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Reactivity of $OsH_2Cl_2(P^iPr_3)_2$ toward Diolefins: New Reactions Involving C−H and C−C Activation and C−C and C−P Bond Formation Processes

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The dihydrido-dichloro complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) reacts with 1,5-cyclooctadiene in toluene under reflux to give the isopropenylphosphine derivative $OsCl_2(\eta^4\text{-COD})\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**2**), which has been characterized by X-ray diffraction analysis. The coordination geometry around the osmium atom of **2** can be rationalized as a highly distorted octahedron. The distortion is due to the ring constraint imposed by the bidentate isopropenylphosphine ligand, which acts with a bite angle of 56.0(1)°. In toluene at 85 °C, the reaction of **1** with 1,5-cyclooctadiene leads to the hydrido compound $OsHCl_2(\eta^4\text{-}C_8H_{11}P^iPr_3)(P^iPr_3)$ (**3**). The molecular structure of this complex has also been determined by an X-ray investigation. The X-ray diffraction analysis of **3** demonstrates the η^4-binding mode of the carbocyclic ligand $[C_8H_{11}P^iPr_3]^+$. The coordination geometry around the osmium center can be rationalized as a distorted octahedron with the triisopropylphosphine, a chlorine atom, and the carbocyclic ligand forming the equatorial plane. Complex **3** reacts with 1,5-cyclooctadiene and 2,5-norbornadiene (NBD) to give **2** and $OsCl_2(\eta^4\text{-NBD})\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**8**), respectively. Complex **8** can also be obtained, under refluxing toluene, from **1** and 2,5-norbornadiene. Similarly, the reaction of **1** with tetrafluorobenzobarrelene (TFB) affords a mixture of the propenylphosphine isomers $OsCl_2(\eta^4\text{-TFB})\{(\eta^2\text{-}CH_2{=}CHCH_2)P^iPr_2\}$ (**9**) and $OsCl_2(\eta^4\text{-TFB})\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**10**), which can also be prepared from **3** and tetrafluorobenzobarrelene. The molecular structure of **9** has been determined by X-ray diffraction analysis. The coordination geometry around the osmium can be described as a distorted octahedron, and as for **2**, the distortion is mainly due to the ring constraint imposed by the bidentate olefin−phosphine ligand, which in this case acts with a bite angle of 74.8(1)°.

Introduction

The complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) is an unusual example of a six-coordinate osmium(IV) molecule, which is prepared by reaction of $OsCl_3{\cdot}xH_2O$ with triisopropylphosphine in refluxing 2-propanol. Its solid-state structure, significantly distorted from octahedral, has only a C_2 symmetry and can be described as a square antiprism with two missing vertices.[1] In solution, it exist as two rapidly interconverting isomers, one having C_2 symmetry and the other with no symmetry.[2]

For this complex, several interesting reactions have been reported. Under hydrogen atmosphere, the reversible coordination of molecular hydrogen affords the nonclassical complex $OsH_4Cl_2(P^iPr_3)_2$, which upon further reaction with hydrogen, rapidly eliminates HCl to form a new d^4 dihydrogen complex $OsH_3Cl(\eta^2\text{-}H_2)(P^iPr_3)_2$ or under basic conditions, affords $OsH_6(P^iPr_3)_2$ and $[OsH_5(P^iPr_3)_2]^-$.[3] Under inert atmosphere, the protonation of **1** with CF_3SO_3H in diethyl ether or dichloromethane yields $[Os_2H_4(\mu{-}Cl)_3(P^iPr_3)_4]CF_3SO_3$, which has been characterized by X-ray diffraction analysis.[4]

Complex **1** is also a useful starting material to prepare new and unusual dihydrogen derivatives. Thus, the reactions of this complex with anionic and neutral bidentate and neutral monodentate nucleophilic ligands lead to $Os(\eta^2\text{-}H_2)$ derivatives. These transformations are a result of the rearrangement of the coordination polyhedron, which changes from a square antiprism with two vacant coordination sites in the starting molecule to an octahedron in the dihydrogen derivatives.[5] The tendency of this compound to form dihydrogen complexes appears to determine its reactivity toward terminal alkynes, 1-alkyn-3-ols, and unsaturated alkynes. The reactions of **1** with terminal alkynes lead to hydrido−carbyne compounds, while hydrido−vinylcarbyne derivatives are formed from 1-alkyn-3-ols and unsaturated alkynes. Dihydrogen−vinylidene−osmium(II) species have been proposed as the key intermediates of these processes; thus, the reactions are rationalized as the electrophilic attack of the acidic hydrogen proton

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(1) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288.

(2) Gusev, D. G.; Kuhlman, R.; Rambo, J. R.; Berke, H.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 281.

(3) (a) Gusev, D. G.; Kuznetsov, V. F.; Eremenko, I. L.; Berke, H. *J. Am. Chem. Soc.* **1993**, *115*, 5831. (b) Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.

(4) Kuhlman, R.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 1788.

(5) (a) Esteruelas, M. A.; Oro, L. A.; Ruiz, N. *Inorg. Chem.* **1993**, *32*, 3793. (b) Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Oñate, E.; Ruiz, N. *Inorg. Chem.* **1994**, *33*, 787.

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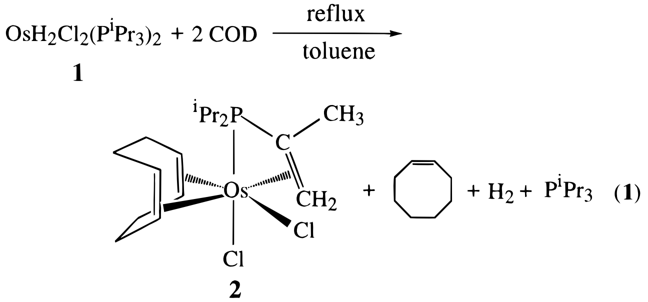
of the dihydrogen ligand on the β−C atom of the vinylidene group.[6]

Complex **1** has also been shown to catalyze the reduction of ketones, olefins, and diolefins.[1] The reduction of ketones is carried out under hydrogen transfer conditions from 2-propanol and in the presence of $NaBH_4$. Under these conditions, complex **1** reacts with $NaBH_4$ to afford $OsH_3(\eta^2\text{-}H_2BH_2)(P^iPr_3)_2$, which decomposes to the catalyst precursor $OsH_6(P^iPr_3)_2$.[7] The reduction of olefins and diolefins occurs under hydrogen atmosphere, and the hydrogenation rates depend on both the solvent and the substrate.[1,8] For the diolefin hydrogenation, the rate law changes during the processes. These changes cannot be rationalized on the basis of the previously mentioned reactions of **1** with molecular hydrogen. This prompted us to explore the reactivity of the complex toward diolefins. During this study, we have discovered a new and unusual reaction pattern between a transition metal−hydrido compound and diolefins, including the transformation of the triisopropylphosphine ligand into new phosphine ligands within the coordination sphere of the metal. More importantly, the new reactions involve C−H and C−C bond activation and C−C and C−P bond formation.

In this paper, we report the results obtained from the study of the reactivity of the complex $OsH_2Cl_2(P^iPr_3)_2$ toward 1,5-cyclooctadiene (COD), 2,5-norbornadiene (NBD), and tetrafluorobenzobarrelene (TFB).

Results and Discussion

Reactions of $OsH_2Cl_2(P^iPr_3)_2$ with 1,5-Cyclooctadiene. Treatment of a refluxing solution of **1** in toluene with 1,5-cyclooctadiene in a 1:3 molar ratio for 5 h leads to a brown solution. Analysis by gas chromatography of this solution reveals the presence of cyclooctene and 1,5-cyclooctadiene in approximately a 1:1 molar ratio. Following removal of the solvent, the $^{31}P\{^1H\}$ NMR spectrum of the residue in benzene-d_6 shows two singlets at 19.7 and −16.5 ppm. The first singlet is due to free triisopropylphosphine, and the second singlet corresponds to the isopropenylphosphine complex $OsCl_2(\eta^4\text{-COD})\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**2**), which is formed according to eq 1 by dehydrogenation of an isopropyl group of a triisopropylphosphine ligand of **1** in the presence of 1,5-cyclooctadiene. Although the hydrogen transfer from alkanes to olefins in the presence of transition metal complexes is a relatively well-studied process[8,9] and the dehydrogenation of coordinated cycloalkylphosphines has been previously reported,[10] the hydrogen transfer from alkanes to diolefins and the dehydrogenation of an acyclic alkylphosphine to give α-vinylphosphines have no precedent.



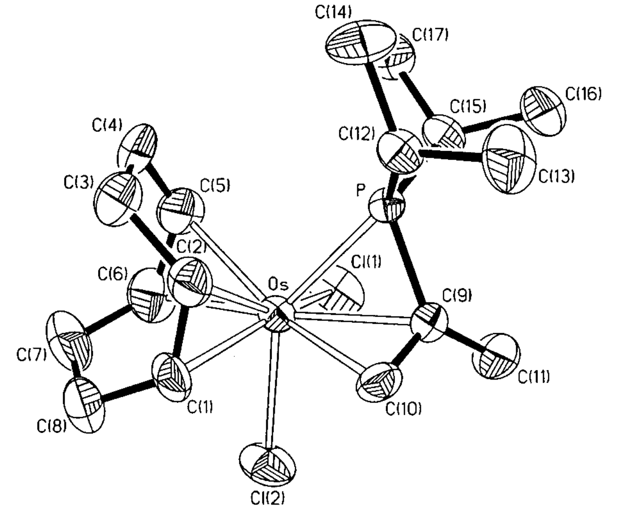


Figure 1. Molecular diagram of $OsCl_2(\eta^4\text{-COD})\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**2**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for $OsCl_2(\eta^4\text{-COD})\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (2)

