4258 *Organometallics* **1994**, *13*, 4258−4265

Reactions of $RuHCl(CO)(P\mathit{i}Pr_3)_2$ with Alkyn-1-ols: Synthesis of Ruthenium(II) Hydroxyvinyl and Vinylcarbene Complexes

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Received March 28, 1994[®]

The monohydrido complex $RuHCl(CO)(P\mathit{i}Pr_3)_2$ (**1**) reacts with $HC{\equiv}CC(OH)R^1R^2$ to give the hydroxyvinyl compounds $RuCl\{(E)\text{-}CH{=}CHC(OH)R^1R^2\}(CO)(P\mathit{i}Pr_3)_2$ ($R^1 = R^2 = H$ (**2**); $R^1 = H$, $R^2 = Ph$ (**3**); $R^1 = R^2 = Ph$ (**4**)), which by reaction with HBF_4 afford $[RuCl({=}CHCH{=}CR^1R^2)(CO)(P\mathit{i}Pr_3)_2]BF_4$ ($R^1 = H$, $R^2 = Ph$ (**5**); $R^1 = R^2 = Ph$ (**6**)). The former cationic compounds react with NaCl to give $RuCl_2({=}CHCH{=}CR^1R^2)(CO)(P\mathit{i}Pr_3)_2$ ($R^1 = H$, $R^2 = Ph$ (**7**); $R^1 = R^2 = Ph$ (**8**)). The molecular structure of **6** was determined by X-ray crystallography. Crystals of **6** are orthorhombic, space group $Pna2_1$, with unit cell dimensions $a = 16.681(1)$ Å, $b = 18.876(1)$ Å, and $c = 11.967(1)$ Å. The structure was solved and refined using 6457 observed reflections; $R = 0.0273$ and $R_w = 0.0281$. The geometry around the ruthenium atom can be described as a square pyramid with the alkylidene ligand located in the apex. The base is formed by the carbonyl ligand and the chlorine atom mutually *trans* disposed, with two triisopropylphosphine groups. The complexes **2**−**4** react with CO to give the *cis*-dicarbonyl compounds $RuCl\{(E)\text{-}CH{=}CHC(OH)R^1R^2\}(CO)_2(P\mathit{i}Pr_3)_2$ ($R^1 = R^2 = H$ (**9**); $R^1 = H$, $R^2 = Ph$ (**10**); $R^1 = R^2 = Ph$ (**11**)). The reaction of **1** with 1-ethynyl-1-cyclohexanol affords $RuCl\{(E)\text{-}CH{=}CHC(OH)(CH_2)_4CH_2\}(CO)(P\mathit{i}Pr_3)_2$ (**12**), which after 4 days in toluene at 60 °C gives $RuCl\{(E)\text{-}CH{=}CHC{=}CH(CH_2)_3CH_2\}(CO)(P\mathit{i}Pr_3)_2$ (**13**). The reaction of **13** with HBF_4 leads to $[RuCl\{{=}CHCH{=}C(CH_2)_4CH_2\}(CO)(P\mathit{i}Pr_3)_2]BF_4$ (**14**), which can also be obtained from the reaction of **12** with HBF_4.

Introduction

Reactions between transition-metal hydrido complexes and alkynes are fundamental steps of many catalytic cycles.[1]

During studies designed to determine the mechanisms of the reduction[2] and hydrosilylation[3] of alkynes catalyzed by unsaturated osmium compounds, we have observed that the reactions of osmium hydrido complexes with terminal alkynes, $HC{\equiv}CR$, allow the preparation of specific organometallic compounds (vinyl,[2a,4] hydrido dihydrogen alkynyl,[2b] hydrido carbyne, hydrido vinylcarbyne,[5] and hydrido vinylidene[6] derivatives) if the number of the hydrido ligands and the electronic properties of the starting complexes are appropriately selected. In general, these compounds play leading roles in homogeneous catalytic processes.[6]

The choice of the nature of the group R of the alkyne also determines the nature of the obtained organometallic complexes. Thus, it has been observed that the monohydrido species $OsHCl(CO)(P\mathit{i}Pr_3)_2$ reacts with acetylene, propyne, and phenylacetylene by insertion to give the five-coordinate vinyl−osmium compounds $OsCl\{(E)\text{-}CH{=}CHR\}(CO)(P\mathit{i}Pr_3)_2$ (R = H, Me, Ph).[4] However, the reactions of this monohydride with $HC{\equiv}CC(OH)R^1R^2$ afford, in one step, vinylcarbene compounds of the type $OsCl_2({=}CHCH{=}CR^1R^2)(CO)(P\mathit{i}Pr_3)_2$ in about 40% yield. When R^1 is hydrogen, small amounts of the complexes $OsCl(CHCHC(O)R^2)(CO)(P\mathit{i}Pr_3)_2$ can also be obtained.[7]

Continuing our work in this field, and in order to show the influence of the metallic center in these type of reactions, we now describe the reactivity of the monohydrido complex $RuHCl(CO)(P\mathit{i}Pr_3)_2$ toward alkyn-1-ols. During these studies, we have isolated cationic five-coordinate (vinylcarbene)ruthenium compounds. Although neutral five-coordinate[8] and cationic six-coordinate[9] (vinylcarbene)ruthenium complexes are already known, as far as we know, cationic five-coordinate (vinylcarbene)ruthenium compounds have not been previously reported.

[®] Abstract published in *Advance ACS Abstracts*, August 1, 1994.

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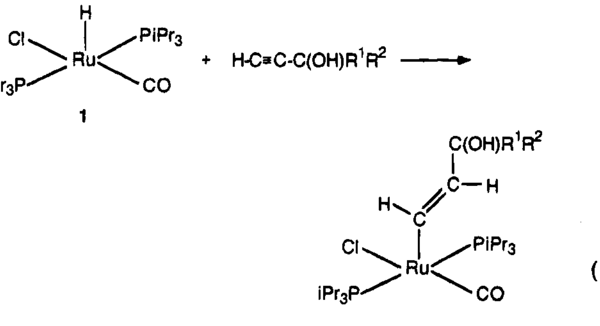
Results and Discussion

Reactions of $RuHCl(CO)(PiPr_3)_2$ with HC≡CC(OH)R^1R^2. Treatment of toluene solutions of the five-coordinate carbonyl hydrido complex $RuHCl(CO)(PiPr_3)_2$ (**1**) with the stoichiometric amount of 2-propyn-1-ol, 1-phenyl-2-propyn-1-ol, and 1,1-diphenyl-2-propyn-1-ol results in the formation of the five-coordinate vinyl compounds RuCl{(*E*)-CH=CHC(OH)R^1R^2}(CO)$(PiPr_3)_2$ (**2**–**4**; eq 1) in 70–90% yield, by insertion of the alkynes into the Ru–H bond of **1**.



