Cyclometalation of 2-Vinylpyridine with $MCl_2(PPh_3)_3$ and $MHCl(PPh_3)_3$ (M = Ru, Os)

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Treatment of $RuCl_2(PPh_3)_3$ in benzene at room temperature with 2-vinylpyridine produces the vinylpyridine complex $RuCl_2(2\text{-}CH_2{=}CHC_5H_4N)(PPh_3)_2$. In the presence of Cs_2CO_3, $RuCl_2(PPh_3)_3$ reacts with 2-vinylpyridine at room temperature to give the cyclometalated complex $RuCl(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(PPh_3)$, which is also produced from the reaction of $RuHCl(PPh_3)_3$ with 2-vinylpyridine. $OsCl_2(PPh_3)_3$ reacts with 2-vinylpyridine/Cs_2CO_3 at room temperature to give the analogous cyclometalated complex $OsCl(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(PPh_3)$. In the presence of $NaBF_4$, the reaction produces $[Os(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(PPh_3)_2]BF_4$. The dihydrogen complex $Os(H_2)Cl(CH{=}CHC_5H_4N)(PPh_3)_2$ is produced from the reaction of $OsHCl(PPh_3)_3$ with 2-vinylpyridine. The mechanism of the cyclometalation reactions has been investigated by computational chemistry.

Introduction

Cyclometalation through C−H bond activation is a very important process, due to its relevance to selective activation and functionalization of hydrocarbons.[1] Cyclometalated complexes have also found increasing applications in catalysis,[2] organometallic chemistry, and materials sciences.[3]

Like many other transition-metal complexes, ruthenium complexes[4] can also effect cyclometalation reactions involving C−H bond activation. Recently, there have been much activity in the development of catalytic reactions involving cyclometalation on ruthenium. These studies have led to the discovery of a number of interesting reactions involving cyclometalation of C−H bonds on the ruthenium center. These include additions of the C−H bonds of aromatics and olefins to unsaturated substrates,[5] coupling reactions of aryl halides with aromatics[6] or olefins,[7] arylation of aromatic ketones with arylboronates,[8] carbonylation of arenes[9] and alkenes,[10] and allylation of 2-pyridylarenes with allyl acetates.[11] In view of the increasing interest in catalytic reactions involving cyclometalated ruthenium species, it is of interest to see how the ligand environment around ruthenium may affect the cyclometalation process. To this end, we have studied the cyclometalation reactions of 2-vinylpyridine with $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$. For comparison, the reactions of 2-vinylpyridine with $OsCl_2(PPh_3)_3$ and $OsHCl(PPh_3)_3$ have also been investigated.

Cyclometalation reactions of 2-vinylpyridine have been reported previously with metal complexes of Pd,[12] Pt,[13] Ir,[14] Rh,[15−17] Co,[18] Re,[19,20] Ru[21−23] and Os.[21,24−28] In the cases of ruthenium and osmium, cyclometalation of 2-vinylpyridine has

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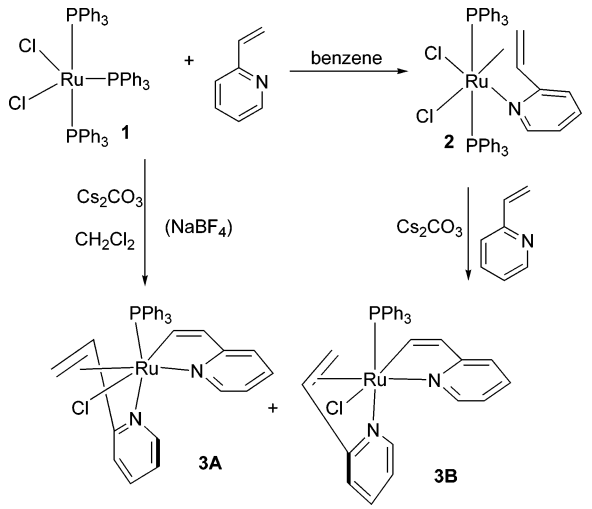
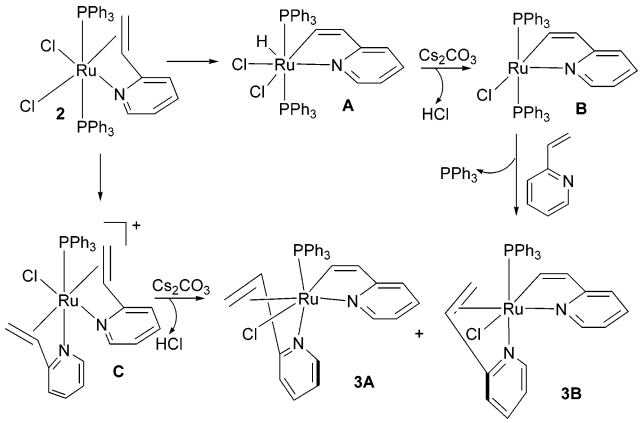
Scheme 1



Scheme 2



been observed in the reactions of 2-vinylpyridine with complexes such as $RuH_4(PhP(CH_2CH_2CH_2PCy_2)_2)$,[22] $[RuHCl(P^iPr_3)_2]_2$,[23] $Ru(R)Cl(CO)(P^iPr_3)_2$ (R = Ph, CH=CHPh),[21] $Os(R)Cl(CO)(P^iPr_3)_2$ (R = Ph, CH=CHPh),[21] $Os_3(CO)_{10}(MeCN)_2$,[24] $OsH_6(P^iPr_3)_2$,[25] $OsH_2Cl_2(P^iPr_3)_2$,[26] and $OsH_3(SnPh_2Cl)(CH_2{=}CHP^iPr_2)(P^iPr_3)$.[27] However, the reactions of $MCl_2(PPh_3)_3$ and $MHCl(PPh_3)_3$ (M = Ru, Os) with 2-vinylpyridine have not been reported, despite the fact that $RuCl_2(PPh_3)_3$ is known to promote the coupling reactions of 2-alkenylpyridines with aryl bromides (the Heck reaction), for which cyclometalation of C−H bonds of alkenylpyridines on a Ru(II) or Ru(0) center has been suggested as one of the key steps.[7]

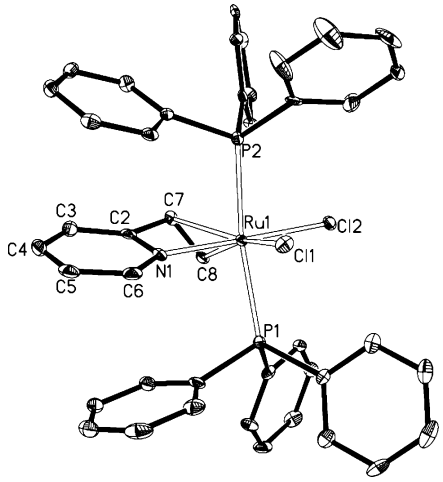


Figure 1. Molecular structure of $RuCl_2(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)_2$ (**2**).

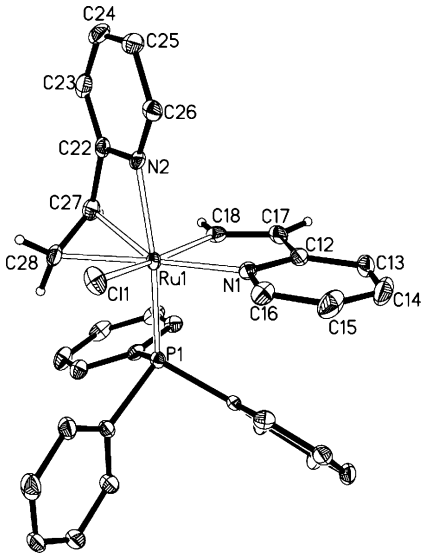


Figure 2. Molecular structure of $RuCl(2\text{-}CH{=}CHC_5H_3N)(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)$ (**3A**).

Results and Discussion

Reaction with $RuCl_2(PPh_3)_3$. Treatment of $RuCl_2(PPh_3)_3$ (**1**) in benzene at room temperature with 2-vinylpyridine produced a brownish yellow solution along with a yellow precipitate, from which the vinylpyridine complex $RuCl_2(2\text{-}CH_2{=}CHC_5H_4N)(PPh_3)_2$ (**2**) can be isolated as a yellow solid in 81% (Scheme 1). Complex **2** is also produced if the reaction is carried out in dichloromethane.

The structure of **2** has been confirmed by an X-ray diffraction study. The crystallographic details, selected bond distances and angles are given in Tables 1 and 2, respectively. The X-ray structure shown in Figure 1 clearly reveals that the complex is a neutral molecule with two trans PPh_3 ligands, two cis chlorides, and an η^3-vinylpyridine ligand coordinated to ruthenium through both the N atom and the olefinic double bond. The complex adopts a distorted-octahedral structure with the two chlorides, N, and the olefinic double bond in the same plane. The $CH_2{=}CH$ vector is essentially perpendicular to the equatorial plane: i.e., parallel with the Ru−P bonds. The Ru−C (2.181(4) and 2.188(4) Å) and C−C bond distances associated with

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Table 1. Crystallographic Data and Structure Refinement Details for $RuCl_2(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)_2$ (2), $RuCl(2\text{-}CH{=}CHC_5H_3N)(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)$ (3A), $OsCl(2\text{-}CH{=}CHC_5H_3N)(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)$ (7B), and $[Os(2\text{-}CH{=}CHC_5H_3N)(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)_2]BF_4$ (8)

	2	3A	7B	8
formula	$C_{44}H_{39}Cl_4NP_2Ru$	$C_{32}H_{28}ClN_2PRu$	$C_{39}H_{36}ClN_2OsP$	$C_{52}H_{47}BCl_4F_4N_2OsP_2$
mol wt	886.57	608.05	789.32	1180.67
symmetry	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	13.4753(8)	9.3139(11)	9.9664(12)	11.4371(7)
b, Å	13.1464(8)	14.6492(18)	10.2744(13)	13.5518(8)
c, Å	21.8713(13)	19.876(2)	16.463(2)	16.7303(10)
α, deg	90	99.525(2)	82.292(2)	73.1180(10)
β, deg	91.0610(10)	97.661(2)	82.888(2)	78.7380(10)
γ, deg	90	91.188(2)	74.077(2)	74.7740(10)
V, Å^3	3873.9(4)	2648.1(6)	1599.8(3)	2374.3(2)
Z	4	4	2	2
D_{calcd}, g cm^{-3}	1.520	1.525	1.639	1.652
μ, mm^{-1}	0.797	0.778	4.150	3.033
2θ range, deg	3.5−50	3.2−52	4.6−50	3.2−50
no. of data collected	19 444	27 552	10 585	15 016
no. of unique data	6795	10367	5553	8184
no. of params/restraints	469/18	667/0	398/0	595/0
goodness of fit on F^2	1.085	0.953	1.040	1.004
R1 ($I > 2\sigma(I)$)	0.0568	0.0447	0.0381	0.0339
wR2 (all data)	0.1192	0.0982	0.0777	0.0783
peak/hole, e Å^{-3}	0.987/−0.805	1.008/−0.680	2.082/−1.385	2.679/−1.094

the $Ru(CH_2{=}CH)$ unit are normal compared with those of reported ruthenium−olefin complexes[29] and show little asymmetry in the binding of the olefin.

