Preparation, X-ray Structure, and Reactivity of an Olefin-Carbene-Osmium Complex: α-Alkenylphosphine to α-Allylphosphine Transformation via an Osmaphosphabicyclopentane Intermediate

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The isopropenyldi(isopropyl)phosphine complex Os(η^5-C_5H_5)Cl{[η^2-CH_2=C(CH_3)]P^{i}Pr$_2$} (**1**) reacts at room temperature with phenyldiazomethane to give the olefin-carbene derivative Os(η^5-C_5H_5)Cl(=CHPh){P^{i}Pr$_2$[C(CH_3)=CH_2]} (**2**), which has been characterized by X-ray diffraction analysis. In toluene at 70 °C, complex **2** evolves into the osmaphosphabicyclopentane compound Os(η^5-C_5H_5)Cl{P^{i}Pr$_2$[C(CH_3)CH_2CHPh]} (**3**). Treatment of **3** with $TlPF_6$ at room temperature leads to a 1:1 mixture of the α-allylphosphine complex [OsH(η^5-C_5H_5)Cl{[η^3-*C*HPh*CH*C(CH_3)]P^{i}Pr$_2$}]PF_6 (**4**) and its α-alkenyl-γ-(η^3-benzyl)phosphine isomer [OsH(η^5-C_5H_5){[η^3-*C*$_6$H$_5$*C*HCH=C(CH_3)]P^{i}Pr$_2$}]PF_6 (**5**). The heating of the mixture in tetrahydrofuran at 66 °C gives rise to the isomerization of **5** into **4**, which has been also characterized by X-ray diffraction analysis. The hydride ligand of **4** is fairly acidic. Its deprotonation with $NaOCH_3$ leads to an equilibrium mixture of the neutral osmium(II) α-allylphosphine OsH(η^5-C_5H_5)Cl{[η^3-*C*HPh*CH*C(CH_3)]P^{i}Pr$_2$} (**6**), α-alkenyl-γ-(η^3-benzyl)phosphine OsH(η^5-C_5H_5)Cl{[η^3-*C*HPh*CH*C(CH_3)]P^{i}Pr$_2$} (**7**), and α-alkenyl-γ-carbenephosphine OsH(η^5-C_5H_5){[=C(Ph)CH=C(CH_3)]P^{i}Pr$_2$} (**8**) isomers. Complex **2** also reacts with $TlPF_6$. The reaction affords the hydride-carbyne derivative [OsH(η^5-C_5H_5)(≡CPh){P^{i}Pr$_2$[C(CH_3)=CH_2]}]PF_6 (**9**), which evolves into **4**. The isomerization is a first-order process with activation parameters of $\Delta H^{\ddagger} = 23 \pm 3$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -4 \pm 4$ cal·K^{-1}·mol^{-1}. The hydride ligand of **9** is also fairly acidic. Its deprotonation with $NaOCH_3$ leads to the neutral carbyne Os(η^5-C_5H_5)(≡CPh){P^{i}Pr$_2$[C(CH_3)=CH_2]} (**10**), which reacts with methanol to give the hydride-alkoxycarbene derivative OsH(η^5-C_5H_5){=C(OMe)Ph}{P^{i}Pr$_2$[C(CH_3)=CH_2]} (**11**). The carbene carbon atom of **2** has amphiphilic character, reacting with electrophiles and nucleophiles. The reaction with HBF_4 leads to the hydride-benzylcyclopentadienyl derivative OsH(η^5-$C_5H_4CH_2$Ph)Cl{[η^2-CH_2=C(CH_3)]P^{i}Pr$_2$}]PF_6 (**14**) via η^1-benzyl intermediates, whereas the reaction with CH_3Li gives the hydride-styrene compound OsH(η^5-C_5H_5)(η^2-CH_2=CHPh){P^{i}Pr$_2$[C(CH_3)=CH_2]} (**15**).

Introduction

Transition-metal carbene complexes are one of the most useful tools in organic and organometallic synthesis. Through [2+2] cycloaddition reactions between M−C double and C−C unsaturated bonds, numerous compounds have been prepared.[1] In particular, half-sandwich complexes of the iron triad have shown to be useful in cyclopropanation and unusual C−C coupling reactions from diazo compounds and terminal alkenes or alkynes.[2]

The osmium derivatives of this type are very scarce, and they have been much less studied than their iron and ruthenium counterparts.[3] In the course of our investigations on the chemistry of the Os(η^5-C_5H_5) unit,[4] we have recently observed that the addition of a toluene solution of phenyldiazomethane to Os(η^5-C_5H_5)Cl(P^{i}Pr$_3$)$_2$

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(1) See for example: (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293. (c) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446. (d) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271. (e) Pariya, C.; Jayaprakash, K. N.; Sarkar, A. *Coord. Chem. Rev.* **1998**, *168*, 1. (f) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (g) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd ed.; University Science Books: Sausalito, 1999; Chapter 6. (h) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (i) Schrock, R. R. *J. Chem. Soc., Dalton Trans.* **2001**, 2541. (j) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (k) Connon, S. J.; Blechert, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1900.

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leads to the osmium-carbene complex Os(η^5-C_5H_5)Cl(=CHPh)(P^iPr_3), which shows a Fischer−Schrock ambivalent behavior.[5]

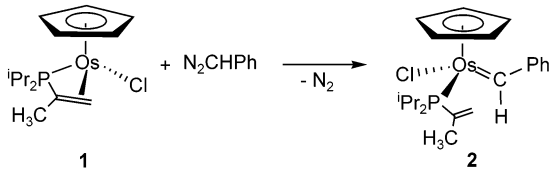
α-Alkenylphosphines are attracting increased attention in the chemistry of the metals.[6] Recently, it has been proved that osmium-α-alkenylphosphine complexes can be formed from alkylphosphine compounds by dehydrogenation of an alkyl substituent of the phosphine.[7] Despite the high kinetic inertia of the Os(η^5-C_5H_5)L_3 systems,[8] the isopropenyldi(isopropyl)-phosphine ligand of the osmium-cyclopentadienyl complex Os(η^5-C_5H_5)Cl{[η^2-CH_2=C(CH_3)]P^iPr_2} displays hemilabile properties.[9]

It is generally accepted that cyclopropanation and olefin metathesis reactions involve the intermediacy of carbene-olefin species, which evolve into metallacycle intermediates. However, these species have been rarely isolated or detected.[10] The presence of an η^2-isopropenyl ligand in Os(η^5-C_5H_5)Cl{[η^2-CH_2=C(CH_3)]P^iPr_2}, and its hemilabile character, prompted us to prepare the olefin-carbene complex Os(η^5-C_5H_5)Cl(=CHPh){P^iPr_2[C(CH_3)=CH_2]}, to study the [2+2] cycloaddition between the carbene and the olefin and the influence of the isopropenyl group on the Fischer−Schrock ambivalent behavior of the carbene ligand.

In this paper, we report the results of these studies and the unprecedented α-alkenylphosphine to α-allylphosphine conversion via carbene and osmaphosphabicyclopentane intermediates. In the context of the latter transformation, it should be mentioned that the catalytic cycles involve short-lived species with variable coordination numbers, which are connected by equilibria. Thus, the selective formation of a particular catalytic product depends on the equilibrium concentration of one or several of these short-lived intermediates. To control their stability, the development of synthetic methods for the preparation of coordinated ligands with a variable number of donor groups is of great interest.

Results and Discussion

1. Preparation and Structure of Os(η^5-C_5H_5)Cl(=CHPh){P^iPr_2[C(CH_3)=CH_2]}. In agreement with the hemilabile character of the α-alkenylphosphine of Os(η^5-C_5H_5)Cl{[η^2-CH_2=C(CH_3)]P^iPr_2} (**1**), the treatment at room temperature of a toluene solution of this compound with 2.0 equiv of phenyldiazomethane in toluene leads after 1 h to the olefin-carbene derivative Os(η^5-C_5H_5)Cl(=CHPh){P^iPr_2[C(CH_3)=CH_2]} (**2**), which is the result of the displacement of the α-alkenylphosphine olefin group from the coordination sphere of the metal by the carbene ligand (eq 1).



1 2 (1)

Complex **2** was isolated as a blue solid in 87% yield and characterized by MS, elemental analysis, IR, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy as well as by an X-ray crystallographic study. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit (enantiomers). A drawing of the *R* enantiomer is shown in Figure 1. Selected bond distances and angles for both enantiomers are listed in Table 1.

The geometry around the osmium center is close to octahedral, with the cyclopentadienyl ligand occupying a face. The C(1)−Os(1)−P(1), C(1)−Os(1)−Cl(1), and P(1)−Os(1)−Cl(1) angles are 87.08(15)°, 102.59(15)°, and 87.49(4)° in *R* and 86.73(15)°, 103.35(14)°, and 87.63(5)° in *S*, respectively.

The X-ray structure reveals that the obtained rotamer contains the phenyl group disposed toward the cyclopentadienyl ligand. The bond lengths of 1.895(5) Å (*R*) and 1.887(5) Å (*S*) are consistent with an Os(1)−C(1) double bond. They agree well with those found in the complexes $OsCl_2$(=$CHCH_2$Ph)(CO)(P^iPr_3) (1.887(9) Å),[11]

(2) See for example: (a) Baratta, W.; Del Zotto, A.; Rigo, P. *Chem. Commun.* **1997**, 2163. (b) Baratta, W.; Del Zotto, A.; Rigo, P. *Organometallics* **1999**, *18*, 5091. (c) Baratta, W.; Herrmann, W. A.; Kratzer, R. M.; Rigo, P. *Organometallics* **2000**, *19*, 3664. (d) Le Paih, J.; Dérien, S.; Özdemir, I.; Dixneuf, P. H. *J. Am. Chem. Soc.* **2000**, *122*, 7400. (e) Guerchais, V. *Eur. J. Inorg. Chem.* **2002**, 783. (f) Priya, S.; Balakrishna, M. S.; Mobin, S. M.; McDonald, R. *J. Organomet. Chem.* **2003**, *688*, 227.

(3) (a) Brumaghim, J. L.; Girolami, G. S. *Chem. Commun.* **1999**, 953. (b) Weberndörfer, B.; Henig, G.; Werner, H. *Organometallics* **2000**, *19*, 4687. (c) Baya, M.; Esteruelas, M. A. *Organometallics* **2002**, *21*, 2332. (d) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 5681. (e) Weberndörfer, B.; Henig, G.; Hockless, D. C. R.; Bennett, M. A.; Werner, H. *Organometallics* **2003**, *22*, 744.

(4) (a) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oro, L. A. *Organometallics* **1996**, *15*, 878. (b) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657. (c) Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E. *Organometallics* **1998**, *17*, 3141. (d) Crochet, P.; Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1998**, *17*, 3479. (e) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Ruiz, N. *Organometallics* **1999**, *18*, 5034. (f) Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **2000**, *19*, 275. (g) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585. (h) Esteruelas, M. A.; López, A. M.; Tolosa, J. I.; Vela, N. *Organometallics* **2000**, *19*, 4650. (i) Baya, M.; Crochet, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 240. (j) Baya, M.; Crochet, P.; Esteruelas, M. A.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **2001**, *20*, 4291. (k) Baya, M.; Esteruelas, M. A.; Oñate, E.; *Organometallics* **2001**, *20*, 4875. (l) Carbó, J. J.; Crochet, P.; Esteruelas, M. A.; Jean, Y.; Lledós, A.; López, A. M.; Oñate, E. *Organometallics* **2002**, *21*, 305. (m) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2004**, *23*, 3021.

(5) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414.

(6) See for example: (a) Ji, H.; Nelson, J. H.; DeCian, A.; Fischer, J.; Slujić, L.; Milosavljević, E. B. *Organometallics* **1992**, *11*, 401. (b) Barthel-Rosa, L. P.; Maitra, K.; Fischer, J.; Nelson, J. H. *Organometallics* **1997**, *16*, 1714. (c) Barthel-Rosa, L. P.; Maitra, K.; Nelson, J. H. *Inorg. Chem.* **1998**, *37*, 633. (d) Hogarth, G.; Shukri, K.; Doherty, S.; Carty, A. J.; Enright, G. D. *Inorg. Chim. Acta* **1999**, 178. (e) Coles, S. J.; Faulds, P.; Hursthouse, M. B.; Kelly, D. G.; Toner, A. J. *Polyhedron* **2000**, *19*, 1271. (f) Hansen, H. D.; Nelson, J. H. *Organometallics* **2000**, *19*, 4740.

(7) (a) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 1316. (b) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2003**, *22*, 2472. (c) Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oliván, M.; Oñate, E.; Tajada, M. A.; Tomàs, J. *Organometallics* **2003**, *22*, 2087.

(8) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; VCH Publisher: New York, 1997; Chapter 3.

(9) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1416.

(10) (a) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241. (b) Tallarico, J. A.; Bonitatebus, P. J., Jr., Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 7157. (c) Álvarez, P.; Lastra, E.; Gimeno, J.; Bassetti, M.; Falvello, L. R. *J. Am. Chem. Soc.* **2003**, *125*, 2386. (d) Mashima, K.; Yonekura, H.; Yamagata, T.; Tani, K. *Organometallics* **2003**, *22*, 3766.

