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Carbon−Carbon Coupling of Two Alkenyl Fragments on a Saturated Compound

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The monohydrido complex RuHCl(CO)(P^{i}Pr$_3$)$_2$ (**1**) reacts with 2-methyl-1-buten-3-yne to give Ru{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$ (**2**) , which has been characterized by X-ray diffraction analysis. The coordination geometry around the ruthenium atom can be rationalized as a square pyramid with the α,*β*-unsaturated alkenyl ligand located in the apex. The ruthenium alkenyl separation is short (1.989(3) Å), suggesting a significant contribution of the zwitterionic resonance form [Ru$^+$]=CHCH=C(CH$_3$)CH$_2^-$ to the structure of **2**. In agreement with this, complex **2** reacts with HBF$_4$ to afford the carbene derivative [Ru{=CHCH=C(CH$_3$)$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (**3**). The coordination number 6 for **2** can be achieved by addition of carbon monoxide. Thus, bubbling carbon monoxide through a hexane solution of **2** results in the formation of Ru{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)$_2$(P^{i}Pr$_3$)$_2$ (**4**). Complex **4** reacts with CH$_3$Li to give Ru(CH$_3$){(*E*)-CH=CHC(CH$_3$)=CH$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$ (**5**) and with CH$_2$=CHMgBr to afford Ru(CH=CH$_2$){(*E*)-CH=CHC(CH$_3$)=CH$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$ (**6**). Complex **6** is stable, and the carbon−carbon coupling between the vinyl and the α,*β*-unsaturated alkenyl fragment is not observed, even at high temperature (refluxing toluene). However, in the presence of 1 equiv of HBF$_4$, complex **6** evolves to a mixture of products containing the α,*β*-unsaturated allyl compound [Ru{η^3-CH$_2$CHCHCH=C(CH$_3$)$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**7**) in about 50% yield. Treatment of this mixture with an excess of NaCl gives Ru{η^3-CH$_2$CHCHCH=C(CH$_3$)$_2$}Cl(CO)$_2$(P^{i}Pr$_3$) (**8**). Similarly, the addition of an excess of K(CH$_3$CO$_2$) to the mixture affords Ru{η^3-CH$_2$CHCHCH=C(CH$_3$)$_2$}{η^1-OC(O)CH$_3$}(CO)$_2$(P^{i}Pr$_3$) (**9**). The molecular structure of **8** has been determined by X-ray diffraction analysis. The complex is pseudooctahedral with the two carbonyl groups, the chlorine atom, the phosphine ligand, and both terminal carbon atoms of the allyl unit of the α,*β*-unsaturated allyl ligand occupying the six coordination sites. The organic ligand has a w-shaped *syn* geometry. The mechanism for the carbon−carbon coupling is discussed on the basis of the reaction of **6** with DBF$_4$, which affords [Ru{η^3-CH$_2$CHCHCH=C(CH$_2$D)CH$_3$}(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**7**-*d*$_1$).

Introduction

The formation of carbon−carbon bonds mediated by transition metal compounds has emerged in its own right over the last few years as an important step in organic synthesis. These reactions can involve migratory *cis*-ligand insertion, the coupling of adjacent carbon−carbon bonds, and the attack of a reagent to an unsaturated organic ligand without metal−reagent bond formation.[1]

In the search for models of homogeneous transition metal systems effective in the synthesis of functionalized organic molecules from basic hydrocarbons, we have recently observed that the treatment of the alkenyl−osmium(II) complexes Os{(*E*)-CH=CHR}Cl(CO)(P^{i}Pr$_3$)$_2$ (R = H, Ph) with main group organometallic compounds leads to osmium(0) species containing olefin ligands.[2,3] For butadiene and phenylbutadiene the osmium(0) species are stable, and they do not undergo a subsequent transformation.[2] However, for *trans*-stilbene and *trans*-methylstyrene, the metallic center is capable of activating a C−H bond of the substituents of the olefins to afford hydridoosmium(II) derivatives. The C−H activation products depend upon the substituents present at the alkene ligand and can be rationalized in light of thermodynamic and kinetic considerations. Thus, when the alkene ligand is *trans*-methylstyrene, the activation of an ortho position of the phenyl ring is kinetically favored. The product of this activation, which shows an agostic interaction between the osmium center and one of the olefinic C−H bonds, evolves to the more favored thermodynamic product, the allyl derivative OsH(η^3-CH$_2$CHCHPh)(CO)(P^{i}Pr$_3$)$_2$.[3]

