$(C_5Me_5)Ru$–Vinylidene Complexes from Terminal Alkynes and Propargyl Alcohol Derivatives

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Received June 10, 1994[⊗]

Complex $(C_5Me_5)(PMe_2Ph)_2RuCl$ (**1**) reacts with phenylacetylene and (trimethylsilyl)-acetylene, in methanol with NH_4PF_6, to afford vinylidene complexes $[(C_5Me_5)(PMe_2Ph)_2Ru{=}C{=}CHR]PF_6$ (R = Ph (**3**), H (**5**), respectively). Complexes **3** and **5** are stable toward the addition of alcohol due to the steric hindrance and electron-releasing capability of the $(C_5Me_5)(PMe_2Ph)_2Ru$ moiety as indicated by an oxidation potential of $E_{1/2}$ = 0.30 VSCE for **1**. Complex **3** is slowly oxidized in the presence of air to give $[(C_5Me_5)(PMe_2Ph)_2RuCO]PF_6$ (**4**). The activation of $HC{\equiv}CCH_2OH$ with **1** leads to the formation of the vinylidene moiety $[Ru{=}C{=}CHCH_2OH]PF_6$ (**7**) in dichloromethane and $[Ru{=}C{=}CHCH_2OMe]PF_6$ (**6**) in methanol, showing the lability of the hydroxy group without dehydration. The activation of $HC{\equiv}CCH(OH)Me$ with **1** allows the formation of chiral vinylidene $[(C_5Me_5)(PMe_2Ph)_2Ru{=}C{=}CHCH(OMe)Me]PF_6$ (**8**). The vinylidenes **3**, **6**, and **8** are easily deprotonated to afford the corresponding alkynylruthenium complexes $(C_5Me_5)(PMe_2Ph)_2RuC{\equiv}CR'$ (R′ = Ph (**9**), CH_2OMe (**10**), CH(OMe)Me (**11**)). The molecular structures of $[(C_5Me_5)(PMe_2Ph)_2Ru{=}C{=}CHPh)][(C_5Me_5)(PMe_2Ph)_2Ru(CO)](PF_6)_2$ (**3·4**) and $[(C_5Me_5)(PMe_2Ph)_2Ru{=}C{=}CHCH(Me)OMe]PF_6$ (**8**) were determined by X-ray crystallographic analysis. Complexes **3·4** crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 12.468(1) Å, b = 14.282(2) Å, c = 36.297(3) Å, z = 4, R = 0.064, and R_w = 0.0069. Complex **8** crystallizes in the orthorhombic space group $Pbcn$ with a = 17.771(2) Å, b = 19.277(3) Å, c = 20.172(6) Å, z = 8, R = 0.045, and R_w = 0.043.

Introduction

During the last decade, the chemistry of metal vinylidene complexes has been the object of a significant development due to the discovery of general synthetic methods[1] and their use to generate new metal carbenes[2,3] and carbynes.[4] Monosubstituted vinylidene complexes, arising from the (η^2-alkyne)metal → (η^1-vinylidene)metal tautomerism (eq 1), have been at the basis of innovation, especially because this process constitutes the first step of terminal alkyne metal activation and provides an electrophilic activation, due to the heteroallene nature of the M=C=CHR moiety. These monosubstituted vinylidenes are excellent precursors, even when they are unstable,[5] of carbene complexes[1-3] *via* nucleophilic addition and of initiation of alkyne polymerization.[6] They have been recognized as active species in selective homogeneous catalytic transformations of terminal alkynes. They were first suggested to explain the regioselective addition of carbamates to the terminal alkyne carbon C(1), catalyzed by (arene)ruthenium(II) complexes,[7] and to alkenylacetylenes.[8] A ruthenium vinylidene intermediate is likely a crucial catalytic species in the dimerization of terminal alkynes into butatriene[9] or enynes,[10] for which the regioselectivity is opposite to that provided by palladium acetate catalysis,[11] and in the anti-Markovnikov addition of carboxylic acids to generate *Z* enol esters.[12] The Ru=C=CHR moiety has been shown to be the effective catalytic species in the coupling reaction of allylic alcohols with terminal alkynes in the presence of $RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)$ to produce unsaturated ketones.[13]

It is noteworthy that **catalytic** reactions involving metal vinylidene intermediates are promoted by ruthe-

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⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1994.
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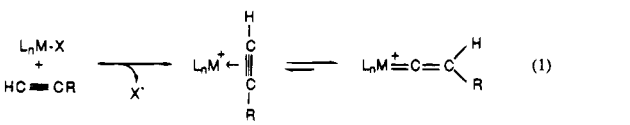
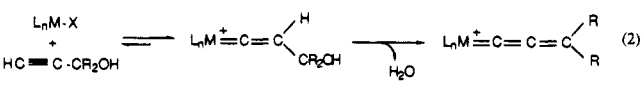
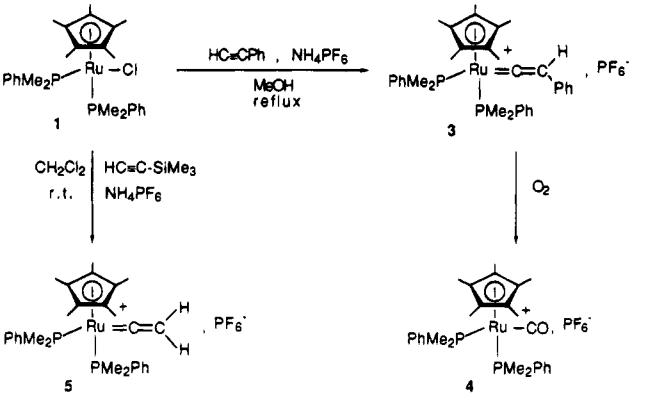
nium(II) precursors. Actually, some ruthenium(II) complexes have been shown to easily give vinylidene complexes, $Ru^{+}=C=CHR$, by displacement of a halide, in the presence of both a noncoordinating anion and a terminal alkyne, from $RuCl(L_2)(\eta^5\text{-}C_5H_5)$ [L_2: $(PPh_3)_2$,[14,15] $(PMe_3)_2$,[16] $(PMe_2Ph)_2$,[17] $Ph_2PCH_2CH_2PPh_2$,[15,18a] or a chiral diphosphine[18]], $RuCl_2(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)_2$,[19] $RuCl_2(\eta^2\text{-}^iPr_2PCH_2CO_2Me)_2$,[19] and $RuCl_2(\eta^2\text{-}Ph_2P(CH_2)_n\text{-}PPh_2)_2$ (n = 1,[20] 2[21]). The comparative study of these reactions suggests that only electron rich ruthenium(II) complexes allow the isolation of ruthenium vinylidene complexes. Indeed, the unsubstituted vinylidene derivatives ($LnRu=C=CH_2$), the most reactive ones, were structurally characterized by X-ray diffraction study only for the most electron-releasing ancillary ligands in $[Ru=C=CH_2(PMe_2Ph)_2(C_5H_5)]BF_4$[17] and $[Ru=C=CH_2(Ph_2PCH_2PPh_2)_2Cl]PF_6$.[20] On the other hand, the very **electrophilic** (arene)ruthenium intermediates, $[Ru=C=CHR(Cl)(PR_3)(C_6R_6)]PF_6$,[5] are very reactive and provide an easy access to a variety of ruthenium carbene complexes. The study of $RuCl_2(dppm)_2$[20] and $RuCl_2(dppe)_2$[21] derivatives toward the activation of terminal alkynes (eq 1) and of propargyl alcohol derivatives (eq 2) suggested that, beside the necessary electron richness of the ruthenium(II) atom, the bulkiness of the ligands was a determining factor for the stabilization of vinylidene- or allenylideneruthenium intermediates.





To check this hypothesis, we have studied the influence of a combination of very bulky and electron-releasing ligands on the ruthenium site. The C_5Me_5 ligand is electron rich enough to stabilize ruthenium(IV) complexes[22] or to favor ruthenium(IV) intermediates in catalytic C−C bond formation.[23] We now report the first example of activation of terminal alkynes with a C_5Me_5Ru complex, $RuCl(PMe_2Ph)_2(C_5Me_5)$ (**1**), and we show that (i) **1** favors the formation of vinylidene complexes, especially from propargyl alcohol derivatives, rather than their dehydration into allenylidene intermediates, (ii) the hydroxy group of (hydroxymethyl)-vinylidenes is labile, and (iii) the corresponding vinylideneruthenium complexes are acidic and provide an easy access to acetylide derivatives. The X-ray structure determinations of $[Ru=C=CHPh(PMe_2Ph)_2(C_5Me_5)]$-$[Ru(CO)(PMe_2Ph)_2(C_5Me_5)](PF_6)_2$ and $[Ru=C=CHCH(OMe)Me(PMe_2Ph)_2(C_5Me_5)]PF_6$ are reported.

Scheme 1



Results and Discussion

(1) Preparation of Ru=C=CHR Complexes and Electron Richness of $RuCl(PMe_2Ph)_2(C_5Me_5)$. Analogously to the preparation of $RuCl(PMe_3)_2(C_5Me_5)$,[24] the precursors $RuCl(PMe_2Ph)_2(C_5Me_5)$ (**1**) and $RuCl(PMePh_2)_2(C_5Me_5)$ (**2**) were obtained by addition of the corresponding phosphine to $[Ru(\mu_3\text{-}Cl)(C_5Me_5)]_4$[25] in 87 and 89% yield, respectively. Complex **1** reacts with phenylacetylene and NH_4PF_6 in methanol at reflux and is completely transformed to give the orange vinylidene complex **3** (85%) (Scheme 1). By contrast, the same reaction with **2** afforded a mixture of the corresponding vinylidene and **2**. The complex **3** shows in ^{31}P [^1H] NMR two types of PMe methyl groups and in ^1H NMR two sets of $X_3AA'X'_3$ patterns for the MePP'Me' groups. A low-field Ru=C ^{13}C NMR resonance (δ = 354.3 ppm, $^2J_{PC}$ = 15.2 Hz) is observed. This low-field resonance is commonly observed with vinylidene complexes[14-21] and has recently been explained as a consequence of a paramagnetic σ_P term rather than of an electron deficiency.[26]

Complex **3** is slowly oxidized in solution in the presence of air to give mixtures of **3** and the carbonyl complex $[RuCO(PMe_2Ph)_2(C_5Me_5)]PF_6$ (**4**). Actually crystallizations of **3** in non-deoxygenated chloroform afforded monocrystals containing both **3** and **4** moieties and allowed their structural study.