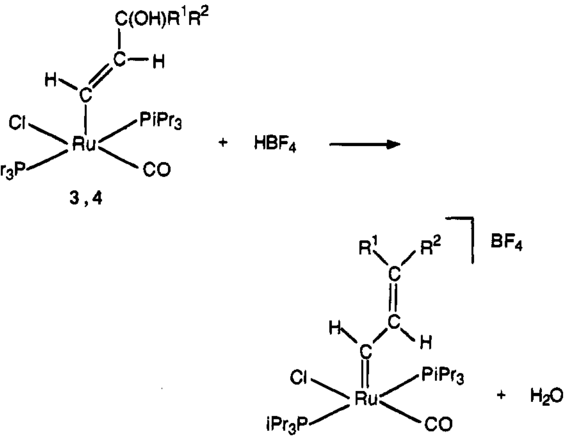
(1)

$R^1=R^2=H$ (**2**); $R^1=H$, $R^2=Ph$ (**3**); $R^1=R^2=Ph$ (**4**)

The IR and ^1H and $^{31}P\{^1H\}$ NMR spectra of **2**–**4** confirm that the obtained products have the molecular structure shown in eq 1. The IR spectra in Nujol contain a resonance at about 3400 cm^{-1}, characteristic of a ν(OH) absorption, while the ^1H NMR spectra in chloroform-*d* show resonances at about 7.5 and 5.0 ppm due to the vinylic hydrogen atoms of the vinyl ligand. The *trans* stereochemistry at the carbon–carbon double bond is strongly supported by the proton–proton coupling constants of about 13 Hz, which is a typical value for this arrangement.[4,10] The $^{31}P\{^1H\}$ NMR spectra show singlets between 38 and 40 ppm, indicating that the two phosphine ligands are equivalent.

The complexes **3** and **4** react with $HBF_4{\cdot}OEt_2$ in diethyl ether to afford the cationic five-coordinate vinylcarbene compounds **5** and **6** (eq 2).

These compounds were fully characterized by elemental analysis and IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The IR spectra in Nujol show the absorption due to the $[BF_4]^-$ anion with T_d symmetry, indicating that this anion is not coordinated to the metallic center of **5** and **6**. The ^1H and $^{31}P\{^1H\}$ NMR spectra in chloroform-*d* are temperature-dependent. At room temperature, the vinylcarbene protons appear as broad signals at about 16 and 8 ppm. At −40 °C, they are doublets with H–H coupling constants of 12.0 (**5**) and 11.1 Hz (**6**). The $^{31}P\{^1H\}$ NMR spectra at −40 °C show singlets at 60.0 (**5**) and 57.4 ppm (**6**), suggesting that the phosphine ligands are equivalent and are mutually *trans* disposed.



(2)

$R^1=H$, $R^2=Ph$ (**5**); $R^1=R^2=Ph$ (**6**)

The definitive characterization of the structures of **5** and **6** came from an X-ray diffraction experiment on a single crystal of **6**. A view of the molecular geometry of the cation of this complex is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The geometry of the cation can be rationalized as a square pyramid with the alkylidene ligand located at the apex. The four atoms P(1), P(2), Cl, and C(16), forming the base, are approximately in one plane, whereas the ruthenium atom is located 0.338(1) Å above this plane toward the apical position.

The most conspicuous features of this structure are first the Ru–C(1) bond length (1.874(3) Å), which is consistent with a Ru–C(1) double-bond formulation, and second the Ru–C(1)–C(2) bond angle (132.8(2)°), which clearly indicates sp^2 hybridization for the C(1) carbon atom. The bond lengths and angles within the alkylidene ligand are consistent with the vinylcarbene proposal; e.g., C(1) and C(2) are separated by 1.411(4) Å and C(2) and C(3) by 1.365(4) Å, and the bond angles around C(2) and C(3) are in the range 120.8–124.1(3)°. Similar values have been reported for related compounds.[9e,11] Furthermore, the deviations observed for the C(1)–C(2) and C(2)–C(3) bond distances from the mean values described for double and single $C(sp^2)$–$C(sp^2)$ bonds (1.34 and 1.48 Å) suggest a weak delocalization of the π-electron density along the C(1)–C(2)–C(3) chain.

Noticeably, the Ru–P lengths (2.4586(8) and 2.4307(8) Å) are significantly longer than the value reported (2.339(4) Å) in the closely related hexacoordinate [RuCl{=C(OMe)CH=CPh_2}$(C_6Me_6)(PMe_3)$}]$^+$ complex.[9e] On the other hand, the Ru–Cl distance (2.3952(9) Å) is comparatively shorter than that reported in the previous example (2.418(4) Å). Most likely the different coordination numbers around the metal, together with the distinct *trans*-situated ligands, are responsible for these variations of the Ru–P and Ru–Cl distances.

The coordination number 6 for **5** and **6** can be achieved by addition of Cl^-. Treatment of solutions of **5** and **6** with sodium chloride in methanol at room temperature results in the formation of brown solids in

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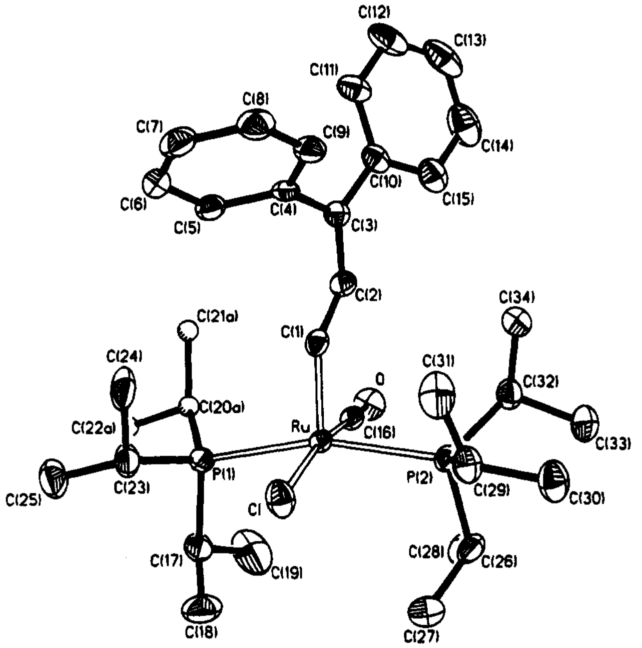
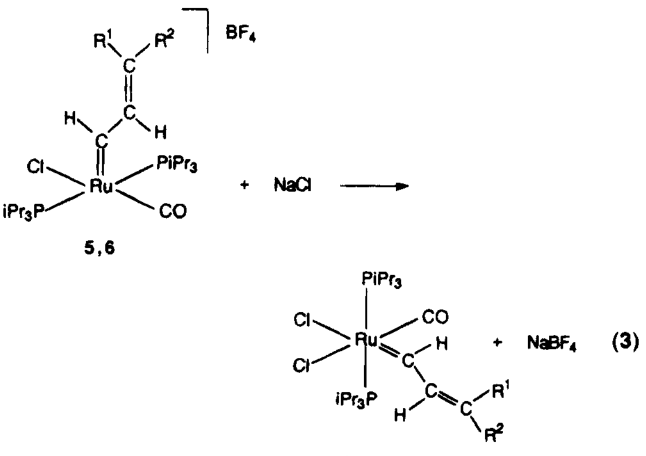


Figure 1. Molecular structure of [RuCl(=CHCH=CPh$_2$)(CO)(PiPr$_3$)$_2$]$^+$ (cation of **6**) showing the labeling scheme.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex [RuCl(=CHCH=CPh$_2$)(CO)(PiPr$_3$)$_2$]BF$_4$ (6)

Ru—Cl	2.3952(9)	C(1)—C(2)	1.411(4)
Ru—P(1)	2.4586(8)	C(2)—C(3)	1.365(4)
Ru—P(2)	2.4307(8)	C(3)—C(4)	1.479(4)
Ru—C(1)	1.874(3)	C(3)—C(10)	1.481(4)
Ru—C(16)	1.843(3)	C(16)—O	1.131(4)
Cl—Ru—P(1)	88.59(3)	P(2)—Ru—C(1)	95.99(9)
Cl—Ru—P(2)	88.73(3)	P(2)—Ru—C(16)	89.15(9)
Cl—Ru—C(1)	102.01(9)	C(1)—Ru—C(16)	88.8(1)
Cl—Ru—C(16)	169.16(9)	Ru—C(1)—C(2)	132.8(2)
P(1)—Ru—P(2)	163.36(3)	C(1)—C(2)—C(3)	124.1(3)
P(1)—Ru—C(1)	100.63(9)	C(2)—C(3)—C(4)	120.8(3)
P(1)—Ru—C(16)	90.40(9)	C(2)—C(3)—C(10)	121.2(3)

excellent yield (ca. 90%). According to the elemental analysis and IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of these solids, they were characterized as the dichloro vinylcarbene complexes **7** and **8** (eq 3).



