Formation and Stereochemistry of Octahedral Cationic Hydride-Azavinylidene Osmium(IV) Complexes

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The complexes $[OsHCl_2(=N=CR_2)(PiPr_3)_2]$ [CR_2 = CMe_2 (**1**), $C^a(CH_2)_4C^bH_2(C^a\text{-}C^b)$ (**3**)] react with $Ag(CF_3SO_3)$ in the presence of ligands L [H_2O, $P(OMe)_3$, CO]. The reactions in the presence of water lead to $[OsHCl(=N=CR_2)(H_2O)(PiPr_3)_2][CF_3SO_3]$ [CR_2 = CMe_2 (**2**), $C^a(CH_2)_4C^bH_2(C^a\text{-}C^b)$ (**4**)], which exist as 1:1 equilibrium mixtures of the isomers **2a**/**4a** (hydride *trans* to Cl) and **2c**/**4c** (hydride *trans* to water) in the solid state and in solution. The structure of **2c** has been determined by an X-ray diffraction study. The geometry around the metal center can be described as a distorted octahedron with *trans* phosphane ligands at opposite sites of an ideal coordination plane defined by the other four ligands. The reactions in the presence of $P(OMe)_3$ afford $[OsHCl(=N=CR_2)\{P(OMe)_3\}(PiPr_3)_2][CF_3SO_3]$ [CR_2 = CMe_2 (**5a**), $C^a(CH_2)_4C^bH_2(C^a\text{-}C^b)$ (**6a**)], with the hydride and chlorine ligands *trans* disposed. Complexes **5a** and **6a** can be also obtained starting from the equilibrium mixtures of **2a** and **2c** or **4a** and **4c**, respectively, and phosphite. Compounds **5c** and **6c**, with $P(OMe)_3$ *trans* to hydride, are formed initially, and subsequently isomerize to **5a** and **6a**. Reactions under carbon monoxide give $[OsHCl(=N=CR_2)(CO)(PiPr_3)_2][CF_3SO_3]$ [CR_2 = CMe_2 (**7a**), $C^a(CH_2)_4C^bH_2(C^a\text{-}C^b)$ (**8a**)], which also contain the chlorine *trans* to the hydride ligand. A theoretical study on $[OsHCl(=N=CH_2)L(PH_3)_2]^+$ [L = H_2O, $P(OH)_3$ and CO] model complexes shows that these stereochemical preferences arise from the properties of the ligands in the plane perpendicular to the P–Os–P axis. Although the structure with the H and Cl *trans* disposed is not the most favorable when the related pentacoordinate $[OsHCl(=N=CR_2)(PiPr_3)_2]^+$ model complex is considered, it maximizes the interaction energy between the pentacoordinate complex and L ligand, and thus it is the most stable as a whole.

Introduction

Transition metal azavinylidene complexes have attracted a great deal of attention in recent years.[1,2] Some of them have been proposed as intermediates in the catalytic and stoichiometric reduction of nitriles[1s][1y,3] and in the ammoxidation of propylene.[1o] However, only two mononuclear hydride-azavinylidene compounds had been reported before 2000: the five-coordinate d^6 species $[MH(=N=CPh_2)(CO)(PiPr_3)_2]$ (M = Ru,[4] Os[5]). These hydride complexes are prepared by reaction of the corresponding chloro-hydrides $[MHCl(CO)(PiPr_3)_2]$ with $LiN=CPh_2$. In agreement with the strong basicity of the imido group, these compounds undergo hydrolysis in methanol or in the presence of traces of water and evolve into the orthometallated benzophenone imine derivatives $[M^aH\{NH=C(Ph)C_6^bH_4\}(CO)(PiPr_3)_2(M^a\text{-}C^b)]$ (M = Ru, Os) by a similar process to the orthopalladation.[4]

We have recently shown that the dihydride-dichloro complex $[OsH_2Cl_2(PiPr_3)_2]$ reacts with acetone oxime and cyclohexanone oxime to give the six-coordinate d^4 hydride-azavinylidene derivatives $[OsHCl_2(=N=CR_2)(PiPr_3)_2]$,[6] via the oximate intermediates $[OsH_2Cl\{\kappa\text{-}N,\kappa\text{-}O[ON=CR_2]\}(PiPr_3)_2]$ [CR_2 = CMe_2, $C^a(CH_2)_4C^bH_2(C^a\text{-}C^b)$].[7] In contrast to $[MH(=N=CPh_2)(CO)(PiPr_3)_2]$, these $[OsHCl_2(=N=CR_2)(PiPr_3)_2]$ complexes are stable in methanol and in the presence of significant amounts of water. Despite the *cis* disposition of the hydride and azavinylidene ligands, they are also stable towards intramolecular reductive elimination to afford d^6-imine species.[6]

The N−H oxidative addition/reductive elimination equilibrium is proposed to be one of the fundamental steps in the hydroamination of olefins and alkynes catalyzed by electron-rich late transition metal centers [Equation (1)]. The $MH(NR_2)$ species are considered the key intermediates of the process.[8]

$$M + H\text{-}NR_2 \rightleftharpoons MH(NR_2) \qquad (1)$$

A homogeneous catalyst must have free coordination sites that allow it to bind the substrates *cis* disposed to the reactive points of the metallic center. However, the complexes $[OsHCl_2(=N=CR_2)(PiPr_3)_2]$ are saturated. So, from the hydroamination point of view, the creation of a coordination vacancy stabilizing the resulting metallic fragment, without producing the intramolecular reductive elimination to Os-imine species, is by itself an objective. This fact prompted us to investigate the reactivity of $[OsHCl_2(=N=$

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$CR_2)(PiPr_3)_2]$ towards $Ag(CF_3SO_3)$ in the presence of water (a usual impurity in amines), trimethylphosphite and carbon monoxide (which are π-acceptor ligands as the olefins and alkynes) and to study the relative stability of the possible isomers resulting from the reactions.

In this paper, we report: *i*) the complexes $[OsHCl(=N=CR_2)L(PiPr_3)_2]^+$ [L = H_2O, $P(OMe)_3$, CO] and their stereochemistries, and *ii*) the factors determining the formation of these stereochemistries.

Results and Discussion

Reactions in the Presence of Water

The treatment of dichloromethane solutions of $[OsHCl_2(=N=CMe_2)(PiPr_3)_2]$ (**1**) with 1.0 equiv. of $Ag(CF_3SO_3)$ in the presence of 2.0 equiv. of water leads to blue solutions and AgCl. The solutions afford a blue solid after the solvent is removed. According to the elemental analysis and MS, the solid corresponds to the complex $[OsHCl(=N=CMe_2)(H_2O)(PiPr_3)_2][CF_3SO_3]$ (**2**). The IR, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra indicate that complex **2** exists as a 1:1 equilibrium mixture of two isomers in the solid state and in solution.

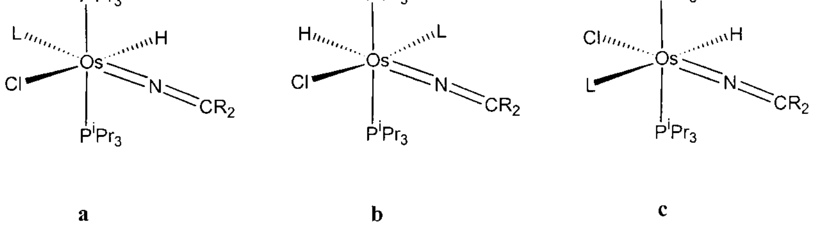
The IR spectrum in KBr shows the ν(Os−H) band of both isomers, at 2164 and 2156 cm^{-1}, along with the characteristic stretching bands of the free $CF_3SO_3^-$ anion (see Exp. Sect.),[9] in agreement with the salt character of the complex. At −90 °C in [D$_2$]dichloromethane, the $^{31}P\{^1H\}$ NMR spectrum contains two singlets at $\delta = -10.3$ and -3.7, corresponding to each isomer. Raising the sample temperature leads to a slight broadening of both resonances, although they show no signs of coalescence at temperatures below 35 °C. The ^1H NMR spectrum at −90 °C agrees well with the $^{31}P\{^1H\}$ NMR spectrum. In the high-field region, it contains two hydride resonances at $\delta = -3.85$ and 0.56, which appear as triplets with H−P coupling constants of 14.1 and 13.2 Hz, respectively. In the low-field region, the spectrum contains two singlets due to the water protons at about $\delta = 4.9$ and four singlets corresponding to the methyl protons of the azavinylidene ligand between $\delta = 4.6$ and 3.4, in addition to the phosphane resonances. The behavior of the resonances due to the hydride and water ligands at this temperature is the same as that of the resonances observed in the $^{31}P\{^1H\}$ NMR spectrum. However, the behavior of the resonances corresponding to the methyl groups of the azavinylidene ligand is significantly different. At −70 °C, the coalescence of two of them is observed, whereas the coalescence of the other two occurs at −30 °C.

The above-mentioned spectra indicate that both isomers have an octahedral structure, with the phosphanes occupying *trans* positions and the C=N group and the carbon atoms bonded to this group lying in a plane that is perpendicular to the P−Os−P axis. In solution, the coordination polyhedron is rigid, although the azavinylidene ligand rotates around the Os−N−C axis.

Three stereochemistries are consistent with the spectroscopic data obtained for **2** (Scheme 1): hydride *trans* to chlorine (**a**), hydride *trans* to azavinylidene (**b**), and hydride *trans* to water (**c**). In order to obtain information about the stereochemistries of the isomers of **2**, we carried out its slow crystallization in dichloromethane/diethyl ether. Unfortunately, the crystals obtained from numerous attempts were in all cases not suitable for an X-ray crystallographic study. The $CF_3SO_3^-$ counterion was therefore exchanged for BF_4^-, and in a crop we obtained a suitable crystal. The remaining crystals of the crop showed the same NMR spectra as **2**.

A view of the molecular geometry of the obtained isomer is shown in Figure 1. Selected bond lengths and angles are listed in Table 1. Although the hydride ligand could not be properly refined, the X-ray study clearly indicates that the isomer formed has the stereochemistry **c**. Thus, the coordination geometry around the osmium atom can be rationalized as being derived from a distorted octahedron, with the triisopropylphosphane ligands occupying *trans* positions [P(1)−Os−P(2) = 168.59(4)°] at opposite sites of an ideal coordination plane defined by the hydride ligand *trans* disposed to the water molecule and the chlorine *trans* disposed to the azavinylidene group [Cl−Os−N = 178.59(12)°].

