Lewis Base-Assisted Hydride-Carbyne to Olefin Transformation versus Carbene Formation

Miguel Baya, Miguel A. Esteruelas,* and Enrique Oñate

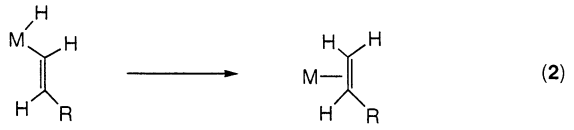
Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza−CSIC, 50009 Zaragoza, Spain

Received July 15, 2002

Summary: Complex $[OsH(\eta^5\text{-}C_5H_5)(\equiv C-CH_2Ph)(P^iPr_3)]BF_4$ (**1**) *reacts with KBr in tetrahydrofuran to give the* π*-olefin derivative* $OsBr(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_2{=}CHPh)(P^iPr_3)$, *which has been characterized by X-ray diffraction analysis. Similarly, the reaction of* $[OsH(\eta^5\text{-}C_5H_5)(\equiv C-CD_2Ph)(P^iPr_3)]BF_4$ (**1-d$_2$**) *with KBr leads to the* π*-dideuterated-olefin complex. On the basis of the deuterium distribution in this complex and the previously reported* $P(OMe)_3$*-assisted hydride-carbyne to carbene transformation, the mechanism of the Br-assisted hydride-carbyne to olefin transformation is discussed.*

Dihydride complexes of platinum group metals have shown to be effective reducing agents for the transformation of terminal alkynes to olefins. It is assumed that the hydrides are transferred sequentially to the alkyne. The transfer of the first hydride yields hydride-alkenyl species, which evolve into the olefin by intramolecular reductive elimination (eqs 1 and 2).[1]

(1)

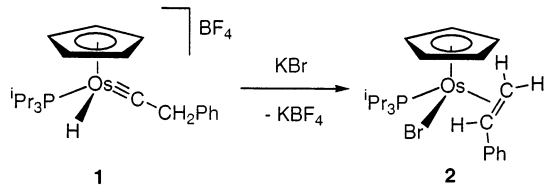


(2)

In contrast to the general trend, the transfer of the first hydride of many osmium-dihydride complexes affords stable hydride-carbyne derivatives.[2] In these cases, the transfer of the second hydride must be forced. However, it does not give olefin derivatives but carbene compounds. Thus, Caulton and co-workers have observed that the complex $OsHCl_2(\equiv CEt)(P^iPr_3)_2$ reacts with carbon monoxide to afford the carbene derivative $OsCl_2(=CHEt)(CO)(P^iPr_3)_2$,[3] which is another member of the $OsCl_2(=CHCH_2R)(CO)(P^iPr_3)_2$ series,[4] and we have reported the $P(OMe)_3$-assisted hydride-carbyne to carbene transformation in the cyclopentadienyl complex $[OsH(\eta^5\text{-}C_5H_5)(\equiv C-CH_2Ph)(P^iPr_3)]BF_4$.[5]

The formation of $[Os(\eta^5\text{-}C_5H_5)(=CH-CH_2Ph)\{P(OMe)_3\}(P^iPr_3)]BF_4$ from $[OsH(\eta^5\text{-}C_5H_5)(\equiv C-CH_2Ph)(P^iPr_3)]BF_4$ and $P(OMe)_3$ takes place via a four-step procedure (Scheme 1) involving (i) deprotonation of the CH_2Ph substituent of the carbyne ligand, (ii) hydride migration to the C_α atom of the resulting vinylidene, (iii) stabilization of the alkenyl intermediate by coordination of the Lewis base, and (iv) protonation of the C_β atom of the alkenyl ligand.

It is now shown that, in contrast to $P(OMe)_3$, bromide promotes the hydride-carbyne to olefin transformation. Furthermore, also in contrast to the $P(OMe)_3$ case, the transformation takes place as a one-pot synthesis. In fact, the treatment of tetrahydrofuran solutions of the hydride-carbyne complex $[OsH(\eta^5\text{-}C_5H_5)(\equiv C-CH_2Ph)(P^iPr_3)]BF_4$ (**1**) with 6 equiv of KBr at room temperature leads after 24 h to the π-olefin derivative $OsBr(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_2{=}CHPh)(P^iPr_3)$ (**2**), which is isolated as red needles in about 60% yield, according to eq 3.



