Reactivity of the Imine−Vinylidene Complexes $OsCl_2(=C=CHPh)(NH=CR_2)(P^iPr_3)_2$ [CR_2 = CMe_2, $\overline{C(CH_2)_4CH_2}$]†

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The reactivity of the imine−vinylidene compounds $OsCl_2(=C=CHPh)(NH=CR_2)(P^iPr_3)_2$ [CR_2 = CMe_2 (**1**), $\overline{C(CH_2)_4CH_2}$ (**2**)] toward amines, ^{n}BuLi, and HBF_4 has been studied. Complexes **1** and **2** react with triethylamine and diallylamine to give equilibrium mixtures of the corresponding starting materials and the five-coordinate azavinylidene derivatives $OsCl(=N=CR_2)(=C=CHPh)(P^iPr_3)_2$ [CR_2 = CMe_2 (**3**), $\overline{C(CH_2)_4CH_2}$ (**4**)], which are obtained as pure microcrystalline solids by reaction of **1** and **2** with ^{n}BuLi. The structure of **3** in the solid state has been determined by an X-ray diffraction study. The geometry around the metal center could be described as a distorted trigonal bipyramid with apical phophines and inequivalent angles within the Y-shaped equatorial plane. The azavinylidene group coordinates in a bent fashion with an Os−N−C angle of 157.2(6)°. Complexes **1** and **2** also react with allylamine and aniline. The reactions initially give **3** and **4**. However, the amount of these compounds decreases by increasing the reaction time. This decrease is accompanied with the formation of mixed amine−phosphine compounds $OsCl_2(=C=CHPh)(NH=CR_2)(NH_2R')(P^iPr_3)$ [R′ = allyl; CR_2 = CMe_2 (**5**), $\overline{C(CH_2)_4CH_2}$, (**6**). R′ = Ph; CR_2 = CMe_2 (**7**), $\overline{C(CH_2)_4CH_2}$ (**8**)]. The structure of **5** in the solid state has been also determined by an X-ray diffraction study. In this case, the geometry around the osmium atom can be rationalized as a distorted octahedron with the amine and phosphine ligands mutually trans disposed and the chlorine ligands mutually cis disposed. The X-ray analysis also shows that the NH-hydrogen atoms of the amine and the chlorines are involved in intra- and intermolecular H···Cl hydrogen bonding. The reactions of **1** and **2** with HBF_4·OEt_2 afford the carbyne derivatives $[OsCl_2(\equiv CCH_2Ph)(NH=CR_2)(P^iPr_3)_2][BF_4]$ [CR_2 = CMe_2 (**9**), $\overline{C(CH_2)_4CH_2}$ (**10**)]. Both **1** and **2** lose the imine ligand to give $OsCl_2(=C=CHPh)(P^iPr_3)_2$ (**11**) in toluene under reflux.

Introduction

Theoretical studies on vinylidene transition metal complexes have identified the electron deficiency at the C_α atom and the localization of the electron density on the C_β atom.[1] The chemical reactivity of the vinylidene unit is thus oriented toward electrophiles at C_β and nucleophiles on C_α.[2]

Examples of additions of water,[3] alcohols,[3g,4] thiols,[4b,5] phosphines,[6] fluoride,[7] and cyanide ions[8] have been reported. Primary amines follow the general trend of the above-mentioned nucleophiles, and their reactions with vinylidenes afford aminocarbene derivatives,[9] which are better described as azoniaalkenyl species.[10]

Transition metal imine compounds are another class of interesting organometallic complexes,[11] which have been found to be intermediate states during the transformations between amine and nitrile derivatives.[12] The reactivity of N-protio imines has not been extensively

† Dedicated to Prof. Juan Bertrán on the occasion of his 70th birthday.

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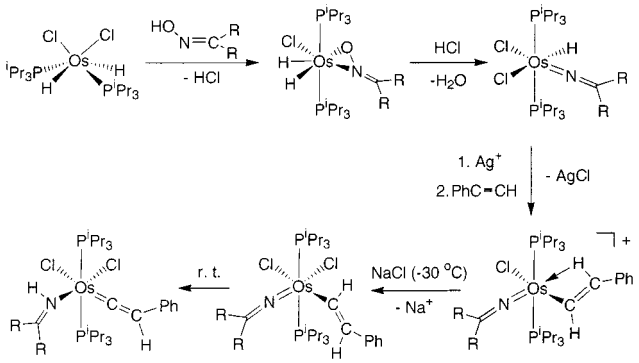
studied. A few experiments show that they can be deprotonated by action of strong bases such as K^t-BuO[11l,13] or KH.[12g]

We have previously reported that the dihydride−dichloro complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with acetone oxime and cyclohexanone oxime, in the presence of Et_3N, to give the dihydride derivatives $OsH_2Cl(\kappa^2\text{-}ON{=}CR_2)(P^iPr_3)_2$ [CR_2 = CMe_2, $\overline{C(CH_2)_4CH_2}$],[14] which afford the corresponding hydride−azavinylidene−osmium(IV) complexes $OsHCl_2(=N{=}CR_2)(P^iPr_3)_2$ by addition of HCl[15] (Scheme 1). Although there were not precedents for compounds containing both vinylidene and imine functional groups, we have recently proven that they can be formed by a novel reaction, the

Scheme 1



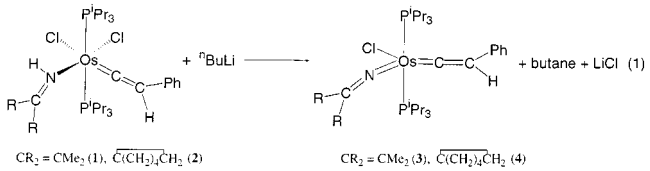
hydrogen transfer from alkenyl ligands to azavinylidene groups. Thus, it was shown that the treatment at room temperature of the hydride−azavinylidene complexes $OsHCl_2(=N{=}CR_2)(P^iPr_3)_2$ with $Ag[CF_3SO_3]$ and the subsequent addition at −25 °C of phenylacetylene leads to the alkenyl−azavinylidene derivatives $[Os\{(E)\text{-}CH{=}CHPh\}Cl(=N{=}CR_2)(P^iPr_3)_2][CF_3SO_3]$, which by addition of NaCl afford the imine−vinylidene compounds $OsCl_2(=C{=}CHPh)(NH{=}CR_2)(P^iPr_3)_2$ via the intermediates $Os\{(E)\text{-}CH{=}CHPh\}Cl_2(=N{=}CR_2)(P^iPr_3)_2$.[16]

The novelty of the imine−vinylidene species prompted us to investigate their reactivity. In this paper, we describe the behavior of the complexes $OsCl_2(=C{=}CHPh)(NH{=}CR_2)(P^iPr_3)_2$ [CR_2 = CMe_2, $\overline{C(CH_2)_4CH_2}$] in the presence of amines, ^{n}BuLi, and HBF_4. In addition, we report the formation of the desired vinylidene complex $OsCl_2(=C{=}CHPh)(P^iPr_3)_2$.[17]

Results and Discussion

1. Reactions of $OsCl_2(=C{=}CHPh)(NH{=}CR_2)(P^iPr_3)_2$ [CR_2 = CMe_2 (1), $\overline{C(CH_2)_4CH_2}$ (2)] with Amines and ^{n}BuLi. The behavior of **1** and **2** in the presence of amines depends on the nature of the amine.

(i) Triethylamine. The addition at room temperature of 1.0 equiv of this amine to dichloromethane-d_2 solutions of **1** gives rise to a 1:5 equilibrium mixture of **1** and the five-coordinate azavinylidene compound $OsCl\{{=}N{=}C(CH_3)_2\}(=C{=}CHPh)(P^iPr_3)_2$ (**3**) according to the ^{1}H and ^{31}P$\{^1$H$\}$ NMR spectra of the mixture. Under the same conditions, the addition of triethylamine to dichloromethane-d_2 solutions of **2** affords a 1:9 equilibrium mixture of **2** and $OsCl\{{=}N{=}\overline{C(CH_2)_4CH_2}\}(=C{=}CHPh)(P^iPr_3)_2$ (**4**). Complexes **3** and **4** are obtained as pure microcrystalline solids in high yield (about 80%), by treatment of tetrahydrofuran solutions of **1** and **2**, respectively, with 1.1 equiv of ^{n}BuLi in hexane (eq 1).