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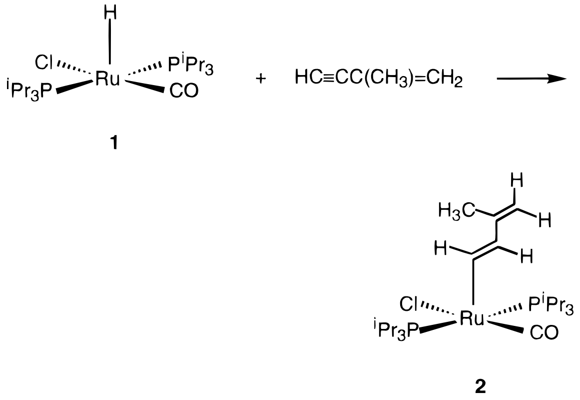
The formation of the osmium(0) species most probably involves the replacement of the Cl$^-$ anion of the alkenyl starting materials by the organic fragments of the main group organometallic compounds, and the subsequent reductive carbon−carbon coupling of the η^1-carbon ligands. In agreement with this, we have also observed that the chloro−styryl ruthenium(II) complex Ru{(*E*)-CH=CHPh}Cl(CO)(P^{i}Pr$_3$)$_2$ reacts with CH$_2$=CHMgBr to give the styryl−vinyl derivative Ru(CH=CH$_2$){(*E*)-CH=CHPh}(CO)(P^{i}Pr$_3$)$_2$, which affords the π-(phenyl)-butadiene Ru(η^4-C$_4$H$_5$Ph)(CO)(P^{i}Pr$_3$)$_2$ by reductive carbon−carbon coupling.

In contrast to the behavior of the five-coordinate complex Ru(CH=CH$_2$){(*E*)-CH=CHPh}(CO)(P^{i}Pr$_3$)$_2$, reductive carbon−carbon coupling between the styryl and vinyl fragments of the saturated compound Ru(CH=CH$_2$){(*E*)-CH=CHPh}(CO)$_2$(P^{i}Pr$_3$)$_2$ does not occur.[2] On the other hand, we have now observed that the alkenyl ligands of the also saturated compound Ru(CH=CH$_2$){(*E*)-CH=CHC(CH$_3$)=CH$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$ undergo carbon−carbon coupling in the presence of HBF$_4$.

In this paper, we report the introduction in a sequential manner of two alkenyl ligands to the ruthenium atom of RuHCl(CO)(P^{i}Pr$_3$)$_2$, to afford the saturated derivative Ru(CH=CH$_2$){(*E*)-CH=CHC(CH$_3$)=CH$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$, and the carbon−carbon coupling between them. In addition the factors governing the coupling are analyzed.

Results and Discussion

1. Introduction of the Alkenyl Ligands. Treatment of a toluene solution of RuHCl(CO)(P^{i}Pr$_3$)$_2$ (**1**) with 1 equiv of 2-methyl-1-buten-3-yne leads to the α,β-unsaturated alkenyl derivative Ru{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$ (**2**), which is a result of the selective addition of the Ru−H bond of **1** to the carbon−carbon triple bond of the enyne (eq 1).