(3)

1 2

As a consequence of the chirality of the osmium atom and the prochirality of the olefin, four pairs of enantiomers could be formed: CPh-carbon atom *cisoid* to the phosphine with the phenyl group toward the osmium atom, CPh-carbon atom *cisoid* to the phosphine with the phenyl group away from the osmium atom, CPh-carbon atom *cisoid* to the bromide with the phenyl group toward the osmium atom, and CPh-carbon atom *cisoid* to the bromide with the phenyl group away from the osmium atom. However, only the pair with the lowest steric hindrance is obtained, suggesting a thermodynamic control of the reaction. Figure 1 shows a view of the structure of one of the enantiomers. The geometry around the osmium atom is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a

(1) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publishers: Dordrecht, 1994.

(2) (a) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683. (b) Werner, H.; Jung, S.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **1999**, 951. (c) Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, *18*, 4949. (d) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2000**, *19*, 5098. (e) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2491.

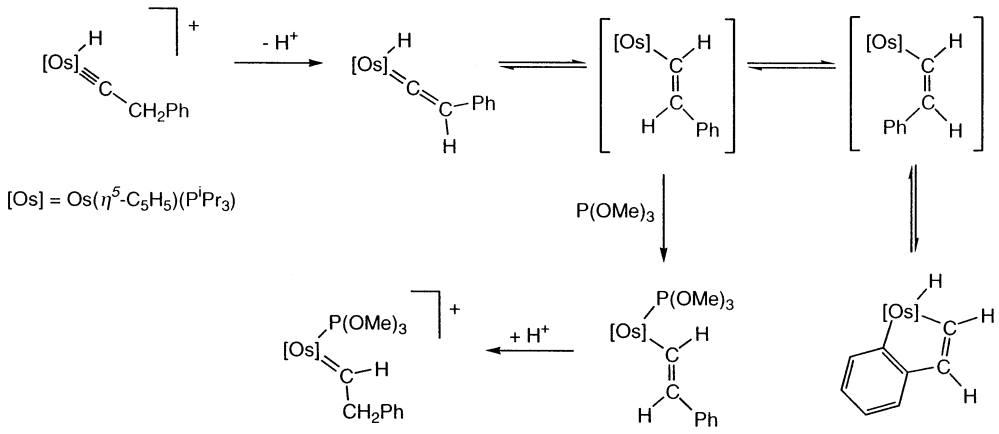
(3) (a) Spivak, G. J.; Coalter, J. N.; Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999. (b) Spivak, G. J.; Caulton, K. G. *Organometallics* **1998**, *17*, 5260.

(4) (a) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935. (b) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3595. (c) Buil, M. L.; Esteruelas, M. A. *Organometallics* **1999**, *18*, 1798.

(5) Baya, M.; Esteruelas, M. A. *Organometallics* **2002**, *21*, 2332.

10.1021/om020546p CCC: $22.00
Publication on Web 11/06/2002

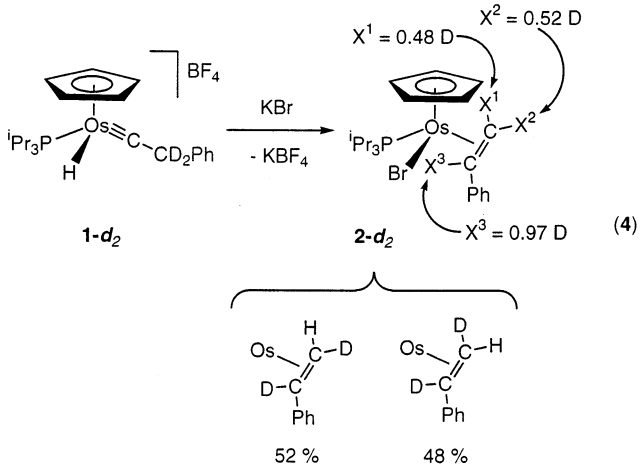
Scheme 1



face, and the CPh-carbon atom C(2) *cisoid* to the bromide with the phenyl group away from the osmium. The osmium-styrene coordination exhibits Os−C distances of 2.161(7) [Os−C(1)] and 2.175(7) Å [Os−C(2)], which agree well with those found in other osmium-olefin complexes (between 2.13 and 2.28 Å).[6] Similarly, the olefinic bond distance C(1)−C(2) [1.422(10) Å] is within the range reported for transition metal olefin complexes (between 1.340 and 1.445 Å).[7]