Under milder conditions than that of the **1** → **3** transformation, complex **1** also reacts with $Me_3SiC{\equiv}CH$

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Table 1. Oxidation Potentials (Ru^{II}/Ru^{III}) of Ruthenium Complexes

complex	$E_{1/2}$ (V)	ΔE_p (mV)[c]	ref
$(C_6Me_6)RuLCl_2$			
L = PMe_2Ph	0.82[a]	70	5
L = PPh_3	0.92[a]	80	5
$(C_5H_5)RuL_2Cl$			
L = PMe_2Ph	0.44[b]	–	28
L = PPh_3	0.53[a]	60	5
$(C_5Me_5)Ru(PMe_2Ph)_2Cl$ (**1**)	0.30[a]	70	–

[a] Cyclic voltammetry in solution in CH_3CN, 200 mV/s, 0.1 M Bu_4NPF_6, Pt/SCE. [b] Cyclic voltammetry in solution in CH_2Cl_2, 0.1 M Bu_4NPF_6, Pt/SCE. [c] ΔE_p: anodic to cathodic peak separation.

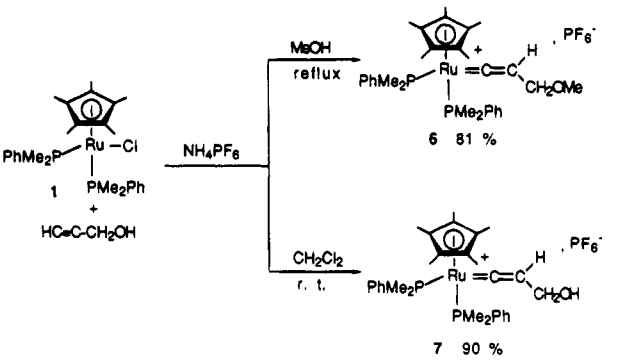
in the presence of NH_4PF_6, in dichloromethane at room temperature for 6 h. The yellow unsubstituted vinylideneruthenium complex **5** (Scheme 1) was obtained in 70% yield. The formation of **5** can be explained *via* the formation of the corresponding (trimethylsilyl)-vinylidene and cleavage of the carbon–silyl bond in the presence of the NH_4^+ cation. Such a cleavage was observed in the formation of ruthenium vinylidene[16] and carbene complexes[5] in methanol. Complex **5** in ^{13}C NMR shows a signal at low field (δ = 347 ppm, $^2J_{PC}$ = 15.7 Hz) for the Ru=C carbon nucleus.

The complex **3** is very stable in methanol and does not give the expected carbene complex $[Ru{=}C(OMe)CH_2Ph(L)_2C_5Me_5]PF_6$ (**A**) *via* addition of the alcohol on carbon C(1), even after a 48 h reflux in methanol. This absence of reaction contrasts with that of electrophilic $[(arene)Cl(PR_3)Ru{=}C{=}CHPh]PF_6$ intermediates[5,27] that lead to carbenes analogous to **A**, within a few seconds, and also with that of the corresponding $[(C_5H_5)(Ph_3P)_2Ru{=}C{=}CHPh]PF_6$ complex that gives a derivative of type **A** on reflux in methanol.[14]

The inertness of **3** toward the formation of **A** can be explained in terms of high electron density at the ruthenium site. The oxidation potential of **3** (E = 0.30 V_{SCE}) can be compared to that of ruthenium complexes leading to vinylidene derivatives (Table 1). This comparison shows that complex **1** is more electron rich than related $(C_5H_5)Ru(PR_3)_2Cl$ derivatives and much more electron rich than the reactive $(arene)RuCl_2(L)$ complexes (L = PR_3,[5] CNR[29]). The oxidation potential of $[LnRu{=}C{=}CHR]PF_6$ complexes cannot be measured, for electrochemical oxidation takes place with decomposition. Assuming that the same sequence of electron richness can be observed in the LnRuCl precursors and their corresponding $[LnRu{=}C{=}CHPh]PF_6$ derivatives, the electron density transfer from the $(C_5Me_5)(PMe_2Ph)_2Ru^+$ moiety to the vinylidene ligand should be the highest and thus the electrophilicity of the C(1) carbon of **3** the lowest. The steric hindrance of the ancillary ligands (C_5Me_5 and 2 PMe_2Ph) is also the most important in **3** as compared to the other ruthenium precursors (Table 1), and the carbon C(1) is expected to be less accessible by the weak nucleophile MeOH.

(2) Activation of Propargyl Alcohol by Complex 1. Propargylic alcohol derivatives are very easily accessible terminal alkynes, and their activation by ruthenium(II) complexes has been shown to generate, *via* spontaneous dehydration, either stable allenylidene complexes (eq 2) such as $[Ru(=C=C=CPh_2)(PMe_3)_2(C_5H_5)]PF_6$,[30] $[Ru(=C=C=C(Ph)(C_5H_4FeC_5H_5))Cl(PMe_3)(C_6Me_6)]PF_6$,[31] and $[Ru{=}C{=}C{=}CR_2(Cl)(Ph_2PCH_2PPh_2)_2]PF_6$[20] or reactive ones to give deprotonation and a dimerization product[32] or, when they are electrophilic, alkenylcarbene complexes such as $[Ru{=}C(OR)CH{=}CR_2(Cl)(PMe_3)(C_6Me_6)]PF_6$[31] on addition of alcohol. The electron rich and sterically hindered ruthenium complex **1** has thus been reacted with three propargylic alcohol derivatives $HC{\equiv}CCR_2OH$ (R,R = H,H; H,Me; Me,Me).

Scheme 2



Complex **1** reacts with prop-2-yn-1-ol, in methanol on reflux, with $NaPF_6$ to give the red (3-methoxyvinylidene)-ruthenium complex **6** (81%) (Scheme 2). When the same compounds were reacted in dichloromethane at room temperature, the orange 3-hydroxyvinylidene complex **7** (90%) was obtained. ^{13}C NMR spectra of **6** and **7** indicate the presence of vinylidene carbon at low field (δ = 329.0 ppm, $^2J_{PC}$ = 15.2 Hz for **6** and δ = 346.4 ppm, ($^2J_{PC}$ = 15.2 Hz for **7**). The ^1H NMR spectra show a vinylidene proton coupled with two identical methylene protons (δ = 4.63 ppm, ($^3J_{HH}$ = 8.0 Hz, $^4J_{PH}$ = 2.2 Hz for **6** and δ = 4.83 ppm, $^3J_{HH}$ = 8.1 Hz, $^4J_{PH}$ = 2.2 Hz for **7**).

The hydroxyvinylidene **7** is especially stable toward dehydration. By contrast, from $RuCl(PR_3)_2C_5H_5$ and $HC{\equiv}CCR_2OH$ ($R \neq H$), such a hydroxyvinylidene intermediate could not be observed but its dehydration complex was obtained[30,33] Moreover, from the reaction of $RuCl_2(PMe_3)(C_6Me_6)$ and $HC{\equiv}CCH_2OH$ in methanol, the formation of $[Ru{=}C(OMe)(CH_2CH_2OMe)(Cl)(PMe_3)(C_6Me_6)]PF_6$[5] was only observed and was consistent with initial dehydration and addition of 2 mol of methanol. It is noteworthy that a hydroxyvinylidene derivative was isolated from $RuCl_2(Ph_2PCH_2PPh_2)_2$ which was electron rich and contained bulky ligands.[20]

The hydroxy group of **7** was shown to be labile and easily replaced by the methoxide group: on reflux of **7** in methanol, complex **6** was isolated in 96% yield. This exchange could take place by dehydration of **7** to give the unsubstituted allenylidene followed by addition of methanol (eq 3). However, the allenylidene intermediate was not observed even on reflux with Ph_3P as an attempt to trap the corresponding phosphonium salt on addition of PPh_3 on carbon C(3) of moiety **I**.

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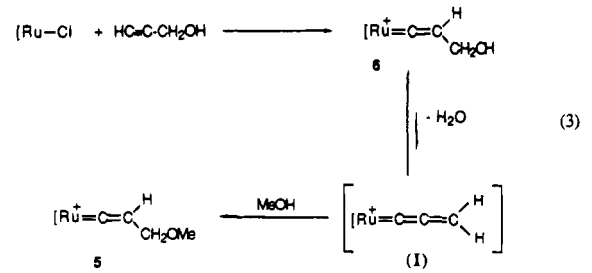
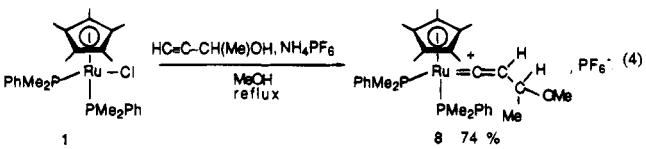


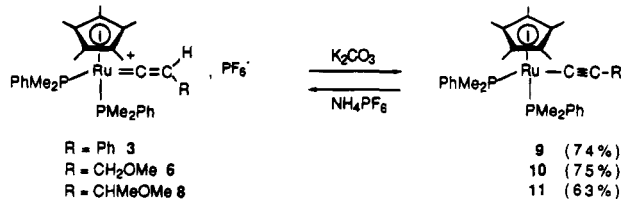
(3) Activation of But-3-yn-2-ol. The activation of the secondary alcohol HC≡CCH(Me)OH by complex **1** in methanol on reflux led to the yellow (3-methoxybut-1-enylidene)ruthenium derivative **8** (74%) containing a C(3) chiral group. Compound **8** results from the hydroxyvinylidene formation followed by the substitution of the hydroxy group by methanol (eq 4). The presence of a chiral group in **8** leads to the nonequivalence of ^{31}P nuclei in ^{31}P NMR (δ = 15.3 and 14.4 ppm, $^2J_{PP}$ = 35.7 Hz). A low-field triplet is observed in ^{13}C NMR at δ = 345 ppm ($^2J_{PC}$ = 15.2 Hz) for the vinylidene Ru=C carbon nucleus. In ^1H NMR the selective irradiation of the *Me*C(3) proton resonance allows to show that the HC(3) proton (δ = 4.47 ppm, $^3J_{HH}$ = 7.6 and 6.1 Hz) is involved in an ABX_3 system (=CH*CH*Me) and that the vinylidene HC(2) resonance (δ = 4.34 ppm, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 2.3 Hz) is part of an ABY_2 system (P_2-Ru=C=*CH*CH). The structure of **8** was confirmed by an X-ray diffraction study.



