3100 *Organometallics* **2000,** *19,* 3100−3108

Synthesis, Characterization, and Theoretical Study of Stable Hydride−Azavinylidene Osmium(IV) Complexes

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Received March 6, 2000

The dihydride−dichloro complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) reacts with cyclohexanone oxime in toluene under reflux to give after 12 h $OsHCl_2\{N{=}\overline{C(CH_2)_4C}H_2\}(P^iPr_3)_2$ (**2**), which can be also obtained by reaction of the oximate compound, $OsH_2Cl\{\kappa\text{-}N,\kappa\text{-}O[ON{=}\overline{C(CH_2)_4C}H_2]\}(P^iPr_3)_2$ (**3**) with HCl. Complex $OsHCl_2\{N{=}C(CH_3)_2\}(P^iPr_3)_2$ (**4**) has been similarly prepared by treatment of compound $OsH_2Cl\{\kappa\text{-}N,\kappa\text{-}O[ON{=}C(CH_3)_2]\}(P^iPr_3)_2$ (**5**) with HCl. When the reaction of **1** and cyclohexanone oxime, in toluene under reflux, was quenched after 1 h, a mixture of **1**, **2**, **3**, and the trichloroazavinylidene $OsCl_3\{N{=}\overline{C(CH_2)_4C}H_2\}(P^iPr_3)_2$ (**6**) was obtained. The structures in the solid state of **2** and **6** have been determined by X-ray diffraction studies. In both cases, the geometry around the metal center can be described as a distorted octahedron with the phosphorus atoms of the phosphines occupying trans positions and the C═N group and the carbon atoms bonded to this group lying in a plane that is parallel to the Cl−Os−Cl plane. CCSD(T)//B3LYP calculations on the model complexes $OsXCl_2(N{=}CH_2)(PH_3)_2$ [X = H (**2t**), X = Cl (**6t**)] state that the above-mentioned conformation is 15.3 (**2t**) or 12.1 (**6t**) kcal mol^{-1} more stable than that with the azavinylidene ligand parallel to the P−Os−P plane. In solution the azavinylidene ligands of **2** and **4** rotate around the Os−N−C axis. The activation parameters of the process are $\Delta H^{\ddagger} = 14.4 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -1.1 \pm 1.3$ cal mol^{-1} K^{-1} for **2** and $\Delta H^{\ddagger} = 13.1 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0.0 \pm 2.8$ cal mol^{-1} K^{-1} for **4**.

Introduction

Vinylidene complexes have attracted a great deal of attention in recent years,[1] in particular, hydride−vinylidene derivatives, which are considered important intermediates in several homogeneous and heterogeneous catalytic reactions, including alkene oligomerization, polimerization, metathesis of olefins,[2] and Fischer−Tropsch synthesis.[3]

Few hydride−vinylidene complexes have been isolated,[4] since they appear to be thermodynamically and kinetically unstable and evolve in solution into the corresponding alkenyl derivatives, as a result of the migratory insertion of the vinylidene group into the M−H bond.[4a,c,e,k] Werner and co-workers have also reported that in solution the hydride−vinylidene cations $[IrHCl(C{=}CHR)(P^iPr_3)_2]^+$ (R = H, CH_3) smoothly rearrange by 1,3-hydride shift to afford the corresponding carbyne isomers $[IrCl(CCH_2R)(P^iPr_3)_2]^+$.[4b]

Azavinylidene complexes, which contain nitrogen instead of carbon in the α-position of the unsaturated

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10.1021/om000208t CCC: $19.00

ligands, have been proposed as intermediates in the catalytic and stoichiometric reduction of nitriles[5] and in the ammoxidation of propylene.[6] In comparison, less is known about azavinylidenes. The azavinylidene compounds previously reported are Sc,[7] Ti,[8] Zr,[9] Cr,[10] Mo,[11] W,[5c,d,6,12] Re,[13] Ru,[14] Os,[15] Ir,[16] and U[17] complexes. The osmium derivatives are cationic arene d^6 species, while neutral d^4 species are not known.

A situation of instability similar to that previously mentioned for the hydride−vinylidene complexes is observed in the related family of the hydride−azavinylidene compounds. Although, the addition of H^+ or H^- to azavinylidenes to give imines and/or nitrenes (the compounds related to alkenyls and carbynes with a nitrogen atom in the α-position) has been described,[5b,12c,e,h] only two hydride−azavinylidene derivatives have been reported: the five-coordinate d^6 species $MH(N{=}CPh_2)(CO)(P^iPr_3)_2$ (M = Ru,[18] Os[19]). These complexes have been obtained by reaction of the corresponding chloro-hydrides $MHCl(CO)(P^iPr_3)_2$ (M = Ru, Os) with $LiN{=}CPh_2$. In methanol, they are unstable and decompose into the orthometalated benzophenone imine derivatives $\overline{\mathrm{MH\{NH{=}C(Ph)C}}{}_6\mathrm{H_4\}(CO)(P^iPr_3)_2}$ (M = Ru, Os) by a process similar to the orthopalladation.[18] The orthometalated benzophenone imine osmium compound can also be prepared by reaction of the dihydride−1-butene complex $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ with benzophenone imine.[20]

Conformational preferences and rotational barriers arise from the π-ligand properties of azavinylidenes. In a nonsymmetrical ligand field, different orientations are possible for both vinylidene and azavinylidene ligands. If the rotational barriers around the M=E (E = C, N) axis are high enough, an equilibrium between the rotational isomers can be detected spectroscopically.[4g,12,21] Several quantitative theoretical studies have been recently reported for the case of vinylidene ligands,[4i,22] but such studies are lacking for the azavinylidene ones.

The six-coordinate complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) is a unique species with a chemical behavior completely different from that of previously reported compounds. It not only catalyzes the reduction of ketones, olefins, and diolefins[23] but also is a useful starting material to prepare dihydrogen,[24] polyhydride,[25] carbyne,[26] diolefin,[27] and cyclopentadienyl[28] derivatives of osmium(II) and osmium(IV). We have now observed that the complex $OsH_2Cl_2(P^iPr_3)_2$ is also useful to prepare

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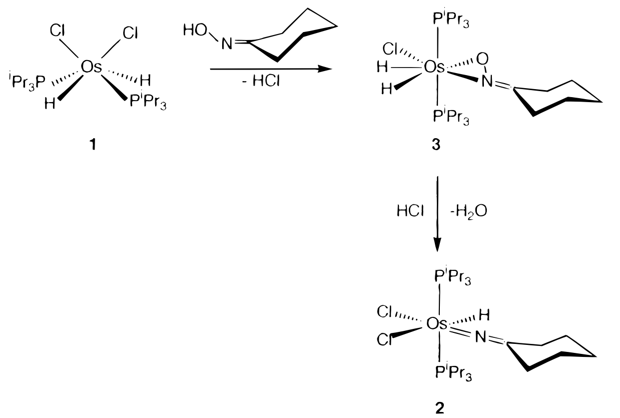
Scheme 1



hydride–azavinylidene compounds of osmium(IV), which are of interest not only because they are the first d^4-hydride–azavinylidene derivatives and the first d^4-azavinylidene species of osmium but also because they are thermodynamically and kinetically more stable than the corresponding imine and nitrene isomers.