5,6

(3)

R^1=H, R^2=Ph (**7**); R^1=R^2=Ph (**8**)

In the IR spectrum of **7**, the most prominent feature is a strong ν(C=C) band at 1550 cm^{-1}, which was assigned to the olefinic bond of the vinylcarbene ligand. In the ^{1}H NMR spectrum, this ligand exhibits resonances at 16.67 (d, J(HH) = 13.4 Hz), 8.53 (dd, J(HH) = 14.5 and 13.4 Hz), and 7.28 (d, J(HH) = 14.5 Hz) ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 40.1 ppm. The IR spectrum of **8** shows the ν(C=C) absorption at 1515 cm^{-1}, whereas in the ^{1}H NMR spectrum the signals of the vinylcarbene ligand appear at 17.05 (Ru=CH—) and 9.02 (CH=) ppm and in the ^{13}C{^{1}H} NMR spectrum at 314.48 (Ru=CH) and 130.75 (CH=) ppm. The signal of the CPh$_2$ carbon atom is masked by the solvent (C$_6$D$_6$). The ^{31}P{^{1}H} NMR spectrum of **8** shows a singlet at 39.2 ppm.

The spectroscopic data for **7** and **8** agree well with those previously reported for the osmium compounds OsCl$_2$(=CHCH=CR^{1}R^2)(CO)(PiPr$_3$)$_2$ (R^1 = H, Ph; R^2 = Ph), where the *cis* disposition of the two chloro ligands was determined by an X-ray diffraction experiment on a single crystal of OsCl$_2$(=CHCH=CHPh)(CO)(PiPr$_3$)$_2$.[7]

As has been previously mentioned, these vinylcarbene—osmium complexes were prepared by direct reaction between OsHCl(CO)(PiPr$_3$)$_2$ and HC≡CC(OH)R^{1}R^2. Then, we suggested that the formation of OsCl$_2$(=CHCH=CR^{1}R^2)(CO)(PiPr$_3$)$_2$ involves the initial insertion of the alkynes into the Os—H bond of OsHCl(CO)(PiPr$_3$)$_2$, to give five-coordinate (E)-vinyl intermediates OsCl{(E)-CH=CHC(OH)R^{1}R^2}(CO)(PiPr$_3$)$_2$, which subsequently isomerize to OsCl{(Z)-CH=CHC(OH)R^{1}R^2}(CO)(PiPr$_3$)$_2$. These six-coordinate (Z)-vinyl species, isolated for R^1 = R^2 = H, decompose in solution by loss of HCl. The acid formed could react with the remaining amount of OsCl{(Z)-CH=CHC(OH)R^{1}R^2}(CO)(PiPr$_3$)$_2$ to afford [OsCl(=CHCH=CR^{1}R^2)(CO)(H$_2$O)(PiPr$_3$)$_2$]$^+$ and Cl$^-$; next, the displacement of the water molecule by Cl$^-$ should give OsCl$_2$(=CHCH=CR^{1}R^2)(CO)(PiPr$_3$)$_2$.

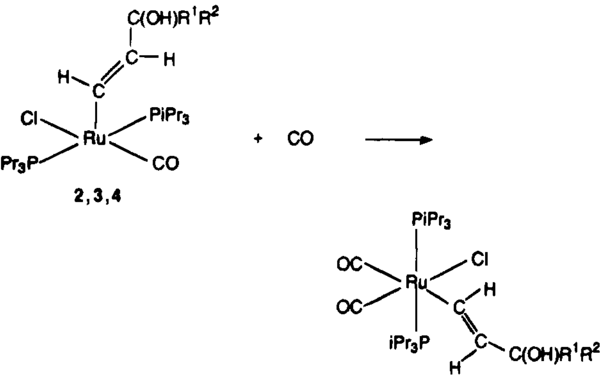
The sequence of eqs 1—3 provides very strong evidence in favor of this proposal. Direct evidence suggesting the participation of six-coordinate cationic aquo vinylcarbene intermediates has been also found. In fact, we have now observed that the complex OsCl{(Z)-CH=CHCH$_2$OH}(CO)(PiPr$_3$)$_2$ reacts with HBF$_4$·OEt$_2$ in diethyl ether to give [OsCl(=CHCH=CH$_2$)(CO)(H$_2$O)(PiPr$_3$)$_2$]BF$_4$, which decomposes in solution to an *ill-defined straw-colored solid.*

The difference in stability between RuCl{(E)-CH=CH(OH)R^{1}R^2}(CO)(PiPr$_3$)$_2$ (**2**—**4**) and their analogous osmium intermediates merits further consideration. The formation of HCl during the reaction of OsHCl(CO)(PiPr$_3$)$_2$ with HC≡CC(OH)R^{1}R^2 was proposed to proceed by heterolytic activation of the H—O bond of a vinyl alcohol ligand, for which it is necessary that the OH group be coordinated to the metallic center. This is only possible if the vinyl alcohol ligand has a Z stereochemistry. Thus, the (E)-vinyl alcohol → (Z)-vinyl alcohol isomerization seems to be the determining step in the formation of HCl. The key to this isomerization is probably the fact that the five-coordinate (E)-vinyl alcohol intermediates are 16-electron species, while the six-coordinate (Z)-vinyl alcohol intermediates are 18-electron derivatives.[7]

In this context, it should be mentioned that the osmium systems containing triisopropylphosphine as ancillary ligands have a higher tendency to give six-coordinate species than their analogous ruthenium systems. Thus, for example, previous studies have shown that the complex OsHCl(CO)(PiPr$_3$)$_2$ reacts with ethylene, methyl acrylate, acrylonitrile, and methyl vinyl ketone in hexane at room temperature to give six-coordinate compounds of the type $OsHCl(\eta^2\text{-}CH_2{=}CHR)(CO)(PiPr_3)_2$, while the ruthenium analogue $RuHCl(CO)(PiPr_3)_2$ is completely inert under the same conditions.[12]

This low tendency of the ruthenium systems to afford six-coordinate derivatives could explain why **2**–**4** are more stable than the analogous osmium compounds and why the cations **5** and **6** can be isolated as five-coordinate species.

The coordination number 6 for **2**–**4** can be achieved by addition of carbon monoxide. Bubbling CO through dichloromethane–hexane solutions of **2**–**4** results in the formation of the derivatives **9**–**11** (eq 4). These compounds are formulated as *cis*-dicarbonyl complexes on the basis of their IR spectra, which show two strong ν(CO) bands in the terminal carbonyl region.