The most conspicuous feature of the structure is the very short Os−N bond length of 1.829(4) Å, which is fully consistent with an Os−N double bond formulation and agrees well with the Os−N(azavinylidene) bond lengths previously reported [between 1.789(2)[6] and 1.882(6)[2d] Å]. The C−N distance [1.285(6) Å] is similar to those found in other azavinylidene transition metal complexes (about 1.30 Å)[1,2] and also agrees with the N−C bond lengths found in organic azaallenium cations (between 1.23 and 1.33 Å)[10] and in the 2-azaallenyl complexes $[Cr\{C(OEt)=N=CtBu_2\}(CO)_5]$ [1.272(5) and 1.264(5) Å],[11] $[Cr\{C(Ph)=N=CHPh\}(CO)_5]$ [1.260(4) and 1.265(4) Å],[12] and $[Ru(\eta^5\text{-}C_5H_5)\{C(CH=$



Scheme 1

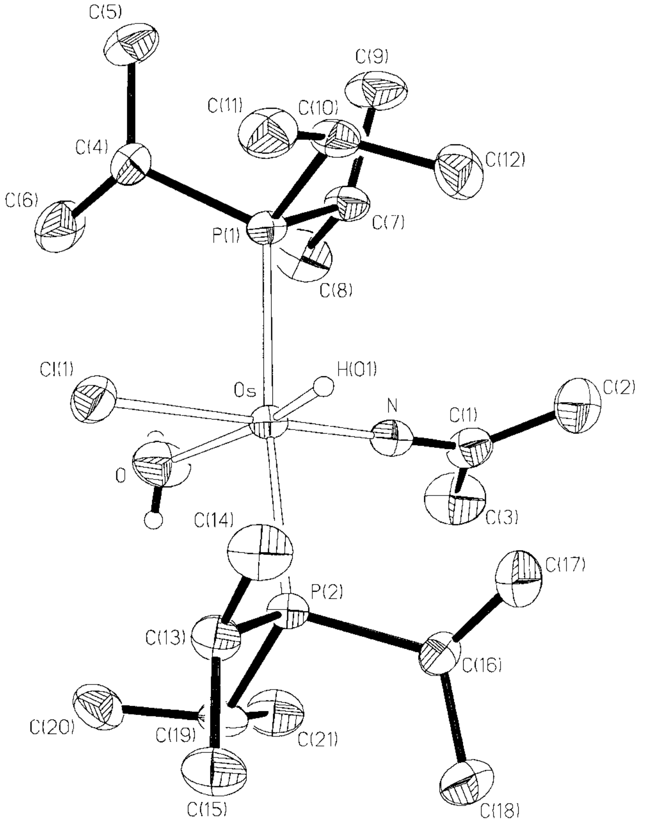


Figure 1. Molecular diagram for $[OsHCl(=N=CMe_2)(H_2O)(PiPr_3)_2]^+$ (**2c**); thermal ellipsoids are shown at 50% probability

Table 1. Selected bond lengths (Å) and angles (deg) for the complex $[OsHCl\{=N=C(CH_3)_2\}(H_2O)(PiPr_3)_2][BF_4]\cdot CH_2Cl_2$ (**2c**)

Os−Cl	2.3972(14)	Os−N	1.829(4)
Os−P(1)	2.4608(14)	N−C(1)	1.285(6)
Os−P(2)	2.4378(14)	C(1)−C(3)	1.518(8)
Os−O	2.306(4)		
Cl−Os−P(1)	88.89(4)	P(2)−Os−O	97.32(11)
Cl−Os−P(2)	90.18(4)	P(2)−Os−N	90.44(12)
Cl−Os−O	83.51(13)	O−Os−N	95.15(17)
Cl−Os−N	178.59(12)	Os−N−C(1)	176.5(4)
P(1)−Os−P(2)	168.59(4)	N−C(1)−C(2)	120.7(5)
P(1)−Os−O	93.88(11)	N−C(1)−C(3)	120.2(5)
P(1)−Os−N	90.74(12)	C(2)−C(1)−C(3)	119.0(5)

$CPh_2)=N=CPh_2\}(CO)(PiPr_3)]^+$ [1.283(9) and 1.252(9) Å].[13]

The Os−N−C chain is almost linear [Os−N−C(1) = 176.5(4)°] and, in agreement with the ^1H and $^{13}C\{^1H\}$ NMR spectra at low temperatures, forms a plane with C(2) and C(3) perpendicular to the best plane containing the phosphorus atoms of the phosphane ligands and the osmium atom [angle: 89.0(2)°]. A similar disposition of the azavinylidene ligand has also been found in the complex $[OsHCl_2\{=N=C^a(CH_2)_4C^bH_2)(PiPr_3)_2(C^a\text{-}C^b)]$ (**3**), where the azavinylidene group is also *trans* disposed to a chlorine ligand.[6]

Since experimental methods have been shown to be ineffective in solving the problem of the determination of the stereochemistry in the other isomer of **2**, we have carried out DFT geometry optimizations on the **a**, **b** and **c** isomers of the model complex $[OsHCl(=N=CH_2)(H_2O)(PH_3)_2]^+$ (**2t**). Single point CCSD(T) calculations on the B3LYP optimized geometries have also been carried out in order to refine further the obtained energetic differences between the three isomers. The results (Table 2) indicate that the stereochemistries **a** (hydride *trans* to chlorine) and **c** (hydride *trans* to water) are clearly more stable (about 20 kcal·mol^{-1}) than stereochemistry **b** (hydride *trans* to azavinylidene) and, in agreement with the spectroscopically observed 1:1 ratio between the isomers, that the difference in stability between **a** and **c** is negligible. Thus, our discussion will be focused on these two isomers. Their main geometrical parameters are listed in Table 3, and their structures are depicted in Figure 2.

Table 2. B3LYP relative energies of the **a**, **b** and **c** isomers of the $[OsHCl(=N=CH_2)L(PH_3)]^+$ (L = H_2O, $P(OH)_3$, CO) model complexes; CCSD(T)//B3LYP single point energies are given in parentheses, where available

	L = H_2O	L = $P(OH)_3$	L = CO
Isomer **a**	0.0(0.0)	0.0	0.(0.0)
Isomer **b**	19.6(21.0)	11.4	3.2(2.2)
Isomer **c**	1.1(0.4)	5.5	7.7(5.4)

A good agreement is found when the optimized structure for isomer **c** of $[OsHCl(=N=CH_2)(H_2O)(PH_3)_2]^+$ and the available X-ray structure of **2c** are compared. The coordination geometry around the Os atom is essentially well reproduced, although the Os−P distances are somewhat shorter (between 0.04 and 0.05 Å) when real phosphanes are substituted by model PH_3 phosphanes. Another minor discrepancy arises from the modeling of the azavinylidene ligand: the substitution of $N=CMe_2$ by $N=CH_2$ decreases the N−Os−O angle in complex **2t**. Our theoretical calculations do, however, allow the determination of the hydride position. The short Os−H distance, similar to that found in the pentacoordinate $[OsHCl(=N=CH_2)(PH_3)_2]^+$ complex (1.601 Å in the former vs. 1.590 Å in the latter) is noteworthy. This reflects the large *trans* influence exerted by the hydride ligand, which is also mirrored by the long Os−O distance (2.341 Å).

Structure **a** shows a distorted octahedral geometry, with almost strictly *trans* arranged phosphanes (P−Os−P = 178.1°) and the angles in the perpendicular plane ranging from 73.8° to 115.0°. The different arrangement of ligands induces some changes in the osmium−ligand distances with regard to structure **c**. Thus, with the chlorine and the strong σ-donor hydride *trans* disposed, the Os−Cl and Os−H distances are significantly longer than in isomer **c** (2.431 Å and 1.622 Å respectively). On the other hand, the Os−N and Os−O distances are shorter (1.792 Å and 2.264 Å), the former being among the smallest Os−N distances found in the literature for Os-azavinylidene complexes. The linearity

Table 3. Most relevant distances (Å) and angles (deg) for the model complexes $[OsHCl(=N=CH_2)L(PH_3)]^+$ [L = H_2O (**a**, **c**), $P(OH)_3$ (**a**), CO (**a**)]

	$[OsHCl(=N=CH_2)(H_2O)(PH_3)_2]^+$		$[OsHCl(=N=CH_2)\{P(OH)_3\}(PH_3)_2]^+$	$[OsHCl(=N=CH_2)(CO)(PH_3)_2]^+$
	a	**c**	**a**	**a**
Os−P	2.404	2.399	2.402	2.415
Os−P	2.404	2.403	2.396	2.415
Os−N	1.792	1.809	1.839	1.846
Os−Cl	2.431	2.405	2.458	2.430
Os−L	2.264	2.341	2.396	2.009
Os−H	1.622	1.601	1.621	1.630
N−C	1.263	1.263	1.261	1.259
P−Os−P	178.08	171.46	178.86	176.07
H−Os−N	94.76	91.67	90.64	90.94
H−Os−Cl	150.28	84.53	151.51	151.84
H−Os−L	73.79	165.16	70.02	71.77
N−Os−Cl	114.95	176.12	117.85	117.22
N−Os−L	167.88	102.98	160.64	162.71
Cl−Os−L	76.61	80.79	81.49	80.07
Os−N−C	179.55	175.39	169.07	169.86

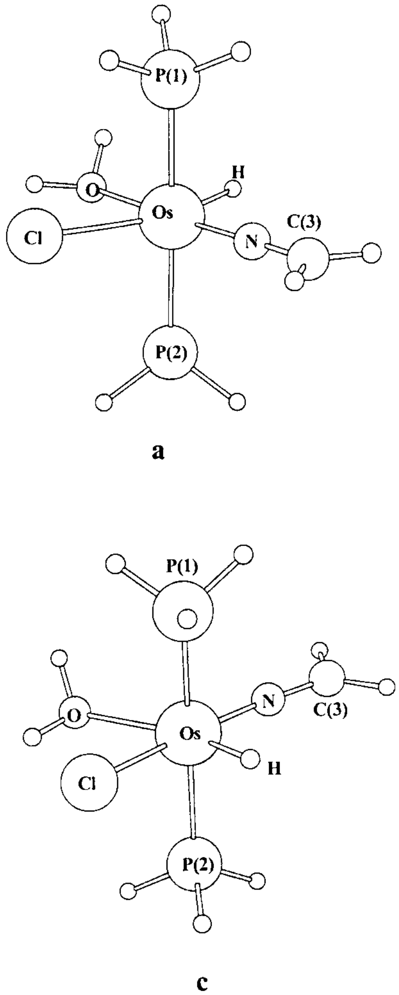


Figure 2. B3LYP optimized structures of the most stable isomers (**a** and **c**) of the $[OsHCl(=N=CH_2)(H_2O)(PH_3)_2]^+$ complex

of the Os-azavinylidene moiety (Os−N−C = 179.5°) should also be noted. In addition, it should be mentioned that in the calculated structures, the azavinylidene ligand is perpendicular to the P−Os−P axis, in agreement with the ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** and the X-ray structure shown in Figure 1.

