

Displacement of Phenyl and Styryl Ligands by Benzophenone Imine and 2-Vinylpyridine on Ruthenium and Osmium

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The phenyl complexes $MPhCl(CO)(P^iPr_3)_2$ ($M = Ru$ (**3**), Os (**4**)) have been prepared by reaction of $MHCl(CO)(P^iPr_3)_2$ ($M = Ru$ (**1**), Os (**2**)) with $HgPh_2$. In solution the phenyl ligand of these compounds rotates around the $M-Ph$ bond. The activation parameters for the process are $\Delta H^\ddagger = 13.0 \pm 0.6 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = 1.5 \pm 1.3 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for **3** and $\Delta H^\ddagger = 11.7 \pm 0.5 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = -5.4 \pm 1.2 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for **4**. The addition of benzophenone imine to dichloromethane solutions of **3** and **4** and the related styryl complexes $M\{(E)\text{-CH=CHPh}\}Cl(CO)(P^iPr_3)_2$ ($M = Ru$ (**7**), Os (**8**)) leads to equilibrium mixtures between the starting compounds and the six-coordinate derivatives $MPhCl(NH=CPh_2)(CO)(P^iPr_3)_2$ ($M = Ru$ (**5**): $\Delta H^\circ = -8.6 \pm 0.4 \text{ kcal}\cdot\text{mol}^{-1}$, $\Delta S^\circ = -42.5 \pm 1.6 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; $M = Os$ (**6**): $\Delta H^\circ = -9.1 \pm 0.8 \text{ kcal}\cdot\text{mol}^{-1}$, $\Delta S^\circ = -31.0 \pm 2.6 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and $M\{(E)\text{-CH=CHPh}\}Cl(NH=CPh_2)(CO)(P^iPr_3)_2$ ($M = Ru$ (**9**): $\Delta H^\circ = -9.5 \pm 0.3 \text{ kcal}\cdot\text{mol}^{-1}$, $\Delta S^\circ = -39.4 \pm 1.1 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; $M = Os$ (**10**): $\Delta H^\circ = -8.8 \pm 0.8 \text{ kcal}\cdot\text{mol}^{-1}$, $\Delta S^\circ = -27.3 \pm 2.6 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). In toluene under reflux complexes **3**, **4**, **7**, and **8** react with benzophenone imine and 2-vinylpyridine to afford the metalated derivatives $M\{C_6H_4C(Ph)=NH\}Cl(CO)P^iPr_3)_2$ ($M = Ru$ (**11**), Os (**12**)) and $M(NC_5H_4\text{-}o\text{-CH=CH})Cl(CO)(P^iPr_3)_2$ ($M = Ru$ (**13**), Os (**14**)), releasing benzene and styrene. Complexes **9**, **12**, and **13** have been characterized by X-ray diffraction analysis. The structure of **9** shows a $Cl\cdots H-N$ hydrogen bond ($2.47 \text{ \AA}$) between the NH hydrogen atom of the imine and the chloride ligand.

Introduction

A ligand substitution reaction is that in which one Lewis base displaces another from a Lewis acid. The replacement of one two-electron donor ligand by another is a fundamental process in the chemistry of the transition metals. In comparison with these substitutions, the Lewis base displacement reactions between one-electron C-donor ligands (eq 1) remain an under-represented area within coordination chemistry.¹



These $M-C$ metathesis reactions do not involve a change in the oxidation state of the metal center and have been observed between alkyl complexes of early transition metals and alkanes.² Exchanges between alkyl groups and arene substrates by late metals have also been reported.³

The stability of a complex in which two or more donor atoms are part of the same ligand often appears much greater than if the same atoms were in separate ligands. Thus, complexes containing chelate rings are usually more stable than similar

compounds without rings. In accordance with this, among the various strategies to stabilize transition metal–carbon bonds, the chelation-assistance strategy is considered to be one of the most promising ways.⁴

As a part of our work on the ability of ruthenium and osmium hydride complexes to act as templates in carbon–carbon and carbon–heteroatom coupling reactions,⁵ we have been exploring

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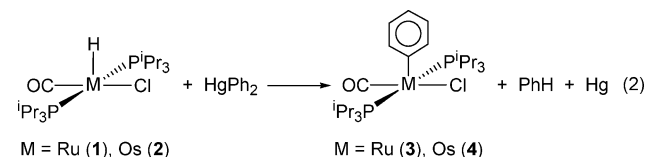
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the ability of benzophenone imine,⁶ aromatic and α,β -unsaturated aldehydes and ketones,^{6c,7} and $\text{CH}_2=\text{Epy}$ ($\text{E} = \text{CH}, \text{N}$) substrates^{7e,8} to afford cyclometalated derivatives, by means of $\text{C}(\text{sp}^2)\text{--H}$ bond activation reactions with osmium polyhydride compounds. We now show the ability of benzophenone imine and 2-vinylpyridine to exchange with phenyl and styryl groups coordinated to ruthenium and osmium.

This paper reports (i) the preparation and characterization of the phenyl complexes $\text{MPhCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$), including the determination of the rotational barrier for the phenyl group, (ii) the thermodynamic parameters of the coordination equilibria of benzophenone imine and 2-vinylpyridine to the unsaturated compounds $\text{MRCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$; $\text{R} = \text{Ph}, \text{CH}=\text{CHPh}$), and (iii) the $\text{M}\text{--}\text{C}$ bond metathesis reactions between the above-mentioned unsaturated compounds and the nitrogenated substrates.

Results and Discussion

1. Preparation and Characterization of $\text{MPhCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$). These compounds have been synthesized starting from the well-known complexes $\text{MHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ($\text{M} = \text{Ru}$ (**1**), Os (**2**)),⁹ by following Roper's protocol.¹⁰ Refluxing **1** and **2** with 1.5 equiv of HgPh_2 in toluene for 24 h gives $\text{MPhCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ($\text{M} = \text{Ru}$ (**3**), Os (**4**)), which are isolated as red solids in high yield (81% (**3**), 72% (**4**)) according to eq 2.



The spectroscopic data of **3** and **4** agree well with those previously reported for other ruthenium (II)- and osmium (II)-aryl derivatives.^{10,11} Furthermore, they are consistent with a structure like that of $\text{RuPhCl}(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$, which on the basis of an X-ray diffraction study has been described as a square-based pyramidal geometry, with the phenyl group *trans* disposed

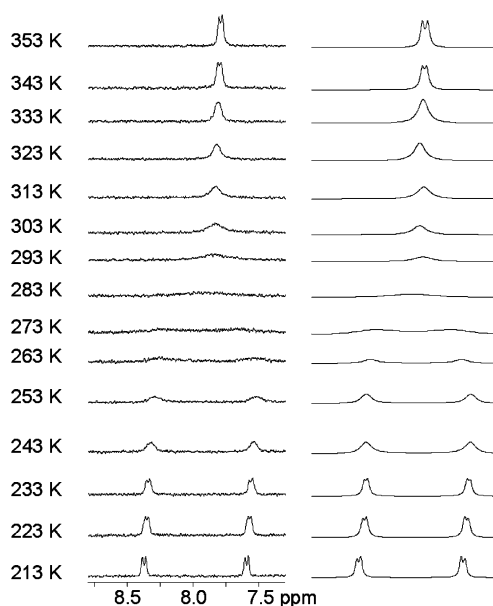


Figure 1. (Left) *ortho* phenyl resonances of $\text{RuPhCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (**3**) as a function of the temperature. (Right) Simulated spectra.

to the vacant site.¹² The ring plane is perpendicular to the $\text{P}\text{--}\text{M}\text{--}\text{P}$ direction. This disposition is strongly supported by the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. At 223 K in dichloromethane- d_2 , the ^1H NMR spectra contain five phenyl resonances between 8.5 and 6.5 ppm, whereas in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra six phenyl signals are observed between 160 and 115 ppm. In agreement with the mutually *trans* disposition of the phosphine ligands, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show singlets at 35.9 (**3**) and 21.3 (**4**) ppm.