The solid-state structure is supported by the solution NMR spectroscopic data. In particular, the ^1H NMR spectrum in CD_2Cl_2 shows the ^1H signals of coordinated $CH{=}CH_2$ at 3.47 (CH_2), 3.73 (CH_2), and 4.59 ppm (CH). In the $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2), the signals of coordinated $CH{=}CH_2$ were observed at 53.3 (CH_2) and 64.8 ppm (CH). The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at 37.0 and 22.2 ppm with a *J*(PP) coupling of 347.5 Hz. Observation of two ^{31}P signals for **2** is expected, due to the unsymmetric nature of the olefinic ligand.

When the reaction was carried out in CH_2Cl_2 in the presence of Cs_2CO_3 and $NaBF_4$ at room temperature (Scheme 1), HCl was eliminated and cyclometalation of 2-vinylpyridine occurred to give $RuCl(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(PPh_3)$ (**3**). Initially, we thought that the $NaBF_4$ might facilitate the cyclometalation through formation of NaCl. However, further study shows that the base Cs_2CO_3 is required, while $NaBF_4$ is not necessary for the cyclometalation reaction. In situ NMR experiments indicate that the reaction of **1** with 2-vinylpyridine in the presence of Cs_2CO_3 initially produces complex **2** as the dominant product, then a mixture of **2** and **3**, and eventually **3** only. The observation implies that complex **3** is formed from complex **2**. Indeed, isolated **2** can be converted to **3** when treated with $CsCO_3$ and additional 2-vinylpyridine (Scheme 1).

The cyclometalated product **3** is found as a mixture of two isomers in a 1:1 ratio, as indicated by its NMR data (in dichloromethane). The presence of both 2-vinylpyridine and a cyclometalated vinylpyridine in complex **3** as ligands is supported by the ^1H and ^{13}C NMR data. The existence of two isomers is clearly indicated by the observations of two singlet ^{31}P signals at 48.5 and 47.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum and two sets of ^1H and ^{13}C signals of Ru(CH=CH) and Ru(η^2-$CH_2{=}CH$) in the ^1H and $^{13}C\{^1H\}$ NMR spectra. The structure of one of the isomers, isomer **3A**, has been determined by X-ray diffraction (see Table 1). A view of the molecular structure of **3A** is shown in Figure 2, and selected bond distances and angles are given in Table 3. As shown in Figure 2, isomer

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $RuCl_2(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)_2$ (2)

Bond Distances			
Ru(1)−C(7)	2.181(4)	Ru(1)−C(8)	2.188 (4)
Ru(1)−N(1)	2.056(3)	Ru(1)−Cl(1)	2.427(1)
Ru(1)−Cl(2)	2.436(1)	Ru(1)−P(1)	2.426(1)
Ru(1)−P(2)	2.377(1)	C(7)−C(8)	1.385(5)
Bond Angles			
C(7)−Ru(1)−C(8)	36.9(1)	N(1)−Ru(1)−Cl(1)	89.09(9)
C(7)−Ru(1)−N(1)	64.2(1)	N(1)−Ru(1)−P(1)	91.16(9)
C(7)−Ru(1)−P(1)	110.6(1)	N(1)−Ru(1)−P(2)	93.74(9)
C(7)−Ru(1)−P(2)	78.8(1)	Cl(1)−Ru(1)−Cl(2)	95.50(3)
C(7)−Ru(1)−Cl(2)	111.3(1)	Cl(1)−Ru(1)−P(1)	86.45(3)
C(8)−Ru(1)−N(1)	85.5(1)	Cl(1)−Ru(1)−P(2)	85.53(3)
C(8)−Ru(1)−P(1)	81.0(1)	Cl(2)−Ru(1)−P(1)	89.72(3)
C(8)−Ru(1)−P(2)	107.5(1)	Cl(2)−Ru(1)−P(2)	86.04(3)
P(1)−Ru(1)−P(2)	170.53(4)		

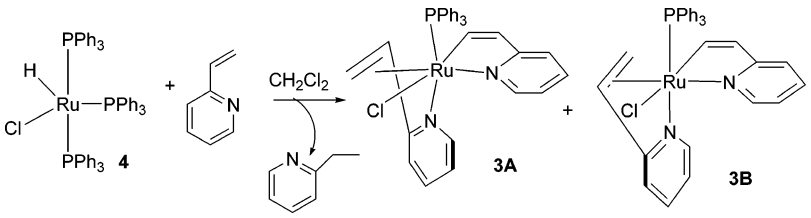
Table 3. Selected Bond Distances (Å) and Angles (deg) for $RuCl(2\text{-}CH{=}CHC_5H_3N)(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)$ (3A)

Bond Distances			
Ru(1)−C(18)	2.018(4)	Ru(1)−N(1)	2.129(3)
Ru(1)−N(2)	2.108(3)	Ru(1)−C(27)	2.151(4)
Ru(1)−C(28)	2.171(4)	Ru(1)−Cl(1)	2.533(1)
Ru(1)−P(1)	2.291(1)	C(17)−C(18)	1.335(5)
C(27)−C(28)	1.376(5)		
Bond Angles			
C(18)−Ru(1)−N(1)	77.1(1)	C(27)−Ru(1)−C(28)	37.1(1)
C(18)−Ru(1)−N(2)	89.8(1)	C(27)−Ru(1)−N(2)	64.3(1)
C(18)−Ru(1)−P(1)	86.0(1)	C(27)−Ru(1)−P(1)	102.5(1)
C(18)−Ru(1)−C(27)	80.6(2)	C(27)−Ru(1)−Cl(1)	110.3(1)
N(1)−Ru(1)−N(2)	96.3(1)	C(28)−Ru(1)−N(2)	82.9(1)
N(1)−Ru(1)−Cl(1)	87.30(8)	C(28)−Ru(1)−P(1)	87.2(1)
N(1)−Ru(1)−P(1)	95.02(8)	C(28)−Ru(1)−Cl(1)	82.4(1)
N(2)−Ru(1)−P(1)	166.70(9)	Cl(1)−Ru(1)−P(1)	105.26(3)
N(2)−Ru(1)−Cl(1)	82.24(8)		

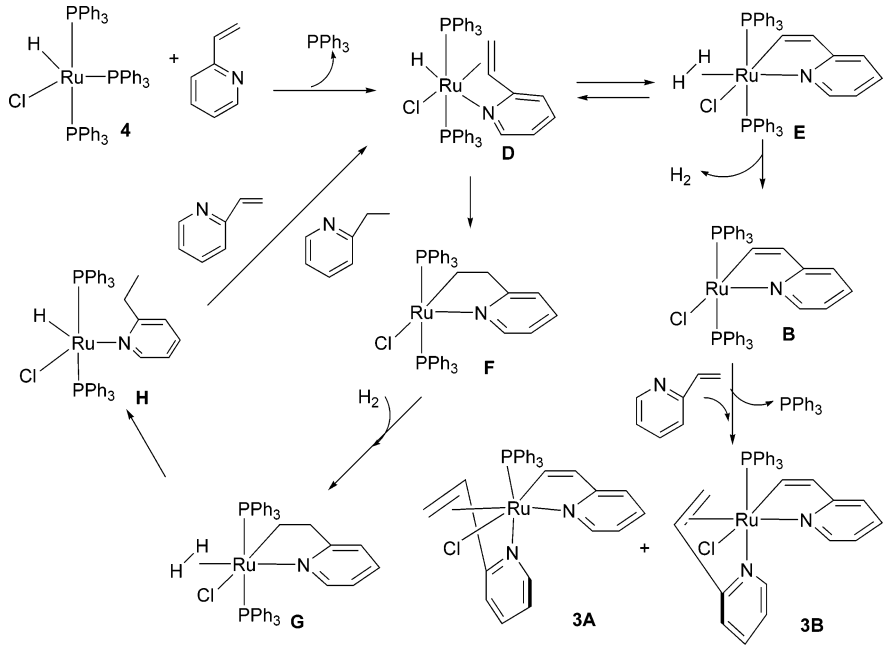
3A is a pseudo-octahedral complex with Cl trans to the η^1-Ru−C(vinyl) group, the η^2-olefin of the neutral 2-vinylpyridine trans to N of the vinylpyridine anion, and PPh_3 trans to N of 2-vinylpyridine. The olefinic group $CH{=}CH_2$ is oriented in such a way that the CH_2 is closer to the chloride ligand. The structural data associated with Ru(η^2-$CH_2{=}CH$) are similar to those of **2**, and the structural data associated with Ru(η^1-CH=CH) are similar to those of $RuCl(CH{=}CHC_6H_4N)(P^iPr_3)_2$.[23]

In view of the similarity of the NMR data of **3A** and **3B**, it is reasonable to assume that isomer **3B** has a coordination sphere

Scheme 3



Scheme 4



similar to that of isomer **3A**. A structure in which the olefinic group is oriented in such a way that the CH is closer to the chloride ligand can be proposed for **3B**. As will be discussed below, the structure of an osmium complex with a structure similar to that of **3B** has been confirmed by an X-ray study. During the course of this work, Esteruelas et al. reported the synthesis of the osmium complex $OsCl(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(P^iPr_3)$, an analogue of complex **3**, from the reaction of $OsH_2Cl_2(P^iPr_3)_2$ with 2-vinylpyridine.[26] The complex $OsCl(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(P^iPr_3)$ also shows similar isomerism. Consistent with the proposed structures, NOE effects were observed for one of the ^1H signals of CH_2 in complex **3B** and for the ^1H signal of $CH{=}CH_2$ in complex **3A** when the Ru*CH* signals in **3B** and **3A** were irradiated.