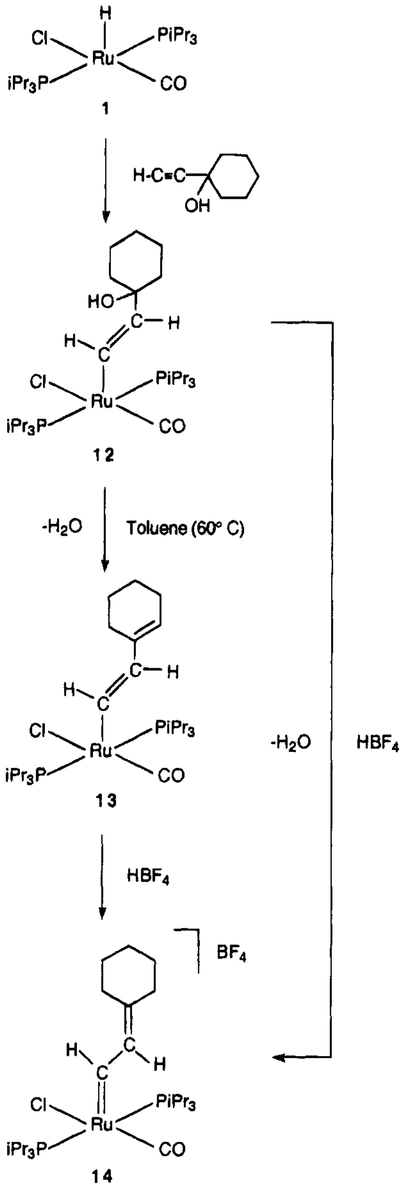


(4)

$R^1{=}R^2{=}H$ (**9**); $R^1{=}H$, $R^2{=}Ph$ (**10**); $R^1{=}R^2{=}Ph$ (**11**)

Reactions of $RuHCl(CO)(PiPr_3)_2$ with 1-Ethynyl-1-cyclohexanol. Similarly to the reactions shown in eq 1, the treatment of **1** with the stoichiometric amount of 1-ethynyl-1-cyclohexanol in toluene at room temperature affords, after 20 min, the hydroxyvinyl complex **12** (Scheme 1), as a violet solid in 75% yield. The IR spectrum of this solid in Nujol contains a broad resonance at 3510 cm^{-1}, characteristic of a ν(OH) absorption. The presence of the vinyl group was inferred from the ^{1}H NMR spectrum in chloroform-*d*, which shows two doublets at 7.49 and 5.01 ppm. The *trans* stereochemistry at the carbon–carbon double bond is supported by the proton–proton coupling constant, which has a value of 13.2 Hz. In agreement with the stereochemistry shown in Scheme 1, the $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at 37.7 ppm, indicating that the two phosphine ligands are equivalent and are mutually *trans* disposed.

Scheme 1



When the reaction between **1** and 1-ethynyl-1-cyclohexanol was carried out in toluene at 60 °C, a new violet solid was obtained after 4 days, in 78% yield. The same compound was prepared directly in 72% yield by heating of **12** in toluene at 60 °C, over 4 days. The IR and ^{1}H, DEPT $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of the solid indicate that it is the vinylvinyl complex **13** (Scheme 1). The IR spectrum of **13** in Nujol shows a ν(C=C) band at 1555 cm^{-1}. The most noticeable data in the ^{1}H NMR spectrum are two doublets at 7.59 (J(HH) = 13.2 Hz) and 5.58 (J(HH) = 13.2 Hz) ppm due to the RuC*H*= and RuCH=C*H* protons, respectively, and a triplet at 5.07 (J(HH) = 3.3 Hz) ppm assigned to the C=C*H* proton. In the DEPT $^{13}C\{^1H\}$ NMR spectrum, the vinylvinyl carbon atoms were assigned to four signals at 143.53 (RuCH=), 139.47 (RuCH=*C*H), 136.24 (CH-*C*=CH), and 118.33 (C=*C*H) ppm. The first three signals appear as triplets with P–C coupling constants of 11.1, 3.2, and 2.1 Hz, respectively, and the fourth appears as a singlet. The $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at 37.4 ppm.

The complex **13** is a result of the dehydration of **12**. Dehydration of hydroxy–η^1-carbon unsaturated ligands has been previously observed. Selegue *et al.* have reported that reactions of 2-alkyn-1-ols with $Ru(\eta^5\text{-}C_5H_5)Cl(PR_3)_2$ in polar media lead to hydroxyvinylidene intermediates, which spontaneously dehydrate in situ.[11a,13,14] In the case of 1,1-diphenyl-2-propyn-1-ol, allenylidene complexes are formed exclusively.[13] However, when hydrogen atoms adjacent to the hydroxy group are present, dehydration can give either alle-

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nylidene or vinylvinylidene.[11a] Dixneuf and co-workers[9] have described that the complex $RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_3)$ reacts at room temperature with $HC{\equiv}CC(OH)R^1R^2$ ($H \neq R^1, R^2$) and $NaPF_6$ in methanol to produce vinylcarbenes. We have reported that the reaction of $OsH_2Cl_2(P\textit{i}Pr_3)_2$ with 3-methyl-1-pentyn-3-ol and 1-ethynyl-1-cyclohexanol leads to hydrido vinylcarbyne complexes via hydrido hydroxycarbyne intermediates.[5] Kolobova and co-workers have observed that the action of SiO_2 or Al_2O_3 on manganese hydroxyvinylidene compounds causes their dehydration to allenylidenes.[15] Some platinum(II) alkynyls with tertiary hydroxy groups can also be dehydrated to enynyls.[16]

The vinylvinyl complex **13** reacts in diethyl ether with the stoichiometric amount of $HBF_4{\cdot}OEt_2$ to give the cationic vinylcarbene compound **14**, as a yellow solid in 87% yield. The complex **14** can be also obtained in excellent yield (85%) by reaction of **12** with $HBF_4{\cdot}OEt_2$ (Scheme 1). The coordination number 5 for **14** can be inferred from its IR spectrum in Nujol, which shows the absorption due to the $[BF_4]^-$ anion with T_d symmetry, indicating that this anion is not coordinated to the metallic center. Similarly to **5** and **6** the ^1H and $^{31}P\{^1H\}$ NMR spectra of **14** in chloroform-*d* are temperature-dependent. At room temperature, the vinylcarbene protons appear as broad signals at 16 and 7.5 ppm. At −40 °C, they are doublets with an H−H coupling constant of 11.4 Hz. The $^{31}P\{^1H\}$ NMR spectrum at −40 °C shows a singlet at 56.4 ppm.

Previous studies of vinyl compounds have identified the localization of electron density at the β-carbon atom. Thus, the reactions of vinyl compounds with electrophiles afford carbene derivatives.[17] The reaction of **13** and HBF_4 to give **14** can be rationalized as the electrophilic attack of a proton at the δ-carbon atom of the vinylvinyl ligand of **13**. Therefore, we now show that the reaction of a vinylvinyl compound with an electrophile leads to a vinylcarbene complex, suggesting that in a vinylvinyl ligand the localization of electron density is on the δ-carbon atom.

Concluding Remarks

This study has shown that the complex $RuHCl(CO)(P\textit{i}Pr_3)_2$ reacts with $HC{\equiv}CC(OH)R^1R^2$ to give hydroxyvinyl compounds of the type $RuCl\{(E)\text{-}CH{=}CHC(OH)R^1R^2\}(CO)(P\textit{i}Pr_3)_2$, which by reaction with HBF_4 afford the five-coordinate cationic vinylcarbene derivatives $[RuCl({=}CHCH{=}CR^1R^2)(CO)(P\textit{i}Pr_3)_2]BF_4$. These compounds react with NaCl to give $RuCl_2({=}CHCH{=}CR^1R^2)(CO)(P\textit{i}Pr_3)_2$. Overall, these reactions must be viewed as supporting evidence for the mechanism of the reactions of $OsHCl(CO)(P\textit{i}Pr_3)_2$ with $HC{\equiv}CC(OH)R^1R^2$, which lead to $OsCl_2({=}CHCH{=}CR^1R^2)(CO)(P\textit{i}Pr_3)_2$. The low tendency of the ruthenium triisopropylphosphine systems to afford six-coordinate derivatives seems to be the reason the reactions of $RuHCl(CO)(P\textit{i}Pr_3)_2$ with $HC{\equiv}CC(OH)R^1R^2$ do not give $RuCl_2({=}CHCH{=}CR^1R^2)(CO)(P\textit{i}Pr_3)_2$.