In solution, the phenyl groups of both compounds rotate around the $\text{M}\text{--}\text{C}_{\text{ipso}}$ bond. At 313 K, the processes proceed at rates sufficient to lead to single *ortho* phenyl resonances in the ^1H NMR spectra (Figure 1 shows the *ortho* phenyl resonances of **3** as a function of the temperature). Lowering the sample temperature produces a broadening of the resonances. Between 283 and 273 K, decoalescence occurs, and at temperatures lower than 273 K two *ortho*-phenyl resonances are observed in the spectra of both compounds.

Line-shape analysis of the *ortho*-phenyl signals allows the calculation of the rate constants for the rotational processes at different temperatures. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^\ddagger = 13.0 \pm 0.6 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = 1.5 \pm 1.3 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for **3** and $\Delta H^\ddagger = 11.7 \pm 0.5 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = -5.4 \pm 1.2 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for **4**. The values of entropy of activation, close to zero, are in agreement with intramolecular processes, whereas the values for the enthalpy of activation are about twice the value obtained by DFT methods for the rotation of the phenyl group of the model compound $\text{OsHPh}(\text{CO})(\text{PH}_3)_2$ ($6.2 \text{ kcal}\cdot\text{mol}^{-1}$).¹³ The calculated barrier underestimates the real value, since the bulky phosphine ligands must certainly increase it.

2. Formation of Six-Coordinate $\text{MRCl}(\text{NH}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ($\text{R} = \text{Ph}, \text{CH}=\text{CHPh}$; $\text{M} = \text{Ru}, \text{Os}$) Complexes. The addition of benzophenone imine to dichloromethane solutions of **3** and **4** gives rise to equilibrium mixtures of these compounds and the six-coordinate derivatives $\text{MPhCl}(\text{NH}=\text{CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ($\text{M} = \text{Ru}$ (**5**), Os (**6**)), according to eq 3.

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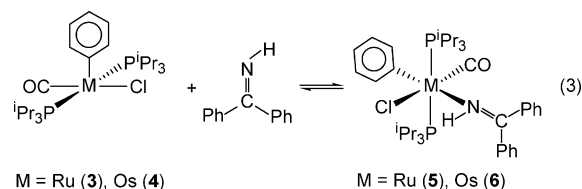
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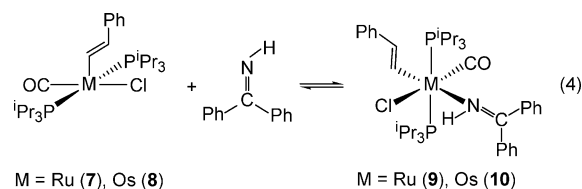
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Complexes **5** and **6** have been characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (see Experimental Section). In accordance with the formation of the new species, at 203 K in dichloromethane- d_2 , the ^1H NMR spectra of the equilibrium mixtures show NH resonances at 11.60 (**5**) and 11.84 (**6**) ppm, shifted about 2 ppm toward lower field with regard to the free ligand. Consistently, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra contain singlets at 19.5 (**5**) and -12.0 (**6**) ppm, which lie 16.4 (**5**) and 33.3 (**6**) ppm toward higher field with regard to **3** and **4**, respectively. Between 188 and 223 K, constants for the equilibria were determined by integration of the $^{31}\text{P}\{^1\text{H}\}$ resonances. Linear-square analyses of $\ln K$ versus $1/T$ provide values of $\Delta H^\circ = -8.6 \pm 0.4 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S^\circ = -42.5 \pm 1.6 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for **5** and $\Delta H^\circ = -9.1 \pm 0.8 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S^\circ = -31.0 \pm 2.6 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for **6**.

Similarly to **3** and **4**, the styryl complexes $\text{M}\{(\text{E})\text{-CH=CHPh}\}\text{Cl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ($\text{M} = \text{Ru}$ (**7**), Os (**8**)) coordinate benzo-phenone imine to afford equilibrium mixtures with the six-coordinate compounds $\text{M}\{(\text{E})\text{-CH=CHPh}\}\text{Cl}(\text{NH=CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ($\text{M} = \text{Ru}$ (**9**), Os (**10**)), according to eq 4.



Crystallization of the mixture of **7** and **9** in toluene at 193 K affords crystals of the latter suitable for an X-ray diffraction study. Figure 2 shows the structure of this complex, whereas selected bond distances and angles are listed in Table 1. The geometry around the metal can be rationalized as a distorted octahedron with the two phosphorus atoms of the phosphine ligands occupying opposite positions ($\text{P}(1)\text{--Ru--P}(2) = 175.34(3)^\circ$). The perpendicular plane is formed by the imine *trans* disposed to the styryl ligand ($\text{N--Ru--C}(1) = 167.23(10)^\circ$) and the chlorine *trans* disposed to the carbonyl group ($\text{Cl--Ru--C}(40) = 175.36(9)^\circ$).

The imine is bound to the ruthenium atom in a bent fashion, with a $\text{Ru--N--C}(9)$ angle of $149.2(2)^\circ$. The Ru--N bond length of $2.182(2) \text{ \AA}$ supports the single bond formulation.¹⁴ The $\text{N--C}(9)$ distance of $1.285(3) \text{ \AA}$ is similar to those observed in other imine transition metal complexes,¹⁵ azavinylidene compounds,¹⁶ organic azaallenium cations,¹⁷ and 2-azaallenyl complexes.¹⁸

At 100 K, the hydrogen atom bonded to the nitrogen of the imine ($\text{H}(01)$) was located in the difference Fourier maps and refined as an isotropic atom together with the rest of the non-

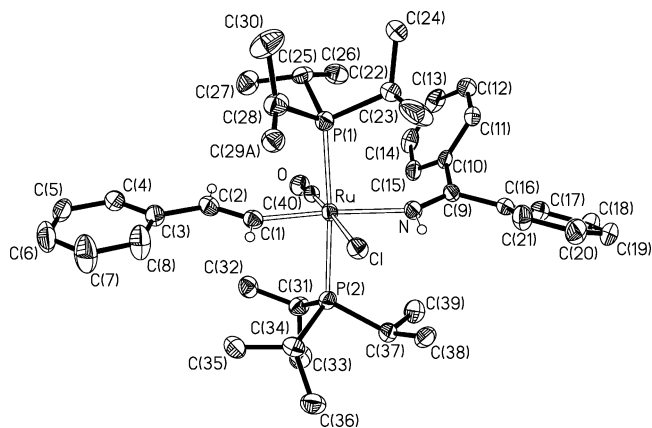


Figure 2. Molecular diagram of the complex $\text{Ru}\{(\text{E})\text{-CH=CHPh}\}\text{Cl}(\text{NH=CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (**9**).