Scheme 2 shows a plausible mechanism for the formation of **3**. Complex **2** can undergo a C−H oxidative addition reaction to give intermediate **A**, which could eliminate HCl with the help of the base Cs_2CO_3 to give intermediate **B**. Complex **3** can then be generated by an addition and substitution reaction of 2-vinylpyridine with intermediate **B**. Alternatively, complex **3** may be formed by initial formation of the cationic species $[RuCl(CH_2{=}CHC_5H_4N)_2(PPh_3)_2]^+$ (**C**) followed by direct deprotonation of the coordinated olefin ligand. However, we feel that the direct deprotonation process is unlikely, because the reaction rate is not significantly different in either the presence or absence of $NaBF_4$. If the direct deprotonation process is involved, one would expect that the reaction should proceed more quickly in the presence of $NaBF_4$, because $NaBF_4$ can help to form cationic species.

Reaction of $RuHCl(PPh_3)_3$. The reaction of $RuHCl(PPh_3)_3$ with 2-vinylpyridine is interesting, because there are several possible outcomes for the reaction. For example, $RuHCl(PPh_3)_3$ may react with 2-vinylpyridine to give a cyclometalated complex by elimination of H_2 or HCl. Since the complex $RuHCl(CO)(PPh_3)_3$ is known to undergo insertion reaction with 2-vinylpyridine,[30] reaction of $RuHCl(PPh_3)_3$ with 2-vinylpyridine may also give an insertion product. Treatment of $RuHCl(PPh_3)_3$ (**4**) in benzene with 2-vinylpyridine produced 2-ethylpyridine and complex **3** (Scheme 3), which was also produced from the reaction of $RuCl_2(PPh_3)_3$ with 2-vinylpyridine in the presence of Cs_2CO_3 (see preceding subsection).

As mentioned previously, elimination of HCl was observed in the reactions of $RuCl_2(PPh_3)_3$ with 2-vinylpyridine in the presence of the base Cs_2CO_3. In order to see if a similar reaction may also occur for the reactions of $RuHCl(PPh_3)_3$ with 2-vinylpyridine, we have carried out the reaction of $RuHCl(PPh_3)_3$ with 2-vinylpyridine in the presence of Cs_2CO_3 and $Cs_2CO_3/NaBF_4$. In both cases, the reaction also produced complex **3** and 2-ethylpyridine, suggesting that the base has no effect on the course of the reaction.

A plausible mechanism for the formation of **3** and 2-ethylpyridine from the reaction of $RuHCl(PPh_3)_3$ (**4**) with 2-vinylpyridine is shown in Scheme 4. The reaction may initially produce the olefin complex **D**. Complex **D** could undergo a cyclometalation reaction to give the dihydrogen complex **E**, which loses the dihydrogen ligand to generate intermediate **B**, which reacts further with 2-vinylpyridine to give complex **3**. Intermediate **B** is structurally related to the cyclometalated complex $RuCl(CH{=}CHC_6H_4N)(P^iPr_3)_2$, which has been previ-

(30) Hiraki, K.; Ochi, N.; Sasada, Y.; Hayashida, H.; Fuchita, Y.; Yamanaka, S. *J. Chem. Soc., Dalton Trans.* **1985**, 873.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $OsCl(2\text{-}CH{=}CHC_5H_3N)(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)$ (7B)

Bond Distances			
Os(1)−C(8)	2.040(6)	Os(1)−C(17)	2.166(6)
Os(1)−C(18)	2.129(6)	Os(1)−N(1)	2.149(5)
Os(1)−N(11)	2.098(4)	Os(1)−Cl(1)	2.510(1)
Os(1)−P(1)	2.298(1)	C(17)−C(18)	1.395(9)
C(7)−C(8)	1.339(9)		
Bond Angles			
C(8)−Os(1)−N(1)	75.9(2)	C(8)−Os(1)−N(11)	89.9(2)
C(8)−Os(1)−C(18)	81.7(3)	C(8)−Os(1)−C(17)	113.5(2)
C(8)−Os(1)−Cl(1)	160.9(2)	C(8)−Os(1)−P(1)	96.4(2)
C(17)−Os(1)−N(11)	64.7(2)	C(17)−Os(1)−C(18)	37.9(2)
C(17)−Os(1)−Cl(1)	79.8(2)	C(17)−Os(1)−P(1)	105.6(2)
C(18)−Os(1)−Cl(1)	115.1(2)	C(18)−Os(1)−N(1)	157.6(2)
C(18)−Os(1)−P(1)	89.9(2)	N(1)−Os(1)−N(11)	95.9(2)
N(1)−Os(1)−Cl(1)	87.0(1)	N(1)−Os(1)−P(1)	93.1(1)
Cl(1)−Os(1)−P(1)	92.95(5)	N(11)−Os(1)−P(1)	170.1(1)

ously isolated by Caulton et al. from the reaction of $[RuHCl(P^iPr_3)_2)]_2$ with 2-vinylpyridine.[23]

Intermediate **D** can also undergo an insertion reaction to give the alkyl complex **F**, which may react with H_2 (released from the formation of **B** from **E**) to give the dihydrogen complex **G**. **G** can undergo intramolecular hydrogen transfer reaction to give **H**, which can react with 2-vinylpyridine to yield 2-ethylpyridine and regenerate **D**. Dihydrogen complexes **E** and **G** are reasonable species, as we have isolated the related dihydrogen complex $OsCl(H_2)(2\text{-}CH{=}CHC_5H_4N)(PPh_3)_2$ from the reaction of $OsHCl(PPh_3)_3$ with 2-vinylpyridine (see below). Intramolecular hydrogen transfer from H_2 to a cis-alkyl ligand has been proposed previously in the mechanisms of catalytic hydrogenation reactions of olefins and alkynes.[31] Unfortunately, we have failed to identify any of the intermediates proposed in Scheme 4.

Reaction with $OsCl_2(PPh_3)_3$. To gain more insight into the cyclometalation reactions of ruthenium complexes, we have investigated the reactions of 2-vinylpyridine with $OsCl_2(PPh_3)_3$ and $OsHCl(PPh_3)_3$, with a view to detecting or isolating some osmium complexes structurally related to the intermediates proposed for the ruthenium-mediated reactions.

The course of the reaction of 2-vinylpyridine with $OsCl_2(PPh_3)_3$ (**5**) in the presence of Cs_2CO_3 was monitored by $^{31}P\{^1H\}$ NMR. The reaction of $OsCl_2(PPh_3)_3$ with excess 2-vinylpyridine in the presence of Cs_2CO_3 initially generated free PPh_3 and several other phosphorus-containing species having doublet $^{31}P\{^1H\}$ signals, which could not be separated or identified. After 4 h, the in situ ^{31}P NMR spectrum mainly showed a singlet signal at −6 ppm for PPh_3, two doublet signals at −7.9 (d, $J(PP) = 15.2$ Hz) and −11.7 (d, $J(PP) = 15.2$ Hz) ppm, and a singlet signal at −22.6 ppm. After 8 h, the doublet signals at −7.9 (d, $J(PP) = 15.2$ Hz) and −11.7 ppm (d, $J(PP) = 15.2$ Hz) disappeared and the singlet signal at −22.6 ppm remained. At this time, two singlets at 0.3 and −4.9 ppm appeared. After 24 h, the singlet signal at −22.6 ppm also disappeared, and only the two singlet signals at 0.3 and −4.9 ppm remained. These observations suggest that the complex with a ^{31}P chemical shift of −22.6 ppm is an intermediate for the formation of complexes with the ^{31}P shifts of 0.3 and −4.9 ppm.

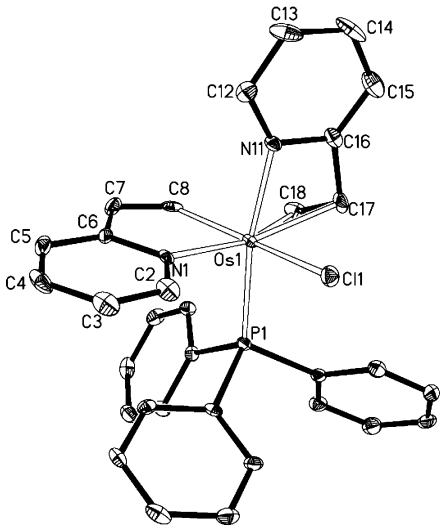


Figure 3. Molecular structure of $OsCl(2\text{-}CH{=}CHC_5H_3N)(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)$ (**7B**).

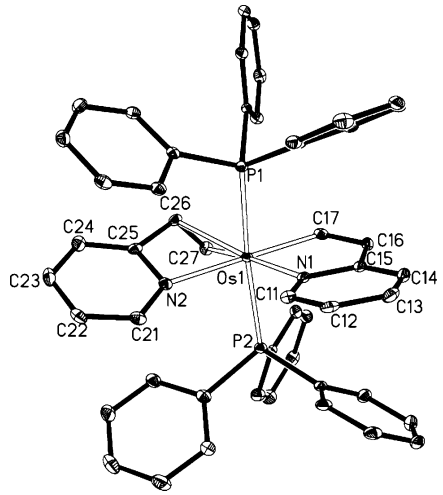


Figure 4. Molecular structure of the cation $[Os(CH{=}CHC_5H_3N)(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)_2]^+$ of complex **8**.