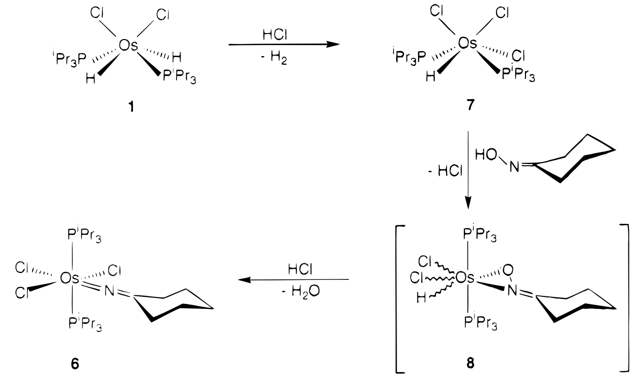
Results and Discussion

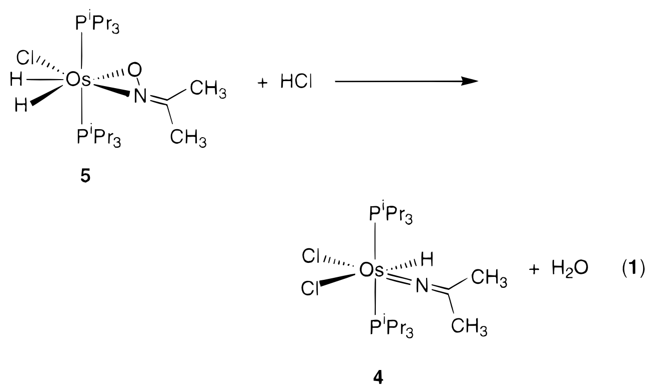
1. Synthesis and Characterization of $OsHCl_2(N{=}CR_2)(P^iPr_3)_2$ [$CR_2{=}\overline{C(CH_2)_4C}H_2$, $C(CH_3)_2$] and $OsCl_3\{N{=}\overline{C(CH_2)_4C}H_2\}(P^iPr_3)_2$.

Treatment of a toluene solution of $OsH_2Cl_2(P^iPr_3)_2$ (**1**) with 1.2 equiv of cyclohexanone oxime under reflux affords after 12 h a green solution, from which the hydride–azavinylidene complex $OsHCl_2\{N{=}\overline{C(CH_2)_4C}H_2\}(P^iPr_3)_2$ (**2**) was isolated by addition of pentane, as a green solid in 70% yield. In addition, a sticky residue was obtained from the resulting pentane solution. The $^{31}P\{^1H\}$ NMR spectrum of this residue in benzene-d_6 shows two singlets at 12.3 and −60.9 ppm, in a 1:4 intensity ratio. The first singlet was assigned to the previously reported oximate complex $OsH_2Cl\{\kappa\text{-}N,\kappa\text{-}O[ON{=}\overline{C(CH_2)_4C}H_2\}(P^iPr_3)_2$[29] (**3**) by comparison of the above-mentioned spectrum with a pure sample.

When the reaction was carried out at room temperature, after 1 h, a brown solid was obtained by addition of methanol. The $^{31}P\{^1H\}$ NMR spectrum of the solid in benzene-d_6 indicates that it is a mixture of four compounds: **1** (about 40%), **3** (about 35%), **2** (about 20%), and that corresponding to the signal at −60.9 ppm (traces). This suggests that the formation of **2** takes place in two steps (Scheme 1). Initially, complex **1** reacts with cyclohexanone oxime to give HCl and the oximate complex **3**. Subsequently, the generated HCl attacks the oximate group of **3** to afford **2** and water. In agreement with Scheme 1, we have also observed that the treatment at room temperature of **1** with a stoichiometric amount of cyclohexanone oxime in the presence of 5 equiv of Et_3N gives **3** in 82% yield and that the addition of 1.7 equiv of HCl in water to a toluene solution of **3** affords **2** in 80% yield. The related hydride–azavinylidene complex $OsHCl_2\{N{=}C(CH_3)_2\}(P^iPr_3)_2$ (**4**) was similarly prepared, by reaction of $OsH_2Cl\{\kappa\text{-}N,\ \kappa\text{-}O\text{-}[ON{=}C(CH_3)_2]\}(P^iPr_3)_2$ (**5**) with HCl (eq 1). Complex **4** was isolated as a green microcrystalline solid in 84% yield.

Scheme 2





When the reaction of **1** and cyclohexanone oxime, in toluene under reflux, was quenched after 1 h, a mixture of complexes **1**, **2**, **3**, and that corresponding to the signal at −60.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum was also obtained. The successive crystallizations of the mixture in toluene–methanol afford a few yellow crystals, which show a singlet at −60.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The crystals were characterized (vide infra) as the azavinylidene complex $OsCl_3\{N{=}\overline{C(CH_2)_4C}H_2\}(P^iPr_3)_2$ (**6**).

The formation of **6** can be rationalized according to Scheme 2. The HCl acid, which is generated from the reaction of **1** with the oxime to give **3**, should react with **1** to afford molecular hydrogen and the previously reported monohydride $OsHCl_3(P^iPr_3)_2$ (**7**).[30] In this way the subsequent reaction of **7** with cyclohexanone oxime should yield **6**, by a process similar to the reaction of **1** with the oxime.

The hydride–azavinylidene complexes **2** and **4** were characterized by MS, elemental analysis, IR, and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. Complex **2** was further characterized by an X-ray crystallographic study. The structure has two chemically equivalent but crystallographically independent molecules of complex **2** in the asymmetric unit. A drawing of one of them is shown in Figure 1. Selected bond distances and angles for both molecules are listed in Table 1.