Table 1. Selected Bond Lengths ($\text{\AA}$) and Angles ($^\circ$) for the Complex $\text{Ru}\{(\text{E})\text{-CH=CHPh}\}\text{Cl}(\text{NH=CPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (**9**)

$\text{Ru--P}(1)$	2.4422(8)	$\text{Ru--P}(2)$	2.4392(8)
Ru--Cl	2.5159(8)	Ru--N	2.182(2)
$\text{Ru--C}(1)$	2.050(3)	$\text{Ru--C}(40)$	1.804(3)
$\text{N--C}(9)$	1.285(3)	$\text{C}(1)\text{--C}(2)$	1.329(4)
$\text{N--H}(01)$	0.82(3)		
$\text{P}(1)\text{--Ru--P}(2)$	175.34(3)	Cl--Ru--N	78.69(6)
$\text{Cl--Ru--C}(1)$	88.56(8)	$\text{Cl--Ru--C}(40)$	175.36(9)
$\text{N--Ru--C}(1)$	167.23(10)	$\text{N--Ru--C}(40)$	101.40(11)
$\text{C}(1)\text{--Ru--C}(40)$	91.37(12)		

hydrogen atoms of the structure, giving a $\text{N--H}(01)$ distance of $0.82(3) \text{ \AA}$. Interestingly, the separation between $\text{H}(01)$ and the chlorine ligand ($2.47 \text{ \AA}$) is shorter than the sum of the van der Waals radii of hydrogen and chlorine ($r_{\text{vdw}}(\text{H}) = 1.20$, $r_{\text{vdw}}(\text{Cl}) = 1.80 \text{ \AA}$),¹⁹ suggesting that there is an intramolecular $\text{Cl}\cdots\text{H--N}$ hydrogen bond between these atoms. The hydrogen bond approaches the imine to the chlorine atom. Thus, as a result of this, the N--Ru--Cl angle ($78.69(6)^\circ$) largely deviates from the ideal value of 90° . Of great importance in biological and organic chemistry,²⁰ the hydrogen bonding is presently attracting considerable interest in the chemistry of transition metals.^{6c,15c,21}

The styryl ligand shows a *trans* disposition for the two substituents, C_6H_5 and $\text{RuCl}(\text{CO})(\text{NH=CPh}_2)(\text{P}^i\text{Pr}_3)_2$, at the C--C double bond. The $\text{Ru--C}(1)$ distance ($2.050(3) \text{ \AA}$) and

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the C(1)–C(2) bond length (1.329(4) Å) support the alkenyl formulation for the complex.²²

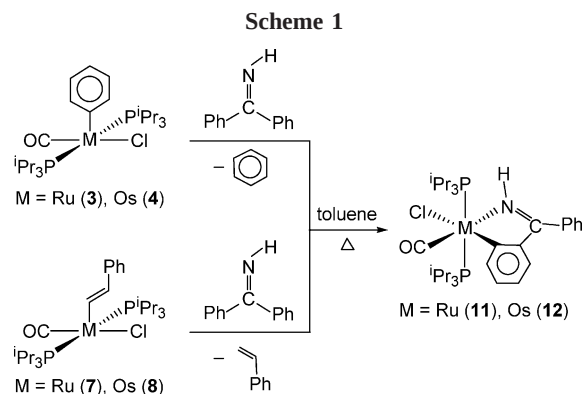
At 193 K in dichloromethane-*d*₂, the ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra of **9** and **10** are consistent with the structure shown in Figure 2. In agreement with the presence of the coordinated imine ligand and with the spectra of **5** and **6**, the ¹H NMR spectra contain broad singlets at 11.26 (**9**) and 11.46 (**10**) ppm. These chemical shifts compare well with that

of the complex OsH₂(SnPh₂Cl){C₆H₄C(Ph)=NH}(P^{*i*}Pr₃)₂ (δ 12.8)^{6c} and suggest that at 193 K the Cl⋯H–N interaction is retained in dichloromethane. The CH_α and CH_β resonances of the styryl ligand are observed at 9.01 (**9**) and 9.46 (**10**), and 6.36 (**9**) and 6.38 (**10**) ppm, respectively. In accordance with the *trans* disposition at the C–C double bond, the H–H coupling constants are 16.5 (**9**) and 13.8 (**10**) Hz. In the ¹³C{¹H} NMR spectra, the C_α and C_β resonances of the alkenyl ligand appear at 160.5 (**9**) and 143.1 (**10**), and 136.8 (**9**) and 135.2 (**10**) ppm, respectively. The ³¹P{¹H} NMR spectra show singlets at 21.1 (**9**) and –10.2 (**10**) ppm, shifted 16.6 and 35.5 ppm, respectively, toward higher field with regard to **7** (δ 37.7) and **8** (δ 33.5).²³

The thermodynamic parameters for the equilibria shown in eq 4 have also been determined in a manner similar to those for the equilibria shown in eq 3, by integration of the ³¹P{¹H} NMR resonances. The values obtained, Δ*H*° = –9.5 ± 0.3 kcal·mol^{–1} and Δ*S*° = –39.4 ± 1.1 cal·mol^{–1}·K^{–1} for **9** and Δ*H*° = –8.8 ± 0.8 kcal·mol^{–1} and Δ*S*° = –27.3 ± 2.6 cal·mol^{–1}·K^{–1} for **10**, agree well with those obtained for **5** and **6**.

According to the values of Δ*H*° and Δ*S*° calculated for the equilibria shown in eqs 3 and 4, the formation constant of the six-coordinate species at 20 °C increases in the sequence **5** (1.4 × 10^{–3}) < **9** (2.8 × 10^{–3}) < **6** (0.96) < **10** (3.8), i.e., Ru < Os and Ph < CH=CHPh. These results elegantly prove that the *trans* influence of phenyl is higher than that of styryl and that the coordination power of osmium(II) is stronger than that of ruthenium(II).

3. Phenyl– and Styryl–Phenyl Exchanges. In toluene under reflux, the equilibrium mixtures shown in eqs 3 and 4 evolve into the orthometalated complexes M{C₆H₄C(Ph)=NH}Cl(CO)–P^{*i*}Pr₃)₂ (M = Ru (**11**), Os (**12**)), releasing benzene and styrene,



respectively. Since at 111 °C, the toluene reflux temperature, the amounts of ruthenium in six-coordinate form are less than 0.06% and those of osmium are less than 9%, it appears to be reasonable to think that the formation of **11** and **12** takes place from the five-coordinate compounds **3**, **4**, **7**, and **8**, according to Scheme 1, without the participation of **5**, **6**, **9**, and **10**. In addition, it should be noted that, in contrast to **5**, **6**, **9**, and **10**, complexes **3**, **4**, **7**, and **8** are 16-electron valence species. This unsaturated character allows the *ortho*-CH bond oxidative addition of one of the phenyl groups of the imine. Thus, the subsequent reductive elimination of benzene or styrene, followed by the coordination of the iminic nitrogen atom to the metal center, could afford the products of these unusual *σ*-bond metathesis processes. The driving force for the substitutions is certainly the chelate nature of the resulting ligand from the displacements.

Complexes **11** and **12** are isolated as yellow (**11**) and pink (**12**) solids in high yields (80–85%) and were characterized by MS, elemental analysis, IR, and ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy. Complex **12** was further characterized by an X-ray crystallographic study. A view of the molecular geometry of this compound is shown in Figure 3. Selected bond distances and angles are listed in Table 2.

The coordination geometry around the osmium atom can be rationalized as derived from a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying *trans* positions (P(1)–Os–P(2) = 173.986(19)°). The perpendicular plane is formed by the atoms C(1) and N of the orthometalated benzophenone imine ligand, which acts with a bite angle of 76.73(8)°, the chlorine *trans* disposed to C(1) (Cl–

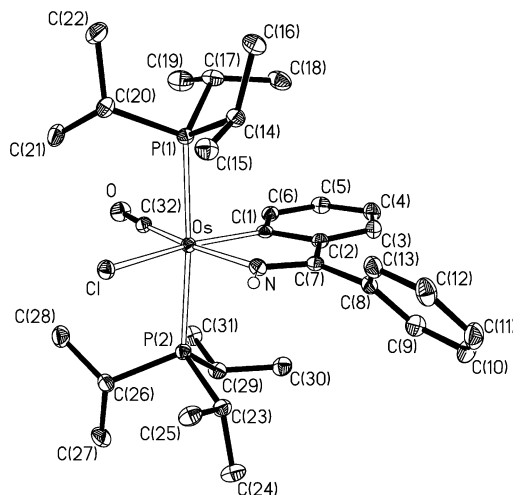


Figure 3. Molecular diagram of the complex Os{C₆H₄C(Ph)=NH}Cl(CO)(P^{*i*}Pr₃)₂ (**12**).