The compounds with ^{31}P signals at 0.3 and −4.9 ppm were isolated from a preparative-scale reaction and identified by NMR and MS to be the two isomers of the cyclometalated complex **7**, an osmium analogue of the ruthenium complex **3**. The structure of **7B** has been confirmed by X-ray diffraction. Selected bond distances and angles are given in Table 4. As shown in Figure 3, the coordination sphere of osmium in **7B** is similar to that of ruthenium in **3A**, except that the olefinic group $CH{=}CH_2$ is oriented in such a way that the CH_2 is closer to the chloride ligand in **3A**, while the olefinic group is oriented in such a way that the CH is closer to the chloride ligand in **7B**. Determination of the X-ray structures of **3A** and **7B** provide strong support for the proposition that the two isomers observed for **3** and **7** are due to the difference in the orientation of the olefinic group $CH{=}CH_2$. Complex **7** is closely related to Esteruelas' complex $OsX(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(P^iPr_3)$ (X = Cl, OTf).[26] The two isomers of **7** are produced in a

(31) (a) Liu, S. H.; Lo, S. T.; Wen, T. B.; Zhou, Z. Y.; Lau, C. P.; Jia, G. *Organometallics* **2001**, *20*, 667. (b) Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Chem. Commun.* **1993**, 1750. (c) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663. (d) Bianchini, C.; Meli, A.; Peruzzini, M.; Frediani, P.; Bohanna, C.; Esteruelas, M. A.; Oro, L. A. *Organometallics* **1992**, *11*, 138. (e) Bianchini, C.; Bohanna, C.; Esteruelas, M. A.; Frediani, P.; Meli, A.; Oro, L. A.; Peruzzini, M. *Organometallics* **1992**, *11*, 3837. (f) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (g) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1992** ,*11*, 3362. (h) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley: New York, 2001; pp 237−238. (i) Chan, W. C.; Lau, C. P.; Chen, Y. Z.; Fang, Y. Q.; Ng, S. M.; Jia, G. *Organometallics* **1997**, *16*, 34.

Scheme 5

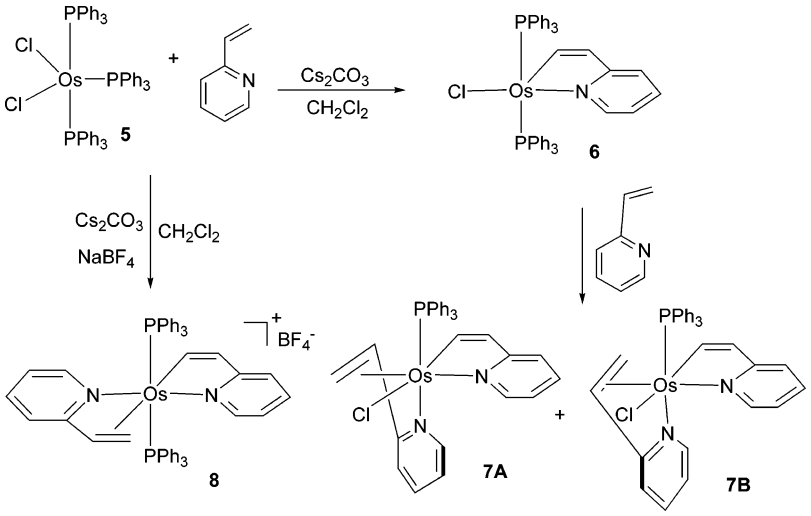


Table 5. Selected Bond Distances (Å) and Angles (deg) for $[Os(2\text{-}CH{=}CHC_5H_3N)(2\text{-}CH_2{=}CHC_5H_3N)(PPh_3)_2]BF_4$ (8)

Bond Distances			
Os(1)−C(17)	2.045(4)	Os(1)−N(1)	2.111(4)
Os(1)−C(27)	2.205(4)	Os(1)−C(26)	2.212(4)
Os(1)−N(2)	2.163(4)	Os(1)−P(1)	2.367(1)
Os(1)−P(2)	2.419(1)	C(16)−C(17)	1.357(6)
C(26)−C(27)	1.427(6)		

Bond Angles			
C(17)−Os(1)−N(1)	76.9(2)	C(26)−Os(1)−N(2)	62.7(2)
C(17)−Os(1)−C(27)	94.7(2)	C(26)−Os(1)−C(27)	37.7(2)
C(17)−Os(1)−C(26)	117.0(2)	C(26)−Os(1)−P(1)	76.3(1)
C(17)−Os(1)−P(1)	87.0(1)	C(26)−Os(1)−P(2)	110.2(1)
C(17)−Os(1)−P(2)	90.5(1)	N(1)−Os(1)−N(2)	103.9(1)
N(1)−Os(1)−P(1)	84.97(9)	N(2)−Os(1)−P(1)	94.18(9)
N(1)−Os(1)−P(2)	84.60(9)	N(2)−Os(1)−P(2)	88.43(9)
P(1)−Os(1)−P(2)	173.48(4)	C(27)−Os(1)−P(1)	105.0(1)
C(27)−Os(1)−P(2)	81.2(1)	C(27)−Os(1)−N(2)	84.4(2)

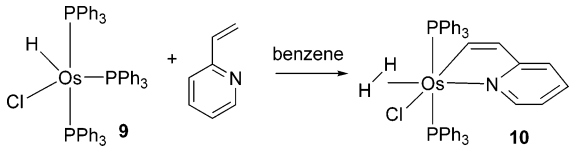
ratio of 63/37. NOE experiments suggest that the major isomer is complex **7B**.

We have also tried to isolate and identify the complex with the ^{31}P shift of −22.6 ppm. However, a pure sample of the compound could not be obtained. We have only been able to obtain a sample of the compound contaminated with ca. 22 mol % of **7**. The MS showed a peak with *m*/*z* 855.15, corresponding to a formula of $OsCl(CH{=}CHC_5H_4N)(PPh_3)_2$. The ^1H NMR spectrum showed two characteristic signals at 11.14 and 6.84 ppm assignable to Os*C*H=CH and OsCH=C*H*, respectively. On the basis of its MS and NMR data and the fact that it can be converted to **7** in the presence of 2-vinylpyridine, we tentatively assign the compound to the structure shown as **6**. This compound can be related to intermediate **B** proposed for the ruthenium-mediated reactions.

When a mixture of $OsCl_2(PPh_3)_3$ and 2-vinylpyridine in CH_2Cl_2 was stirred at room temperature in the presence of $CsCO_3$ and $NaBF_4$ for 24 h, the predominant product of the reaction is the cationic complex **8** (Scheme 5). As indicated by an in situ NMR experiment, a small amount of complex **7** was produced from the reaction. Complex **8** was isolated as a yellow solid. Its structure has also been confirmed by single-crystal X-ray diffraction (Figure 4). Selected bond distances and angles are given in Table 5. As shown in Figure 4, the complex has two trans PPh_3 ligands, two trans pyridines, and the η^2-olefin is trans to η^1-vinyl. The solution NMR spectroscopic data are in agreement with the solid-state structure.

The cationic complex **8** is likely formed via substitution of the chloride in **6** by 2-vinylpyridine. Obviously, $NaBF_4$ can provide Na^+, an electrophile that can remove the Cl^- ligand from the osmium center of **6** to give the cationic complex **8**. It should be noted that $NaBF_4$ is not required for the cyclometalation reaction to proceed to give **7**. It is also interesting to note that the analogous cationic ruthenium complex was not generated from the reaction of $RuCl_2(PPh_3)_3$ with 2-vinylpyridine in the presence of $Cs_2CO_3/NaBF_4$. Apparently, Os has a higher affinity for PPh_3. Isolation of the cationic complex **8** from the reaction of $OsCl_2(PPh_3)_3$ with 2-vinylpyridine in the presence of $CsCO_3$ and $NaBF_4$ supports the idea that cyclometalation does not proceed through direct deprotonation.

Scheme 6



Reaction of $OsHCl(PPh_3)_3$. In the reaction of $RuHCl(PPh_3)_3$ with 2-vinylpyridine, we assume that the reaction proceeds through the dihydrogen intermediate $RuCl(H_2)(CH{=}CHC_5H_4N)(PPh_3)_2$ (**E**) (Scheme 4). However, we have failed to isolate or observe the intermediate. It is known that osmium dihydrogen complexes could have higher thermal stability than analogous ruthenium dihydrogen complexes. Thus, we have studied the reaction of 2-vinylpyridine with $OsHCl(PPh_3)_3$ (**9**) with a hope to isolate the dihydrogen complex $OsCl(H_2)(CH{=}CHC_5H_4N)(PPh_3)_2$ (**10**).

Indeed, complex **10** was isolated in 63% yield as a yellow solid by treatment of $OsHCl(PPh_3)_3$ (**9**) or $OsH_3Cl(PPh_3)_3$ with 2-vinylpyridine (Scheme 6). Its structure can be readily assigned on the basis of NMR spectroscopic data. The presence of the dihydrogen ligand is confirmed by the observation of a hydride signal at −6.96 ppm, which has a T_1(min) value of 41.2 ms at 230 K and 300 MHz. The T_1(min) value suggests that complex **10** can be classified as an elongated dihydrogen complex (or a compressed dihydride complex).[32] Reported osmium alkyl dihydrogen complexes closely related to **10** include $Os(H_2)Cl$-

(32) Reviews on dihydrogen complexes: (a) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (b) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (c) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Esteruelas, M. A.; Oro, L. A. *Chem. Rev.* **1998**, *98*, 577. (e) Kubas, G. J. *Dihydrogen and s-Bond Complexes*; Kluwer Academic/Plenum Press: New York, 2001. (f) Peruzzini, M.; Poli, R. *Recent Advances in Hydride Chemistry*; Elsevier: Amsterdam, 2001.