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

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex Os(η^5-C_5H_5)Cl(=CHPh){P^{i}Pr$_2$[C(CH$_3$)=CH$_2$]} (2)

	R	*S*		*R*	*S*
Os(1)−P(1)	2.3019(13)	2.2952(13)	Os(1)−C(20)	2.299(5)	2.196(5)
Os(1)−Cl(1)	2.3853(13)	2.3870(13)	Os(1)−C(21)	2.191(5)	2.301(5)
Os(1)−C(1)	1.895(5)	1.887(5)	C(1)−C(2)	1.470(6)	1.491(6)
Os(1)−C(17)	2.188(5)	2.368(5)	P(1)−C(11)	1.843(5)	1.855(5)
Os(1)−C(18)	2.332(5)	2.326(5)	C(11)−C(12)	1.331(6)	1.313(6)
Os(1)−C(19)	2.364(5)	2.170(5)	C(11)−C(13)	1.490(6)	1.494(6)
M[a]−Os(1)−P(1)	130.6	130.0	C(1)−Os(1)−Cl(1)	102.59(15)	103.35(14)
M[a]−Os(1)− Cl(1)	115.4	115.5	Os(1)−C(1)−C(2)	130.8(3)	130.6(4)
M[a]−Os(1)− C(1)	125.0	125.1	P(1)−C(11)−C(12)	123.6(4)	123.1(4)
P(1)−Os(1)−Cl(1)	87.49(4)	87.63(5)	P(1)−C(11)−C(13)	115.9(3)	116.0(3)
C(1)−Os(1)−P(1)	87.08(15)	86.73(15)	C(12)−C(11)−C(13)	120.4(5)	120.8(4)

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

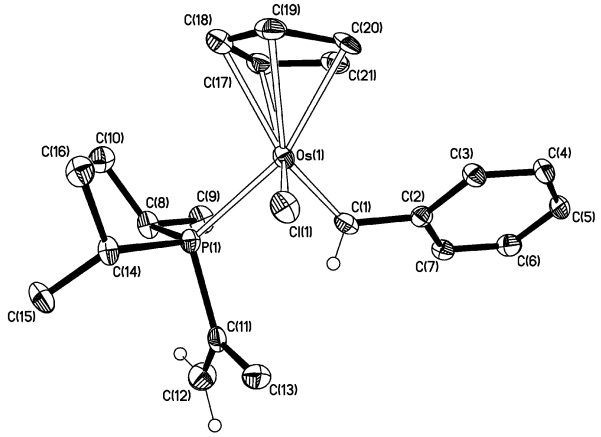


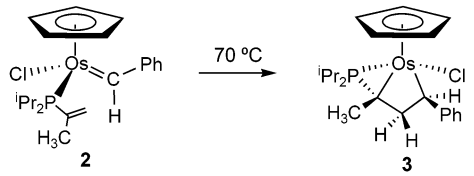
Figure 1. Molecular diagram of the *R* enantiomer of Os(η^5-C_5H_5)Cl(=CHPh){P^{i}Pr$_2$[C(CH$_3$)=CH$_2$]} (**2**).

[OsH(κ^2-O_2CCH_3){=C(Ph)CH$_2$}(P^{i}Pr$_3$)2]BF$_4$ (1.895(10) and 1.882(11) Å),[12] [OsH(κ^2-O_2CCH_3){=C(Ph)CH$_2$}-(P^{i}Pr$_3$)2]BF$_4$ (1.879(6) Å),[13] and [OsCl{=CHCH(Ph)N=CMe$_2$}(CO)](P^{i}Pr$_3$)$_2$][CF_3SO_3] (1.890(10) Å),[14] where an Os−C double bond has also been proposed to exist. The Os(1)−C(1)−C(2) (130.8(3)° in *R* and 130.6(4)° in *S*) angles support the sp^2 hybridization of C(1). The C(11)−C(12) distances (1.331(6) Å in *R* and 1.313(6) Å in *S*) as well as the angles around C(11), close to 120°, support the presence of a double bond between these atoms of the phosphine.

In the ^{1}H NMR spectrum of **2** in benzene-d_6, the most noticeable resonance of the carbene ligand is that corresponding to the C$_\alpha$-H proton, which appears at 18.50 ppm as a doublet with a H−P coupling constant of 16.8 Hz. In the ^{13}C{^{1}H} NMR spectrum, the C$_\alpha$ atom of the carbene displays a broad resonance at 234.2 ppm. The ^{13}C{^{1}H} and ^{1}H NMR spectra also reveal the presence of a free isopropenyl substituent in the phosphine. In the ^{13}C{^{1}H} NMR spectrum, the C(sp^2) carbon atoms of the phosphine give rise to a doublet at 142.5 (CP) ppm, with a C−P coupling constant of 33 Hz, and a singlet at 125.8 (CH$_2$) ppm. These resonances appear shifted 93.2 (CH$_2$) and 106.4 (CP) ppm to lower field with regard to those of **1** (δ, 32.6 (CH$_2$), 36.1 (CP)).[9] In addition, it should be mentioned that the CP resonance has significantly increased the C−P coupling constant as a consequence of the decoordination (from 19.7 to 33 Hz). In the ^{1}H NMR spectrum, the resonances due to the CH$_2$ protons of the isopropenyl group are observed at 5.67 (*trans* to P) and 5.34 (*cis* to P) ppm, as doublets with H−P coupling constants of 28.5 and 12.0 Hz, respectively. These resonances are shifted 1.57 (*trans* to P) and 2.47 (*cis* to P) ppm toward lower field with regard to those found in the spectrum of **1** (δ, 4.10 and 2.87).[9] The H−P coupling constant of the resonance corresponding to the proton disposed *cis* to the phosphorus atom also increases as a consequence of the decoordination (from 7.2 to 12.0 Hz).

The ^{31}P{^{1}H} NMR spectrum of **2** contains a singlet at 31.6 ppm, shifted 34.5 ppm to lower field compared with the observed one in the spectrum of **1** (δ, −2.9).

2. [2+2] Cycloaddition between the Olefin and Carbene Groups. In toluene the olefin-carbene complex **2** very slowly evolves to give the unprecedented osmaphosphabicyclopentane derivative Os(η^5-C_5H_5)Cl-{P^{i}Pr$_2$[C(CH$_3$)CH$_2$CHPh]} (**3**). At 70 °C in an NMR tube the transformation is quantitative after 50 h. Under the same conditions at Schlenk-tube scale, complex **3** was isolated as an orange solid in 72% yield (eq 2).

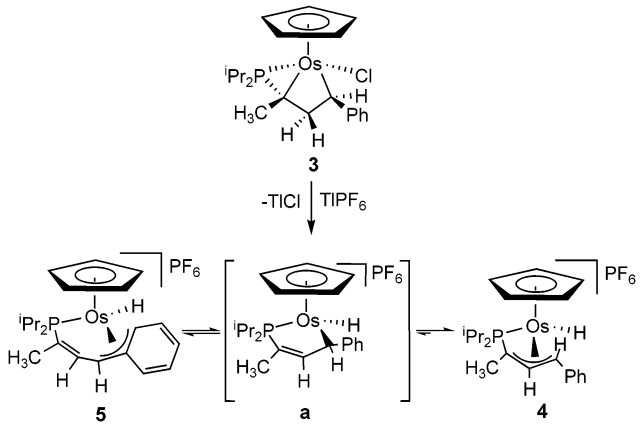


(2)

The presence of Os−CHPh and Os−C(CH$_3$)P single bonds in **3** is strongly supported by its ^{13}C{^{1}H} NMR spectrum, which shows doublets at −9.5 and −22.4 ppm, with C−P coupling constants of 3 and 13 Hz, respectively. In the ^{1}H NMR spectrum, the resonance corresponding to the OsCH proton of the bicycle appears at 3.99 ppm. The CH$_2$ group displays two resonances: one of them at 4.47 ppm, overlapped by the Cp signal, and the other one at 3.45 ppm. The resonance due to the methyl substituent of the bicycle is observed at 0.55 ppm. The ^{31}P{^{1}H} NMR spectrum contains a singlet at −23.3 ppm, shifted 54.9 ppm to higher field compared with the observed one in the spectrum of **2**.

(12) 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.
(13) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184.
(14) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2294.

Scheme 1



The stereochemistry shown in eq 2 was inferred on the basis of a NOE experiment; the saturation of the CH_3 resonance of the bicycle increases the intensity of the Ph (6.4%) and Cp (7.0%) resonances, while a NOE effect with the OsCH resonance is not observed. The exclusive formation of this diastereomer proves that the reaction is diastereoselective and involves a [2+2] cycloaddition process between the C−C double bond of the phosphine and the Os−C double bond in the rotamer shown in Figure 1.

The extraction of the chloride ligand from **3** provokes the destruction of the bicycle. At room temperature, the treatment of acetone solutions of **3** with 1.0 equiv of $TlPF_6$ leads to a 1:1 mixture of the α-allylphosphine complex $OsH(\eta^5\text{-}C_5H_5)Cl\{[\eta^3\text{-}CHPhCHC(CH_3)]P^iPr_2\}]PF_6$ (**4**) and its α-alkenyl-γ-(η^3-benzyl)phosphine isomer $OsH(\eta^5\text{-}C_5H_5)\{[\eta^3\text{-}C_6H_5CHCH{=}C(CH_3)]P^iPr_2\}]PF_6$ (**5**). The transformation initially affords the hydride-η^1-allylphosphine intermediate **a** (Scheme 1), as a result of the Os−C(CH_3)P bond cleavage and a β-hydrogen elimination reaction on the CH_2 group of the bicycle. From a thermodynamic point of view, complex **4** is more stable than **5**. Thus, the heating of the mixture in tetrahydrofuran at 66 °C gives rise to the isomerization of **5** into **4**, and the latter can be isolated as a pure white solid in 70% yield.

It should be noted that a β-H elimination rather than a metathesis process, driven by the presence of the vacant site, is observed in the metallacyclobutane of **3**. Although intermediates have not been isolated, it has been proposed that an intramolecular [2+2] cycloaddition reaction in olefin-carbene-metal complexes and the subsequent transformation of the resulting metallacyclobutane into hydrido-η^3-allyl-metal derivatives are the key steps for the catalytic formation of C_n olefins, by addition of diazoalkanes to C_{n-1} olefins.[2c,f,15] The reactions shown in eqs 1 and 2 and the formation of **4** according to Scheme 1 are strong evidence in favor of this proposal. Kirchner et al. have also postulated that ruthenium complexes react with terminal alkynes, in the presence of base, to yield η^3-butadienyl compounds via metallacyclobutane intermediates related to **3**.[16]

Figure 2 shows a view of the structure of the cation of **4**. Table 2 collects selected bond distances and angles. The structure proves the formation of the α-allylphosphine ligand, which is coordinated to the metallic center

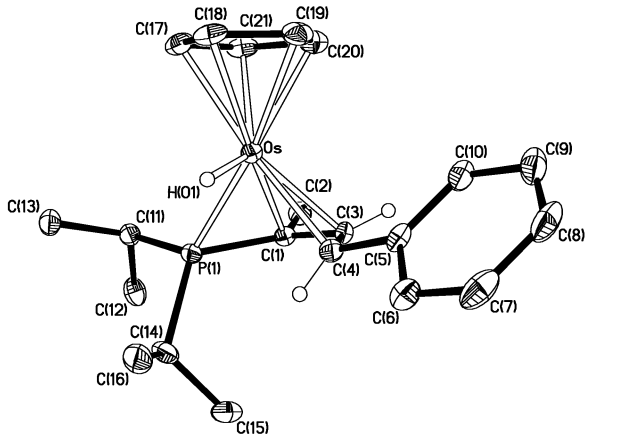


Figure 2. Molecular diagram of the cation of $OsH(\eta^5\text{-}C_5H_5)Cl\{[\eta^3\text{-}CHPhCHC(CH_3)]P^iPr_2\}]PF_6$ (**4**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex $OsH(\eta^5\text{-}C_5H_5)Cl\{[\eta^3\text{-}CHPhCHC(CH_3)]P^iPr_2\}]PF_6$ (4)

Os−P(1)	2.2634(9)	Os−C(21)	2.212(3)
Os−C(1)	2.221(3)	Os−H(01)	1.33(4)
Os−C(3)	2.173(3)	C(1)−C(2)	1.507(4)
Os−C(4)	2.209(3)	C(1)−C(3)	1.414(4)
Os−C(17)	2.224(3)	C(3)−C(4)	1.415(5)
Os−C(18)	2.230(3)	C(4)−C(5)	1.484(4)
Os−C(19)	2.232(3)	P(1)−C(1)	1.772(3)
Os−C(20)	2.214(3)		
M[a]−Os−P(1)	138.6	C(1)−Os−C(3)	37.52(12)
M[a]−Os−C(1)	130.8	C(1)−Os−C(4)	67.91(12)
M[a]−Os−C(3)	130.2	C(3)−Os−C(4)	37.67(12)
M[a]−Os−C(4)	137.9	C(1)−C(3)−C(4)	122.1(3)
M[a]−Os−H(01)	106.1	P(1)−C(1)−C(2)	122.9(2)
P(1)−Os−C(1)	46.53(8)	P(1)−C(1)−C(3)	115.8(2)
P(1)−Os−C(3)	75.11(9)	C(2)−C(1)−C(3)	120.6(3)
P(1)−Os−C(4)	83.01(9)	C(3)−C(4)−C(5)	121.6(3)
P(1)−Os−H(01)	85.2(15)		

[a] M represents the midpoint of the C(23)−C(27) Cp ring.

by the phosphorus and the C(1), C(3), and C(4) carbon atoms. The angles C(1)−Os−C(4), C(3)−Os−P(1), C(1)−C(3)−C(4), and C(3)−C(1)−P(1) are 67.91(12)°, 75.11(9)°, 122.1(3)°, and 115.8(2)°, respectively. The phenyl substituent is *syn* disposed with regard to C(3), with a C(3)−C(4)−C(5) angle of 121.6(3)°. The allyl moiety coordinates in an asymmetrical fashion, with the separation between the central carbon atom, C(3), and the metal (2.173(3) Å) shorter than the separation between the metal and the terminal carbon atoms C(4) (2.209(3) Å) and C(1) (2.221(3) Å). The carbon−carbon distances are 1.414(4) Å for C(1)−C(3) and 1.415(5) Å for C(3)−C(4). The Os−P(1) and P(1)−C(1) bond lengths reflect the peculiarities of the α-allylphosphine. The Os−P(1) distance (2.2634(9) Å) is about 0.09 Å shorter than the separation between the metal and the triisopropylphosphine ligand in the hydride-η^3-allyl-osmium(IV) derivative $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{\eta^3\text{-}CH_2C(Ph)CH_2\}(P^iPr_3)]BF_4$ (2.3500(11) Å),[4k] whereas the P(1)−C(1) distance (1.772(3) Å) is about 0.04 and 0.07 Å shorter than the P(1)−C(11) (1.816(3) Å) and P(1)−C(14) (1.848(3) Å) distances, respectively. The P(1)−C(1) distance is also about 0.07 Å shorter than the P−(Csp2) bond length in the α-alkenylphosphine of **2**, suggesting that some electron density of the allyl unit extends toward the phosphorus.

