, *10*, 1516. (c) Reference 24.

Scheme 1



C−H activation reactions the selectivity is determined by the thermodynamic stability of the reaction products rather than by the strength of the C−H bond to be activated.[7h]

Products obtained from the oxidative addition of the olefinic C−H bonds have not been observed during this work, in spite of the fact that the activation of these bonds is an expected process in intermediates such as **9** and **10**.[3ab,7gl,10c,28] The lack of products from these activations does not necessarily imply that these processes are kinetically disfavored with regard to the activations of the *ortho* phenyl or methyl group C−H bonds. In fact, low activation barriers should be expected for all the possible intramolecular C−H activations in osmium(0) intermediates like **10**, in view of the mild isomerization conditions and the values of activation enthalpies reported for this kind of reactions.[7j] Thus, the nonobservation of hydrido−vinyl complexes could be a consequence of their lower thermodynamic stability compared to the hydrido−phenyl derivatives.[29] This was also suggested by previous studies showing that metal−phenyl bonds are stronger that metal−vinyl ones.[2f,7h] In the light of these considerations, the hydrido−phenyl complexes **2** and **4** may be tentatively considered as products of thermodynamic control among those C−H activations kinetically favored. In this context, the additional stabilization given by the agostic interaction found in **2** and **4**, albeit small, may have an influence in directing the selectivity of the C−H activation to the *ortho* C−H bonds.

Conclusion

This study has revealed that the five-coordinate complex OsCl(*E*-CH═CHPh)(CO)(P^iPr_3)$_2$ (**1**) is an useful starting material to perform, in consecutive steps, carbon−carbon bond formation and C−H activation reactions.

Treatment of complex **1** with RLi (R = Ph, CH_3) leads to new hydridoosmium(II) derivatives, via osmium(0) intermediates containing an olefinic ligand. This ligand is a result of the reductive carbon−carbon coupling between the styryl and R groups. The metallic center of these osmium(0) intermediates is capable of activating a C−H bond of one substituent of the coordinated olefin to afford hydridoosmium(II) derivatives. The nature of the C−H activation products can be rationalized on the basis of the substituents present at the alkene ligand of the osmium(0) intermediate and in the light of thermodynamic and kinetic considerations. When the alkene ligand has a phenyl substituent, the activation of an *ortho* position of this phenyl ring is kinetically favored. The products of these activations show an agostic interaction between the osmium center and one of the olefinic C−H bonds. When the alkene ligand has a methyl substituent, the final product of the reaction is a hydrido−allyl complex. This reaction requires larger activation energy but gives a complex thermodynamically more stable.

In recent years our group has studied a series of catalytic processes performed by phosphino−osmium complexes. The mechanistic studies carried out in catalytic reactions such as hydrogenation,[30,11b] hydrosililation,[31] or hydrogen transfer re-

Table 4. Atomic Coordinates ($\times 10^4$; $\times 10^5$ for Os Atom) and Equivalent Isotropic Displacement Coefficients (Å^2, $\times 10^3$; Å^2, $\times 10^4$ for Os Atom) for the Compound OsH{C_6H_4-2-(*E*-CH═CHPh)}(CO)(P^iPr_3)$_2$ (**2a**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	U_{eq}[a]
H(1)[b]	9375	5703	7116	
H(8)[c]	5456(94)	7882(79)	7639(41)	53(22)
Os	76029(3)	64831(2)	74446(1)	276(1)
P(1)	8197(2)	4519(2)	8256(1)	30(1)
P(2)	7710(2)	8036(2)	6474(1)	33(1)
O(1)	8829(8)	8009(6)	8533(3)	62(2)
C(1)	6482(7)	5441(6)	6784(3)	31(1)
C(2)	4908(8)	5627(7)	6946(3)	36(1)
C(3)	4073(9)	4964(8)	6559(4)	47(2)
C(4)	4753(11)	4121(8)	5982(4)	58(2)
C(5)	6294(10)	3902(8)	5812(4)	51(2)
C(6)	7107(9)	4522(7)	6205(3)	39(2)
C(7)	4089(8)	6571(7)	7544(3)	42(2)
C(8)	4633(7)	7501(7)	7854(3)	35(1)
C(9)	3877(8)	8455(7)	8438(3)	40(2)
C(10)	2492(10)	8461(9)	8772(4)	55(2)
C(11)	1801(11)	9386(9)	9316(5)	67(2)
C(12)	2475(12)	10334(9)	9554(4)	68(3)
C(13)	3832(12)	10352(8)	9221(5)	65(2)
C(14)	4524(9)	9419(8)	8677(4)	50(2)
C(15)	8391(8)	7427(7)	8100(3)	37(1)
C(16)	7131(9)	3241(7)	8204(4)	46(2)
C(17)	7908(12)	1730(8)	8425(5)	66(2)
C(18)	5566(11)	3762(10)	8614(6)	72(3)
C(19)	8231(9)	4974(7)	9231(3)	43(2)
C(20)	8743(12)	3718(9)	9746(4)	63(2)
C(21)	6802(11)	6081(9)	9507(4)	62(2)
C(22)	10203(9)	3339(8)	8093(4)	48(2)
C(23)	11397(10)	4055(11)	8235(5)	72(3)
C(24)	10474(11)	2755(9)	7317(4)	64(2)
C(25)	5874(9)	9300(8)	6152(4)	52(2)
C(26)	4842(10)	8541(11)	5892(6)	74(3)
C(27)	5044(13)	10399(10)	6725(6)	86(4)
C(28)	8579(9)	7088(7)	5626(3)	41(2)
C(29)	8360(13)	7934(9)	4909(4)	68(3)
C(30)	10277(10)	6256(10)	5686(4)	64(2)
C(31)	8823(10)	9226(7)	6683(4)	48(2)
C(32)	10411(10)	8520(10)	6928(5)	60(2)
C(33)	8840(15)	10320(10)	6098(5)	83(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *Uij* tensor. [b] The coordinates of the hydride were calculated by the HYDEX program. [c] The agostic hydrogen H(8) was refined as a free isotropic atom.