Os−Cl(1)	2.439(1)	P−C(15)	1.846(4)
Os−Cl(2)	2.459(1)	C(1)−C(2)	1.406(6)
Os−P	2.347(1)	C(1)−C(8)	1.525(8)
Os−C(1)	2.221(5)	C(2)−C(3)	1.514(9)
Os−C(2)	2.244(5)	C(3)−C(4)	1.530(8)
Os−C(5)	2.230(5)	C(4)−C(5)	1.498(8)
Os−C(6)	2.202(6)	C(5)−C(6)	1.407(7)
Os−C(9)	2.284(5)	C(6)−C(7)	1.515(11)
Os−C(10)	2.259(5)	C(7)−C(8)	1.527(8)
P−C(9)	1.794(4)	C(9)−C(10)	1.413(6)
P−C(12)	1.844(4)	C(9)−C(11)	1.505(8)
Cl(1)−Os−Cl(2)	81.50(4)	M(1)−Os−M(2)[a]	96.4(2)
Cl(1)−Os−P	86.08(4)	M(1)−Os−M(3)[a]	167.9(2)
Cl(1)−Os−M(1)[a]	99.0(1)	M(2)−Os−M(3)[a]	82.7(2)
Cl(1)−Os−M(2)[a]	164.6(1)	Os−P−C(9)	65.4(1)
Cl(1)−Os−M(3)[a]	82.4(2)	Os−P−C(12)	123.6(1)
Cl(2)−Os−P	140.84(4)	Os−P−C(15)	122.2(1)
Cl(2)−Os−M(1)[a]	89.5(1)	C(9)−P−C(12)	111.7(2)
Cl(2)−Os−M(2)[a]	98.4(1)	C(9)−P−C(15)	109.9(2)
Cl(2)−Os−M(3)[a]	102.6(2)	C(12)−P−C(15)	111.7(2)
P−Os−M(1)[a]	56.0(1)	P−C(9)−C(10)	108.0(3)
P−Os−M(2)[a]	102.9(1)	P−C(9)−C(11)	128.1(3)
P−Os−M(3)[a]	112.3(2)	C(10)−C(9)−C(11)	123.8(4)

[a] M(1), M(2), and M(3) are the midpoints of the olefin double bonds C(9)−C(10), C(1)−C(2), and C(5)−C(6), respectively.

After pentane extraction of the residue and cooling at −78 °C of the resulting solution, complex **2** was isolated as a yellow solid and characterized by elemental analysis, IR ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies, and X-ray diffraction. The molecular structure of **2** is presented in Figure 1. Selected bond distances and angles are listed in Table 1.

Complexes containing $R_2PC(R'){=}CH_2$ ligands are rare. In those complexes previously reported, the vi-

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(6) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683.

(7) Esteruelas, M. A.; Jean, Y.; Lledós, A.; Oro, L. A.; Ruiz, N.; Volatron, F. *Inorg. Chem.* **1994**, *33*, 3609.

(8) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publishers: Dordrecht, 1994; Chapter 2.

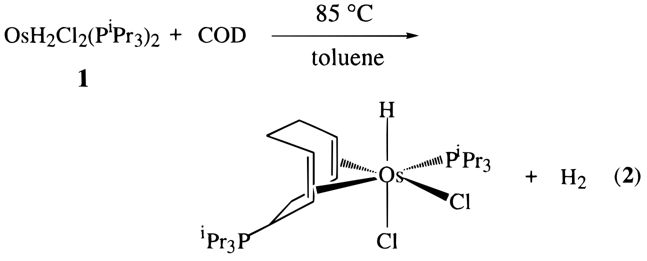
(9) (a) Crabtree, R. H.; *Chem. Rev.* **1985**, *85*, 245. (b) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025. (c) Aoki, T.; Crabtree, R. H. *Organometallics* **1993**, *12*, 294.

(10) (a) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978**, *152*, 347. (b) Arliguie, T.; Chaudret, B.; Jalon, F.; Lahoz, F. J. *J. Chem. Soc., Chem. Commun.* **1988**, 998. (c) Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5527.

nylphosphine acts as a monodentate ligand,[11] a bridge for two metal centers,[12] and a chelating ligand (η^3-phosphaallyl).[13] Complex **2** is the first osmium compound stabilized by a chelating vinylphosphine ligand. The coordination geometry around the osmium atom of **2** could be rationalized as being derived from a highly distorted octahedron. The distortion is due to the ring constraint imposed by the bidentate isopropenylphosphine ligand, which acts with a bite angle of 56.0(1)°. The phosphorus atom is situated *pseudo-trans* to one of the two chlorine atoms (Cl(2); P−Os−Cl(2) = 140.84(4)°), at opposite sides of an ideal coordination plane defined by the other chlorine atom (Cl(1)) and the midpoint of the olefinic C(1)−C(2), C(5)−C(6), and C(9)−C(10) bonds. If M(1) is the midpoint of the C(9)−C(10) bond and M(2) and M(3) are the midpoints of the olefinic cyclooctadiene C(1)−C(2) and C(5)−C(6) bonds, respectively, the deviations of M(1), M(2), M(3), and Cl(1) from a mean plane passing through them are −0.144(4), 0.047(4), −0.299(5), and 0.003(1) Å, respectively, with the osmium atom deviating from this plane by 0.0005(2) Å. The olefinic carbon atoms of the isopropenylphosphine ligand (C(9) and C(10)) are out of this coordination plane; C(9) is shifted toward the phosphorus atom by 0.504(4) Å, while C(10) is shifted toward Cl(2) by 0.215(4) Å. Thus, the dihedral angle between the coordination plane and the C(9)−C(10) bond is 30.6(2) Å. The C(9)−C(10) distance (1.413(6) Å) is statistically identical with the bond lengths of the coordinated double bonds C(1)−C(2) (1.406(6) Å) and C(5)−C(6) (1.407(7) Å) of the 1,5-cyclooctadiene ligand, which takes its customary "tub" conformation. These distances are greater than those found in the free 1,5-cyclooctadiene molecule (1.34 Å),[14] in agreement with the usual Chatt, Dewar, and Duncanson metal−olefin bonding scheme. The P−C(9) distance (1.794(4) Å) is about 0.05 Å shorter than the P−C(12) (1.844(4) Å) and P−C(15) (1.846(4) Å) bond lengths. In accordance with the sp^2 hybridization for C(9), the angles P−C(9)−C(11) and C(10)−C(9)−C(11) are 128.1(3)° and 123.8(4)°, respectively. In addition, the Os−Cl(1) distance (Cl *trans* to C(1)−C(2), 2.439(1) Å) is shorter than the Os−Cl(2) distance (Cl *trans* to P, 2.459(1) Å), possibly due to the different *trans* influence of the olefin and phosphine groups.

The disposition of the ligands, as shown in Figure 1, leaves the molecule with no overall symmetry. In agreement with this, the ^{1}H NMR spectrum of **2** contains, between 5.2 and 1.5 ppm, 12 signals for the inequivalent protons of the 1,5-cyclooctadiene ligand and the ^{13}C{^{1}H} shows 4 resonances for the olefinic carbon atoms and 4 resonances for the CH$_2$ carbon atoms of the diolefin, between 86 and 72 ppm and between 40 and 24 ppm, respectively. In the ^{1}H NMR spectrum, the most noticeable phosphine signals are those corresponding to the isopropenyl protons, which appear as doublets at 3.81 (CH= *trans* to P), 2.46 (−CH$_3$), and 2.31 (CH= *cis* to P) ppm, with P−H coupling constants of 34.2, 8.1, and 11.6 Hz, respectively. In the ^{13}C{^{1}H} NMR spectrum, the carbon atoms of the isopropenyl group give rise to doublets at 77.7 (P−C=), 71.3 (=CH$_2$), and 24.3 (−CH$_3$) ppm, with P−C coupling constants of 22.0, 4.6, and 6.9 Hz, respectively.

Previously, it has been reported that the thermolytic decomposition of RuH(η^5-C$_5$Me$_5$)(η^2-CH$_2$=SiR$_2$)(PCy$_3$) affords HSiMeR$_2$ (R = Ph, Me) and the dicyclohexyl(cyclohexenyl)phosphine complex RuH(η^5-C$_5$Me$_5$){(η^2-C$_6$H$_9$)PCy$_2$}.[10c] This reaction appears to involve migration of the hydride to produce 16-electron intermediate silyl complexes Ru(η^5-C$_5$Me$_5$){Si(Me)R$_2$}(PCy$_3$), which then undergo cyclometallation to form the final product. In favor of this proposal, it has also been observed that the thermolytic decomposition of the related compound RuH(η^5-C$_5$Me$_5$)(η^2-CH$_2$=SiPh$_2$)(P^{i}Pr$_3$) gives the metallated complex RuH(η^5-C$_5$Me$_5$){Si(Me)Ph$_2$}{P[C(Me)H-CH$_2$]^{i}Pr$_2$}, which is stable. This stability prompted us to carry out the reaction of **1** with 1,5-cyclooctadiene at a lower temperature than that used in the reaction shown in eq 1. Treatment of a toluene solution of **1** with 1,5-cyclooctadiene in a 1:3 molar ratio at 85 °C leads, after 3 days, to a white precipitate and a brown solution. The isolated white solid (47%) was characterized as the complex OsHCl$_2$(η^4-C$_8$H$_{11}$P^{i}Pr$_3$)(P^{i}Pr$_3$) (**3**) by elemental analysis, IR, ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopies, and X-ray diffraction (vide infra). Analysis by gas chromatography of the brown toluene solution reveals the presence of 1,5-cyclooctadiene and cyclooctene in approximately a 6:1 molar ratio. The brown toluene solution affords a sticky residue after solvent removal. The ^{31}P{^{1}H} NMR spectrum of the residue in chloroform-*d* shows the presence of complexes **1**, **2**, and **3** in a 1:3.5:3 molar ratio. This suggests that at 85 °C, the reaction of **1** with 1,5-cyclooctadiene leads to complexes **2** (eq 1) and **3** (eq 2) in approximately 30% and 65% yield, respectively.