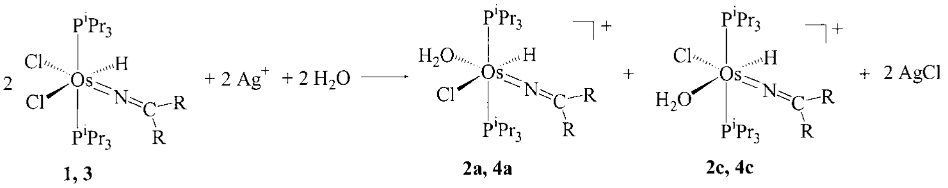
The spectroscopic data of **2** together with the results of the theoretical calculations strongly support that the reaction of **1** with $Ag(CF_3SO_3)$ and water leads to an equimolar mixture of the isomers shown in Equation (2). Similarly, the treatment of **3** with $Ag(CF_3SO_3)$ and water gives $[OsHCl\{=C=C^a(CH_2)_4C^bH_2\}(H_2O)(PiPr_3)_2(C^a\text{-}C^b)][CF_3SO_3]$ (**4**), which according to the IR, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra is a 1:1 mixture of the isomers **4a** and **4c**.

The IR spectrum of **4** in KBr contains two ν(Os−H) bands at 2145 and 2135 cm^{-1}. In the ^1H NMR spectrum, the hydride resonances appear at $\delta = -4.40$ and 0.43 as triplets, with H−P coupling constants of 13.8 and 13.2 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets at $\delta = -10.9$ and 4.8.

Reactions in the Presence of Trimethylphosphite

The treatment of dichloromethane solutions of **1** at −40 °C with 1.0 equiv. of $Ag(CF_3SO_3)$ and 1.1 equiv. of trimethylphosphite leads, after 2 h at this temperature, to brown solutions and AgCl. The solutions afford a brown-orange solid after the solvent is removed. According to the elemental analysis and MS, the solid corresponds to the complex $[OsHCl(=N=CMe_2)\{P(OMe_3)\}(PiPr_3)_2][CF_3SO_3]$ (**5**).

In contrast to **2** and **4**, the IR spectrum of **5** in KBr shows only one ν(Os−H) band, at 2155 cm^{-1}, suggesting that in the solid state this complex exists as only one isomer. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra in [D$_2$]dichloromethane at −40 °C also indicate that there is also only one isomer in solution. Thus, the $^{31}P\{^1H\}$ NMR spectrum contains a triplet at $\delta = 57.5$ [$P(OMe_3)$] and a doublet at $\delta = 47.6$ ($PiPr_3$). The multiplicity of the signals and the value of the P−P coupling constant (19.4 Hz) strongly support the *trans* disposition of the phosphanes, which lie *cis* to the phosphite. In the ^1H NMR spectrum the hydride ligand appears as a doublet of triplets at $\delta = -7.20$, with

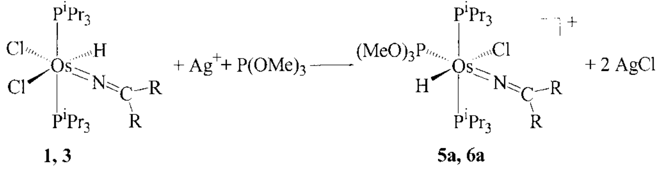


CR$_2$ = CMe$_2$ (**1, 2**), $\overline{\mathrm{C(CH_2)_4CH_2}}$ (**3, 4**)

(2)

H−P coupling constants of 39.6 and 13.8 Hz, indicating that the hydride is *cis* to the phosphorus donor ligands. At temperatures higher than room temperature the decomposition of **5** to [HP*i*Pr$_3$]$^+$ and unidentified products is observed.

The above-mentioned spectroscopic data are consistent with the stereochemistries **a** and **b** shown in Scheme 1. In order to determine the most stable isomer of **5** DFT calculations on the model complex [OsHCl(=N=CH$_2$){P(OH)$_3$}(PH$_3$)$_2$]$^+$ (**5t**) were also carried out. In this case, the results of the B3LYP calculations (Table 2) indicate that the stereochemistry **a** (hydride *trans* to chlorine) is again favored, while **b** and **c** lie higher in energy (11.4 kcal·mol^{-1} and 5.5 kcal·mol^{-1} respectively). This excludes the possibility of an equilibrium similar to that found in the previous case. So, the spectroscopic data of **5** together with the results of the theoretical calculations support that the reaction of **1** with Ag(CF$_3$SO$_3$) in the presence of trimethylphosphite leads to **5a** [Equation (3)]. Similarly the treatment of **3** with Ag(CF$_3$SO$_3$) and trimethylphosphite affords **6a**.



CR$_2$ = CMe$_2$ (**1, 5**), $\overline{\mathrm{C(CH_2)_4CH_2}}$ (**3, 6**)

(3)

The spectroscopic data of **6a** agree well with those of **5a**. The IR spectrum in KBr shows the ν(OS−H) band at 2154 cm^{-1}. In the ^{1}H NMR spectrum in [D$_2$]dichloromethane at −40 °C, the resonance corresponding to the hydride ligand appears at δ = −7.07 as a doublet of triplets with H−P coupling constants of 40.0 and 13.2 Hz. The ^{31}P{^{1}H} NMR spectrum shows a triplet at δ = 59.2 and a doublet at δ = 49.1. The value of the P−P coupling constant is 12.3 Hz.

The geometrical parameters for isomer **a** of the [OsHCl(=N=CH$_2$){P(OH)$_3$}(PH$_3$)$_2$]$^+$ model complex are listed in Table 3 and its structure is depicted in Figure 3. This complex can be described as a distorted octahedron with *trans* phosphanes (P−Os−P = 178.9°). In the perpendicular plane, the angles N−Os−P and Cl−Os−H are 160.6° and 151.5°, respectively. The Os−N (1.839 Å) and N−C (1.261 Å) distances and Os−C−N angle (169.7°) are consistent with the azavinylidene formulation. In agreement with the structures shown in Figure 1, the azavinylidene lies in the plane containing the osmium atom, the hydride, the chlorine and the phosphorous atom of the phosphite ligand.

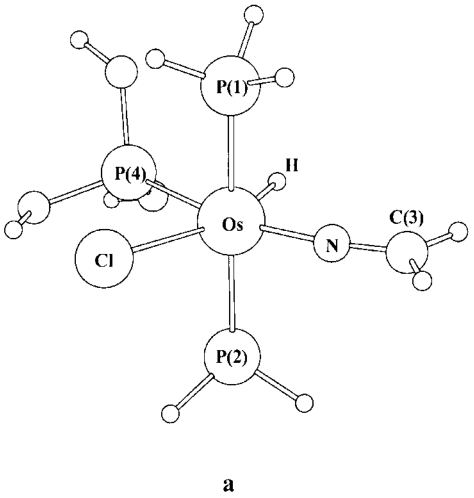
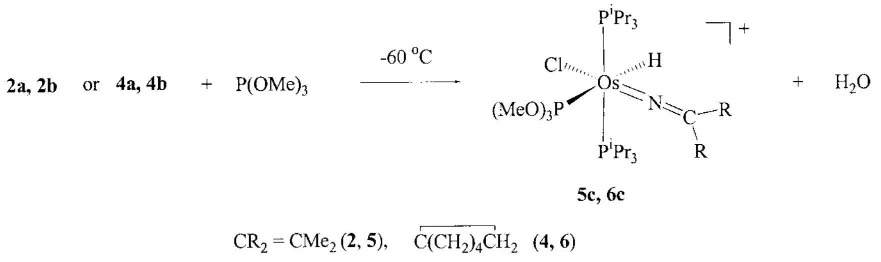


Figure 3. B3LYP optimized structure of the most stable isomer of the [OsHCl(=N=CH$_2$){P(OH)$_3$}(PH$_3$)$_2$]$^+$ complex

Theoretical results also indicate that the stability of the stereochemistry of **c** (hydride *trans* to phosphite) is between those of the stereochemistries of **a** and **b**. The corresponding isomers **5c** and **6c** can be isolated from [D$_2$]dichloromethane solutions at −60 °C. Thus, the addition of 1.0 equiv. of trimethylphosphite to [D$_2$]dichloromethane solutions of the equilibrium mixtures of **2a** and **2c** or **4a** and **4c** at −60 °C gives rise to the immediate and selective formation of **5c** or **6c** [Equation (4)] (in quantitative yield, in both cases). Under these conditions the isomers **5c** and **6c** are moderately stable and slowly isomerize to **5a** or **6a**. At −20 °C, about 50% of conversion is observed after 10 min. Isomers with **b** stereochemistry are not observed during the isomerization process, in agreement with the higher energy of this stereochemistry.

The *trans* disposition of the hydride and phosphite ligands in **5c** and **6c** is strongly supported by the ^{1}H NMR



(4)

spectra of these compounds, which show a doublet of triplets at δ = 0.95 (**5c**) and δ = 0.65 (**6c**) with H−P coupling constants of 125.0 and 16.3 Hz (**5c**) and 122.7 and 17.7 Hz (**6c**).

Reactions Under a Carbon Monoxide Atmosphere

The reaction of **1** with $Ag(CF_3SO_3)$ under a carbon monoxide atmosphere affords only one isomer of the carbonyl derivative $[OsHCl\{=N=C(CH_3)_2\}(CO)(P\mathit{i}Pr_3)_2][CF_3SO_3]$ (**7**), according to the IR, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of the yellow solid obtained.

In the IR spectrum, the most noticeable features are the presence of a ν(Os−H) band at 1951 cm^{-1} and a ν(CO) vibration at 1981 cm^{-1}. In the high field region of the ^1H NMR spectrum, the hydride ligand appears as a triplet at δ = −5.74, with an H−P coupling constant of 34.5 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ = 63.0.

The chemical shift of the hydride ligand of **7** is similar to that of both **5a** and **6a**. At first glance, this suggests that the stereochemistry of **7** is the same as that of **5a** and **6a** (hydride *trans* to chloride), since the chemical shift of a hydride ligand is highly dependent on the *trans* effect of the ligand located *trans* to the hydride. In order to corroborate this, DFT calculations were also carried out on the model complex $[OsHCl(=N=CH_2)(CO)(PH_3)_2]^+$ (**7t**). As expected, the results of the single point CCSD(T) calculations on the B3LYP optimized geometries (Table 2) indicate that the stereochemistry **a** is the most stable. The spectroscopic data of **7** together with the results of the theoretical calculations both suggest that the reaction of **1** with $Ag(CF_3SO_3)$ under carbon monoxide atmosphere leads to **7a** [Equation (5)]. Similarly, the treatment of **3** with $Ag(CF_3SO_3)$ under a carbon monoxide atmosphere gives **8a**. These isomers are also the species formed by the reaction of **2** or **4** with carbon monoxide at −60 °C in [D₂]dichloromethane as solvent.