(28) For examples on oxidative addition of alkenes to give hydrido vinyl complexes, see: (a) Stoutland, P. O.; Bergman, R. G.; *J. Am. Chem. Soc.* **1985**, *107*, 4581. (b) Silvestre, J.; Calhorda, M. J.; Hoffman, R.; Stoutland, P. O.; Bergman, R. G. *Organometallics* **1986**, *5*, 1841. (c) Haddleton, D. M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1986**, 1734. (d) Bell, T. W.; Haddleton, D. M.; McCamley, A.; Partridge, M. G.; Perutz, R. N.; Willner, H *J. Am. Chem. Soc*. **1990**, *112*, 9212. (e) Bianchini, C.; Barbaro, P.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1993**, *12*, 2505.

(29) Recent work on styrene derivatives of osmium indicates that the products of activation of the phenyl ring are thermodynamically favored with respect to the activation of the olefinic C−H bonds. Nevertheless, in solution the products of both C−H activation processes are in equilibrium. Albéniz, M. J.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Oro, L. A.; Sola, E.; Zeier, B. Submitted for publication.

(30) (a) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563. (c) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1992**, *11*, 3362.

Table 5. Crystal Data and Data Collection and Refinement for OsH{C_6H_4-2-(*E*-CH═CHPh)}(CO)(P^iPr_3)$_2$ (**2a**)

Crystal Data	
formula	$C_{33}H_{54}OOsP_2$
mol wt	718.94
color and habit	yellow, irregular prism
crystal size, mm	0.29 × 0.27 × 0.12
space group	triclinic, *P*$\bar{1}$ (no. 2)
a, Å	9.230(1)
b, Å	10.092(1)
c, Å	18.525(2)
α, deg	88.667(7)
β, deg	87.172(7)
γ, deg	71.110(6)
V, Å^3	1630.6(3)
Z	2
D(calcd), g cm^{-1}	1.464
Data Collection and Refinement	
diffractometer	4-Circle Siemens-P4
λ(Mo Kα), Å; technique	0.71073, bisecting geometry
monochromator	graphite oriented
μ, mm^{-1}	4.034
scan type	*θ*/2*θ*
2*θ* range, deg	3 ≤ 2*θ* ≤ 53°
temp, K	298
no. of data collected	7458
no. of unique data	6171
no. of params refined	339
R^a ($F_o \geq 4.0\sigma(F_o)$)	0.0401
wR^b (all data)	0.0994
S^c	1.008

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$, $a = 0.0381$ and $b = 0$. [c] $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0.5}$, where n is the number of number of data and p is the number of parameters.

ductions[32] indicate that the catalytic cycles of these processes involve osmium(II) and osmium(IV) intermediates. The present work has shown that very reactive osmium(0) intermediates can also be generated under mild conditions, suggesting that the field of application of these osmium complexes can be extended to other catalytic processes involving carbon−carbon bond formation and C−H oxidative addition steps.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Perkin-Elmer 883 or a Nicolet 550 spectrometer. NMR spectra were recorded on a Varian UNITY 300 or on a Bruker ARX 300. The probe temperature of the NMR spectrometers was calibrated against a methanol standard. ^{1}H and ^{13}C{^{1}H} chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. ^{31}P{^{1}H} chemical shifts are reported relative to H_3PO_4 (85%). ^{2}H chemical shifts were measured relative to C_6D_6 (7.15 ppm) used as internal reference. Coupling constants *J* and *N* (*N* = *J*(HP) + *J*(HP′′ for ^{1}H, and *N* = *J*(CP) + *J*(CP′) for ^{13}C) are given in Hertz. In general, spectra assignment was achieved with the aid of ^{1}H COSY and ^{13}C DEPT experiments. C,H analysis were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Synthesis. All reactions were carried out with exclusion of air by using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The complex OsCl(*E*-CH═CHPh)(CO)(P^iPr_3)$_2$ (**1**) was prepared according with the literature method.[11a]