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $\text{Os}\{\text{C}_6\text{H}_4\text{C}(\text{Ph})=\text{NH}\}\text{Cl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (**12**)

Os–P(1)	2.4144(6)	Os–P(2)	2.4215(6)
Os–Cl	2.5143(6)	Os–N	2.1041(18)
Os–C(1)	2.038(2)	Os–C(32)	1.844(2)
N–C(7)	1.296(3)	N–H(01)	0.75(2)
P(1)–Os–P(2)	173.986(19)	Cl–Os–N	87.75(5)
Cl–Os–C(1)	164.47(6)	Cl–Os–C(32)	102.50(7)
N–Os–C(1)	76.73(8)	N–Os–C(32)	169.75(8)
C(1)–Os–C(32)	93.02(9)	Os–N–C(7)	119.18(15)

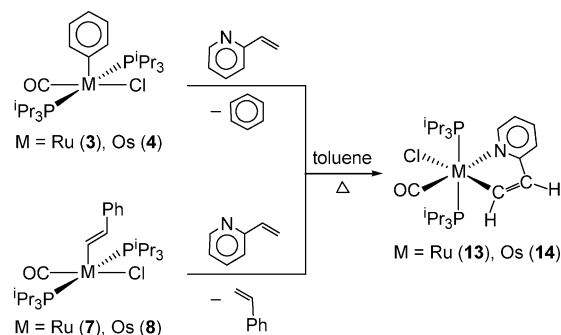
Os–C(1)) = 164.47(6)° and the carbonyl group *trans* located to the nitrogen atom (C(32)–Os–N = 169.75(8)°).

The five-membered ring formed by the metalated imine and the osmium atom is almost planar. The Os–N bond length of 2.1041(18) Å and the Os–C(1) distance of 2.038(2) Å are typical for Os–N and Os–C(aryl) single bonds, respectively, and are in agreement with the values previously found for

the complexes $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}_6\text{H}_4\text{C}(\text{Ph})=\text{NH}\}(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (2.078(18) and 2.080(19) Å, and 2.10(2) and 2.137(19) Å),²⁴ $\text{Os}\{\text{C}_6\text{H}_4\text{C}(\text{Ph})=\text{NH}\}\text{Cl}(\eta^2\text{-H}_2)(\text{P}^i\text{Pr}_3)_2$ (2.097(3) and 2.069(4) Å),^{6a} $\text{Os}\{\text{C}_6\text{H}_4\text{C}(\text{Ph})=\text{NH}\}(\text{C}_2\text{Ph})(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (2.106(7) and 2.089(7) Å),²⁵ $[\text{Os}\{\text{C}_6\text{H}_4\text{C}(\text{Ph})=\text{NH}\}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{P}^i\text{Pr}_3)]\text{-PF}_6$ (2.083(4) and 2.072(4) Å),²⁶ $\text{OsH}\{(\text{C}_6\text{H}_3\text{-}p\text{-Me})\text{C}(\text{p-tolyl})=\text{NN}=\text{C}(\text{p-tolyl})_2\}(\text{CO})_2(\text{PPh}_3)$ (2.119(5) and 2.100(7) Å),²⁷ *fac*- $\text{Os}\{\text{C},N\text{-3-Me}[2\text{-(MeC}_6\text{H}_4)\text{NCMe}_3]\text{C}_6\text{H}_3\}(2\text{-MeC}_6\text{H}_4\text{-}(\text{CN}^i\text{Bu})_3)$ (2.193(24) and 2.077(20) Å),²⁸ $\text{OsH}_2(\text{SnPh}_2\text{Cl})\text{-}\{\text{C}_6\text{H}_3\text{C}(\text{Ph})=\text{NH}\}(\text{P}^i\text{Pr}_3)_2$ (2.094(3) and 2.108(4) Å), and $\text{OsH}_2(\text{SnPh}_2\text{OH})\{\text{C}_6\text{H}_4\text{C}(\text{Ph})=\text{NH}\}(\text{P}^i\text{Pr}_3)_2$ (2.102(5) and 2.114(5) Å).^{6c} The N–C(7) distance of 1.296(3) Å is similar to that observed in **9** and agrees well with those found in other orthometalated imine complexes.²⁹

The ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **11** and **12** are consistent with the structure shown in Figure 3. In the ^1H NMR spectra, the most noticeable resonances are those corresponding to the NH protons, which, as a consequence of the absence of $\text{Cl}\cdots\text{H}-\text{N}$ hydrogen bonds, appear at 9.56 (**11**) and 9.40 (**12**) ppm, shifted about 2 ppm toward higher field with regard to **5**, **6**, **9**, and **10**. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the resonances due to the metalated carbon atom of the imine are observed at 191.9 (**11**) and 193.8 (**12**) ppm, as triplets with C–P coupling constants of 8.3 and 9.1 Hz, respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show singlets at 36.1 (**11**) and 3.0 (**12**) ppm.

4. Phenyl– and Styryl–Vinyl Exchanges. In contrast to benzophenone imine, the addition of 2-vinylpyridine to toluene- d_8 or dichloromethane- d_2 solutions of **3**, **4**, **7**, and **8** does not give rise to the formation of the corresponding six-coordinate

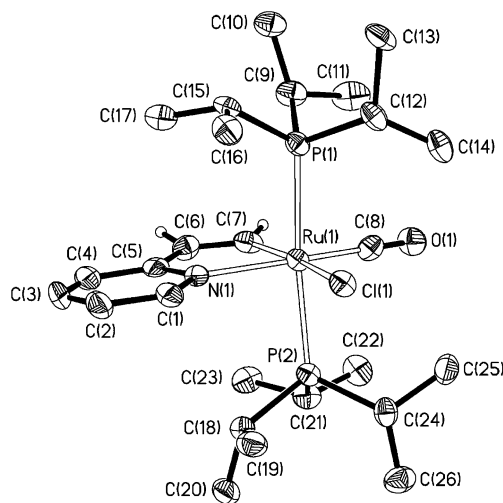
Scheme 2

derivatives. The larger steric requirement of 2-vinylpyridine with regard to benzophenone imine prevents the coordination of the nitrogen atom of the pyridine ring to the coordination vacancy of the five-coordinate compounds. However, in toluene under reflux these compounds react with 2-vinylpyridine to afford the

metalated complexes $\text{M}(\text{NC}_5\text{H}_4\text{-}o\text{-CH}=\text{CH})\text{Cl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ ($\text{M} = \text{Ru}$ (**13**), Os (**14**)) and benzene (**3** and **4**) or styrene (**7** and **8**), as result of phenyl– and styryl–vinyl metathesis reactions (Scheme 2). These processes can be rationalized in a manner similar to the previously mentioned phenyl- and styryl-phenyl exchanges; that is, the oxidative addition of one of the terminal $\text{C}(\text{sp}^2)\text{-H}$ bonds of the vinyl substituent of the pyridine to the ruthenium and osmium centers of **3**, **4**, **7**, and **8**, followed by the reductive elimination of benzene or styrene and the subsequent coordination of the pyridinic nitrogen atom to the metal centers, should give **13** and **14**.

These compounds are isolated as yellow (**13**) and orange (**14**) solids in high yields (70–76%) and were characterized by MS, elemental analysis, IR, and ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Complex **13** was further characterized by an X-ray crystallographic study. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. A drawing of one of them is shown in Figure 4. Selected bond distances and angles for both molecules are listed in Table 3.

The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying mutually *trans* positions (P(1)–Ru(1)–P(2) = 172.95(6)° molecule *a* and

**Figure 4.** Molecular diagram of the complex $\text{Ru}(\text{NC}_5\text{H}_4\text{-}o\text{-CH}=\text{CH})\text{Cl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (**13**).