The spectroscopic data of **8a** agree well with those of **7a**. The IR spectrum of **8b** in KBr shows the ν(Os−H) band at 1940 cm^{-1} and the ν(CO) vibration at 1977 cm^{-1}. In the ^1H NMR spectrum in [D₂]dichloromethane, the hydride ligand appears as a triplet at δ = −5.56, with an H−P coupling constant of 34.5 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ = 63.2.

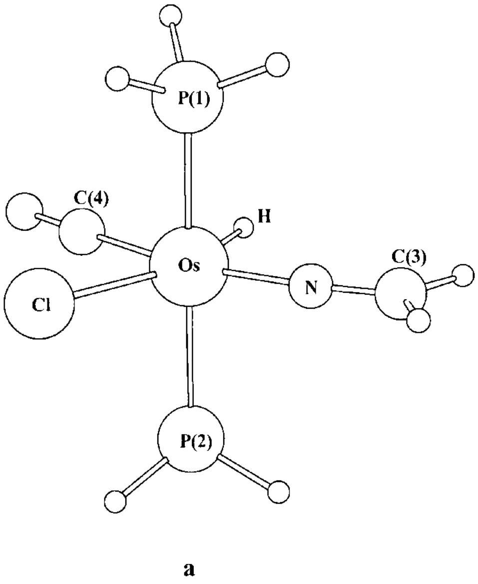
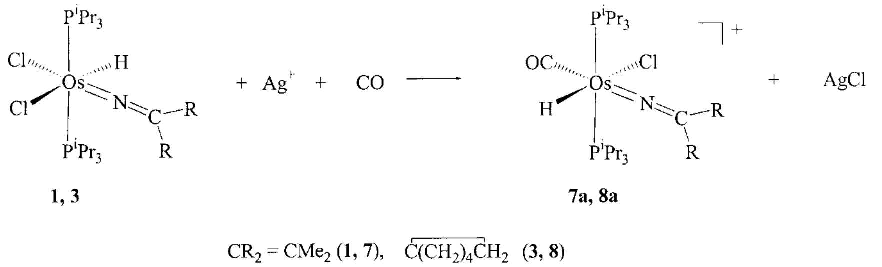


Figure 4. B3LYP optimized structure of the most stable isomer of the $[OsHCl(=N=CH_2)(CO)(PH_3)_2]^+$ complex

Figure 4 shows the optimized geometry at the B3LYP level for the **a** isomer of the $[OsHCl(=N=CH_2)(CO)(PH_3)_2]^+$ model complex; its main geometrical parameters are listed in Table 3. This isomer exhibits similar patterns to the $[OsHCl(=N=CH_2)(H_2O)(PH_3)_2]^+$ and



(5)

$[OsHCl(=N=CH_2)\{P(OH)_3\}(PH_3)_2]^+$ model complexes i.e. a distorted octahedral geometry where the P−Os−P angle is almost linear, although the angles between the ligands in the plane containing the H, Cl, N and C atoms clearly deviate from ideality (H−Os−Cl = 151.5°, N−Os−Cl = 162.7°). As in the $[OsHCl(=N=CH_2)\{P(OH)_3\}(PH_3)_2]^+$ complex, the Os−azavinylidene axis is slightly tilted (Os−N−C = 169.9°). The Os−N distance is the longest of our family of complexes (1.846 Å). As in the previous cases the azavinylidene ligand lies in the plane perpendicular to the P−Os−P axis.

Stereochemical Preferences of $[OsHCl(=N=CH_2)L(PH_3)_2]^+$ [L = H_2O, $P(OH)_3$ and CO] Complexes

In octahedral hexacoordinate complexes containing ligands with different electronic properties, as in $[OsHCl(=N=CH_2)L(PH_3)_2]^+$ [L = H_2O, $P(OH)_3$ and CO] model complexes, the presence of a strong σ-donor hydride will have a pronounced influence on the rest of the ligands, and the ability of a given ligand to remain *trans* to the hydride will govern the stereochemistry of the complex. To illustrate this general idea, a DFT theoretical study on $[OsHCl(=N=CH_2)(PH_3)_2]^+$ and $[OsHCl(=N=CH_2)L(PH_3)_2]^+$ [L = H_2O, $P(OH)_3$ and CO] complexes is offered in this section.

Pentacoordinate Complexes

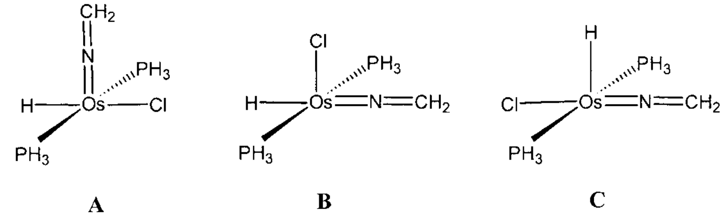
To begin our study the parent pentacoordinate $[OsHCl(=N=CH_2)(PH_3)_2]^+$ model complex, from which the hexacoordinate $[OsHCl(=N=CH_2)L(PH_3)_2]^+$ complexes are obtained, is analyzed in some detail. The structures of the related hexacoordinate complexes (i.e. phosphanes must be equivalent by symmetry), with available NMR spectroscopic data, have been fully optimized at the DFT level of theory using the B3LYP functional. Regular square-planar pyramids and trigonal bipyramids have been taken as starting points and no symmetry constraints have been imposed in order to allow free rotation of the azavinylidene ligand. The seven initial structures that were obtained are depicted in Scheme 2.

After geometry optimization, no trigonal bipyramid is found to be stable, and they all revert to a square-planar pyramid structure. Within the square-planar pyramid's family, only two isomers are obtained (**B** and **C** according to our labelling), although **B** lies much higher in energy than **C** (by 33.8 kcal·mol^{-1}). Thus, it is obvious that despite the apparent possibility of isomerism, there is only one available structure for the pentacoordinate complex. This result agrees perfectly with the ligand site preferences in a square-planar pyramid, where the stronger σ-donor ligand tends to occupy the apical position.[14] The geometrical parameters of complex **C** are listed in Table 4, and its structure is depicted in Figure 5.

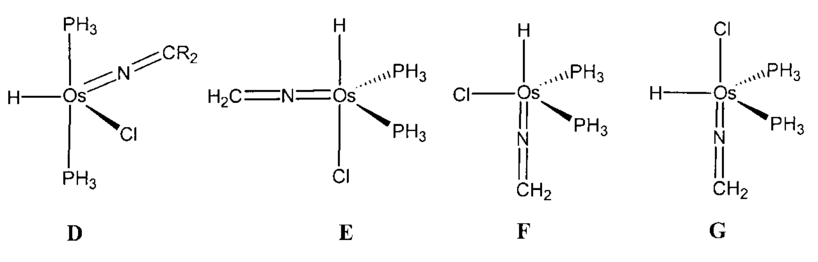
Table 4. Selected bond lengths (Å) and angles (deg) for the most stable isomer of the B3LYP optimized $[OsHCl(=N=CH_2)(PH_3)]^+$ model complex

Os−P(1)	2.411	Os−P(2)	2.411
Os−N	1.809	Os−H(1)	1.590
Os−Cl	2.328	N−C	1.263
C−H(2)	1.091	C−H(3)	1.090
H(1)−Os−P(1)	88.9	H(1)−Os−P(2)	88.9
H(1)−Os−N	94.4	H(1)−Os−Cl	109.1
P(1)−Os−P(2)	174.0	N−Os−Cl	156.5
P(1)−Os−N	92.8	N−Os−P(2)	92.8
P(2)−Os−Cl	87.8	Cl−Os−P(1)	87.8
Os−N−C	171.2	N−C−H(2)	119.8
N−C−H(3)	121.6		

Square Planar Pyramids



Trigonal Bipyramids



Scheme 2

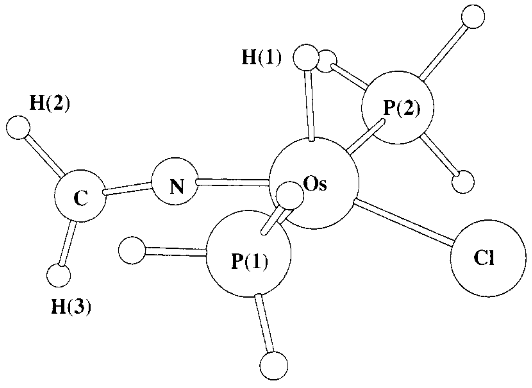


Figure 5. B3LYP optimized structure of the most stable isomer of the $[OsHCl(=N=CH_2)(PH_3)]^+$ complex

Complex **C** can be described as a slightly distorted square-planar pyramid with the strongest σ-donor hydride occupying the apical position *trans* to the vacant site. The phosphanes are located almost strictly *trans* to each other (P−Os−P = 174.0°), and the other ligands of the basal plane (azavinylidene and chloride) form an angle of 156.5°, thus making the whole structure somewhat distorted. It is noteworthy that the $Os=N=CH_2$ plane is perpendicular to the P−Os−P axis. As a matter of fact, the structure with the azavinylidene plane parallel to the P−Os−P axis, which would correspond to the transition state for the azavinylidene ligand rotation process, was found to be 9.2 kcal·mol^{-1} higher in energy than the minimum at the B3LYP//CCSD(T) level of theory.

Hexacoordinate Complexes

From the structural data and the calculated relative energies for the different isomers of $[OsHCl(=N=CH_2)L(PH_3)_2]^+$ complexes (Table 2), some initial trends may be drawn: (a) No matter what the electronic character of L (from a σ-donor H_2O ligand to a strong π-acceptor CO ligand), the structure with H *trans* to Cl turns out to be the most stable. (b) If the **b** and **c** structures are taken into account, opposite trends are found when the π-acceptor character of L is enhanced i.e. **b** is stabilized and **c** is destabilized. For the $[OsHCl(=N=CH_2)(H_2O)(PH_3)_2]^+$ complex the relative energies of **a** and **c** are similar (a difference of only 0.4 kcal·mol^{-1} is found at the CCSD(T)//B3LYP level of theory), but **c** is 5.4 kcal·mol^{-1} higher in energy than **a** in $[OsHCl(=N=CH_2)(CO)(PH_3)_2]^+$. At the same time, structure **b** is 21.0 kcal·mol^{-1} higher in energy than **a** in $[OsHCl(=N=CH_2)(H_2O)(PH_3)_2]^+$, although the difference between them is lowered to 2.2 kcal·mol^{-1} for the $[OsHCl(=N=CH_2)(CO)(PH_3)_2]^+$ complex. It should be noted at this point that even on purely thermodynamic grounds this difference might be somewhat large to allow an equilibrium between these two isomers. However, it should be possible in principle for **a** and **b** to exist simultaneously by using an even stronger π-acceptor ligand. (c) The addition of a sixth ligand to the most favorable pentacoordinate isomer (H *trans* to the empty coordination site) would lead to the **c** isomer. As a consequence, it is reasonable to suppose that this is the isomer that would be obtained under kinetic control conditions; structure **c** is indeed observed for L = $P(OMe)_3$ (**5c**, **6c**) and rapidly evolves into the isomer **a**.