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The single-crystal X-ray diffraction analysis of **3** shows the η^4-binding mode of the unusual carbocyclic ligand [C$_8$H$_{11}$P^{i}Pr$_3$]$^+$. The coordination geometry about the osmium center can be rationalized as a distorted octahedron with the phosphorus atom of the triisopropylphosphine ligand, a chlorine atom Cl(1), mutually *cis* disposed (Cl(1)−Os−P(2) = 94.0(1)°), and the carbocyclic ligand forming the equatorial plane. The apical positions are occupied by the other chlorine atom (Cl(2)) and the hydrido ligand (Figure 2), which could not be

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[11] (a) Holt, M. S.; Nelson, J. H.; Alcock, N. W. *Inorg. Chem.* **1986**, *25*, 2288. (b) Rahn, J. A.; Holt, M. S.; O'Neil-Johnson, M.; Nelson, J. H. *Inorg. Chem.* **1988**, *27*, 1316. (c) Rahn, J. A.; DeCian, A.; Nelson, J. H. *Inorg. Chem.* **1989**, *28*, 215. (d) Rahn, J. A.; Holt, M. S.; Gray, G. A.; Alcock, N. W.; Nelson, J. H. *Inorg. Chem.* **1989**, *28*, 217. (e) Bhaduri, D.; Nelson, J. H.; Day, C. L.; Jacobson, R. A.; Solujić, L.; Milosavljević, E. B. *Organometallics* **1992**, *11*, 4069. (f) Adams, H.; Bailey, N. A.; Blenkiron, P.; Morris, M. J. *J. Organomet. Chem.* **1993**, *460*, 73. (g) Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *Inorg. Chim. Acta* **1994**, *220*, 201.

[12] (a) Hogarth, G. *J. Organomet. Chem.* **1991**, *407*, 91. (b) Wilson, W. L.; Nelson, J. H.; Alcock, N. W. *Organometallics* **1990**, *9*, 1699. (c) Doyle, M. J.; Duckworth, T. J.; Manojlovic-Muir, L.; Mays, M. J.; Raithby, P. R.; Robertson, F. J. *J. Chem. Soc., Dalton Trans.* **1992**, 2703. (d) Acurm, G. A.; Mays, M. J.; Raithby, P. R.; Solan, G. A. *J. Organomet. Chem.* **1996**, *508*, 137.

[13] Ji, H.; Nelson, J. H.; DeCian, A.; Fischer, J.; Solujic, L.; Milosavijevic, E. B. *Organometallics* **1992**, *11*, 401.

[14] Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1973**, *12*, 531.

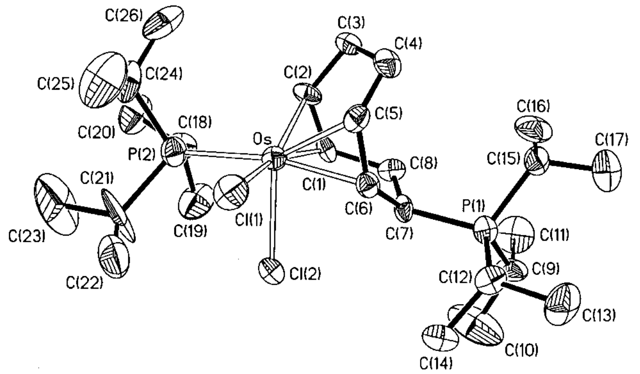

Figure 2. Molecular diagram of $OsHCl_2(\eta^4\text{-}C_8H_{11}P^iPr_3)(P^iPr_3)$ (**3**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $OsHCl_2(\eta^4\text{-}C_8H_{11}P^iPr_3)(P^iPr_3)$ (3)

Os−Cl(1)	2.478(4)	P(2)−C(18)	1.88(2)
Os−Cl(2)	2.551(4)	P(2)−C(21)	1.85(3)
Os−P(2)	2.418(4)	P(2)−C(24)	1.86(2)
Os−C(1)	2.15(1)	C(1)−C(2)	1.38(2)
Os−C(2)	2.15(1)	C(1)−C(8)	1.56(2)
Os−C(5)	2.19(1)	C(2)−C(3)	1.53(2)
Os−C(6)	2.19(1)	C(3)−C(4)	1.55(2)
P(1)−C(7)	1.84(1)	C(4)−C(5)	1.52(2)
P(1)−C(9)	1.82(2)	C(5)−C(6)	1.44(2)
P(1)−C(12)	1.83(1)	C(6)−C(7)	1.54(2)
P(1)−C(15)	1.84(1)	C(7)−C(8)	1.53(2)

Cl(1)−Os−Cl(2)	87.2(1)	C(9)−P(1)−C(12)	111.7(7)
Cl(1)−Os−P(2)	94.0(1)	C(9)−P(1)−C(15)	107.0(7)
Cl(1)−Os−M(1)[a]	167.6(4)	C(12)−P(1)−C(15)	108.5(7)
Cl(1)−Os−M(2)[a]	84.6(4)	Os−P(2)−C(18)	113.0(5)
Cl(2)−Os−P(2)	86.4(1)	Os−P(2)−C(21)	118.6(7)
Cl(2)−Os−M(1)[a]	102.0(4)	Os−P(2)−C(24)	113.5(6)
Cl(2)−Os−M(2)[a]	101.4(4)	C(18)−P(2)−C(21)	102.5(9)
P(2)−Os−M(1)[a]	94.8(4)	C(18)−P(2)−C(24)	103.3(7)
P(2)−Os−M(2)[a]	172.0(4)	C(21)−P(2)−C(24)	104.3(8)
M(1)−Os−M(2)[a]	85.5(5)	C(6)−C(7)−C(8)	112.6(10)
C(7)−P(1)−C(9)	110.0(7)	C(6)−C(7)−P(1)	113.7(9)
C(7)−P(1)−C(12)	107.3(6)	C(8)−C(7)−P(1)	116.9(9)
C(7)−P(1)−C(15)	112.4(6)		

[a] M(1) and M(2) are the midpoints of the olefin double bonds C(1)−C(2) and C(5)−C(6), respectively.

accurately located. The presence of the hydrido ligand in the complex is confirmed from the IR and ^1H NMR spectra. The IR spectrum of **3** in Nujol shows a strong ν(Os−H) absorption at 2140 cm^{-1}, while the ^1H NMR spectrum in dichloromethane-d_2 contains a doublet at −10.46 ppm, with a P−H coupling constant of 21.9 Hz.

Table 2 lists selected bond distances and angles for the structure of **3**. The C(5)−C(6) bond distance (1.44(2) Å) is about 0.03 Å longer than those found in **2** for the coordinated olefinic bonds (between 1.406(6) and 1.413(6) Å), while the C(1)−C(2) bond length (1.38(2) Å) is about 0.03 Å shorter. Furthermore, the Os−C(1) and Os−C(2) distances (both 2.15(1) Å) are 0.04 Å shorter than the Os−C(5) and Os−C(6) distances (both 2.19(1) Å). Thus, we observe the carbon atoms of the longest carbon−carbon double bond possess the longest bonds to the osmium atom. Interestingly, P(1) is bonded to C(7), the α-carbon atom with regard to the C(5)−C(6) olefinic bond, but the β-carbon atom with regard to the C(2)−C(1) double bond. Thus, the P^iPr_3 group of the carbocyclic ligand seems to have a significant influence on the structural parameters of the metal−olefin bonds of the $Os(\eta^4\text{-}C_8H_{11}P^iPr_3)$ unit. A similar situation has been previously observed for the complexes $[Fe(\eta^4\text{-}C_7H_9\text{-}5\text{-}exo\text{-}\eta^1\text{-dppm})(CO)_3]BF_4$[15] and $[Fe(\eta^4\text{-}C_6H_7\text{-}5\text{-}exo\text{-}PPh_3)(CO)_3]BF_4$.[16]

P(1) is bonded to C(7) in an *exo* stereochemistry. The environment of this phosphorus atom is tetrahedral, with angles between 107.0(7)° and 112.4(6)°. All P(1)−carbon distances are similar, between 1.82(2) and 1.84(1) Å, and slightly shorter than the P(2)−carbon bond length in the triisopropylphosphine ligand, between 1.85(3) and 1.88(2) Å.

As for **2**, the osmium−chlorine distances are different. The Os−Cl(1) distance (Cl *trans* to C(5)−C(6), 2.478(4) Å) is shorter than the Os−Cl(2) bond length (Cl *trans* to hydrido, 2.551(4) Å), in agreement with the different *trans* influence of the olefin and hydrido ligands.

In the $^{13}C\{^1H\}$ NMR spectrum of **3** in chloroform-*d*, the carbon atoms of the olefinic C(1)−C(2) bond appear as a doublet (J(PC) = 9 Hz) at 60.7 ppm and a singlet at 50.1 ppm. Both carbon atoms of the C(5)−C(6) double bond, which is *trans* to the triisopropylphosphine ligand, display doublets at 61.6 and 44.2 ppm, with P−C coupling constants of 22 and 18 Hz, respectively. We assign the doublet at 61.6 ppm, which shows the greatest P−C coupling constant, to C(6) because the value of P(2)−Os−C(6) angle (168.7(4)°) is closest to the ideal value of 180° (P(2)−Os−C(5) angle (153.0(4) Å)). The C(7) resonance appears at 35.3 ppm as a double doublet with P−C coupling constants of 2 and 22 Hz, while the aliphatic atom C(8) displays a doublet at 41.8 (J(PC) = 3 Hz) ppm, and C(3) and C(4) give rise to singlets at 29.9 and 28.6 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **3** shows two doublets at 37.6 and 2.3 ppm. The doublet at 2.3 ppm was assigned to the triisopropylphosphine ligand on the basis of the $^{31}P\{^1H\}$ NMR spectrum recorded under off-resonance conditions, where this doublet is split into a virtual triplet (vt) as a result of the P−H coupling with the hydrido ligand.

In order to obtain information about the reaction pathway leading to **3**, we carried out the reaction of $OsCl_3\cdot xH_2O$ with triisopropylphosphine in 2-propanol-d_8. Under the same experimental conditions as those previously reported for the preparation of **1**,[1] a mixture of **1** and $OsD_2Cl_2(P^iPr_3)_2$ (**1**-*d*) was obtained in approximately a 1:1 molar ratio. Treatment of a toluene solution of this mixture with 3 equiv of 1,5-cyclooctadiene at 85 °C led to **3**. Deuterium was not observed in the hydrido position or on the carbocyclic ligand, which suggests that the hydrido ligand of **3** originates from the 1,5-cyclooctadiene molecule. A plausible mechanism which accounts for this observation is shown in Scheme 1.