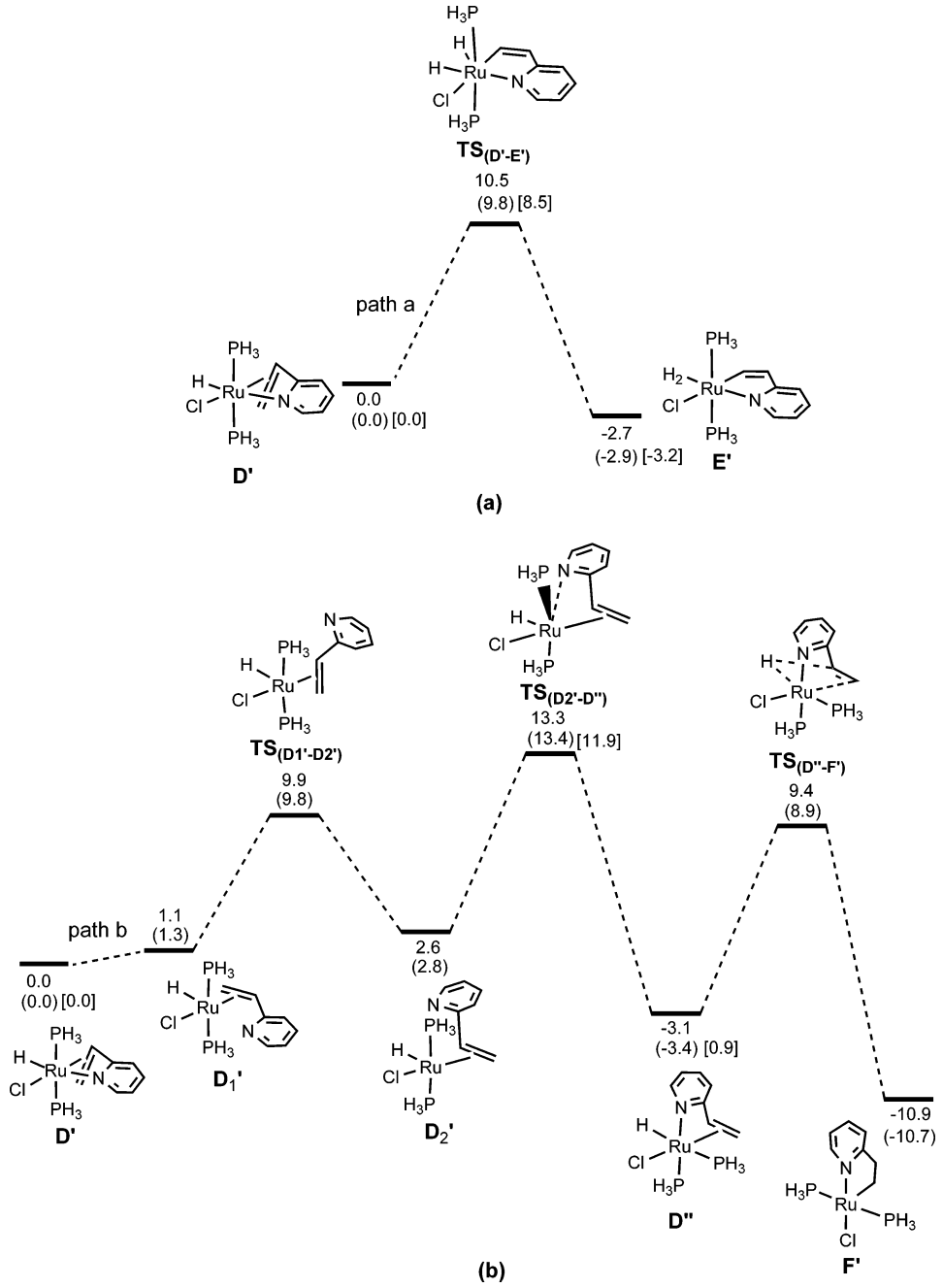


Figure 5. Energy profiles calculated for the reactions of the model complex $RuHCl(CH_2{=}CHC_5H_4N)(PH_3)_2$ (**D′**): (a) cyclometalation reaction to give the dihydrogen complex **E′**; (b) insertion reaction to generate the alkyl complex **F′**. The calculated relative free energies and zero point energy corrected electronic energies (in parentheses) are given in kcal/mol. The relative electronic energies (kcal/mol) in brackets were obtained on the basis of the ONIOM calculations, which consider the steric effect of the realistic PPh_3 ligands.

$(CH{=}CHC_5H_4N)(P^iPr_3)_2$,[25] $Os(H_2)(SnClPh_2)(CH{=}CHC_5H_4N)(P^iPr_3)_2$,[27] $Os(H_2)ClH(PPh_3)_3$,[33] $Os(H_2)X(C_6H_4COMe)(P^iPr_3)_2$ (X = Cl, F)[34] and $Os(H_2)Cl(PPh_3)(PCP)$.[35]

Theoretical Studies. Reaction of $RuHCl(PPh_3)_3$ with 2-vinylpyridine in benzene produces both ethylpyridine and complex **3** (Scheme 3). Mechanistically, we believe that the reaction initially produces the intermediate olefin complex **D** (Scheme 4). In order to generate both ethylpyridine, a hydrogenated product, and complex **3**, the intermediate complex **D** should undergo simultaneously an insertion reaction to give the alkyl complex **F** and a cyclometalation reaction to generate the dihydrogen complex **E** (Scheme 4). In other words, only if both of the two reactions occurred could ethylpyridine and complex **3** be produced. Energetically, the two reactions should be comparable in their reaction barriers. To see if this is the case, we carried out density functional calculations based on the model complex $RuHCl(CH_2{=}CHC_5H_4N)(PH_3)_2$ (**D′**). Figure 5 shows the relevant energy profiles calculated for the two reactions. Figure 6 gives the optimized structures with selected structural parameters for the species involved in these two reactions. It can be clearly seen from Figure 5 that the barrier difference between the two reactions is within 3.0 kcal/mol, supporting the mechanistic proposal shown in Scheme 4. The steric effect

(33) Yousufuddin, M.; Wen, T. B.; Mason, S. A.; McIntyre, G. J.; Jia, G.; Bau, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7227.

(34) Barrio, P.; Esteruelas, M. A.; Lledos, A.; Onate, E.; Tomas, J. *Organometallics* **2004**, *23*, 3008.

(35) Liu, S. H.; Lo, S. T.; Wen, T. B.; Williams, I. D.; Zhou, Z. Y.; Lau, C. P.; Jia, G. *Inorg. Chim. Acta* **2002**, *334*, 122.

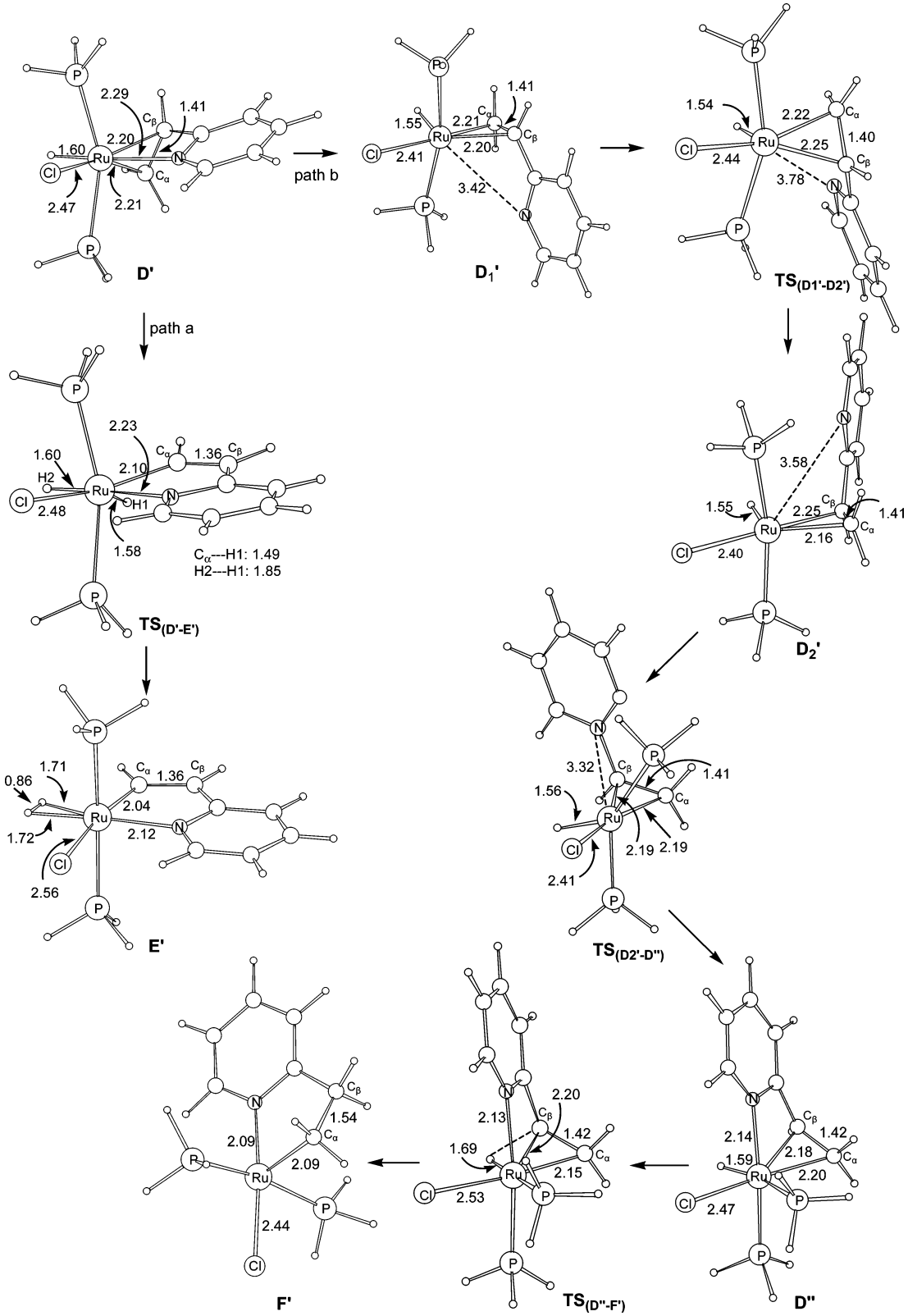


Figure 6. Selected structural parameters (Å) calculated for the species shown in paths a and b of Figure 5.

missed from the small model PH_3 calculations was studied with two-layer ONIOM calculations using the real PPh_3 ligand for several selected species (see those data in brackets in Figure 5 for the relative electronic energies derived from the ONIOM calculations and the Experimental Section for the computational details). The results show that the use of PPh_3 in the models does not significantly alter the reaction barriers. More discussion on the ONIOM results will be given below.