In agreement with the presence of a coordinated styrene ligand in **2**, the ^{1}H NMR spectrum of this compound in benzene-d_6 at room temperature shows the resonances corresponding to the vinylic protons of the olefin at 5.11, 3.77, and 2.20 ppm. In the ^{13}C{^{1}H} NMR spectrum, the resonances due to the coordinated atoms of the olefin are observed at 44.3 and 15.7 ppm, the first of them as a singlet, while the second one as a doublet, with a C−P coupling constant of 5.5 Hz. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 3.5 ppm.

The treatment of the dideuterated hydride-carbyne complex [OsH(η^5-C_5H_5)(≡C−CD_2Ph)(P^iPr_3)]BF_4 (**1-*d*$_2$**) with KBr, under the same conditions as those previously mentioned for the formation of **2**, leads to the dideuterated π-olefin derivative OsBr(η^5-C_5H_5)(η^2-CDH=CDPh)(P^iPr_3) (**2-*d*$_2$**, eq 4) with the following deuterium distribution: 0.97 deuterium atom at C(2) and 1.00 deuterium atom at C(1). The latter are distributed 0.48 *trans* to the phenyl group and 0.52 *cis* to the phenyl group. This distribution suggests that the addition of KBr to **1-*d*$_2$** affords the mixture of complexes containing the isomeric dideuterated olefins *trans*-D_2 (52%) and *cis*-D_2 (48%).



(4)

The previously mentioned deuterium distribution is strongly supported by the ^{2}H and ^{1}H NMR spectra of **2-*d*$_2$**. The ^{2}H NMR spectrum contains three broad singlets at 5.0, 3.7, and 2.2 ppm in a 0.97:0.52:0.48 intensity ratio, whereas in the ^{1}H NMR spectrum the intensity ratio of the resonances at 5.11, 3.77, and 2.20 ppm is 0.03:0.48:0.52.

On the basis of the reactions shown in Scheme 1, the results summarized in eq 4 can be rationalized according to Scheme 2. Because in **1** the benzyl group has proved to be fairly acidic, it is reasonable to assume that the first step of the deuterated Br-assisted hydride-carbyne to olefin transformation involves the dissociation of D^+. The resulting hydride-vinylidene exists as an equilibrium mixture of the two possible rotational isomers, that containing the deuterium atom toward the

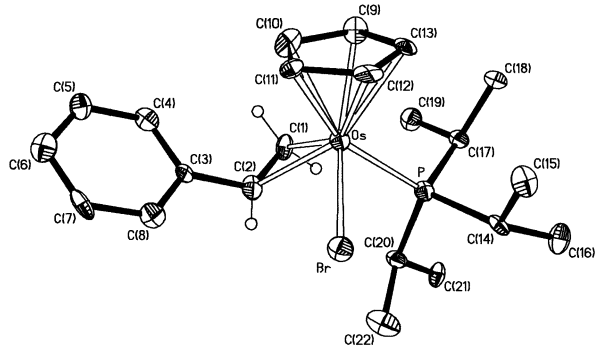
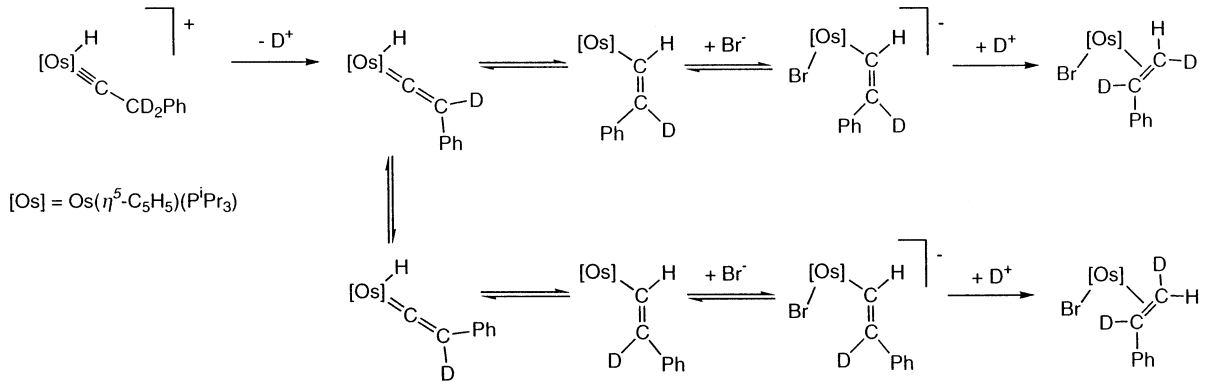