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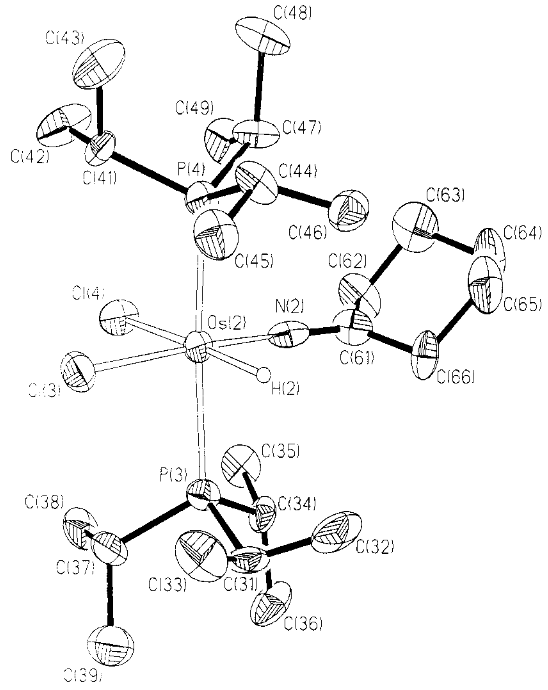

Figure 1. Molecular diagram for $OsHCl_2\{N{=}\overline{C(CH_2)_4C}H_2\}(P^iPr_3)_2$ (**2**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $OsHCl_2\{N{=}\overline{C(CH_2)_4C}H_2\}(P^iPr_3)_2$ (2)

molecule **a**		molecule **b**	
Os(1)−P(1)	2.414(4)	Os(2)−P(3)	2.420(4)
Os(1)−P(2)	2.410(4)	Os(2)−P(4)	2.402(4)
Os(1)−Cl(2)	2.418(4)	Os(2)−Cl(3)	2.425(3)
Os(1)−Cl(1)	2.474(3)	Os(2)−Cl(4)	2.463(4)
Os(1)−N(1)	1.789(12)	Os(2)−N(2)	1.777(12)
		Os(2)−H(2)	1.65(11)
N(1)−C(51)	1.30(2)	N(2)−C(61)	1.28(2)
P(1)−Os(1)−P(2)	169.27(13)	P(3)−Os(2)−P(4)	169.86(14)
P(1)−Os(1)−Cl(2)	89.31(14)	P(3)−Os(2)−Cl(3)	88.36(12)
P(1)−Os(1)−Cl(1)	94.88(13)	P(3)−Os(2)−Cl(4)	94.27(13)
P(1)−Os(1)−N(1)	90.1(4)	P(3)−Os(2)−N(2)	90.0(3)
		P(3)−Os(2)−H(2)	82(4)
P(2)−Os(1)−Cl(2)	89.39(13)	P(4)−Os(2)−Cl(3)	89.39(13)
P(2)−Os(1)−Cl(1)	95.70(12)	P(4)−Os(2)−Cl(4)	95.47(13)
P(2)−Os(1)−N(1)	90.3(4)	P(4)−Os(2)−N(2)	90.6(3)
		P(4)−Os(2)−H(2)	88(4)
Cl(2)−Os(1)−Cl(1)	87.23(13)	Cl(3)−Os(2)−Cl(4)	86.60(14)
Cl(2)−Os(1)−N(1)	175.1(4)	Cl(3)−Os(2)−N(2)	170.6(4)
		Cl(3)−Os(2)−H(2)	80(3)
Cl(1)−Os(1)−N(1)	97.6(4)	Cl(4)−Os(2)−N(2)	102.7(4)
		Cl(4)−Os(2)−H(2)	167(3)
		N(2)−Os(2)−H(2)	90(3)
Os(1)−N(1)−C(1)	173.1(12)	Os(2)−N(2)−C(61)	179.3(10)

The coordination geometry around the osmium atom can be rationalized as derived from a distorted octahedron with the triisopropylphosphine ligands occupying trans positions [P(1)−Os(1)−P(2) = 169.27(13)°, P(3)−Os(2)−P(4) = 169.86(14)°] at opposite sites of an ideal coordination plane defined by the two chloride ligands mutually cis disposed [Cl(2)−Os(1)−Cl(1) = 87.23(13)°, Cl(3)−Os(2)−Cl(4) = 86.60(14)°], the hydride, and the nitrogen atom of the azavinylidene group disposed trans to Cl(2) in molecule **a** [Cl(2)−Os(1)−N(1) = 175.1(4)°] and to Cl(3) in molecule **b** [Cl(3)−Os(2)−N(2) = 170.6(4)°].

The most conspicuous feature of the structure is the very short Os−N bond length of 1.789(12) Å in molecule **a** and 1.777(12) Å in molecule **b**, which are fully consistent with a Os−N double-bond formulation. Os−N(azavinylidene) bond lengths previously reported are between 1.81(2)[15f] and 1.882(6)[15c] Å. So, the Os−N bond lengths in **2** are the shortest known osmium−azavinylidene distances. This could be related to the different oxidation states of the metallic centers, IV in **2** and II in the previously reported compounds.

The C−N distances in **2** [N(1)−C(15) = 1.30(2) Å, N(2)−C(61) = 1.28(2) Å] are similar to those in other azavinylidene transition metal complexes (about 1.30 Å)[7−15] and also agree with the N−C bond lengths found in organic azaallenium cations (between 1.23 and 1.33 Å)[31] and in the 2-azaallenyl complexes $Cr\{C(OEt){=}N{=}C^tBu_2\}(CO)_5$ [1.272(5) and 1.264(5) Å],[32] $Cr\{C(Ph){=}N{=}CHPh\}(CO)_5$ [1.260(4) and 1.265(4) Å],[33] and $[Ru(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}N{=}CPh_2\}(CO)(P^iPr_3)]BF_4$ [1.283(9) and 1.252(9) Å].[34]

The Os−N−C chain is almost linear [Os(1)−N(1)−C(1) = 173.1(12)°, Os(2)−N(2)−C(61) = 179.3(10)°] and forms a plane with C(52) and C(56) (molecule **a**) or C(62) and C(66) (molecule **b**) perpendicular to the best plane containing the phosphorus atoms of the phosphine ligands and the osmium atom (angle: 89.4° in molecule **a**, and 88.1° in molecule **b**).

In addition, it should be mentioned that the distance between the osmium atom and the chloride disposed trans to the azavinylidene group [Os(1)−Cl(2) = 2.418(4) Å, Os(2)−Cl(3) = 2.425(3) Å] is between 0.04 and 0.06 Å shorter than between the osmium atom and the chloride disposed trans to the hydride [Os(1)−Cl(1) = 2.474(3) Å, Os(2)−Cl(4) = 2.463(4) Å], which can be assigned to the different trans-influence of the azavinylidene and hydride ligands.

The ^1H NMR spectrum in toluene-d_8 of **2** agrees well with the structure shown in Figure 1. Because the azavinylidene ligand is disposed cis to both hydride and chloride ligands and the C=N group and the CH_2 carbon atoms bonded to the C=N group lie within the plane containing the metallic center, the hydride, and the chloride ligands (the dihedral angle formed by the least-squares planes through both groups of atoms is 7.0° in molecule **a** and 7.9° in molecule **b**), the CH_2 groups are inequivalent. In accordance with this, the spectrum at 263 K shows two CH_2CN resonances at 3.65 and 3.25 ppm. On raising the temperature, they coalesce to give one resonance. This behavior can be understood as the result of the rotation of the azavinylidene ligand around the Os−N−C axis. Line-shape analysis of the spectra of Figure 2 allows the calculation of the rate constants

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(34) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E. Oro, L. A. *Organometallics* **1996**, *15*, 3423.