To give a simple explanation of these facts, it has been assumed that, starting from the most stable pentacoordinate isomer, the corresponding hexacoordinate complexes can be obtained in two steps (of course, this has nothing to do with the actual mechanism; it is only a theoretical way of thinking). In a first step, the pentacoordinate complex is distorted towards the geometry that it would have in the hexacoordinate complex. The energy related to this distortion (ΔE_{dist}) is evaluated by simply removing the L ligand from the optimized hexacoordinate structure and calculating the B3LYP energy of the resulting fragment. In the second step, a crude interaction energy (ΔE_{int}) of the $[OsHCl(=N=CH_2)(PH_3)_2]^+$ fragment with the L ligand fragment is obtained as the difference between the sum of the energies of both fragments and the energy of the optimized hexacoordinate structure. The results of this decomposition are shown in Figures 6 and 7.

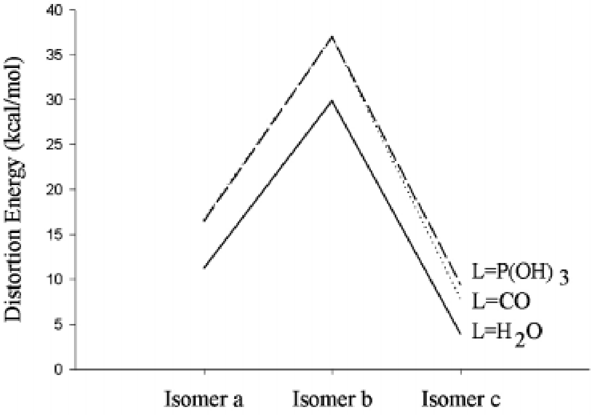


Figure 6. Distortion energies of the $[OsHCl(=N=CH_2)(PH_3)_2]^+$ fragments calculated at the B3LYP level of theory

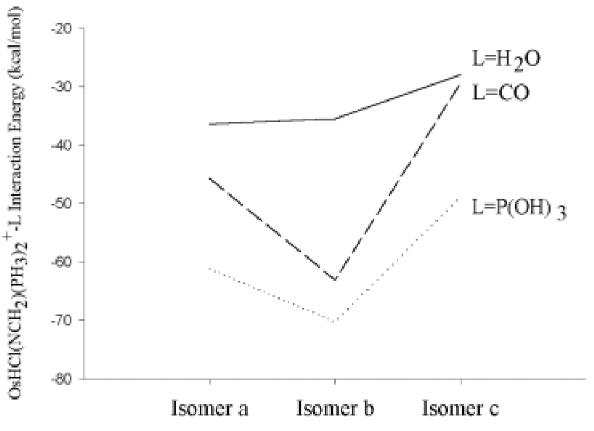


Figure 7. Interaction energies between $[OsHCl(=N=CH_2)(PH_3)_2]^+$ distorted fragments and L ligands (L = H_2O, $P(OH)_3$, CO) calculated at the B3LYP level of theory

The distortion term (Figure 6) is in fact related to the stability of the pentacoordinate fragment. This term is clearly smaller for isomer **c**, which is related to the best pentacoordinate structure previously described. The highest distortion energy arises from isomer **b**. In this fragment, the chloride ligand occupies the apical position *trans* to the vacant site, which is a very unfavorable arrangement for a square-planar pyramid. As a consequence, this would, in principle, be a factor that works against this hexacoordinate isomer. The distortion energy of isomer **a** lies in between the **b** and **c** isomers. Another interesting fact is that although the distortion energy is smaller for L = H_2O (as we shall see later, this is a consequence of the weaker interaction of water with the pentacoordinate fragment), the trends are almost identical in all cases [for L = $P(OH)_3$ and L = CO, the distortion term is not only parallel, but practically coincident]. Thus, the same consequences for the three isomers would be drawn if only this term is considered, and the energetic ordering of the hexacoordinate isomers would be **c** < **a** < **b**. It is obvious that the different behavior arises from the interaction term. Just looking at the shapes of the lines in Figure 7, it is clear that H_2O, $P(OH)_3$ and CO interact very differently with the distorted $[OsHCl(=N=CH_2)(PH_3)_2]^+$ fragment. Our theoretical results show that water interacts only weakly with the metallic fragment; the long Os−O distance in **2c** confirms this. The strongest interaction would correspond to the phosphite ligand, and carbonyl lies in between both of these. It is evident that in all cases isomer **c** is clearly disfavored, because this isomer is obtained by adding a σ-donor or a π-acceptor ligand *trans* to the strong σ-donor hydride. The strong *trans* influence exerted by this hydride would then destabilize the bond between Os and the L ligand, and this would lead to a small interaction energy. The next isomer in our ordering of interaction energies is isomer **a**. For this isomer, an equilibrium is reached between interaction and distortion, and the immediate consequence is that this is the most stable isomer as a whole. Lastly, isomer **b** exhibits a large interaction energy except for L = H_2O, but this energy is in general not enough to compensate the distortion term.

The relative interaction energies within each group (see the slope of the lines in Figure 7) follow a definite trend in enhancing the π-acceptor character of L: taking the most stable isomer **a** as the reference, the interaction energy due to isomer **b** increases, while that due to isomer **c** decreases. Again, this is a consequence of the electronic nature of the ligands, because in isomer **b** the L ligand is trans to a π-donor chloride, while in isomer **c** L is trans to a hydride. Thus, for L = H_2O, the interaction energy of isomer **c** is not very small and the distortion term can compensate nicely for the disadvantage of having an H_2O ligand *trans* to the hydride. This compensation leads to the observed equilibrium between **a** and **c**. For L = $P(OH)_3$, both hexacoordinate isomers **b** and **c** are far more unstable than isomer **a**, because in isomer **b** the interaction cannot compensate for the distortion and in isomer **c** the distortion cannot compensate for the interaction. Finally, for L = CO, the interaction term is so small for isomer **c** that the corresponding hexacoordinate structure is highly unstable, while the interaction term in **b**, although bigger than in the other cases, does not compensate for the distortion.

Concluding Remarks

Although the imido groups [$R_2C=N$] are strong bases, this study has revealed that the azavinylidene ligand of the complexes $[OsHCl_2(=N=CR_2)(P\textit{i}Pr_3)_2]$ are stable towards hydrolysis when they are treated with $Ag(CF_3SO_3)$ in the presence of water. The reactions lead to the six-coordinate hydride-azavinylidene-osmium(IV) derivatives $[OsHCl(=N=CR_2)(H_2O)(P\textit{i}Pr_3)_2]^+$, which are the first cationic species of this type.

Hydride-azavinylidene-osmium(IV) compounds are stable, not only towards hydrolysis of the azavinylidene, but also towards reductive elimination into imino species. It is well-known that the oxidative addition/reductive elimination equilibrium is governed by the amount of electron density at the metal. Electron-rich donor ligands favor the oxidized species, while π-acceptor ligands favor the reduced one. However, the extraction of a strong π-donor chlorine from $[OsHCl_2(=N=CR_2)(P\textit{i}Pr_3)_2]$ and the coordination of π-acceptor ligands [i.e. CO, $P(OMe)_3$] does not induce a reductive elimination to afford the corresponding d^6-imine derivatives, but results in the formation of $[OsHCl(=N=CR_2)L(P\textit{i}Pr_3)_2]^+$ [L = $P(OMe)_3$, CO].

Three stereochemistries are possible for complexes $[OsHCl(=N=CR_2)L(P\textit{i}Pr_3)_2]^+$ [L = H_2O, $P(OMe)_3$, CO]: hydride *trans* to chlorine (**a**), hydride *trans* to azavinylidene (**b**) and hydride *trans* to L (**c**). Theoretical calculations indicate that structure **a** is the most favored in all cases from a thermodynamic point of view, whereas structure **c** is kinetically favored. The relative stability of structures **b** and **c** depends upon the electronic character of L. When the π-acceptor character of L increases, **b** is stabilized and **c** is destabilized; however, even with L=CO, the **b** isomer is never observed.

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 $[OsHCl_2(=N=CMe_2)(P\textit{i}Pr_3)_2]$ (**1**) and $[OsHCl_2\{=N=C^a(CH_2)_4C^bH_2\}(P\textit{i}Pr_3)_2(C^a\text{-}C^b)]$ (**3**) were prepared by the published method.[6] ^1H NMR spectra were recorded at 300 MHz and chemical shifts are expressed in ppm downfield from Me_4Si. $^{13}C\{^1H\}$ NMR spectra were recorded at 75.4 MHz and chemical shifts are expressed in ppm downfield from Me_4Si. $^{31}P\{^1H\}$NMR spectra were recorded at 121.4 MHz and chemical shifts are expressed in ppm downfield from 85% H_3PO_4. Coupling constants, *J* and *N*, are given in Hertz.

Preparation of $[OsHCl\{=N=C(CH_3)_2\}(H_2O)(P\textit{i}Pr_3)_2][CF_3SO_3]$ (2a,c): A pale green solution of **1** (200 mg, 0.313 mmol) in 10 mL of acetone was treated with 81 mg (0.315 mmol) of $Ag(CF_3SO_3)$ and 12 μL (0.666 mmol) of water. The suspension was stirred for 3 hours and was filtered through Celite to remove the AgCl formed. After the solvent was removed, addition of diethyl ether yielded a blue precipitate that was washed (2 × 2 mL) with diethyl ether and dried in vacuo. The resulting blue microcrystalline solid was a mixture of two isomers with an **a**:**c** ratio of 1:1. Yield: 180 mg (74%). − $C_{22}H_{51}ClF_3NO_4OsP_2S$ (770.30): calcd. C 34.30, H 6.67, N 1.82, S 4.16; found C 34.51, H 6.52, N 1.73, S 3.99. − MS (FAB$^+$): *m*/*z* = 604 [M$^+$ − H_2O].

Isomer a) IR (KBr): ν(Os−H) 2164 cm^{-1} (m), ν(C=N) 1686 (m), $\nu_a(SO_3)$ 1296 (s), $\nu_s(CF_3)$ 1242 (s), $\nu_a(CF_3)$ 1174 (s), $\nu_s(SO_3)$ 1024 (s), $\delta_a(SO_3)$ 636 (s). − ^{1}H NMR (CD_2Cl_2, −90 °C): δ = 4.91 (br, 2 H, H_2O), 4.46 and 4.16 (both s, 6 H, $\{CH_3\}_2C{=}N$), 2.47 (m, 6 H, PCH), 1.30 (br. {at −40 °C dvt, J_{H-H} = 6.3, *N* = 12.6}, 36 H, PCHC*H*$_3$), −3.85 (t, J_{H-P} = 14.1, 1 H, OsH). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ = 151.0 (s, Os=N=C), 121.4 (q, J_{C-F} = 316.7, CF_3), 22.5 (vt, *N* = 24.4, PCH), 19.3 and 18.7 (both s, PCH*C*H$_3$), 5.1 and 2.5 (both s, $\{CH_3\}_2C{=}N$). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C): δ = −10.3 (s).