In Figure 5, path a gives the energy profile for the cyclometalation reaction. Interestingly, the cyclometalation reaction is a one-step process and the transition-state structure (**TS$_{(D'-E')}$**) corresponds to an oxidatively added species having a formal Ru(IV) metal center. In this transition-state structure, the Cα−H1 and H2−H1 distances are 1.49 and 1.85 Å, respectively (see Figure 6 for the atom-labeling scheme). Transition-state structures that correspond to a Ru(IV) oxidatively added species

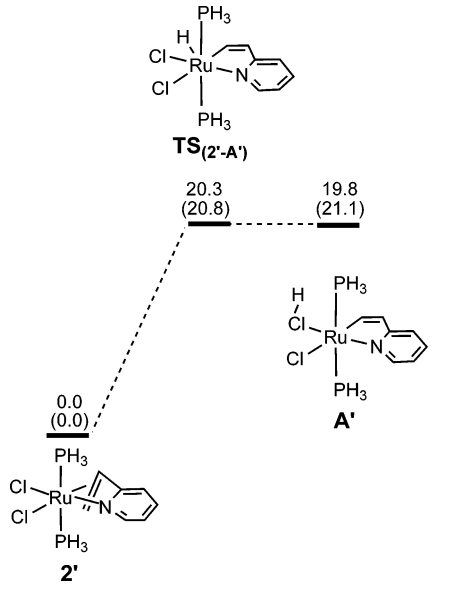
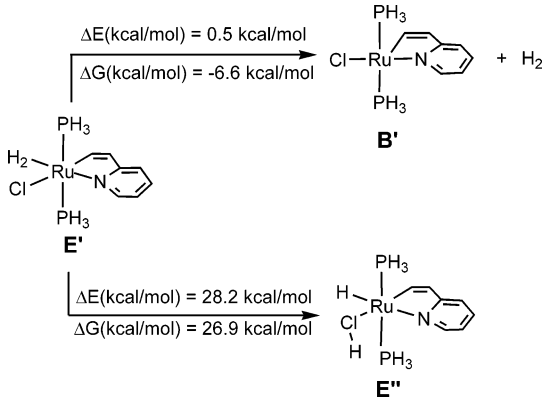


Figure 7. Energy profile calculated for the conversion of **2′** to **A′**. The calculated relative free energies and zero point energy corrected electronic energies (in parentheses) are given in kcal/mol.

Scheme 7



have been found in many other Ru systems.[36] Path b of Figure 5 gives the energy profile for the insertion reaction. Path b starts with a trans-to-cis isomerization from **D′** to **D″**. The cis isomer **D″** is slightly more stable than the trans isomer **D′** when the PH_3 models were considered. It becomes slightly less stable when the PPh_3 models were considered. From **D″**, olefin insertion into the Ru−H bond occurs to give **F′**. We were unable to locate a transition state directly linking **D′** and **F′**. The failure to locate a transition state directly linking **D′** and **F′** is understandable because the hydride ligand and the η^2-olefin ligand are approximately perpendicular to each other, not in an optimal (coplanar) arrangement for olefin insertion. In the cis isomer **D″**, the hydride ligand and the η^2-olefin ligand are approximately coplanar (Figure 6), facilitating the insertion process.

In the trans to cis isomerization (**D′** → **D″**) (Figure 5b), a ligand dissociation occurs to form the five-coordinate intermediate $\mathbf{D_1}'$ followed by a rotation of the vinylpyridine ligand to give $\mathbf{D_2}'$. The intermediates $\mathbf{D_1}'$ and $\mathbf{D_2}'$ are both only slightly less stable than **D′**. The high stability of the five-coordinate intermediates can be understood as follows. In **D′**, the vinylpyridine ligand is highly strained to secure that both the N atom and the vinyl group are coordinated to the metal center. The strained geometry of the vinylpyridine ligand can be clearly seen in the calculated structure of **D′** (Figure 6) and the X-ray structure of **2** (Figure 1). In $\mathbf{D_1}'$ and $\mathbf{D_2}'$, there is no strain in the ligand and the strength of the strong trans-influencing metal−hydride bond is enhanced. From $\mathbf{D_2}'$, a ligand recoordination occurs to give the cis isomer **D″**.

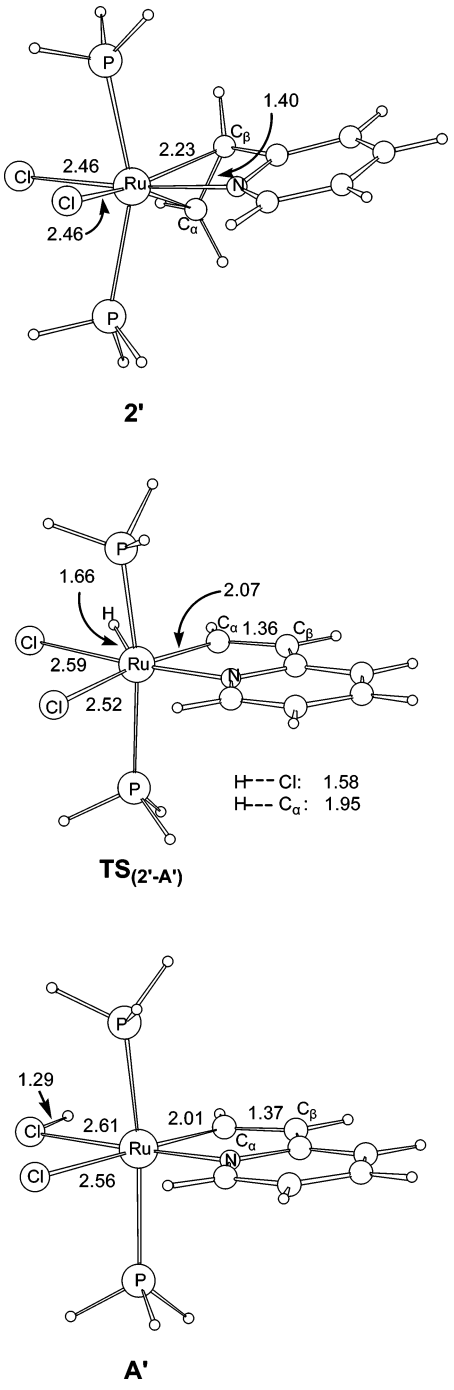


Figure 8. Selected structural parameters (Å) calculated for the species involved in the conversion of **2′** to **A′**.

It is of interest to make a few comments on the ONIOM results that consider the effect of PPh_3. Comparing the data in the parentheses with those in the brackets in Figure 5, we have the following findings. In the PPh_3 models, both the $\mathbf{TS_{(D'-E')}}$

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and $\mathbf{TS_{(D2'-D'')}}$ transition states are relatively stabilized with respect to the PH_3 models. **E′** is also stabilized, but to a less significant extent. Interestingly, **D″** is relatively destabilized. These results suggest that the steric effect from the PPh_3 ligands in both **D′** and **D″** is more significant than that in other species and that the steric effect in **D″** is the most significant. Explanations of these unexpected results can be given as follows. When both the N atom and the vinyl group are coordinated with the metal center, the strained geometry of the vinylpyridine ligands creates the most steric crowdedness in the coordination sphere of the ligands, leading to the observation that **D′** and **D″** experience the most steric crowdedness. In **D″**, the cis arrangement of the two phosphine ligands further increases the crowdedness in comparison with **D′**.

Scheme 2 shows that the vinylpyridine dichloro complex $RuCl_2(2\text{-}CH_2{=}CHC_5H_4N)(PPh_3)_2$ (**2**) can eliminate HCl in the presence of a base. **2** is an analogue of **D** but does not contain a hydride ligand. Therefore, we expect that the elimination of HCl from **2** should follow a pathway similar to the conversion of **D** to **E**, generating an intermediate having hydrochloride as a ligand. Figure 7 shows the energy profile calculated for the formation of the hydrochloride intermediate (**A′**) from the model complex $RuCl_2(CH_2{=}CHC_5H_4N)(PH_3)_2$ (**2′**). Figure 8 gives the optimized structures with selected structural parameters for the species involved. Indeed, we see that the formation of the intermediate (**A′**) having HCl as a ligand also corresponds to a one-step process with a reaction barrier of 20.3 kcal/mol and the transition-state structure ($\mathbf{TS_{(2'-A')}}$) is an oxidatively added species having a formal Ru(IV) metal center, similar to what we found for the conversion of **D** to **E** (Figure 5). The intermediate **A′**, which contains HCl as a ligand, is less stable than **2′** by ca. 19.8 kcal/mol. Therefore, the presence of a base is absolutely necessary to make the HCl elimination feasible. In comparison to the conversion of **D** to **E**, the formation of **A′** from **2′** has a much higher reaction barrier. The difference is understandable in view of the fact that hydrochloride complexes are rarely found while dihydrogen complexes are prevalent.[37]

It is also interesting to see that in the experiment **E**, which is a dihydrogen complex, is ready to dissociate the dihydrogen ligand to generate **B** (Scheme 4). However, elimination of HCl from **E** does not occur, even in the presence of a base. To understand the difference between the two processes, we calculated the reaction energies of the H_2 dissociation from **E′** and the metathetical conversion of **E′** to **E″**, a species containing HCl as a ligand (Scheme 7). From Scheme 7, we can conclude that H_2 can easily dissociate from **E′**, with a reaction free energy of −6.6 kcal/mol. In **E′**, the H_2 ligand is only weakly coordinated to the metal center. The 16e species **B′**, which is formed after the H_2 dissociation, is relatively stable, due to the presence of the π-donor chloride ligand. From Scheme 7, we can also conclude that the formation of **E″** is not possible. **E″** is less stable than **E′** by ca. 27 kcal/mol. It is therefore expected that, even in the presence of a base, it is not possible to eliminate HCl from **E′** because the relevant precursor complex **E″** is very unstable compared with **E′**.