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complex $\text{Ru}\{(E)\text{-Ru}(\text{NC}_5\text{H}_4\text{-o-CH=CH})\text{Cl}(\text{CO})(\text{P}^i\text{Pr}_3)_2\}$ (**13**)

molecule <i>a</i>		molecule <i>b</i>	
Ru(1)–P(1)	2.4214(18)	Ru(2)–P(3)	2.4183(19)
Ru(1)–P(2)	2.4315(17)	Ru(2)–P(4)	2.4232(18)
Ru(1)–Cl(1)	2.5090(16)	Ru(2)–Cl(2)	2.5122(17)
Ru(1)–N(1)	2.157(5)	Ru(2)–N(2)	2.172(6)
Ru(1)–C(7)	2.009(7)	Ru(2)–C(33)	2.003(7)
Ru(1)–C(8)	1.798(6)	Ru(2)–C(34)	1.827(7)
C(6)–C(7)	1.343(9)	C(32)–C(33)	1.347(10)
P(1)–Ru(1)–P(2)	172.95(6)	P(3)–Ru(2)–P(4)	175.27(7)
Cl(1)–Ru(1)–N(1)	90.89(14)	Cl(2)–Ru(2)–N(2)	89.99(15)
N(1)–Ru(1)–C(7)	76.9(3)	N(2)–Ru(2)–C(33)	78.1(3)
N(1)–Ru(1)–C(8)	166.8(3)	N(2)–Ru(2)–C(34)	169.0(3)
Cl(1)–Ru(1)–C(7)	167.5(2)	Cl(2)–Ru(2)–C(33)	168.1(2)
Cl(1)–Ru(1)–C(8)	102.0(2)	Cl(2)–Ru(2)–C(34)	101.0(3)
C(7)–Ru(1)–C(8)	90.4(3)	C(33)–Ru(2)–C(34)	91.0(3)
Ru(1)–C(7)–C(6)	118.2(6)	Ru(2)–C(33)–C(32)	116.8(5)
C(5)–C(6)–C(7)	116.8(7)	C(31)–C(32)–C(33)	118.3(7)

175.27(7)° molecule *b*). The ruthenium sphere is completed by the metalated group, which acts with bite angles of 76.9(3)° (*a*) and 78.1(3)° (*b*), the chlorine ligand *trans* disposed to C(7) (C(7)–Ru(1)–Cl(1) = 167.5(2)° (*a*) and 168.1(2)° (*b*)), and the carbonyl group *trans* disposed to N(1) (C(8)–Ru(1)–N(1) = 166.8(3)° (*a*) and 169.0(3)° (*b*)).

The Ru(1)–C(7) bond lengths of 2.009(7) Å (*a*) and 2.003(7) Å (*b*) are as expected for a Ru–C(sp²) single bond and similar to the ruthenium–styryl distance in **9**. The C(7)–C(6) bond lengths of 1.343(9) and 1.347(10) Å also agree with the related parameter in **9** and with the average carbon–carbon double bond distances in vinyl groups (1.35(2) Å).³⁰ In accordance with the sp² hybridization at C(6) and C(7), the angles C(5)–C(6)–C(7) and Ru(1)–C(7)–C(6) are 116.8(7)° (*a*) and 118.3(7)° (*b*), and 118.2(6)° (*a*) and 116.8(5)° (*b*), respectively.

The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra of **13** and **14** are consistent with the structure shown in Figure 4. In the ¹H NMR spectrum in benzene-*d*₆ the MCH resonances of the vinyl group appear at 9.81 (**13**) and 10.63 (**14**) ppm as doublets with H–H coupling constants of about 8 Hz, whereas the HC-py resonances are observed at 6.78 (**13**) and 7.01 (**14**) ppm. The ¹³C{¹H} NMR spectra agree well with those of other transition metal compounds containing a metalated 2-vinylpyridine ligand.³¹ In this context, it should be mentioned that the chemical shifts of the MC signals (δ, 200.4 (**13**) and 184.8 (**14**)) indicate a low contribution of the carbene resonance form at the metal–vinyl bonds.³² The ³¹P{¹H} NMR spectra show singlets at 32.3 (**13**) and 0.8 (**14**) ppm.

Concluding Remarks

In dichloromethane, the five-coordinate complexes MPhCl(CO)(PⁱPr₃)₂ and M{(E)-CH=CHPh}Cl(CO)(PⁱPr₃)₂ (M = Ru, Os) coordinate benzophenone imine to give equilibrium mixtures between the starting compounds and the six-coordinate derivatives MPhCl(NH=CPh₂)(CO)(PⁱPr₃)₂ and M{(E)-CH=CHPh}-

Cl(NH=CPh₂)(CO)(PⁱPr₃)₂, where the NH hydrogen atoms of the imines and the chlorine ligands are involved in Cl⋯H–N hydrogen bonds. The values of Δ*H*° and Δ*S*° for these equilibria prove that the *trans* influence of phenyl is higher than that of styryl and that the coordination power of osmium(II) is stronger than that of ruthenium(II).

In toluene under reflux, these five-coordinate complexes react with benzophenone imine and 2-vinylpyridine to afford the metalated derivatives M{C₆H₄C(Ph)=NH}Cl(CO)(PⁱPr₃)₂ and M(NC₅H₄-o-CH=CH)Cl(CO)(PⁱPr₃)₂ (M = Ru, Os), as a consequence of novel phenyl–phenyl, styryl–phenyl, phenyl–vinyl, and styryl–vinyl exchanges. Although the driving force for these displacements is undoubtedly the chelate character of the metalated nitrogen donor ligands, it should be mentioned that the thermodynamic parameters for the coordination equilibria of benzophenone imine to the five-coordinate starting compounds and the fact that the latter complexes do not coordinate 2-vinylpyridine suggest that six-coordinate species of the type MRCIL(CO)(PⁱPr₃)₂ (L = NH=CPh₂, NC₅H₄-o-CH=CH₂) are not involved in the ligand exchanges. It seems that the carbon–carbon replacements occur before the coordination of the nitrogen atoms.

In conclusion, using the chelation-assistance strategy, we have achieved novel C(sp²)/C(sp²) metathesis reactions on ruthenium and osmium.

Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. Complexes MHCl(CO)(PⁱPr₃)₂ (M = Ru (**1**), Os (**2**))^{3a} and M{(E)-CH=CHPh}Cl(CO)(PⁱPr₃)₂ (M = Ru (**8**), Os (**9**))²³ were prepared as previously described. Infrared spectra were recorded on a Perkin-Elmer Spectrum One spectrometer as solids (Nujol mull). ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on either a Varian Gemini 2000, a Bruker AXR 300, and a Bruker Avance 400 instrument. Chemical shifts are referenced to residual solvent peaks (¹H and ¹³C{¹H}) or external H₃PO₄ (³¹P{¹H}). Coupling constants *J* and *N* (*N* = *J*_{P–H} + *J*_{P'–H} for ¹H; *N* = *J*_{P–C} + *J*_{P'–C} for ¹³C{¹H}) are given in hertz. C, H, and N analyses were measured on a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of RuPhCl(CO)(PⁱPr₃)₂ (3**).** A solution of **1** (250 mg, 0.52 mmol) and HgPh₂ (277 mg, 0.78 mmol) in toluene (15 mL) was heated at reflux for 24 h. After this time it was filtered through Celite and evaporated to dryness. The addition of methanol caused the formation of a brick red solid, which was washed with methanol and dried in vacuo. Yield: 234 mg (81%). Anal. Calcd for C₂₅H₄₇ClP₂Ru: C, 53.42; H, 8.43. Found: C, 53.15; H, 8.69. IR (Nujol, cm^{−1}): ν(CO) 1906 (s). ¹H NMR (400 MHz, CD₂Cl₂, 223 K): δ 7.76 (d, *J*_{H–H} = 7.6, 1H, *o*-Ph), 7.07 (d, *J*_{H–H} = 7.6, 1H, *o*-Ph), 6.63–6.56 (m, 3H, Ph), 2.57 (m, 6H, PCH), 1.13 (dvt, *N* = 13.5, *J*_{H–H} = 7.2, 18H, PCH(CH₃)₂), 0.98 (dvt, *N* = 13.8, *J*_{H–H} = 7.2, 18H, PCH(CH₃)₂). ³¹P{¹H} NMR (121.42 MHz, CD₂Cl₂, 293 K): δ 35.9 (s). ¹³C{¹H} NMR (100.56 MHz, CD₂Cl₂, 223 K): δ 204.0 (t, *J*_{P–C} = 13.7, Ru–CO), 155.6 (t, *J*_{P–C} = 9.3, *C*_{ipso} Ph), 140.5, 135.8, 126.0, 124.5, 119.7 (all s, Ph), 23.4 (vt, *N* = 15.5, PCH), 19.1, 18.7 (both s, PCH(CH₃)₂). MS (FAB⁺): *m/z* 562 (M⁺), 527 (M⁺ – Cl).