Figure 1. Molecular diagram for the complex OsBr(η^5-C_5H_5)(η^2-CH_2=CHPh)(P^iPr_3) (**2**). Thermal ellipsoids are shown at 50% probability. Selected bond distances (Å) and angles (deg): Os−C(1): 2.161(7); Os−C(2): 2.175(7); C(1)−C(2): 1.422(10); P−Os−Br: 88.95(5); P−Os−M: 94.5(2); Br−Os−M: 102.2(2); Os−C(2)−C(1): 70.3(4); C(1)−Os−C(2) 38.3(3); C(1)−C(2)−C(3) 123.6(7). [M is the midpoint of the C(1)−C(2) bond.]

(6) (a) Johnson, T. J.; Albinati, A.; Koetzle, T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 4966. (b) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 636. (c) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828. (d) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E. *Organometallics* **2000**, *19*, 3260.

(7) Allen, F. H.; Davis, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.

Scheme 2



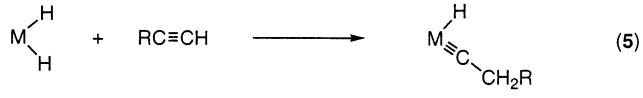
hydride ligand and that containing the deuterium atom toward the phosphine ligand. The migration of the hydride ligand from the metallic center to the C_α atom of the vinylidenes should afford the corresponding unsaturated styryl intermediates, which should be stabilized by coordination of bromide. The electrophilic addition of D^+ to the C_α atom of the styryl ligand of the resulting saturated species should give the olefins.

The formation of **2** and **2-*d*$_2$** together with the preparation of the carbene derivative $[Os(\eta^5\text{-}C_5H_5)(=CH-CH_2Ph)\{P(OMe)_3\}(P^iPr_3)]BF_4$ according to Scheme 1 suggest that, in this cyclopentadienyl-osmium-triisopropylphosphine system, the position of the nucleophilic center of the styryl ligand is strongly dependent upon the nature of the incoming ligand in the coordination vacancy of the unsaturated $Os(\eta^5\text{-}C_5H_5)(CH=CHPh)(P^iPr_3)$ intermediate. When the incoming ligand is a π-acceptor, as $P(OMe)_3$, the nucleophilic center of the alkenyl group is the C_β atom (Scheme 1). However, when the incoming ligand is a π-donor, as bromide, the nucleophilic center is the C_α atom (Scheme 2).

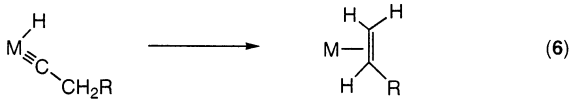
The nucleophilicity of C_α is only formal. At first glance, an $Os(\eta^5\text{-}C_5H_5)(CH=CHPh)L(P^iPr_3)$ species should have two nucleophilic centers, the metal and the C_β atom of the alkenyl group. The π-acidic nature of L decreases the nucleophilic power of the metal; as a result, the electrophiles add at C_β, and carbene derivatives are formed. In contrast, the donor nature of L increases the nucleophilic power of the metal, favoring the electrophilic addition at this atom. The subsequent reductive elimination affords olefins. This explains why the behavior of **1** toward bromide is different from the behavior toward $P(OMe)_3$.