Preparation of OsH{C_6H_4-2-(*E*-CH═CHPh)}(CO)(P^iPr_3)$_2$ (2). A solution of OsCl(*E*-CH═CHPh)(CO)(P^iPr_3)$_2$ (**1**) (150 mg, 0.23 mmol) in 6 mL of toluene was treated with 0.3 mL of a 1 M solution of C_6H_5-Li in diethyl ether, and the resulting solution was heated at 60 °C for 1 h. The resultant suspension was filtered through kieselgur, and the solvent was removed to yield a yellow residue. Treatment of this residue with methanol gave a yellow solid, which was washed with methanol and dried in vacuo: yield 98.6 mg (65%); IR (Nujol mull, cm^{-1}) 2197 (m, *ν*(OsH)), 1904 (s, *ν*(CO)); ^{1}H NMR ($CDCl_3$, 293 K) *δ* −17.83 (t, J_{HP} = 21.0 Hz, 1H, Os-H), 0.97 (dvt, N = 13.8 Hz, J_{HH} = 6.8 Hz, 18H, PCH(C*H*$_3$)$_2$), 1.09 (dvt, N = 13.8 Hz, J_{HH} = 6.8 Hz, 18H, PCH(C*H*$_3$)$_2$), 2.2 (m, 6H, PC*H*(CH$_3$)$_2$), 6.72 (vt, J_{HH} = 7.2 Hz, 1H), 6.80 (vt, J_{HH} = 7.2, 1H), 7.09 (d, J_{HH} = 7.2 Hz, 1H), 7.15 (t, J_{HH} = 7.6 Hz, 1H, $H_{para\text{-}Ph}$), 7.29 (vt, J_{HH} = 7.6 Hz, 2H, $H_{meta\text{-}Ph}$), 7.51 (d, J_{HH} = 7.2 Hz, 1H), 7.56 (d, J_{HH} = 13.6 Hz, 1H, ═CH), 7.61 (d, J_{HH} = 7.6 Hz, 2H, $H_{ortho\text{-}Ph}$); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) *δ* 22.8 (s); ^{13}C{^{1}H} NMR (C_6D_6, 293 K) *δ* 19.5 (s, PCH(*C*H$_3$)$_2$), 19.9 (s, PCH(*C*H$_3$)$_2$), 27.3 (vt, N = 22.8 Hz, P*C*H(CH$_3$)$_2$), 106.2 (br, ═CH), 121.8 (s, ═CH), 126.5 (s, CH), 127.0 (s, $CH_{para\text{-}Ph}$), 127.2 (s, $CH_{meta\text{-}Ph}$), 128.7 (s, $CH_{ortho\text{-}Ph}$), 129.8 (brt, CH), 139.7 (brt, CH), 141.0 (s, $C_{ipso\text{-}Ph}$), 142.9 (brt, CH), 155.4 (t, J_{CP} = 2.3 Hz, *C*−CH═), 177.3 (t, J_{CP} = 10.6 Hz, Os-C), 191.3 (t, J_{CP} = 8.8 Hz, CO). Anal. Calcd for $C_{33}H_{54}OP_2Os$: C, 55.14; H, 7.57. Found: C, 54.71, H, 8.26.

Preparation of OsH{C_6H_4-2-(*E*-CH═CHPh)}(CO)$_2$(P^iPr_3)$_2$ (3). Carbon monoxide was bubbled through a suspension of OsH{C_6H_4-2-(*E*-CH═CHPh)}(CO)(P^iPr_3)$_2$ (**2**) (100 mg, 0.14 mmol) in 5 mL of methanol. After a 10 min reaction a white solid was formed, which was decanted, washed with methanol, and dried in vacuo: yield 88.0 mg (84%); IR (Nujol mull, cm^{-1}) 2032 (s, *ν*(OsH)), 1966, 1894 (s, *ν*(CO)); ^{1}H NMR (C_6D_6, 293 K) *δ* −6.09 (t, J_{HP} = 21.3 Hz, 1H, Os-H), 1.06 (dvt, N = 12.3 Hz, J_{HH} = 6.3 Hz, 18H, PCH(C*H*$_3$)$_2$), 1.08 (dvt, N = 12.3 Hz, J_{HH} = 6.3 Hz, 18H, PCH(C*H*$_3$)$_2$), 2.06 (m, 6H, PC*H*(CH$_3$)$_2$), 6.77 (td, J_{HH} = 7.8 Hz, J_{HH} = 1.2 Hz, 1H), 6.97 (d, J_{HH} = 16.2 Hz, 1H, ═CH), 7.02 (vt, J_{HH} = 7.8 Hz, 1H), 7.06 (t, J_{HH} = 7.5 Hz, 1H, $H_{para\text{-}Ph}$), 7.28 (vt, J_{HH} = 7.6 Hz, 2H, $H_{meta\text{-}Ph}$), 7.71 (dd, J_{HH} = 7.8 Hz, J_{HH} = 1.2 Hz 1H), 7.84 (d, J_{HH} = 7.5 Hz, 2H, $H_{ortho\text{-}Ph}$), 8.37 (d, J_{HH} = 16.2 Hz, 1H, ═CH), 8.63 (d, J_{HH} = 7.8 Hz, 1H); ^{31}P{^{1}H} NMR (C_6D_6, 293 K) *δ* 19.1 (s); ^{13}C{^{1}H} NMR (C_6D_6, 293 K) *δ* 19.3 (s, PCH(*C*H$_3$)$_2$), 20.0 (s, PCH(*C*H$_3$)$_2$), 26.5 (vt, N = 27.0 Hz, P*C*H(CH$_3$)$_2$), 123.5 (br, CH), 125.5 (br, CH), 126.0 (br, CH), 126.8 (s, $CH_{para\text{-}Ph}$), 126.9 (s, $CH_{meta\text{-}Ph}$), 128.9 (s, $CH_{ortho\text{-}Ph}$), 139.5 (s, $C_{ipso\text{-}Ph}$), 141.7 (s, ═CH), 148.8 (brt, *C*−CH═), 152.6 (t, J_{CP} = 12.0 Hz, Os-C), 156.9 (s, ═CH), 185.2 (t, J_{CP} = 8.3 Hz, CO), 190.4 (t, J_{CP} = 5.5 Hz, CO). Anal. Calcd for $C_{34}H_{54}O_2P_2Os$: C, 54.68; H, 7.29. Found: C, 54.26 , H, 7.10.