On the other hand, it is interesting to note that the high tendency of the ruthenium triisopropylphosphine systems to afford five-coordinate derivatives could be the reason for the formation of five-coordinate cationic vinylcarbene complexes. These compounds can be prepared by reaction between a five-coordinate hydroxyvinyl complex and HBF_4 and by electrophilic attack at the δ-carbon atom of a vinylvinyl ligand of a five-coordinate vinylvinyl complex.

Experimental Section

General Considerations. All reactions were carried out with rigorous exclusion of air by using Schlenk-tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. 2-Propyn-1-ol (Aldrich), 1-phenyl-2-propyn-1-ol (ABCR), and 1,1-diphenyl-2-propyn-1-ol (ABCR) were used without further purification. $RuHCl(CO)(P\textit{i}Pr_3)_2$[12] was prepared by a published method.

Physical Measurements. NMR spectra were recorded on a Varian XL-200 or on a Varian UNITY 300 spectrophotometer. Chemical shifts are expressed in ppm upfield from Me_4Si (^{13}C, ^1H) and 85% H_3PO_4 (^{31}P). Coupling constants J and N ($N = J(HP) + J(HP')$ for ^1H and $N = J(CP) + J(CP')$ for ^{13}C) are given in hertz. Infrared spectra were recorded with a Perkin-Elmer 783 spectrophotometer or a Perkin-Elmer 883 spectrophotometer (Nujol mulls on polyethylene sheets). C and H analyses were carried out with a Perkin-Elmer 240C microanalyzer or a Perkin-Elmer 2400 CHNS/O analyzer.

Reaction of 1 with 2-Propyn-1-ol: Preparation of $RuCl(CH{=}CHCH_2OH)(CO)(P\textit{i}Pr_3)_2$ (2). A solution of **1** (135 mg, 0.28 mmol) in 10 mL of toluene was treated with 2-propyn-1-ol (17 μL, 0.30 mmol). After the mixture was stirred for 5 h at room temperature, it was concentrated until a rose-colored solid precipitated. Hexane was then added to complete precipitation. The solid was filtered off, washed with hexane, and dried in vacuo. Yield: 136 mg (89%). Anal. Calcd for $C_{22}H_{47}ClO_2P_2Ru$: C, 48.45; H, 8.69. Found: C, 48.19; H, 9.62. IR (Nujol): ν(OH) 3345 (m, br), ν(C=O) 1906 (vs), ν(C=C) 1584 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, J(HH) = 12.8; RuCH=), 5.20 (m; =CH−), 3.90 (dd, J(HH) = 6.4, J(HH) = 5.8; $-CH_2-$), 2.69 (m; PCH), 1.24 (dvt, N = 14.2, J(HH) = 6.9; $PCCH_3$), 1.21 (dvt, N = 14.0, J(HH) = 6.9; $PCCH_3$), 0.90 (t, J(HH) = 5.8; −OH). $^{31}P\{^1H\}$ NMR (80.90 MHz, $CDCl_3$): δ 38.00 (s).

Reaction of 1 with 1-Phenyl-2-propyn-1-ol: Preparation of $RuCl\{CH{=}CHCH(OH)Ph\}(CO)(P\textit{i}Pr_3)_2$ (3). The experimental procedure was analogous to that described for **2**; starting materials were **1** (135 mg, 0.28 mmol) and 1-phenyl-2-propyn-1-ol (38 mg, 0.29 mmol) in 10 mL of toluene. The product is a rose-colored solid. Yield: 125 mg (72%). Anal. Calcd for $C_{28}H_{51}ClO_2P_2Ru$: C, 54.40; H, 8.31. Found: C, 54.41; H, 9.28. IR (Nujol): ν(OH) 3300 (m, br), ν(C≡O) 1907 (vs), ν(C=C) 1584 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, J(HH) = 11.4; RuCH=), 7.51 (H_{Ph}), 5.06 (dt, J(HH) = 11.4, J(HP) = 1.8; =CH−), 5.04 (d, J(HH) = 2.5; C*H*(OH)Ph), 2.43 and 2.33 (both m; PCH), 1.49 (d, J(HH) = 2.5; −OH), 1.21 (dvt, N = 13.1, J(HH) = 6.0; $PCCH_3$), 1.19 (dvt, N = 13.0, J(HH) = 6.5; $PCCH_3$), 1.04 (dvt, N = 13.5, J(HH) = 6.2; $PCCH_3$), 1.01 (dvt, N = 13.3, J(HH) = 6.2; $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.90 MHz, $CDCl_3$): δ 38.36 (s).

Reaction of 1 with 1,1-Diphenyl-2-propyn-1-ol: Preparation of $RuCl\{CH{=}CHC(OH)Ph_2\}(CO)(P\textit{i}Pr_3)_2$ (4). The procedure was analogous to that described for **2**; starting materials were **1** (151 mg, 0.31 mmol) and 1,1-diphenyl-2-propyn-1-ol (38 mg, 0.31 mmol) in 10 mL of toluene. The product is a rose-colored solid. Yield: 167 mg (79%). Anal. Calcd for $C_{33}H_{55}ClO_2P_2Ru$: C, 58.10; H, 8.13. Found: C, 58.01;

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H, 8.75. IR (Nujol): ν(OH) 3587 (m, br), ν(C≡O) 1900 (vs), ν(C=C) 1576 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.46 (dt, *J*(HH) = 13.0, *J*(HP) = 0.9; RuCH=), 7.20 (H_{Ph}), 5.54 (dt, *J*(HH) = 13.0, *J*(HP) = 1.8; =CH−), 2.56 (m; PCH), 2.03 (s; −OH), 1.19 (dvt, *N* = 13.5, *J*(HH) = 6.9; $PCCH_3$), 1.16 (dvt, *N* = 14.1, *J*(HH) = 6.9; $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.90 MHz, $CDCl_3$): δ 39.90 (s).

Reaction of 3 with HBF_4·OEt_2: Preparation of [RuCl(=CHCH=CHPh)(CO)(P*i*Pr_3)$_2$]BF_4 (5). A solution of **3** (150 mg, 0.24 mmol) in 10 mL of Et_2O was treated at room temperature dropwise with HBF_4·OEt_2 (54%; 40 μL, 0.30 mmol). The yellow solid formed was filtered off and washed repeatedly with cold Et_2O and hexane. Yield: 138 mg (83%). Anal. Calcd for $C_{28}H_{50}BClF_4OP_2Ru$: C, 48.89; H, 7.32. Found: C, 49.02; H, 7.90. IR (Nujol): ν(C≡O) 1991 (vs), ν(C=C) 1565 (s), ν(BF_4^-) 1052 (s, br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, −40 °C): δ 16.04 (d, *J*(HH) = 12.0; Ru=CH−), 8.61 (dd, *J*(HH) = 15.8, *J*(HH) = 12.0; −CH=), 8.13 (d, *J*(HH) = 15.8; =C*H*Ph), 7.47 (H_{Ph}), 2.87 (m; PCH), 1.37 (dvt, *N* = 14.4, *J*(HH) = 7.2; $PCCH_3$), 1.34 (dvt, *N* = 15.0, *J*(HH) = 7.8; $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$, −40 °C): δ 59.96 (s).