The **1** → **8** transformation shows that monosubstitution at C(3) does not favor dehydration of the vinylidene complex. However complex **8** may result from the formation of the secondary allenylideneruthenium moiety (Ru^+=C=C=CHMe) that was previously observed only in the isolated complexes [Ru=C=C=CHAr(Cl)-$(Ph_2PCH_2PPh_2)_2$]PF_6.[34] The latter were shown to be the object of addition of methoxide at the secondary C(3) carbon atom.[34]

The reaction of **1** with HC≡CCMe$_2$OH and $NaPF_6$ in methanol on reflux leads to the formation of a violet oil. When the reaction was performed in dichloromethane at room temperature, the same violet oily product was obtained. This compound could not be characterized but shows in ^1H NMR two multiplets between 1 and 2 ppm (δ = 1.6 and 1.4 ppm), consistent with the presence of two different $C_5Me_5RuP_2$ moieties. The cyclic voltammetry of this violet complex in propylene carbonate shows two reversible oxidation waves: $E_{1/2}$ = −0.10 V_{SCE} and $E_{1/2}$ = 0.24 V_{SCE}. This observation is consistent with the presence of two different ruthenium moieties and their reversible Ru^{II} ⇌ Ru^{III} oxidation. We can suggest for the compound a bimetallic structure on the basis of the characterized product obtained by Selegue et al.[32] on reaction of $RuCl(PPh_3)_2C_5H_5$ with HC≡C-CMe$_2$OH and corresponding to the coupling of two dehydrated species (Ru^+=C=CHCMe=CH$_2$ and Ru^+=C=C=CMe$_2$). Another coupling reaction of the propargylic alcohol derivative promoted by $RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)$ has just been reported.[35]

Scheme 3



The comparative activation by **1** of HC≡CCH$_2$OH, HC≡CCHMeOH, and HC≡CCMe$_2$OH shows that the presence of a hydrogen atom on carbon C(3) favors the formation of stable 3-hydroxyvinylidene derivatives rather than their dehydration.

(4) Access to Ruthenium Acetylides by Deprotonation of Vinylidenes. The direct access to ruthenium acetylide complexes by classical substitution of a chloride by a lithium, magnesium, or tin acetylide is not straightforward, especially with hindered ruthenium complexes.[20c] The ease of access to cationic vinylidenes directly from terminal alkynes and complex **1** allowed the study of their deprotonation, as a route to (C_5Me_5)-RuC≡CR derivatives.

Complexes **3**, **6**, and **8** can be easily deprotonated into their corresponding acetylides by a variety of basic reagents such as alumina, sodium methoxide, and DBU (diazabicycloundecene). However, potassium carbonate offers the best compromise for the ease of separation and yields. Thus complexes **3**, **6**, and **8** in dichloromethane were treated with an excess of K_2CO_3 at room temperature for 0.5−2 h to give the yellow complexes **9** (74%), **10** (75%), and **11** (63%), respectively (Scheme 3). The spectroscopic data of **9**−**11** are given in Table 2. It is noteworthy that the alkynyl derivative **11** that possesses a chiral group shows nonequivalent diastereotopic ^{31}P nuclei. The acetylide **9** was obtained in one pot in 74% yield directly from **1** in methanol by successive addition of an excess of phenylacetylene and sodium methoxide. However, this method cannot be used for propargyl alcohol derivatives.

The alkynylruthenium derivatives **9**−**11** can be reprotonated to give back the vinylidenes **3**, **6**, and **8**, respectively. Alkynyl complexes **9**−**11** are basic enough to be protonated simply by NH_4PF_6. After 15 min of reaction at room temperature, complexes **3** (86%), **6** (97%), and **8** (95%) were obtained from **9**−**11**, respectively.

(5) X-ray Crystal Structure of [Ru=C=CHPh-(C_5Me_5)(PMe_2Ph)$_2$][Ru(CO)(C_5Me_5)(PMe_2Ph)$_2$]-(PF_6)$_2$ (3·4). Successive crystallizations of complex **3** in non-deoxygenated chloroform afforded monocrystals for which the X-ray diffraction study revealed in the cell two different molecules, [Ru=C=CHPh(C_5Me_5)(PMe_2Ph)$_2$]PF_6 (**3**) and [Ru(CO)(C_5Me_5)(PMe_2Ph)$_2$]PF_6 (**4**). The molecular structures of **3** and **4** are shown in Figures 1 and 2, respectively. Experimental crystallographic data, selected bond distances and angles, and positional parameters are given in Tables 3−5, respectively. The ruthenium vinylidene Ru=C=C moiety is almost linear (Ru−C(51)−C(52): 174(1)°). The (vinylidene)C−Ru bond

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Table 2. Spectroscopic Data of $(C_5Me_5)(PMe_2Ph)RuC{\equiv}CR$ Complexes

R	IR ($\nu_{C\equiv C}$, cm^{-1})	$^{31}P[^1H]$ NMR (δ, ppm)	^1H NMR (δ, ppm) (J, Hz)	
			C_5Me_5 ($^4J_{PH}$)	PMe ($^2J_{PH} + {}^4J_{PH}$)
Ph (**9**)	2045	21.86	1.52 (1.3)	1.66 (8.5) 1.61 (8.0)
CH_2OMe (**10**)	2070	20.60	1.43 (1.5)	1.60 (8.5) 1.55 (8.1)
CHMeOMe (**11**)	2064	22.06 21.74 ($^2J_{PP}$ = 33 Hz)	1.42 (1.5)	1.60 (7.9) 1.56 (7.6)

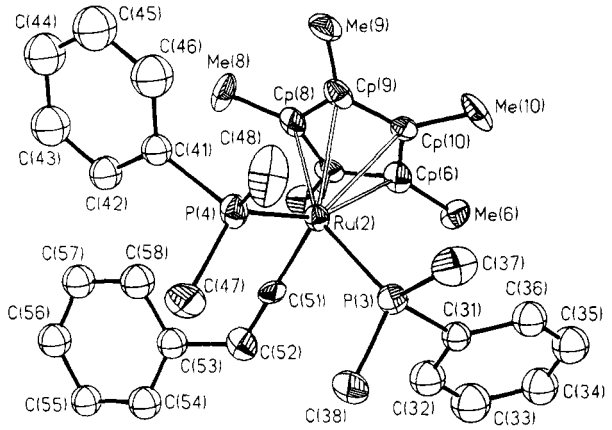

Figure 1. Molecular diagram of complex $[(C_5Me_5)(PMe_2Ph)_2Ru{=}C{=}CHPh]PF_6$ (**3**).

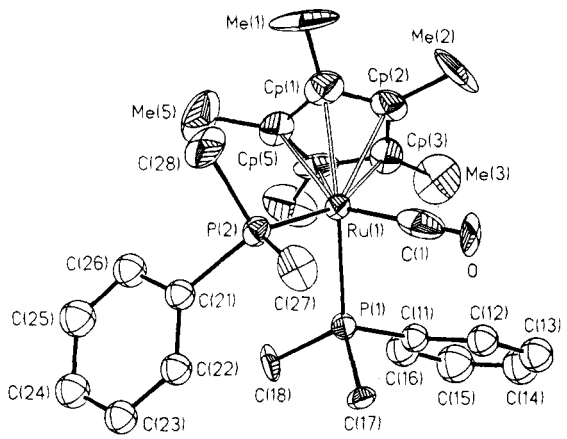

Figure 2. Molecular diagram of complex $[(C_5Me_5)(PMe_2Ph)_2Ru(CO)]PF_6$ (**4**).

length Ru(2)–C(51) of 1.76(1) Å is very short as compared to that of other vinylideneruthenium complexes (Table 6). Only in $Ru{=}C{=}CHPh(Cl)_2(^iPr_2PCH_2CH_2OMe)_2$ [19] was a shorter Ru=C bond distance observed. This is likely to result from the electron-releasing capability of the $(C_5Me_5)(PhMe_2P)_2Ru$ moiety toward the electron-withdrawing vinylidene ligand. It is noteworthy that the molecular structure of **4** is closely related to that of **3**. The CO ligand does not modify significantly the arrangement of ligands and the structural data of the $(C_5Me_5)(PhMe_2P)_2Ru$ moiety with respect to the C=CHPh ligand in **3**. For instance, the P–Ru–P angle is 92.1(1)° in **3** and 92.7(1)° in **4**, and the P–Ru–C angles are 88.4(4)° and 89.4(5)° in **3** and 89.0(4)° and 88.9(4)° in **4**. This similarity is likely responsible for the inclusion in the cell of the two different molecules, **3** and **4**.

(6) X-ray Crystal Structure of $[Ru{=}C{=}CHCH(OMe)Me(PMe_2Ph)_2(C_5Me_5)]PF_6$, (8). The molecular structure of **8** is shown in Figure 3. Experimental crystallographic data, selected bond distances and angles, and positional parameters are given in Tables 3, 7, and 8, respectively. The molecular structure of **8** revealed a chiral vinylidene group coordinated to the ruthenium metal center. The Ru-vinylidenic Cα atom bond distance, Ru–C(11) (1.854(8) Å), is comparable to the double bond Ru=C observed in the $[(C_5H_5)Ru(PR_3)_2(=C{=}CR^1R^2)]^+$ complexes (Table 6). The C(11)–C(12) distance (1.29(1) Å) corresponds to a double-bond length. The ruthenium vinylidene carbon atoms are almost in a linear assembly with the Ru–C(11)–C(12) angle of 174.6(7)°. In $[(C_5H_5)Ru(PR_3)_2(=C{=}CR^1R^2)]^+$ cations, the vinylidene plane is orthogonal to the plane bisecting the

Table 3. Experimental Crystallographic Data

	complex **3**·**4**	complex **8**
formula	$Ru_2P_4C_{61}H_{80}O{\cdot}2PF_6$	$RuP_2C_{31}OH_{35}{\cdot}PF_6{\cdot}^1/_2CH_3OH$
mol wt	1445.3	731.6
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	*Pbcn*
a, Å	12.468(1)	17.771(2)
b, Å	14.282(2)	19.277(3)
c, Å	36.297(3)	20.172(6)
V, Å^3	6463(1)	6910(2)
Z	4	8
D_{calc}, g/cm^{-3}	1.49	1.41
cryst size, mm	0.24 × 0.28 × 0.55	0.15 × 0.24 × 0.35
2θ range, deg	3–44	50
diffractometer	CAD4	CAD4
λ (Mo Kα radiation), Å	0.7107	0.71069
T, K	292	294
F(000)	2960	2976
abs coeff μ, cm^{-1}	6.1	6.34
scan type	ω-scan	ω/2θ
no. of reflcns measured	5579	
no. of unique reflcns	5369	8235
no. of observed reflcns, $F_0 > 3\sigma(F_0)$	5032	1921
R; R_w	0.064; 0.069	0.045; 0.043

Table 4. Selected Bond Distances and Angles for 3 and 4[a]

atoms	bond distances (Å)	atoms	bond angles (deg)
	Compound **3**		
Ru(2)–C(51)	1.76(1)	C(51)–Ru(2)–P(3)	88.4(4)
Ru(2)–P(3)	2.341(4)	C(51)–Ru(2)–P(4)	89.4(5)
Ru(2)–P(4)	2.314(4)	C(51)–Ru(2)–Cp(2)	125.9(8)
Ru(2)–C(Cp(2))	2.25–2.35	P(3)–Ru(2)–P(4)	92.1(1)
Ru–Cp(2)	1.96(1)	Ru(2)–C(51)–C(52)	174(1)
C(51)–C(52)	1.34(2)	C(51)–C(52)–C(53)	128(1)
C(52)–C(53)	1.58(2)	Ru(2)–P(3)–C(Cp(2))	110–117(1)
P(3,4)–C(Cp(2))	1.79–1.86(2)	Ru(2)–P(4)–C(Cp(2))	116–118
		C(47)–P(4)–C(48)	101(1)
	Compound **4**		
Ru–C(1)	1.86(1)	C(1)–Ru–P(1)	89.0(4)
Ru–P(1)	2.329(4)	C(1)–Ru–P(2)	88.9(4)
Ru–P(2)	2.347(4)	C(1)–Ru–Cp	121.6(7)
Ru–C(Cp)	2.25–2.29	P(1)–Ru–P(2)	92.7(1)
Ru–Cp	1.92(2)	Ru–C(1)–O(2)	178(1)
C(1)–O(2)	1.14(2)		
P(1,2)–C(Cp)	1.82–1.85		

[a] C(Cp) = C_5 carbon atoms of the C_5Me_5 ring.