Preparation of OsH{C_6H_4-2-(*E*-CH═CHCH$_3$)}(CO)(P^iPr_3)$_2$ (4). A solution of OsCl(*E*-CH═CHPh)(CO)(P^iPr_3)$_2$ (**1**) (100 mg, 0.15 mmol) in 10 mL of hexane was treated with 0.1 mL of a 1.6 M solution of CH_3Li in diethyl ether. The reaction mixture became yellow, was cooled to 0 °C and quickly filtered through kieselgur. The solvent was removed at 0 °C to yield a yellow residue. Treatment of this residue with cold methanol gave a yellow solid, which was washed with methanol and dried in vacuo: yield 86.4 mg (89%); IR (Nujol mull, cm^{-1}) 2245 (m, *ν*(OsH)), 1910 (s, *ν*(CO)); ^{1}H NMR (C_6D_6, 293 K) *δ* −13.33 (t, J_{HP} = 24.0 Hz, 1H, Os-H), 1.06 (dvt, N = 12.9 Hz, J_{HH} = 6.9 Hz, 18H, PCH(C*H*$_3$)$_2$), 1.11 (dvt, N = 12.9 Hz, J_{HH} = 6.9 Hz, 18H, PCH(C*H*$_3$)$_2$), 2.14 (d, J_{HH} = 5.7 Hz, 3H, CH_3), 2.20 (m, 6H, PC*H*(CH$_3$)$_2$), 2.67 (m, 1H, CH_3-C*H*═), 5.82 (d, J_{HH} = 10.8 Hz, 1H, CH_3-CH═C*H*), 6.81 (d, J_{HH} = 7.2 Hz, 1H), 6.97 (vt, J_{HH} = 7.2 Hz, 1H), 7.05 (vt, J_{HH} = 7.2 Hz, 1H), 7.54 (d, J_{HH} = 7.2 Hz, 1H); ^{31}P{^{1}H} NMR (C_6D_6, 293 K) *δ* 18.8 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 263 K): *δ* 16.2 (s, CH_3), 19.6 (s, PCH(*C*H$_3$)$_2$), 20.2 (s, PCH(*C*H$_3$)$_2$), 26.7 (vt, N = 25.7 Hz, P*C*H(CH$_3$)$_2$), 75.3 (br, ═CH), 87.1 (br, ═CH), 119.9 (t, J_{CP} = 1.0 Hz, CH), 123.9 (s, CH), 125.2 (t, J_{CP} = 2.0 Hz, CH), 142.9 (t, J_{CP} = 1.5 Hz, CH), 155.4 (t, J_{CP} = 2.5 Hz, *C*−CH═), 177.3 (t, J_{CP} = 10.6 Hz, Os-C), 191.3 (t, J_{CP} = 8.3 Hz, CO). Anal. Calcd for $C_{28}H_{52}OP_2Os$: C, 51.20; H, 7.98. Found: C, 50.79, H, 7.78.

Preparation of OsH{C_6H_4-2-(*E*-CH═CHCD$_3$)}(CO)(P^iPr_3)$_2$ (4-*d*$_3$). A solution of OsCl(*E*-CH═CHPh)(CO)(P^iPr_3)$_2$ (**1**) (100 mg, 0.15 mmol) in 10 mL of hexane was treated with 0.3 mL of a 0.5 M solution of CD_3Li in diethyl ether. After 5 min of reaction, the resulting

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

(32) (a) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H; Meyer, U. *J. Mol. Catal.* **1988**, *45*, 1. (b) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H; Meyer, U. *J. Mol. Catal.* **1989**, *53*, 43. (c) Esteruelas, M. A.; Valero, C.; Oro, L. A.; Meyer, U.; Werner, H. *Inorg. Chem.* **1991**, *30*, 1159. (d) 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.

suspension was filtered through kieselgur, and the solvent was removed to leave a yellow residue. Treatment of this residue with methanol gave a yellow solid, which was washed with methanol and dried in vacuo: yield 81.6 mg (84%); IR (Nujol mull, cm^{-1}) 2245 (m, ν(OsH)), 1910 (s, ν(CO)); ^{1}H NMR (C_6D_6, 293 K) δ −13.22 (t, J_{HP} = 24.6 Hz, 1H, Os-H), 1.05 (dvt, N = 13.0 Hz, J_{HH} = 7.0 Hz, 18H, PCH(CH_3)$_2$), 1.11 (dvt, N = 12.9 Hz, J_{HH} = 6.9 Hz, 18H, PCH(CH_3)$_2$), 2.20 (m, 6H, PC*H*(CH$_3$)$_2$), 2.69 (d, J_{HH} = 10.9 Hz, 1H, CD$_3$C*H*═), 5.80 (d, J_{HH} = 10.9 Hz, 1H, CD$_3$CH═C*H*), 6.81 (d, J_{HH} = 7.4 Hz, 1H), 6.98 (vt, J_{HH} = 7.4 Hz, 1H), 7.04 (vt, J_{HH} = 7.4 Hz, 1H), 7.54 (d, J_{HH} = 7.4 Hz, 1H); ^{31}P{^{1}H} NMR (C_6D_6, 293 K) δ 18.6 (s); ^{2}H NMR (C_6H_6, 293 K) δ 2.0 (s, CD$_3$). Anal. Calcd for $C_{28}H_{49}D_3OP_2Os$: C, 50.95; H, 7.97. Found: C, 50.47 , H, 8.43.