In addition, it should be noted that the formation of hydride-carbyne complexes by reaction of dihydride compounds and terminal alkynes together with the hydride-carbyne to olefin transformation shown in eq 3 suggest that, for the reduction of terminal alkynes by action of dihydride complexes, there is an alternative pathway to that summarized in eqs 1 and 2. This pathway involves hydride-carbyne intermediates (eqs 5 and 6), and its relevance in the reduction process seems to be highly dependent on the electronic properties of the co-ligands of the complex. The reason for this dependence is a consequence of the ionic nature of the mechanisms of formation of the carbyne ligand[2] and of its transformation into olefin.

In conclusion, when a carbyne ligand has a CHR_2 substituent, the hydride-carbyne complexes can be transformed into olefin or carbene derivatives by action of Lewis bases. In the $Os(\eta^5\text{-}C_5H_5)(P^iPr_3)$ system, π-acceptor ligands favor the transformation into carbene, while π-donor ligands favor the transformation into olefin. In both cases the mechanism is ionic.



(5)



(6)

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material $[OsH(\eta^5\text{-}C_5H_5)(\equiv C-CH_2Ph)(P^iPr_3)]BF_4$ (**1**) was prepared by the published method.[5]

NMR spectra were recorded at 293 K, and chemical shifts are expressed in ppm downfield from Me_4Si (^1H, ^2H, and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, J, are given in hertz.

Preparation of $[OsH(\eta^5\text{-}C_5H_5)(\equiv C-CD_2Ph)(P^iPr_3)]BF_4$ (1-*d*$_2$). This product was prepared from $OsH(\eta^5\text{-}C_5H_5)(C\equiv CPh)(SiPh_3)(P^iPr_3)$ by the same procedure as its nondeuterated counterpart **1**, but using DBF_4 instead HBF_4. DBF_4 was prepared by adding D_2O (1 mL, 50 mmol) to a commercial solution of HBF_4 in diethyl ether (1 mL, 7.3 mmol). ^1H NMR (300 MHz, $CDCl_3$): δ 7.40−7.10 (5 H, −Ph); 5.74 (s, 5 H, η^5-C_5H_5); 2.04 (m, 3 H, PCH); 1.19 (dd, 9 H, PCHC*H*$_3$, $^3J_{HP}$ = 11.7, $^3J_{HH}$ = 7.2); 1.16 (dd, 9 H, PCHC*H*$_3$, $^3J_{HP}$ = 11.7, $^3J_{HH}$ = 7.2); −12.15 (d, 1 H, Os−H, $^2J_{HP}$ = 24.0). ^2H NMR (46.1 MHz, $CHCl_3$): δ 3.04 (br, $-CD_2-$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 48.0 (s, d in off-resonance).

Preparation of $OsBr(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_2=CHPh)(P^iPr_3)$ (2). A solution of $[OsH(\eta^5\text{-}C_5H_5)(\equiv C-CH_2Ph)(P^iPr_3)]BF_4$ (124 mg, 0.20 mmol) in tetrahydrofuran (12 mL) was treated with an excess of KBr (151 mg, 1.27 mmol) during 24 h. The mixture was then vacuum-dried, and the residue was extracted with diethyl ether (30 mL). The solution was vacuum-dried and purified through an alumina column. Diethyl ether eluted an orange fraction, which was vacuum-dried. The subsequent residue was crystallized by slow diffusion of a dichloromethane solution (1 mL) into methanol (15 mL). The product was isolated as red needles. Yield: 70 mg (57%). Anal. Calcd for $C_{22}H_{34}BrOsP$: C, 44.07; H, 5.71. Found: C, 43.84; H, 5.67. ^1H NMR (300.0 MHz, C_6D_6): δ 7.80−7.00 (5 H, −Ph); 5.11 (dd, 1 H, =C*H*Ph, $^3J_{HH}$ = 10.5, $^3J_{HH}$ = 7.5); 4.58 (s, 5 H, η^5-C_5H_5);