In agreement with the presence of a hydride ligand in the complex, the ^{1}H NMR spectrum shows at −13.74 ppm a double doublet by spin coupling with the phosphorus (20.5 Hz) and the CHPh proton of the allyl unit (2.4 Hz). The resonance due to the latter appears at 3.40 ppm with a H−H$_{meso}$ coupling constant of 7.8 Hz. The resonance corresponding to the H$_{meso}$ is observed at 6.19 ppm, as a double doublet with a H−P coupling constant of 23.5 Hz. In the ^{13}C{^{1}H} NMR spectrum, the most noticeable resonances are three doublets at 79.3, 53.5, and 41.6 ppm, with C−P coupling constants of 7, 14, and 5 Hz, respectively. On the basis of the ^{1}H−^{13}C HMQC spectrum, these resonances are assigned to the C(3), C(1), and C(4) atoms of the allyl moiety, respectively. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 32.6 ppm.

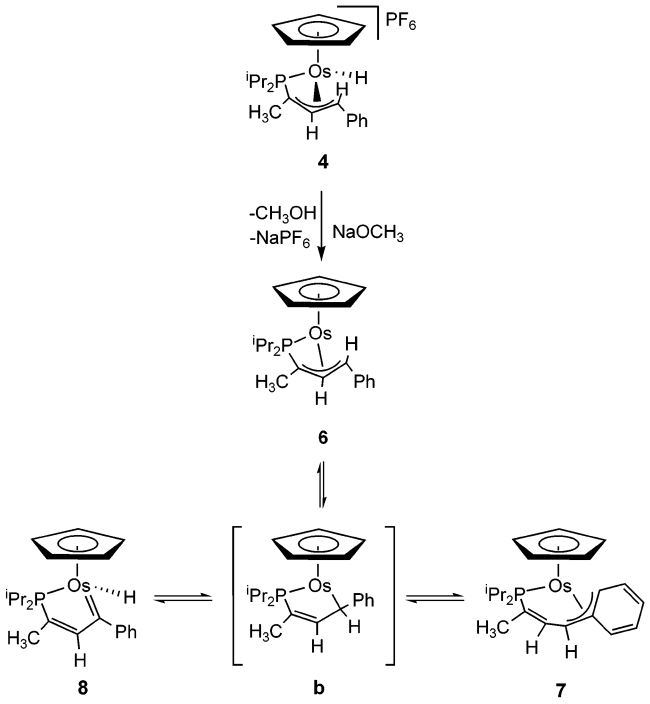
In the ^{1}H NMR spectrum of **5**, the hydride resonance appears at −13.27 ppm, as a doublet with a H−P coupling constant of 27.9 Hz. The resonance corresponding to the olefinic proton of the alkenyl unit of the phosphine is observed at 6.29 ppm, as a double multiplet with a H−P coupling constant of 52.0 Hz, whereas the protons of the η^3-unit of the benzyl group display multiplets at 6.03 and 4.66 ppm. In the ^{13}C{^{1}H} NMR spectrum, the most noticeable feature is the presence of singlets at 87.7, 67.1, and 47.8 ppm, due to the carbon atoms of the η^3-moiety of the benzyl group. These spectroscopic data are in accordance with those reported previously for other η^3-benzyl complexes.[5,17] The ^{31}P-{^{1}H} NMR spectrum contains a singlet at 74.0 ppm.

The hydride ligand of **4** is fairly acidic. Thus, the addition of 2.0 equiv of sodium methoxide to tetrahydrofuran solutions of this compound results in its deprotonation to afford a white solid in 58% yield. According to the elemental analysis, the composition of the solid is Os(C$_5$H$_5$)(^{i}Pr$_2$PC$_{10}$H$_{10}$).

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of the solid in toluene-d_8 indicate that in solution it gives rise to an equilibrium mixture of the neutral osmium(II) α-allylphosphine OsH(η^5-C$_5$H$_5$)Cl{[η^3-*C*HPh*CH**C*(CH$_3$)]P-^{i}Pr$_2$}]PF$_6$ (**6**), α-alkenyl-γ-(η^3-benzyl)phosphine OsH(η^5-C$_5$H$_5$){[η^3-*C*$_6$H$_5$*C*HCH=C(CH$_3$)]P^{i}Pr$_2$}]PF$_6$ (**7**), and α-alkenyl-γ-carbenephosphine OsH(η^5-C$_5$H$_5$){[=C(Ph)CH=C(CH$_3$)]P^{i}Pr$_2$} (**8**) isomers. The equilibrium is highly dependent on the temperature. At 80 °C, isomer **6** is favored with regard to **8**, and the latter with regard to **7**. Thus, at this temperature the **6**:**8**:**7** molar ratio is 20:6:1. Lowering the sample temperature produces a decrease of the amount of **6** and an increase in the amounts of **7** and **8**. At room temperature the **6**:**8**:**7** molar ratio is 2:1:1. At −20 °C, only traces of **6** are observed, while the **8**:**7** molar ratio is 1:2.

The formation of this equilibrium mixture can be rationalized according to Scheme 2. It is reasonable to assume that the deprotonation of **4** initially affords **6**. The $\eta^3-\eta^1$ conversion of the allyl moiety of the phosphine ligand of **6** should lead to intermediate **b**, where the η^1-allyl unit is also a η^1-benzyl moiety. Thus, the $\eta^1-\eta^3$ conversion of the benzyl group could yield the α-alkenyl-γ-(η^3-benzyl)phosphine isomer **7**. Intermediate **b** is an unsaturated osmaphosphacyclopentene species

Scheme 2



with H$_\alpha$ and H$_\beta$ hydrogen atoms with regard to the σ,Os−C bond. As a consequence of the rigidity imposed by the sp^2-hybridization of the CH$_\beta$ carbon atom of the metallacycle, the H$_\beta$ hydrogen atom points in the opposite direction of the metallic center and, therefore, the β-hydrogen elimination is disfavored with regard to the α-hydrogen elimination reaction. The migration of the H$_\alpha$ hydrogen from the CPh carbon atom to the osmium should yield isomer **8**. The formation of carbene derivatives by α-elimination on alkyl species, which have no accessible β-hydrogen atoms, is a well-known process.[18]

In the ^{1}H NMR spectrum of **6**, at 80 °C, the resonance corresponding to the CHPh proton of the allyl unit appears at 3.05 ppm, as a double doublet with H−P and H−H$_{meso}$ coupling constants of 10.6 and 5.7 Hz, respectively. The H$_{meso}$ resonance is observed at 5.59 ppm, also as a double doublet but with a H−P coupling constant of 23.4 Hz. In the ^{13}C{^{1}H} NMR spectrum the most noticeable features are two doublets at 70.4 and 39.0 ppm, with C−P coupling constants of 13 and 15 Hz, respectively, assigned to the C$_{meso}$ and PC(sp^2) carbon atoms, and a singlet at 29.0 ppm corresponding to the CHPh carbon atom. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 0.9 ppm.

In the ^{1}H NMR spectrum of **7** at −20 °C, the resonance corresponding to the olefinic proton of the alkenyl unit of the phosphine is observed at 5.95 ppm,

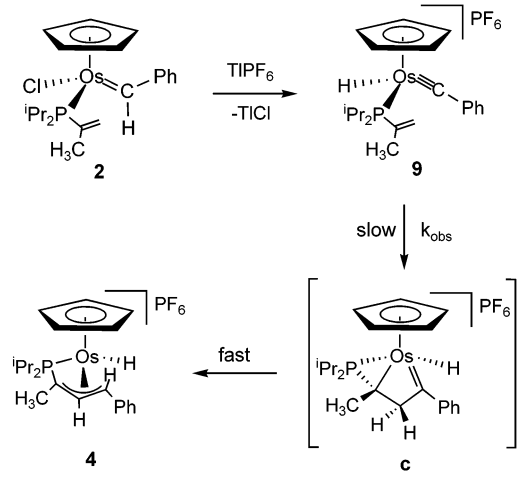
(15) (a) Wolf, J.; Brandt, L.; Fries, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 510. (b) Werner, H.; Möhring, U. *J. Organomet. Chem.* **1994**, *475*, 277. (c) Werner, H. *J. Organomet. Chem.* **1995**, *500*, 331.

(16) (a) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Am. Chem. Soc.* **1998**, *120*, 6175. (b) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Eur. J. Inorg. Chem.* **1999**, 1141. (c) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 1011.

(17) See for example: (a) Carmona, E.; Paneque, M.; Poveda, M. L. *Polyhedron* **1989**, *8*, 285. (b) Lee, B. Y.; Bazan, G. C.; Vela, J.; Komon, Z. J. A.; Bu, X. *J. Am. Chem. Soc.* **2001**, *123*, 5352.

(18) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley-Interscience: New York, 2001; Chapter 7, p 190.

Scheme 3



as a double multiplet with a H−P coupling constant of 46.2 Hz, whereas the protons of the η^3-unit of the benzyl group display a multiplet at 4.88 ppm and a double doublet at 3.12 ppm with H−P and H−H coupling constants of 13.8 and 5.6 Hz, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the carbon atoms of the η^3-moiety of the benzyl group display two singlets at 73.5 and 39.5 ppm and a doublet at 38.2 ppm with a C−P coupling constant of 3 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 65.1 ppm.

In agreement with the presence of a hydride ligand in **8**, its ^1H NMR spectrum at −20 °C contains at −14.03 ppm a doublet with a H−P coupling constant of 31.6 Hz. The olefinic resonance of the alkenyl group is observed at 6.58 ppm, as a double quartet with H−P and H−H coupling constants of 43.8 and 1.8 Hz, respectively. The presence of an Os−C double bond in the complex is strongly supported by the $^{13}C\{^1H\}$ NMR spectrum, which contains a singlet at 238.4 ppm. The olefinic resonances appear at 173.7 and 141.3 ppm, as doublets with C−P coupling constants of 31 and 35 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 73.4 ppm.

3. Transformation of 2 into 4 via a Hydride-Carbyne Intermediate. An alternative method to prepare **4** is shown in Scheme 3. The addition of 1.0 equiv of $TlPF_6$ to acetone solutions of **2** produces the extraction of the chloride ligand and the migration of the hydrogen atom of the carbene from the carbon atom to the metallic center. As a result, the hydride-carbyne derivative $[OsH(\eta^5\text{-}C_5H_5)(\equiv CPh)\{P^iPr_2[C(CH_3)=CH_2]\}]PF_6$ (**9**) is formed. This compound was isolated as a yellow solid in 82% yield.

In agreement with the presence of a hydride ligand in the complex, its ^1H NMR spectrum in dichloromethane-d_2 at room temperature shows a doublet at −12.04 ppm, with a H−P coupling constant of 22.5 Hz. In the low-field region of the spectrum the CH_2 olefinic protons of the phosphine display two doublets at 5.95 and 5.70 ppm, with H−P coupling constants of 38.4 and 17.7 Hz, respectively. In the $^{13}C\{^1H\}$ NMR spectrum the resonance corresponding to the C_α atom of the carbyne appears at 280.1 ppm, as a doublet with a C−P coupling constant of 9.0 Hz. The C(sp^2) atoms of the phosphine give rise to a singlet at 135.1 (CH_2) ppm and a doublet at 134.0 (CP) ppm, with a C−P coupling constant of 8 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 42.0 ppm.