Reaction of 4 with HBF_4·OEt_2: Preparation of [RuCl(=CHCH=CPh_2)(CO)(P*i*Pr_3)$_2$]BF_4 (6). The procedure was analogous to that described for **5**; starting materials were **4** (123 mg, 0.18 mmol) and HBF_4·OEt_2 (54%; 30 μL, 0.20 mmol) in 10 mL of Et_2O. The product is a red solid. Yield: 121 mg (88%). Anal. Calcd for $C_{34}H_{54}BClF_4OP_2Ru$: C, 53.45; H, 7.12. Found: C, 53.36; H, 7.75. IR (Nujol): ν(C≡O) 1976 (vs), ν(C=C) 1584 (w), ν(BF_4^-) 1045 (s, br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, −40 °C): δ 15.42 (d, *J*(HH) = 11.1; Ru=CH−), 8.54 (d, *J*(HH) = 11.1; −CH=), 7.52 (H_{Ph}), 2.86 (m; PCH), 1.36 (dvt, *N* = 14.8, *J*(HH) = 6.9; $PCCH_3$), 1.33 (dvt, *N* = 15.4, *J*(HH) = 6.9; $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$, −40 °C): δ 57.40 (s).

Reaction of 5 with NaCl: Preparation of $RuCl_2$(=CHCH=CHPh)(CO)(P*i*Pr_3)$_2$ (7). A solution of **5** (120 mg, 0.18 mmol) in 10 mL of methanol was treated with NaCl (12 mg, 0.20 mmol) for 15 min at room temperature. A dark brown precipitate was formed. The solvent was removed, and the residue was dissolved in 15 mL of toluene and filtered. After the solvent was removed, the dark brown solid was washed repeatedly with methanol, Et_2O and hexane and then dried in vacuo. Yield: 105 mg (92%). Anal. Calcd for $C_{28}H_{50}Cl_2OP_2Ru$: C, 52.83; H, 7.92. Found: C, 53.00; H, 8.00. IR (Nujol): ν(C≡O) 1927 (vs), ν(C=C) 1550 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 16.67 (d, *J*(HH) = 13.4; Ru=CH−), 8.53 (dd, *J*(HH) = 14.5, *J*(HH) = 13.4; −CH=), 7.72 (d, *J*(HH) = 8.0; H_{oPh}), 7.55 (t, *J*(HH) = 7.2; H_{mPh}), 7.43 (t, *J*(HH) = 8.0; H_{pPh}), 7.28 (d, *J*(HH) = 14.5; =C*H*Ph), 2.78 (m; PCH), 1.37 (dvt, *N* = 14.1, *J*(HH) = 7.2; $PCCH_3$), 1.21 (dvt, *N* = 13.6, *J*(HH) = 7.0; $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ 40.07 (s).

Reaction of 6 with NaCl: Preparation of $RuCl_2$(=CHCH=CPh_2)(CO)(P*i*Pr_3)$_2$ (8). The procedure was analogous to that described for **7**; starting materials were **6** (267 mg, 0.35 mmol) and NaCl (23 mg, 0.39 mmol) in 12 mL of methanol. The product is a brown solid. Yield: 222 mg (89%). Anal. Calcd for $C_{34}H_{54}Cl_2OP_2Ru$: C, 57.30; H, 7.64. Found: C, 57.48; H, 8.16. IR (Nujol): ν(C≡O) 1940 (vs), ν(C=C) 1515 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 17.05 (d, *J*(HH) = 14.1; Ru=CH−), 9.02 (d, *J*(HH) = 14.1; −CH=), 7.36 (H_{Ph}), 2.77 (m; PCH), 1.39 (dvt, *N* = 13.8, *J*(HH) = 6.9; $PCCH_3$), 1.14 (dvt, *N* = 13.5, *J*(HH) = 6.6; $PCCH_3$). $^{13}C\{^1H\}$ NMR (75.33 MHz, C_6D_6): δ 314.48 (t, *J*(CP) = 8.7; RuC=), 202.29 (t, *J*(CP) = 12.4; RuCO), 146.42 (s; C_{ipsoPh}), 130.75 (s; −CH=), 129.54, 129.47, 128.56 (both s, C_{Ph}), 25.54 (vt, *N* = 19.7; PCH), 20.15, 19.74 (both s; $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ 39.19 (s).

Reaction of 2 with Carbon Monoxide: Preparation of RuCl{CH=CHCH_2(OH)}(CO)$_2$(P*i*Pr_3)$_2$ (9). Carbon monoxide was bubbled through a solution of **2** (162 mg, 0.29 mmol) in 10 mL of a hexane−CH_2Cl_2 mixture (8:1) for 2 min at room temperature. The solution was filtered, and the solvent was removed. The remaining pale yellow residue was recrystallized from CH_2Cl_2−hexane at −78 °C. The product is a colorless solid. Yield: 131 mg (79%). Anal. Calcd for $C_{23}H_{47}ClO_3P_2Ru$: C, 48.14; H, 8.26. Found: C, 48.09; H, 8.25. IR (Nujol): ν(OH) 3380 (m, br), ν(C≡O) 2010 (vs), 1942 (vs), ν(C=C) 1580 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, *J*(HH) = 17.5; RuCH=), 5.89 (d, br, *J*(HH) = 17.5; =CH−), 4.05 (s, br; −CH_2−), 2.67 (m; PCH), 1.35 (dvt, *N* = 13.7, *J*(HH) = 6.9; $PCCH_3$), 1.28 (dvt, *N* = 12.9, *J*(HH) = 6.5; $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ 35.77 (s).

Reaction of 3 with Carbon Monoxide: Preparation of RuCl{CH=CHCH(OH)Ph}(CO)$_2$(P*i*Pr_3)$_2$ (10). The procedure was analogous to that described for **9**; the starting material was **3** (130 mg, 0.21 mmol) in 10 mL of CH_2Cl_2. The product is a colorless solid. Yield: 92 mg (68%). Anal. Calcd for $C_{29}H_{51}ClO_3P_2Ru$: C, 53.90; H, 7.96. Found: C, 54.46; H, 8.00. IR (Nujol): ν(OH) 3445 (m, br), ν(C≡O) 2005 (vs), 1950 (vs), ν(C=C) 1585 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.43 (d, *J*(HH) = 17.1; RuCH=), 7.25 (H_{Ph}), 5.85 (ddt, br, *J*(HH) = 17.1, *J*(HH) = 7.1, *J*(HP) = 2.2; =CH−), 5.72 (d, br, *J*(HH) = 7.1; C*H*(OH)Ph), 2.70 and 2.44 (both m; PCH), 1.81 (d, *J*(HH) = 2.5; OH), 1.37 (dvt, *N* = 14.0, *J*(HH) = 6.9; $PCCH_3$), 1.29 (dvt, *N* = 12.9, *J*(HH) = 5.8; $PCCH_3$), 1.23 (dvt, *N* = 14.3, *J*(HH) = 7.2; $PCCH_3$), 1.07 (dvt, *N* = 12.9, *J*(HH) = 6.8; $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ 35.91 (s).

Reaction of 4 with Carbon Monoxide: Preparation of RuCl{CH=CHC(OH)Ph_2}(CO)$_2$(P*i*Pr_3)$_2$ (11). Carbon monoxide was bubbled through a suspension of **4** (121 mg, 0.18 mmol) in 10 mL of hexane for 3 min at room temperature, which led to the formation of a yellow solution. The mixture was concentrated to ca. 2 mL. The pale yellow solid that formed was filtered off and repeatedly washed with cold hexane. The product is a colorless solid. Yield: 109 mg (85%). Anal. Calcd for $C_{34}H_{55}ClO_3P_2Ru$: C, 57.67; H, 7.76. Found: C, 57.17; H, 8.69. IR (Nujol): ν(OH) 3435 (m, br), ν(C≡O) 2002 (vs), 1935 (vs), ν(C=C) 1597 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.26 (m; H_{Ph} + RuCH=), 6.41 (dt, *J*(HH) = 18.1, *J*(HP) = 1.7; =CH−), 2.66 (s; −OH), 2.55 (m; PCH), 1.30 (dvt, *N* = 14.6, *J*(HH) = 7.1; $PCCH_3$), 1.13 (dvt, *N* = 13.6, *J*(HH) = 6.1; $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ 37.55 (s).