It has been previously mentioned that the addition of nucleophilic ligands to **1** produces the transformation of the hydrido ligands into a coordinated dihydrogen molecule.[5] Thus, the initial interaction of **1** with the diolefin could afford a dihydrogen intermediate containing 1,5-cyclooctadiene coordinated in an η^2-bonding mode (**4**). The release of molecular hydrogen and the subsequent coordination of the free olefin bond of the diene could lead to an η^4-cyclooctadiene complex **5**, in which the dissociation of a phosphine ligand should be favored as a result of the large steric hindrance expe-

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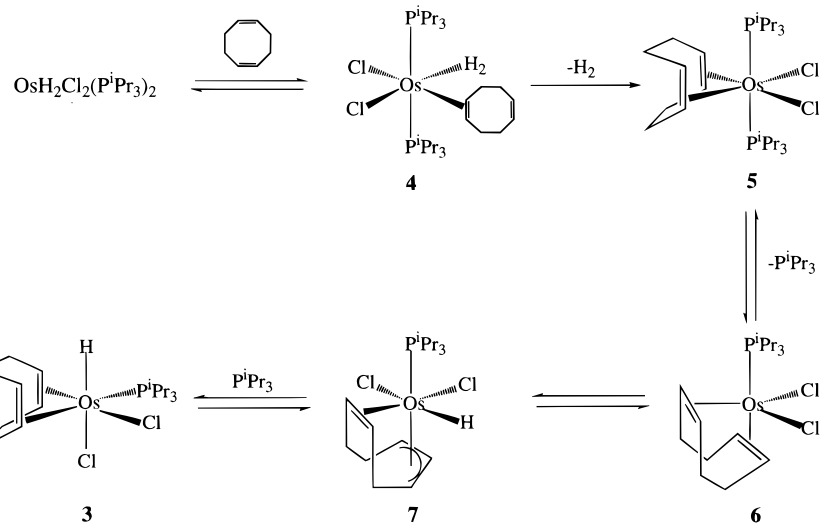
(15) Brown, D. A.; Burns, J.; El-Gamati, I.; Glass, W. K.; Kreddan, K.; Salama, M.; Cunningham, D.; Higgins, T.; McArdle, P. *J. Chem. Soc., Chem. Commun.* **1992**, 701.

(16) Guy, J. J.; Reichert, B. E.; Sheldrick, G. M. *Acta Crystallogr.* **1976**, *B32*, 2504.

Scheme 1

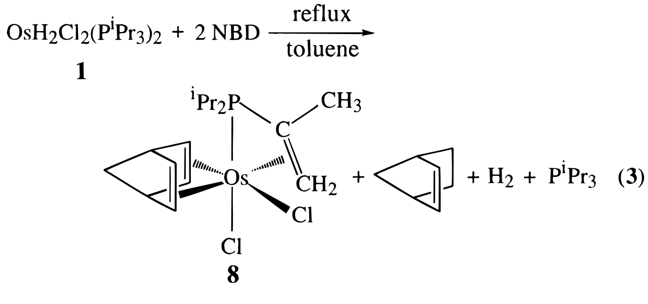


rienced by the phosphine and diolefin ligands, mutually *cis* disposed. The dissociation of a phosphine ligand from **5** should give the 16-electron complex **6**, which could afford the hydrido−allyl complex **7** by oxidative addition of one of the C(sp^3)−H bonds of the coordinated cyclooctadiene. A similar process has been previously proposed to rationalize the formation of $[Ru(1\text{-}3:5,6\text{-}\eta\text{-}C_8H_{11})(\eta^6\text{-}1,3,5\text{-cyclooctatriene})]^+$ from $[RuH(\eta^4\text{-}C_8H_{12})(NH_2NMe_2)_3]^+$ and 1,5-cyclooctadiene.[17] Finally, the addition of the triisopropylphosphine molecule, released during the formation of **6**, to one of the terminal carbon atoms of the allyl unit of **7**, a well-known process,[18] should give **3**.

Treatment of a toluene suspension of **3** with 1,5-cyclooctadiene in a 1:5 molar ratio at 85 °C leads, after 1 day, to **2**. At first glance, this suggest that complex **3** may be an intermediate for the formation of **2**. According to Scheme 1, the formation of **3** involves the allyl intermediate **7**, which is the result of the C−H activation of a −CH$_2$− group of the coordinated 1,5-cyclooctadiene ligand of **6**. In order to further investigate this proposal, we carried out the reactions of **1** with 2,5-norbornadiene and tetrafluorobenzobarrelene, two diolefins which unlike 1,5-COD, do not allow the formation of an allyl intermediate, such as **7**.

Reaction of $OsH_2Cl_2(P^iPr_3)_2$ with 2,5-Norbornadiene. Treatment of a refluxing solution of **1** in toluene with 2,5-norbornadiene in a 1:3 molar ratio for 5 h leads to a brown solution, from which the isopropenylphosphine complex $OsCl_2(\eta^4\text{-NBD})\{[(\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**8**, eq 3) was isolated as a white solid by the addition of pentane.

Although the reaction shown in eq 3 spectroscopically proceeds nearly quantitatively, complex **8** was obtained in about 30% yield as a result of its moderate solubility in pentane. The most noticeable features in the ^{1}H NMR spectrum are the resonances corresponding to the isopropenyl protons of the phosphine, which appear at 3.51, 2.47, and 2.10 ppm. The 2,5-norbornadiene gives rise to five signals. The olefinic protons display two double doublet of doublets at 4.82 and 2.80 ppm and two overlapped double doublets at about 4.20 ppm. The −CH bridge protons appear as broad resonances at 4.06 and 3.65 ppm, while the −CH$_2$ group gives rise to a second-order system centered at 1.28 ppm. In the APT ^{13}C{^{1}H} spectrum, the carbon atoms of the isopropenyl group appear at 64.2 (=CH$_2$), 63.7 (P−C=), and 23.4 (−CH$_3$) ppm as doublets with P−C coupling constants of 4.6, 22.5, and 6.9 Hz, respectively, and the olefinic carbon atoms of the coordinated diene are observed at 56.7, 47.5, 44.9, and 42.1 ppm, also as doublets, with P−C coupling constants of 2, 3, 3, and 4 Hz, respectively. The ^{31}P{^{1}H} NMR spectrum shows a singlet at −11.6 ppm.



Complex **8** is structurally related to **2** but contains a 2,5-norbornadiene molecule in the place of the 1,5-cyclooctadiene ligand. The formation of this compound under the same conditions as those described for **2** indicates that the synthesis of **2** does not require the formation of **3** via the allyl intermediate **7**. In favor of this, we have also observed that at 85 °C, **3** not only reacts with 1,5-cyclooctadiene to give **2** but also with 2,5-norbornadiene to afford **8**.

From the reaction of **3** with 2,5-norbornadiene, in addition to **8**, triisopropylphosphine, 1,5-cyclooctadiene, and norbornene were obtained. This suggests that under the reaction conditions, complex **3** decomposes to triisopropylphosphine, 1,5-cyclooctadiene, and an unsaturated osmium fragment, which is capable of dehydrogenating an isopropyl group of the triisopropylphosphine to probably give a dihydrido intermediate. The hydrido ligands formed should be removed by the excess diolefin; furthermore, the formation of both isoprope-

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[17] Ashworth, T. V.; Chalmuers, A. A.; Liles, D. C.; Meintjies, E.; Singleton, E. *Organometallics* **1987**, *6*, 1543.

[18] See, for example: (a) Connely, N. G.; Mills, R. N.; Whiteley, M. W.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 17. (b) Connelly, N. G.; Lucy, A. R.; Mills, R. N.; Whiteley, M. W.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 161. (c) Ittel, S. D.; Whitney, J. F.; Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1988**, *7*, 1323.

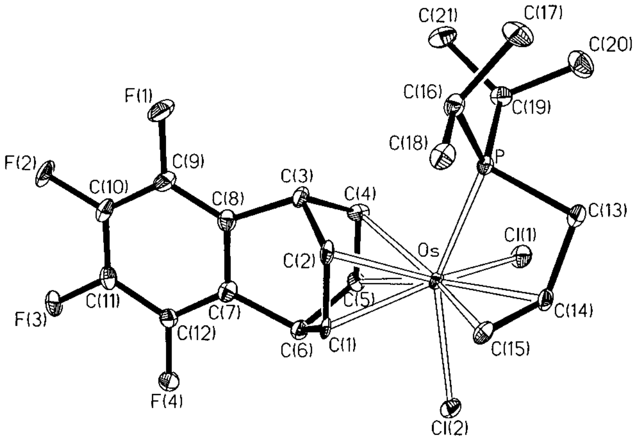
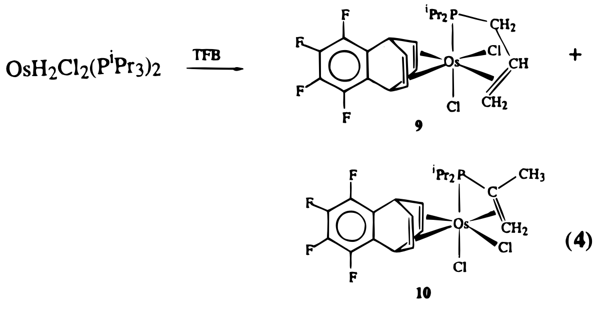


Figure 3. Molecular diagram of $OsCl_2(\eta^4\text{-TFB})\{(\eta^2\text{-}CH_2{=}CHCH_2)P^iPr_2\}$ (**9**).

nylphosphine compounds **2** and **8** from **1** and **3** suggests that the reaction pathways starting from **1** and **3** have a common intermediate. Thus, the reactions shown in eqs 1 and 2 can be seen as two competitive C–H activation processes on an undetected unsaturated osmium fragment. One of them, favored under refluxing toluene, consists of the activation of an isopropyl group of the triisopropylphosphine ligand. The other, which requires a lower temperature, involves the diene.

Reaction of $OsH_2Cl_2(P^iPr_3)_2$ with Tetrafluorobenzobarrelene. Treatment of a refluxing solution of **1** in toluene with tetrafluorobenzobarrelene in a 1:3 molar ratio for 5 h leads to a white precipitate (38%) and a brown solution. The white precipitate was characterized as the allylphosphine complex $OsCl_2(\eta^4\text{-TFB})\{(\eta^2\text{-}CH_2{=}CHCH_2)P^iPr_2\}$ (**9**) by elemental analysis, IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies, and X-ray diffraction, while from the brown solution, the isopropenylphosphine complex $OsCl_2(\eta^4\text{-TFB})\{[(\eta^2\text{-}CH_2{=}C\text{-}(CH_3)]P^iPr_2\}$ (**10**) (41%) was isolated as a yellow solid by addition of pentane. In addition, 1 equiv of diolefin was hydrogenated to the corresponding monoolefin (eq 4).