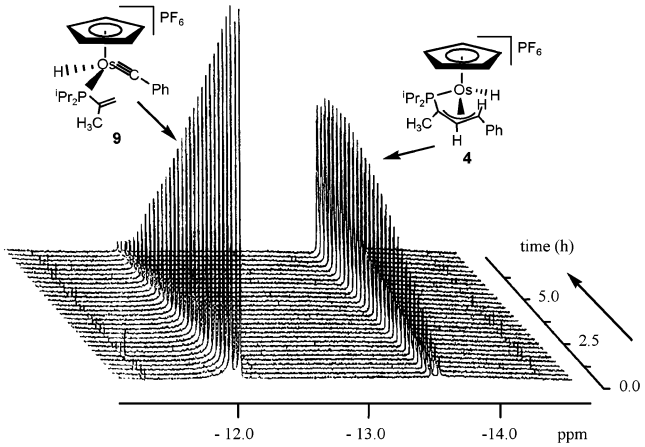


Figure 3. Stacked ^1H NMR spectra (hydride region) illustrating the isomerization of complex **9** into **4** in acetone-d_6 at 308 K.

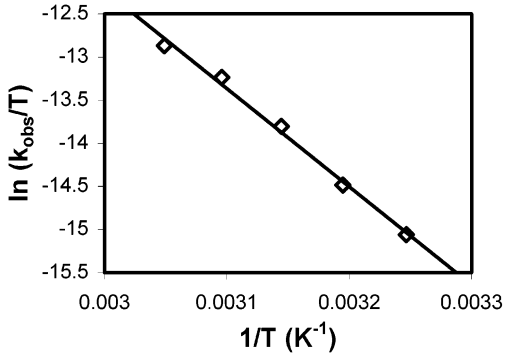


Figure 4. Eyring plot of the first-order rate constants (k_{obs}) for the isomerization of **9** into **4** in acetone-d_6 at 308 K.

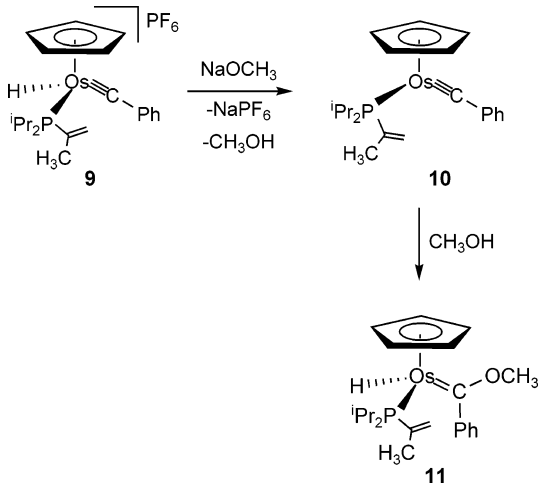
Table 3. Rate Constants of Isomerization of Complex 9 into 4 in Acetone-d_6

temperature (K)	k_{obs} (10^5 s^{-1})
308	8.9 ± 0.1
313	16 ± 0.1
318	32 ± 0.5
323	58 ± 0.6
328	84 ± 2.6

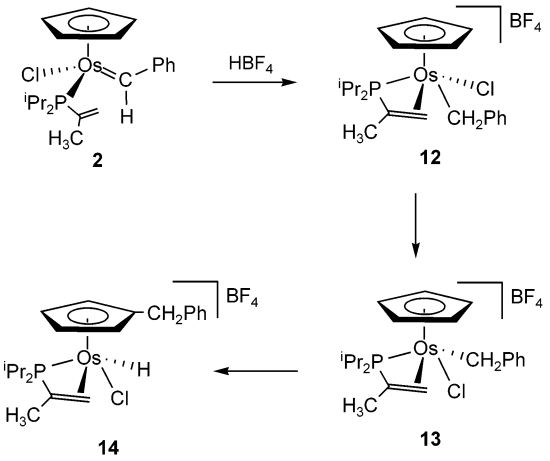
In acetone as solvent, the hydride-carbyne complex **9** evolves selectively into **4**. At first glance, one could think that the rearrangement occurs through a hydride-carbyne/carbene backward step, which should afford an unsaturated osmaphosphabicyclopentane intermediate. However, it should be pointed out that the transformation is unaffected by the presence of chloride and that traces of **5** are not observed during the reaction.

The rearrangement was followed by ^1H NMR spectroscopy by measuring the disappearance of the hydride resonance of **9** as a function of time. As shown in Figure 3, the decrease of **9** (with the corresponding increase of **4**) 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 4, giving values of $\Delta H^\ddagger = 23 \pm 3$ kcal·mol^{-1} and $\Delta S^\ddagger = -4 \pm 4$ cal·K^{-1}·mol^{-1}.

Scheme 4



Scheme 5



The above-mentioned observations are consistent with an intramolecular [2+2] cycloaddition process between the isopropenyl substituent of the phosphine and the carbyne ligand. The cycloaddition leads to the short-lived intermediate **c** (Scheme 3), which rapidly affords **4**, by 1,2-hydrogen shift from the CH_2 group to the $C(sp^2)$ atom of the bicycle.

The hydride ligand of **9** is fairly acidic, as the hydride of **4**. Thus, similarly to **4**, the addition of 2.0 equiv of sodium methoxide to tetrahydrofuran solutions of **9** produces its deprotonation, to afford the neutral carbyne derivative $Os(\eta^5\text{-}C_5H_5)(\equiv CPh)\{P^iPr_2[C(CH_3)=CH_2]\}$ (**10**), which was isolated as a dark brown oil in 73% yield (Scheme 4).

In the ^1H NMR spectrum of **10** in benzene-d_6 at room temperature, the most noticeable feature is the presence of two doublets at 5.72 and 5.39, with H−P coupling constants of 14.7 and 32.5 Hz respectively, corresponding to the olefinic CH_2 protons of the phosphine. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the C_α atom of the carbyne is observed at 263.1 ppm as a doublet with a C−P coupling constant of 14, whereas the olefinic resonances of the phosphine appear at 142.0 and 127.8 ppm, the first of them (CP) as a doublet with a C−P coupling constant of 33 Hz, and the second one (CH_2) as a singlet. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 50.2 ppm.

Complex **10** is soluble in hydrocarbon solvents. Its solutions are stable for up to several days if kept under argon at −20 °C. In toluene at 75 °C, it decomposes to give a complex mixture of 10 unidentified products; according to the $^{31}P\{^1H\}$ NMR spectrum of the mixture, none of them is **6**, **7**, or **8**. In methanol at room temperature complex **10** evolves into the hydride-alkoxycarbene derivative $OsH(\eta^5\text{-}C_5H_5)\{=C(OMe)Ph\}\{P^iPr_2[C(CH_3)=CH_2]\}$ (**11**), as a consequence of the addition of the O−H bond of the alcohol to the Os−C triple bond (Scheme 4).

Complex **11** was isolated as an orange oil in 79% yield. The presence of a hydride ligand in the complex is strongly supported by the ^1H NMR spectrum in benzene-d_6 at room temperature, which contains at −14.98 ppm a doublet with a H−P coupling constant of 31.5 ppm. In the low-field region of the spectrum, the most noticeable resonances are two doublets at 5.49 and 5.28 ppm, with H−P coupling constants of 28.2 and 12.3 Hz, respectively, corresponding to the olefinic CH_2 protons of the phosphine and a singlet at 3.13 ppm due to the methoxy group. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the C_α atom of the carbene is observed at 244.6 ppm, as a doublet with a C−P coupling constant of 9 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 44.7 ppm.

4. Amphiphilic Character of the C_α Atom of the Carbene Ligand of 2. The C_α atom of **2** has nucleophilic character, adding electrophiles. Thus, at −40 °C, the addition of 1.0 equiv of HBF_4 to an NMR tube containing a dichloromethane-d_2 solution of **2** leads to the instantaneous formation of the benzyl-osmium(IV) derivative $[Os(\eta^5\text{-}C_5H_5)(CH_2Ph)Cl\{[\eta^2\text{-}CH_2=C(CH_3)]P^iPr_2\}]BF_4$ (**12**), as a result of the addition of the proton of the acid to the C_α atom of the carbene of **2**, and the coordination of the isopropenyl substituent of the phosphine to the osmium atom (Scheme 5).

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **12** are consistent with the structure proposed for this compound in Scheme 5. In the ^1H NMR spectrum, the olefinic CH_2 protons of the phosphine display two doublets at 4.92 and 3.51 ppm, with H−P coupling constants of 10.7 and 32.7 Hz, respectively, whereas the CH_2 protons of the benzyl group give rise to a double doublet at 4.06 ppm, with both H−P and H−H coupling constants of 8.8 Hz, and a doublet at 3.12 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the olefinic resonances of the phosphine are observed at 71.9 (CP) and 40.0 (CH_2) ppm, as doublets with C−P coupling constants of 20 and 4 Hz, respectively, whereas the CH_2 resonance of the benzyl group appears at 4.1 ppm as a doublet with a C−P coupling constant of 5 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −7.2 ppm.

At room temperature complex **12** isomerizes into **13**. After 5 min the transformation is quantitative. The isomerization probably involves the decoordination of the isopropenyl group in **12**, which lies between the phosphorus atom and the benzyl ligand, and its subsequent coordination between the phosphorus and chlorine atoms. The driving force for the isomerization seems to be the greater size of the benzyl group with regard to the chlorine atom, which makes unfavorable the isopropenyl-benzyl *cisoid* disposition with regard to the isopropenyl-chlorine *cisoid* disposition.

There are some significant differences between the ^1H and $^{13}C\{^1H\}$ NMR spectra of **12** and **13**. In contrast to **12**, in the ^1H NMR spectrum of **13**, the low-field resonance corresponding to the CH_2 protons of the benzyl group (δ, 3.57) does not show any H−P coupling constant. In the $^{13}C\{^1H\}$ NMR spectrum of **13**, the CH_2 benzyl resonance appears at 18.8 ppm, shifted 14.7 ppm toward low field compared with that of **12**. Furthermore, the C−P coupling constant reflects the change of the relative position of the benzyl group with regard to the phosphorus atom, from *transoid* to *cisoid*, increasing its value up to 10 Hz.[4k] The singlet in the $^{31}P\{^1H\}$ NMR spectrum of **13** (δ −12.2) appears shifted to higher field than that of **12**.

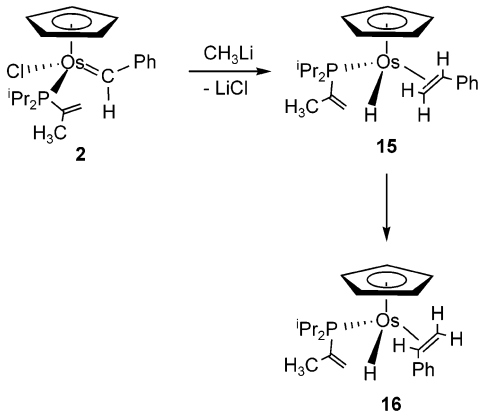
In dichloromethane-d_2 at room temperature, the benzyl group of **13** and one of the hydrogen atoms of the cyclopentadienyl ligand slowly exchange their positions. As a result, the isomerization of **13** into the hydride-benzylcyclopentadienyl derivative [Os(η^5-C_5H_5)(CH_2Ph)Cl{[η^2-CH_2═C(CH_3)]P^{i}Pr$_2$}]BF_4 (**14**) is observed. After 72 h, the transformation is quantitative. When the protonation of **2** is carried out in a Schlenk tube at room temperature, complex **14** is directly obtained after 72 h as a yellow solid in 81% yield.

We note that the carbene-rhodium complex Rh(η^5-C_5H_5)(═CPh_2)(P^{i}Pr$_3$) reacts with HX to give the rhodium(III) derivatives RhH(η^5-$C_5H_4CHPh_2$)X(P^{i}Pr$_3$) (X = Cl, Br, I, CF_3CO_2). Similarly to the formation of **14** these reactions involve the initial addition of the proton of the acids to the carbene carbon atom to give nondetected alkyl intermediates, which evolve by alkyl(Rh)/H(Cp) exchange into the observed products.[19] The generation of functionally substituted cyclopentadienyl ligands in the osmium(IV) chemistry, by ligand(Os)/H(Cp) exchange, has been recently shown.[4i] In contrast to **2**, the protonation of Rh(η^5-C_5H_5)(═CPh_2)(P^{i}Pr$_3$) with HBF_4 affords an η^3-benzylrhodium derivative.[19b]

The presence of a hydride ligand in **14** is strongly supported by its ^1H NMR spectrum, which contains a doublet at −11.67 ppm. In agreement with the *cisoid* disposition of the phosphorus atom and the hydride ligand,[4e] the value of the H−P coupling constant is 26.7 Hz. The spectrum is also consistent with the presence of a benzylcyclopentadienyl ligand and a coordinated isopropenyl group. The benzylcyclopentadienyl ligand displays an AB spin system, centered at 3.77 ppm and defined by $\Delta\nu = 57$ Hz and $J_{A-B} = 16.2$ Hz, for the CH_2 benzyl protons, and between 6.28 and 5.36 ppm the expected ABCD spin system for the ring protons. The resonances corresponding to the CH_2 olefinic protons of the phosphine appear at 4.70 and 3.53 ppm with H−P coupling constants of 10.9 and 26.6 Hz, respectively, and a H−H coupling constant of 1.7 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the C(sp^2) atoms of the phosphine give rise to doublets at 72.1 (CP) and 43.2 (CH_2) ppm, with C−P coupling constants of 22 and 5 Hz, respectively, whereas the CH_2 benzyl resonance is observed at 34.5 ppm as a singlet. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 13.6 ppm.