Preparation of OsH{C_6H_4-2-(*E*-CH═CHCH$_3$)}(CO){(P(OMe)$_3$}-(P^{i}Pr$_3$)$_2$ (5). A solution of OsCl(*E*-CH═CHPh)(CO)(P^{i}Pr$_3$)$_2$ (**1**) (100 mg, 0.15 mmol) in 10 mL of hexane was treated with 0.1 mL of a 1.6 M solution of CH_3Li in diethyl ether. The reaction mixture became yellow, was cooled to 0 °C, and quickly filtered through kieselgur. Addition of P(OMe)$_3$ (18 μL, 0.15 mmol) gave a colorless solution which was dried to leave a white residue. Treatment of this residue with methanol gave a white solid, which was washed with methanol and dried in vacuo: yield 70 mg (59%); IR (Nujol mull, cm^{-1}) 2110 (m, ν(OsH)), 1895 (s, ν(CO)); ^{1}H NMR (C_6D_6, 293 K) δ −8.34 (dt, J_{HP} = 143.4 Hz, J_{HP} = 24.1 Hz, 1H, Os-H), 1.18 (dvt, N = 12.0 Hz, J_{HH} = 6.9 Hz, 18H, PCH(CH_3)$_2$), 1.24 (dvt, N = 13.6 Hz, J_{HH} = 7.0 Hz, 18H, PCH(CH_3)$_2$), 1.98 (d, J_{HH} = 6.3 Hz, 3H, CH$_3$), 2.35 (m, 6H, PC*H*(CH$_3$)$_2$), 3.41 (d, J_{HP} = 9.6 Hz, 9H, P(OCH$_3$)$_3$), 5.94 (dq, J_{HH} = 15.6 Hz, J_{HH} = 6.6 Hz, 1H, CH$_3$C*H*═), 6.90 (vt, J_{HH} = 7.5 Hz, 1H), 7.15 (vt, J_{HH} = 7.5 Hz, 1H), 7.69 (d, J_{HH} = 7.5 Hz, 1H), 8.06 (d, J_{HH} = 15.6 Hz, 1H, CH$_3$CH═C*H*), 8.55 (d, J_{HH} = 7.5 Hz, 1H); ^{31}P{^{1}H} NMR (C_6D_6, 293 K) δ 12.5 (d, J_{PP} = 19.4 Hz, P^{i}Pr$_3$), 95.3 (d, J_{PP} = 19.4 Hz, P(OMe$_3$)$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 293 K) δ 18.8 (s, CH$_3$), 20.5 (s, PCH(*C*H$_3$)$_2$), 27.0 (vtd, N = 25.3 Hz, J_{CP} = 2.8 Hz, P*C*H-(CH$_3$)$_2$), 53.3 (d, J_{CP} = 11.54 Hz, P(OCH$_3$)$_3$), 119.1 (s, CH), 122.74 (s, CH), 124.4 (dt, J_{CP} = 4.1 Hz, J_{CP} = 1.4 Hz, CH), 124.6 (brt, CH), 147.0 (dbrt, J_{CP} = 5.0 Hz, CH), 147.7 (dt, J_{CP} = 2.3 Hz, J_{CP} = 1.3 Hz, CH), 153.8 (dt, J_{CP} = 18.4 Hz, J_{CP} = 1.4 Hz, *C*−CH═), 155.6 (vq, J_{CP} = 12.0 Hz, Os-C), 188.5 (vq, J_{CP} = 9.53 Hz, CO). Anal. Calcd for $C_{31}H_{61}O_4P_3Os$: C, 47.67; H, 7.87. Found: C, 48.29, H, 7.76.

Preparation of OsH{C_6H_4-2-(*E*-CH═CHCH$_3$)}(CO)$_2$(P^{i}Pr$_3$)$_2$ (6). A solution of OsCl(*E*-CH═CHPh)(CO)(P^{i}Pr$_3$)$_2$ (**1**) (100 mg, 0.15 mmol) in 10 mL of hexane was treated with 0.1 mL of a 1.6 M solution of CH_3Li in diethyl ether. The reaction mixture became yellow, was cooled to 0 °C, and quickly filtered through kieselgur. Carbon monoxide was bubbled until the solution became colorless (ca. 10 min), and then the solvent was removed to leave a white residue. Treatment of this residue with methanol gave a white solid, which was washed with methanol and dried in vacuo: yield 79 mg (76%); IR (Nujol mull, cm^{-1}) 2010 (s, ν(OsH)), 1965, 1890 (s, ν(CO)); ^{1}H NMR (C_6D_6, 293 K) δ −6.23 (t, J_{HP} = 21.7 Hz, 1H, Os-H), 1.09 (dvt, N = 13.0 Hz, J_{HH} = 7.1 Hz, 18H, PCH(CH_3)$_2$), 1.11 (dvt, N = 13.4 Hz, J_{HH} = 7.2 Hz, 18H, PCH(CH_3)$_2$), 2.05 (dd, J_{HH} = 6.7 Hz, J_{HH} = 1.6 Hz, 3H, CH$_3$), 2.10 (m, 6H, PC*H*(CH$_3$)$_2$), 5.91 (dq, J_{HH} = 15.5 Hz, J_{HH} = 6.7 Hz, 1H, CH$_3$C*H*═), 6.80 (vtd, J_{HH} = 7.6 Hz, J_{HH} = 1.6 Hz, 1H), 7.07 (vt, J_{HH} = 7.6 Hz, 1H), 7.51 (dd, J_{HH} = 7.6 Hz, J_{HH} = 1.6 Hz, 1H), 7.59 (dq, J_{HH} = 15.5 Hz, J_{HH} = 1.6 Hz, 1H, CH$_3$CH═C*H*), 8.55 (d, J_{HH} = 7.6 Hz, 1H); ^{31}P{^{1}H} NMR (C_6D_6, 293 K) δ 18.4 (s); ^{13}C{^{1}H} NMR (C_6D_6, 293 K) δ 18.5 (s, CH$_3$), 19.4 (s, PCH(*C*H$_3$)$_2$), 20.0 (s, PCH-(*C*H$_3$)$_2$), 26.6 (vt, N = 27.2 Hz, P*C*H(CH$_3$)$_2$), 123.1 (s, CH), 123.4 (t, J_{CP} = 1.4 Hz, CH), 124.9 (t, J_{CP} = 1.4 Hz, CH), 126.0 (t, J_{CP} = 1.4 Hz, CH), 144.4 (s, CH), 149.8 (t, J_{CP} = 1.4 Hz, CH), 149.9 (t, J_{CP} = 6.9 Hz, Os-C), 156.1 (t, J_{CP} = 1.8 Hz, *C*−CH═), 185.3 (t, J_{CP} = 8.3 Hz, CO), 190.3 (t, J_{CP} = 6.0 Hz, CO). Anal. Calcd for $C_{29}H_{52}O_2P_2Os$: C, 50.85; H, 7.65. Found: C, 50.91, H, 8.62.