Table 5. Positional and Equivalent Isotropic Thermal Parameters for 3 and 4[a]

atom	x	y	z	U_{eq} (Å^2)	atom	x	y	z	U_{eq} (Å^2)
				Compound **4**					
Ru(1)	0.05383(9)	0.01879(8)	0.04292(3)	0.0366(4)	C(15)	0.4925(6)	0.0826(5)	0.0254(2)	0.096(4)
Cp(1)	−0.065(1)	0.137(1)	0.0418(6)	0.079(3)	C(16)	0.3970(6)	0.0410(5)	0.0140(2)	0.071(4)
Cp(2)	0.019(2)	0.165(1)	0.0621(5)	0.068(3)	C(17)	0.230(1)	−0.1774(9)	0.0486(4)	0.040(3)
Cp(3)	0.116(2)	0.169(1)	0.0413(6)	0.073(3)	C(18)	0.231(1)	−0.093(1)	−0.0224(4)	0.065(3)
Cp(4)	0.084(1)	0.144(1)	0.0047(6)	0.076(3)	C(21)	−0.0348(6)	−0.1826(5)	−0.0073(2)	0.047(3)
Cp(5)	−0.021(2)	0.123(1)	0.0033(6)	0.074(3)	C(22)	0.0111(6)	−0.2715(5)	−0.0050(2)	0.050(3)
Me(1)	−0.189(1)	0.139(1)	0.0548(8)	0.145(3)	C(23)	0.0356(6)	−0.3208(5)	−0.0371(2)	0.057(4)
Me(2)	0.009(2)	0.197(1)	0.1014(5)	0.132(3)	C(24)	0.0143(6)	−0.2813(5)	−0.0715(2)	0.066(4)
Me(3)	0.221(3)	0.210(1)	0.0489(8)	0.141(3)	C(25)	−0.0316(6)	−0.1924(5)	−0.0738(2)	0.075(4)
Me(4)	0.162(2)	0.153(1)	−0.0309(6)	0.138(3)	C(26)	−0.0562(6)	−0.1430(5)	−0.0417(2)	0.061(4)
Me(5)	−0.087(2)	0.111(2)	−0.0322(6)	0.138(3)	C(27)	−0.058(1)	−0.193(1)	0.0715(4)	0.065(3)
C(1)	0.074(1)	−0.019(1)	0.0916(4)	0.054(3)	C(28)	−0.201(1)	−0.089(1)	0.0311(5)	0.083(3)
O	0.0893(8)	−0.042(1)	0.1212(3)	0.083(3)	P(5)	0.1040(4)	0.5199(4)	0.0811(1)	0.065(2)
P(1)	0.2080(3)	−0.0635(3)	0.0267(1)	0.040(1)	F(1)	0.121(1)	0.540(2)	0.0416(3)	0.264(3)
P(2)	−0.0567(3)	−0.1122(3)	0.0339(1)	0.045(1)	F(2)	0.091(1)	0.508(2)	0.1197(3)	0.303(3)
C(11)	0.3281(6)	0.0009(5)	0.0398(2)	0.048(3)	F(3)	0.075(2)	0.431(1)	0.0710(9)	0.433(3)
C(12)	0.3548(6)	0.0024(5)	0.0771(2)	0.058(4)	F(4)	0.134(2)	0.616(1)	0.0874(7)	0.291(3)
C(13)	0.4504(6)	0.0440(5)	0.0886(2)	0.074(4)	F(5)	−0.007(1)	0.547(2)	0.0733(4)	0.251(3)
C(14)	0.5192(6)	0.0841(5)	0.0627(2)	0.087(4)	F(6)	0.213(1)	0.490(2)	0.0854(5)	0.305(3)
				Compound **3**					
Ru(2)	0.28369(9)	0.04764(9)	0.28110(3)	0.0374(4)	C(42)	0.4894(7)	−0.0433(5)	0.3603(2)	0.061(4)
Cp(6)	0.282(1)	0.038(1)	0.2165(4)	0.057(3)	C(43)	0.5761(7)	−0.1019(5)	0.3679(2)	0.089(4)
Cp(7)	0.390(1)	0.031(1)	0.2309(3)	0.052(3)	C(44)	0.5612(7)	−0.1986(5)	0.3698(2)	0.094(4)
Cp(8)	0.397(1)	−0.052(1)	0.2528(3)	0.052(3)	C(45)	0.4595(7)	−0.2366(5)	0.3640(2)	0.105(4)
Cp(9)	0.294(1)	−0.100(1)	0.2530(4)	0.049(3)	C(46)	0.3727(7)	−0.1780(5)	0.3565(2)	0.091(4)
Cp(10)	0.222(1)	−0.046(1)	0.2312(3)	0.048(3)	C(47)	0.284(2)	0.082(1)	0.3787(4)	0.090(3)
Me(6)	0.244(1)	0.107(1)	0.1868(4)	0.059(3)	C(48)	0.161(1)	−0.074(2)	0.3545(5)	0.095(3)
Me(7)	0.484(1)	0.094(1)	0.2199(5)	0.065(3)	C(51)	0.352(1)	0.149(1)	0.2960(4)	0.047(3)
Me(8)	0.505(1)	−0.092(1)	0.2673(4)	0.068(3)	C(52)	0.409(1)	0.226(1)	0.3041(4)	0.059(3)
Me(9)	0.271(1)	−0.198(1)	0.2671(4)	0.063(3)	C(53)	0.5279(7)	0.2328(6)	0.3189(2)	0.059(4)
Me(10)	0.109(1)	0.072(1)	0.2187(4)	0.071(3)	C(54)	0.5689(7)	0.3185(6)	0.3308(2)	0.069(4)
P(3)	0.1222(3)	0.1292(3)	0.2884(1)	0.049(2)	C(55)	0.6755(7)	0.3251(6)	0.3422(2)	0.063(4)
P(4)	0.2796(3)	−0.0055(3)	0.3413(1)	0.051(1)	C(56)	0.7412(7)	0.2460(6)	0.3416(2)	0.075(4)
C(31)	0.1013(7)	0.2076(6)	0.2505(2)	0.047(3)	C(57)	0.7002(7)	0.1603(6)	0.3296(2)	0.072(4)
C(32)	0.1714(7)	0.2833(6)	0.2472(2)	0.074(4)	C(58)	0.5936(7)	0.1538(6)	0.3183(2)	0.074(4)
C(33)	0.1628(7)	0.3440(6)	0.2173(2)	0.097(4)	P(6)	0.7672(4)	0.0072(5)	0.1644(2)	0.099(2)
C(34)	0.0841(7)	0.3291(6)	0.1906(2)	0.086(4)	F(7)	0.715(1)	−0.056(1)	0.1861(5)	0.233(3)
C(35)	0.0140(7)	0.2535(6)	0.1939(2)	0.084(4)	F(9)	0.773(2)	0.082(1)	0.1826(9)	0.454(3)
C(36)	0.0226(7)	0.1927(6)	0.2238(2)	0.071(4)	F(10)	0.799(1)	−0.023(2)	0.1306(5)	0.312(3)
C(37)	−0.005(1)	0.064(1)	0.2906(5)	0.076(3)	F(11)	0.680(1)	0.048(2)	0.1489(5)	0.278(3)
C(38)	0.112(1)	0.211(1)	0.3282(4)	0.074(3)	F(12)	0.869(1)	0.005(2)	0.1745(6)	0.300(3)
C(41)	0.3877(7)	−0.0813(5)	0.3546(2)	0.049(3)					

Table 6. Comparative Structural Data for LnRu=C=CRR′ Complexes

LnRu[a]	ion	R	R′	Ru−C (Å)	C−C (Å)	Ru−C−C (deg)	ref
$CpRu(PMe_2Ph)_2$ (**1**)	PF_6	H	Ph	1.76(1)	1.34(2)	174(1)	
$CpRu(PMe_2Ph)_2$ (**8**)	PF_6	H	CHMeOMe	1.854(8)	1.29(1)	174(6)	
$CpRu(PPh_3)_2$	I	Me	Ph	1.86(1)	1.29(2)	173	36
$CpRu(PMe_3)_2$	PF_6	H	Me	1.845(7)	1.313(1)	180(2)	37
$CpRu(PMe_2Ph)_2$	BF_4	H	H	1.843(1)	1.287(1)	174.1(8)	17
$(^iPr_2PCH_2CH_2OMe)_2RuCl_2$	−	H	Ph	1.749(7)	1.34(1)	176.6(7)	19
$(dppm)_2RuCl$	PF_6	H	H	1.882(8)	1.22(1)	178.3(8)	20c

[a] Cp = C_5Me_5; dppm = $Ph_2PCH_2PPh_2$.

P(1)−Ru−P(2) angle.[38] Theoretical calculations[39] showed that a maximal π-stabilization between the metal and the Cα atom arises from interaction of the p orbitals of the Cα atom with the 2a″ orbitals of the metallic fragment. Interestingly, in cation **8** the vinylidene Ru−C(11)−C(12)−C(13) plane makes an angle of 73.1(4)° with the plane bisecting the P(1)−Ru−P(2) plane, thus showing a clear distortion with respect to complexes in the $(C_5H_5)Ru$ series. This distortion is observed in Figure 4. The rotation barrier around a (vinylidene)-Cα=Ru bond of a $[(C_5H_5)Ru(PR_3)_2(=C=CR_2)]^+$ complex is relatively weak, in the order of 15 kJ mol^{-1}.[40] Therefore, steric factors might be responsible for the distortion observed in **8**. Indeed the molecular structure shows an interaction of the OMe group with the C_5Me_5 methyl groups which can explain the distortion. The increase of the Ru−C(α) distance in **8** with respect to that of **3** may also result from this interaction.