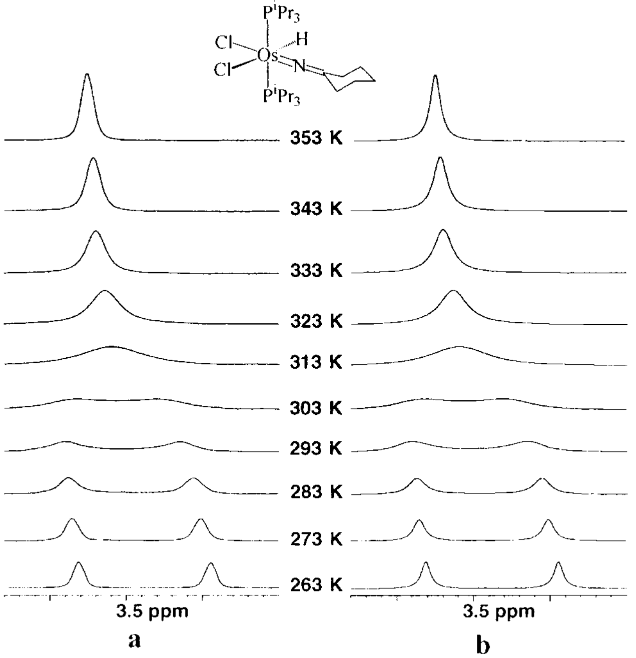

Figure 2. Experimental (a) and calculated (b) variable-temperature 300 MHz ^{1}H NMR spectra in the CH_2 region of $OsHCl_2\{N{=}C(CH_2)_4CH_2\}(P^iPr_3)_2$ (**2**) in toluene-d_8.

Table 2. Rate Constants for Azavinylidene Rotation around the Os−N−C Axis of Complexes 2 and 4

	rates (s^{-1})	
T (K)	**2**	**4**
353	6.76×10^3	
343	2.25×10^3	
333	8.41×10^2	
323	6.56×10^2	
313	3.30×10^2	
308		3.23×10^3
303	1.76×10^2	1.73×10^3
293	95.3	8.22×10^2
283	30.0	5.80×10^2
273	9.81	2.05×10^2
268		1.63×10^2
263	2.39	99.0
258		68.6
253		42.1
248		23.5
243		7.26
233		1.20

for the rotation (Table 2). The activation parameters obtained from the Eyring analysis (Figure 3) are $\Delta H^\ddagger = 14.4 \pm 0.8$ kcal mol^{-1} and $\Delta S^\ddagger = -1.1 \pm 1.3$ cal mol^{-1} K^{-1}. The activation entropy is nearly zero, suggesting that the process is intramolecular, whereas the value of the activation enthalpy is in agreement with those found in azavinylidene−tungsten complexes (between 9 and 19 kcal mol^{-1}).[12d,e,h]

The ^{1}H NMR spectrum also shows at −0.89 ppm the hydride resonance as a triplet with a H−P coupling constant of 14.1 Hz. It should be noted the unusual chemical shift of this signal, which appears to significant lower field than that observed for the previously reported hydride−osmium(IV) complexes.[25] Similar chemical shifts to the hydride of **2** have been observed for hydrides disposed trans to a linear nitrosyl group in six-coordinate dihydride−nitrosyl−osmium(II) complexes.[35]

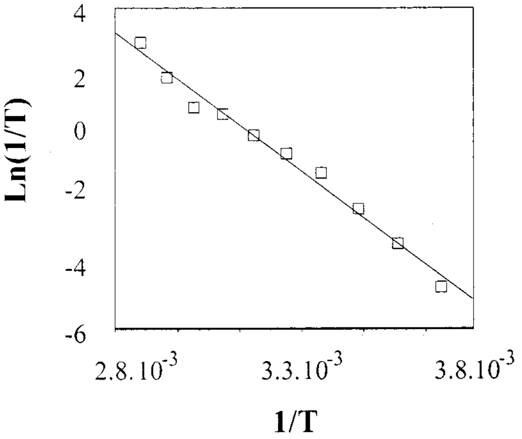

Figure 3. Eyring plot of the rate constants for the $(CH_2)_2C{=}N$ proton exchange for $OsHCl_2\{N{=}C(CH_2)_4CH_2\}(P^i\text{-}Pr_3)_2$ (**2**).

The hydride ligand also gives rise to a ν(Os−H) band at 2146 cm^{-1} in the IR spectrum in KBr. In addition, the spectrum contains a ν(C=N) absorption at 1679 cm^{-1}. The $^{13}C\{^1H\}$ NMR spectrum at 233 K is consistent with the ^{1}H NMR spectrum at the same temperature. Thus, it shows two CH_2 resonances due to the carbon atoms bonded to the C=N group at 13.4 and 9.9 ppm. The C=N carbon atom gives rise to a broad signal at 148.7 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows at −13.8 ppm a singlet, which under off-resonance conditions is split into a doublet, as a consequence of the spin-coupling with the hydride ligand.

The spectroscopic data of **4** agree well with those of **2**. In the ^{1}H NMR spectrum in toluene-d_8 at 233 K, the methyl groups of the azavinylidene ligand give rise to two singlets at 3.82 and 3.66 ppm, whereas the hydride ligand displays at −0.90 ppm a triplet with a H−P coupling constant of 14.4 Hz. On raising the temperature, the methyl resonances coalesce to give one resonance. As for **2**, line-shape analysis of the obtained spectra (Figure 4) allows the calculation of the rate constants for the rotation process (Table 2). The activation parameters obtained from the corresponding Eyring analysis (Figure 5) are in this case $\Delta H^\ddagger = 13.1 \pm 0.8$ kcal mol^{-1} and $\Delta S^\ddagger = 0.0 \pm 2.8$ cal mol^{-1} K^{-1}. The IR spectrum in KBr contains the ν(Os−H) and ν(C=N) bands at 2155 and 1685 cm^{-1}. The $^{13}C\{^1H\}$ NMR spectrum at 233 K shows two triplets at 1.9 and −2.0 ppm with C−P coupling constants of 18.9 and 17.6 Hz, respectively, corresponding to the methyl groups of the azavinylidene ligand. The resonance of the C=N carbon atom is observed at 147.4 ppm as a broad signal. The $^{31}P\{^1H\}$ spectrum contains a singlet at −14.9 ppm, which is split into a doublet under off-resonance conditions.