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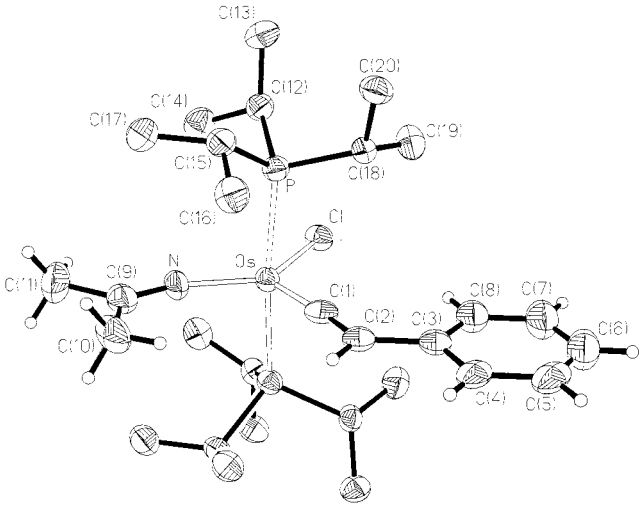

Figure 1. Molecular diagram for $OsCl_2(=N=CMe_2)(=C=CHPh)(P^iPr_3)_2$ (**3**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $OsCl(=C=CHPh)(=N=CMe_2)(P^iPr_3)_2$ (3)

Os−Cl	2.409(2)	N−C(9)	1.237(9)
Os−C(1)	1.812(6)	C(1)−C(2)	1.331(9)
Os−P(1)	2.416(2)	C(9)−C(10)	1.531(10)
Os−N	1.873(5)	C(9)−C(11)	1.537(10)
N−Os−C(1)	115.7(3)	Os−N−C(9)	157.2(6)
N−Os−Cl	128.2(2)	C(1)−C(2)−C(3)	124.6(7)
N−Os−P(1)	92.77(3)	C(10)−C(9)−C(11)	115.0(7)
Cl−Os−C(1)	116.1(2)	C(10)−C(9)−N	124.8(7)
Cl−Os−P(2)	87.7(3)	C(11)−C(9)−N	120.2(7)
C(1)−Os−P(2)	89.46(3)	C(1)−C(2)−H(2)	117(4)
P(1)−Os−P(2)	174.26(6)	C(3)−C(2)−H(2)	118(4)
Os−C(1)−C(2)	174.7(6)		

The reaction shown in eq 1 agrees well with the reactivity of the N-protio imine ligands in transition metal compounds, which are deprotonated by strong bases. In this context it should be pointed out that, although the deprotonation of vinylidene metal species is a general method to prepare alkynyl derivatives,[18] the formation of alkynyl-N-protio imine complexes is not observed during the formation of **3** and **4**. This fact elegantly proves that under the same conditions the NH-hydrogen atom of an imine ligand is stronger Brönsted acid than the =CH hydrogen atom of a vinylidene group.

Complexes **3** and **4**, which are isolated as orange solids, were characterized by MS, elemental analysis, IR, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Complex **3** was further characterized by an X-ray crystallographic study. A view of the molecular geometry of this complex is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The geometry around the osmium atom can be rationalized as a distorted trigonal bipyramid with apical phosphines [P(1)−Os−P(2) = 174.26(6)°] and inequivalent angles within the Y-shaped equatorial plane. The angles C(1)−Os−N, N−Os−Cl, and C(1)−Os-Cl are 115.7(3)°, 128.2(2)°, and 116.1(2)°, respectively. This Y structure is similar to that calculated for $RuHCl(=C=CH_2)(PH_3)_2$;[19] however, it contrasts with that found for the carbene complexes $RuCl_2(=CR_2)(PR_3)_2$, in which the carbene ligand occupies the apical position of a square pyramid.[20]

The vinylidene ligand is bound to the metal in a nearly linear fashion, with an Os−C(1)−C(2) angle of 174.7(6)°. The Os−C(1) [1.812(6) Å] and C(1)−C(2) [1.331(9) Å] bond lengths compare well with those found in other osmium−vinylidene complexes[21] and support the vinylidene formulation.

The azavinylidene ligand coordinates to the osmium atom in a bent fashion with an Os−N−C(9) angle of 157.2(6)°. A similar coordination mode has been observed for the azavinylidene ligands of the osmium complexes $[Os\{=N=C(Me)^tBu\}(\eta^6\text{-}C_6H_6)(P^iPr_3)]PF_6$ [167-(2)°, 168(2)°, and 155(2)°][22] and *cis*-$[OsCl_2\{=N=C(Ph)(2\text{-}PhCOC_6H_4)\}(terpy)]PF_6$ [168.2(3)°].[23] This type of structure has been described as corresponding to organometallic heteroallene type Schiff base derivatives.[24] The Os−N distance of 1.873(5) Å is intermediate between that found in **1** [2.072(7) Å][16] and in the complexes $[Os\{=N=C(Me)^tBu\}(\eta^6\text{-}C_6H_6)(P^iPr_3)]PF_6$ [1.81-(2) and 1.83(2) Å] [22] and *cis*-$[OsCl_2\{=N=C(Ph)(2\text{-}PhCOC_6H_4)\}(terpy)]PF_6$ [1.812(6) Å],[23] while the N−C(9) distance of 1.237(9) Å is similar to that found in the above-mentioned compounds.

In agreement with the presence of the azavinylidene and vinylidene ligands in **3** and **4**, the IR spectra of these compounds in KBr contain ν(C=N) and ν(Os=C=C) bands at 1671 (**3**) and 1655 (**4**) cm^{-1}, and 1608 (**3**) and 1605 (**4**) cm^{-1}, respectively. In the ^1H NMR spectra of both compounds the most noticeable resonances are triplets at 3.4 ppm, with H−P coupling constants of about 2.5 Hz, corresponding to the =CH hydrogen atom of the phenylvinylidene ligand. In the $^{13}C\{^1H\}$ NMR spectra the resonances corresponding to the C_α atom of this ligand appear at about 275.0 ppm as triplets with C−P coupling constants of about 11 Hz, whereas the resonances due to the C_β atom are observed at about 113 ppm, also as triplets but with C−P coupling constants of about 3 Hz. The resonances corresponding to the C=N carbon atom of the azavinylidene ligands appear at 153.8 (**3**) and 158.2 (**4**), as triplets with C−P coupling constants of about 2.5 Hz. The $^{31}P\{^1H\}$ NMR spectra of both compounds show a singlet at 4.2 ppm.

(ii) Diallylamine. The pK_a of this amine (9.29) is similar to that of the triethylamine (10.8). As a consequence, the behavior of **1** and **2** in the presence of both amines is similar. The addition at room temperature of 1.0 equiv of diallylamine to dichlorometane-d_2 solutions of **1** affords a 2:1 equilibrium mixture of **1** and **3**, whereas, under the same conditions, the treatment of

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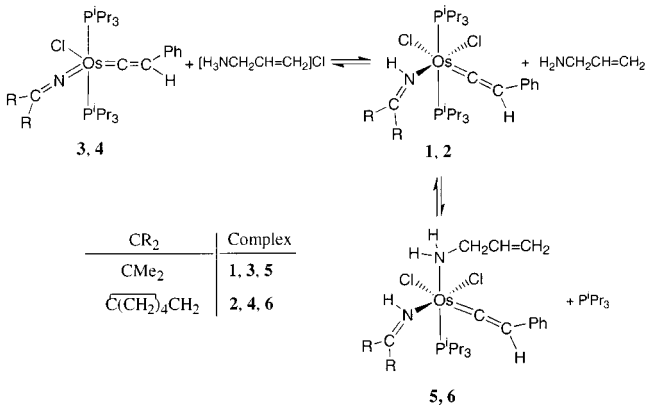
Scheme 2



dichlorometane-d_2 solutions of **2** with 1.0 equiv of diallylamine gives a 3:2 equilibrium mixture of **2** and **4**. These molar ratios and those previously mentioned indicate that the pK_a of the coordinated imine of **2** is lower than that of the coordinated imine of **1**.

(iii) Allylamine. Although the pK_a of allylamine (9.7) is similar to those of triethylamine and diallylamine, the behavior of **1** and **2** in the presence of this amine is significantly different of that previously mentioned for the other amines. In contrast to triethylamine and diallylamine, the addition at room temperature of 1.0 equiv of allylamine to dichlorometane-d_2 solutions of **1** leads to equilibrium mixtures of **1** (22%), **3** (8%), P^{i}Pr$_3$ (35%), and the mixed amine−phosphine complex OsCl$_2$(=C=CHPh){NH=C(CH$_3$)$_2$}(NH$_2$CH$_2$CH=CH$_2$)(P^{i}Pr$_3$) (**5**; 35%), according to the ^{1}H and ^{31}P{^{1}H} NMR spectra of the mixture. Similarly, the treatment at room temperature of dichloromethame-d_2 solutions of **2** with 1.0 equiv of allylamine affords equilibrium mixtures of **2** (9%), **4** (11%), P^{i}Pr$_3$ (40%), and OsCl$_2$(=C=CHPh){NH=C(CH$_2$)$_4$CH$_2$}(NH$_2$CH$_2$CH=CH$_2$)(P^{i}Pr$_3$) (**6**; 40%) (Scheme 2). In both cases, the addition of a second equivalent of allylamine to the above-mentioned solutions produces the shift of the equilibria toward the formation of **5** and **6**, which are isolated as orange solids in high yield (about 87%), by stirring at room temperature dichlorometane solutions of **1** and **2** in the presence of 1.5 equiv of allylamine for 4 h.

Figure 2 shows, as a function of the time, the ^{31}P-{^{1}H} NMR spectrum of the dichloromethane-d_2 solution of **1** with 2.0 equiv of allylamine. Initially the deprotonation of the imine occurs and complex **3** is formed. However, the amount of **3** decreases by increasing the reaction time. This decrease is accompanied with the formation of **5** and free phosphine. According to Figure 2, complex **3** is the product of kinetic control in the reaction of **1** with allylamine, whereas complex **5** is the product of thermodynamic control.