Preparation of OsPhCl(CO)(PⁱPr₃)₂ (4**).** This complex was prepared as described for **3** starting from 200 mg (0.35 mmol) of **2** and HgPh₂ (185 mg, 0.52 mmol). Yield (garnet solid): 163 mg (72%). Anal. Calcd for C₂₅H₄₇ClP₂Os: C, 46.10; H, 2.27. Found: C, 46.24; H, 7.39. IR (Nujol, cm^{−1}): ν(CO) 1894 (s). ¹H NMR (400 MHz, CD₂Cl₂, 223 K): δ 7.40 (d, *J*_{H–H} = 8.0, 1H, *o*-Ph),

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6.91 (d, $J_{\text{H-H}} = 8.0$, 1H, *o*-Ph), 6.63–6.56 (m, 3H, Ph), 2.75 (m, 6H, PCH), 1.18 (dvt, $N = 12.9$, $J_{\text{H-H}} = 6.9$, 18H, $\text{PCH}(\text{CH}_3)_2$), 1.02 (dvt, $N = 12.9$, $J_{\text{H-H}} = 6.6$, 18H, $\text{PCH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, CD_2Cl_2 , 293 K): δ 20.4 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.56 MHz, CD_2Cl_2 , 223 K): δ 183.0 (t, $J_{\text{P-C}} = 8.7$, Os–CO), 141.1, 135.4 (both s, Ph), 126.4 (t, $J_{\text{P-C}} = 5.5$, C_{ipso} Ph), 125.8, 124.3, 119.8 (all s, Ph), 24.0 (vt, $N = 24$, PCH), 19.4, 18.9 (both s, $\text{PCH}(\text{CH}_3)_2$). MS (FAB^+): m/z 652 (M^+).

Spectroscopic Characterization of $\text{RuPhCl}(\text{CO})(\text{NH}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)_2$ (5). In a 5 mm NMR tube **3** (20 mg, 0.036 mmol) and benzophenone imine (6 μL , 0.036 mmol) were dissolved in 0.4 mL of dichloromethane- d_2 , and the sample was cooled at -70°C , changing the color of the solution from brick-red to orange. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded at this temperature showed a mixture of **3** and **5** in a ratio of 1:1.8. NMR data of $\text{RuPhCl}(\text{CO})(\text{NH}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)_2$ (**5**): ^1H NMR (400 MHz, CD_2Cl_2 , 203 K): δ 11.60 (br, 1H, NH), 7.66 (d, $J_{\text{H-H}} = 7.2$, 1H, *o*-Ph), 7.58–6.75 (m, 14H, Ph), 2.27 (br, 6H, PCH), 1.30 (br, 18H, $\text{PCH}(\text{CH}_3)_2$), 0.80 (br, 18H, $\text{PCH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CD_2Cl_2 , 203 K): δ 19.5 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.56 MHz, CD_2Cl_2 , 203 K plus apt): δ 206.2 (t, $J_{\text{P-C}} = 13.0$, Ru–CO), 177.2 (s, $\text{N}=\text{C}$), 158.7 (t, $J_{\text{P-C}} = 10.0$, C_{ipso} Ph), 144.9, 142.1 (both s, Ru–Ph), 139.2 and 137.3 (both s, C_{ipso} imine), 128.8, 128.0, 129.7, 127.7, 127.4, 126.6 (all s, Ph imine), 125.2, 123.6 (both s, Ru–Ph), 24.8 (br, PCH), 19.8, 20.4 (both s, $\text{PCH}(\text{CH}_3)_2$).

Spectroscopic Characterization of $\text{OsPhCl}(\text{CO})(\text{NH}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)_2$ (6). In a 5 mm NMR tube **4** (20 mg, 0.031 mmol) and benzophenone imine (5.1 μL , 0.036 mmol) were dissolved in 0.4 mL of dichloromethane- d_2 , and the sample was cooled at -50°C , changing the color of the solution from garnet to dark orange. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded at this temperature showed the formation of the title compound. NMR data of $\text{OsPhCl}(\text{CO})(\text{NH}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)_2$ (**6**): ^1H NMR (300 MHz, CD_2Cl_2 , 223 K): δ 11.84 (br, 1H, NH), 8.44 (d, $J_{\text{H-H}} = 7.7$, 1H, *o*-Ph, Os–Ph), 7.80 (d, $J_{\text{H-H}} = 7.7$, 1H, *o*-Ph, Os–Ph), 7.73–6.64 (m, 13H, Ph), 2.43 (br, 6H, PCH), 1.27–0.60 (m, 36H, $\text{PCH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CD_2Cl_2 , 223 K): δ –12.0 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CD_2Cl_2 , 223 K plus apt): δ 182.5 (t, $J_{\text{P-C}} = 9.0$, Os–CO), 175.1 (s, $\text{N}=\text{C}$), 158.7 (t, $J_{\text{P-C}} = 10.0$, C_{ipso} Ph), 145.3, 141.9 (both s, *Ortho* Os–Ph), 139.3 (s, C_{ipso} imine), 136.1 (t, $J_{\text{P-C}} = 7.9$, C_{ipso} , Os–Ph), 130.5, 128.7, 128.3, 128.2, 127.9, 127.7 (all s, Ph), 125.6, 124.5, 119.6 (s, Os–Ph), 25.2 (br, PCH), 20.5, 20.3 (both s, $\text{PCH}(\text{CH}_3)_2$).

Preparation of $\text{Ru}\{(\text{E})\text{-CH}=\text{CHPh}\}\text{Cl}(\text{CO})(\text{NH}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)_2$ (9). A deep red solution of **7** (30 mg, 0.051 mmol), in 5 mL of CH_2Cl_2 at -80°C , was treated with benzophenone imine (8.6 μL , 0.051 mmol) and was kept for 0.5 h at this temperature. The solvent of the resulting solution was removed under reduced pressure, until the formation of orange crystals. The remaining solution was decanted, and the crystals were dried in a vacuum. Yield: 23 mg (59%). Anal. Calcd for $\text{C}_{40}\text{H}_{60}\text{NClORuP}_2$: C, 62.44; H, 7.86; N, 1.82. Found: C, 62.41; H, 7.72; N, 1.78. IR (Nujol, cm^{-1}): $\nu(\text{N-H})$ 3229 (m), $\nu(\text{C}=\text{O})$ 1904 (s). ^1H NMR (300 MHz, CD_2Cl_2 , 193 K): δ 11.26 (br, 1H, NH), 9.01 (d, 1H, $J_{\text{H-H}} = 16.5$, $\text{RuCH}=\text{}$), 7.64–6.86 (m, 15H, Ph), 6.36 (d, 1H, $J_{\text{H-H}} = 16.5$, CHPh), 2.42 (m, 6H, PCH), 1.01 (br, 36H, $\text{PCH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CD_2Cl_2 , 193 K): δ 21.1 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CD_2Cl_2 , 193 K): δ 206.4 (t, $J_{\text{C-P}} = 12.5$, CO), 178.2 (s, $\text{N}=\text{C}$), 160.5 (s, $\text{RuC}=\text{}$), 140.7, 139.1, and 136.4 (all s, C_{ipso} Ph); 136.8 (s, $=\text{CH}$); 131.3, 130.9, 130.7, 129.2, 128.6, 128.5, 128.1, 127.3, 123.7, and 123.4 (all s, Ph), 24.9 (br m, PCH), 20.3 and 20.1 (both br s, PCHCH_3).