Similarly to **2**, the trichloroazavinylidene complex **6** was characterized by MS, elemental analysis, IR, and ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy and an X-ray crystallographic study. In this case, the structure also has two chemically equivalent but crystallographically independent molecules of complex **6** in the asymmetric unit. A drawing of one of them is shown in Figure

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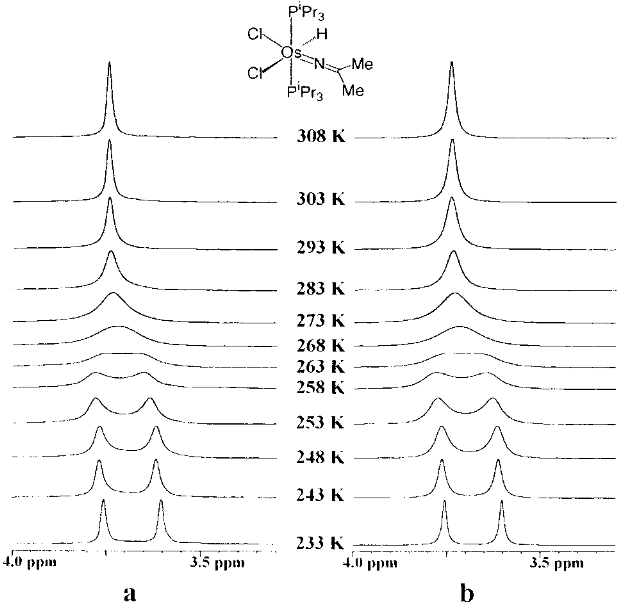


Figure 4. Experimental (a) and calculated (b) variable-temperature 300 MHz ^1H NMR spectra in the CH_3 region of $OsHCl_2\{N{=}C(CH_3)_2\}(P^iPr_3)_2$ (**4**) in toluene-d_8.

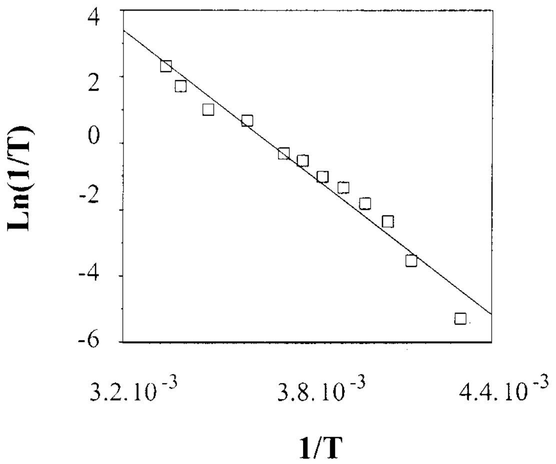


Figure 5. Eyring plot of the rate constants for the $(CH_3)_2C{=}N$ proton exchange for $OsHCl_2\{N{=}C(CH_3)_2\}(P^iPr_3)_2$ (**4**).

6. Selected bond distances and angles for both molecules are listed in Table 3.

The coordination geometry around the osmium atom can be rationalized as derived from a distorted octahedron with the triisopropylphosphine ligands occupying trans positions [P(11)−Os(1)−P(12) = 177.05(11)°, P(21)−Os(2)−P(22) = 178.09(11)°] at opposite sites of an ideal coordination plane defined by the chloride and azavinylidene ligands. The Os−N [Os(1)−N(1) = 1.808(10) Å, Os(2)−N(21) = 1.806(10) Å] bond lengths as well as the N−C [N(11)−C(11) = 1.26(2), N(21)−C(21) = 1.28(2) Å] distances are similar to those found in **2** and fully consistent with the azavinylidene formulation. The Os−N−C chain is also almost linear [Os(1)−N(11)−C(11) = 175.4(11)°, Os(2)−N(21)−C(21) = 176.5(10)°] and forms a plane with C(12) and C(16) (molecule **a**) or C(22) and C(26) (molecule **b**) perpendicular to the best plane containing the phosphorus atoms of the phosphine ligands and the osmium atom (angle: 91.8° in molecule **a**, and 89.4° in molecule **b**).

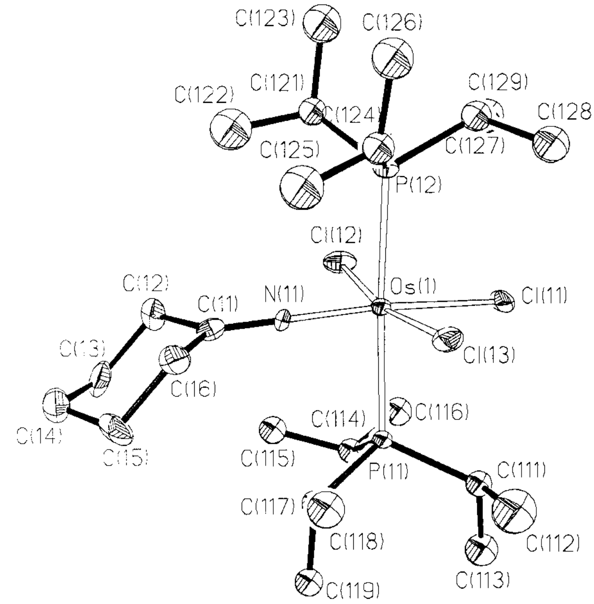


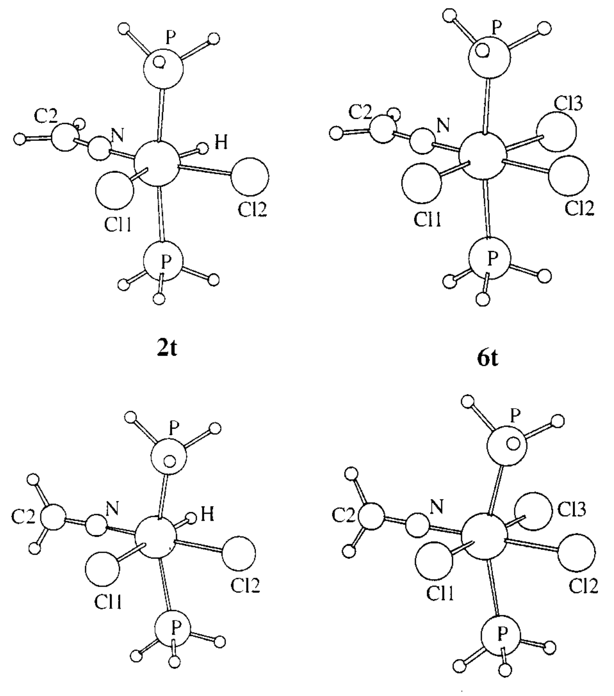
Figure 6. Molecular diagram for $OsCl_3\{N{=}C(CH_2)_4CH_2\}(P^iPr_3)_2$ (**6**). Thermal ellipsoids are shown at 50% probability.