Because evidence for the dissociation of triisopropylphosphine from **1** has not been found, we have carried out the reaction of **3** with [H$_3$NCH$_2$CH=CH$_2$]Cl in the presence and in the absence of NaCl, to know how the substitution of phosphine by amine occurs. The addition in an NMR tube of 1.0 equiv of [H$_3$NCH$_2$CH=CH$_2$]Cl to a dichloromethane-d_2 solution of **3** leads after 10 min to a 7:2 mixture of **5** and **1** plus free triisopropylphosphine, while the addition of 1.0 equiv of [H$_3$NCH$_2$CH=CH$_2$]Cl to a saturated NaCl acetone-d_6 solution of **3** gives rise after 10 min to a 1:4 mixture of **5** and **1** plus free phosphine. These results suggest that the substitution process takes place via the previous dissociation of a chlorine ligand from **1**, according to Scheme 3. Since the formation of **3** is faster than the formation of **5**, the dissociation of phosphine from the intermediate [OsCl(=C=CHPh)(NH=CR$_2$)(NH$_2$R′)(P^{i}Pr$_3$)$_2$]$^+$ appears to be the rate-determining step of the substitution.

In contrast to what is expected, during the reactions shown in Scheme 2, the addition of the primary amine to the phenylvinylidene ligands of **1**−**6** is not observed. This suggests that in these compounds the electrophilic character of the vinylidene ligand is not significant. In addition, it should be noted that the excess of amine or the displaced phosphine does not deprotonate the coordinated imine ligands of **5** and **6**, indicating that the pK_a of this group depends not only on the substituents of the imine but also on the co-ligands of the complex.

The displacement of a triisopropylphosphine ligand in **1** and **2** by allylamine is surprising, due to the soft nature of the phosphine and osmium atom and the hard nature of the amine, and in view of the known sentences *soft coordinates to soft* and *hard coordinates to hard*. In the search for some clue that will allow us to understand the stability of **5** and **6**, we carried out an X-ray diffraction experiment on a single crystal of **5**. A view of the molecular geometry of this complex is shown in Figure 3. Selected bond distances and angles are listed in Table 2.

The geometry around the osmium atom can be rationalized as a distorted octahedron with the nitrogen atom of the allylamine ligand [N(2)] and the phosphorus atom of triisopropylphosphine in trans positions [P−Os−N(2) = 176.08(19)°]. The perpendicular plane is formed by the chloride ligands mutually cis disposed [Cl(1)−Os−Cl(2) = 84.35(6)°] and the nitrogen atom of the imine [N(1)] and the C$_\alpha$ atom [C(1)] of the vinylidene also in cis position [N(1)−Os−C(1) = 99.3(3)°].

The vinylidene ligand is bound to the metal in a nearly linear fashion with an Os−C(1)−C(2) angle of 177.5(6)°. The Os−C(1) [1.812(7) Å] and C(1)−C(2) [1.316(10) Å] distances are similar to the related parameters previously mentioned for **3**.

The imine ligand is bound to the osmium atom in a bent fashion, with a Os−N(1)−C(9) angle of 141.8(6)°, which compares well with the Os−N−C angle found in **1** [142.5(6)°], in [OsCl(=C=CHPh){NH=C(CH$_3$)$_2$}-(H$_2$O)(P^{i}Pr$_3$)$_2$][CF$_3$SO$_3$] [142.7(6)°],[16] and in the rhenium complex [Re(η^5-C$_5$H$_5$)(NO)(NH=CPh$_2$)(PPh$_3$)] [136.2-(3)°].[11l] The Os−N(1) bond length [2.052(6) Å] supports the Os−N single bond formulation. It is statistically identical with the Os−N bond length found in **1** [2.072-(7) Å] and in the above-mentioned cationic-osmium compound [2.067(5) Å],[16] and about 0.2 Å longer than that found in **3**. The N(1)−C(9) [1.279(9) Å] distance is similar to those observed in other imine transition metal complexes,[11] azavinylidene compounds,[15,22,23] organic azaallenium cations,[25] and 2-azaallenyl complexes.[26]

At 173 K, the hydrogen atoms bonded to the nitrogen atoms of the imine [H(02)] and amine [H(03) and H(04)] ligands were located in the difference Fourier maps and refined as isotropic atoms together with the rest of the

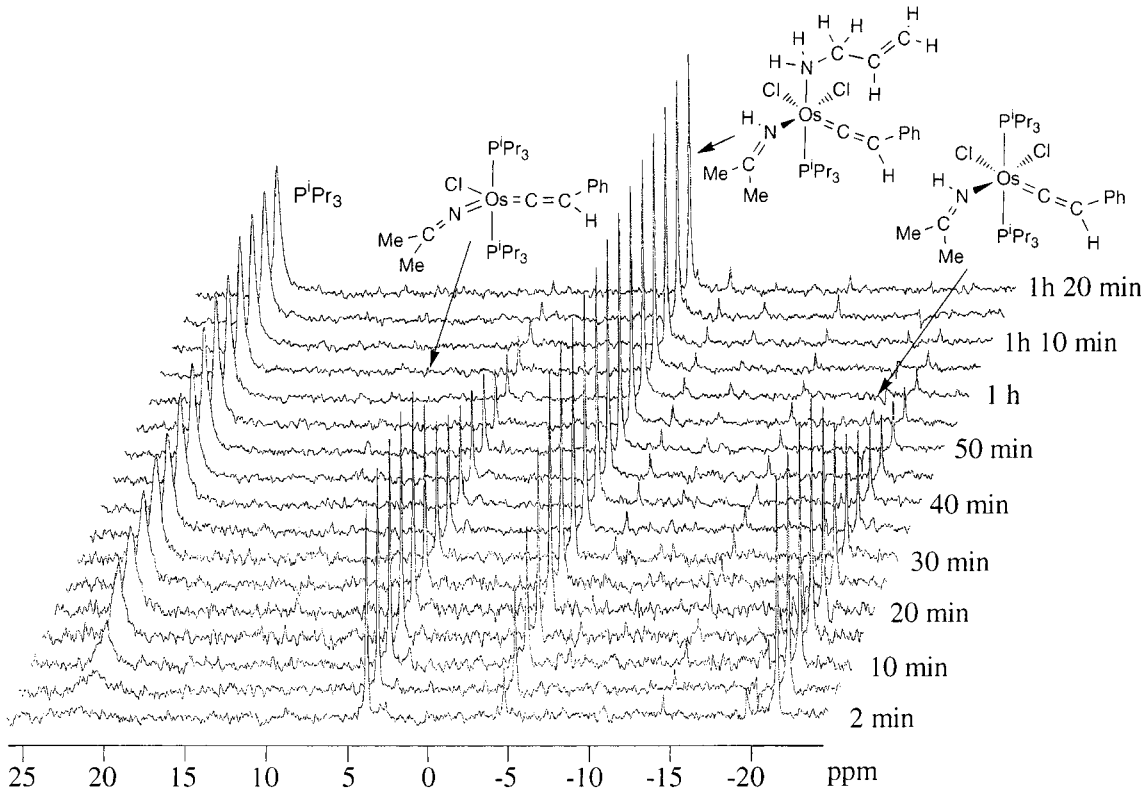
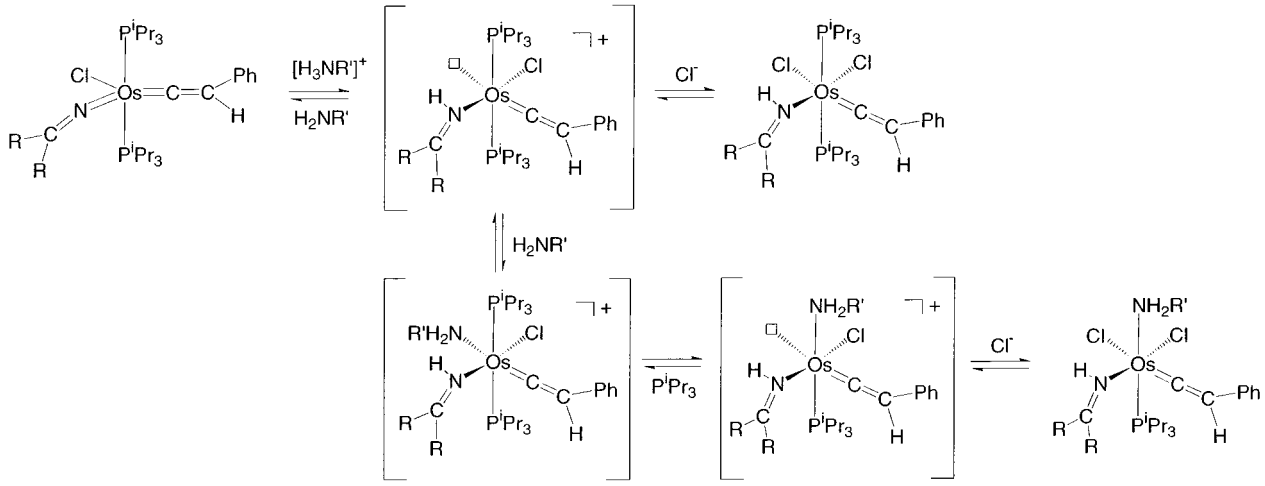


Figure 2. $^{31}P\{^{1}H\}$ NMR spectrum as a function of the time of the reaction of **1** with 2 equiv of allylamine.