Isomer c) IR (KBr): ν(Os−H) 2156 cm^{-1} (m), ν(C=N) 1671 (m), $\nu_a(SO_3)$ 1296 (s), $\nu_s(CF_3)$ 1242 (s), $\nu_a(CF_3)$ 1174 (s), $\nu_s(SO_3)$ 1024 (s), $\delta_a(SO_3)$ 636 (s). − ^{1}H NMR (CD_2Cl_2, −90 °C): δ = 4.85 (br, 2 H, H_2O), 3.56 and 3.45 (both s, 6 H, $\{CH_3\}_2C{=}N$), 2.27 (m, 6 H, PCH), 1.23 (br. {at −40 °C dvt, J_{H-H} = 6.6, *N* = 13.6}, 36 H, PCHC*H*$_3$), 0.56 (t, J_{H-P} = 13.2, 1 H, OsH). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ = 148.7 (s, Os=N=C), 121.4 (q, J_{C-F} = 316.7, CF_3), 22.7 (vt, *N* = 24.4, PCH), 18.6 and 18.3 (both s, PCH*C*H$_3$), −1.6 (both s, $\{CH_3\}_2C{=}N$). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C): δ = −3.7 (s).

Preparation of [OsHCl{=N=C^a(CH$_2$)$_4$C^{b}H$_2$}(H$_2$O)(P*i*Pr$_3$)$_2$(*C*^{a}-*C*^{b})][CF$_3$SO$_3$] (4a,c): This complex was prepared as described for **2** starting from 200 mg (0.311 mmol) of **3**, 80 mg (0.311 mmol) of $Ag(CF_3SO_3)$, and 12 μL (0.666 mmol) of water. The resulting blue microcrystalline solid was a mixture of two isomers with an **a**:**c** ratio of 1:1. Yield: 180 mg (71%). − $C_{25}H_{55}ClF_3NO_4OsP_2S$ (810.37): calcd. C 37.05, H 6.84, N 1.73, S 3.96; found C 37.17, H 6.92, N 1.69, S 4.01. − MS (FAB$^+$): *m*/*z* = 644 [M$^+$ − H_2O].

Isomer a) IR (KBr): ν(Os−H) 2135 cm^{-1} (m), ν(C=N) 1686 (m), $\nu_a(SO_3)$ 1294 (s), $\nu_s(CF_3)$ 1247 (s), $\nu_a(CF_3)$ 1160 (s), $\nu_s(SO_3)$ 1031 (s), $\delta_a(SO_3)$ 637 (s). − ^{1}H NMR (CD_2Cl_2, −40 °C): δ = 4.60 (br, 2 H, H_2O), 4.13 (br, 4 H, $\{CH_2\}_2C{=}N$) 2.57 (m, 6 H, PCH), 2.6−2.4 (m, 6 H, Cy), 1.30 (m, 36 H, PCHC*H*$_3$), −4.40 (t, J_{H-P} = 13.8, 1 H, OsH). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ = 152.3 (s, Os=N=C), 121.4 (q, J_{C-F} = 316.7, CF_3), 28.6 and 23.6 (both s, Cy), 22.5 (vt, *N* = 24.4, PCH), 19.3 and 18.8 (both s, PCH*C*H$_3$), 16.2 and 13.5 (both s, $\{CH_2\}_2C{=}N$). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ = −10.9 (s).

Isomer c) IR (KBr): ν(Os−H) 2145 cm^{-1} (m), ν(C=N) 1671 (m), $\nu_a(SO_3)$ 1294 (s), $\nu_s(CF_3)$ 1247 (s), $\nu_a(CF_3)$ 1160 (s), $\nu_s(SO_3)$ 1031 (s), $\delta_a(SO_3)$ 637 (s). − ^{1}H NMR (CD_2Cl_2, −40 °C): δ = 4.48 (br, 2 H, H_2O), 3.74 (br, 4 H, $\{CH_2\}_2C{=}N$) 2.32 (m, 6 H, PCH), 1.23 (m, 36 H, PCHC*H*$_3$), 0.43 (t, J_{H-P} = 13.2, 1 H, OsH). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ = 149.2 (s, Os=N=C), 121.4 (q, J_{C-F} = 316.7, CF_3), 27.1 and 22.8 (both s, Cy), 22.5 (vt, *N* = 24.4, PCH), 18.9 and 18.4 (both s, PCH*C*H$_3$), 10.5 (br, $\{CH_2\}_2C{=}N$). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ = −4.8 (s).

Preparation of [OsHCl{=N=C(CH$_3$)$_2$}{P(OMe)$_3$}(P*i*Pr$_3$)$_2$][CF$_3$SO$_3$] (5a): A pale green solution of **1** (200 mg, 0.313 mmol), at 40 °C, in a mixture of dichloromethane (10 mL) and acetone (0.2 mL) was treated with 81 mg (0.315 mmol) of $Ag(CF_3SO_3)$ and 38 μL (0.322 mmol) of $P(OMe)_3$. The suspension was stirred for 2 h at this temperature and was then filtered through Celite to remove the AgCl formed. The resulting brown solution was evaporated to dryness at the same temperature. Addition of diethyl ether yielded a brown-orange solid that was washed (3 × 2 mL) with diethyl ether at −40 °C and dried in vacuo. Yield: 200 mg (73%). − $C_{25}H_{58}ClF_3NO_6OsP_3S$ (876.36): calcd. C 34.26, H 6.67, N 1.60, S 3.66; found C 34.05, H 6.55, N 1.70, S 3.55. − IR (KBr): ν(Os−H) 2155 cm^{-1} (m), ν(C=N) 1686 (m), $\nu_a(SO_3)$ 1276 (s), $\nu_s(CF_3)$ 1225 (s), $\nu_a(CF_3)$ 1158 (s), $\nu_s(SO_3)$ 1034 (s), $\delta_a(SO_3)$ 639 (s). − ^{1}H NMR (CD_2Cl_2, −40 °C): δ = 3.69 (d, J_{H-P} = 10.8, 9 H, P{OMe}$_3$), 2.69 (br, 6 H, $\{CH_3\}_2C{=}N$) 2.47 (m, 6 H, PCH), 1.32 and 1.30 (both dvt, J_{H-H} = 7.2, *N* = 15, 36 H, PCHC*H*$_3$), −7.20 (td, J_{H-P} = 39.6, J_{H-P} = 13.8, 1 H, OsH). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ = 161.5 (s, Os=N=C), 120.7 (q, J_{C-F} = 320.3, CF_3), 54.9 (d, J_{C-P} = 11.5, P{OMe}$_3$), 23.4 (vt, *N* = 25.3, PCH), 19.6 and 18.8 (both s, PCH*C*H$_3$), 17.4 (br, $\{CH_3\}_2C{=}N$). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ = 57.5 (t, J_{P-P} = 19.4, P{OMe}$_3$), 47.6 (d, J_{P-P} = 19.4, P*i*Pr$_3$). − MS (FAB$^+$): *m*/*z* = 728 [M$^+$], 604 [M$^+$ − P(OMe)$_3$].

Reaction of an Equilibrium Mixture of 2a and 2c with P(OMe)$_3$. Formation of 5c: A solution of an equilibrium mixture of **2a** and **2c** (30 mg, 0.040 mmol) in 0.5 mL of [D$_2$]dichloromethane in an NMR tube at −60 °C was treated with $P(OMe)_3$ (5 μL, 0.042 mmol). The NMR tube was sealed under argon and measurements were made immediately. − ^{1}H NMR (CD_2Cl_2, −60 °C): δ = 3.93 (d, J_{H-P} = 9.9, 9 H, P{OMe}$_3$), 3.65 (br, 6 H, $\{CH_3\}_2C{=}N$), 2.47 (m, 6 H, PCH), 1.28 and 1.22 (both dvt, J_{H-H} = 6.6, *N* = 13.5, 36 H, PCHC*H*$_3$), 0.95 (dt, J_{H-P} = 125.0, J_{H-P} = 16.3, 1 H, OsH). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ = 149.3 (s, Os=N=C), 120.7 (q, J_{C-F} = 320.3, CF_3), 56.5 (d, J_{C-P} = 12.0, P{OMe}$_3$), 23.4 (vt, *N* = 25.3, PCH), 19.4 and 18.8 (both s, PCH*C*H$_3$), 2.4 (br, $\{CH_3\}_2C{=}N$). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ = 56.2 (t, J_{P-P} = 17.8, P{OMe}$_3$), −8.0 (d, J_{P-P} = 17.8, P*i*Pr$_3$).

Preparation of [OsHCl{=N=C^a(CH$_2$)$_4$C^{b}H$_2$}{P(OMe)$_3$}(P*i*Pr$_3$)$_2$(*C*^{a}-*C*^{b})][CF$_3$SO$_3$] (6a): This complex was prepared as described for **5a** starting from 200 mg (0.311 mmol) of **3**, 80 mg (0.311 mmol) of $Ag(CF_3SO_3)$, and 38 μL (0.321 mmol) of $P(OMe)_3$. Yield: 210 mg (74%). − $C_{28}H_{62}ClF_3NO_6OsP_3S$ (916.43): calcd. C 36.70, H 6.82, N 1.53, S 3.50; found C 36.55, H 6.67, N 1.65, S 3.42. − IR (KBr): ν(Os−H) 2154 cm^{-1} (m), ν(C=N) 1686 (m), $\nu_a(SO_3)$ 1276 (s), $\nu_s(CF_3)$ 1225 (s), $\nu_a(CF_3)$ 1158 (s), $\nu_s(SO_3)$ 1034 (s), $\delta_a(SO_3)$ 639 (s). − ^{1}H NMR (CD_2Cl_2, −40 °C): δ = 3.68 (d, J_{H-P} =10.5, 9 H, P{OMe}$_3$), 2.9 (br, 4 H, $\{CH_2\}_2C{=}N$), 2.6 (m, 6 H, PCH), 1.68 (m, 6 H, Cy), 1.4−1.2 (m, 36 H, PCHC*H*$_3$), −7.07 (td, J_{H-P} = 40.0, J_{H-P} = 13.2, 1 H, OsH). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ = 165.2 (s, Os=N=C), 120.3 (q, J_{C-F} = 320.3, CF_3), 54.9 (d, J_{C-P} = 11.5, P{OMe}$_3$), 28.2 and 27.0 (both s, Cy), 24.6 (m, PCH), 20.3 and 19.9 (both s, PCH*C*H$_3$), 17.3 (br, $\{CH_2\}_2C{=}N$). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C): δ = 59.5 (t, J_{P-P} = 12.3, P{OMe}$_3$), 49.1 (d, J_{P-P} = 12.3, P*i*Pr$_3$). − MS (FAB$^+$): *m*/*z* = 768 [M$^+$], 644 [M$^+$ − P(OMe)$_3$].