(4)

Figure 3 shows the molecular structure of **9**. Selected bond distances and angles are listed in Table 3. The coordination geometry around the osmium atom can be described as a distorted octahedron. Although the allylphosphine acts with a bigger bite angle (74.8(1)°) than that of the isopropenylphosphine of **2** (56.0(1)°), the most important distortion from the ideal octahedron is again the result of the ring constraint imposed by the bidentate phosphine ligand. The phosphorus atom is situated *trans* to one of the two chlorine atoms (Cl(2); P–Os–Cl(2) = 152.36(3)°), at opposite sides of an ideal coordination plane defined by the other chlorine atom (Cl(1)) and the midpoints of the olefinic C(1)–C(2), C(4)–C(5), and C(14)–C(15) bonds. If M(1), M(2) and M(3) are the midpoints of the C(14)–C(15), C(1)–C(2), and C(4)–C(5) bonds, respectively, the deviations of M(1), M(2), M(3), and Cl(1) from a mean plane passing through them are −0.034(4), 0.056(4), −0.056(4), and 0.003(1) Å, with the osmium in the plane (maximum deviation 0.0000(2) Å). The olefinic carbon atoms of the allyl group are out of this plane; C(14) is shifted toward the phosphorus atom by 0.212(4) Å, while C(15) is shifted toward Cl(2) by 0.144(4) Å. As expected, the dihedral angle between the coordination plane and the C(14)–C(15) bond (14.6(2)°) is smaller than the equivalent angle in **2** (30.6(2) Å). The three carbon–carbon bond lengths for the coordinated olefinic bonds are statistically identical and in agreement with the usual Chatt, Dewar, and Duncanson metal–olefin bonding scheme (see Table 3). The P–allyl distance (P–C(13), 1.836(4) Å) is slightly shorter than the P–isopropyl bond lengths (P–C(16), 1.856(4) Å and P–C(19), 1.857(4) Å). In accordance with the sp^2 hybridization for C(14), the angle C(13)–C(14)–C(15) is 122.6(3)°. As for **2**, and in agreement with the different *trans* influence of the olefin and phosphine groups, the Os–Cl(1) distance (Cl *trans* to C(1)–C(2), 2.4251(13) Å) is shorter than the Os–Cl(2) distance (Cl *trans* to P, 2.4720(9) Å).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $OsCl_2(\eta^4\text{-TFB})\{(\eta^2\text{-}CH_2{=}CHCH_2)P^iPr_2\}$ (9)

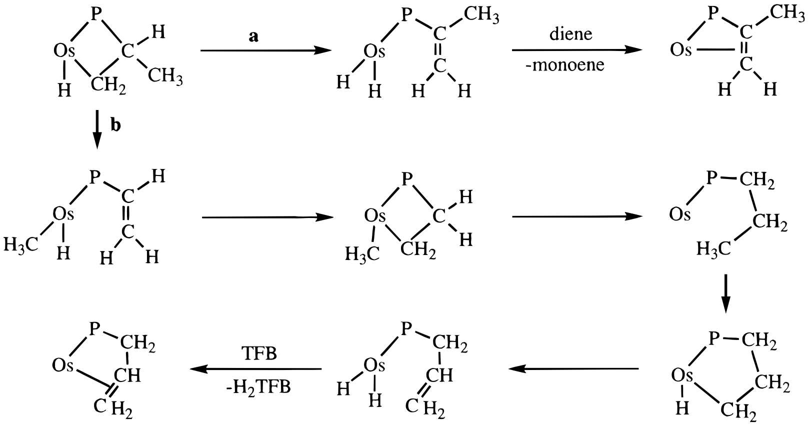
Os–Cl(1)	2.4251(13)	P–C(16)	1.856(4)
Os–Cl(2)	2.4720(9)	P–C(19)	1.857(4)
Os–P	2.3805(9)	C(1)–C(2)	1.403(5)
Os–C(1)	2.197(5)	C(1)–C(6)	1.538(5)
Os–C(2)	2.224(5)	C(2)–C(3)	1.532(5)
Os–C(4)	2.220(4)	C(3)–C(4)	1.542(7)
Os–C(5)	2.196(3)	C(4)–C(5)	1.397(5)
Os–C(14)	2.207(4)	C(5)–C(6)	1.530(6)
Os–C(15)	2.215(4)	C(13)–C(14)	1.526(5)
P–C(13)	1.836(4)	C(14)–C(15)	1.414(7)

Cl(1)–Os–Cl(2)	82.97(3)	M(1)–Os–M(2)[a]	106.0(2)
Cl(1)–Os–P	83.09(3)	M(1)–Os–M(3)[a]	172.9(2)
Cl(1)–Os–M(1)[a]	99.0(1)	M(2)–Os–M(3)[a]	67.4(2)
Cl(1)–Os–M(2)[a]	155.0(1)	Os–P–C(13)	87.5(1)
Cl(1)–Os–M(3)[a]	87.7(1)	Os–P–C(16)	127.5(1)
Cl(2)–Os–P	152.36(3)	Os–P–C(19)	115.2(1)
Cl(2)–Os–M(1)[a]	83.9(1)	C(13)–P–C(16)	106.3(2)
Cl(2)–Os–M(2)[a]	98.3(1)	C(13)–P–C(19)	112.1(2)
Cl(2)–Os–M(3)[a]	99.4(1)	C(16)–P–C(19)	105.8(2)
P–Os–M(1)[a]	74.8(1)	P–C(13)–C(14)	99.3(3)
P–Os–M(2)[a]	104.4(1)	C(13)–C(14)–C(15)	122.6(3)
P–Os–M(3)[a]	103.8(1)		

[a] M(1), M(2,) and M(3) are the midpoints of the olefin double bonds C(14)–C(15), C(1)–C(2), and C(4)–C(5), respectively.

Molecule **9** has no symmetry. In agreement with this, the ^1H NMR spectrum in chloroform-*d* shows six resonances for the six protons of the diolefin. The resonances due to the CH– aliphatic protons appear at 5.63 and 4.93 ppm, while the olefinic resonances are observed at 4.55, 4.40, 4.04, and 3.85 ppm. The olefinic allyl protons give rise to a multiplet at 3.77 ($CH_2{-}CH{=}$) ppm and two doublets at 3.34 (CH *trans* to H) and 3.23 (CH *cis* to H) ppm, with H–H coupling constants of 11.1 and 8.0 Hz, respectively, while the CH_2 group displays two multiplets at 4.49 and 4.32 ppm. In the APT $^{13}C\{^1H\}$ NMR spectrum, the allyl carbon atoms give rise to doublets. The sp^2-carbon atoms appear at 62.1 ($=CH_2$, $J(PC) = 3.2$ Hz) and 40.4 ($CH{=}$, $J(PC) = 6.0$ Hz) ppm, while the sp^3-CH_2 carbon atom is observed at 30.4 ppm, with a P–C coupling constant of 33.5 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −69.6 ppm.

Scheme 2



In accordance with the structure proposed for **10** in eq 4, which is related to the X-ray structure of **2**, the ^{1}H NMR spectrum of **10** in chloroform-*d* shows two aliphatic $-CH$ resonances at 5.71 and 4.81 ppm and four olefinic resonances at 4.69, 4.10, 4.02, and 2.75 ppm. In addition, the spectrum also contains the three characteristic doublets corresponding to the isopropenyl protons at 3.61 ($CH=$ *trans* to P, $J(PH) = 34.6$ Hz), 2.58 ($-CH_3$, $J(PH) = 8.8$ Hz), and 2.46 ($CH=$ *cis* to P, $J(PH) = 12.1$ Hz) ppm. In the APT $^{13}C\{^{1}H\}$ NMR spectrum, the carbon atoms of the coordinated isopropenyl group appear at 65.8 ($P-C=$), 62.8 ($=CH_2$), and 24.8 ($-CH_3$) ppm as doublets with P−C coupling constants of 22.5, 4.2, and 7.4 Hz, respectively, while the olefinic carbon atoms of the diene are observed at 46.3, 44.3, 40.6, and 35.5 ppm as doublets with P−C coupling constants of 1.5, 5.0, 3.2, and 3.2 Hz, respectively. The $^{31}P\{^{1}H\}$ NMR spectrum shows a singlet at −12.2 ppm.

As for **2** and **8**, complexes **9** and **10** can also be obtained from the reaction of **3** with tetrafluorobenzobarrelene, again indicating that the participation of an allyl intermediate **7** is not necessary in the formation of **2** and, therefore, for the transformation of triisopropylphosphine into isopropenyl(diisopropyl)phosphine.

In addition, complexes **9** and **10** are isomers. The formation of **10**, as for **2** and **8**, should involve an osmium intermediate containing a metallated triisopropylphosphine ligand. The β-hydrogen extraction on the metallated group should yield the isopropenylphosphine ligand (route a of Scheme 2). If the β-elimination process on the metallated group occurs on the $PC-CH_3$ bond instead of the PC−H bond (route b of Scheme 2), the reactions should yield allylphosphine ligands, most probably via the reaction pathway shown in Scheme 2. C−C cleavage via β-alkyl elimination has been observed rarely. Only in the past 15 years it has become recognized as an important chain-termination step in early transition metal-based, model Ziegler−Natta polymerization systems.[19] In late transition metal systems there are some reports in which β-alkyl elimination has proposed.[20] The formation of the allylphosphine complex **10** indicates that on the metallated group of a triisopropylphosphine ligand, two β-activation processes, C−H and C−C, are possible when the diolefin is tetrafluorobenzobarrelene. In other words, the formation of the isopropenylphosphine complexes **2**, **8**, and **10** and the allylphosphine derivative **9** can be understood as two competitive β-elimination processes on the metallated group of a metallated triisopropylphosphine ligand. The β-elimination of hydrogen leads to isopropenylphosphine compounds and takes place in the presence of 1,5-cyclooctadiene, 2,5-norbornadiene, and tetrafluorobenzobarrelene, while the β-elimination of the methyl group, which leads to allylphosphine species, is only observed in the presence of tetrafluorobenzobarrelene.