Experimental Section

All reactions were performed under an argon or nitrogen atmosphere, unless otherwise stated, with the use of Schlenk techniques. The solvents were dried and deoxygenated by standard methods. NMR spectra were recorded on Bruker AC 300 P or Bruker AC 200 P spectrometers. Infrared spectra

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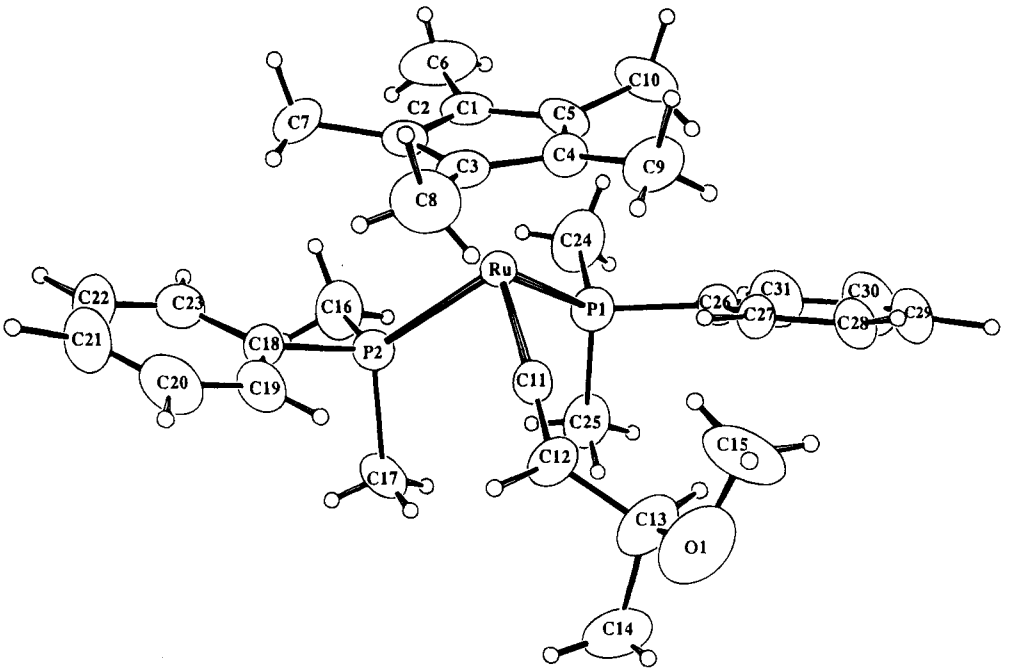

Figure 3. Molecular diagram of complex $[(C_5Me_5)(PMe_2Ph)_2Ru{=}C{=}CHCH(Me)OMe]PF_6$ (**8**).

Table 7. Selected Bond Distances and Angles for Complex 8[a]

atoms	bond distances (Å)	atoms	bond angles (deg)
Ru–C(11)	1.854(8)	C(11)–Ru–P(1)	92.1(2)
Ru–P(1)	2.312(2)	C(11)–Ru–P(2)	88.1(2)
Ru–P(2)	2.314(2)	Ru–C(11)–C(12)	174.6(7)
Ru–C(Cp)	2.255–2.301	P(1)–Ru–P(2)	92.88(8)
C(11)–C(12)	1.29(1)	C(11)–C(12)–C(13)	126.2(8)
C(12)–C(13)	1.52(1)	C(24)–P(1)–C(25)	100.6(5)
		C(16)–P(2)–C(17)	101.7(5)

[a] C(Cp) = C_5 carbon atoms of the C_5Me_5 ring.

were recorded on FT-IR Nicolet 20 C or Perkin-Elmer 1310 spectrometers. Elemental analyses were performed by the Service Central de Microanalyse of CNRS at Vernaison, France. The complex $[(C_5Me_5)RuCl]_4$ was prepared by the literature method.[25]

Electrochemical measurements were recorded by using a EGG PAR Model 362 scanning potentiostat with an XY recorder. Cyclic voltammograms were recorded in a single cell by using a 2 mm Pt disk working electrode and a 2 mm Pt disk auxiliary electrode. The reference electrode was an aqueous saturated calomel electrode (SCE). Purified Bu_4NPF_6 was used as electrolyte.

Synthesis of $(C_5Me_5)(PMe_2Ph)_2RuCl$ (1). In a Schlenk tube were successively introduced 3.0 g (2.8 mmol) of $[(C_5Me_5)RuCl]_4$, 50 mL of freshly distilled THF, and 3.4 mL (23.9 mmol) of dimethylphenylphosphine. The solution was stirred at room temperature for 30 min and rapidly became red. The solution was filtered and evaporated to dryness. The oily residue was triturated in 15 mL of petroleum ether to give a yellow solid which was filtered, washed with 4 × 5 mL of petroleum ether, and dried under vacuum; yield: 5.30 g (87%). The yellow powder could be recrystallized in hot petroleum ether to give orange needles. ^1H NMR ($CDCl_3$, 300.133 MHz, 297 K): δ 7.68–7.61 (m, 4 H, PPh), 7.29–7.22 (m, 6 H, PPh), 1.50–1.45 (m, 12 H, PMe_2), 1.14 (t, 15 H, $^4J_{PH}$ = 1.6 Hz, C_5Me_5). $^{31}P[^1H]$ NMR ($CDCl_3$, 121.496 MHz, 297 K): δ 13.58 (s, PMe_2Ph). Anal. Calcd for $C_{26}H_{37}ClP_2Ru$: C, 56.98; H, 6.80. Found : C, 57.20. H 6.95.

Synthesis of $(C_5Me_5)(PMePh_2)_2RuCl$ (2). In a Schlenk tube were successively introduced 2.5 g (2.3 mmol) of $[(C_5Me_5)RuCl]_4$, 50 mL of freshly distilled THF, and 3.6 mL (19.3 mmol) of methyldiphenylphosphine. The solution was stirred at room temperature for 30 min, rapidly became red, and was filtered and concentrated to about 10 mL. The addition of 15 mL of hexane caused the precipitation of a yellow solid which was filtered, washed with 5 mL of hexane, and dried under vacuum to yield 4.80 g of yellow powder. The mother solution was concentrated to half of its volume and cooled to −20 °C to give orange crystals which were filtered, washed with 5 mL of hexane, and vacuum-dried (0.72 g). Overall yield of **2**: 5.72 g (89%). ^1H NMR ($CDCl_3$, 300.133 MHz, 297 K): δ 7.55 (m, 4 H, PPh), 7.37 (m, 6 H, PPh), 7.11 (m, 10 H, Ph), 1.32 (t, 6 H, J = 4.1 Hz, PMe), 1.25 (t, 15 H, $^4J_{PH}$ = 1.6 Hz, C_5Me_5). $^{31}P[^1H]$ NMR ($CDCl_3$, 121.496 MHz, 297 K): δ 26.36 (s, PMe_2Ph). Anal. Calcd for $C_{36}H_{41}ClP_2Ru$: C, 64.32; H, 6.15; Cl, 5.27. Found: C, 64.22; H, 6.41; Cl, 5.37.

Synthesis of $[(C_5Me_5)(PMe_2Ph)_2Ru{=}C{=}CHPh]PF_6$ (3). Method A, from 1. In a Schlenk tube were successively introduced 0.5 g (0.9 mmol) of $(C_5Me_5)(PMe_2Ph)_2RuCl$ (**1**), 0.15 g (0.9 mmol) of NH_4PF_6, and 25 mL of methanol. To the yellow solution was added 0.15 mL (1.4 mmol) of phenylacetylene with a syringe. The mixture was heated to reflux for 2 h. The color progressively turned to orange. The solution was evaporated to dryness affording an orange solid which was dissolved in 15 mL of dichloromethane and then filtered. After removal of the dichloromethane under vacuum, the solid was recrystallized from the minimum amount of hot methanol, yielding 0.60 g (87%) of orange crystals of **3**.

Method B, from 9. In a Schlenk tube were successively introduced 0.12 g (0.2 mmol) of $(C_5Me_5)(PMe_2Ph)_2Ru(C_2Ph)$ (**9**), 0.16 g (1.0 mmol) of NH_4PF_6, and 10 mL of dichloromethane. The solution was stirred at room temperature for 10 min, and the color progressively changed from yellow to orange. The solution was filtered and concentrated to about 4 mL. Ether (30 mL) was added in order to maintain two phases. Orange crystals were formed, separated by decantation, washed with 3 × 5 mL of ether, and dried under vacuum; yield: 0.12 g (86%). ^1H NMR ($CDCl_3$, 300.133 MHz, 297 K): δ 7.40–7.06 (m, 15 H, PPh), 5.42 (t, 1 H, $^4J_{PH}$ = 2.2 Hz, =CH), 1.68 (s, 15 H, C_5Me_5), 1.56 (v t, 6 H, $|^2J_{PH} + {}^4J_{PH}|$ = 9.2 Hz, PMe_A + $P'Me'_A$), 1.52 (v t, 6 H, $|^2J_{PH} + {}^4J_{PH}|$ = 9.3 Hz, PMe_B + $P'Me'_B$). $^{31}P[^1H]$ NMR (CD_2Cl_2, 121.496 MHz, 297 K): δ 12.80 (s, PMe_2Ph), −143.86 (sept, $^1J_{PF}$ = 709.4 Hz, PF_6). $^{13}C[^1H]$ NMR ($CDCl_3$, 75.469 MHz, 297 K): δ 354.31 (t, $^2J_{PC}$ = 15.2 Hz, Ru=C=), 135.85 (m, Ph), 130.8–125.7 (m, Ph), 113.88 (s,