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Complex $OsCl_3\{N{=}C(CH_2)_4CH_2\}(P^iPr_3)_2$ (6)

molecule **a**		molecule **b**	
Os(1)−P(11)	2.480(3)	Os(2)−P(21)	2.481(3)
Os(1)−P(12)	2.481(3)	Os(2)−P(22)	2.482(4)
Os(1)−Cl(11)	2.402(3)	Os(2)−Cl(21)	2.410(3)
Os(1)−Cl(12)	2.383(4)	Os(2)−Cl(22)	2.382(3)
Os(1)−Cl(13)	2.365(4)	Os(2)−Cl(23)	2.372(3)
Os(1)−N(11)	1.808(10)	Os(2)−N(21)	1.806(10)
N(11)−C(11)	1.26(2)	N(21)−C(21)	1.28(2)
P(11)−Os(1)−P(12)	177.05(11)	P(21)−Os(2)−P(22)	178.09(11)
P(11)−Os(1)−Cl(11)	84.88(11)	P(21)−Os(2)−Cl(21)	85.08(11)
P(11)−Os(1)−Cl(12)	95.39(12)	P(21)−Os(2)−Cl(22)	94.55(12)
P(11)−Os(1)−Cl(13)	90.94(12)	P(21)−Os(2)−Cl(23)	92.13(11)
P(11)−Os(1)−N(11)	89.1(3)	P(21)−Os(2)−N(21)	89.6(4)
P(12)−Os(1)−Cl(11)	93.09(11)	P(22)−Os(2)−Cl(21)	93.19(11)
P(12)−Os(1)−Cl(12)	86.54(12)	P(22)−Os(2)−Cl(22)	86.10(12)
P(12)−Os(1)−Cl(13)	86.80(12)	P(22)−Os(2)−Cl(23)	86.95(12)
P(12)−Os(1)−N(11)	93.1(3)	P(22)−Os(2)−N(21)	92.2(4)
Cl(11)−Os(1)−Cl(12)	85.11(13)	Cl(21)−Os(2)−Cl(22)	84.92(13)
Cl(11)−Os(1)−Cl(13)	86.53(13)	Cl(21)−Os(2)−Cl(23)	86.65(13)
Cl(11)−Os(1)−N(11)	172.7(3)	Cl(21)−Os(2)−N(21)	174.3(4)
Cl(12)−Os(1)−Cl(13)	169.01(12)	Cl(22)−Os(2)−Cl(23)	168.76(12)
Cl(12)−Os(1)−N(11)	91.4(4)	Cl(22)−Os(2)−N(21)	93.7(3)
Cl(13)−Os(1)−N(11)	97.6(4)	Cl(23)−Os(2)−N(21)	95.4(3)
Os(1)−N(11)−C(11)	175.4(11)	Os(2)−N(21)−C(21)	176.5(10)

The previously mentioned $^{31}P\{^1H\}$ NMR spectrum and the IR and the ^1H and $^{13}C\{^1H\}$ NMR spectra of **6** are consistent with the structure shown in Figure 6. The IR spectrum in KBr shows the $\nu(C{=}N)$ band at 1671 cm^{-1}. The ^1H NMR spectrum in benzene-d_6 contains a multiplet at 4.18 ppm, corresponding to the four CH_2-CN protons. In the $^{13}C\{^1H\}$ NMR spectrum both CH_2 carbon atoms bonded to the C=N group give rise to a singlet at 10.0 ppm, whereas the resonance corresponding to the C=N carbon atom appears at 154.1 ppm, as a triplet with a C−P coupling constant of 2.5 Hz. As has been previously mentioned, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −60.9 ppm.

2. Theoretical Analysis on Conformational Preferences and Rotational Barriers. The structures shown in Figures 1 and 6 and the ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** and **4** indicate that the C=N group and the



2t **6t**

2t-TS **6t-TS**

Figure 7. B3LYP optimized structures of $OsHCl_2(N{=}CH_2)(PH_3)_2$ (**2t**, **2t-TS**) and $OsCl_3(N{=}CH_2)(PH_3)_2$ (**6t**, **6t-TS**).

Table 4. B3LYP Optimized Geometrical Parameters Associated with $OsHCl_2(N{=}CH_2)(PH_3)_2$ (2t, 2t-TS) and $OsCl_3(N{=}CH_2)(PH_3)_2$ (6t, 6t-TS) Complexes

	2t	2t-TS	6t	6t-TS
Os−Cl(1)	2.474	2.568	2.434	2.465
Os−Cl(2)	2.475	2.491	2.434	2.484
Os−H	1.621	1.619		
Os−Cl(3)			2.448	2.465
Os−N	1.808	1.779	1.808	1.783
Os−P	2.369	2.383	2.382	2.392
N−C(2)	1.267	1.269	1.261	1.265
N−Os−Cl(1)	107.8	89.9	95.2	89.9
Cl(1)−Os−Cl(2)	86.8	90.8	86.8	90.1
Cl(2)−Os−H	74.7	87.3		
Cl(2)−Os−Cl(3)			85.9	90.1
H−Os−N	90.7	91.9		
Cl(3)−Os−N			92.1	89.9
P−Os−P	170.5	154.6	171.2	154.2

carbon atoms bonded to this group lie in a plane that is parallel to the plane containing the chlorine and osmium atoms. Furthermore, the behavior of the ^1H NMR spectra of **2** and **4** with the temperature suggests that in solution the azavinylidene ligands of these compounds rotate around the Os−N−C axis (Table 2). To understand these results, high-level ab initio calculations have been performed on the $OsXCl_2(N{=}CH_2)(PH_3)_2$ [X = H (**2t**), Cl (**6t**)] model complexes.

The structures of complexes **2t** and **6t** were optimized within the C_s symmetry constraint at the B3LYP level of theory. Two conformations were studied, the $N{=}CH_2$ ligand lying either in the Cl−Os−Cl ($\theta = 0°$) plane or perpendicular to that plane ($\theta = 90°$). The main geometrical parameters are listed in Table 4, while the optimized structures are depicted in Figure 7.

The conformational preference of the azavinylidene ligand is well reproduced by the calculations. In the preferred orientation (minima structures) the azavinylidene ligand is in the Cl−Os−Cl plane (**2t** and **6t**, $\theta = 0°$), whereas conformations with $\theta = 90°$ correspond to the transition states for the rotational process around the N=C bond (**2t-TS** and **6t-TS**, respectively). A slight distortion from the regular octahedron is found in the **2t-TS** and **6t-TS** structures. The distortion is due to the bending of the phosphine ligands toward the chloride trans to the azavinylidene ligand. Other interesting geometrical features are the Os−Cl(1) bond elongation that can be seen for the **2t-TS** complex compared to **2t** and the subtle balance in the Os−N and Os−Cl(2) distances on going from the minimum to the transition state structures, reflecting the competition between the chloride and azavinylidene ligands for the electronic density.