Scheme 3



non-hydrogen atoms of the structure, giving N(1)−H(02), N(2)−H(03), and N(2)−H(04) distances of 0.88(8), 0.80(6), and 0.80(6) Å, respectively. Interestingly, the separations between the H(02) hydrogen atom of the imine and the chlorine ligand Cl(2) [2.58(7) Å] and the H(03) hydrogen atom of the amine and the chlorine ligand Cl(1) [2.59(8) Å] are shorter than the sum of the van der Waals radii of hydrogen and chlorine [r_{vdw}(H) = 1.20, r_{vdw}(Cl) = 1.80 Å], suggesting that there are intramolecular Cl···H−N hydrogen bonds between these atoms.[27] The interactions give rise to four-membered Os−Cl---H−N rings. An extended view of the structure (Figure 4) indicates also short intermolecular interactions [2.52(7) Å] between the H(04) hydrogen atoms of the amines and the chlorine ligands Cl(2) of two adjacent molecules in the crystal. Of great importance in biological and organic chemistry,[28] the hydrogen

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(27) Analysis of the hydrogen bonds was made over all hydrogens bonded to electronegative elements present in the structure and for which Distance($H\cdots A_{acceptor-atom}$) < r(A, N = 0.7) + 2.0 Å and Angle($D_{donor-atom}$ − $H\cdots A_{acceptor-atom}$) > 110°.

(28) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer: Berlin, 1991.

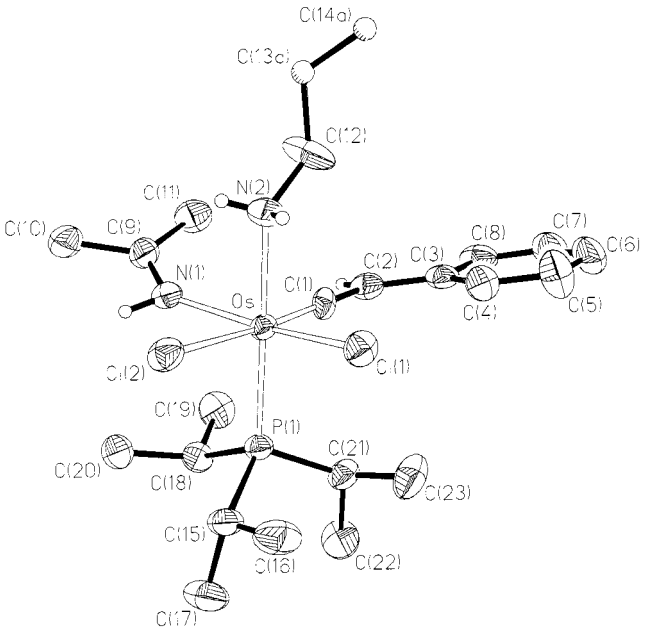


Figure 3. Molecular diagram for $OsCl_2(=C=CHPh)(NH=CMe_2)(NH_2CH_2CH=CH_2)(P^iPr_3)$ (**5**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selcted Bond Lengths (Å) and Angles (deg) for the Complex $OsCl_2(=C=CHPh)(NH=CMe_2)(NH_2CH_2CH=CH_2)(P^iPr_3)$ (5)

Os−C(1)	1.812(7)	C(2)−H(01)	0.92(7)
Os−N(1)	2.052(6)	N(1)−C(9)	1.279(9)
Os−N(2)	2.186(6)	N(1)−H(02)	0.88(8)
Os−P	2.3507(18)	N(2)−C(12)	1.484(11)
Os−Cl(1)	2.3938(17)	N(2)−H(03)	0.80(6)
C(1)−C(2)	1.316(10)	N(2)−H(04)	0.79(6)
C(1)−Os−Cl(1)	97.0(2)	Cl(2)−Os−P	93.88(6)
C(1)−Os−Cl(2)	176.5(2)	Cl(2)−Os−N(1)	78.67(19)
C(1)−Os−P	89.2(2)	Cl(2)−Os−N(2)	82.65(19)
C(1)−Os−N(1)	99.3(3)	P−Os−N(1)	95.24(17)
C(1)−Os−N(2)	94.4(3)	P−Os−N(2)	176.08(19)
Cl(1)−Os−Cl(2)	84.35(6)	N(1)−Os−N(2)	85.9(3)
Cl(1)−Os−P	97.10(6)	Os−C(1)−C(2)	177.5(6)
Cl(1)−Os−N(1)	159.62(19)	Os−N(1)−C(9)	141.8(6)
Cl(1)−Os−N(2)	80.8(2)	Os−N(2)−C(12)	119.8(5)

hydrogen bonds	$D_{(H-acceptor\ atom)}$	$A_{(donor\ atom-H\cdots acceptor\ atom)}$
N(1)−H(02)···Cl(2)	2.58(7)	104(6)
N(2)−H(03)···Cl(1)	2.59(8)	110(7)
N(2)−H(04)···Cl(2)	2.52(7)	162(6)
(−*x*+2, −*y*+1, −*z*+1)		

bonding is presently attracting considerable interest in the chemistry of transition metals.[16,29]

Are the interactions H(03)···Cl(1) and H(04)···Cl(2) the reason for the formation of **5**? We cannot assure this but the fact is that, although one should expect that the stabilization achieved by means of the H···Cl interactions is small, it may be enough. Furthermore, it should be noted that triethylamine and even diallylamine do not afford compounds related to **5** and **6**.

In agreement with the presence of the imine and amine ligands in **5** and **6**, the IR spectra in KBr of these compounds contain three ν(N−H) bands between 3300 and 3100 cm^{-1}. In addition, the spectra show ν(C=N) and ν(Os=C=C) absorptions at about 1660 and 1610 cm^{-1}, respectively. In the ^1H NMR spectra the resonances corresponding to the NH-hydrogen atom of the imines appear at about 10.6 ppm, as broad signals, whereas the NH-hydrogen atoms of the amine display

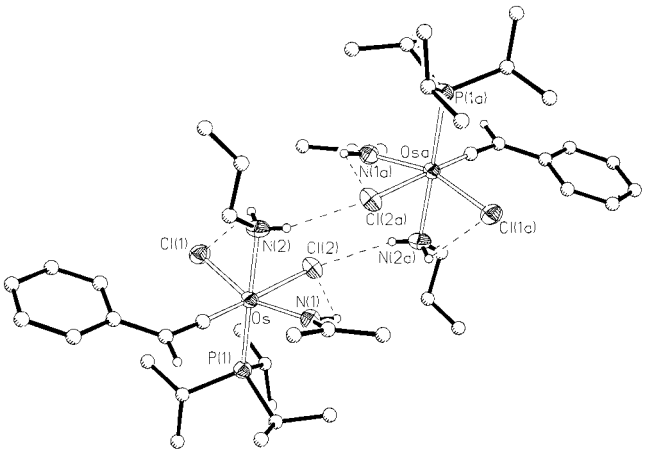
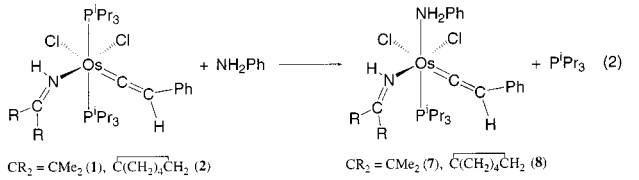


Figure 4. Intra- and intermolecular Os−Cl···H−N interactions in $OsCl_2(=C=CHPh)(NH=CMe_2)(NH_2CH_2CH=CH_2)(P^iPr_3)$ (**5**).

two resonances, masked with that due to the CH_2 group, between 4.0 and 3.5 ppm. The resonances due to the =CH proton of the vinylidene are observed at 2.18 (**5**) and 2.25 (**6**) ppm as doublets with coupling constants of 2.0 Hz. In the $^{13}C\{^1H\}$ NMR spectra, the C_α atom of the vinylidene gives rise to doublets at about 296 ppm with C−P coupling constants of about 11 Hz, and the C_β atom displays singlets at about 113 ppm. The resonances corresponding to the C=N carbon atom of the imines are observed at 181.4 (**5**) and 187.5 (**6**) ppm, as singlets. The $^{31}P\{^1H\}$ NMR spectra contain singlets at about −4.5 ppm.

(iv) Aniline. The generality of the substitution of a phosphine in **1** and **2** by primary amines is evident in the synthesis of $OsCl_2(=C=CHPh)(NH=CR_2)(NH_2Ph)(P^iPr_3)$ [CR_2 = CMe_2 (**7**), $\overline{C(CH_2)_4CH_2}$ (**8**)]. These compounds are prepared, similarly to **5** and **6**, by addition at room temperature of 1.5 equiv of aniline to dichloromethane solutions of **1** and **2**, respectively (eq 2).