Preparation of OsH(η^3-CH$_2$CHCHPh)(CO)(P^{i}Pr$_3$)$_2$ (11). A solution of OsCl(*E*-CH═CHPh)(CO)(P^{i}Pr$_3$)$_2$ (**1**) (100 mg, 0.15 mmol) in 10 mL of hexane was treated with 0.1 mL of a 1.6 M solution of CH_3Li in diethyl ether, and the resulting suspension was stirred for 2 h at room temperature. The resultant suspension was filtered through kieselgur, and the solvent was removed to leave a yellow residue. Treatment of this residue with methanol gave a white solid, which was washed with methanol and dried in vacuo: yield 84 mg (85%); IR (Nujol mull, cm^{-1}) 2120 (m, ν(OsH)), 1875 (s, ν(CO)); ^{1}H NMR (C_6D_6, 293 K) δ −11.52 (dd, J_{HP} = 31.5 Hz, J_{HP} = 23.5 Hz 1H, Os-H), 0.98 (dd, J_{HP} = 12.8 Hz, J_{HH} = 7.1 Hz, 9H, PCH(CH_3)$_2$), 0.99 (dd, J_{HP} = 12.0 Hz, J_{HH} = 6.7 Hz, 9H, PCH(CH_3)$_2$), 1.21 (dd, J_{HP} = 12.7 Hz, J_{HH} = 6.0 Hz, 9H, PCH(CH_3)$_2$), 1.23 (dd, J_{HP} = 12.7 Hz, J_{HH} = 6.0 Hz, 9H, PCH(CH_3)$_2$), 1.78 (m, J_{HH} = 6.6 Hz, J_{HH} = 2.0 Hz, J_{HP} = 2.0 Hz, 1H, allyl-CH$_2$ ($_{syn}$)), 2.01 (m, 3H, PC*H*(CH$_3$)$_2$), 2.22 (m, 3H, PC*H*(CH$_3$)$_2$), 4.79 (dd, J_{HP} = 9.6 Hz, J_{HH} = 8.7 Hz, 1H, allyl-C*H*Ph), 5.32 (m, J_{HH} = 8.9 Hz, J_{HH} = 8.7 Hz, J_{HH} = 6.6 Hz, J_{HP} = 8.0 Hz, 1H, allyl-CH$_{meso}$), 7.07 (t, J_{HH} = 7.5 Hz, 1H, H$_{para\text{-}Ph}$), 7.25 (vt, J_{HH} = 7.5 Hz, 2H, H$_{meta\text{-}Ph}$), 7.82 (d, J_{HH} = 7.5 Hz, 2H, H$_{ortho\text{-}Ph}$); ^{31}P{^{1}H} NMR (C_6D_6, 293 K) AB system δ_A = 20.5, δ_B = 23.3, J_{AB} = 208.9 Hz; ^{13}C{^{1}H} NMR (C_6D_6, 293 K) δ 16.3 (dd, J_{CP} = 6.0 Hz, J_{CP} = 3.2 Hz, allyl-CH$_2$), 20.1 (s, PCH(*C*H$_3$)$_2$), 20.2 (s, PCH(*C*H$_3$)$_2$), 20.6 (s, PCH(*C*H$_3$)$_2$), 20.7 (s, PCH(*C*H$_3$)$_2$), 27.7 (dd, J_{CP} = 21.6 Hz, J_{CP} = 2.8 Hz, P*C*H(CH$_3$)$_2$), 28.4 (dd, J_{CP} = 23.2 Hz, J_{CP} = 3.5 Hz, P*C*H(CH$_3$)$_2$), 49.7 (s, allyl-*C*HPh), 79.8 (d, J_{CP} = 1.0 Hz, allyl-CH$_{meso}$), 124.7 (s, CH$_{para\text{-}Ph}$), 128.2 (s, CH$_{meta\text{-}Ph}$), 129.4 (s, CH$_{ortho\text{-}Ph}$), 145.4 (s, C$_{ipso\text{-}Ph}$), 192.9 (dd, J_{CP} = 10.8 Hz, J_{CP} = 8.8 Hz, CO). Anal. Calcd for $C_{28}H_{52}OP_2Os$: C, 51.20; H, 7.98. Found: C, 51.89, H, 8.98.