(**1**)

A behavior similar to that of **1** has been observed previously for the five-coordinate monohydrido complexes OsHCl(CO)(P^{i}Pr$_3$)$_2$[4] and RhH(SnPh$_3$)(acac)(PCy$_3$).[5] However, the reaction of *cis*-(Me$_3$Si)CH=CHC≡CSiMe$_3$ with the six-coordinate RuHCl(CO)(PPh$_3$)$_3$ gives a stable complex whose molecular structure is formally regarded as the result of either 1,2-addition of the H−Ru to the double bond or 1,4-addition of the H−Ru to the conjugated enyne.[6]

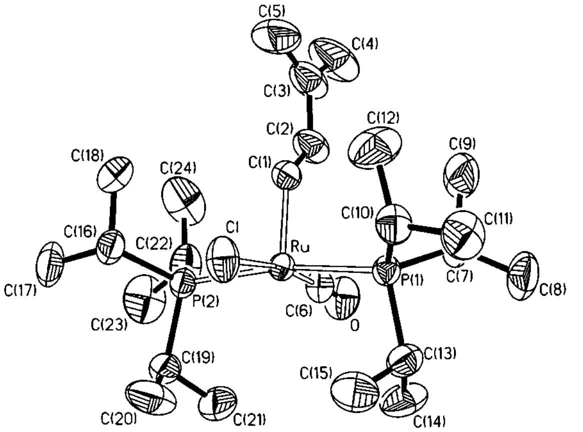


Figure 1. Molecular diagram of complex Ru{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$ (**2**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex Ru{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$ (2)

Ru−Cl	2.4208(7)	C(1)−C(2)	1.340(4)
Ru−P(1)	2.4101(6)	C(2)−C(3)	1.469(5)
Ru−P(2)	2.4052(7)	C(3)−C(4)	1.342(5)
Ru−C(1)	1.989(3)	C(3)−C(5)	1.499(6)
Ru−C(6)	1.812(2)	C(6)−O	1.127(3)
Cl−Ru−P(1)	89.56(2)	P(2)−Ru−C(6)	89.61(8)
Cl−Ru−P(2)	88.75(2)	C(1)−Ru−C(6)	90.2(1)
Cl−Ru−C(1)	99.83(7)	Ru−C(6)−O	178.8(2)
Cl−Ru−C(6)	169.92(9)	Ru−C(1)−C(2)	134.6(2)
P(1)−Ru−P(2)	169.49(2)	C(1)−C(2)−C(3)	124.3(3)
P(1)−Ru−C(1)	95.48(7)	C(2)−C(3)−C(4)	118.8(4)
P(1)−Ru−C(6)	90.26(8)	C(2)−C(3)−C(5)	119.2(3)
P(2)−Ru−C(1)	95.03(7)	C(4)−C(3)−C(5)	122.0(4)

Complex **2** was isolated as a violet solid in 88% yield and characterized by elemental analysis, IR, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy, and an X-ray crystallographic study. The molecular structure is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The geometry can be rationalized as a square pyramid with the alkenyl ligand located at the apex. The four atoms P(1), P(2), Cl, and C(6), forming the base, are approximately in a plane, whereas the ruthenium atom is located 0.2171(2) Å above this plane toward the apical position. The alkenyl, chloride, and carbonyl groups are disposed in a T shape. This is in agreement with previous results obtained by Caulton and co-workers[7] and by us,[8] from related compounds. The high stability of the *trans* Cl, CO disposition seems to be the result of a push−pull mechanism between the π-donor Cl and the π-acceptor CO groups.[7] Furthermore, the stereodiagram shown in Figure 2 illustrates that also in the sixth (formally unoccupied) position of the octahedron the ruthenium atom is well-shielded. Four of the 12 methyl groups of the phosphine ligands surround the metal like an umbrella. The shielding effect of the

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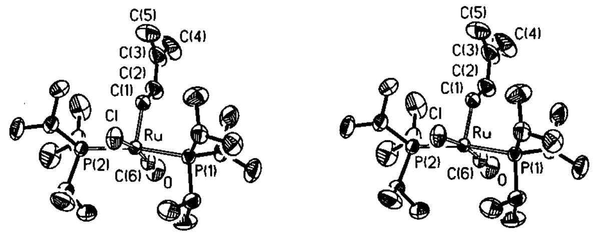


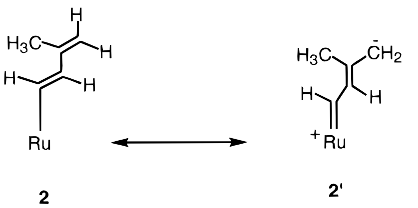
Figure 2. Stereoview of the molecule Ru{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$ (**2**).