Concluding Remarks

This study has revealed that the reactions of $OsH_2Cl_2(P^iPr_3)_2$ with diolefins leads to osmium products which result from C−H and C−C activation and C−C and C−P bond formation processes. They are competitive and depend upon the nature of the diolefin. When the diene is 1,5-cyclooctadiene, the dehydrogenation of an isopropyl group of triisopropylphosphine affords the isopropenylphosphine complex **2**, under refluxing toluene. However, at 85 °C, the C−H activation of a coordinated 1,5-cyclooctadiene molecule occurs, and the reaction produces, by a subsequent C−P bond formation, the osmium derivative **3** containing the carbocyclic ligand $[C_8H_{11}P^iPr_3]^+$. In the presence of 2,5-norbornadiene, the diolefin is not activated, the activation of the triisopropylphosphine leads to the isopropenylphosphine complex **8**. During the reaction of $OsH_2Cl_2(P^iPr_3)_2$ with tetrafluorobenzobarrelene, the diene is not activated either. However, the C−H activation of the triisopropylphosphine leads to a mixture of two propenyl phosphine isomers, as a result of two competitive β-elimination processes on one metallated group of a metallated triisopropylphosphine ligand. The β-elimination of

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[19] (a) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (c) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976. (d) Bercaw, J. E. *Pure Appl. Chem.* **1990**, *62*, 1151. (e) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277. (f) Kesti, M. R.; Waymonth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565. (g) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362. (h) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025. (i) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993,** *115*, 3392. (j) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147.

[20] (a) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795. (b) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076. (c) Thomsons, S. K.; Young, G. B. *Organometallics* **1989**, *8*, 2068. (d) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3344. (e) Ermer, S. P.; Struck, G. E.; Bitler, S. P.; Richards, R.; Bau, R.; Flood, T. C. *Organometallics* **1993**, *12*, 2634. (f) Ankianiec, B. C.; Christou, V.; Hardy, D. T.; Thompson, S. K.; Young, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9963. (g) McNeil, K.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 3625.

hydrogen leads to the isopropenylphosphine complex **10**, while the β-elimination of the CH_3 group affords the allylphosphine derivative **9** by a subsequent C−C bond formation process.

The reactions shown in eqs 1−4, as well as the compounds reported in this paper, have no precedent. The reactivity of $OsH_2Cl_2(P^iPr_3)_2$ toward diolefins, terminal alkynes, and 1-alkyn-3-ols to afford carbyne and vinylcarbyne derivatives[6] and Lewis bases to give dihydrogen compounds,[5] together with its particular structure in the solid state,[1] dynamic behavior in solution,[2] and catalytic properties,[1] demonstrate that the complex $OsH_2Cl_2(P^iPr_3)_2$ is a unique species with a completely different chemical behavior than that of previously reported compounds.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Perkin-Elmer 883 or a Nicolet 550 spectrometer. NMR spectra were recorded on a Varian UNITY 300 or on a Bruker ARX 300. ^1H and $^{13}C\{^1H\}$ chemical shifts were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane. $^{31}P\{^1H\}$ chemical shifts are reported relative to H_3PO_4 (85%). Coupling constants, J, are given in hertz. The gas chromatography (GC) experiments were carried out using a FFAP (free fatty acids phase) on Chromosorb W-HP 80/100-mesh column on a Perkin Elmer 8500 gas chromatograph with a flame ionization detector. The diolefins and olefins in the reaction solutions were characterized by comparison with the pure olefins and diolefins. C and H analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectral analyses were performed with a VG Auto Spec instrument. The ions were produced, FAB^+ mode, with the standard Cs^+ gun at *ca.* 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

Synthesis. All reactions were carried out with exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) was prepared according to the literature method.[1]

Reaction of $OsH_2Cl_2(P^iPr_3)_2$ (1) with 1,5-Cyclooctadiene. Preparation of $OsCl_2(COD)\{^iPr_2PC(CH_3){=}CH_2\}$ (2). A solution of $OsH_2Cl_2(P^iPr_3)_2$ (200 mg, 0.34 mmol) in 17 mL of toluene was treated with 126 μL (1.02 mmol) of 1,5-cyclooctadiene. The mixture was heated under reflux for 5 h. The resulting brown solution was filtered through Kieselguhr. GC analysis of the solution (0.3 μL) showed the presence of cyclooctene and 1,5-cyclooctadiene in a 1:1 molar ratio. The solution was concentrated to dryness, and 10 mL of pentane was added. The solvent was partially evaporated until a yellow solid began to precipitate, and the suspension was stored at −78 °C for 1 h. The yellow solid was separated by decantation, washed with 3 mL of pentane, and dried in vacuo: yield 63 mg (35%). ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 5.21 (m, 1 H, $=CH$, COD), 4.64 (m, 1 H, $=CH$, COD), 4.37 (m, 1 H, $=CH$, COD), 4.11 (m, 1 H, PCH), 3.81 (d, J(PH) = 34.2 Hz, 1 H, $PC{=}CHH_{trans}$), 3.63 (m, 1 H, $=CH$, COD), 3.26 (m, 1 H, $-CH_2$, COD), 2.88 (m, 1 H, $-CH_2$, COD), 2.79 (m, 1 H, $-CH_2$, COD), 2.52−2.36 (3 H, $-CH_2$, COD), 2.46 (d, J(PH) = 8.1 Hz, 3 H, $PC(CH_3){=}$), 2.31 (d, J(PH) = 11.6 Hz, 1 H, $PC{=}CHH_{cis}$), 2.07 (m, 2 H, PCH and $-CH_2$, COD), 1.87 (m, 1 H, $-CH_2$, COD), 1.59 (dd, J(HH) = 7.4 Hz, J(PH) = 12.7 Hz, 3 H, $PCCH_3$), 1.54 (dd, J(HH) = 7.4 Hz, J(PH) = 12.1 Hz, 3 H, $PCCH_3$), 1.53 (dd, J(HH) = 7.5 Hz, J(PH) = 13.2 Hz, 3 H, $PCCH_3$), 1.47 (dd, J(HH) = 7.5 Hz, J(PH) = 12.3 Hz, 3 H, $PCCH_3$). $^{31}P\{^1H\}$NMR (121.42 MHz, $CDCl_3$, 293 K): δ −16.7 (s). $^{13}C\{^1H\}$NMR (75.42 MHz, $CDCl_3$, 293 K, plus APT): δ 86.3 (+, s, $=CH$ COD), 79.6 (+, d, J(PC) = 3.2 Hz, $=CH$ COD), 77.7 (−, d, J(PC) = 22.0 Hz, $C{=}CH_2$), 77.5 (+, s, $=CH$, COD), 72.1 (+, d, J(PC) = 5.0 Hz, $=CH$, COD), 71.3 (−, d, J(PC) = 4.6 Hz, $C{=}CH_2$), 40.1 (−, d, J(PC) = 3.7 Hz, $-CH_2$, COD), 35.8 (−, s, $-CH_2$, COD), 32.3 (−, d, J(PC) = 1.3 Hz, $-CH_2$, COD), 24.5 (−, s, $-CH_2$, COD), 24.3 (+, d, J(PC) = 6.9 Hz, $PC(CH_3){=}$), 21.8 (+, d, J(PC) = 26.7 Hz, PCH), 20.8 (+, d, J(PC) = 6.9 Hz, $PCCH_3$), 20.3 (+, d, J(PC) = 22.5 Hz, PCH), 18.7 (+, s, $PCCH_3$), 18.6 (+, d, J(PC) = 2.8 Hz, $PCCH_3$), 16.1 (+, s, $PCCH_3$) Anal. Calcd for $C_{17}H_{31}Cl_2OsP$: C, 38.70; H, 5.92. Found: C, 38.37; H, 5.82

Reaction of 1 with 1,5-Cyclooctadiene. Preparation of $OsHCl_2(\eta^4\text{-}C_8H_{11}P^iPr_3)(P^iPr_3)$ (3). A solution containing $OsH_2Cl_2(P^iPr_3)_2$ (400 mg, 0.68 mmol) and 252 μL (2.05 mmol) of 1,5-cyclooctadiene in 17 mL of toluene was heated at 85 °C for 3 days, giving a white precipitate and a brown solution. GC analysis of the solution (0.3 μL) showed the presence of cyclooctene and 1,5-cyclooctadiene in a 1:6 molar ratio. After the mixture was cooled to room temperature, the white solid was separated by decantation, washed with pentane, and dried in vacuo: yield 220 mg (47%). IR (Nujol): ν (OsH) 2140 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 293 K):[21,22] δ 5.41 (m, 1 H, $C_8H_{11}P^iPr_3$), 3.88 (m, 1 H, $C_8H_{11}P^iPr_3$), 3.16 (m, 1 H, $C_8H_{11}P^iPr_3$), 3.09 (m, 1 H, $C_8H_{11}P^iPr_3$), 2.88−2.69 (5 H, P(1)CH and $C_8H_{11}P^iPr_3$), 2.47 (m, 3 H, P(2)CH), 2.31−2.05 (2 H, $C_8H_{11}P^iPr_3$), 1.59 (dd, J(HH) = 6.9 Hz, J(P(1)H) = 14.4 Hz, 9 H, $P(1)CCH_3$), 1.56 (d, J(PH) = 36.0 Hz, 1 H, $CHP(1)^iPr_3$),[23] 1.47 (dd, J(HH) = 6.6 Hz, J(P(1)H) = 14.7 Hz, 9 H, $P(1)CCH_3$), 1.35 (m, 1 H, $C_8H_{11}P^iPr_3$),[23]1.29 (dd, J(HH) = 6.0 Hz, J(P(2)H) = 12.6 Hz, 9 H, $P(2)CCH_3$), 1.27 (dd, J(HH) = 6.0 Hz, J(P(2)H) = 12.6 Hz, 9 H, $P(2)CCH_3$), 1.07 (br, 1 H, $C_8H_{11}P^iPr_3$), −10.46 (d, J(P(2)H) = 21.9 Hz, 1 H, OsH). $^{31}P\{^1H\}$NMR (121.42 MHz, CD_2Cl_2, 293 K):[21] δ 37.6 (d, J(PP) = 13.0 Hz, P(1)), 2.3 (d, J(PP) = 13.0 Hz, vt in off-resonance, P(2)). $^{13}C\{^1H\}$NMR (75.42 MHz, $CDCl_3$, 293 K, plus DEPT):[21] δ 61.6 (+, d, J(PC) = 21.7 Hz, $=C(6)H$), 60.7 (+, d, J(PC) = 9.1 Hz, $=CH$), 50.1 (+, s, $=CH$), 44.2 (+, d, J(PC) = 18.2 Hz, $=C(5)H$), 41.8 (−, d, J(PC) = 3.5 Hz, $-C(8)H_2$), 35.3 (+, dd, J(P(1)C) = 21.9 Hz, J(P(2)C) = 2.3 Hz, $-C(7)H$), 30.0, 28.6 (−, both s, $-C(3)H_2$ and $-C(4)H_2$), 24.1 (+, d, J(PC) = 20.7 Hz, PCH), 21.3 (+, d, J(PC) = 38.9 Hz, PCH), 20.3 (+, s, $PCCH_3$), 19.8 (+, s, $PCCH_3$), 17.8 (+, d, J(PC) = 3.5 Hz, $PCCH_3$), 17.6 (+, d, J(PC) = 3.5 Hz, $PCCH_3$). Anal. Calcd for $C_{26}H_{54}Cl_2OsP_2$: C, 45.29; H, 7.89. Found: C, 45.04; H, 7.12. MS (FAB^+): *m/e* 655 ($M^+ - Cl$).