Reaction of an Equilibrium Mixture of 4a and 4c with P(OMe)$_3$. Formation of 6c: This complex was prepared as described for **5c** starting from an equilibrium mixture of **4a** and **4c** (30 mg, 0.037) and $P(OMe)_3$ (5 μL, 0.042 mmol). − ^{1}H NMR (CD_2Cl_2, −60 °C): δ = 3.91 (d, J_{H-P} = 10.2, 9 H, P{OMe}$_3$), 3.87 (br, 4 H, $\{CH_2\}_2C{=}N$), 2.48 (m, 6 H, PCH), 1.7−1.3 (m, 6 H, CH_2 Cy), 1.29 and 1.20 (m, 36 H, PCHC*H*$_3$), 0.65 (dt, J_{H-P} = 122.7, J_{H-P} = 17.7, 1 H, OsH). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ = 149.4 (s, Os=N=C), 120.5 (q, J_{C-F} = 321.3, CF_3), 56.1 (d, J_{C-P} = 11.5, P{OMe}$_3$), 26.8 and 23.5 (both s, Cy), 23.0 (br, PCH), 19.5 and 18.6 (both s, PCH*C*H$_3$), 13.2 (br, $\{CH_2\}_2C{=}N$). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2,

−60 °C): δ = 59.4 (t, $J_{P\text{-}P}$ = 11.5, P{OMe}$_3$), −6.6 (d, $J_{P\text{-}P}$ = 11.5, P*i*Pr$_3$).

Preparation of [OsHCl{=N=C(CH$_3$)$_2$}(CO)(P*i*Pr$_3$)$_2$][CF$_3$SO$_3$] (7a): A pale green solution of **1** (200 mg, 0.313 mmol) in a mixture of dichloromethane (10 mL) and acetone (0.2 mL) was treated with 81 mg (0.315 mmol) of Ag(CF$_3$SO$_3$) and was then stirred for 10 min. under a carbon monoxide atmosphere. The suspension was filtered through Celite to remove the AgCl formed and the resulting yellow solution was evaporated to dryness. Subsequent addition of diethyl ether yielded a yellow solid, which was washed with diethyl ether (3 × 2 mL) and dried in vacuo. Yield: 225 mg (86%). − $C_{23}H_{49}ClF_3NO_4OsP_2S$ (780.30): calcd. C 35.40, H 6.33, N 1.80, S 4.11; found C 35.33, H 6.12, N 1.77, S 3.80. − IR (KBr): ν(CO) 1981 cm^{-1} (s), ν(Os−H) 1950 (m), ν(C=N) 1687 (m), ν_a(SO$_3$) 1270 (s), ν_s(CF$_3$) 1236 (s), ν_a(CF$_3$) 1140 (s), ν_s(SO$_3$) 1032 (s), δ_a(SO$_3$) 637 (s). − ^{1}H NMR (CDCl$_3$, 20 °C): δ = 2.88 (m, 6 H, PCH), 2.60 (br, 6 H, {CH$_3$}$_2$C=N), 1.43 and 1.37 (both dvt, $J_{H\text{-}H}$ = 6.9, *N* = 16.8, 36 H, PCHC*H*$_3$), −5.74 (t, $J_{H\text{-}P}$ = 34.5, 1 H, OsH). − ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 169.5 (t, $J_{C\text{-}P}$ = 6.9, CO), 165.9 (t, $J_{C\text{-}P}$ = 6.0, Os=N=C), 121.2 (q, $J_{C\text{-}F}$ = 316.9, CF$_3$), 27.8 (vt, *N* = 29.3, PCH), 19.4 and 19.2 (both s, PCH*C*H$_3$), 18.7 (br, {*C*H$_3$}$_2$C=N). − ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 63.0 (s, d off resonance). − MS (FAB$^+$): *m*/*z* = 632 [M$^+$].

Reaction of an Equilibrium Mixture of 2a and 2c with CO at −60 °C: CO was bubbled through a solution of an equilibrium mixture of **2a** and **2c** (30 mg, 0.040 mmol), in 0.5 mL of [D$_2$]dichloromethane in an NMR tube at −60 °C, for 5 minutes. The NMR tube was then sealed under argon and measurements were made immediately. A mixture of **2a**, **2c**, and **7a** was obtained.

Preparation of [OsHCl{=N=C^a(CH$_2$)$_4$C^{b}H$_2$}(CO)(P*i*Pr$_3$)$_2$(*C*^{a}-*C*^{b})]-[CF$_3$SO$_3$] (8a): This complex was prepared as described for **7a** starting from 200 mg (0.311 mmol) of **3** and 80 mg (0.311 mmol) of Ag(CF$_3$SO$_3$). Yield: 230 mg (85%). − $C_{26}H_{53}ClF_3NO_4OsP_2S$ (820.36): calcd. C 38.07, H 6.51, N 1.77, S 3.80; found C 37.75, H 6.82, N 1.51, S 3.83. − IR (KBr): ν(CO) 1977 cm^{-1} (s), ν(Os−H) 1940 (m), ν(C=N) 1687 (m), ν_a(SO$_3$) 1271 (s), ν_s(CF$_3$) 1222 (s), ν_a(CF$_3$) 1139 (s), ν_s(SO$_3$) 1031 (s), δ_a(SO$_3$) 637 (s). − ^{1}H NMR (CDCl$_3$, 20 °C): δ = 3.0−2.8 (m, 10 H, {CH$_2$}$_2$C=N and PCH), 1.9−1.7 (m, 6 H, Cy), 1.42 and 1.37 (both dvt, $J_{H\text{-}H}$ = 7.2, *N* = 16.8, 36 H, PCHCH$_3$), −5.56 (t, $J_{H\text{-}P}$ = 34.5, 1 H, OsH). − ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 168.5 (t, $J_{C\text{-}P}$ = 6.9, CO), 168.0 (t, $J_{C\text{-}P}$ = 6.0, Os=N=C), 121.2 (q, $J_{C\text{-}F}$ = 316.9, CF$_3$), 28.1 (br, {*C*H$_2$}$_2$C=N), 25.9 (vt, *N* = 29.5, PCH), 25.4 and 22.7 (both s, Cy), 17.2 and 17.0 (both s, PCH*C*H$_3$). − ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 63.2 (s, d off resonance). − MS (FAB$^+$): *m*/*z* = 672 [M$^+$].

Reaction of an Equilibrium Mixture of 4a and 4c with CO at −60 °C: CO was bubbled through a solution of an equilibrium mixture of **4a** and **4c** (30 mg, 0.037 mmol) in 0.5 mL of [D$_2$]dichloromethane in an NMR tube at −60 °C for 5 minutes. Then, the NMR tube was sealed under argon and measurements were made immediately. A mixture of **4a**, **4c**, and **8a** was obtained.

X-ray Structure Analysis of Complex 2: Crystals suitable for X-ray diffraction analysis were mounted onto a glass fiber and transferred to a Bruker-Siemens P4 automatic diffractometer (173 K, Mo-K_α radiation, graphite monochromator, λ = 0.71073 Å). A summary of crystal data and refinement parameters is reported in Table 5. Accurate unit cell parameters were determined by least-squares fitting from the setting of high angle reflections. Data were collected by the ω/2θ scan method. Lorentz and polarization corrections were applied. Measuring three standards throughout the data collection monitored the decay. Corrections for decay and absorption (semiempirical psi-scan method) were applied.

Table 5. Crystal data and data collection and refinement for complex [OsHCl{=N=C(CH$_3$)$_2$}(H$_2$O)(P*i*Pr$_3$)$_2$][BF$_4$]·CH$_2$Cl$_2$ (**2c**)

	2c
Formula	$C_{21}H_{51}BClF_4NOOsP_2 \cdot CH_2Cl_2$
Mol wt	792.95
Color and habit	Irregular block
Space group	Triclinic, $P\bar{1}$
a, *b*, *c* Å	9.323(4), 11.941(4), 16.249(6)
α, β, γ °	77.653(9), 82.73(1), 79.09(1)
V, Å^3	1728.2(11)
Z	2
D $_{calc}$, g cm^{-3}	1.524
Data Collection and Refinement	
Diffractometer	Bruker-Siemens P4
λ(Mo-K_α), Å	0.71073
Monochromator	Graphite oriented
μ, mm^{-1}	4.051
Scan type	ω/2θ
2θ range, deg	3 ≤ 2θ ≤ 50°
Temp, K	173.0(2)
No. of data collected	6385 (*h*: −10, 0; *k*: −13, 13; *l*: −19, 19)
No. of unique data	5977 (merging *R* factor 0.0526)
No. of params refined/restraints	337/2
R_1 [a][$F^2 > 2\sigma(F^2)$]	0.0302
wR_2 [b] [all data]	0.0748
S[c] [all data]	1.052

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

The structure was solved by Patterson methods and refined by full-matrix least-squares on F^2.[16] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms were observed or included at idealized positions. The hydride ligand H(01) was observed in the difference Fourier maps as a peak of adequate intensity and expected geometry, but does not support an appropriate refinement, and was not included in the atom list. However, the water hydrogen atoms H(02) and H(03) were located and refined as isotropic atoms with the same distance to the O atom.