Preparation of $\text{Os}\{(\text{E})\text{-CH}=\text{CHPh}\}\text{Cl}(\text{CO})(\text{NH}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)_2$ (10). This complex was prepared as described for **9** starting from 30 mg (0.044 mmol) of **9** and benzophenone imine (7.4 μL , 0.044 mmol). Yield (orange crystals): 23 mg (61%). Anal. Calcd for $\text{C}_{40}\text{H}_{60}\text{NClOOSp}_2$: C, 55.96; H, 7.04; N, 1.63. Found: C, 55.72;

H, 6.90; N, 1.59. IR (Nujol, cm^{-1}): $\nu(\text{N-H})$ 3206 (m), $\nu(\text{C}=\text{O})$ 1886 (s). ^1H NMR (300 MHz, CD_2Cl_2 , 193 K): δ 11.46 (br, 1H, NH), 9.46 (d, 1H, $J_{\text{H-H}} = 13.8$, $\text{OsCH}=\text{}$), 7.63–6.36 (m, 15H, Ph), 6.38 (d, 1H, $J_{\text{H-H}} = 13.8$, CHPh), 2.51 (br, 6H, PCH), 1.24 (br, 36H, $\text{PCH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CD_2Cl_2 , 193 K): δ –10.2 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CD_2Cl_2 , 193 K): δ 182.2 (br, CO), 174.7 (s, $\text{N}=\text{C}$), 143.1 (br, $\text{OsC}=\text{}$), 141.6, 139.0, and 135.5 (all s, C_{ipso} Ph), 135.2 (s, $=\text{CH}$), 130.2, 129.9, 128.5, 127.9, 127.6, 127.3, 122.9, and 122.4 (all s, Ph), 24.9 (br m, PCH), 19.5 and 19.2 (both br s, PCHCH_3).

Preparation of $\text{Ru}\{\text{C}_6\text{H}_4\text{C}(\text{Ph})=\text{NH}\}\text{Cl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (11). This complex can be prepared either starting from **3** (100 mg, 0.18 mmol) and benzophenone imine (30.2 μL , 0.18 mmol) or from **7** (291 mg, 0.495 mmol) and benzophenone imine (83.0 μL , 0.495 mmol) in toluene (15 mL). In both cases, the mixtures were heated under reflux conditions for 24 h. The resulting reddish-orange solutions were filtered and then concentrated almost to dryness. The addition of pentane caused the formation of a yellow solid. The solutions were decanted, and the solid was washed with pentane (2×3 mL). Yield: starting from **3**, 98 mg (82%); starting from **7**, 280 mg (85%). Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{ClONP}_2\text{Ru}$: C, 57.78; H, 7.88; N, 2.11. Found: C, 58.17; H, 8.20; N, 2.30. IR (Nujol, cm^{-1}): $\nu(\text{N-H})$ 3325 (m), $\nu(\text{C}=\text{O})$ 1910 (s). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 9.56 (br, 1H, NH), 8.57 (d, $J_{\text{H-H}} = 7.8$, 1H, Ph), 7.43–7.11 (m, 6H, Ph), 6.92 (t, $J_{\text{H-H}} = 7.8$, 1H, Ph), 6.73 (t, $J_{\text{H-H}} = 7.3$, 1H, Ph), 2.32 (m, 6H, PCH), 1.49 (dvt, $N = 14.1$, $J_{\text{H-H}} = 7.2$, 18H, PCHCH_3), 0.78 (dvt, $N = 12.0$, $J_{\text{H-H}} = 6.9$, 18H, PCHCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 36.1 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, C_6D_6 , 293 K): δ 211.7 (t, $J_{\text{C-P}} = 14.4$, CO), 191.9 (t, $J_{\text{C-P}} = 8.3$, Ru–C), 181.9 (t, $J_{\text{C-P}} = 3.5$, $\text{N}=\text{C}$), 145.0, 144.3, 144.2, 138.9, 138.7, 138.3, 132.5, 132.2, 130.6, 129.7, 129.2, 126.1, and 120.3 (all s, Ph and C_6H_4); 24.2 (vt, $N = 19.2$, PCH); 20.8 and 18.9 (both s, PCHCH_3). MS (FAB^+): m/z 665 (M^+).

Preparation of $\text{Os}\{\text{C}_6\text{H}_4\text{C}(\text{Ph})=\text{NH}\}\text{Cl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (12). This complex was prepared as described for **11** starting either from **4** (100 mg, 0.153 mmol) and benzophenone imine (26 μL , 0.153 mmol) or from **8** (100 mg, 0.147 mmol) and benzophenone imine (25 μL , 0.147 mmol). Yield (pink solid): starting from **4**, 98 mg (85%); starting from **8**, 89 mg (80%). Anal. Calcd for $\text{C}_{32}\text{H}_{52}\text{ClONOsP}_2$: C, 50.95; H, 6.95; N, 1.86. Found: C, 50.53; H, 7.07; N, 1.62. IR (Nujol, cm^{-1}): $\nu(\text{N-H})$ 3327 (m), $\nu(\text{C}=\text{O})$ 1893 (s). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 9.40 (br, 1H, NH), 8.61–6.69 (m, 9H, Ph), 2.41 (m, 6H, PCH), 1.45 (dvt, $N = 13.9$, $J_{\text{H-H}} = 7.1$, 18H, PCHCH_3), 0.81 (dvt, $N = 12.1$, $J_{\text{H-H}} = 6.7$, 18H, PCHCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 3.0 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, C_6D_6 , 293 K): δ 193.8 (t, $J_{\text{C-P}} = 9.1$, Os–C), 183.4 (t, $J_{\text{C-P}} = 13.1$, CO), 174.5 (s, $\text{N}=\text{C}$), 143.1, 138.2, 132.2, 130.3, 130.2, 129.2, 127.1, 126.8, 118.8 (all s, Ph and C_6H_4), 24.0 (vt, $N = 23.5$, PCH); 20.6 and 18.8 (both s, PCHCH_3). MS (FAB^+): m/z 755 ($\text{M}^+ + \text{H}$).

Preparation of $\text{Ru}(\text{NC}_5\text{H}_4\text{-o-CH}=\text{CH})\text{Cl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (13). This complex can be prepared either starting from **3** (100 mg, 0.18 mmol) and 2-vinylpyridine (29 μL , 0.27 mmol) or from **7** (100 mg, 0.150 mmol) and 2-vinylpyridine (24 μL , 0.23 mmol) in toluene (15 mL). In both cases, the mixtures were heated under reflux conditions for 24 h. The resulting orange solution was filtered through Celite and concentrated to dryness, getting an orange residue. The addition of pentane (25 mL) led to an orange solution, which was filtered and concentrated to ca. 5 mL. Cooling of this solution overnight afforded yellow crystals. The pentane was decanted and the crystals were washed with pentane. Yield: starting from **3**, 77 mg (73%); starting from **7**, 76 mg (75%). Anal. Calcd for $\text{C}_{26}\text{H}_{48}\text{ClNOP}_2\text{Ru}$: C, 53.00; H, 8.21; N, 2.38. Found: C, 53.02; H, 8.16; N, 2.15. IR (Nujol, cm^{-1}): $\nu(\text{C}=\text{O})$ 1923 (s), $\nu(\text{C}=\text{C})$ 1600 (m). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 9.90 (ddd, $J_{\text{H-H}} = 6.0$, $J_{\text{H-H}} = 1.5$, $J_{\text{H-H}} = 0.6$, 1H, py), 9.81 (d, $J_{\text{H-H}} = 8.0$, 1H,