Reaction of a 1:1 Mixture of $OsH_2Cl_2(P^iPr_3)_2$ and $OsD_2Cl_2(P^iPr_3)_2$ with 1,5-Cyclooctadiene. A suspension of a 1:1 mixture of $OsH_2Cl_2(P^iPr_3)_2$ and $OsD_2Cl_2(P^iPr_3)_2$ (100 mg, 0.17 mmol) in 13 mL of toluene was treated with 63 μL (0.52 mmol) of 1,5-cyclooctadiene. The mixture was heated at 85 °C for 2 days, and a white precipitate was obtained. After the mixture was cooled to room temperature, the white solid was separated by decantation, washed with toluene, and dried in vacuo. By comparison of the IR and ^1H NMR spectra of this solid with those of pure **3**, only partial deuteration of both triisopropylphosphine groups was observed.

Reaction of 3 with 1,5-Cyclooctadiene. A suspension of $OsHCl_2(\eta^4\text{-}C_8H_{11}P^iPr_3)(P^iPr_3)$ (100 mg, 0.14 mmol) in 13 mL of toluene was treated with 89 μL (0.72 mmol) of 1,5-cyclooctadiene. The mixture was heated at 85 °C for 1 day, and a yellow solution was obtained. After the mixture was cooled to room temperature, the solution was filtered through Kieselguhr and concentrated to dryness. Addition of pentane precipitated a yellow solid, which was separated by decantation, washed with pentane, and dried in vacuo. The product was characterized as **2** by ^1H and $^{31}P\{^1H\}$ NMR: yield 60 mg (79%).

Reaction of 1 with 2,5-Norbornadiene. Preparation of $OsCl_2(\eta^4\text{-}NBD)\{[(\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (8). A solution of **1** (175 mg, 0.30 mmol) in 12 mL of toluene was treated with 86 μL (0.90 mmol) of 2,5-norbornadiene. The mixture was heated under reflux for 5 h, and a brown solution was obtained.

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[21] Atoms labeled according to Figure 2.

[22] The assignment of the PCH and $PCCH_3$ of $P(1)^iPr_3$ and $P(2)\text{-}^iPr_3$ are based on selective $^1H\{^{31}P\}$ experiments.

[23] Observed in the ^1H NMR COSY spectrum.

After the mixture was cooled to room temperature, the solution was filtered through Kieselguhr and concentrated to dryness. Five milliliters of pentane was added, and the solution was concentrated to dryness. An aliquot of toluene (5 mL) was added and then concentrated to dryness, followed by the addition of 5 mL of pentane. This procedure was repeated until a white solid could be obtained in a toluene suspension, which was separated by decantation, washed with 3 mL of pentane, and dried in vacuo: yield 39 mg (26%). ^{1}H NMR (300 MHz, CDCl$_3$, 293 K): δ 4.82 (ddd, J(PH) = 7.1 Hz, J(HH) = 4.2 Hz, J(HH) = 4.2 Hz, 1 H, ═CH, NBD), 4.22 (dd, J(HH) = 4.3 Hz, J(HH) = 4.3 Hz, 1 H, ═CH, NBD), 4.21 (dd, J(HH) = 4.1 Hz, J(HH) = 4.1 Hz, 1 H, ═CH, NBD), 4.06 (br, 1H, −CH bridge, NBD), 3.85 (m, 1H, PCH), 3.65 (br, 1H, −CH bridge, NBD), 3.51(d, J(PH) = 34.5 Hz, 1 H, PC═CHH_{trans}), 2.80 (ddd, J(PH) = 7.4 Hz, J(HH) = 4.1 Hz, J(HH) = 4.1 Hz, 1 H, ═CH, NBD), 2.47(d, J(PH) = 8.6 Hz, 3 H, PC(CH$_3$)═), 2.10 (d, J(PH) = 11.8 Hz, 1 H, PC═CHH_{cis}), 1.89 (m, 1H, PCH), 1.61−1.43 (12 H, PCCH$_3$), 1.28 (second-order system, 2 H, −CH$_2$, NBD). ^{31}P{^{1}H} NMR (121.42 MHz, CDCl$_3$, 293 K): δ −11.6 (s). ^{13}C{^{1}H}NMR (75.42 MHz, CDCl$_3$, 293 K, plus APT): δ 64.2 (−, d, J(PC) = 4.6 Hz, C═CH$_2$), 63.7 (−, d, J(PC) = 22.5Hz, C═CH$_2$), 60.8 (−, s, −CH$_2$, NBD), 56.7 (+, d, J(PC) = 2.3 Hz, ═CH, NBD), 47.5 (+, d, J(PC) = 3.2 Hz, ═CH, NBD), 46.1 (+, d, J(PC) = 1.9 Hz, −CH bridge, NBD), 45.8 (+, d, J(PC) = 1.4 Hz, −CH bridge, NBD), 44.9 (+, d, J(PC) = 2.8 Hz, ═CH, NBD), 42.1 (+, d, J(PC) = 4.1 Hz, ═CH, NBD), 23.4 (+, d, J(PC) = 6.9 Hz, PC(CH$_3$)═), 22.9 (+, d, J(PC) = 23.0 Hz, PCH), 21.5 (+, d, J(PC) = 28.5 Hz, PCH), 20.4 (+, d, J(PC) = 6.9 Hz, PCCH$_3$), 18.9 (+, s, PCCH$_3$), 18.4 (+, d, J(PC) = 2.7 Hz, PCCH$_3$), 14.6 (+, d, J(PC) = 2.3 Hz, PCCH$_3$). Anal. Calcd for C$_{16}$H$_{27}$Cl$_2$OsP: C, 37.57; H, 5.32. Found: C, 37.93; H, 5.63.

Reaction of 3 with 2,5-Norbornadiene. A suspension of OsHCl$_2$(η^4-C$_8$H$_{11}$P^{i}Pr$_3$)(P^{i}Pr$_3$) (55 mg, 0.08 mmol) in 13 mL of toluene was treated with 38 μL (0.40 mmol) of 2,5-norbornadiene and heated at 85 °C for 1 day. After the mixture was cooled to room temperature, the solution was filtered through Kieselguhr. GC analysis of the solution (0.3 μL) showed the presence of norbornene and 1,5-cyclooctadiene. After concentration of the solvent to dryness, 5 mL of pentane was added and then concentrated to dryness. An aliquot of toluene (3 mL) was added and then concentrated to dryness, followed by the addition of 3 mL of pentane. This procedure was repeated until a white solid could be obtained in a toluene suspension, which was separated by decantation, washed with 2 mL of pentane, and dried in vacuo. The product was characterized as **8** by ^{1}H and ^{31}P{^{1}H} NMR: yield 14 mg (35%)

Reaction of 1 with Tetrafluorobenzobarrelene. Preparation of OsCl$_2$(η^4-TFB){(η^2-CH$_2$═CHCH$_2$)P^{i}Pr$_2$} (9) and OsCl$_2$(η^4-TFB){[(η^2-CH$_2$═C(CH$_3$)]P^{i}Pr$_2$} (10). A solution of **1** (200 mg, 0.34 mmol) in 12 mL of toluene was treated with 232 mg (1.02 mmol) of tetrafluorobenzobarrelene. The mixture was heated under reflux for 5 h, giving a white solid and a brown toluene solution. GC analysis of the solution (0.3 μL) showed the presence of TFB and H$_2$TFB in a 1:1 molar ratio. After the mixture was cooled to room temperature, the white solid was separated by decantation, washed with toluene, and dried in vacuo. The white solid obtained was characterized as OsCl$_2$(η^4-TFB){(η^2-CH$_2$═CHCH$_2$)P^{i}Pr$_2$} (**9**): yield 85 mg (38%). ^{1}H NMR (300 MHz, CDCl$_3$, 293 K): δ 5.63 (dd, J(HH) = 5.7 Hz, J(HH) = 5.7 Hz, 1 H, −CH bridge, TFB), 4.93 (dd, J(HH) = 5.7 Hz, J(HH) = 5.7 Hz, 1 H, −CH bridge, TFB), 4.55 (ddd, J(PH) = 6.0 Hz, J(HH) = 6.0 Hz, J (HH) = 6.0 Hz, 1 H, ═CH, TFB), 4.49 (m, 1 H, PCH$_2$), 4.40 (dd, J(HH) = 6.3 Hz, J(HH) = 5.1 Hz, 1 H, ═CH, TFB), 4.32 (m, 1 H, PCH$_2$), 4.04 (dd, J(HH) = 5.4 Hz, J(HH) = 5.1 Hz, 1 H, ═CH, TFB), 3.85 (ddd, J(PH) = 6.6 Hz, J(HH) = 6.0 Hz, J(HH) = 6.0 Hz, 1 H, ═CH TFB), 3.77 (m, 1 H, PCCH═), 3.50 (m, 1 H, PCH), 3.34 (d, J(HH) = 11.1 Hz, 1 H, CH═CHH_{trans}), 3.23 (d, J(HH) = 8.0 Hz, 1 H, C═CHH_{cis}), 2.39 (m, 1 H, PCH), 1.61 (dd, J(HH) = 7.2 Hz, J(PH) = 14.7 Hz, 3 H, PCCH$_3$), 1.52 (dd, J(HH) = 7.5 Hz, J(PH) = 16.5 Hz, 3 H, PCCH$_3$), 1.39 (dd, J(HH) = 6.3 Hz, J(PH) = 13.5 Hz, 3 H, PCCH$_3$), 1.37 (dd, J(HH) = 7.5 Hz, J(PH) = 15.0 Hz, 3 H, PCCH$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, CDCl$_3$, 293 K): δ −69.6 (s). ^{13}C{^{1}H}NMR (75.42 MHz, CDCl$_3$, 293 K, plus APT): δ 67.3 (+, br, −CH bridge, TFB), 62.7 (+, d, J(PC) = 10.1 Hz, ═CH, TFB), 62.1 (−, d, J(PC) = 3.2 Hz, CH═CH$_2$), 57.7 (+, d, J(PC) = 1.3 Hz, ═CH, TFB), 48.4 (+, br, −CH bridge, TFB), 40.5 (+, br, ═CH, TFB), 40.4 (+, d, J(PC) = 6.0 Hz, CH═CH$_2$), 36.62 (+, d, J(PC) = 1.8 Hz, ═CH, TFB), 30.4 (−, d, J(PC) = 33.5 Hz, PCH$_2$), 27.61 (+, d, J(PC) = 19.3 Hz, PCH), 24.5 (+, d, J(PC) = 23.9 Hz, PCH), 20.5 (+, s, PCCH$_3$), 20.4 (+, d, J(PC) = 1.4 Hz, PCCH$_3$), 20.3 (+, d, J(PC) = 5.6 Hz, PCCH$_3$), 20.1 (+, d, J(PC) = 5.1 Hz, PCCH$_3$). Anal. Calcd for C$_{21}$H$_{25}$Cl$_2$F$_4$OsP: C, 39.07; H, 3.89. Found: C, 39.19; H, 3.96. MS (FAB$^+$): m/e 646 (M$^+$), 611 (M$^+$ − Cl).