Complexes **7** and **8** were isolated as orange solids in high yield (about 80%) and characterized by MS,

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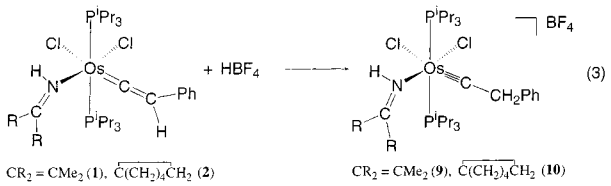
elemental analysis, IR, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. As in the IR spectra of **5** and **6**, the IR spectra of **7** and **8** contain three ν(N−H) bands between 3300 and 3100 cm^{-1} along with the ν(C═N) and ν(Os═C═C) absorptions at about 1660 and 1610 cm^{-1}, respectively. In the ^1H NMR spectra, the resonances corresponding to the NH-hydrogen atom of the imines appear at about 10.6 ppm, whereas the NH-hydrogen atoms of the aniline display two resonances between 5.8 and 5.5 ppm. For both compounds, the resonance due to the ═CH hydrogen atom of the vinylidene group is observed at about 2.1 ppm, as a doublet with a H−P coupling constant of about 1.5 Hz. The $^{13}C\{^1H\}$ NMR spectra agree well with those of **5** and **6**; the C_α atom of the vinylidene displays at about 297 ppm doublets with C−P coupling constants of about 11 Hz, whereas the resonances due to the C_β atom are observed at about 115 ppm as singlets. The resonances corresponding to the C═N carbon atom of the imines appear at about 182 ppm, as singlets. The $^{31}P\{^1H\}$ NMR spectra show singlets at about −1 ppm.

2. Reactions of 1 and 2 with HBF_4. Equation 1 and Scheme 2 show that complexes **1** and **2** have typical behavior of a Brönsted acid, transferring one proton to bases such as ^{n}BuLi and amines. Although, at first glance, these compounds could have two electrophilic hydrogen atoms, the NH of the imines and ═CH of the vinylidene, only one of them is transferred, that of the imine ligands. This fact, together with the inertia of the vinylidene toward the addition of primary amines, suggests that the vinylidene is a nucleophile, and therefore, compounds **1** and **2** should also shown Brönsted base behavior, accepting a proton of strong acids. To corroborate this, we have also carried out the reactions of **1** and **2** with HBF_4.

The addition at room temperature of 1.0 equiv of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of **1** and **2** leads to the immediate formation of the carbyne−imine derivatives $[OsCl_2(\equiv CCH_2Ph)(NH{=}CR_2)(P^iPr_3)_2][BF_4]$ [CR_2 = CMe_2 (**9**), $C(CH_2)_4CH_2$ (**10**)], as a result of the addition of the proton from the acid to the C_β atom of the vinylidene (eq 3). The regioselectivity of the addition is in agreement with the previously mentioned theoretical studies on vinylidene compounds, which have identified the localization of the electron density on the C_β atom.[1]

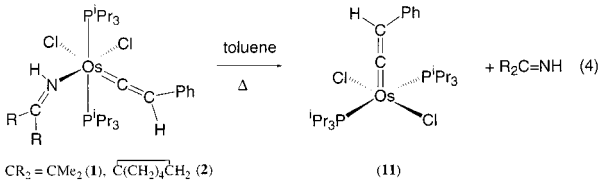


The reactions shown in eq 3 are reversible. Thus, the addition of 1.0 equiv of triethylamine to dichloromethane-d_2 solutions of **9** and **10** regenerates **1** and **2**, respectively. The selectivity of these deprotonations agrees well with the high stability of **1** and **2**, which do not evolve into azavinylidene−carbyne species by hydrogen transfer from the imines to the vinylidene group.

Complexes **9** and **10** were isolated as yellow solids in high yield (about 85%). In the IR spectra in KBr, the ν(NH) absorptions of the coordinated imine groups appear at 3271 (**9**) and 3254 (**10**) cm^{-1}. In addition the spectra show ν(C═N) bands at 1637 (**9**) and 1621 (**10**) cm^{-1} and the absorptions due to the $[BF_4]^-$ anions with T_d symmetry, centered at 1053 (**9**) and 1061 (**10**) cm^{-1}. In the solid state, these compounds are stable for one month if kept under argon at −20 °C. At this temperature, in dichloromethane solutions, they are stable for a few hours. In the ^1H NMR spectra of **9** and **10** in dichloromethane-d_2 at −40 °C, the most noticeable resonances are broad signals at about 9.8 ppm corresponding to the NH proton of the imines and broad singlets at about 3.8 ppm, due to the CH_2 protons of the carbyne. In the $^{13}C\{^1H\}$ NMR spectra at −40 °C, the C_α resonances of the carbyne appear at about 282 ppm as triplets with C−P coupling constants of about 9 Hz, whereas the C_β resonances are observed at about 61 ppm as singlets. The C═N carbon atoms of the imines display singlets at 188.1 (**9**) and 192.3 (**10**) ppm. The $^{31}P\{^1H\}$ NMR spectra contain singlets at about 5 ppm.

3. Formation of $OsCl_2(=C=CHPh)(P^iPr_3)_2$. Ruthenium vinylidene complexes of the type $RuCl_2(=C=CHR)(PR'_3)_2$ have been known since 1991.[30] Since the advent of Grubbs ROMP catalysts $RuCl_2(=CR_2)(PR'_3)_2$,[31] the synthesis of this type of vinylidene derivatives has experienced an increased interest.[32] However, pathways for the preparation of the osmium counterparts have not been found, although their search has been intense.[17]

Complexes **1** and **2** are precursors of $OsCl_2(=C=CHPh)(P^iPr_3)_2$ (**11**), in agreement with the weak Lewis basicity of the imine nitrogen atom.[33] The heating of toluene solutions of these compounds under reflux for 24 h affords purple solutions, from which complex **11** is isolated as a purple solid in about 60% yield (eq 4). The formation of **11** is probably favored by the low stability of the free aliphatic N−H ketimines, which in the presence of traces of water evolve into ketones.[34]



In the IR spectrum of **11** in KBr, the most noticeable features are the absence of any ν(NH) band and the presence of the ν(Os═C═C) vibration corresponding to

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the vinylidene ligand at 1611 cm^{-1}. In the ^1H NMR spectrum in benzene-d_6, the resonance due to the CH= vinylidene proton is observed at 2.14 ppm, as a triplet with a H−P coupling constant of 2.7 Hz. In the $^{13}C\{^1H\}$ spectrum the C_α atom of the vinylidene gives rise at 278.9 ppm to a triplet with a C−P coupling constant of 9.6 Hz, and the C_β atom displays at 110 ppm another triplet but with a C−P coupling constant of 4.0 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 5.5 ppm. These spectroscopic data agree well with those previously reported for the ruthenium counterpart, where the square-pyramidal structure has been proven by X-ray diffraction analysis.[32c,d]

Concluding Remarks

This study has revealed that the reactivity of imine−vinylidene compounds of the type $OsCl_2(=C=CHPh)(NH=CR_2)(P^iPr_3)_2$ is the result of (i) the electrophilic character of the NH-hydrogen atom of the imine and the nucleophilic character of the vinylidene ligand, (ii) the electronegativity of the chlorine ligands, which favor the formation of hydrogen bonds, and (iii) the weak Lewis basicity of the imine nitrogen atom.

As a consequence of the electrophilic character of the NH-hydrogen atom of the imine and the nucleophilic character of the vinylidene, these compounds have amphoteric nature, transferring the NH-hydrogen proton to bases such as amines and ^{n}BuLi and accepting the proton from HBF_4. In their reactions as acids, the conjugated bases are the five-coordinate azavinylidene−vinylidene compounds $OsCl(=N=CR_2)(=C=CHPh)(P^iPr_3)_2$, which coordinate the azavinylidene ligands in a bent fashion. In their reactions as bases, the conjugated acids are the carbyne−imine derivatives $[OsCl_2(\equiv CCH_2Ph)(NH=CR_2)(P^iPr_3)_2]^+$.

The high electronegativity of the chlorine does makes this ligand efficient for forming inter- and intramolecular hydrogen bonds with ligands containing hydrogen atoms bonded to the donor atom. The additional stabilization resulting from these H···Cl interactions appears to be the reason for the surprising formation of the mixed amine−phosphine complexes $OsCl_2(=C=CHPh)(NH=CR_2)(NH_2R')(P^iPr_3)$, which are obtained as a result of the displacement of a triisopropylphosphine ligand from $OsCl_2(=C=CHPh)(NH=CR_2)(P^iPr_3)_2$ by primary amines.

As a result of the weak Lewis basicity of the nitrogen atom of the imines, complexes $OsCl_2(=C=CHPh)(NH=CR_2)(P^iPr_3)_2$ dissociate the N−H ketimine in toluene under reflux, to give $OsCl_2(=C=CHPh)(P^iPr_3)_2$. The driving force of this reaction could be the low stability of the free aliphatic N−H ketimines.

In conclusion, complexes $OsCl_2(=C=CHPh)(NH=CR_2)(P^iPr_3)_2$ are electrophiles at the NH-hydrogen atom and nucleophiles at the C_β atom of the vinylidene group. They exchange a phosphine ligand by primary amines and lose the imine ligand in toluene under reflux.

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, $OsCl_2(=C=CHPh)\{NH=C(CH_3)_2\}(P^iPr_3)_2$ (**1**) and $OsCl_2(=C=CHPh)\{NH=C(CH_2)_4CH_2\}(P^iPr_3)_2$ (**2**), were prepared by the published method.[16] ^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.