Computational Details: DFT[17] optimizations without any symmetry constraint were carried out with the Gaussian94 series of programs[18] using the B3LYP functional.[19] Furthermore, for [OsHCl(=N=CH$_2$)(PH$_3$)$_2$]$^+$, [OsHCl(=N=CH$_2$)(H$_2$O)(PH$_3$)$_2$]$^+$, [OsHCl(=N=CH$_2$){P(OH)$_3$}(PH$_3$)$_2$]$^+$ and [OsHCl(=N=CH$_2$)-(CO)(PH$_3$)$_2$]$^+$ complexes CCSD(T)[20] single-point calculations on the DFT-optimized structures were performed in order to obtain more reliable energies. A quasi-relativistic effective core potential operator was used to represent the 60 innermost electrons of the osmium atom.[21] The basis set for the osmium atom was that associated with the pseudopotential[21] with a standard valence double-ζ LANL2DZ contraction.[18] The 6-31G(d) basis set[22c] was used for all the atoms directly attached to the metal, except for the hydride atom, which was described using a 6-31G(p) basis set.[22a,22b] For the oxygen atom in the carbonyl ligand a 6-31G(d) basis was used.[22c] The rest of the atoms were described with a 6-31G basis set.[22a]

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-162318. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ. UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

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[1] [1a] K. Farmery, M. Kilner, C. Midcalf, *J. Chem. Soc. A* **1970**, 2279−2285. − [1b] M. Kilner, C. Midcalf, *J. Chem. Soc. A* **1971**, 292−297. − [1c] J. Chatt, R. J. Dosser, F. King, G. J. Leigh, *J. Chem. Soc., Dalton Trans.* **1976**, 24352−444. − [1d] G. Erker, W. Frömberg, J. L. Atwood, W. E. Hunter, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 68−69. − [1e] R. E. Cramer, K. Panchanatheswaran, J. W. Gilje, *J. Am. Chem. Soc.* **1984**, *106*, 1853−1854. − [1f] W. Frömberg, G. Erker, *J. Organomet. Chem.* **1985**, *280*, 343−354. − [1g] M. Green, R. J. Mercer, C. E. Morton, A. G. Orpen, *Angew. Chem. ; Int. Ed. Engl.* **1985**, *24*, 422−424. − [1h] J. E. Bercaw, D. L. Davies, P. T. Wolczanski, *Organometallics* **1986**, *5*, 443−450. − [1i] M. Bochmann, L. M. Wilson, *J. Chem. Soc., Chem. Commun.* **1986**, 1610−1611. − [1j] I. A. Latham, G. J. Leigh, G. Huttner, I. Jibril, *J. Chem. Soc., Dalton Trans.* **1986**, 377−383. − [1k] R. F. Jordan, C. S. Bajgur, W. E. Dasher, A. L. Rheingold, *Organometallics* **1987**, *6*, 1041−1051. − [1l] H. Werner, W. Knaup, M. Dziallas, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 248−250. − [1m] A. Dormond, A. Aaliti, A. Elbouadili, C. Moise, *J. Organomet. Chem.* **1987**, *329*, 187−199. − [1n] A. R. Barron, J. E. Salt, G. Wilkinson, M. Motevalli, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **1987**, 2947−2954. − [1o] G. Erker, W. Frömberg, C. Krüger, E. Raabe, *J. Am. Chem. Soc.* **1988**, *110*, 2400−2405. − [1p] M. Bochmann, L. M. Wilson, M. B. Hursthouse, M. Motevalli, *Organometallics* **1988**, *7*, 1148−1154. − [1q] E. A. Maatta, Y. Du, *J. Am. Chem. Soc.* **1988**, *110*, 8249−8250. − [1r] H. M. Colquhoun, A. E. Crease, S. A. Taylor, D. J. Williams, *J. Chem. Soc, Dalton Trans.* **1988**, 2781−2786. − [1s] S. G. Feng, J. L. Templeton, *J. Am. Chem. Soc.* **1989**, *111*, 6477−6478. − [1t] H. G. Woo, T. D. Tilley, *J. Organomet. Chem.* **1990**, *393*, C6−C9. − [1u] S. L. Borkowsky, R. F. Jordan, G. D. Hinch, *Organometallics* **1991**, *10*, 1268−1274. − [1v] T. Daniel, H. Müller, H. Werner, *Inorg. Chem.* **1991**, *30*, 3118−3120. − [1x] Y. W. Alelyunas, R. F. Jordan, S. F. Echols, S. L. Borkowsky, P. K. Bradley, *Organometallics* **1991**, *10*, 1406−1416. − [1y] J. D. Debad, P. Legzdins, R. J. Batchelor, F. W. B. Einstein, *Organometallics* **1992**, *11*, 6−8. − [1z] S. G. Feng, J. L. Templeton, *Organometallics* **1992**, *11*, 1295−1303.

[2] [2a] S. G. Feng, P. S. White, J. L. Templeton, *Organometallics* **1993**, *12*, 1765−1774. − [2b] S. G. Feng, P. S. White, J. L. Templeton, *Organometallics* **1993**, *12*, 2131−2139. − [2c] H. Werner, T. Daniel, W. Knaup, O. Nürnberg, *J. Organomet. Chem.* **1993**, *462*, 309−318. − [2d] T. Daniel, W. Knaup, M. Dziallas, H. Werner, *Chem. Ber.* **1993**, *126*, 1981−1993. − [2e] S. G. Feng, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1994**, *116*, 8613−8620. − [2f] K. R. Powell, P. J. Pérez, L. Luan, S. G. Feng, P. S. White, M. Brookhart, J. L. Templeton, *Organometallics* **1994**, *13*, 1851−1864. − [2g] T. Daniel, H. Werner, *J. Chem. Soc., Dalton Trans.* **1994**, 221−227. − [2h] H. Werner, T. Daniel, T. Braun, O. Nürnberg, *J. Organomet. Chem.* **1994**, *480*, 145−153. − [2i] M. A. Esteruelas, F. J. Lahoz, M. Oliván, E. Oñate, L. A. Oro, *Organometallics* **1994**, *13*, 3315−3323. − [2j] S. G. Feng, P. S. White, J. L. Templeton, *Organometallics* **1995**, *14*, 5184−5192. − [2k] L. W. Francisco, P. S. White, J. L. Templeton, *Organometallics* **1996**, *15*, 5127−5136. − [2l] T. B. Gunnoe, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1996**, *118*, 6916−6923. [2m] H. Werner, T. Daniel, M. Müller, N. Mahr, *J. Organomet. Chem.* **1996**, *512*, 197−205. − [2n] J. A. Cabeza, I. del Rio, V. Riera, *J. Organomet. Chem.* **1997**, *548*, 255−261. − [2o] J. A. Cabeza, I. del Rio, R. J. Franco, F. Grepioni, V. Riera, *Organometallics* **1997**, *16*, 2763−2764. − [2p] J. A. Cabeza, I. del Rio, M. Moreno, V. Riera, F. Grepioni, *Organometallics* **1998**, *17*, 3027−3033. − [2q] J. A. Cabeza, I. del Rio, V. Riera, D. Ardura, *J. Organomet. Chem.* **1998**, *554*, 117−121. − [2r] C. Bois, J. A. Cabeza, R. J. Franco, V. Riera, E. Savorit, *J. Organomet. Chem.* **1998**, *564*, 201207. − [2s] P. Schollhammer, M. Pichon, K. W. Muir, F. Y. Petillon, R. Pichon, J. Talarmin, *Eur. J. Inorg. Chem.* **1999**, 221−223. − [2t] S. N. Brown, *Inorg. Chem.* **2000**, *39*, 378−381. − [2u] M. A. Jiménez-Tenorio, M. Jiménez-Tenorio, M. C. Puerta, P. Valerga, *Inorg. Chim. Acta* **2000**, *300*, 869−874. − [2v] R. Castarlenas, M. A. Esteruelas, E. Oñate, *Organometallics* **2000**, *19*, 5454−5463. − [2x] R. Castarlenas, M. A. Esteruelas, E. Gutiérrez-Puebla, E. Oñate, *Organometallics* **2001**, *20*, 1545−1554.

[3] [3a] R. C. Wade, *Catalysis of Organic Reactions* (Ed.: W. R. Moser); Marcel Dekker: New York, 1981. − [3b] L. F. Rhodes, L. M. Venanzi, *Inorg. Chem.* **1987**, *26*, 2692−2695. −

[4] C. Bohanna, M. A. Esteruelas, A. M. López, L. A. Oro, *J. Organomet. Chem.* **1996**, *526*, 73−83.

[5] T. Daniel, H. Werner, *Z. Naturforsch, B* **1992**, *47*, 1707−1710.

[6] R. Castarlenas, M. A. Esteruelas, E. Gutiérrez-Puebla, Y. Jean, A. Lledós, M. Martín, E. Oñate, J. Tomàs, *Organometallics* **2000**, *19*, 3100−3108.

[7] R. Castarlenas, M. A. Esteruelas, E. Gutiérrez-Puebla, Y. Jean, A. Lledós, M. Martín, J. Tomàs, *Organometallics* **1999**, *18*, 4296−4303.

[8] T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675−703.

[9] G. A. Lawrence, *Chem. Rev.* **1986**, *86*, 17−33.

[10] [10a] J. C. Jochims, R. Abu-El-Halawa, I. Jibril, G. Huttner, *Chem. Ber.* **1984**, *117*, 1900−1912. − [10b] M. Al-Talib, J. C. Jochims, *Chem. Ber.* **1984**, *117*, 3222−3230. − [10c] M. Al-Talib, I. Jibril, E.-U. Würthwein, J. C. Jochims, G. Huttner, *Chem. Ber.* **1984**, *117*, 3365−3373. − [10d] R. Kupfer, E.-U. Würthwein, M. Nagel, R. Allmann, *Chem. Ber.* **1985**, *118*, 643−652. − [10e] M. Al-Talib, I. Jibril, G. Huttner, J. C. Jochims, *Chem. Ber.* **1985**, *118*, 1876−1886. − [10f] M. Al-Talib, J. C. Jochims, L. Zsolnai, G. Huttner, *Chem. Ber.* **1985**, *118*, 1887−1902. − [10g] E.-U. Würthwein, R. Kupfer, R. Allmann, M. Nagel, *Chem. Ber.* **1985**, *118*, 3632−3642. − [10h] M. Krestel, R. Kupfer, R. Allmann, E.-U. Würthwein, *Chem. Ber.* **1987**, *120*, 1271−1279.

[11] F. Seitz, H. Fischer, J. Riede, *J. Organomet. Chem.* **1985**, *287*, 87−101.

[12] R. Aumann, S. Althaus, S. Krüger, P. Betz, *Chem. Ber.* **1989**, *122*, 357−364.

[13] M. A. Esteruelas, A. V. Gómez, F. J. Lahoz, A. M. López, E. Oñate, L. A. Oro, *Organometallics* **1996**, *15*, 3423−3435.

[14] A. R. Rossi, R. Hoffmann, *Inorg. Chem.* **1975**, *14*, 365−374.

[15] [15a] J. T. Poulton, M. P. Sigalas, K. Folting, W. E. Streib, O. Eisenstein, K. G. Caulton, *Inorg. Chem.* **1994**, *33*, 1476−1485. − [15b] K. G. Caulton, *New J. Chem.* **1994**, *18*, 25−41.

[16] G. M. Sheldrick, University of Göttingen, Göttingen, Germany, **1997**.

[17] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., **1989**.

[18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y.

Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian 94; Gaussian Inc.: Pittsburgh PA, **1995**.

[19] [19a] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785−789. – [19b] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652. – [19c] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623−11627.

[20] [20a] R. J. Bartlett, *J. Phys. Chem.* **1989**, *93*, 1697−1708. – [20b] R. J. Bartlett, J. D. Watts, S. A. Kucharski, J. Noga, *Chem. Phys. Lett.* **1990**, *165*, 513−522.

[21] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299−310.

[22] [22a] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257−2261. – [22b] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213−218. – [22c] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654−3665.

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