The behavior of **2** agrees well with that previously observed for the triisopropylphosphine complex Os(η^5-C_5H_5)Cl(═CHPh)(P^{i}Pr$_3$).[5] However, it must be noted that the replacement of an isopropyl group by an isopropenyl substituent in the phosphine has a marked influence on the nature of the resulting products of the H^+ addition to the carbene carbon atom. In contrast to **2**, the addition of the acid to the carbene carbon atom of the triisopropylphosphine complex initially leads to a η^3-benzyl derivative, which loses HCl to give the hydride-carbyne compound [OsH(η^5-C_5H_5)(≡CPh)(P-^{i}Pr$_3$)]BF_4. The stronger coordinating power of an isopropenyl group with regard to an isopropyl substituent explains the observed difference in behavior.

Scheme 6



The carbene-carbon atom of **2** also shows a marked electrophilicity, characteristic of the Fischer-type derivatives. Thus, the treatment at 0 °C of tetrahydrofuran solutions of **2** with the stoichiometric amount of methyllithium in diethyl ether affords the hydride-styrene derivative OsH(η^5-C_5H_5)(η^2-CH_2═CHPh){P^{i}Pr$_2$-[C(CH_3)═CH_2]} (**15**), which was isolated as an orange oil in 60% yield (Scheme 6).

The formation of **15** can be rationalized as the addition of the nucleophilic organic fragment to the carbene carbon atom of **2**, followed by the elimination of chloride and subsequent β-hydrogen extraction. An alternative pathway involving a carbene-methyl-metal species, which evolves into the same intermediate as that resulting from the direct attack of the organic fragment to the carbene carbon atom, may also be considered.[20]

The stereochemistry shown in Scheme 6 for **15**, with the phenyl group disposed *cisoid-anti* with regard to the phosphorus atom, is strongly supported by the ^1H NMR spectrum of this compound. In this context, it should be mentioned that X-ray diffraction analysis together with spectroscopic studies have proved for this type of system that hydrogen atoms of coordinated olefins disposed *cisoid-syn* with regard to hydride and phosphine ligands undergo spin coupling with the respective active nuclei of these ligands, in the ^1H NMR spectrum.[3d,5] According to this, in the ^1H NMR spectrum of **15**, the resonance corresponding to the olefinic CHPh proton, which is *cisoid-syn* disposed to the phosphorus atom, appears at 3.24 ppm as a double doublet of doublets, by spin coupling with the phosphorus of the phosphine (8.1 Hz) and the CH_2 hydrogens of the styrene (J_{trans} =

(19) (a) Herber, U.; Bleuel, E.; Gevert, O.; Laubender, M.; Werner, H. *Organometallics* **1998**, *17*, 10. (b) Bleuel, E.; Schwab, P.; Laubender, M.; Werner, H. *J. Chem. Soc., Dalton Trans.* **2001**, 266.

(20) Braun, T.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1995**, *117*, 7291.

7.5 Hz, J_{cis} = 6.6 Hz). The resonance due to the CH_2 proton disposed *trans* to the phenyl group, which is *cisoid-syn* disposed with regard to the hydride ligand, is observed at 2.30 ppm with a H−H coupling constant with the hydride of 3.6 Hz. The other CH_2 resonance appears at 2.93 ppm with a gem H−H coupling constant of 3.6 Hz. The hydride ligand gives rise to a double doublet at −15.96 ppm with a H−P coupling constant of 34.2 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the styrene resonances appear at 23.2 (CHPh) and 3.4 (CH_2) ppm, as singlets, while the olefinic resonances of the isopropenyl substituent of the phosphine are observed at 140.9 (CP) and 128.9 (CH_2) ppm as doublets with C−P coupling constants of 32 and 11 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 39.1 ppm.

In benzene-d_6 at 80 °C complex **15** isomerizes into **16** (Scheme 6), containing the phenyl group of the styrene ligand *cisoid-anti* with regard to the hydride ligand. According to this, in the ^1H NMR spectrum of **16**, the olefinic CHPh resonance (δ 3.78) shows spin coupling with the hydride (2.4 Hz) and does not show spin coupling with the phosphorus atom, whereas the resonance corresponding to the CH_2 proton of styrene, disposed *cis* (7.3 Hz) to the CHPh proton and *trans* to the phenyl group (δ 1.21), shows a H−P coupling constant of 10.5 Hz. The other CH_2 resonance appears at 2.98 ppm, with H−P and *gem* H−H coupling constants of 2.9 and 3.0 Hz, respectively. The hydride ligand is observed at −15.23 with a H−P coupling constant of 32.8 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the styrene resonances appear at 24.8 (CHPh) and 2.2 (CH_2) ppm, the first of them as a singlet and the second one as a doublet with a C−P coupling constant of 5 Hz. The olefinic resonances of the isopropenyl substituent of the phosphine are observed at 140.3 (CP) and 128.6 (CH_2) ppm as doublets with C−P coupling constants of 33 and 10 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 40.0 ppm.

The chemical shifts of the styrene resonances in the $^{13}C\{^1H\}$ NMR spectra of both isomers are typical for $C(sp^3)$ atoms. This suggests that the acceptor component of the osmium−styrene bond has a very important contribution to the structure of both **15** and **16**.

Complexes **15** and **16** are diastereoisomers resulting from the chirality of the osmium atom and the prochirality of the olefin. The conversion of **15** into **16** involves the decoordination of the styrene ligand and its subsequent coordination by the other face. The process probably takes place via a short-lived hydride-isopropenyldi(isopropyl)phosphine intermediate stabilized by coordination of the isopropenyl substituent of the phosphine. The driving force for the isomerization could be the steric hindrance experienced by the phosphine and the phenyl group, which makes unfavorable the *cisoid* phosphine-CHPh disposition with regard to the *cisoid* phosphine-CH_2 disposition observed in **16**.

Complex **2** shows a Fischer−Schrock ambivalent behavior, which is supported by the amphiphilic character of its carbene carbon atom. Complexes $Ru(=CF_2)(CO)_2(PPh_3)_2$, $Re(\eta^5\text{-}C_5H_5)(=CHCH_2CH_2CMe_3)(CO)_2$, and $Re\{=C(CH_3)C(CH_3)_2CH_2(\eta^5\text{-}C_5H_4)\}(CO)_2$ also show amphiphilic reactivity at the carbene carbon atom.[21]

Concluding Remarks

This paper reveals that *coordinated α-alkenylphosphines can be transformed into α-allylphosphines by reaction with diazoalkanes via [2+2] cycloaddition processes*. As a result of the hemilabile character of the α-alkenylphosphine of the complex $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}H_2C{=}C(CH_3)]P^iPr_2\}$, the treatment of this compound with phenyldiazomethane affords the olefin-carbene-osmium(II) derivative $Os(\eta^5\text{-}C_5H_5)Cl(=CHPh)\{P^iPr_2[C(CH_3){=}CH_2]\}$, which is converted into the α-allylphosphine $OsH(\eta^5\text{-}C_5H_5)Cl\{[\eta^3\text{-}CHPhCHC(CH_3)]P^iPr_2\}]PF_6$ compound by two alternative pathways.

In toluene at 70 °C, the complex $Os(\eta^5\text{-}C_5H_5)Cl(=CHPh)\{P^iPr_2[C(CH_3){=}CH_2]\}$ isomerizes into the unprecedented osmaphosphabicyclopentane derivative $Os(\eta^5\text{-}C_5H_5)Cl\{P^iPr_2[C(CH_3)CH_2CHPh]\}$, by a [2+2] cycloaddition reaction between the C−C double bond of the phosphine and the Os−C double bond. The extraction of the chloride ligand from this complex provokes the destruction of the bicycle and the formation of $OsH(\eta^5\text{-}C_5H_5)Cl\{[\eta^3\text{-}CHPhCHC(CH_3)]P^iPr_2\}]PF_6$. The alternative pathway involves the initial extraction of the chloride ligand of $Os(\eta^5\text{-}C_5H_5)Cl(=CHPh)\{P^iPr_2[C(CH_3){=}CH_2]\}$ to give the hydride-carbyne-olefin intermediate $[OsH(\eta^5\text{-}C_5H_5)(\equiv CPh)\{P^iPr_2[C(CH_3){=}CH_2]\}]PF_6$, which also evolves into the α-alkenylphosphine complex. The osmaphosphabicyclopentane-allylphosphine transformation indicates that *a β-H elimination rather than a metathesis process, driven by the presence of a vacant site, is favored in the metallacyclobutane of the osmaphosphabicyclopentane*.

The carbene carbon atom of the complexes $Os(\eta^5\text{-}C_5H_5)Cl(=CHPh)(PR_3)$ has amphiphilic character, reacting with both nucleophiles and electrophiles. However, there are marked differences in the nature of the resulting products of the H^+ addition, which depend on the substituent R of the phosphine. Thus, while the reaction of the triisopropylphosphine complex $Os(\eta^5\text{-}C_5H_5)Cl(=CHPh)(P^iPr_3)$ with H^+ affords a η^3-benzyl derivative, which loses HCl to give $[OsH(\eta^5\text{-}C_5H_5)(\equiv CPh)(P^iPr_3)]^+$, the addition of H^+ to the isopropenyldi(isopropyl)phosphine compound $Os(\eta^5\text{-}C_5H_5)Cl(=CHPh)\{P^iPr_2[C(CH_3){=}CH_2]\}$ leads to the hydride-benzylcyclopentadienyl derivative $[OsH(\eta^5\text{-}C_5H_4CH_2Ph)Cl\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}]BF_4$.

In conclusion, this paper reports the preparation, X-ray structure, and reactivity of the olefin-carbene complex $Os(\eta^5\text{-}C_5H_5)Cl(=CHPh)\{P^iPr_2[C(CH_3){=}CH_2]\}$, which shows Fischer−Schrock ambivalent behavior. This complex can be transformed into the α-allylphosphine compound $OsH(\eta^5\text{-}C_5H_5)Cl\{[\eta^3\text{-}CHPhCHC(CH_3)]P^iPr_2\}]PF_6$ by a [2+2] cycloaddition process via the

(21) (a) Clark, G. R.; Hoskins, S. V.; Jones, T. C.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1983**, 719. (b) Casey, C. P.; Vosejpka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713. (c) Casey, C. P.; Czerwinski, C. J.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1997**, *119*, 5750.

unprecendented osmaphosphabicyclopentane Os(η^5-C_5H_5)Cl{P^{i}Pr$_2$[C(CH$_3$)CH$_2$CHPh]}, which is isolated and characterized.

Experimental Section

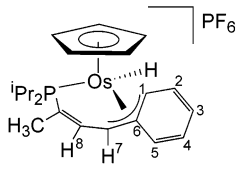
All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials Os(η^5-C_5H_5)Cl{[η^2-CH$_2$=C(CH$_3$)]P^{i}Pr$_2$}[9] (**1**) and N$_2$=CHPh[22] were prepared by the published methods.

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

Preparation of Os(η^5-C_5H_5)Cl(=CHPh){P^{i}Pr$_2$[C(CH$_3$)=CH$_2$]} (2). A yellow solution of **1** (146 mg, 0.32 mmol) in 3 mL of toluene was treated with 5 mL of a red solution of N$_2$=CHPh in toluene (0.128 M, 0.64 mmol). The reaction mixture was allowed to react at room temperature for 1 h, it was filtered through Kieselguhr, and the solvent was removed in vacuo. The resultant green oil was washed with cold pentane (5 × 3 mL), and a blue solid was obtained. The solid was separated by decantation and dried in vacuo. Yield: 152 mg (87%). Anal. Calcd for $C_{21}H_{30}ClOsP$: C, 46.78; H, 5.61. Found: C, 46.71; H, 5.46. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 18.50 (d, J_{H-P} = 16.8, 1H, Os=CH), 7.91−7.11 (m, 5H, Ph), 5.67 (d, J_{H-P} = 28.5, 1H, =CH$H_{trans\ to\ P}$), 5.34 (d, J_{H-P} = 12.0, 1H, =CH$H_{cis\ to\ P}$), 5.00 (s, 5H, C_5H_5), 2.66 (m, 1H, PCH), 2.27 (m, 1H, PCH), 1.91 (d, J_{H-P} = 9.3, 3H, PC(CH$_3$)=), 1.20 (dd, J_{H-P} = 15.1, J_{H-H} = 7.2, 3H, PCHCH_3), 1.09 (dd, J_{H-P} = 12.3, J_{H-H} = 7.3, 3H, PCHCH_3), 0.83 (dd, J_{H-P} = 14.2, J_{H-H} = 7.3, 3H, PCHCH_3), 0.80 (dd, J_{H-P} = 14.7, J_{H-H} = 7.3, 3H, PCHCH_3). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 31.6 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 234.2 (br, Os=C), 167.1 (d, J_{C-P} = 5, C_{ipso}Ph), 142.5 (d, J_{C-P} = 33, PC=), 129.8 and 125.9 (both s, Ph), 125.8 (s, =CH$_2$), 125.2 (s, Ph), 86.0 (s, Cp), 25.5 (d, J_{C-P} = 32, PCH), 23.6 (d, J_{C-P} = 32, PCH), 21.1 (d, J_{C-P} = 9, CH$_3$), 20.5 (d, J_{C-P} = 2, CH$_3$), 19.5 (d, J_{C-P} = 3, CH$_3$), 18.3 (s, CH$_3$), 16.8 (d, J_{C-P} = 3, CH$_3$). MS (FAB$^+$): *m*/*z* 506 (M$^+$ − Cl + H).