Reaction of 1 with Triethylamine. A solution of **1** (13 mg, 0.018 mmol) in 0.5 mL of dichloromethane-d_2 in an NMR tube was treated with triethylamine (2.5 μL, 0.018 mmol). The NMR tube was sealed under argon, and after 10 min ^1H and $^{31}P\{^1H\}$ NMR measurements were made. An 1:5 equilibrium mixture of **1** and **3** was obtained.

Reaction of 2 with Triethylamine. A solution of **2** (13 mg, 0.018 mmol) in 0.5 mL of dichloromethane-d_2 in an NMR tube was treated with triethylamine (2.5 μL, 0.018 mmol). The NMR tube was sealed under argon, and after 10 min ^1H and $^{31}P\{^1H\}$ NMR measurements were made. An 1:9 equilibrium mixture of **2** and **4** was obtained.

Reaction of 1 with ^{n}BuLi: Preparation of $OsCl\{=N=C(CH_3)_2\}(=C=CHPh)(P^iPr_3)_2$ (3). An orange solution of **1** (100 mg, 0.134 mmol) in 10 mL of THF was treated with ^{n}BuLi (60 μL, 0.150 mmol, 2.5 M in hexanes). After 10 min, 0.5 mL of 2-propanol was added to eliminate the excess ^{n}BuLi. Then, the solvent was removed and dichloromethane (10 mL) was added to filter the ionic salts. The resulting orange solution was evaporated to dryness, and addition of methanol (2 mL) yielded an orange solid that was washed with methanol (2 × 2 mL) and dried in vacuo. Yield: 75 mg (79%). Anal. Calcd for $C_{29}H_{54}NClOsP_2$: C, 49.45; H, 7.73; N, 1.99. Found: C, 49.15; H, 7.58; N, 1.83. IR (KBr, cm^{-1}): ν(C=N) 1671 (m); ν(Os=C=C) 1608 (s). ^1H NMR (C_6D_6, 20 °C): δ 7.3−7.2 (m, 4H, H_{Ph}); 6.85 (t, J_{H-H} = 6.5, 1H, $H_{para-Ph}$); 3.40 (t, J_{H-P} = 2.1, 1H, Os=C=C*H*Ph); 2.71 (m, 6H, PCH); 2.17 and 1.98 (both s, 6H, $\{CH_3\}_2C=N$); 1.35 and 1.13 (both dvt, J_{H-H} = 6.9, N = 13.5, 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR plus DEPT (C_6D_6, 20 °C): δ 275.0 (t, J_{C-P} = 11.2, Os=C); 153.8 (t, J_{C-P} = 3.2, C=N); 135.5 (t, J_{C-P} = 2.3, $C_{ipso-Ph}$); 128.1, 124.0, and 122.5 (all s, C_{Ph}); 113.2 (t, J_{C-P} = 3.9, Os=C=*C*); 22.9 (vt, N = 22.8, PCH); 19.7 and 19.3 (both s, PCH*C*H$_3$); 19.5 and 19.2 (both s, $\{CH_3\}_2C=N$). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 4.2 (s). MS (FAB$^+$): m/z 705 (M^+).

Reaction of 2 with ^{n}Buli: Preparation of $OsCl\{=N=C(CH_2)_4CH_2\}(=C=CHPh)(P^iPr_3)_2$ (4). This complex was prepared as described for **3** starting from 100 mg (0.128 mmol) of **2** and ^{n}BuLi (55 μL, 0.137 mmol, 2.5 M in hexanes). Yield: 75 mg (78%). Anal. Calcd for $C_{32}H_{58}NClOsP_2$: C, 51.63; H, 7.85; N, 1.88. Found: C, 51.53; H, 7.79; N, 1.78. IR (KBr, cm^{-1}): ν(C=N) 1655 (m); ν(Os=C=C) 1605 (s). ^1H NMR (C_6D_6, 20 °C): δ 7.31 (t, J_{H-H} = 7.5, 2H, $H_{meta-Ph}$); 7.27 (d, J_{H-H} = 7.8, 2H, $H_{ortho-Ph}$); 6.85 (t, J_{H-H} = 6.9, 1H, $H_{para-Ph}$); 3.41 (t, J_{H-P} = 3.0, 1H, Os=C=C*H*Ph); 2.76 (m, 6H, PCH); 2.62 and 2.29 (both m, 4H, $\{CH_2\}_2C=N$); 1.38 and 1.15 (both dvt, J_{H-H} = 6.9, N = 13.5, 36H, PCHC*H*$_3$) 1.4−1.2 (m, 6H, Cy). $^{13}C\{^1H\}$ NMR plus APT (C_6D_6, 20 °C): δ 275.0 (t, J_{C-P} = 10.9, Os=C); 158.2 (t, J_{C-P} = 2.0, C=N); 135.3 (s, $C_{ipso-Ph}$); 127.4, 123.4, and 121.3 (all s, C_{Ph}); 112.6 (t, J_{C-P} = 2.5, Os=C=*C*); 33.1, 32.7, 26.7, and 25.2 (all s, CH_2 Cy); 22.4 (vt, N = 22.9, PCH); 19.4 and 19.3 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 4.2 (s). MS (FAB$^+$): m/z 745 (M^+).

Reaction of 1 with Diallylamine. A solution of **1** (15 mg, 0.020 mmol) in 0.5 mL of dichloromethane-d_2 in an NMR tube was treated with diallylamine (2.5 μL, 0.020 mmol). The NMR tube was sealed under argon, and after 10 min ^1H and $^{31}P\{^1H\}$ NMR measurements were made. A 2:1 equilibrium mixture of **1** and **3** was obtained.

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Reaction of 2 with Diallylamine. A solution of **2** (15 mg, 0.019 mmol) in 0.5 mL of dichloromethane-d_2 in an NMR tube was treated with diallylamine (2.5 μL, 0.020 mmol). The NMR tube was sealed under argon, and after 10 min ^{1}H and ^{31}P-{^{1}H} NMR measurements were made. A 3:2 equilibrium mixture of **2** and **4** was obtained.

Reaction of 1 with Allylamine. A solution of **1** (15 mg, 0.020 mmol) in 0.5 mL of dichloromethane-d_2 in an NMR tube was treated with allylamine (1.5 μL, 0.020 mmol). The NMR tube was sealed under argon, and after 6 h ^{1}H and ^{31}P{^{1}H} NMR measurements were made. An equilibrium mixture of **1** (22%), **3** (8%), P^{i}Pr$_3$ (35%), and **5** (35%) was obtained.

Reaction of 2 with Allylamine. A solution of **2** (15 mg, 0.020 mmol) in 0.5 mL of dichloromethane-d_2 in an NMR tube was treated with allylamine (1.5 μL, 0.020 mmol). The NMR tube was sealed under argon, and after 6 h ^{1}H and ^{31}P{^{1}H} NMR measurements were made. An equilibrium mixture of **2** (9%), **4** (11%), P^{i}Pr$_3$ (40%), and **6** (40%) was obtained.

Preparation of $OsCl_2(=C=CHPh)\{NH=C(CH_3)_2\}(NH_2CH_2CH=CH_2)(P^iPr_3)$ (5). An orange solution of **1** in dichloromethane (100 mg, 0.135 mmol) was treated with allylamine (15 μL, 0.200 mmol). After stirring for 4 h at room temperature the solvent was removed to dryness. Addition of pentane caused the precipitation of an orange solid that was washed (4 × 3 mL) with pentane and dried in vacuo. Yield: 75 mg (87%). Anal. Calcd for $C_{23}H_{41}N_2Cl_2OsP$: C, 43.32; H, 6.48; N, 4.39. Found: C, 43.46; H, 6.53; N, 4.19. IR (KBr, cm^{-1}): ν(N−H) 3293 (m), 3206 (m), and 3125 (m); ν(C=N) 1660 (m); ν(Os=C=C) 1617 (s). ^{1}H NMR (acetone-d_6, 20 °C): δ 10.61 (s, 1H, C=N−H); 7.34 (d, J_{H-H} = 7.5, 2H, $H_{ortho-Ph}$); 7.14 (t, J_{H-H} = 7.5, 2H, $H_{meta-Ph}$); 6.65 (t, J_{H-H} = 7.5, 1H, $H_{para-Ph}$); 5.7 (m, 1H, −C*H*=CH$_2$); 4.85 (d, J_{H-H} = 17.1, −CH=CH_{trans}); 4.74 (d, J_{H-H} = 10.2, −CH=CH_{cis}); 3.9−3.5 (m, 4H, CH$_2$ and NH$_2$); 2.73 (m, 3H, PCH); 2.18 (d, J_{H-H} = 1.8 Hz, 1H, C=C*H*Ph); 2.04 and 1.96 (both s, 6H, {CH$_3$}$_2$C=N); 1.19 (dd, J_{H-H} = 7.5, J_{H-P} = 6.3, 18H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR plus APT (acetone-d_6, 20 °C): δ 296.1 (d, J_{C-P} = 10.6, Os=C); 181.4 (s, C=N); 137.4 (s, −CH=); 130.8 (s, $C_{ipso-Ph}$); 127.3, 125.4, and 123.6 (both s, C_{Ph}); 116.5 (s, =CH$_2$); 113.6 (s, Os=C=*C*); 46.9 (s, N−CH$_2$); 30.5 and 24.1 (both s,{*C*H$_3$}$_2$C=N); 26.3 (d, J_{C-P} = 28.0, PCH); 19.5 and 19.2 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (acetone-d_6, 20 °C): δ −4.6 (s). MS (FAB$^+$): *m*/*z* 638 (M$^+$), 602 (M$^+$ − Cl) and 581 [M$^+$ − (NH$_2$CH$_2$CH=CH$_2$)].