The brown toluene solution was concentrated to dryness. Addition of pentane caused the precipitation of a yellow solid, which was separated by decantation, washed with pentane, and dried in vacuo. The yellow solid obtained was characterized as OsCl$_2$(η^4-TFB){[(η^2-CH$_2$═C(CH$_3$)]P^{i}Pr$_2$} (**10**): yield 90 mg (41%). ^{1}H NMR (300 MHz, CDCl$_3$, 293 K): δ 5.71 (br, 1 H, −CH bridge, TFB), 4.81 (br, 1 H, −CH bridge, TFB), 4.69 (ddd, J(PH) = 5.8 Hz, J(HH) = 5.0 Hz, J(HH) = 5.0 Hz, 1 H, ═CH, TFB), 4.10 (dd, J(HH) = 5.0 Hz, J(HH) = 5.0 Hz, 1 H, ═CH TFB), 4.02 (dd, J(HH) = 4.9 Hz, J(HH) = 4.9 Hz, 1 H, ═CH, TFB), 3.88 (m, 1H, PCH), 3.61 (d, J(PH) = 34.6 Hz, 1 H, PC═CHH_{trans}), 2.75 (ddd, J(PH) = 5.2 Hz, J(HH) = 4.9 Hz, J(HH) = 4.9 Hz, 1 H, ═CH, TFB), 2.58 (d, J(PH) = 8.8 Hz, 3 H, PC(CH$_3$)═), 2.46 (d, J(PH) = 12.1 Hz, 1 H, PC═CHH_{cis}), 1.99 (m, 1H, PCH), 1.72−1.51 (12 H, PCCH$_3$). ^{31}P{^{1}H}NMR (121.42 MHz, CDCl$_3$, 293 K): δ −12.2 (s). ^{13}C{^{1}H}NMR (75.42 MHz, CDCl$_3$, 293 K, plus APT): δ 65.8 (−, d, J(PC) = 22.5 Hz, C═CH$_2$), 62.8 (−, d, J(PC) = 4.2 Hz, C═CH$_2$), 58.9 (+, s, −CH bridge, TFB), 47.2 (+, d, J(PC) = 1.0 Hz, −CH bridge, TFB), 46.3 (+, d, J(PC) = 1.5 Hz, ═CH, TFB), 44.3 (+, d, J(PC) = 5.0 Hz, ═CH, TFB), 40.6 (+, d, J(PC) = 3.2 Hz, ═CH, TFB), 35.5 (+, d, J(PC) = 3.2 Hz, ═CH, TFB), 24.8 (+, d, J(PC) = 7.4 Hz, PC(CH$_3$)═), 24.4 (+, d, J(PC) = 22.0 Hz, PCH), 21.9 (+, d, J(PC) = 28.0 Hz, PCH), 20.6 (+, d, J(PC) = 5.9 Hz, PCCH$_3$), 19.3 (+, d, J(PC) = 6.9 Hz, PCCH$_3$), 19.2 (+, s, PCCH$_3$), 14.4 (+, s, PCCH$_3$). Anal. Calcd for C$_{21}$H$_{25}$Cl$_2$F$_4$OsP + 0.5C$_5$H$_{12}$: C, 41.40; H, 4.58. Found: C, 41.65; H, 4.71. MS (FAB$^+$): m/e 646 (M$^+$), 611 (M$^+$ − Cl).

Reaction of 3 with Tetrafluorobenzobarrelene. A suspension of OsHCl$_2$(η^4-C$_8$H$_{11}$P^{i}Pr$_3$)(P^{i}Pr$_3$) (90 mg, 0.13 mmol) in 13 mL of toluene was treated with tetrafluorobenzobarrelene (147 mg, 0.65 mmol) and heated under reflux for 3 h. After the mixture was cooled to room temperature, a white precipitate and a brown solution were obtained. The white solid was separated by decantation, washed with toluene, and dried in vacuo. The product was characterized as **9** by ^{1}H and ^{31}P{^{1}H} NMR: yield 35 mg (42%). The yellow solution was concentrated to dryness. Addition of pentane caused the precipitation of a yellow solid, which was separated by decantation, washed with pentane, and dried in vacuo. The product was characterized as **10** by ^{1}H and ^{31}P{^{1}H} NMR: yield 38 mg (45%).

Crystal Data for 2, 3, and 9: Crystals suitable for the X-ray diffraction study were obtained from dichloromethane/pentane (**2** and **3**) or dichloromethane/methanol solutions (**9**). The crystals (light yellow crystalline prism, 0.46 × 0.42 × 0.39 mm (**2**); colorless crystalline rectangular plate, 0.28 × 0.18 × 0.06 mm (**3**); and a colorless crystalline prism, 0.60 × 0.58 × 0.33 mm (**9**)) were glued onto the tip of a glass fiber. A set of randomly searched reflections were indexed to monoclinic (**2** and **3**) or triclinic (**9**) symmetry, and accurate unit cell dimensions were determined by a least-squares refinement of 44 (**2**), 24 (**3**), and 59 (**9**) carefully centered reflections ($10 \le 2\theta \le 30$ (**2**); $25 \le 2\theta \le 30$ (**3**); and $20 \le 2\theta \le 50$ (**9**)). Data were collected on Siemens P4 (**2** and **3**) or Siemens Stoe AED four-circle (**9**) diffractometers, with graphite-monochromated Mo Kα radiation, by the $\omega/2\theta$ scan method. Three orientation and intensity standards were monitored at intervals through-

Table 4. Crystallographic Data for Complexes 2, 3, and 9

	2	3	9
mol form	$C_{17}H_{31}Cl_2OsP$	$C_{26}H_{54}Cl_2OsP_2$	$C_{21}H_{25}Cl_2F_4OsP$
mol wt	527.512	689.766	645.502
a, Å	9.4882(19)	8.521(2)	7.6816(13)
b, Å	15.9515(19)	12.414(4)	11.0435(21)
c, Å	13.8635(18)	28.432(8)	13.2247(30)
α, deg	n/a	n/a	76.969(9)
β, deg	108.915(11)	96.53(2)	73.975(1)
γ, deg	n/a	n/a	74.852(9)
V, Å^3	1985.0(6)	2988(2)	1026.5(4)
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Z	4	4	2
temp, °C	20	20	−117
θ min−max, deg	1−25	2−22.5	1.5−25
octants	$h, \pm k, \pm l$	$h, \pm k, \pm l$	$-h, \pm k, \pm l$
no. measd reflns	8338	5340	5552
no. indep reflns	3503	3900	3609
no. of params	192	296	264
GOF	1.077	1.086	1.049
ρ_{calcd}, g cm^{-3}	1.7652	1.5333	2.0884
μ, mm^{-1}	6.767	4.572	6.591
trans coeff	0.428/0.865	n/a	0.329/1.000
R_1[a]	0.0235	0.0556	0.0227
R_2[a]	0.0577	0.1441	0.0616

[a] SHELXL-93: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, calculated using 3015, 2718, and 3564 observed reflections [$F_o > 4\sigma(F_o)$] for complexes **2**, **3**, and **9**, respectively. $R_2 = \sqrt{\{\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4\}}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = F_o^2 + 2F_c^2/3$.

out the data collection; no variation was observed. Data were corrected for absorption using a semiempirical method (ψ-scan[24], **2** and **9**). For the complex **3**, an empirical method (DIFABS)[25] was used because it gave better results, althrough not perfect. The structures were solved by Patterson (SHELXTL PLUS)[26] and conventional Fourier techniques, and refined by full-matrix least-squares on F^2 (SHELXL-93).[27] All non-hydrogen atoms were refined anisotropically, and all hydrogens were observed or calculated but refined riding on C atoms with common thermal parameters. The largest peaks and holes in the final difference maps were 0.78 and −0.75 e·Å^{-3} (**2**), 1.584 and −1.177 e·Å^{-3} (**3**) and 1.2 and −2.2 e·Å^{-3} (**9**). The crystallographic data for complexes **2**, **3**, and **9** are summarized in Table 4.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, distances and angles, interatomic distances, and least-squares planes for **2**, **3**, and **9** (42 pages). Ordering information is given on any current masthead page.

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(24) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351.

(25) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

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

(27) Sheldrick, G. M. *SHELXL-93*; University of Göttingen, Göttingen, Germany, 1993.