Table 8. Positional Parameters and Estimated Standard Deviations for 8[a]

atom	x	y	z	B (A2)
Ru	0.25176(3)	0.04051(2)	0.00201(3)	2.094(8)
P(1)	0.1681(1)	0.1320(1)	0.0095(1)	2.97(4)
P(2)	0.2225(1)	0.0197(1)	−0.10801(9)	3.05(4)
P(3)	0.000	0.4072(2)	0.250	3.76(7)
P(4)	0.5090	0.3570(2)	0.250	4.87(8)
F(1)	0.000	0.3243(4)	0.250	7.4(2)*
F(2)	0.0057(4)	0.4027(3)	0.1727(3)	7.6(1)*
F(3)	0.0892(3)	0.4111(3)	0.2493(3)	6.6(1)*
F(4)	0.000	0.4887(4)	0.250	7.1(2)*
F(11)	0.4845(6)	0.3732(6)	0.3270(5)	6.3(2)*
F(12)	0.500	0.276(1)	0.250	10.7(6)*
F(13)	0.4191(8)	0.3298(7)	0.2344(7)	10.0(4)*
F(14)	0.500	0.437(1)	0.250	9.3(5)*
F(15)	0.415(1)	0.3825(9)	0.2281(8)	4.0(4)*
F(16)	0.470(1)	0.284(1)	0.215(1)	6.8(6)*
F(21)	0.988(2)	0.440(1)	0.176(1)	9.3(7)*
F(22)	0.087(1)	0.382(1)	0.270(1)	7.4(6)*
F(31)	0.455(1)	0.427(1)	0.227(1)	7.5(6)*
F(32)	0.460(1)	0.342(1)	0.318(1)	6.0(5)*
F(33)	0.413(1)	0.357(1)	0.261(1)	6.6(6)*
F(34)	0.498(2)	0.335(1)	0.175(1)	7.5(7)*
O(1)	0.4687(4)	0.2225(4)	−0.0100(4)	8.3(2)
O(2)	0.000	0.124(2)	0.250	11.9(8)*
C(1)	0.1967(4)	−0.0461(4)	0.0634(4)	3.3(2)
C(2)	0.2580(5)	−0.0740(4)	0.0291(3)	3.1(1)
C(3)	0.3247(4)	−0.0402(4)	0.0511(4)	3.2(2)
C(4)	0.3040(4)	0.0091(4)	0.1009(4)	3.3(2)
C(5)	0.2242(4)	0.0058(4)	0.1084(4)	3.5(2)
C(6)	0.1181(6)	−0.0737(5)	0.0622(6)	6.6(3)
C(7)	0.2555(6)	−0.1391(4)	−0.0113(4)	5.1(2)
C(8)	0.4048(5)	−0.0586(5)	0.0331(5)	5.4(2)
C(9)	0.3574(6)	0.0467(5)	0.1443(5)	5.8(2)
C(10)	0.1814(6)	0.0398(5)	0.1627(4)	6.2(2)
C(11)	0.3285(4)	0.0982(4)	−0.0270(3)	2.5(1)
C(12)	0.3859(4)	0.1332(4)	−0.0479(4)	3.8(2)
C(13)	0.4005(5)	0.2097(5)	−0.0360(5)	5.5(2)
C(14)	0.4021(6)	0.2486(5)	−0.1050(6)	7.2(3)
C(15)	0.4684(6)	0.2040(7)	0.0568(5)	7.9(3)
C(16)	0.1254(5)	−0.0019(5)	−0.1251(4)	5.0(2)
C(17)	0.2413(6)	0.0858(4)	−0.1707(4)	4.4(2)
C(18)	0.2757(5)	−0.0521(4)	−0.1440(4)	3.7(2)
C(19)	0.3534(5)	−0.0473(4)	−0.1462(4)	4.5(2)
C(20)	0.3971(6)	−0.1005(5)	−0.1725(5)	6.0(2)
C(21)	0.3612(7)	−0.1591(5)	−0.1966(5)	7.2(3)
C(22)	0.2865(7)	−0.1639(5)	−0.1963(4)	6.7(3)
C(23)	0.2416(6)	−0.1110(4)	−0.1704(4)	5.1(2)
C(24)	0.0703(5)	0.1092(5)	0.0235(5)	5.4(2)
C(25)	0.1585(5)	0.1921(4)	−0.0593(4)	4.6(2)
C(26)	0.1894(4)	0.1936(4)	0.0763(4)	3.2(2)
C(27)	0.2621(5)	0.2003(4)	0.0988(3)	3.3(2)
C(28)	0.2809(6)	0.2514(4)	0.1442(4)	4.7(2)
C(29)	0.2254(7)	0.2952(5)	0.1682(4)	6.2(3)
C(30)	0.1537(6)	0.2886(5)	0.1462(5)	6.6(3)
C(31)	0.1346(5)	0.2387(5)	0.1003(5)	5.1(2)
C(32)	0.030(2)	0.151(2)	0.241(2)	6(1)*

[a] Atoms labeled with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

=CH), 103.79 (s, C_5), 19.23 (v t, $|^1J_{PC} + {}^3J_{P'C}| = 34.9$ Hz, $PMe_A + P'Me'_A$), 17.55 (v t, $|^1J_{PC} + {}^3J_{P'C}| = 35.4$ Hz, $PMe_B + P'Me'_B$), 10.02 (s, Me_5). IR (KBr): $\nu_{C=C}$ 1645, 1624 cm^{-1}; ν_{PF6} 840 cm^{-1}. Anal. Calcd for $C_{34}H_{43}F_6P_3Ru$: C, 53.75; H, 5.70. Found : C, 53.66; H, 5.83.

Synthesis of [(C_5Me_5)(PMe_2Ph)$_2$Ru=C=CHPh]BF_4 (3'). Method C, from 9. In a Schlenk tube were introduced 0.10 g (0.16 mmol) of (C_5Me_5)(PMe_2Ph)$_2$Ru(C_2Ph) (**9**) and 30 mL of methanol, and then with rapid stirring an excess of a HBF_4·OEt_2 solution (100 mg of a 85% in ether solution) was added. The yellow solid readily dissolved, and the orange solution was stirred at room temperature for 10 min. The solution was filtered and concentrated to about 5 mL. A pink powder was precipitated by addition of 50 mL of ether. The solid was separated by decantation, washed with 3 × 5 mL of ether, and dried under vacuum; yield: 0.11 g (98%). IR (KBr): $\nu_{C=C}$ 1640, 1620 cm^{-1}; ν_{BF4} 1050 cm^{-1}.

Synthesis of [(C_5Me_5)(PMe_2Ph)$_2$Ru=C=CH_2]PF_6 (5). In a Schlenk tube were successively introduced 0.50 g (0.9 mmol) of (C_5Me_5)(PMe_2Ph)$_2$RuCl, 0.20 g (1.2 mmol) of NH_4PF_6, 20 mL of dichloromethane, and, with a syringe, 0.2 mL (1.4 mmol) of (trimethylsilyl)acetylene. The mixture was stirred at room temperature for 6 h, and the color progressively changed from orange to yellow. The solution was filtered and concentrated to 10 mL. Ether (100 mL) was slowly added in order to maintain two phases. Yellow crystals were formed, separated by decantation, washed with 3 × 10 mL of ether, and dried under vacuum; yield: 0.43 g (70%). ^{1}H NMR ($CDCl_3$, 300.133 MHz, 293 K): δ 7.46−7.43 (m, 6 H, PPh), 7.37−7.31 (m, 4 H, PPh), 3.89 (t, 2 H, $^4J_{PH}$ = 2.4 Hz, =CH_2), 1.79 (v t, 6 H, $|^2J_{PH} + {}^4J_{P'H}| = 9.0$ Hz, $PMe_A + P'Me'_A$), 1.62 (v t, 6 H, $|^2J_{PH} + {}^4J_{P'H}| = 9.4$ Hz, $PMe_B + P'Me'_B$), 1.46 (t, 15 H, $^4J_{PH} = 1.4$ Hz, Me_5). ^{31}P [^{1}H] NMR ($CDCl_3$, 121.496 MHz, 293 K): δ 17.09 (s, PMe_2Ph), −143.68 (sept, $^1J_{PF}$ = 711.6 Hz, PF_6). ^{13}C [^{1}H] NMR ($CDCl_3$, 75.469 MHz, 297 K): δ 346.95 (t, $^2J_{PC}$ = 15.7 Hz, Ru=C=), 136.81−136.14 (m, Ph), 130.69−128.92 (m, Ph), 102.66 (s, =CH_2), 92.02 (s, C_5), 19.94 (v t, $|^1J_{PC} + {}^3J_{P'C}| = 35.9$ Hz, $PMe_A + P'Me'_A$), 17.00 (v t, $|^1J_{PC} + {}^3J_{P'C}| = 34.1$ Hz, $PMe_B + P'Me'_B$), 9.78 (s, Me_5). IR (KBr): $\nu_{C=C}$ 1622 cm^{-1}; ν_{PF6} 835 cm^{-1}. Anal. Calcd for $C_{28}H_{39}F_6OP_3Ru$: C, 49.20; H, 5.75; P, 13.59. Found: C, 49.14; H, 5.52; P, 13.54.

Synthesis of [(C_5Me_5)(PMe_2Ph)$_2$Ru=C=$CHCH_2OMe$]PF_6 (6). Method A. In a Schlenk tube were successively introduced 1.1 g (2.0 mmol) of (C_5Me_5)(PMe_2Ph)$_2$RuCl, 0.33 g (2.0 mmol) of NH_4PF_6, and 50 mL of methanol. To the solution was added 0.18 mL (3.0 mmol) of propargyl alcohol. The mixture was heated to reflux for 1.5 h. The color progressively changed from yellow to red. The solution was evaporated to dryness, the residue was dissolved in 15 mL of dichloromethane, and the solution was filtered. After evaporation of the solvent, the brown residue was crystallized from the minimum amount of hot methanol, yielding 1.18 g (81%) of red crystals of **6**.

Method B. Following the procedure described for the preparation of **3**, from 0.04 g (0.07 mmol) of (C_5Me_5)(PMe_2Ph)$_2$Ru(C_2CH_2OMe) (**10**) and 0.05 g (0.3 mmol) of NH_4PF_6, 0.05 g (97%) of **6** were obtained. ^{1}H NMR ($CDCl_3$, 300.133 MHz, 297 K): δ 7.40−7.29 (m, 10 H, PPh), 4.63 (tt, 1 H, $^3J_{HH}$ = 8.0 Hz, $^4J_{PH}$ = 2.2 Hz, =CH), 4.20 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, CH_2), 3.34 (s, 3 H, OMe), 1.63 (v t, 6 H, $|^2J_{PH} + {}^4J_{P'H}| = 8.8$ Hz, $PMe_A + P'Me'_A$), 1.5 (masked t, 6 H, $PMe_B + P'Me'_B$), 1.48 (t, 15 H, $^4J_{PH}$ = 1.2 Hz, C_5Me_5). ^{31}P [^{1}H] NMR ($CDCl_3$, 121.496 MHz, 297 K): δ 16.11 (s, PMe_2Ph), −143.68 (sept, $^1J_{PF}$ = 713.4 Hz, PF_6). ^{13}C [^{1}H] NMR ($CDCl_3$, 75.47 MHz, 297 K): δ 329.02 (t, $^2J_{PC}$ = 15.2 Hz, Ru=C), 136.2 (m, Ph), 130.8−128.9 (m, Ph), 106.13 (t, $^3J_{PC}$ = 1.3 Hz, =CH), 103.05 (t, $^2J_{PC}$ = 1.4 Hz, C_5), 63.51 (s, CH_2), 57.92 (s, OMe), 20.05 (v t, $|^1J_{PC} + {}^3J_{P'C}| = 35.3$ Hz, $PMe_A + P'Me'_A$), 17.57 (v t, $|^1J_{PC} + {}^3J_{P'C}| = 34.3$ Hz, $PMe_B + P'Me'_B$), 10.02 (s, Me_5). IR (KBr): $\nu_{C=C}$ 1610 cm^{-1}; ν_{PF6} 820 cm^{-1}. Anal. Calcd for $C_{30}H_{43}F_6P_3Ru$: C, 49.51; H, 5.96. Found: C, 49.33; H, 6.04.