Preparation of Os(η^5-C_5H_5)Cl{P^{i}Pr$_2$[C(CH$_3$)CH$_2$CHPh]} (3). A bluish green solution of **2** (125 mg, 0.23 mmol) in 10 mL of toluene was allowed to react at 70 °C for 50 h. The resultant orange solution was concentrated to dryness, and the product was extracted from the dark orange oil with 10 mL of diethyl ether and was filtered through Kieselguhr. The orange solution was concentrated to about 1 mL and stored at − 78 °C for 15 min, and cold pentane was added (2 mL). After 5 min, an orange solid appeared. The solid was separated by decantation, washed with cold pentane, and dried in vacuo. Yield: 90 mg (72%). Anal. Calcd for $C_{21}H_{30}ClOsP$: C, 46.78; H, 5.61. Found: C, 46.60; H, 5.23. IR (Nujol, cm^{-1}): ν(Ph) 1593 (m). ^{1}H NMR (300 MHz, C_6D_6, 293 K, plus COSY): δ 7.66−7.05 (m, 5H, Ph), 4.47 (s, 6H, C_5H_5 + 1H of CH$_2$), 3.99 (dd, J_{H-H} = J_{H-H} = 9.0, 1H, C*H*Ph), 3.45 (ddd, J_{H-P} = 23.2, J_{H-H} = 14.5, J_{H-H} = 9.0, 1H, CH$_2$), 2.79 (m, 1H, PCH), 1.60 (dd, J_{H-P} = 18.0, J_{H-H} = 7.2, 3H, PCHCH_3), 1.26 (dd, J_{H-P} = 18.0, J_{H-H} = 6.0, 3H, PCHCH_3), 1.21 (dd, J_{H-P} = 14.7, J_{H-H} = 6.3, 4H, PCHCH_3 + PCH), 1.00 (dd, J_{H-P} = 14.2, J_{H-H} = 6.4, 3H, PCHCH_3), 0.55 (d, J_{H-P} = 8.1, 3H, PC(CH$_3$)). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ − 23.3 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT, plus HSQC): δ 157.3 (s, C_{ipso}-Ph), 128.3, 125.1, and 122.5 (all s, Ph), 87.8 (s, Cp), 48.7 (s, CH$_2$), 26.9 (d, J_{C-P} = 28, PCH), 24.9 (s, CH$_3$), 22.8 (d, J_{C-P} = 24, PCH), 22.3 (d, J_{C-P} = 8, CH$_3$), 21.5 (d, J_{C-P} = 5, CH$_3$), 20.8 (s, CH$_3$), 20.4 (d, J_{C-P} = 3, CH$_3$), −9.5 (d, J_{C-P} = 3, *C*HPh), − 22.4 (d, J_{C-P} = 13, P*C*(CH$_3$)). MS (FAB$^+$): *m*/*z* 540 (M$^+$).

Reaction of Os(η^5-C_5H_5)Cl{P^{i}Pr$_2$[C(CH$_3$)CH$_2$CHPh]} (3) with TlPF$_6$: Formation of OsH(η^5-C_5H_5)Cl{[η^3-*C*HPh*C*HC-(CH$_3$)]P^{i}Pr$_2$}]PF$_6$ (4) and OsH(η^5-C_5H_5){[η^3-C_6H_5*C*HCH=C(CH$_3$)]P^{i}Pr$_2$}]PF$_6$ (5). An orange solution of **3** (192 mg, 0.36 mmol) in 10 mL of acetone was treated with thallium(I) hexafluorophosphate (124 mg, 0.36 mmol). The resulting mixture was stirred for 15 min in the absence of light and filtered through Kieselguhr. The resultant dark orange solution was concentrated to ca. 1 mL and cooled to − 50 °C. Diethyl ether was added (5 mL), and 20 min later, a yellow solid appeared, which was separated by decantation, washed with 2 mL of diethyl ether, and dried in vacuo. The NMR spectra at room temperature in CD_2Cl_2 showed the presence of **4** and **5** in a 1:1 molar ratio. Yield of the mixture: 167 mg (72%). Spectroscopic data for **5**: ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K, plus COSY): δ 7.43−7.11 (m, 4H, H^2−H^5), 6.29 (dm, J_{H-P} = 52.0, 1H, H^8), 6.03 (m, 1H, H^7), 4.98 (s, 5H, C_5H_5), 4.66 (m, 1H, H^1), 2.64 (m, 1H, PCH), 2.00 (m, 1H, PCH), 1.90 (ddd, J_{H-P} = 8.4, J_{H-H^7} = J_{H-H^8} = 1.3, 3H, PC(CH$_3$)=), 1.37 (dd, J_{H-P} = 16.9, J_{H-H} = 6.7, 3H, PCHCH_3), 1.31−1.20 (6H, PCHCH_3), 1.12 (dd, J_{H-P} = 16.8, J_{H-H} = 6.9, 3H, PCHCH_3), −13.27 (d, J_{H-P} = 27.9, 1H, Os-H). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 74.0 (s, P^{i}Pr$_2$), −144.2 (sept, J_{F-P} = 714, PF$_6$). ^{13}C-{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus APT, plus HSQC): δ 146.0 (s, C^8), 138.2 (d, J_{C-P} = 39, PC=), 135.9, 132.5, 130.6, and 127.3 (all s, C^2−C^5), 87.7 (s, C^6), 85.5 (s, Cp), 67.1 (s, C^1), 47.8 (s, C^7), 30.2 (d, J_{C-P} = 33, PCH), 24.0 (d, J_{C-P} = 36, PCH), 18.1 (d, J_{C-P} = 3, CH$_3$), 18.1, 17.9, and 17.8 (all s, CH$_3$), 15.4 (d, J_{C-P} = 4, CH$_3$).



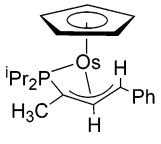
5

A suspension of the obtained 1:1 mixture of **4** and **5** (167 mg) in 10 mL of tetrahydrofuran was stirred at reflux temperature for 30 h. The solvent was removed under vacuum, and the yellow residue was solved in ca. 1 mL of acetone and cooled to 0 °C. Addition of diethyl ether caused the precipitation of **4** as a white solid. Yield: 162 mg (70%). Anal. Calcd for $C_{21}H_{30}F_6OsP_2$: C, 38.89; H, 4.66. Found: C, 38.80; H, 4.44. IR (Nujol, cm^{-1}): ν(Ph) 1597 (m), ν(PF$_6$) 836 (vs). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.33−7.18 (m, 5H, Ph), 6.19 (dd, J_{H-P} = 23.5, J_{H-H} = 7.8, 1H, H_{meso}), 5.38 (s, 5H, C_5H_5), 3.40 (dd, $J_{H-Hmeso}$ = 7.8, J_{H-Hhyd} = 2.4, 1H, C*H*Ph), 2.46 (m, 1H, PCH), 2.34 (d, J_{H-P} = 7.8, 3H, PC(CH$_3$)), 2.24 (m, 1H, PCH), 1.54 (dd, J_{H-P} = 15.9, J_{H-H} = 6.9, 3H, PCHCH_3), 1.39 (dd, J_{H-P} = 20.5, J_{H-H} = 7.3, 3H, PCHCH_3), 1.28 (dd, J_{H-P} = 17.1, J_{H-H} = 7.5, 3H, PCHCH_3), 1.27 (dd, J_{H-P} = 22.5, J_{H-H} = 7.5, 3H, PCHCH_3), −13.74 (dd, J_{H-P} = 20.5, J_{H-H} = 2.4, 1H, Os-H). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 32.6 (s, P^{i}Pr$_2$), −144.3 (sept, J_{F-P} = 712, PF$_6$). ^{13}C{^{1}H} NMR (75.42 MHz, CD$_2$-

(22) Jiménez, A. I.; López, P.; Oliveros, L.; Cativiela, C. *Tetrahedron* **2001**, *57*, 6019.

Cl_2, 293 K, plus APT, plus HSQC): δ 141.7 (s, C_{ipso}Ph), 129.2, 127.2, and 126.0 (all s, Ph), 84.1 (s, Cp), 79.3 (d, $J_{C-P} = 7$, CH_{meso}), 53.5 (d, $J_{C-P} = 14$, P*C*(CH_3)), 41.6 (d, $J_{C-P} = 5$, *C*HPh), 31.9 (d, $J_{C-P} = 39$, PCH), 23.5 (d, $J_{C-P} = 6$, CH_3), 20.4 (d, $J_{C-P} = 36$, PCH), 19.1 (d, $J_{C-P} = 7$, CH_3), 17.9 (d, $J_{C-P} = 4$, CH_3), 17.2 and 16.8 (both s, CH_3). MS (FAB$^+$): *m/z* 505 (M^+).

Deprotonation of OsH(η^5-C_5H_5)Cl{[η^3-*CHPhCHC*-(CH_3)]P^{i}Pr$_2$}]PF_6 with $NaOCH_3$. A yellowish solution of **4** (165 mg, 0.25 mmol) in 10 mL of tetrahydrofuran was treated with sodium methoxide (27 mg, 0.51 mmol). The slurry was allowed to react for 15 h at room temperature. The solvent was removed. The product was extracted with 15 mL of pentane, and the slurry was filtered through Kieselguhr. The resultant dark orange solution was concentrated to 2 mL and cooled to −40 °C. Immediately, a light orange solid appeared. The solid was separated by decantation, washed with 1 mL of cold pentane, and dried in vacuo. The NMR spectra at room temperature showed the presence of **6**, **7**, and **8** in a molar ratio 2:1:1. Yield of the mixture: 75 mg (58%). Anal. Calcd for $C_{21}H_{29}OsP$: C, 50.18; H, 5.81. Found: C, 49.92; H, 5.95. MS (FAB$^+$): *m/z* 503 (M^+). Spectroscopic data for **6**: ^{1}H NMR (300 MHz, toluene-d_8, 353 K): δ 7.32−7.02 (m, 5H, Ph), 5.59 (dd, $J_{H-P} = 23.4$, $J_{H-H} = 5.7$, 1H, H_{meso}), 4.52 (s, 5H, C_5H_5), 3.05 (dd, $J_{H-P} = 10.6$, $J_{H-H} = 5.7$, 1H, C*H*Ph), 1.85 (d, $J_{H-P} = 6.0$, 3H, PC(CH_3)), 1.74 (m, 2H, PCH), 1.13 (dd, $J_{H-P} = 13.8$, $J_{H-H} = 6.9$, 3H, CH_3), 1.11 (dd, $J_{H-P} = 11.7$, $J_{H-H} = 7.2$, 3H, CH_3), 1.02 (dd, $J_{H-P} = 23.1$, $J_{H-H} = 7.5$, 3H, CH_3), 1.02 (dd, $J_{H-P} = 18.1$, $J_{H-H} = 7.3$, 3H, CH_3). ^{31}P{^{1}H} NMR (121.42 MHz, toluene-d_8, 353 K): δ 0.9 (s). ^{13}C{^{1}H} NMR (75.42 MHz, toluene-d_8, 353 K, plus APT, plus HSQC): δ 137.5 (s, C_{ipso}-Ph), 128.1, 124.9, and 122.5 (all s, Ph), 70.4 (s, Cp), 70.4 (d, $J_{C-P} = 13$, C_{meso}), 39.0 (d, $J_{C-P} = 15$, P*C*(CH_3)), 32.6 (d, $J_{C-P} = 42$, PCH), 29.0 (s, *C*HPh), 24.7 (d, $J_{C-P} = 3$, PCH*C*H_3), 22.1 (s, PC(*C*H_3)), 20.4 (d, $J_{C-P} = 7$, PCH(*C*H_3)), 19.3 (d, $J_{C-P} = 6$, PCH(*C*H_3)), 18.3 (s, PCH(*C*H_3)), 12.5 (d, $J_{C-P} = 12$, PCH). Spectroscopic data for **7**: ^{1}H NMR (400 MHz, toluene-d_8, 253 K, plus COSY): δ 7.12−6.95 (m, 2H, H^2 and H^5), 6.40 and 6.29 (both m, each 1H, H^3 and H^4), 5.95 (dm, $J_{H-P} = 46.2$, 1H, H^8), 4.88 (m, 1H, H^7), 4.05 (s, 5H, C_5H_5), 3.12 (dd, $J_{H-P} = 13.8$, $J_{H-H^2} = 5.6$, 1H, H^1), 2.01 and 1.51 (both m, each 1H, PCH), 1.51 (ddd, $J_{H-P} = 6.6$, $J_{H-H^7} = J_{H-H^8} = 1.5$, 3H, PC($CH_3$)═), 1.09 (dd, $J_{H-P} = 14.2$, $J_{H-H} = 7.2$, 3H, PCHC*H*$_3$), 1.07 (dd, $J_{H-P} = 14.2$, $J_{H-H} = 7.2$, 3H, PCHC*H*$_3$), 0.98 (dd, $J_{H-P} = 15.2$, $J_{H-H} = 6.8$, 3H, PCHC*H*$_3$), 0.95−0.89 (3H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (161.89 MHz, toluene-d_8, 253 K): δ 65.1 (s). ^{13}C{^{1}H} NMR (100.56 MHz, toluene-d_8, 253K, plus APT, plus HMQC): δ 149.4 (d, $J_{C-P} = 34$, C^8), 142.1 (s, C^2 or C^5), 133.3 (d, $J_{C-P} = 35$, PC═), 127.9 (s, C^5 or C^2), 123.3 and 116.7 (both s, C^3 and C^4), 74.6 (s, Cp), 73.5 (s, C^6), 39.5 (s, C^7), 38.2 (d, $J_{C-P} = 3$, C^1), 30.5 (d, $J_{C-P} = 31$, PCH), 25.1 (d, $J_{C-P} = 27$, PCH), 20.7−18.1 (*C*H_3 of the P^{i}Pr$_2$ fragment), 16.0 (d, $J_{C-P} = 2$, PC(*C*H_3)═). Spectroscopic data for **8**: ^{1}H NMR (400 MHz, toluene-d_8, 253 K, plus COSY): δ 7.42−6.95 (m, 5H, Ph), 6.58 (dq, $J_{H-P} = 43.8$, $J_{H-H} = 1.8$, 1H, C_{sp2}-H), 4.97 (s, 5H, C_5H_5), 1.87 and 1.61 (both m, each 1H, PCH), 0.95−0.89 (9H, PC(CH_3)═ + PCHC*H*$_3$), 0.79 (dd, $J_{H-P} = 13.0$, $J_{H-H} = 6.6$, 3H, PCHC*H*$_3$), 0.74 (dd, $J_{H-P} = 15.0$, $J_{H-H} = 6.6$, 3H, PCHC*H*$_3$), −14.03 (d, $J_{H-P} = 31.6$, 1H, Os-H). ^{31}P{^{1}H} NMR (161.89 MHz, toluene-d_8, 253 K): δ 73.4 (s). ^{13}C{^{1}H} NMR (100.56 MHz, toluene-d_8, 253 K, plus APT, plus HMQC): δ 238.4 (s, Os═C), 173.7 (d, $J_{C-P} = 31$, C_{sp2}-H), 169.9 (s, C_{ipso}Ph), 141.3 (d, $J_{C-P} = 35$, PC═), 132.6, 124.5, and 120.7 (all s, Ph), 82.9 (s, Cp), 23.3 (d, $J_{C-P} = 32$, PCH), 22.3 (d, $J_{C-P} = 33$, PCH), 20.7−18.1 (all CH_3 groups).