methyl groups is certainly supported by the bending of the phosphorus−ruthenium−phosphorus axis, resulting in a P(1)−Ru−P(2) angle of 169.49(2)°. A similar situation has been observed in the complexes Os{(*E*)-CH=CHPh}Cl(CO)(P^{i}Pr$_3$)$_2$ (P−Os−P = 167.4(1)°),[8a] [RuCl(=CHCH=CPh$_2$)(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (P−Ru−P = 163.36(3)°),[8b] and Ru{C(O)CH$_3$}Cl(CO)(P^{i}Pr$_3$)$_2$ (P−Ru−P = 166.54(4)°).[8c] In agreement with the disposition of the phosphine ligands in Figure 1, the ^{31}P{^{1}H} NMR spectrum of **2** shows a singlet at 38.2 ppm.

The alkenyl ligand shows a *trans* disposition for the two substituents, C(CH$_3$)=CH$_2$ and RuCl(CO)(P^{i}Pr$_3$)$_2$, at the C(1)−C(2) double bond. This agrees well with the ^{1}H NMR spectrum, which contains, for the =CH− and RuCH= protons, two doublets at 6.29 and 8.37 ppm, respectively, with a H−H coupling constant of 12.9 Hz, a value which is typical for this arrangement.[8a] The signals corresponding to the =CCH$_3$ and CH$_2$ protons appear as singlets at 1.96, 4.49, and 4.70 ppm. In the ^{13}C{^{1}H} NMR spectrum, the alkenyl ligand gives rise to two triplets at 150.2 (J_{CP} = 10.3 Hz) and 138.9 (J_{CP} = 5.6 Hz) ppm and three singlets at 141.6, 105.6 and 20.0 ppm, which were assigned to C(1), C(2), C(3), C(4), and C(5), respectively.

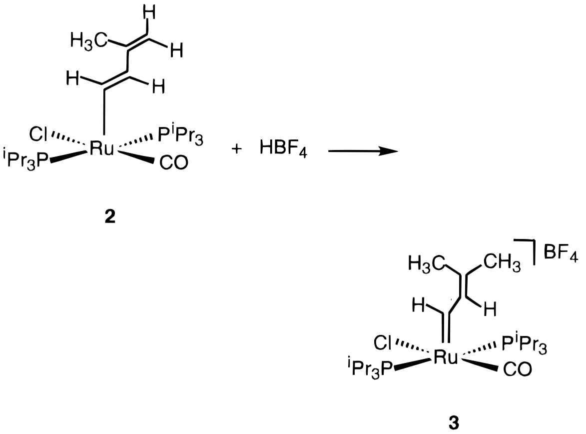
The Ru−C(1) distance (1.989(3) Å) is significantly shorter than the Ru−C distances previously found in the alkenylruthenium(II) derivatives Ru{(*E*)-CH=CHPh}(η^2-O$_2$CCH$_3$)(CO)(PPh$_3$)$_2$ (2.030(15) Å),[9] Ru{(*E*)-CH=CHC$_3$H$_7$}Cl(CO)(Me$_2$Hpz)(PPh$_3$)$_2$ (2.05(1) Å),[10] Ru{(*E*)-CH=CHC(CH$_3$)$_3$}Cl(CO)(Me$_2$Hpz)(PPh$_3$)$_2$ (2.063(7) Å),[11] Ru{(*E*)-CH=CHPh}(η^2-O$_2$CH)(CO)(PPh$_3$)$_2$ (2.036(8) Å),[12] [Ru{(*E*)-CH=CHC(CH$_3$)$_3$}Cl(CO){NH=C(Me$_2$Hpz)CH$_3$}(PPh$_3$)$_2$]PF$_6$ (2.067(8) Å),[13] Ru(CH$_3$){(*E*)-CH=CHPh}(CO)$_2$(P^{i}Pr$_3$)$_2$ (2.141(3) Å),[8c] and Ru{C(CO$_2$Me)=C(CO$_2$Me)Cl}Cl(CO)$_2$(PPh$_3$)$_2$ (2.16(2) Å),[14] where a Ru−C(sp^2) single bond has been proposed. The Ru−C(1) distance is similar to the Ru−C bond lengths reported for the derivatives Ru(η^5-C$_5$H$_5${C=CHCO$_2$CH$_3$)OC(O)CH$_3$}(PPh$_3$) (2.00(2) Å)[15] and [Ru{C(=CHPh)OC(O)CH$_3$}{η^1-OC(CH$_3$)$_2$}(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (1.967(8) Å),[16] containing an alkenylacetato ligand, and where some character of double bond has been proposed for the junction between the ruthenium and the carbon atom of the alkenylacetato ligand.