A reliable energetic comparison between the minima and TS structures can be obtained through CCSD(T) single-point energy calculations on the B3LYP optimized structures. A good agreement was actually found between the experimental $\Delta H^{\ddagger}$ values and the calculated energy for the corresponding model complex **2t** (about 14.4 vs 15.3 kcal mol^{-1}). For complex **6t**, in which the hydride ligand of complex **2t** has been replaced by a chloride ligand, the rotational barrier is slightly lower (12.1 kcal/mol at the CCSD(T)/B3LYP level of theory).

The nitrene and imine isomers of **2t**, resulting from the 1,3- and 1,2-hydride shifts, are respectively 2.7 and 6.9 kcal mol^{-1} more stable than **2t-Ts**. However, the participation of these intermediates in the rotation of the azavinylidene must be rejected, since the activation barriers for the 1,3- and 1,2-hydride shifts are very high, more than 90 kcal mol^{-1} for the 1,3-hydride shift and 43.8 kcal mol^{-1} for the 1,2-hydride shift.

The above-mentioned values indicate that the 1,3- and 1,2-hydride shifts in hydride−azavinylidene complexes of the type $OsHCl_2(N{=}CR_2)(PR'_3)_2$ are thermodynamically and kinetically unfavorable processes.

Concluding Remarks

This study has revealed that the dihydride−dichloro complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with oximes to afford the novel hydride−azavinylidene compounds $OsHCl_2(N{=}CR_2)(P^iPr_3)_2$, via the oximate intermediates $OsH_2Cl\{\kappa\text{-}N,\kappa\text{-}O[ON{=}CR_2]\}(P^iPr_3)_2$.

The structure of these azavinylidene complexes is octahedral, with the phosphines occupying trans positions and the C=N group and the carbon atoms bonded to this group lying in a plane that is parallel to the Cl−Os−Cl plane. This conformation is about 14−15 kcal mol^{-1} more stable than that with the azavinylidene ligand parallel to the P−Os−P plane. In solution, the azavinylidene ligands rotate around the Os−N−C axis. The mechanism of the process can be described as the change of position of the substituents of the unsaturated ligands through the less favored conformation and involves only minor motion of the other ligands. In these compounds, the hydride and azavinylidene ligands are mutually cis disposed. Despite this, they are stable and do not evolve by 1,3- or 1,2-hydride shifts into the corresponding $OsCl_2(NCHR_2)(P^iPr_3)_2$ or $OsCl_2(NH{=}CR_2)(P^iPr_3)_2$ isomers. The reason for their stability is both thermodynamic and kinetic in origin.

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 $OsH_2Cl_2(P^iPr_3)_2$ (**1**), $OsH_2Cl\{\kappa\text{-}N,\kappa\text{-}O[ON{=}\overline{C(CH_2)_4CH_2}]\}(P^iPr_3)_2$ (**3**), and $OsH_2Cl\{\kappa\text{-}N,\kappa\text{-}O[ON{=}C(CH_3)_2]\}(P^iPr_3)_2$ (**5**) were prepared by the published method.[23,29]

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

Kinetic Analysis. Complete line-shape analyses of the ^1H NMR spectra of **2** and **4** were achieved using the program gNMR v3.6 for Macintosh, Cherwell Scientific Publishing Limited. The transverse relaxation time T_2 used was common for the two signals for all temperatures recorded and was obtained from the line width of the exchange-averaged resonance above the fast-exchange limit. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated by least-squares fit of $\ln(k/T)$ vs $1/T$ (Eyring equation). Error analysis assumed a 2% error in the rate constant and 1 K in the temperature. Errors were computed by published methods.[36]

Computational Details. Calculations were performed with the GAUSSIAN94 series of programs.[37] Geometry optimizations were carried out using the density functional theory (DFT)[38] with the B3LYP functional.[39] An effective core potential operator was used to represent the 60 innermost electrons of the osmium atom.[40] The basis set for the metal was that associated with the pseudopotential,[40] with a standard valence double-ζ LANL2DZ contraction.[37] The basis set for the hydrogen atom directly attached to the metal was a double-ζ supplemented with a polarization p shell.[41a,b] A 6-31G(d) basis was used for Cl, P, and N atoms.[41c] The rest of the atoms were described using a 6-31G basis set.[41a]

To obtain accurate energetic estimations, the geometries were optimized at the B3LYP level and energies recalculated using coupled-cluster theory with single, double, and a noniterative estimation of triple excitations (CCSD(T)//B3LYP).[42]

Preparation of $OsHCl_2\{N{=}\overline{C(CH_2)_4CH_2}\}(P^iPr_3)_2$ (2). Method A: A brown solution of **1** (200 mg, 0.34 mmol) in toluene was treated with cyclohexanone oxime (40 mg, 0.35 mmol) and was heated under reflux during 12 h. After concentrating the toluene to ca. 1 mL addition of pentane yielded a green precipitate that was washed two times with pentane and dried in vacuo. Yield: 144 mg (70%). Method B: A yellow solution of **3** (200 mg, 0.30 mmol) in toluene was treated with HCl in water (500 μL, 1 N, 0.5 mmol) and was stirred for 25 min at room temperature. The blue solution was evaporated to dryness, and addition of 5 mL of methanol yielded a green precipitate that was decanted and washed with methanol (2 × 2 mL) and pentane (4 × 5 mL) and dried in vacuo. Yield: 165 mg (80%). Anal. Calcd for $C_{24}H_{53}NCl_2OsP_2$: C, 42.47; H, 7.87; N, 2.06. Found: C, 42.33; H, 7.67; N, 2.06. IR (KBr, cm^{-1}): ν(Os−H) 2146 s; ν(C=N) 1679 m. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 3.65 (br, 2H, $-CH_2C{=}N$); 3.25 (br, 2H, $-CH_2C{=}N$); 2.54 (m, 6H, PCH); 1.43 and 1.29 (both dvt, $J_{H-H} = 6.6$ Hz, $N = 12.9$ Hz, 36H, $PCHCH_3$); 1.00 (m, 6H, Cy); −0.89 (t, $J_{P-H} = 14.1$, 1H, OsH). $^{13}C\{^1H\}$ plus DEPT NMR (75.4 MHz, toluene-d_8, 233 K): δ 148.7 (br, C=N=Os); 28.3, 28.1 and 24.2 (all s, CH_2 Cy); 23.4 (vt, $N = 23.7$ Hz, PCH); 19.5 and 19.2 (both s, $PCHCH_3$); 13.4 and 9.9 (both s, $CH_2C{=}N$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ −13.8 (s, d off resonance). MS (FAB$^+$): m/z = 679 (M^+) and 644 ($M^+ - Cl$).