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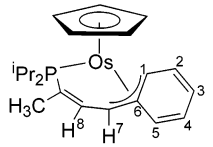

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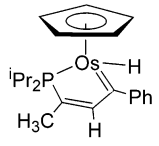


8

Preparation of [OsH(η^5-C_5H_5)(≡CPh){P^{i}Pr$_2$[C(CH_3)═CH_2]}]PF_6 (9). A bluish green solution of **2** (160 mg, 0.30 mmol) in 10 mL of acetone was treated with thallium(I) hexafluorophosphate (104 mg, 0.30 mmol). The slurry was allowed to react for 5 min in the absence of light at room temperature. After that, it was filtered through Kieselguhr. The resultant light orange solution was concentrated to ca. 1 mL and cooled to 0 °C. Diethyl ether was added (5 mL), and 2 min later, a yellow solid appeared, which was separated by decantation and dried in vacuo. Yield: 157 mg (82%). Anal. Calcd for $C_{21}H_{30}F_6OsP_2$: C, 38.89; H, 4.66. Found: C, 39.06; H, 4.66. IR (Nujol, cm^{-1}): ν(OsH) 2128 (w), ν(Ph) 1586 (m), ν(PF_6) 908 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.86−7.47 (m, 5H, Ph), 5.95 (d, $J_{H-P} = 38.4$, 1H, ═CH*H*$_{trans\ to\ P}$), 5.84 (s, 5H, C_5H_5), 5.70 (d, $J_{H-P} = 17.7$, 1H, ═CH*H*$_{cis\ to\ P}$), 2.31 (m, 3H, PCH), 2.15 (m, 3H, PCH), 2.03 (d, $J_{H-P} = 10.2$, 3H, PC(CH_3)═), 1.23 (dd, $J_{H-P} = 17.4$, $J_{H-H} = 6.9$, 3H, PCHC*H*$_3$), 1.17 (dd, $J_{H-P} = 17.4$, $J_{H-H} = 6.9$, 3H, PCHC*H*$_3$), 1.16 (dd, $J_{H-P} = 12.0$, $J_{H-H} = 6.9$, 3H, PCHC*H*$_3$), 1.10 (dd, $J_{H-P} = 10.8$, $J_{H-H} = 6.9$, 3H, PCHC*H*$_3$), −12.04 (d, $J_{H-P} = 22.5$, 1H, Os-*H*). ^{31}P-{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 42.0 (s, P^{i}Pr$_2$), −144.2 (sept, $J_{F-P} = 712$, PF_6). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2-Cl_2, 233 K, plus APT): δ 280.1 (d, $J_{C-P} = 9.0$, Os≡C), 144.6 (s, C_{ipso}Ph), 135.1 (s, ═CH_2), 134.6 (s, Ph), 134.0 (d, $J_{C-P} = 8$, PC═), 131.8 and 129.1 (both s, Ph), 88.6 (s, Cp), 28.8 (d, $J_{C-P} = 37$, PCH), 26.8 (d, $J_{C-P} = 35$, PCH), 23.6 (d, $J_{C-P} = 8$, CH_3), 18.4, 18.4, 18.2, and 18.0 (all s, CH_3). MS (FAB$^+$): *m/z* 505 (M^+).

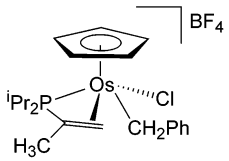
Isomerization of [OsH(η^5-C_5H_5)(≡CPh){P^{i}Pr$_2$[C(CH_3)═CH_2]}]PF_6 (9) into OsH(η^5-C_5H_5)Cl{[η^3-*CHPhCHC*-(CH_3)]P^{i}Pr$_2$}]PF_6 (4). A yellowish solution of **9** (150 mg, 0.23 mmol) in 8 mL of dichloromethane was stirred for 40 h at room temperature. The resulting yellowish solution was filtered through Kieselguhr and concentrated to ca. 1 mL. Diethyl ether was added (5 mL) and, immediately, a white solid appeared, which was separated by decantation, washed with 2 mL of diethyl ether, and dried in vacuo. The solid was characterized by ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} as compound **4**. Yield: 134 mg (89%).

Preparation of Os(η^5-C_5H_5)(≡CPh){P^{i}Pr$_2$[C(CH_3)═CH_2]} (10). A slurry of **9** (175 mg, 0.27 mmol) in 10 mL of tetrahydrofuran was treated with 30 mg (0.55 mmol) of sodium methoxide. The mixture was allowed to react for 1 h at room temperature. Then, the solvent was removed and a brown oil was obtained. The product was extracted with 15 mL of pentane, and the slurry was filtered through Kieselguhr. The solution was concentrated to dryness, and the product was isolated as a dark brown oil. Yield: 99 mg (73%). IR (Nujol, cm^{-1}): ν(Ph) 1583 (w). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.77−6.90 (m, 5H, Ph), 5.72 (d, $J_{H-P} = 14.7$, 1H, ═CH*H*$_{cis\ to\ P}$), 5.39 (d, $J_{H-P} = 32.5$, 1H, ═CH*H*$_{trans\ to\ P}$), 4.82 (s, 5H, C_5H_5), 1.86 (d, $J_{H-H} = 8.7$, 3H, PC(CH_3)═), 1.73 (m, 2H, PCH), 1.19 (dd, $J_{H-P} = 16.2$, $J_{H-H} = 7.0$, 6H, PCHC*H*$_3$), 0.90 (dd, $J_{H-P} = 14.5$, $J_{H-H} = 6.7$, 6H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 50.2 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 263.1 (d, $J_{C-P} = 14$, Os≡C), 150.5 (s, C_{ipso}Ph), 142.0 (d, $J_{C-P} = 33$, PC═), 128.5 and 128.3 (both s, Ph), 127.8 (s, ═CH_2), 126.8 (s, Ph), 76.4 (s, Cp), 28.1 (d, $J_{C-P} = 34$, PCH), 23.9 (d, $J_{C-P} = 10$, CH_3), 19.6 (d, $J_{C-P} = 4$, CH_3), 18.7 (s, CH_3). MS (FAB$^+$): *m/z* 504 ($M^+ + H$).

Preparation of OsH(η^5-C_5H_5){═C(OCH$_3$)Ph}{P^{i}Pr$_2$-[C(CH_3)═CH_2]} (11). An orange solution of **10** (125 mg, 0.25 mmol) in 5 mL of methanol was stirred for 2 h at room temperature. The solvent was removed, and the product was isolated as an orange oil. Yield: 105 mg (79%). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.21−6.96 (m, 5H, Ph), 5.49 (d, $J_{H-P} = 28.2$, 1H, ═CH*H*$_{trans\ to\ P}$), 5.28 (d, $J_{H-P} = 12.3$, 1H, ═CH*H*$_{cis\ to\ P}$), 4.79 (s, 5H, C_5H_5), 3.13 (s, 3H, OCH_3), 2.01 (d, $J_{H-P} = 8.7$, 4H, PC(CH_3)═ + PCH), 1.73 (m, 1H, PCH), 1.10−0.95 (12H, CH_3), − 14.98 (d, $J_{H-P} = 31.5$, 1H, Os-H). ^{31}P{^{1}H} NMR (121.42

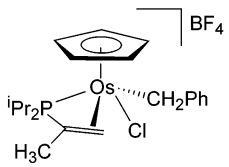
MHz, C_6D_6, 293 K): δ 44.7 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 244.6 (d, $J_{C-P} = 9$, Os=C), 160.5 (s, C_{ipso}-Ph), 143.0 (d, $J_{C-P} = 32$, PC=), 126.8, 125.6, and 122.7 (all s, Ph), 122.0 (d, $J_{C-P} = 4$, $=CH_2$), 83.3 (s, Cp), 58.0 (s, OCH_3), 28.5 (d, $J_{C-P} = 32$, PCH), 26.4 (d, $J_{C-P} = 31$, PCH), 19.5, 19.5, 18.8, 18.2, and 18.2 (all s, CH_3). MS (FAB^+): *m*/*z* 535 ($M^+ - H$).

Reaction of Os(η^5-C_5H_5)Cl(=CHPh){P^iPr_2[$C(CH_3)$=CH_2]} (2) with HBF_4. An NMR tube containing a bluish green solution of **2** (44 mg, 0.08 mmol) in 0.4 mL of CD_2Cl_2, at − 40 °C, was treated with HBF_4·Et_2O (11 μL, 0.08 mmol). The solution color changed immediately from green to dark red, and the NMR spectra showed the presence of the species **12**. Spectroscopic data for **12**: ^1H NMR (300 MHz, CD_2Cl_2, 233 K): δ 7.30−7.09 (m, 5H, Ph), 5.62 (s, 5H, C_5H_5), 4.92 (d, J_{H-P} = 10.7, 1H, =CH$H_{cis\ to\ P}$), 4.06 (dd, $J_{H-P} = 8.8$, $J_{gem} = 8.8$, 1H, CH_2Ph), 3.51 (d, $J_{H-P} = 32.7$, 1H, =CH$H_{trans\ to\ P}$), 3.12 (d, J_{gem} = 8.8, 1H, CH_2Ph), 2.90 (m, 1H, PCH), 2.50 (d, $J_{H-P} = 9.8$, 3H, PC(CH_3)=), 1.95 (m, 1H, PCH), 1.79−1.62 (9H, PCHCH_3), 1.48 (dd, $J_{H-P} = 20.8$, $J_{H-H} = 6.3$, 3H, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 233 K): δ − 7.2 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 233 K, plus APT, plus HSQC): δ 149.0 (s, C_{ipso}-Ph), 128.5, 127.8, and 125.3 (all s, Ph), 94.7 (s, Cp), 71.9 (d, $J_{C-P} = 20$, PC=), 40.0 (d, $J_{C-P} = 4$, $=CH_2$), 33.5 (d, $J_{C-P} = 28$, PCH), 26.7 (d, $J_{C-P} = 7$, CH_3), 20.2 (d, $J_{C-P} = 4$, CH_3), 19.7 (d, $J_{C-P} = 29$, PCH), 17.4 and 17.1 (both s, CH_3), 10.3 (d, J_{C-P} = 2, CH_3), 4.1 (d, $J_{C-P} = 5$, CH_2Ph).