Preparation of OsD(η^3-CD$_2$CHCHPh)(CO)(P^{i}Pr$_3$)$_2$ (11-d_3). A solution of OsCl(*E*-CH═CHPh)(CO)(P^{i}Pr$_3$)$_2$ (**1**) (100 mg, 0.15 mmol) in 10 mL of hexane was treated with 0.3 mL of a 0.5 M solution of CD_3Li in diethyl ether, and the resulting suspension was stirred during 2 h at 50 °C. The obtained suspension was filtered through kieselgur, and the solvent was removed to leave a yellow residue. Treatment of this residue with methanol gave a white solid, which was washed with methanol and dried in vacuo: yield 82 mg (82%); IR (Nujol mull, cm^{-1}) 1875 (s, ν(CO)); ^{1}H NMR (C_6D_6, 293 K) δ 0.99 (dd, J_{HP} = 13.2 Hz, J_{HH} = 6.9 Hz, 9H, PCH(CH_3)$_2$), 1.01 (dd, J_{HP} = 13.2 Hz, J_{HH} = 6.9 Hz, 9H, PCH(CH_3)$_2$), 1.21 (dd, J_{HP} = 12.1 Hz, J_{HH} = 6.6 Hz, 9H, PCH(CH_3)$_2$), 1.23 (dd, J_{HP} = 12.1 Hz, J_{HH} = 6.6 Hz, 9H, PCH(CH_3)$_2$, 2.02 (m, 3H, PC*H*(CH$_3$)$_2$), 2.22 (m, 3H, PC*H*(CH$_3$)$_2$), 4.79 (vt, J_{HP} = 8.7 Hz, J_{HH} = 8.7 Hz, 1H, allyl-C*H*Ph), 5.35 (vt, J_{HH} = 8.7 Hz, J_{HP} = 8.7 Hz, 1H, allyl-CH$_{meso}$), 7.10 (t, J_{HH} = 7.6 Hz, 1H, H$_{para\text{-}Ph}$), 7.30 (vt, J_{HH} = 7.6 Hz, 2H, H$_{meta\text{-}Ph}$), 7.85 (d, J_{HH} = 7.6 Hz, 2H, H$_{ortho\text{-}Ph}$); ^{31}P{^{1}H} NMR (C_6D_6, 293 K) ABX system (X = ^{2}H) δ_A = 20.5, δ_B = 23.3, J_{AB} = 208.9 Hz, J_{AX} = J_{BX} = 3.6 Hz; ^{2}H NMR (C_6H_6, 293 K) δ −11.5 (brdd, OsD), 1.0 (br, allyl-CD$_2$($_{anti}$)), 1.7 (br, allyl-CD$_2$($_{syn}$)).

Preparation of OsH(η^1-CH$_2$CH═CHPh)(CO)$_2$(P^{i}Pr$_3$)$_2$ (12). A solution OsH(η^3-CH$_2$CHCHPh)(CO)(P^{i}Pr$_3$)$_2$ (**11**) (100 mg, 0.15 mmol) in 10 mL of hexane was stirred under CO atmosphere (P = 1 atm) during 24 h at room temperature. The resulting suspension was decanted, and the white solid was washed with hexane and dried in vacuo: yield 76 mg (74%); IR (Nujol mull, cm^{-1}) 2015 (s, ν(OsH)), 1950, 1885 (s, ν(CO)); ^{1}H NMR (C_6D_6, 293 K) δ −7.54 (t, J_{HP} = 22.6 Hz, 1H, Os-H), 1.15 (dvt, N = 13.5 Hz, J_{HH} = 6.9 Hz, 18H, PCH(CH_3)$_2$), 1.16 (dvt, N = 13.5 Hz, J_{HH} = 6.9 Hz, 18H, PCH-(CH_3)$_2$), 1.82 (dt, J_{HH} = 9.0 Hz, J_{HP} = 8.2 Hz, 2H, Os-CH$_2$), 2.25 (m, 6H, PC*H*(CH$_3$)$_2$), 6.14 (d, J_{HH} = 15.3 Hz, 1H, Os-CH$_2$-CH═C*H*), 7.01 (t, J_{HH} = 7.5 Hz, 1H, H$_{para\text{-}Ph}$), 7.10 (dt, J_{HH} = 15.3 Hz, J_{HH} = 9.0 Hz, 1H, Os-CH$_2$C*H*═), 7.25 (vt, J_{HH} = 7.5 Hz, 2H, H$_{meta\text{-}Ph}$), 7.53 (d, J_{HH} = 7.5 Hz, 2H, H$_{ortho\text{-}Ph}$); ^{31}P{^{1}H} NMR (C_6D_6, 293 K) 22.8 (s); ^{13}C{^{1}H} NMR (C_6D_6, 293 K) δ −4.5 (t, J_{CP} = 6.9 Hz, Os-CH$_2$), 19.1 (s, PCH(*C*H$_3$)$_2$), 19.2 (s, PCH(*C*H$_3$)$_2$), 25.5 (vt, N = 13.3 Hz, P*C*H(CH$_3$)$_2$), 121.0 (s, Os-CH$_2$*C*H═), 125.1 (s, CH$_{para\text{-}Ph}$), 125.4 (s, CH$_{meta\text{-}Ph}$), 128.8 (s, CH$_{ortho\text{-}Ph}$), 140.8 (s, C$_{ipso\text{-}Ph}$), 147.8 (s, Os-CH$_2$-CH═*C*H), 182.4 (t, J_{CP} = 8.2 Hz, CO), 190.6 (t, J_{CP} = 6.0 Hz, CO). Anal. Calcd for $C_{29}H_{52}O_2P_2Os$: C, 50.85; H, 7.65. Found: C, 50.45, H, 7.03.