Table 4. Crystal Data and Data Collection and Refinement for **9**, **12**, and **13**

	9	12	13
Crystal Data			
formula	C ₄₀ H ₆₀ ClNOP ₂ Ru	C ₃₂ H ₅₂ ClNOOsP ₂	C ₂₆ H ₄₈ ClNOP ₂ Ru·1/2C ₁₆ H ₁₄ ·1/4C ₅ H ₁₂
molecular wt	769.35	754.34	710.29
color and habit	orange, irregular block	red, irregular block	yellow, prism
size, mm	0.14, 0.10, 0.06	0.30, 0.18, 0.12	0.46, 0.10, 0.10
symmetry, space group	monoclinic, <i>P</i> 2(1)/ <i>c</i>	monoclinic, <i>P</i> 2(1)/ <i>n</i>	monoclinic, <i>P</i> 2(1)
<i>a</i> , Å	11.2101(16)	9.9565(19)	19.639(4)
<i>b</i> , Å	11.3142(16)	18.275(3)	9.7366(17)
<i>c</i> , Å	30.803(4)	17.730(3)	20.438(4)
β , deg	93.101(3)	96.908(3)	110.208(3)
<i>V</i> , Å ³	3901.2(10)	3202.7(10)	3667.6(11)
<i>Z</i>	4	4	4
<i>D</i> _{calc} , g cm ⁻³	1.310	1.564	1.286
Data Collection and Refinement			
diffractometer		Broker Smart APEX	
λ (Mo K α), Å		0.71073	
monochromator		graphite oriented	
scan type		ω scans	
μ , mm ⁻¹	0.583	4.190	0.614
2 θ , range, deg	3, 57	3, 57	3, 57
temp, K	100.0(2)	100.0(2)	100.0(2)
no. of data collected	46 533	37 259	45 835
no. of unique data	9371 (<i>R</i> _{int} = 0.0612)	7680 (<i>R</i> _{int} = 0.0290)	17 649 (<i>R</i> _{int} = 0.0541)
no. of params/restraints	436/2	358/0	663/12
Flack parameter			0.36(4)
<i>R</i> ₁ ^a [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0369	0.0188	0.0579
<i>wR</i> ₂ ^b [all data]	0.0710	0.0399	0.1368
<i>S</i> ^c [all data]	0.898	0.991	0.995

^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 $\text{Goof} = S = \{\sum [F_o^2 - F_c^2] / (n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

Ru-CH), 6.97 (ddd, *J*_{H-H} = 7.6, *J*_{H-H} = 7.2, *J*_{H-H} = 1.5, 1H, py), 6.78 (dt, *J*_{H-H} = 8.1, *J*_{p-H} = 1.3, 1H, Ru-CH=CH), 6.76 (dd, *J*_{H-H} = 7.2, *J*_{H-H} = 0.6, 1H, py), 6.40 (ddd, *J*_{H-H} = 7.2, *J*_{H-H} = 6.0, *J*_{H-H} = 1.5, 1H, py), 2.22 (m, 6H, PCH), 1.23 (dvt, *J*_{H-H} = 7.2, *N* = 13.5, 18H, PCH(CH₃)₂), 1.01 (dvt, *J*_{H-H} = 6.9, *N* = 12.0, 18H, PCH(CH₃)₂). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 293 K): δ 32.3 (s). ¹³C{¹H} NMR (75.4 MHz, C₆D₆, 293 K): δ 209.0 (t, *J*_{C-P} = 15.5, CO), 200.4 (t, *J*_{C-P} = 9.1, Ru-CH), 166.5 (s, N=C-CH=CHRu), 152.8 (s, py), 135.8 (s, py), 128.7 (s, CH=CH), 119.2, 115.4 (both s, py), 24.8 (vt, *N* = 18, PCH), 20.5 and 19.7 (both s, PCH(CH₃)₂). MS (FAB⁺): *m/z* 589 (M⁺), 554 (M⁺ - Cl).

Preparation of Os(NC₅H₄-o-CH=CH)Cl(CO)(PⁱPr)₂ (**14**).

This complex was prepared as described for **13** starting either from **4** (100 mg, 0.153 mmol) and 2-vinylpyridine (25 μ L, 0.23 mmol) or from **8** (100 mg, 0.147 mmol) and 2-vinylpyridine (24 μ L, 0.22 mmol). Yield (orange solid): starting from **4**, 75 mg (72%); starting from **8**, 70 mg (70%). Anal. Calcd for C₂₆H₄₈ClNOOsP₂: C, 46.04; H, 7.16; N, 2.06. Found: C, 46.15; H, 6.95; N, 1.94. IR (Nujol, cm⁻¹): ν (C=O) 1910 (s), ν (C=C) 1603 (m). ¹H NMR (300 MHz, C₆D₆, 293 K): δ 10.63 (d, *J*_{H-H} = 8.2, 1H, Os-CH), 9.83 (br d, *J*_{H-H} = 5.1, 1H, py), 7.01 (d, *J*_{H-H} = 8.2, 1H, Os-CH=CH), 6.89 (ddd, *J*_{H-H} = 7.5, *J*_{H-H} = 0.9, 1H, py), 6.78 (ddd, *J*_{H-H} = 7.5, *J*_{H-H} = 1.2, *J*_{H-H} = 1.2, 1H, py), 6.34 (ddd, *J*_{H-H} = 7.5, *J*_{H-H} = 5.1, *J*_{H-H} = 1.2, 1H, py), 2.33 (m, 6H, PCH), 1.21 (dvt, *J*_{H-H} = 7.2, *N* = 13.5, 18H, PCH(CH₃)₂), 1.02 (dvt, *J*_{H-H} = 6.9, *N* = 12.0, 18H, PCH(CH₃)₂). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 293 K): δ 0.8 (s). ¹³C{¹H} NMR (75.4 MHz, C₆D₆, 293 K): δ 190.9 (t, *J*_{C-P} = 10.8, CO), 184.8 (t, *J*_{C-P} = 5.8, Os-CH), 169.1 (s, N=C-CH=CHOs), 152.1 (s, py), 135.9 (s, py), 126.2 (s, CH=CH), 118.7, 114.4 (both s, py), 24.9 (vt, *N* = 24.0, PCH), 20.4 and 19.5 (both s, PCH(CH₃)₂). MS (FAB⁺): *m/z* 679 (M⁺), 644 (M⁺ - Cl).

Structural Analysis of Complexes 9, 12, and 13. X-ray data were collected for all complexes on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering 0.3° in

ω . Data were corrected for absorption by using a multiscan method applied with the SADABS program.³³ The structures of all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on *F*² with SHELXL97,³⁴ was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters. For **13** the asymmetric unit shows two independent, but chemically equivalent, molecules, a molecule of 1,4-diphenylbutadiene, and a half molecule of pentane in the unit cell. The 1,4-diphenylbutadiene and the pentane molecule were refined as isotropic with geometrical restraints. The PLATON program³⁵ suggests that the structure of complex **13** has an 85% probability of being *P*2(1)/*c*. However, all our attempts to solve it within this space group have been unsuccessful. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model. The hydrogen atoms of the imine groups of complexes **9** and **12** were observed in the difference Fourier maps and refined as free isotropic atoms. All the highest electronic residuals were observed in close proximity of the metal centers and make no chemical sense. Crystal data and details of the data collection and refinement are given in Table 4.

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Supporting Information Available: Tables of positional and displacement parameters, crystallographic data, and bond lengths and angles of complexes **3**, **12**, and **13**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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