Preparation of $OsCl_2(=C=CHPh)\{NH=C(CH_2)_4CH_2\}(NH_2CH_2CH=CH_2)(P^iPr_3)$ (6). This complex was prepared as described for **5** starting from 100 mg (0.128 mmol) of **2** and 15 μL (0.200 mmol) of allylamine. Yield: 75 mg (86%). Anal. Calcd for $C_{26}H_{45}N_2Cl_2OsP$: C, 46.08; H, 6.69; N, 4.13. Found: C, 46.42; H, 6.73; N, 4.24. IR (KBr, cm^{-1}): ν(N−H) 3290 (m), 3206 (m), and 3123 (m); ν(C=N) 1655 (m); ν(Os=C=C) 1610 (s). ^{1}H NMR (acetone-d_6, 20 °C): δ 10.58 (s, 1H, C=N−H); 7.23 (d, J_{H-H} = 7.5, 2H, $H_{ortho-Ph}$); 7.13 (t, J_{H-H} = 7.5, 2H, $H_{meta-Ph}$); 6.72 (t, J_{H-H} = 7.5, 1H, $H_{para-Ph}$); 5.9 (m, 1H, −C*H*=CH$_2$); 5.16 (d, J_{H-H} = 17.1, −CH=CH_{trans}); 5.09 (d, J_{H-H} = 10.2, −CH=CH_{cis}); 4.2−3.7 (m, 4H, CH$_2$ and NH$_2$); 2.82 (m, 3H, PCH); 2.25 (d, J_{H-P} = 2.0, 1H, C=C*H*Ph); 2.0−1.4 (m, 10H, Cy); 1.38 (dd, J_{H-H} = 7.5, J_{H-P} = 6.3, 18H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR plus APT (acetone-d_6, 20 °C): δ 295.8 (d, J_{C-P} = 11.9, Os=C); 187.5 (s, C=N); 137.1 (s, −CH=); 131.1 (s, $C_{ipso-Ph}$); 128.0, 125.3, and 123.1 (all s, C_{Ph}); 116.5 (s, =CH$_2$); 112.8 (s, Os=C=*C*); 46.8 (s, N−CH$_2$); 42.4, 34.1, 27.2, 26.7, and 24.8 (all s, CH$_2$ Cy); 26.1 (d, J_{C-P} = 28.0, PCH); 19.5 and 19.2 (both s, PCH*C*H$_3$). ^{31}P-{^{1}H} NMR (acetone-d_6, 20 °C): δ −4.0 (s). MS (FAB$^+$): *m*/*z* 678 (M$^+$), 642 (M$^+$ − Cl) and 621 [M$^+$ − (NH$_2$CH$_2$CH=CH$_2$)].

Reaction of 3 with $[H_3NCH_2CH=CH_2]Cl$. A solution of **3** (15 mg, 0.021 mmol) in 0.5 mL of dichloromethane-d_2 in an NMR tube was treated with [H$_3$NCH$_2$CH=CH$_2$]Cl (2 mg, 0.021 mmol). The NMR tube was sealed under argon, and after 10 min ^{1}H and ^{31}P{^{1}H} NMR measurements were made. A 7:2 equilibrium mixture of **5** and **1** plus free triisopropylphosphine was obtained.

Reaction of 3 with $[H_3NCH_2CH=CH_2]Cl$ in the Presence of NaCl. A solution of **3** (15 mg, 0.021 mmol) in 0.5 mL of acetone-d_6 in an NMR tube was treated with [H$_3$NCH$_2$CH=CH$_2$]Cl (2 mg, 0.021 mmol) and NaCl (10 mg, 0.170 mmol). The NMR tube was sealed under argon, and after 10 min ^{1}H and ^{31}P{^{1}H} NMR measurements were made. A 1:4 equilibrium mixture of **5** and **1** plus free triisopropylphosphine was obtained.

Preparation of $OsCl_2\{=C=CHPh\}\{NH=C(CH_3)_2\}(NH_2Ph)(P^iPr_3)$ (7). An orange solution of **1** in dichloromethane (100 mg, 0.135 mmol) was treated with aniline (18 μL, 0.197 mmol). After stirring for 36 h at room temperature the solvent was removed to dryness. Addition of pentane caused the precipitation of an orange solid that was washed (4 × 3 mL) with pentane and dried in vacuo. Yield: 75 mg (83%). Anal. Calcd for $C_{26}H_{41}N_2Cl_2OsP$: C, 46.35; H, 6.13; N, 4.16. Found: C, 46.42; H, 6.28; N, 3.94. IR (KBr, cm^{-1}): ν(N−H) 3224 (m) and 3158 (m); ν(C=N) 1655 (m); ν(Os=C=C) 1613 (s). ^{1}H NMR (C_6D_6, 20 °C): δ 10.57 (s, 1H, C=N−H); 7.5−6.8 (m, 10H, H_{Ph}); 5.8 and 5.5 (both m, 2H, NH$_2$); 2.68 (m, 3H, PCH); 2.08 (d, J_{H-H} = 1.8, 1H, Os=C=C*H*Ph); 1.53 and 1.09 (both s, 6H, {CH$_3$}$_2$C=N); 1.20 (m, 18H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR plus APT (acetone-d_6, 20 °C): δ 297.4 (d, J_{C-P} = 11.0, Os=C); 180.4 (s, C=N); 142.1 (s, N−C_{Ph}); 130.4 (s, $C_{ipso-Ph}$); 128.6, 125.9, 124.0, and 121.4 (all s, C_{Ph}); 114.5 (s, Os=C=*C*); 30.2 and 22.8 (both s,{*C*H$_3$}$_2$C=N); 30.0 (s, *C*H$_2$Ph); 26.6 (d, J_{C-P} = 28.0, PCH); 19.5 and 19.3 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ −1.1 (s). MS (FAB$^+$): *m*/*z* 581 [M$^+$ − (NH$_2$Ph)].

Preparation of $OsCl_2(=C=CHPh)(NH_2Ph)\{NH=C(CH_2)_4CH_2\}(P^iPr_3)$ (8). This complex was prepared as described for **7** starting from 100 mg (0.128 mmol) of **2** and 18 μL (0.197 mmol) of aniline. Yield: 75 mg (82%). Anal. Calcd for $C_{29}H_{45}N_2Cl_2OsP$: C, 48.80; H, 6.35; N, 3.92. Found: C, 48.95; H, 6.66; N, 3.63. IR (KBr, cm^{-1}): ν(N−H) 3220 (m) and 3160 (m); ν(C=N) 1660 (m); ν(Os=C=C) 1615 (s). ^{1}H NMR (C_6D_6, 20 °C): δ 10.62 (s, 1H, C=N−H); 7.8−6.8 (m, 10H, H_{Ph}); 5.8 and 5.5 (both m, 2H, NH$_2$); 2.67 (m, 3H, PCH); 2.14 (d, J_{H-H} = 1.5, 1H, Os=C=C*H*Ph); 1.8−0.7 (m, 10H, Cy); 1.2 (m, 18H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR plus APT (acetone-d_6, 20 °C): δ 296.8 (d, J_{C-P} = 11.5, Os=C); 184.6 (s, C=N); 142.3 (s, N−C_{Ph}); 130.1 (s, $C_{ipso-Ph}$); 128.7, 126.0, 124.4, 123.9, and 121.3 (all s, C_{Ph}); 114.6 (Os=C=*C*); 41.6, 32.8, 26.4, 25.4, and 24.2 (all s, CH$_2$ Cy); 26.5 (d, J_{C-P} = 28.0, PCH); 19.4 and 19.1 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ −0.8 (s). MS (FAB$^+$): *m*/*z* 621 [M$^+$ − (NH$_2$Ph)].

Preparation of $[OsCl_2(\equiv C-CH_2Ph)\{NH=C(CH_3)_2\}(P^iPr_3)_2]BF_4$ (9). An orange solution of **1** (100 mg, 0.135 mmol) in 10 mL of diethyl ether was treated with tetrafluoroboric acid (18 μL, 0.135 mmol, 54% in diethyl ether). A yellow solid was formed immediately, and after 10 min of stirring, it was washed with diethyl ether (2 × 3 mL) and dried in vacuo. Yield: 95 mg (85%). Anal. Calcd for $C_{29}H_{56}NBCl_2F_4OsP_2$: C, 42.04; H, 6.81; N, 1.69. Found: C, 42.33; H, 7.14; N, 1.77. IR (KBr, cm^{-1}): ν(N−H) 3271 (m); ν(C=N) 1637 (s); ν(BF$_4$) 1053 (vs, br). ^{1}H NMR (CD_2Cl_2, −40 °C): δ 9.82 (br, 1H, N−H); 7.4−7.2 (m, 5H, Ph); 3.83 (s, 2H, C*H*$_2$Ph); 2.68 (m, 6H, PCH); 2.58 (s, 6H, {CH$_3$}$_2$C=N); 1.28 (m, 36H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, −40 °C): δ 281.7 (t, J_{C-P} = 9.0, Os≡C); 188.1 (s, C=N); 129.5, 129.3, 128.6, and 127.2 (all s, C_{Ph}); 60.8 (s, *C*H$_2$Ph); 31.8 and 26.6 (both s, {*C*H$_3$}$_2$C=N); 25.5 (vt, *N* = 23.2, PCH); 19.7 (br, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, −40 °C): δ 4.0 (s). MS (FAB$^+$): *m*/*z* 742 (M$^+$); 706 (M$^+$ − HCl); 685 (M$^+$ − HN=C{CH$_3$}$_2$).