X-ray Structure Analysis of OsH{C_6H_4-2-(*E*-CH═CHPh)}(CO)-(P^{i}Pr$_3$)$_2$ (2a). Crystals suitable for X-ray diffraction were obtained from a saturated solution of **2** in methanol at −20 °C. Atomic coordinates and U_{eq} values are listed in Table 4. A summary of crystal data, intensity collection procedure, and refinement is reported in Table 5. A yellow prismatic crystal was glued on a glass fiber and mounted on a Siemens P4 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 37 reflections in the range $10 \le 2\theta \le 30$. The 7458 recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitorized every 100 reflections; variation was less than 5%.

Reflections were also corrected for absorption by an semiempirical (Ψ-scan) method.[33] The structure was solved by Patterson (Os atom) and conventional Fourier techniques. Refinement was carried out by full-matrix least-squares with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms, except the hydride H(1) and the agostic hydrogen H(8), were observed or calculated (C−H = 0.96 Å) and included in the refinement riding on carbon atoms with a common isotropic thermal parameter. The agostic hydrogen H(8) was located in the difference Fourier maps and refined as a free isotropic atom. Although a reasonable peak was observed in the spatial zone assignable to the hydrido ligand, it does not support a proper refinement. As alternative, an electrostatic potential energy calculation based on the whole molecule with an ideal value for the Os−H bond distance of 1.66 Å[12] was carried out, giving only one minimum. Atomic scattering factors, corrected for anomalous dispersion for Os and P, were taken from ref 34. Final $R(F, F_o > 4.0\sigma(F_o))$ and $wR(F^2$, all reflections) values were 0.0401 and 0.0994. All calculations were performed by the use of the SHELXTL-PLUS[35] and SHELXL93[36] system of computer programs.

Kinetic Analysis. The equilibrium constants $K = k_1/k_{-1} =$ [**2a**]/[**2b**] were calculated by ^{1}H NMR spectroscopy in toluene-d_8. At temperatures below the coalescence point the ratio was calculated by integration of the hydrido signals corresponding to **2a** and **2b**, and above the coalescence temperature by measuring the chemical shift of the exchange averaged hydrido resonance. A least-squares fit of the values of ln K vs $1/T$ gave the thermodynamic magnitudes $\Delta H°$ and $\Delta S°$ involved in this equilibrium. Error analysis assumed a 10% error in the value of the equilibrium constant, whereas the error in temperature was estimated at 1 K. Errors were computed by standard error propagation formulas for least-squares fitting.[37]

The two parameters K and k_1 (or k_{-1}) are sufficient to characterize and simulate the hydrido regions of the variable-temperature ^{1}H NMR spectra. Complete line shape analysis of the spectra was achieved using the program DNMR6 (QCPE, Indiana University). The rate constants (k_{-1}) for various temperatures were obtained by visually matching observed and calculated spectra. Due to the broadness of the signals obtained at the lowest temperature reached, the individual coupling constants J_{HP} for the two hydrides could not be evaluated; thus the averaged value of J_{HP} was used for both hydrides. The transverse relaxation time T_2 used was common for the two signals and was obtained from the line width of the exchange averaged resonance above the fast exchange limit. To avoid the influence of these mentioned simplifications in the calculation of activation parameters, only data for the spectra that exhibited significant line broadening were included. The activation parameters $\Delta H^‡$ and $\Delta S^‡$ were calculated by least-squares fit of $\ln(k_{-1}/T)$ vs $1/T$ (Eyring equation). Error analysis assumed a 10% error in the rate constant and 1 K in the temperature. Errors were computed by published methods.[18]

The isomerization of complex **4** to **11** was followed quantitatively by ^{1}H NMR spectroscopy in $CDCl_3$. The decrease of the intensity of the hydrido signal of complexes **4** and **4-d_3** was measured automatically at intervals in a Varian UNITY 300 spectrometer. The rate constants and the errors were obtained by fitting the data to an exponential decay function, using the routine programs of the spectrometer. Activation parameters $\Delta H^‡$ and $\Delta S^‡$ were obtained by a least-squares fit of the Eyring plot. Error analysis assumed a 4.3% error in the rate constant (the maximun value found in the experimental determinations) and 1 K in the temperature. Errors were computed by published methods.[18]

Acknowledgment. We thank the D.G.I.C.Y.T. (Project PB 92-0092, Programa de Promoción General del Conocimiento) and E.U. (Project: Selective Processes and Catalysis Involving Small Molecules) for financial support. E.O. thanks the Diputación General de Aragón (D.G.A.) for a grant.

Supporting Information Available: Tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, experimental details of the X-ray study, bond distances and angles, and interatomic distances for **2a** (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA952186L

(33) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

(34) *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

(35) Sheldrick, G. M. SHELXTL PLUS; Siemens Analytical X-ray Instruments: Madison, WI, 1990.

(36) Sheldrick, G. M. *J. Appl. Crystallogr.*, manuscript in preparation.

(37) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill, New York, 1969; Chapter 4.