Table 5. Crystal Data and Data Collection and Refinement for Complex $OsHCl_2\{N{=}\overline{C(CH_2)_4CH_2}\}(P^iPr_3)_2$ (2) and $OsCl_3\{N{=}\overline{C(CH_2)_4CH_2}\}(P^iPr_3)_2$ (6)

	2	6
formula	$C_{24}H_{53}Cl_2NOsP_2 0.5CH_3OH$	$C_{24}H_{52}Cl_3NOsP_2$
mol wt	694.73	713.16
color, habit	green, prismatic	yellow, prismatic
space group	monoclinic, $P2_1$	monoclinic, $P\bar{1}$
a, Å	11.5766(8)	11.8753(8)
b, Å	15.7639(11)	15.2571(10)
c, Å	18.0123(12)	17.2013(11)
α, deg	90	89.348(1)
β, deg	108.536(1)	73.346(1)
χ, deg	90	89.644(1)
V, Å^3	3116.6(4)	2985.6(3)
Z	4	4
D(calc), g cm^{-3}	1.480	1.587
μ, mm^{-1}	4.379	4.660
scan type	ω scans at different φ values	
θ range, deg	$2 \leq \theta \leq 24$	
temp, K	193.0(2)	153.0(2)
no. of data collected	8166	11 856
no. of unique data	5370 ($R_{int} = 0.0384$)	8181 ($R_{int} = 0.0686$)
no. of params refined	695	391
$R_1{}^a$ ($F^2 > 2\sigma(F^2)$)	0.0384	0.0621
$wR_2{}^b$ (all data)	0.0827	0.1598
S^c (all data)	1.056 ($a = 0.0323$, $b = 0$)	0.996 ($a = 0.0765$, $b = 51.1130$)

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2\ (F^2) = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$; $w^{-1} = [\sigma^2(F_o{}^2) + (aP)^2 + bP]$, where $P = [\max(F_o{}^2, 0) + 2F_c{}^2)]/3$. [c] $S = [\sum[w(F_o{}^2 - F_c{}^2)^2/(n-p)]]^{1/2}$, where n is the number of reflections and p the number of refined parameters.

Preparation of $OsHCl_2\{N{=}C(CH_3)_2\}(P^iPr_3)_2$ (4). This complex was prepared as described for **2** (method b) starting from 200 mg (0.32 mmol) of **5** and 500 μL of a water solution of HCl (1 N, 0.5 mmol). A green microcrystaline solid was obtained. Yield: 173 mg (84%). Anal. Calcd for $C_{21}H_{49}NCl_2OsP_2$: C, 39.49; H, 7.73; N, 2.19. Found: C, 39.39; H, 7.52; N, 2.10. IR (KBr, cm^{-1}): ν(Os−H) 2155 s; ν(C=N) 1685 m. ^1H NMR (300 MHz, CD_2Cl_2, 233 K): δ 3.82 and 3.66 (both s, 6H, $CH_3C{=}N$); 2.55 (m, 6H, PCH); 1.35 and 1.27 (both dvt, $J_{H-H} = 6.3$ Hz, $N = 12.9$ Hz, 36H, $PCHCH_3$); −0.90 (t, $J_{P-H} = 14.4$, 1H, OsH). $^{13}C\{^1H\}$ plus DEPT NMR (75.4 MHz, CD_2Cl_2, 233 K): δ 147.4 (br, C=N=Os); 23.3 (br, PCH); 19.3−18.6 (m, $PCHCH_3$); 1.9 (d, $J_{P-C} = 18.9$ Hz, $CH_3C{=}N$) −2.0 (d, $J_{P-C} = 17.6$ Hz $CH_3C{=}N$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 233 K): δ −14.9 (s, d off resonance). MS (FAB$^+$): m/z = 604 ($M^+ - Cl$).

Preparation of $OsCl_3\{N{=}\overline{C(CH_2)_4CH_2}\}(P^iPr_3)_2$ (6). A brown solution of **1** (200 mg, 0.34 mmol) in 30 mL of toluene was treated with cyclohexanone oxime (40 mg, 0.35 mmol) and was heated under reflux during 1 h. The solution was concentrated to 3 mL, and addition of methanol yielded a

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yellow precipitate that was washed (3 × 2 mL) and dried in vacuo. Yield: 25 mg (15%). Anal. Calcd for $C_{24}H_{52}NCl_3OsP_2$: C, 40.42; H, 7.35; N, 1.96. Found: C, 40.43; H, 7.39; N, 1.77. IR (KBr, cm^{-1}): $\nu(C{=}N)$ 1671 m. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 4.18 (m, 4H, $CH_2C{=}N$); 3.00 (m, 6H, PCH); 1.44 (dvt, J_{H-H} = 6.9 Hz, N = 13.2 Hz, 36H, $PCHCH_3$); 1.30−1.00 (m, 6H, Cy). $^{13}C\{^1H\}$ plus DEPT NMR (75.4 MHz, C_6D_6, 293 K): δ 154.1 (t, J_{C-H} = 2.5 Hz, $C{=}N{=}Os$); 28.2, (s, $N{=}CCH_2CH_2$); 24.2 (s,$N{=}CCH_2CH_2CH_2$); 23.4 (t, J_{C-H} = 10.6, PCH); 19.2 (s, $PCHCH_3$); 10.0 (s, $N{=}CCH_2$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ −60.9 (s). MS (FAB$^+$): m/z 677 ($M^+ - Cl$).

X-ray Structure Determination of $OsHCl_2\{N{=}\overline{C(CH_2)_4C}H_2\}(P^iPr_3)_2$ (2) and $OsCl_3\{N{=}\overline{C(CH_2)_4C}H_2\}(P^iPr_3)_2$ (6). A summary of the fundamental crystal and refinement data of the compounds **2** and **6** is given in Table 5. Crystals of **2** and **6** showing well-defined faces were mounted on a Bruker-Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 20 mA. Data were collected over a quadrant of the reciprocal space by a combination of two frame sets for **2** and over a hemisphere by a combination of three sets for **6**. The cell parameter were determinated and refined by least-squares fit of all reflections collected. Each frame exposure time was 10 s, covering 0.3° in ω. The crystal to detector distance was 6.05 cm. Coverage of the unique sets was over 100% complete to at least 27° in θ. The first 50 frames were recollected at the end of the data collection to monitor crystal decay. The absorption correction was made using SADABS.[43] The structure was solved by Multan and Fourier methods using SHELXS.[43] Full-matrix least-squares refinement was carried out using SHELXTL[43] minimizing $w(F_o^2 - F_c^2)^2$. Weighted R factors (R_w) and all goodness of fit S values are based on F^2; conventional R factors (R) are based on F.

Acknowledgment. Financial support from the DGES of Spain (Projects PB98-0916-02-01 and PB98-1591) is acknowledged. J.T. acknowledges the “Direcció General de Recerca de la Generalitat de Catalunya” for a grant. R.C. thanks also the “Ministerio de Educación y Cultura” for a grant. The use of computational facilities of the Centre de Supercomputació i Comunicacions de Catalunya is gratefully appreciated as well.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **2** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000208T

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