Synthesis of [(C_5Me_5)(PMe_2Ph)$_2$Ru=C=$CHCH_2OH$]PF_6 (7). In a Schlenk tube were successively introduced 0.50 g (0.9 mmol) of (C_5Me_5)(PMe_2Ph)$_2$RuCl, 0.20 g (1.2 mmol) of NH_4PF_6, and 30 mL of dichloromethane. Then 0.1 mL (1.7 mmol) of propargyl alcohol was added with a syringe. The mixture was stirred at room temperature for 4 h, and the color changed from yellow to orange. The solution was filtered and concentrated to about 10 mL. Ether (100 mL) was slowly added in order to maintain two phases. Orange crystals were formed, separated by decantation, washed with 10 mL of ether, and dried under vacuum; yield: 0.58 g (90%). ^{1}H NMR ($CDCl_3$, 200.13 MHz, 293 K): δ 7.44−7.37 (m, 10 H, PPh), 4.83 (tt, 1H, $^4J_{PH}$ = 2.2 Hz, $^3J_{HH}$ = 8.1 Hz, =CH), 4.54 (d, 2 H, $^2J_{HH}$ = 8.1 Hz, CH_2O), 2.3 (broad, 1 H, OH), 1.70 (v t, 6 H, $|^2J_{PH} + {}^4J_{P'H}| = 8.9$ Hz, $PMe_A + P'Me'_A$), 1.6 (masked v t, 6 H, PMe_B

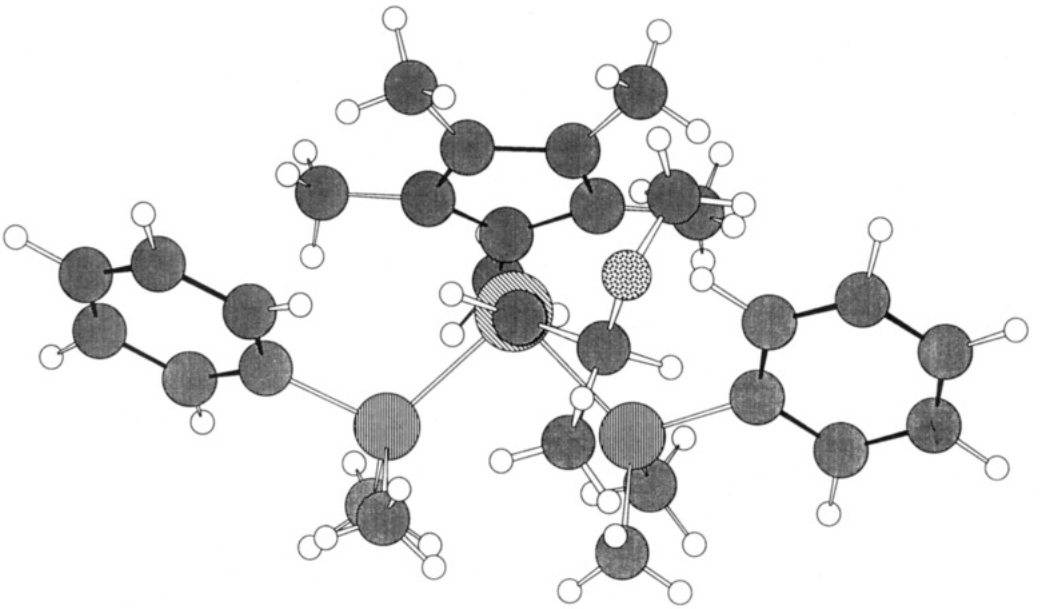

Figure 4. Molecular diagram of complex $[(C_5Me_5)(PMe_2Ph)_2Ru{=}C{=}CHCH(Me)OMe]PF_6$ (**8**) showing the distortion of the vinylidene plane.

+ P′Me′$_B$), 1.57 (t, 15 H, $^4J_{PH}$ = 1.3 Hz, Me_5). ^{31}P [^1H] NMR ($CDCl_3$, 81.01 MHz, 293 K): δ 13.53 (s, PMe_2Ph), −145.67 (sept, $^1J_{PF}$ = 713.4 Hz, PF_6). ^{13}C [^1H] NMR ($CDCl_3$, 75.469 MHz, 297 K): δ 346.36 (t, $^2J_{PC}$ = 15.2 Hz, Ru=C), 136.1 (m, Ph), 130.8−128.9 (m, Ph), 105.88 (s, =CH), 103.23 (s, C_5), 75.25 (s, CH_2), 20.01 (v t, $|^1J_{PC} + {}^3J_{PC}| = 35.5$ Hz, PMe_A + P′Me′$_A$), 17.68 (v t, $|^1J_{PC} + {}^3J_{PC}| = 34.64$ Hz, PMe_A + P′Me′$_A$), 10.08 (s, Me_5). IR (KBr): $\nu_{C=C}$ 1640 cm^{-1}; ν_{PF6} 830 cm^{-1}. Anal. Calcd for $C_{29}H_{41}F_6OP_3Ru$: C, 48.81; H, 5.79; P, 13.02. Found: C, 49.41; H, 5.77; P, 12.93.

Synthesis of $[(C_5Me_5)(PMe_2Ph)_2Ru{=}C{=}CHCHMeOMe]PF_6$ (8). Method A, from 1. In a Schlenk tube were introduced 0.9 g (1.6 mmol) of $(C_5Me_5)(PMe_2Ph)_2RuCl$ (**1**), 0.40 g (2.5 mmol) of NH_4PF_6, and 40 mL of methanol. To the solution was added 0.20 mL (2.5 mmol) of 3-butyn-2-ol. The mixture was heated to reflux for 1.5 h, and the color progressively changed from yellow to orange. The solution was evaporated to dryness, and the yellow residue was washed with ether (2 × 5 mL) and then dissolved in 15 mL of dichloromethane. The solution was filtered and evaporated to dryness. The solid was crystallized from the minimum amount of hot methanol, yielding 0.88 g (74%) of orange crystals of **8**.

Method B, from 11. Following the procedure described for the preparation of **3**, from 0.10 g (0.17 mmol) of $(C_5Me_5)(PMe_2Ph)_2Ru(C_2CHMeOMe)$ (**11**) and 0.10 g (0.6 mmol) of NH_4PF_6, 0.12 g (95%) of **8** were obtained. ^1H NMR ($CDCl_3$, 200.13 MHz, 293 K): δ 7.46−7.33 (m, 10 H, PPh), 4.47 (ABX_3 system, 1 H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 6.1 Hz, $CHCH_3$), 4.34 (ABY_2 system, 1 H, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 2.3 Hz, =C=CH), 1.75 (d, 3 H, $^2J_{PH}$ = 8.8 Hz, PMe_A), 1.72 (d, 3 H, $^2J_{PH}$ = 8.8 Hz, P′Me′$_A$), 1.64 (d, 3 H, $^2J_{PH}$ = 9.0 Hz, PMe_B), 1.56 (t, 15 H, $^4J_{PH}$ = 1.3 Hz, C_5Me_5), 1.53 (d, 3 H, $^2J_{PH}$ = 9.0 Hz, P′Me′$_B$), 1.44 (d, 3 H, $^3J_{HH}$ = 6.0 Hz, $CHCH_3$). ^{31}P [^1H] NMR ($CDCl_3$, 81.01 MHz, 293 K): δ 15.30, 14.40 (AB system, $^2J_{PP}$ = 35.7 Hz, PMe_2Ph), −145.71 (sept, $^1J_{PF}$ = 712.4 Hz, PF_6). ^{13}C [^1H] NMR ($CDCl_3$, 50.320 MHz, 293 K): δ 345.06 (t, $^2J_{PC}$ = 15.3 Hz, Ru=C=), 136.7−135.6 (m, Ph), 130.8−128.8 (m, Ph), 112.97 (t, $^3J_{PC}$ = 1.3 Hz, =CH), 102.95 (t, $^2J_{PC}$ = 1.3 Hz, C_5), 70.33 (s, −CH), 55.77 (s, OMe), 22.93 (s, C-CH_3), 20.85−19.60 (m, PMe_A), 18.08−16.98 (m, PMe_B), 10.06 (s, Me_5). IR (KBr): $\nu_{C=C}$ 1643 cm^{-1}; ν_{PF6}: 840 cm^{-1}. Anal. Calcd for $C_{31}H_{45}F_6OP_3Ru$: C, 50.20; H, 6.11. Found: C, 50.01; H, 6.29.

Synthesis of $(C_5Me_5)(PMe_2Ph)_2Ru(C_2Ph)$ (9). Method A, from HC≡CPh. In a Schlenk tube containing a solution of 1.0 g (1.8 mmol) of $(C_5Me_5)(PMe_2Ph)_2RuCl$ (**1**) in 30 mL of methanol was added 0.30 mL (3.7 mmol) of phenylacetylene with a syringe. The mixture was heated to reflux for 45 min. The color changed from yellow to red. Then 2.6 mL of freshly prepared 1 N NaOMe solution was added. The solution immediately turned yellow and was stirred at room temperature for 1 h. The methanol was evaporated and the residue dissolved in 20 mL of dichloromethane. The solution was concentrated to about 10 mL and 10 mL of methanol added. The mixture was concentrated until a yellow precipitate appeared. The precipitate was dissolved by heating, and the yellow solution was separated from an insoluble oily residue through a cannula. After the solution was cooled to −20 °C, 0.80 g (74%) of yellow crystals was obtained.