Reaction of 1 with 1-Ethynyl-1-cyclohexanol: Preparation of RuCl{(*E*)-CH=CHC(OH)(CH_2)$_4$$CH_2$}(CO)(P*i*$Pr_3$)$_2$ (12). A solution of **1** (113 mg, 0.23 mmol) in 10 mL of toluene was treated with 1-ethynyl-1-cyclohexanol (29 mg, 0.23 mmol). After the mixture was stirred for 20 min at room temperature, the violet solution was filtered off and concentrated until a violet precipitate was formed. Then pentane was added to complete precipitation. The solid was filtered off, washed with pentane, and dried in vacuo. Yield: 105 mg (75%). Anal. Calcd for $C_{27}H_{55}ClO_2P_2Ru$: C, 53.15; H, 9.09. Found: C, 53.01; H, 9.10. IR (Nujol): ν(OH) 3510 (m), ν(C≡O) 1913 (vs), ν(C=C) 1588 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J*(HH) = 13.2; RuCH=), 5.01 (d, *J*(HH) = 13.2; =CH), 2.72 (m; PCH), 1.38 (m; Cy H), 1.26 (dvt, *N* = 13.2, *J*(HH) = 7.2; $PCCH_3$), 1.25 (dvt, *N* = 14.7, *J*(HH) = 7.4; $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ 37.68 (s).

Reaction of 1 with 1-Ethynyl-1-cyclohexanol at 60 °C: Preparation of RuCl{(*E*)-CH=CHC=CH(CH_2)$_3$$CH_2$}(CO)(P*i*$Pr_3$)$_2$ (13). A solution of **1** (127 mg, 0.26 mmol) in 10 mL of toluene was treated with 1-ethynyl-1-cyclohexanol (34 mg, 0.27 mmol). After the solution was stirred for 4 days at 60 °C, it was filtered off and concentrated until a violet precipitate was formed. Then pentane was added to complete precipitation. The solid was filtered off, washed with pentane, and dried in vacuo. Yield: 120 mg (78%). Anal. Calcd for $C_{27}H_{53}ClOP_2Ru$: C, 54.76; H, 9.02. Found: C, 54.20; H, 9.01. IR

Table 2. Atomic Coordinates (×10^4; ×10^5 for Ru, Cl, and P Atoms) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3; ×10^4 for Ru, Cl, and P Atoms) for the Compound [RuCl(=CHCH=CPh$_2$)(CO)(P*i*Pr$_3$)$_2$]BF$_4$ (6)

atom	*x/a*	*y/b*	*z/c*	U_{eq}^{a}/U_{iso}
Ru	88106(1)	81115(1)	50000	189(1)
Cl	100637(5)	84844(4)	57804(7)	348(2)
P(1)	86165(5)	73481(4)	66425(7)	239(2)
P(2)	92438(5)	85800(4)	32070(7)	228(2)
O	7427(1)	7425(1)	3865(2)	36(1)
C(1)	8137(2)	8872(2)	5363(2)	22(1)
C(2)	7360(2)	9064(1)	5009(3)	26(1)
C(3)	6970(2)	9661(1)	5354(2)	23(1)
C(4)	7259(2)	10069(2)	6330(3)	23(1)
C(5)	7324(2)	9737(2)	7370(3)	29(1)
C(6)	7567(2)	10115(2)	8299(3)	35(1)
C(7)	7779(2)	10824(2)	8192(3)	37(1)
C(8)	7723(2)	11157(2)	7178(3)	37(1)
C(9)	7459(2)	10786(2)	6240(3)	29(1)
C(10)	6226(2)	9902(2)	4797(3)	28(1)
C(11)	5713(2)	10372(2)	5341(3)	34(1)
C(12)	4999(2)	10582(2)	4854(4)	47(1)
C(13)	4799(2)	10348(2)	3792(4)	54(1)
C(14)	5304(2)	9887(2)	3235(4)	53(1)
C(15)	6021(2)	9669(2)	3723(3)	39(1)
C(16)	7956(2)	7683(2)	4295(2)	26(1)
C(17)	9106(2)	6483(2)	6387(3)	36(1)
C(18)	10010(2)	6542(2)	6308(4)	55(1)
C(19)	8737(3)	6110(2)	5378(4)	82(2)
C(20a)^b	7542(3)	7055(3)	6815(5)	32(2)
C(21a)^b	6964(3)	7664(3)	7055(6)	43(2)
C(22a)^b	7420(5)	6452(4)	7660(8)	50(2)
C(20b)^b	7605(6)	7257(6)	7310(10)	30(3)
C(21b)^b	6928(7)	7435(6)	6533(11)	36(3)
C(22b)^b	7457(7)	6588(6)	7994(11)	28(3)
C(23)	9117(2)	7689(2)	7902(3)	35(1)
C(24)	8832(3)	8438(2)	8200(3)	50(1)
C(25)	9085(3)	7207(2)	8927(3)	49(1)
C(26)	9760(2)	7838(2)	2490(3)	32(1)
C(27)	10487(2)	7580(2)	3142(3)	48(1)
C(28)	9199(2)	7226(2)	2233(3)	42(1)
C(29)	9999(2)	9299(2)	3297(3)	32(1)
C(30)	10300(2)	9563(2)	2161(3)	40(1)
C(31)	9748(3)	9917(2)	4037(3)	45(1)
C(32)	8423(2)	8857(2)	2255(3)	30(1)
C(33)	8628(2)	8804(2)	1003(3)	41(1)
C(34)	8113(2)	9598(2)	2489(3)	42(1)
H(1)^c	8356(16)	9183(14)	5817(24)	11(7)
H(2)^c	7138(18)	8811(16)	4430(25)	21(8)
B	8369(3)	3081(3)	5442(5)	58(2)
F(1)	8215(2)	3502(2)	4509(2)	87(1)
F(2)	7743(2)	2610(1)	5558(3)	89(1)
F(3)	8413(2)	3516(2)	6352(3)	89(1)
F(4)	9075(2)	2733(2)	5338(3)	93(1)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^{b} These atoms were involved in disorder of a isopropyl group and refined isotropically. ^{c} The vinylcarbene hydrogen atoms were refined as free isotropic atoms.

(Nujol): ν(C≡O) 1902 (vs), ν(C=C) 1555 (s) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.59 (d, *J*(HH) = 13.2; RuCH=), 5.58 (d, *J*(HH) = 13.2; RuCH=C*H*), 5.07 (t, *J*(HH) = 3.3; =C*H*−CH$_2$−), 2.68 (m; PCH), 2.02, 1.50 (both m; Cy H), 1.27 (dvt, *N* = 13.2, *J*(HH) = 6.3; PCCH$_3$), 1.23 (dvt, *N* = 13.2, *J*(HH) = 6.0; PCCH$_3$). ^{13}C{^{1}H} NMR (75.43 MHz, C$_6$D$_6$): δ 203.84 (t, *J*(PC) = 13.1; RuCO), 143.53 (t, *J*(PC) = 11.1; RuCH=), 139.47 (t, *J*(PC) = 3.2; RuCH=*C*H), 136.24 (t, *J*(PC) = 2.1; RuCH=CH*C*=), 118.33 (s, RuCH=CHC=*C*H), 38.95, 25.88 (both s; CH$_2$), 24.66 (vt, *N* = 19.3; PCH), 23.42, 22.67 (both s; CH$_2$), 20.04, 19.81 (both s; PC*C*H$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, CDCl$_3$): δ 37.39 (s).