3.77 (ddd, 1 H, =CH$H_{\text{cis to Ph}}$, $^3J_{HH}$ = 10.5, $^2J_{HH}$ = 3.3, $^3J_{HP}$ = 1.5); 2.31 (m, 3 H, PCH); 2.20 (ddd, 1 H, =CH$H_{\text{trans to Ph}}$, $^3J_{HP}$ = 13.8, $^3J_{HH}$ = 7.5, $^2J_{HH}$ = 3.3); 1.02 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 13.2, $^3J_{HH}$ = 7.2); 0.84 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 13.2, $^3J_{HH}$ = 7.2). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, plus APT): δ 149.4 (−, s, C*ipso* of Ph); 128.5, 125.7 (+, both s, C*ortho*, C*meta* of Ph); 125.1 (+, s, C*para* of Ph); 83.0 (+, s, η^5-C_5H_5); 44.3 (+, s, =*C*HPh); 24.9 (+, d, PCH, $^1J_{CP}$ = 29.2); 21.0, 20.0 (+, both s, PCH*C*H_3); 15.7 (−, d, =CH_2, $^2J_{CP}$ = 5.5). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 3.5 (s). MS (FAB$^+$): *m*/*z* 496 (M^+ − CH_2= CHPh).

Preparation of OsBr(η^5-C_5H_5)(η^2-CDH=CDPh)(P^iPr_3) (2-*d*$_2$). A solution of [OsH(η^5-C_5H_5)(≡C−CD_2Ph)(P^iPr_3)]BF_4 (202 mg, 0.33 mmol) in tetrahydrofuran (10 mL) was treated with an excess of KBr (251 mg, 2.11 mmol) during 24 h. The mixture was then vacuum-dried, and the residue was extracted with diethyl ether (30 mL). The solution was vacuum-dried and purified through an alumina column. Diethyl ether eluted an orange fraction, which was vacuum-dried. The subsequent residue was washed with methanol (2 × 3 mL). The product was isolated as a red solid. Yield: 127 mg (64%). ^1H NMR (300.0 MHz, C_6D_6): δ 7.80−7.00 (5 H, −Ph); 5.11 (br, 0.03 H, =CHPh); 4.58 (s, 5 H, η^5-C_5H_5); 3.77 (br, 0.48 H, =$CDH_{\text{cis to Ph}}$); 2.29 (m, 3 H, PCH); 2.20 (m, 0.52 H, =$CDH_{\text{trans to Ph}}$); 1.02 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 13.2, $^3J_{HH}$ = 7.2); 0.84 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 13.2, $^3J_{HH}$ = 7.2). ^2H NMR (46.1 MHz, C_6H_6): δ 5.04 (br, 0.97 D, =CDPh); 3.72 (br, 0.52 D, =$CHD_{\text{cis to Ph}}$); 2.17 (br, 0.48 D, =$CHD_{\text{trans to Ph}}$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 3.5 (s).

Crystallographic Data for 2. Crystals are orthorhombic, *Fdd*2; a red needle was used (0.12 × 0.06 × 0.05 mm) in a Smart APEX CCD diffractometer at 100.0(2) K equipped with a normal focus, 2.4 kW sealed tube source (molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering 0.3° in ω. The cell parameters [25.0801(16) Å, 42.146(3) Å, 7.8607(5) Å; Z = 16] were determined and refined by least-squares fit of 2989 collected reflections. The first 100 frames were collected at the end of the data collection to monitor crystal decay. Absorption correction was performed with the SADABS program (this is based on the method of Blessing[8]). Lorentz and polarization corrections were also performed. The structures were solved by Patterson and Fourier methods and refined by full matrix least-squares using the Bruker SHELXTL program package[9] minimizing $\omega(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were anisotropically refined. The anisotropic parameters of carbon atom C(3) refined improperly, so a restrained refinement was used. The hydrogen atoms were observed or calculated and refined freely or riding to bonded carbon atoms. Weighted R factors (R_w) and goodness of fit (S) are based on F^2; conventional R factors are based on F. R_1 = 0.0374 [$I > 2\sigma(I)$] and wR_2 = 0.0488; GOOF = 0.780 (SHELXL97 program).

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

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020546P

(8) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
(9) *SHELXTL* v. 6.1; Bruker Analytical, X-ray Systems: Madison, WI, 2000.