Conclusion

We have found that cyclometalation of 2-vinylpyridine with $MCl_2(PPh_3)_3$ and $MHCl(PPh_3)_3$ (M = Ru, Os) can proceed at room temperature. In the presence of Cs_2CO_3, $RuCl_2(PPh_3)_3$ reacts with 2-vinylpyridine at room temperature to give the cyclometalated complex $RuCl(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(PPh_3)$, which is also produced from the reaction of $RuHCl(PPh_3)_3$ with 2-vinylpyridine. The reaction with $RuHCl(PPh_3)_3$ is kinetically more favorable than $RuCl_2(PPh_3)_3$. $OsCl_2(PPh_3)_3$ reacts with 2-vinylpyridine/Cs_2CO_3 at room temperature to give the analogous cyclometalated complex $OsCl(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(PPh_3)$. In the presence of $NaBF_4$, the reaction produces $[Os(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(PPh_3)_2]BF_4$. The dihydrogen complex $Os(H_2)Cl(CH{=}CHC_5H_4N)(PPh_3)_2$ is produced from the reaction of $OsHCl(PPh_3)_3$ with 2-vinylpyridine. All of the cyclometalation reactions proceed through initial oxidative addition of the cis C−H bond of vinylpyridine. In the case of $RuHCl(PPh_3)_3$, both cyclometalation and insertion reaction were found to have very similar reaction barriers.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, ether, THF), sodium (benzene), or calcium hydride (CH_2Cl_2). The starting materials $RuCl_2(PPh_3)_3$,[38] $OsCl_2(PPh_3)_3$,[39] $RuHCl(PPh_3)_3$,[40] and $OsH_3Cl(PPh_3)_3$ and $OsHCl(PPh_3)_3$[41] were prepared following the procedures described in the literature. All other reagents were used as purchased from Aldrich Chemical Co. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were collected on a JEOL EX-400 spectrometer (400 MHz) or a Bruker ARX-300 spectrometer (300 MHz). ^1H and ^{13}C NMR shifts are relative to TMS, and ^{31}P chemical shifts are relative to 85% H_3PO_4. MS spectra were recorded on a Finnigan TSQ7000 spectrometer.

$RuCl_2(CH_2{=}CHC_5H_4N)(PPh_3)_2$ (2). To a solution of $RuCl_2(PPh_3)_3$ (0.40 g, 0.42 mmol) in benzene was added 2-vinylpyridine (0.18 mL, 1.68 mmol). The reaction mixture was stirred at room temperature for 30 min to give a brownish yellow solution with a yellow precipitate. The volume of the mixture was reduced to half, and the solid was collected by filtration, washed with diethyl ether (10 mL), and dried under vacuum (0.19 g). The filtrate was concentrated to ca. 1 mL under reduced pressure, and diethyl ether (20 mL) was added to the residue with stirring to give additional yellow solid, which was collected by filtration, washed with diethyl ether (10 mL × 2), and dried under vacuum (84 mg). Total yield: 81%. Anal. Calcd for $C_{43}H_{37}Cl_2NRuP_2$: C, 64.42; H, 4.65; N, 1.75. Found: C, 64.65; H, 4.80; N, 1.63. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): AB pattern, δ 37.0 (d), 22.2 (d), J(PP) = 347.5 Hz). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 8.25 (br, 6 H, PPh_3), 7.23−7.36 (br m, 24 H, PPh_3), 6.74 (t, J(HH) = 7.4 Hz, 1 H, C*H*, py), 6.21 (d, J(HH) = 5.2 Hz, 1 H, C*H*, py), 5.94 (t, J(HH) = 6.4 Hz, 1 H, C*H*, py), 5.64 (d, J(HH) = 7.6 Hz, 1 H, C*H*, py), 4.59 (m, 1 H, C*H*=CH_2), 3.73 (m, 1 H, CH=CH_2), 3.47 (d, J(HH) = 7.3 Hz, 1 H, CH=CH_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ 163.87 (s, *C*(ipso-py)), 147.32 (s, CH, py), 134.82−127.96 (m, PPh_3), 133.58 (s, CH, py), 121.80 (s, CH, py), 119.39 (s, *CH*, py), 64.75 (s, *C*H=CH_2), 53.28 (s, CH=*C*H_2, obscured by the CD_2Cl_2 resonance and confirmed by $^1H-^{13}C$ COSY and DEPT-135).

$RuCl(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(PPh_3)$ (3A and 3B). To a suspension of $RuHCl(PPh_3)_3$ (0.45 g, 0.48 mmol) in benzene (20 mL) was added 2-vinylpyridine (0.31 mL, 2.87 mmol). The reaction mixture was stirred at room temperature for 3 h to give a clear yellow solution. The volume of the solution was concentrated to ca. 1 mL under reduced pressure. Hexane (30 mL) was added

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slowly with stirring to give a yellow solid, which was collected by filtration. The solid was then stirred in 20 mL of diethyl ether cooled with an ice bath for 10 min, collected on a filter frit, and dried under vacuum, to give a mixture of isomers **3A** and **3B** in about a 1:1 ratio. Yield: 0.21 g, 71%. Anal. Calcd for $C_{32}H_{28}ClN_2RuP$: C, 63.21; H, 4.64; N 4.61; Found: C, 63.22; H, 4.43; N, 4.71. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 48.48 (s), 47.68 (s) (in about 1:1 ratio). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 9.75 (d, J(HH) = 7.8 Hz, 1 H, Ru*CH*=CH of **3B**), 9.49 (br s, 2 H, $W_{1/2}$ = 13.2 Hz, py), 8.98 (dd, J(HH) = 7.6 Hz, J(PH) = 3.2 Hz, 1 H, Ru*CH*=CH of **3A**), 7.52−6.92 (m, 40 H, PPh_3, py), 6.86−6.76 (m, 4 H, py, RuCH=CH of **3** (the resonance of RuCH=*CH* of **3A** appears at ca. 6.77 and that of RuCH=*CH* of **3B** at ca. 6.82, as confirmed by $^1H-^1H$ COSY)), 6.67 (t, J(HH) = 6.3 Hz, 2 H, py), 4.60−4.53 (m, 2 H, a doublet at ca. 4.58 ppm (C*H*$_2$=CH of **3A**) partially overlapped with a triplet at ca. 4.55 ppm (CH_2=C*H* of **3B**), 4.12 (t, J(HH) = 9.3 Hz, 1 H, CH_2=C*H* of **3A**), 3.92 (dd, J(HH) = 8.1 Hz, J(PH) = 4.8 Hz, 1 H, C*H*$_2$=CH of **3A**), 3.77 (dd, J(HH) = 8.5 Hz, J(PH) = 5.3 Hz, 1 H, C*H*$_2$=CH of **3B**), 3.49 (d, J(HH) = 10.4 Hz, 1 H, C*H*$_2$=CH of **3B**). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ 204.17 (d, J(PC) = 10.9 Hz, Ru*C*H=CH of **3B**), 198.24 (d, J(PC) = 15.2 Hz, Ru*C*H=CH of **3A**), 167.02, 166.47, 166.40, 165.75 (s, 4 C(ipso-py)), 152.65, 151.97 (s, 2 CH, py), 146.46, 145.94 (s, 2 CH, py), 136.05 (s, *C*H, py), 135.73 (s, 2 *C*H, py), 135.32 (s, *C*H, py), 134.89−127.26 (m, PPh_3), 132.78, 129.58 (s, 2 *C*H, py), 122.53 (s, RuCH=*C*H of **3B**), 121.71 (s, RuCH=*C*H of **3A**), 120.64, 119.98, 119.66, 118.54, 117.23, 117.18 (s, 6 CH, py), 68.03 (s, CH_2=*C*H), 67.48 (s, CH_2=*C*H), 66.40 (s, *C*H$_2$=CH), 65.57 (s, *C*H$_2$=CH).

Observation of 6. A mixture of $OsCl_2(PPh_3)_3$ (0.798 g, 0.762 mmol), Cs_2CO_3 (0.620 g, 1.90 mmol), and 2-vinylpyridine (0.310 mL, 2.87 mmol) in DCM (50 mL) was stirred at room temperature. The reaction mixture turned from green to brick red. After 4 h, the $^{31}P\{^1H\}$ signal of **6** appeared as a singlet at −22.6 ppm, together with two doublet signals at −7.9 (d, J(PP) = 15.2 Hz) and −11.7 ppm (d, J(PP) = 15.2 Hz) and a singlet signal at −6.0 ppm for PPh_3 in the ^{31}P NMR spectrum. After 8 h, the doublet signals at −7.9 (d, J(PP) = 15.2 Hz) and −11.7 ppm (d, J(PP) = 15.2 Hz) disappeared and the singlet signal at −22.6 ppm for **6** remained. At this time, two singlet signals at 0.3 and −4.9 ppm also appeared. The reaction was stopped by the removal of inorganic salts by filtration and most of the solvent of DCM, at which point the $^{31}P\{^1H\}$ NMR spectrum showed five major peaks: a singlet signal at −22.6 ppm for **6**, a singlet signal at −6.0 ppm for PPh_3, two singlet signals at 0.3 and −4.9 ppm for **7**, and a singlet signal at 24.8 ppm for O=PPh_3. To the filtrate was added a small amount of diethyl ether to give a small amount of brown precipitate. The obtained precipitate was a 82/18 mixture of **6** and **7**. (The ratio varies depending on when the reaction was stopped. The product might be contaminated with other unknown byproducts, if the reaction was stopped too early.) Spectroscopic data for **6** are as follows. MS (FAB): m/z 855 (M^+). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ −22.6. ^1H NMR(300.13 MHz, $CDCl_3$): δ 11.36 (br d, J(HH) = 8.1 Hz, 1 H, OsC*H*=CH), 8.55 (d, J(HH) = 6.3 Hz, 1 H, py), 7.88−7.102 (m, PPh_3 and py), 6.84 (d, J(HH) = 7.8 Hz, 1 H, OsCH=C*H*), 6.12 (t, J(HH) = 6.9 Hz, 1 H, py).