Heating of 12 in Toluene at 60 °C: Preparation of RuCl{(*E*)-CH=CHC=CH(CH$_2$)$_3$CH$_2$}(CO)(P*i*Pr$_3$)$_2$ (13). A solution of **12** (120 mg, 0.20 mmol) was heated in 10 mL of toluene for 4 days at 60 °C. The solution was filtered off and concentrated until a violet precipitate was formed; addition of pentane completed precipitation. The violet solid was filtered off, washed with pentane, and dried in vacuo. Yield: 85 mg (72%).

Table 3. Crystal Data and Data Collection and Refinement for [RuCl(=CHCH=CPh$_2$)(CO)(P*i*Pr$_3$)$_2$]BF$_4$ (6)

Crystal Data	
formula	$C_{34}H_{54}BClF_4OP_2Ru$
mol wt	764.07
color and habit	red, transparent prism
cryst size, mm	0.466 × 0.312 × 0.581
cryst syst	orthorhombic
space group	*Pna*2$_1$ (No. 33)
a, Å	16.681(1)
b, Å	18.876(1)
c, Å	11.967(1)
V, Å^3	3768.1(4)
Z	4
D(calcd), g cm^{-3}	1.347
Data Collection and Refinement	
diffractometer	4-circle Siemens-STOE AED
λ(Mo K$_\alpha$), Å; technique	0.710 73; bisecting geometry
monochromator	graphite oriented
μ, mm^{-1}	0.61
scan type	ω/2θ
2θ range, deg	$3 \le 2\theta \le 50$
temp (K)	173
no. of data collect	8051
no. of unique data	6666 (R_{int} = 0.017)
no. of unique obsd data	6457 ($F_o \ge 4.0\sigma(F_o)$)
no. of params refined	404
R, R_w^{a}	0.0273, 0.0281

^{a} $R = (\Sigma[|F_o| - |F_c|])/\Sigma F_o$; $R_w = (\Sigma([|F_o| - |F_c|])w^{1/2})/\Sigma(|F_o|w^{1/2})$, $w^{-1} = \sigma^2(F_o) + 0.000033(F_o)^2$.

Reaction of 12 with HBF$_4$·OEt$_2$: Preparation of {RuCl{=CHCH=C(CH$_2$)$_4$CH$_2$}(CO)(P*i*Pr$_3$)$_2$]BF$_4$ (14). A solution of **12** (65 mg, 0.11 mmol) in 10 mL of Et$_2$O was treated dropwise at room temperature with HBF$_4$·OEt$_2$ (54%; 17 μL, 0.12 mmol). The orange solution was evaporated to dryness. The residue was recrystallized from CH$_2$Cl$_2$−Et$_2$O at −78 °C. The product is a yellow solid. Yield: 64 mg (85%). Anal. Calcd for $C_{27}H_{52}BClF_4OP_2Ru$: C, 47.83; H, 7.73. Found: C, 47.56; H, 7.73. IR (Nujol): ν(C≡O) 1968 (vs), ν(C=C) 1550 (s), ν(BF$_4^-$) 1050 (s, br) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, −40 °C): δ 15.95 (d, *J*(HH) = 11.7; Ru=CH−), 7.53 (d, *J*(HH) = 11.4; −CH=), 2.81 (m; PCH), 2.50, 2.29, 1.78, 1.66 (all m, br; Cy H), 1.28 (dvt, *N* = 14.3, *J*(HH) = 7.0; PCCH$_3$), 1.25 (dvt, *N* = 14.8, *J*(HH) = 7.3; PCCH$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, CDCl$_3$, −40 °C): δ 56.35 (s).

Reaction of OsCl{(*Z*)-CH=CHCH$_2$OH}(CO)(P*i*Pr$_3$)$_2$ with HBF$_4$·OEt$_2$: Preparation of [OsCl(=CHCH=CH$_2$)(CO)(H$_2$O)(P*i*Pr$_3$)$_2$]BF$_4$. A solution of OsCl{(*Z*)-CH=CHCH$_2$OH}(CO)(P*i*Pr$_3$)$_2$ (150 mg, 0.24 mmol) in 10 mL of Et$_2$O was treated dropwise at room temperature with HBF$_4$·OEt$_2$ (54%; 32 μL, 0.24 mmol) and stirred at room temperature. After 6 h the dark brown precipitate was filtered off and washed repeatedly with Et$_2$O. Yield: 130 mg (75%). Anal. Calcd for $C_{22}H_{47}BClF_4O_2P_2Os$: C, 36.75; H, 6.43. Found: C, 36.98; H, 6.63. IR (Nujol): ν(OH) 3500 (m, br), ν(C≡O) 1950 (vs), ν(C=C) 1535 (w), ν(BF$_4^-$) 1070 (s, br) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 17.06 (br; Os=CH−), 6.85 (s; −CH=), 4.56 (m; =CH$_2$), 2.61 (m; PCH), 2.19 (m; OH$_2$), 1.41 (dvt, *N* = 14.8, *J*(HH) = 9.8; PCCH$_3$), 1.07 (dvt, *N* = 13.6, *J*(HH) = 9.0; PCCH$_3$). ^{13}C{^{1}H} NMR (75.33 MHz, CDCl$_3$): δ 289.86 (br, Os=CH), 179.30 (t, *J*(PC) = 9.65; OsCO), 66.74 (s; −CH=), 57.13 (s; =CH$_2$), 24.03 (vt, *N* = 13.1; PCH), 19.93, 18.58 (both s: PC*C*H$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, CDCl$_3$): δ 24.84 (s).

X-ray Structure Analysis of [RuCl(=CHCH=CHPh$_2$)(CO)(P*i*Pr$_3$)$_2$]BF$_4$ (6). Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of Et$_2$O into a concentrated solution of **6** in CH$_2$Cl$_2$. Atomic coordinates and U_{eq} values are listed in Table 2. A summary of crystal data, intensity collection procedure, and refinement data is reported in Table 3. The prismatic crystal studied was glued on a glass fiber and mounted on a Siemens AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 56 reflections in the range $20 \leq 2\theta \leq 47°$. The 8051 recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no variation was observed. Reflections were also corrected for absorption by a numerical method based on indexed morphological faces.[18]

The structure was solved by Patterson (Ru atom) and conventional Fourier techniques. An isopropyl group of a phosphine ligand (C(20)–C(22) atoms) was observed to be disordered. The disordered group was modeled by including two different isopropyl groups with a complementary occupancy factor refined to a final value of 0.67(1) for C(20a), C(21a), and C(22a). Refinement was carried out by full-matrix least squares with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms, except those involved in disorder. Hydrogen atoms were located from difference Fourier maps and included in the refinement riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Ru, Cl, and P, were taken from ref 19. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weight defined as $w = 1/(\sigma^2(F_o) + 0.000033(F_o)^2)$. Final R and R_w values were 0.0273 and 0.0281. All calculations were performed by use of the SHELXTL-PLUS system of computer programs.[20]

Acknowledgment. We thank the DGICYT (Project PB 92-0092, Programa de Promoción General del Conocimiento) and EU (Project: Selective Processes and Catalysis Involving Small Molecules) for financial support. E.O. thanks the DGA (Diputación General de Aragón) for a grant.

Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, experimental details of the X-ray study, bond distances and angles, selected least-squares planes, and interatomic distances (12 pages). Ordering information is given on any current masthead page.

OM940241D

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