Method B, from 3. In a Schlenk tube were successively introduced 0.18 g (0.24 mmol) of $[(C_5Me_5)(PMe_2Ph)_2Ru(C{=}CHPh)]PF_6$ (**3**), 20 mL of dichloromethane, and 0.5 g (excess) of K_2CO_3. The mixture was stirred at 25 °C for 1 h, changing progressively from orange to yellow. The solution was evaporated to dryness and the yellow residue dissolved in 20 mL of ether. The solution was filtered and then evaporated. The yellow solid was dissolved in 10 mL of hot methanol and the solution cooled to −20 °C. The bright yellow crystals formed were separated by decantation, washed with 3 mL of cold methanol, and dried under vacuum; yield: 0.11 g (74%). ^1H NMR ($CDCl_3$, 300.133 MHz, 297 K): δ 7.80 (m, 4 H, Ph), 7.38−7.32 (m, 8 H, Ph), 7.22 (m, 2 H, Ph), 7.02 (m, 1H, Ph), 1.66 (v t, 6 H, $|^2J_{PH} + {}^4J_{PH}| = 8.5$ Hz, PMe_A + P′Me′$_A$), 1.61 (v t, 6 H, $|^2J_{PH} + {}^4J_{PH}| = 8.0$ Hz, PMe_B + P′Me′$_B$), 1.52 (t, 15 H, $^4J_{PH}$ = 1.3 Hz, C_5Me_5). ^{31}P [^1H] NMR ($CDCl_3$, 121.496 MHz, 297 K): δ 21.86 (s, PMe_2Ph). ^{13}C [^1H] NMR (CD_2Cl_2, 75.469 MHz, 297 K) δ 142.5 (m, Ph), 131.7−127.5 (m, Ph), 122.43 (s, RuC), 107.65 (s, C≡C), 92.07 (t, $^3J_{PC}$ = 2.2 Hz, C_5), 20.80 (v t, $|^1J_{PC} + {}^3J_{PC}| = 30.4$ Hz, PMe_A + P′Me′$_A$), 19.94 (v t, $|^1J_{PC} + {}^3J_{PC}| = 28.8$ Hz, PMe_B + P′Me′$_B$), 10.30 (s, Me_5). IR (KBr): $\nu_{C=C}$ 2045 cm^{-1}. Anal. Calcd for $C_{34}H_{42}P_2Ru$: C, 66.54; H, 6.90; P, 10.09. Found: C, 65.97; H, 6.93; P, 10.06.

Synthesis of $(C_5Me_5)(PMe_2Ph)_2Ru(C_2CH_2OMe)$ (10). In a Schlenk tube containing a solution of 0.30 g (0.41 mmol) of $[(C_5Me_5)(PMe_2Ph)_2Ru(C{=}CHCH_2OMe)]PF_6$ (**6**) in 20 mL of dichloromethane was added 1.0 g (excess) of K_2CO_3. The mixture was stirred for 2 h at 30 °C, changing progressively from orange to yellow. The solution was evaporated to dryness and the residue dissolved in 20 mL of petroleum ether. The yellow solution was filtered and then evaporated to dryness, affording an oily residue which slowly crystallized at −20 °C. The yellow solid was dried under vacuum; yield: 0.18 g (75%).

^{1}H NMR (CD_2Cl_2, 300.134 MHz, 297 K): δ 7.71−7.64 (m, 4 H, PPh), 7.26−7.10 (m, 6 H, PPh), 4.22 (t, 2 H, $^5J_{PH}$ = 2.0 Hz, $-CH_2$), 3.31 (s, 3 H, OMe), 1.49 (v t, 6 H, $|^2J_{PH} + {}^4J_{P'H}|$ = 8.5 Hz, $PMe_A + P'Me'_A$), 1.45 (v t, 6 H, $|^2J_{PH} + {}^4J_{P'H}|$ = 8.1 Hz, $PMe_B + P'Me'_B$), 1.33 (t, 15 H, $^4J_{PH}$ = 1.5 Hz, C_5Me_5). ^{31}P [^{1}H] NMR (CD_2Cl_2, 121.496 MHz, 297 K): δ 21.81 (s, PMe_2Ph). ^{13}C [^{1}H] NMR (CD_2Cl_2, 75.469 MHz, 297 K): δ 143.6 (m, Ph), 131.55−127.75 (m, Ph), 120.41 (t, $^2J_{PC}$ = 25.0 Hz, RuC), 100.44 (s, C≡*C*), 91.91 (t, $^3J_{PC}$ = 2.2 Hz, C_5), 63.58 (s, CH_2), 56.20 (s, OMe), 21.00 (v t, $|^1J_{PC} + {}^3J_{P'C}|$ = 29.9 Hz, $PMe_A + P'Me'_A$), 20.20 (v t, $|^1J_{PC} + {}^3J_{P'C}|$ = 28.5 Hz, $PMe_B + P'Me'_B$), 10.37 (s, Me_5). IR (KBr): $\nu_{C\equiv C}$ 2070 cm^{-1}. Complex **10** was not stable enough to obtain a correct elemental analysis but gave back **6** (identified by NMR) on protonation with NH_4PF_6.

Synthesis of (C_5Me_5)(PMe_2Ph)$_2$Ru($C_2CHMeOMe$) (11). In a Schlenk tube containing a solution of 0.30 g (0.40 mmol) of [(C_5Me_5)(PMe_2Ph)$_2$Ru(C=CHCHMeOMe)]PF_6 (**8**) in 20 mL of dichloromethane was added 1.0 g (excess) of K_2CO_3. The solution was stirred at about 35 °C for 2 h, changing progressively from orange to yellow. The solution was evaporated to dryness and the residue dissolved in 20 mL of petroleum ether. The yellow solution was filtered, and the slow evaporation of the solvent caused the precipitation of a microcrystalline yellow solid which was dried under vacuum; yield: 0.15 g (63%). ^{1}H NMR (CD_2Cl_2, 300.134 MHz, 297 K): δ 7.74−7.68 (m, 4 H, PPh), 7.26−7.201 (m, 6 H, PPh), 4.25 (qt, 1 H, $^3J_{HH}$ = 6.4 Hz, $^5J_{PH}$ = 1.6 Hz, CH-), 3.36 (s, 3 H, OMe), 1.50 (v t, 6 H, $|^2J_{PH} + {}^4J_{P'H}|$ = 7.9 Hz, $PMe_A + P'Me'_A$), 1.46 (v t, 6 H, $|^2J_{PH} + {}^4J_{P'H}|$ = 7.6 Hz, $PMe_B + P'Me'_B$), 1.35 (masked d, CCH_3), 1.32 (t, 15 H, $^4J_{PH}$ = 1.5 Hz, C_5Me_5). ^{31}P [^{1}H] NMR (CD_2Cl_2, 121.496 MHz, 297 K): δ 22.06, 21.74 (AB system, $^2J_{PP}$ = 33 Hz, PMe_2Ph). ^{13}C [^{1}H] NMR (CD_2Cl_2, 75.469 MHz, 297 K): δ 143.90−143.50 (m, Ph), 131.58−127.69 (m, Ph), 117.08 (t, $^2J_{PC}$ = 25.0 Hz, RuC), 105.17 (s, C≡*C*), 91.83 (t, $^3J_{PC}$ = 2.2 Hz, C_5), 69.72 (s, CHO), 55.28 (s, OMe), 25.02 (s, CCH_3), 21.26−20.85 (m, $PMe_A + P'Me'_A$), 20.40−20.00 (m, $PMe_B + P'Me'_B$), 10.13 (s, Me_5). IR (KBr): $\nu_{C=C}$ 2064 cm^{-1}. Complex **11** was not stable enough to obtain a correct elemental analysis but gave back **8** (identified by NMR) on protonation with NH_4PF_6.

Crystal Structure Analysis of 3·4. Orange crystals suitable for X-ray analysis were obtained by slow diffusion of petroleum ether into a chloroform solution of **3·4**. The sample crystal (0.24 x 0.28 × 0.55 mm^3) was studied on an automatic diffractometer, CAD4 ENRAF-NONIUS, with graphite monochromatized Mo Kα radiation. The cell parameters were determined from 25 reflections in the range 14° < θ < 17°. Data collection was by ω scan, $\Delta\omega$ = 1.0 + 0.35 tan θ°, $2\theta_{max}$ = 44°, t_{max} = 30 s; *hkl* range: *h* 0.12, *k* 0.14, *l* 0.35. Intensity control reflexions showed 2.6% decay; 5565 reflections were measured, 5369 unique and 5032 with $F < \sigma 3(F)$.

After Lorentz, polarization, and absorption corrections, the structure was solved with a Patterson synthesis which revealed the Ru positions and subsequent difference Fourier syntheses. To reduce the large number of parameters, the phenyl groups including H atoms were treated as rigid groups with isotropic temperature factors. The cyclopentadienyl groups showed large anisotropic motion. The H atoms of the methyl groups were neglected. The PF_6^- ions showed very large thermal motion; one F atom could not be located. Refinement was performed by full-matrix least squares based on *F* values with weights $1/\sigma^2$. Final R = 0.064 and R_w = 0.069. Residual electron density < 0.88 e/Å^3. Programs used were SHELXS-86 and SHELXTS.[41,42] Atomic scattering factors are from ref 43; dispersion values are from ref 44.

Crystal Structure Analysis of 8. Yellow crystals of [C_5Me_5(PMe_2Ph)$_2$Ru=C=CHCHMeOMe]PF_6 (**8**) suitable for X-ray analysis were obtained by slow cooling of a hot saturated solution of **8** in methanol. The sample (prism, 0.15 × 0.24 × 0.35 mm^3) was studied on an automatic diffractometer, CAD4 ENRAF-NONIUS, with graphite monochromatized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high θ reflections. The data collection ($2\theta_{max}$ = 50°, scan $\omega/2\theta$ = 1, t_{max} = 60 s; *hkl* range: *h* 0.22, *k* 0.24, *l* 0.25; intensity controls without appreciable decay (0.2%)) gave 8235 reflections, 1921 with $I < \sigma 3(I)$.

After Lorentz and polarization corrections, the structure was solved with a Patterson map which revealed the Ru atom. The remaining non-hydrogen atoms of the structure were found after successive scale factor refinements and Fourier differences. During these calculations, two half-anions, PF_6^-, appeared as disordered and located on symmetry elements. After isotropic refinement (R = 0.072), one molecule of methanol appeared (multiplicity about 0.5). After anisotropic refinement (R = 0.053), a Fourier difference allowed the location of many hydrogen atoms, the remaining ones being set in theoritical position. The whole structure was refined by the full-matrix least squares-technique (use of *F* magnitude; *x*, *y*, *z*, and β_{ij} for Ru, P, O, and C atoms, *x*, *y*, *z*, and B_{iso} for F atoms, *x*, *y*, and *z* for fixed H atoms; 254 variables and 1921 observations; $\omega = 1/\sigma(F_0)^2 = [\sigma^2(I) + (0.04F_0^2)^2]^{-1/2}$) with the resulting R = 0.045, R_w = 0.043, and S_ω = 3.38 (residual $\Delta\rho \leq 0.59$ eÅ^{-3}). Atomic scattering factors are from *International Tables for X-ray Crystallography*.[45] All the calculations were performed on a Digital Micro VAX 3100 computer with the MolEN package.[46]

Acknowledgment. The authors are grateful to J. P. Guéguan for NMR technical assistance and the Ministère des Affaires Etrangères for a research stay of R.L.L. in Chile.

Supplementary Material Available: Tables of bond lengths and angles, least-squares planes, atomic fractional coordinates, and thermal parameters for **3·4** and **8** (16 pages). Ordering information is given on any current masthead page.

OM940445U

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