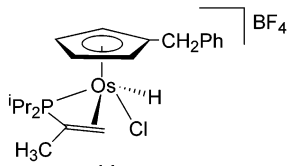
12

Isomerization of 12 into 13. The sample used to measure spectroscopic data for **12** was warmed to room temperature for 5 min. The entire transformation of **12** into **13** was observed. Spectroscopic data for **13**: ^1H NMR (300 MHz, CD_2Cl_2, 233 K): δ 7.30−7.14 (m, 5H, Ph), 5.62 (s, 5H, C_5H_5), 4.72 (d, $J_{H-P} = 12.3$, 1H, =CH$H_{cis\ to\ P}$), 3.57 (d, $J_{gem} = 8.4$, 1H, CH_2-Ph), 3.56 (d, $J_{H-P} = 34.2$, 1H, =CH$H_{trans\ to\ P}$), 3.21 (d, J_{gem} = 8.4, 2H, CH_2Ph + PCH), 2.54 (d, $J_{H-P} = 9.6$, 3H, PC(CH_3)=), 1.95 (m, 1H, PCH), 1.70 (dd, $J_{H-P} = 17.0$, $J_{H-H} = 7.4$, 3H, PCHCH_3), 1.65 (dd, $J_{H-P} = 17.0$, $J_{H-H} = 7.4$, 3H, PCHCH_3), 1.52 (dd, $J_{H-P} = 13.1$, $J_{H-H} = 7.0$, 3H, PCHCH_3), 1.46 (dd, J_{H-P} = 20.4, $J_{H-H} = 7.0$, 3H, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 233 K): δ − 12.2 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 233 K, plus APT, plus HSQC): δ 149.4 (s, C_{ipso}Ph), 128.6, 128.4, and 125.9 (all s, Ph), 92.5 (s, Cp), 69.7 (d, $J_{C-P} = 19$, PC=), 44.1 (s, $=CH_2$), 29.0 (d, $J_{C-P} = 25$, PCH), 26.6 (d, J_{C-P} = 8, CH_3), 21.6 (d, $J_{C-P} = 29$, PCH), 19.8 (d, $J_{C-P} = 5$, CH_3), 18.8 (d, $J_{C-P} = 10$, CH_2Ph), 18.4, 17.7, and 10.9 (all s, CH_3). The sample used to measure spectroscopic data for **13** was kept at room temperature for 72 h. After that period of time, the quantitative formation of [Os(η^5-C_5H_5)(CH_2Ph)Cl{[η^2-CH_2=C(CH_3)]P^iPr_2}]BF_4 (**14**) was observed.



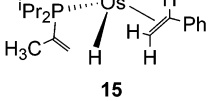
13

Preparation of [Os(η^5-C_5H_5)(CH_2Ph)Cl{[η^2-CH_2=C(CH_3)]P^iPr_2}]BF_4 (14). A bluish green solution of **2** (210 mg, 0.39 mmol) in 10 mL of dichloromethane was treated with HBF_4·Et_2O (53 μL, 0.39 mmol). The resulting yellowish solution was stirred for 72 h at room temperature and then was concentrated almost to dryness. The addition of diethyl ether (7 mL) caused the formation of a yellow solid. The solid was washed with diethyl ether and dried in vacuo. Yield: 197 mg (81%). Anal. Calcd for $C_{21}H_{31}BClF_4OsP$: C, 40.23; H, 4.98. Found: C, 39.91; H, 4.68. IR (Nujol, cm^{-1}): $\nu(BF_4)$ 1062 (s). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.43−7.23 (m, 5H, Ph), 6.28−5.36 (ABCD spin system, 4H, C_5H_4), 4.70 (dd, J_{H-P} = 10.9, $J_{H-H} = 1.7$, 1H, =CH$H_{cis\ to\ P}$), 3.77 (AB spin system, $\Delta\nu$ = 57.0, $J_{A-B} = 16.2$, 2H, CH_2Ph), 3.53 (dd, $J_{H-P} = 26.6$, J_{H-H} = 1.7, 1H, =CH$H_{trans\ to\ P}$), 2.80 (m, 1H, PCH), 2.57 (d, J_{H-P} = 9.9, 3H, PC(CH_3)=), 2.05 (m, 1H, PCH), 1.69−1.21 (12H, PCHCH_3), −11.67 (d, $J_{H-P} = 26.7$, 1H, Os-H). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 13.6 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 293 K, plus APT, plus HSQC): δ 136.6 (s, C_{ipso}-Ph), 129.8, 129.4, and 127.8 (all s, Ph), 126.7 (s, C_{ipso}Cp), 102.4, 84.3, 81.5, and 74.6 (all s, Cp), 72.1 (d, $J_{C-P} = 22$, PC=), 43.2 (d, $J_{C-P} = 5$, $=CH_2$), 34.5 (s, CH_2Ph), 32.3 (d, $J_{C-P} = 37$, PCH), 29.1 (d, $J_{C-P} = 24$, PCH), 22.2 (d, $J_{C-P} = 3$, CH_3), 18.8 and 17.8 (both s, CH_3), 16.3 (d, $J_{C-P} = 2$, CH_3). MS (FAB^+): *m*/*z* 540 ($M^+ - H$); 541 (M^+).



14

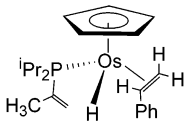
Preparation of [OsH(η^5-C_5H_5)(η^2-CH_2=CHPh){P^iPr_2[$C(CH_3)$=CH_2]}] (15). A bluish green solution of **2** (261 mg, 0.48 mmol) in 10 mL of tetrahydrofuran at 0 °C was treated with methyllithium (0.45 mL, 0.72 mmol) 1.6 M in diethyl ether. Immediately, the reaction mixture became orange. It was allowed to react at 0 °C for 30 min. Then, the solvent was removed, and the resultant oil was extracted with pentane (15 mL) and filtered through Kieselguhr. The pentane solution was concentrated to dryness, and **15** was obtained as an orange oil. Yield: 150.7 mg (60%). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.27−6.95 (m, 5H, Ph), 5.65 (dd, $J_{H-P} = 14.7$, $J_{H-H} = 1.8$, 1H, =CH$H_{cis\ to\ P}$), 5.55 (dd, $J_{H-P} = 32.5$, $J_{H-H} = 1.8$, 1H, = CH$H_{trans\ to\ P}$), 4.51 (s, 5H, C_5H_5), 3.24 (ddd, $J_{H-P} = 8.1$, J_{trans} = 7.5, $J_{cis} = 6.6$, 1H, =CHPh), 2.93 (dd, $J_{trans} = 7.5$, $J_{gem} = 3.6$, 1H, =CH$H_{cis\ to\ Ph}$), 2.30 (ddd, $J_{cis} = 6.6$, $J_{gem} = J_{H-Hhyd} = 3.6$, 1H, =CH$H_{trans\ to\ Ph}$), 1.99 (m, 1H, PCH), 1.84 (m, 1H, PCH), 1.75 (d, $J_{H-P} = 7.8$, 3H, PC(CH_3)=), 1.07 (dd, $J_{H-P} = 13.8$, J_{H-H} = 6.9, 3H, PCHCH_3), 0.95−0.84 (9H, PCHCH_3), −15.96 (dd, $J_{H-P} = 34.2$, $J_{H-H} = 3.6$, 1H, Os-H). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 39.1 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT, plus HSQC): δ 153.6 (s, C_{ipso}Ph), 140.9 (d, $J_{C-P} = 32$, PC=), 128.9 (d, $J_{C-P} = 11$, PC=CH_2), 128.1, 125.4, and 122.9 (all s, Ph), 80.4 (s, Cp), 30.0 (d, $J_{C-P} = 31$, PCH), 28.5 (d, $J_{C-P} = 32$, PCH), 23.2 (s, =CHPh), 21.2 (d, $J_{C-P} = 6$, CH_3), 20.4, 20.1, 19.9, and 19.7 (all s, CH_3), 3.4 (s, $=CH_2$). MS (FAB^+): *m*/*z* 520 (M^+).



15

Isomerization of 15 into 16. An orange solution of **15** (40 mg, 0.08 mmol) in 0.4 mL of benzene-d_6 was heated to 80 °C for 24 h. The NMR spectra showed the presence of **15** and **16** in a molar ratio 3:8. Spectroscopic data for **16**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.35−6.93 (m, 5H, Ph), 5.56 (dd, J_{H-P} =

14.8, $J_{H-H} = 2.2$, 1H, $=CH H_{cis\ to\ P}$), 5.45 (dd, $J_{H-P} = 33.0$, $J_{H-H} = 2.2$, 1H, $=CH H_{trans\ to\ P}$), 4.49 (s, 5H, C_5H_5), 3.78 (ddd, $J_{H-Hhyd} = 2.4$, $J_{trans} = 9.4$, $J_{cis} = 7.3$, 1H, $=CH Ph$), 2.98 (ddd, $J_{H-P} = 2.9$, $J_{trans} = 9.4$, $J_{gem} = 3.0$, 1H, $=CH H_{cis\ to\ Ph}$), 1.83 (m, 1H, PCH), 1.70 (d, $J_{H-P} = 7.8$, 4H, $PC(CH_3)= + PCH$), 1.21 (ddd, $J_{H-P} = 10.5$, $J_{cis} = 7.3$, $J_{gem} = 3.0$, 1H, $=CH H_{trans\ to\ Ph}$), 1.07 (dd, $J_{H-P} = 13.8$, $J_{H-H} = 6.9$, 3H, $PCHCH_3$), 0.89 (dd, $J_{H-P} = 14.1$, $J_{H-H} = 7.2$, 3H, $PCHCH_3$), 0.86 (dd, $J_{H-P} = 13.2$, $J_{H-H} = 7.2$, 3H, $PCHCH_3$), 0.76 (dd, $J_{H-P} = 13.8$, $J_{H-H} = 7.2$, 3H, $PCHCH_3$), −15.23 (dd, $J_{H-P} = 32.8$, $J_{H-H} = 2.4$, 1H, Os−H). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 40.0 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT, plus HSQC): δ 152.6 (s, $C_{ipso}Ph$), 140.3 (d, $J_{C-P} = 33$, $PC=$), 128.6 (d, $J_{C-P} = 10$, $PC=CH_2$), 127.7, 126.4, and 122.7 (all s, Ph), 80.3 (s, Cp), 29.4 (d, $J_{C-P} = 32$, PCH), 25.6 (d, $J_{C-P} = 31$, PCH), 24.8 (s, $=CHPh$), 21.7 (d, $J_{C-P} = 6$, CH_3), 19.8 (d, $J_{C-P} = 2$, CH_3), 19.4 (d, $J_{C-P} = 2$, CH_3), 19.3 and 19.1 (both s, CH_3), 2.2 (d, $J_{C-P} = 5$, $=CH_2$). MS (FAB^+): m/z 431 ($M^+ - C_7H_6 + H$).



16

Kinetic Analysis. The isomerization of complex **6** into **4** was followed quantitatively by ^1H NMR spectroscopy in acetone-d_6. The decrease of the intensity of the hydride ligand of **6** was measured automatically at intervals in a Varian Gemini 2000 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 $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained by least-squares fit of the Eyring plot. Error analysis assumed a 3.1% error in the rate constants (the maximum value found in the experimental determinations) and 1 K in the temperature. Errors were computed by published methods.[23]

Structural Analysis of Complexes 2 and 4. Crystals suitable for the X-ray diffraction were obtained by cooling at 4 °C a solution of **2** in pentane and by slow diffusion of diethyl ether into a concentrated solution of **4** in dichloromethane. X-ray data were collected for both complexes at low temperature on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using ω scans. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[24] The structures for the two compounds were solved by direct methods. Refinement, by full-matrix least squares on F^2 with SHELXL97,[25] was similar for both complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen atoms. The hydride ligand of **4** was located and refined freely. The rest of the hydrogen atoms were observed or calculated and refined freely or using a restricted riding mode in the last cycles of refinement. All the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense.

A summary of crystal data and data collection and refinement details is reported in Table 4.

Table 4. Crystal Data and Data Collection and Refinement for 2 and 4

	2	**4**
Crystal Data		
formula	$C_{21}H_{30}ClOsP$	$C_{21}H_{30}F_6OsP_2$
molecular wt	539.07	648.59
color and habit	dark red, irregular block	yellow, irregular prism
size, mm	0.14, 0.12, 0.04	0.18, 0.08, 0.02
symmetry, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$
a, Å	12.189(3)	8.3356(13)
b, Å	13.368(4)	16.209(3)
c, Å	13.614(4)	17.149(3)
α, deg	101.590(5)	
β, deg	102.886(5)	101.913(3)
γ, deg	102.962(5)	
V, Å^3	2032.7(10)	2267.2(6)
Z	4	4
D_{calc}, g cm^{-3}	1.761	1.900
Data Collection and Refinement		
diffractometer	Bruker Smart APEX	
λ(Mo Kα), Å	0.71073	
monochromator	graphite oriented	
scan type	ω scans	
μ, mm^{-1}	6.483	5.82
2θ, range, deg	3, 57	3, 57
temp, K	100.0(2)	100.0(2)
no. of data collect	24 928	27 240
no. of unique data	9454 ($R_{int} = 0.0396$)	5460 ($R_{int} = 0.0406$)
no. of params/ restraints	449/0	289/0
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0299	0.0236
wR_2[b] [all data]	0.0523	0.0419
S[c] [all data]	0.840	0.884

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

Acknowledgment. Financial support from the MCYT of Spain (Proyects BQU2002-00606 and PPQ2000-0488-P4-02) is acknowledged.

Supporting Information Available: Crystal structure determinations, including bond lengths and angles of compounds **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0496075

(23) Morse, P. M.; Spencer, M. O.; Wilson, S. R.; Girolami; G. S. *Organometallics* **1994**, *13*, 1646.
(24) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38. *SADABS*: Area-detector absorption correction; Bruker-AXS: Madison, WI, 1996.
(25) *SHELXTL* Package v. 6.10; Bruker-AXS: Madison, WI, 2000. Sheldrick, G. M. *SHELXS-86* and *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.