$OsCl(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(PPh_3)$ (7A and 7B). A mixture of $OsCl_2(PPh_3)_3$ (0.798 g, 0.762 mmol), Cs_2CO_3 (0.620 g, 1.90 mmol), and 2-vinylpyridine (0.310 mL, 2.87 mmol) in DCM (50 mL) was stirred at room temperature. The color of the reaction mixture turned from green to brick red. After 24 h, the inorganic solid was removed by filtration and the volume of the mixture was concentrated to ca. 5 mL under vacuum. To the filtrate was added diethyl ether (30 mL) to give a brown precipitate. The brown precipitate was filtered off. Addition of hexane (30 mL) to the filtrate gave a brick red precipitate. The brick red precipitate was removed by filtration, and the filtrate was concentrated to ca. 5 mL to give a crystalline brick red precipitate. The crystalline brick red precipitate was collected, washed with hexane (15 mL) twice, and dried under vacuum. The NMR data shows that it is a mixture of **7A** and **7B** in a ratio of 37/63. Yield: 249 mg (47%). Anal. Calcd for $C_{32}H_{28}N_2ClPOs$: C, 55.13; H, 4.05; N, 4.02. Found: C, 55.97; H, 4.41; N, 3.67. As indicated by ^1H NMR, the sample contains a small amount of hexane. Anal. Calcd for $C_{32}H_{28}N_2ClPOs\cdot 0.25C_6H_{14}$: C, 56.35; H, 4.38; N, 3.87. MS (FAB): m/z 698 (M^+), 663([M − Cl]$^+$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 0.3 (s, **7B**), −4.9 (s, **7A**). ^1H NMR of **7** (300.13 MHz, C_6D_6; the number of protons is not specified, because **7A** and **7B** are not present in equimolar amounts): δ 10.51 (d, J(HH) = 8.7 Hz, OsC*H*=CH of **7B**), 10.08 (m, ortho CH of py of **7A** and **7B**), 9.90 (dd, J(HH) = 8.6 Hz, J(HP) = 1.5 Hz, OsC*H*=CH of **7A**), 7.61−7.60 (m, phenyl and py), 7.30 (d, J(HH) = 8.7 Hz, OsCH=C*H* of **7B**), 7.11−6.89 (m, phenyl and py, OsCH=C*H* of **7A**), 6.74−6.62 (m, py), 6.48 (d, J(HH) = 7.8 Hz, py), 6.33−6.22 (m, py), 5.96 (m, py), 4.62 (d, J(HH) = 8.1 Hz, C*H*$_2$=CH of **7A**), 4.42 (m, C*H*$_2$=CH of **7A** and **7B**), 3.98 (m, CH_2=C*H* of **7A** and **7B**) and 3.54 (d, J(HH) = 8.1 Hz, C*H*$_2$=CH of **7B**).

$[Os(CH{=}CHC_5H_4N)(CH_2{=}CHC_5H_4N)(PPh_3)_2]BF_4$ (8). A mixture of $OsCl_2(PPh_3)_3$ (0.585 g, 0.558 mmol), $NaBF_4$ (0.766 g, 6.98 mmol), Cs_2CO_3 (0.567 g, 1.74 mmol), and vinylpyridine (0.602 mL, 5.58 mmol) in DCM (30 mL) was stirred at room temperature. The reaction mixture turned from green to brick red. After 24 h, the inorganic solid was removed by filtration and the solvent was removed under vacuum. The residue was extracted with methanol (10 mL). The flask containing the methanol solution was stored in an ice bath. After 3 h, a yellow powder precipitated from the solution. The methanol was evaporated to half its original volume to give more yellow powder. The yellow powder was collected by filtration, washed with diethyl ether, and dried under vacuum. Yield, 0.26 g, 46%. Anal. Calcd for $C_{50}H_{43}BF_4N_2P_2Os$: C, 59.41; H, 4.29; N, 2.77. Found: C, 59.26; H, 4.66; N, 2.75. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 8.3 (d, J(PP) = 234.5 Hz), 0.6 (d, J(PP) = 234.6 Hz). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 9.85 (d, 1 H, J(HH) = 8.3 Hz, 1 H, OsC*H*=CH), 8.48 (d, 1 H, J(HH) = 5.5 Hz, 1 H, py), 8.07 (d, 1 H, J(HH) = 5.1 Hz, 1 H, py), 7.07−7.55 (m, 33 H, PPh_3, py), 6.82 (m, 2 H, OsCH=C*H*, and py), 6.31 (d, 1 H, J(HH) = 7.9 Hz, 1 H, py), 6.13 (d, 1 H, J(HH) = 7.8 Hz, 1 H, py), 3.87 − 3.97 (m, 2 H, C*H*$_2$=CH), 3.53−3.62 (m, 1 H, CH_2=C*H*). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ 169.9 (t, J(PC) = 10.0 Hz, Os*C*H=CH), 169.6 (s, C(ipso-py), 165.4, (s, C(ipso-py)), 150.4−119.9 (m, PPh_3, OsCH=*C*H, and other CH signals of py), 44.3 (d, J(PC) = 6.3 Hz, *C*H$_2$=CH), 43.3 (d, J(PC) = 4.3 Hz, CH_2=*C*H).

$OsCl(H_2)(CH{=}CHC_5H_4N)(PPh_3)_2$ (10). To a suspension of $OsH_3Cl(PPh_3)_3$ (0.60 g, 0.59 mmol) in benzene (10 mL) and CH_2Cl_2 (2 mL) was added 2-vinylpyridine (0.26 mL, 2.41 mmol) with stirring. The reaction mixture turned to an orange solution after ca. 2 min, which produced a yellow precipitate after stirring at room temperature for 2 h. The solution was then concentrated to ca. 5 mL, and the yellow solid was collected on a filter frit, washed with benzene (3 mL × 2), and dried under vacuum overnight (0.18 g). The orange filtrate and the washing solution were combined and concentrated to ca. 2 mL. Hexane (20 mL) was added to the residue slowly with stirring to give a pale yellow precipitate. The solid was collected by filtration, washed with diethyl ether (15 mL × 2), and dried under vacuum to give additional yellow product (0.14 g). Total yield: 0.32 g, 63%. The complex could also be obtained by reacting $OsHCl(PPh_3)_3$ with excess 2-vinylpyridine at room temperature in benzene. Anal. Calcd for $C_{43}H_{38}NClP_2Os$: C, 60.31; H, 4.47; N, 1.64. Found: C, 60.11; H, 4.66; N, 1.61. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 11.2 (s). ^1H NMR (300.13 MHz, CD_2Cl_2): δ 9.14 (dt, J(HH) = 8.9 Hz, J(PH) = 3.9 Hz, 1 H, Os*C*H=CH), 8.39 (d, J(HH) = 6.1 Hz, 1 H, py), 7.40−7.46 (m, 12 H, PPh_3), 7.14−7.24 (m, 18 H, PPh_3), 7.00 (t, J(HH) = 7.4 Hz, 1 H, py), 6.68 (d, J(HH) = 8.9 Hz, 1 H, OsCH=*CH*), 6.62 (d, J(HH) =

7.9 Hz, 1 H, py), 6.04 (t, J(HH) = 6.4 Hz, 1 H, py), −6.96 (td, J(PH) = 11.9 Hz, J(HH) = 3.9 Hz, 2 H, OsH_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ 174.06 (t, J(PC) = 8.2 Hz, Os*C*H═CH), 165.56 (s, C(ipso py)), 148.77 (s, CH, ortho py), 134.86 (s, CH, para py), 134.45 (t, J(PC) = 5.7 Hz) and 128.26 (t, J(PC) = 4.6 Hz, CH of ortho and meta PPh_3), 134.5 ppm (t, J(PC) = 23.8 Hz, the ipso carbon signal of the PPh_3), 129.77 (s, para PPh_3), 127.24 (s, OsCH═*CH*), 119.04 (s) and 116.83 (s, CH, meta-py). T_1 (ms, Os(H_2), 300.13 MHz, CD_2Cl_2): 90.1 (298 K), 61.2 (273 K), 52.8 (262 K), 47.2 (252 K), 43.3 (241 K), 41.2 (230 K), 49.9 (220 K).

Crystallographic Analysis of 2, 3A, 7B, and 8. All compounds are sufficiently air stable to be mounted on glass fibers with epoxy adhesive. The diffraction intensity data were collected with a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 100 K under a cold N_2 stream. Lattice determination and data collection were carried out using SMART v.5.625 software. Data reduction and absorption correction by empirical methods were performed using SAINT v 6.26 and SADABS v 2.03, respectively. Structure solution and refinement were performed using the SHELXTL v.6.10 software package. The structures were all solved by direct methods. All of the structures were refined smoothly, with the exception of **2**, which showed extensive phenyl ring disorder that was modeled with restraints. Otherwise, all non-hydrogen atoms were refined anisotropically by full-matrix least squares, with a riding model for the hydrogen atoms.

Computational Details. Full geometry optimizations of all the model complexes were done at the Becke3LYP (B3LYP) level of density functional theory (DFT).[42] Frequency calculations had also been performed at the same level of theory to identify all the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency) and to provide free energy at 298.15 K which includes entropic contributions by taking into account the vibrational, rotational, and translational motions of the species under consideration. Transition states were located using the Berny algorithm. Intrinsic reaction coordinates (IRC)[43] were calculated for the transition states to confirm that such structures are indeed connecting two relevant minima. The effective core potentials (ECPs) of Hay and Wadt with double-ζ valence basis sets (LanL2DZ)[44] were used to describe Ru, Cl, and P. Polarization functions were also added for Ru (ζ_f = 1.235), Cl (ζ_d = 0.640), and P (ζ_d = 0.387).[45] The 6-311G(d,p) Pople basis set was used for those C and H atoms that were directly bonded to the metal center.[46] The 6-31G basis set was used for all of the other atoms.[47] All of the calculations were performed with the Gaussian 03[48] software package.

In most of our DFT calculations, we used PH_3 as a model for PPh_3. To study the steric effect missed from the small-model calculations, we performed two-layer ONIOM (B3LYP/BSI:HF/Lanl2MB)[49] calculations with the real PPh_3 ligand for several selected species. In the ONIOM calculations, the phenyl groups on the phosphine ligand were treated as the second layer, while the rest were treated as the first layer. BSI represents the basis set described above.

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Supporting Information Available: CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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