Preparation of $[OsCl_2(\equiv C\text{-}CH_2Ph)\{NH=C(CH_2)_4CH_2\}(P^iPr_3)_2]BF_4$ (10). This complex was prepared as described for **9** starting from 100 mg (0.128 mmol) of **2** and tetrafluo-

roboric acid (17 μL, 0.128 mmol, 54% in diethyl ether). Yield: 95 mg (86%). Anal. Calcd for $C_{32}H_{60}NBCl_2F_4OsP_2$: C, 44.25; H, 6.96; N, 1.61. Found: C, 44.45; H, 7.31; N, 1.56. IR (KBr, cm^{-1}): ν(N−H) 3254 (m); ν(C=N) 1621 (s); $\nu(BF_4)$ 1061 (vs, br). ^{1}H NMR (CD_2Cl_2, −40 °C): δ 9.84 (br, 1H, N−H); 7.4−7.2 (m, 5H, Ph); 3.86 (s, 2H, CH_2Ph); 2.9−2.7 (m, 10H, PCH, {CH_2}$_2$C=N); 1.73 and 1.58 (both m, 6H, Cy); 1.30 (m, 36H, PCHCH_3). ^{13}C{^{1}H} NMR plus DEPT (CD_2Cl_2, −40 °C): δ 281.9 (t, J_{C-P} = 8.6, Os≡C); 192.3 (s, C=N); 129.7, 129.4, and 128.7 (all s, C_{Ph}); 127.4 (s, $C_{ipso-Ph}$); 61.2 (s, CH_2Ph); 43.3, 36.1, 26.9, 26.2, and 22.8 (all s, CH_2, Cy); 25.5 (br, PCH); 19.9 and 19.1 (both br, PCHCH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, −40 °C): δ 4.8 (s). MS (FAB$^+$): *m*/*z* 782 (M$^+$); 746 (M$^+$ − HCl); 685 (M$^+$ − NH=C(CH_2)$_4$$CH_2$).

Reaction of 9 with Triethylamine. A solution of **9** (15 mg, 0.018 mmol) in 0.5 mL of dichloromethane-d_2 in an NMR tube was treated with triethylamine (2.5 μL, 0.018 mmol). The NMR tube was sealed under argon, and after 10 min measurements were made. Complex **1** was obtained.

Reaction of 10 with Triethylamine. A solution of **10** (15 mg, 0.018 mmol) in 0.5 mL of dichloromethane-d_2 in an NMR tube was treated with triethylamine (2.5 μL, 0.018 mmol). The NMR tube was sealed under argon, and after 10 min measurements were made. Complex **2** was obtained.

Preparation of $OsCl_2$(=C=CHPh)(P^iPr_3)$_2$ (11). Method A: A solution of **1** (100 mg, 0.135 mmol) in toluene was heated to reflux during 24 h. The resulting purple solution was evaporated to dryness, and addition of methanol yielded a purple solid that was washed with methanol (2 × 2 mL) and dried in vacuo. Yield: 55 mg (60%). Method B: As described for method A starting from 100 mg (0.128 mmol) of **2**. Yield: 50 mg (57%). Anal. Calcd for $C_{26}H_{48}Cl_2OsP_2$: C, 45.67; H, 7.08. Found: C, 45.50; H, 7.26. IR (KBr, cm^{-1}): ν(Os=C=C) 1611 (s). ^{1}H NMR (C_6D_6, 20 °C): δ 7.10 (t, J_{H-H} = 7.5, 2H, $H_{meta-Ph}$); 6.72 (d, J_{H-H} = 7.5, 2H, $H_{ortho-Ph}$); 6.66 (t, J_{H-H} = 7.5, 1H, $H_{para-Ph}$); 3.04 (m, 6H, PCH); 2.14 (t, J_{H-P} = 2.7, 1H, Os=C=C*H*Ph); 1.34 (dvt, J_{H-H} = 7.2, *N* = 13.5, 36H, PCHCH_3). ^{13}C{^{1}H} NMR plus DEPT (C_6D_6, 20 °C): δ 278.9 (t, J_{C-P} = 9.6, Os=C); 131.1 (t, J_{C-P} = 2.0, $C_{ipso-Ph}$); 127.8, 125.1, and 123.7 (all s, C_{Ph}); 110.0 (t, J_{C-P} = 4.0, Os=C=*C*); 23.7 (vt, *N* = 23.3, PCH); 19.6 (s, PCHCH_3). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 5.5 (s). MS (FAB$^+$): *m*/*z* 684 (M$^+$ − Cl).

Crystal Data for $OsCl$(=N=CMe_2)(=C=CHPh)(P^iPr_3)$_2$ (3) and $OsCl_2$(=C=CHPh)(NH=C(Me)$_2$}(NH_2CH_2CH=CH_2)(P^iPr_3) (5). A summary of the fundamental crystal and refinement data of the compounds **3** and **5** is given in Table 3. Crystals of **3** and **5** were mounted on a Bruker Smart CCD(3) and Bruker Smart APEX CCD diffractometers equipped with a normal focus, 2.4 kW sealed tube X-ray source (molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA. Data were collected over a hemisphere by a combination of three sets. The cell parameters were determined and refined by least-squares fit of all collected reflections. Each frame exposure time was 20 s (**3**) or 10 s (**5**) covering 0.3° in ω. Coverage of the unique sets was over 100% complete to al least 25° in θ. The first 50 (**3**) or 100 (**5**) frames were collected at the end of the data collection to monitor crystal decay. The absorption correction was made using SADABS.[35] The structure was solved by Multan and Fourier methods using SHELXS.[36] Full-matrix least-squares refinement was carried out using SHELXL97[35] minimizing $w(F_o^2 - F_c^2)_2$. Weighted *R* factors (R_w) and goodness of fit *S* are based on F^2; conventional *R* factors are based on *F*.

(35) *SADABS*, Smart Apex v. 5; Bruker Analytical X-ray Systems: Madison, WI.

(36) Sheldrick, G. M. *SHELXS*; University of Göttingen: Göttingen, Germany, 1997.

Table 3. Crystal Data and Data Collection and Refinement for Complexes $OsCl$(=N=CMe_2)(=C=CHPh)(P^iPr_3)$_2$ (3) and [$OsCl_2$(=C=CHPh)(NH=CMe_2)-(NH_2CH_2CH=CH_2)(P^iPr_3) C_7H_8 (5)

	3	**5**
formula	$C_{29}H_{54}ClNOsP_2$	$C_{23}H_{41}Cl_2N_2OsP\ C_7H_8$
mol wt	704.36	729.78
color and habit	red block	red block
space group	monoclinic, $P2_1/m$	triclinic, $P\bar{1}$
a, Å	9.4978(8)	9.4244(9)
b, Å	13.0692(12)	10.6728(10)
c, Å	13.5472(12)	16.6864(15)
α, deg		81.515(2)
β, deg	105.837(1)	83.561(2)
γ, deg		82.244(2)
V, Å^3	1617.8(2)	1637.5(3)
Z	2	2
D_{calc}, g cm^{-3}	1.446	1.480
Data Collection and Refinement		
diffractometer	Bruker-Siemens CCD	
λ(Mo Kα), Å	0.71073	
monochromator	graphite oriented	
F, mm^{-1}	4.14	4.13
scan type	ω scans at different *n* values	
2θ range, deg	$5 \le 2\theta \le 52$	$5 \le 2\theta \le 50$
temp, K	293.0(2)	173.0(2)
no. of data collect	4640 (*h*: −10, 11; *k*: −12, 14; *l*: −16, 6)	8996 (*h*: −11, 11; *k*: −11, 12; *l*: −18, 19)
no. of unique data	2406 (merging *R* factor 0.0261)	5667 (merging *R* factor 0.0481)
no. of params refined	184	318
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0282	0.0456
wR_2[b] [all data]	0.0714	0.1113
S[c] [all data]	1.009	0.897

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

Complex **3** was solved and refined in both $P2_1$ and $P2_1/m$ space groups, according to the observed value of $Z = 2$ and systematic absences. However, a careful check of the refined geometry revealed the $P2_1/m$ space group as more appropriate.

The −CH=CH_2 group of the allylamine ligand of **5** was found to be disordered. This disorder was modeled with two moieties (C(13a), C(14a) and C(13b), C(14b)) and refined with complementary occupancy factors (0.53(3) *a*, and 0.47(3) *b*) as isotropic atoms.

Complex **5** crystallizes with two molecules of toluene with occupancy 0.5, which were refined with restrained geometry. The vinylidene (H01), imine (H02), and amine (H(03) and H(04)) hydrogen atoms of complex **5** were refined as free isotropic atoms, with the same bond distance to the N(2) nitrogen atom for H(03) and H(04).

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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 **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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