Scheme 1



The short Ru−C(1) distance, which may be a reflection of the situation of the C(1) atom in the apical position of the metal coordination sphere with no *trans* ligand present, suggests that for an adequate description of the bonding situation in **2** a second zwitterionic resonance form as **2′** (Scheme 1) should be considered. This seems to be also supported for the C(1)−C(2) (1.340(4) Å) and C(3)−C(4) (1.342(5) Å) bond lengths, which are statistically identical with the related distance of the styrylacetato complex [Ru{C(=CHPh)OC(O)CH$_3$}{η^1-OC(CH$_3$)$_2$}(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (1.350(13) Å)[16] and longer than the carbon−carbon bond lengths reported for the double bond of the single alkenyl ligands of the above mentioned complexes.

As a result of the significant contribution of the zwitterionic resonance form **2′** to the structure of **2**, the C(4) atom of the alkenyl ligand has a marked nucleophilic character. Thus, in diethyl ether as solvent, complex **2** reacts with 1 equiv of HBF$_4$ to afford the α,β-unsaturated carbene derivative [Ru{=CHCH=C(CH$_3$)$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (**3**), which was isolated as a green solid in 85% yield (eq 2).



(2)

In the IR spectrum of **3** in Nujol, the most prominent features are a strong ν(C=C) band at 1563 cm^{-1}, which was assigned to the olefinic bond of the vinylcarbene ligand, and the absorption due to the [BF$_4$]$^-$ anion with T_d symmetry at about 1100 cm^{-1} indicating that, although the metallic center of **3** is coordinatively unsaturated, the anion is not coordinated to the ruthenium atom. In the ^{1}H NMR spectrum at room temperature, the alkenyl ligand exhibits resonances at 15.92 (br d, J_{HH} = 11.0 Hz), 7.64 (br d, J_{HH} = 11.0 Hz), and 1.99 ppm, which were assigned to Ru=CH− and −CH= protons and both CH$_3$ groups, respectively. The resonance of the Ru=CH− carbon atom appears in the ^{13}C{^{1}H} NMR spectrum at 240 K as a broad signal at 285.3

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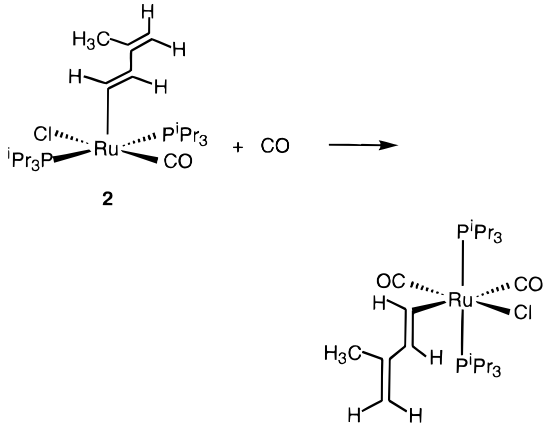
ppm, while the resonances due to the vinylic carbon atoms are observed as singlets at 167.3 and 146.3 ppm. At the same temperature the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 56.8 ppm. These spectroscopic data agree well with those previously reported for the compounds $[Ru(=CHCH=CR^1R^2)Cl(CO)(P^iPr_3)_2]BF_4$ (R^1 = H, R^2 = Ph; R^1 = R^2 = Ph), where the square pyramidal geometry with the carbene ligand in the apical position was determined by an X-ray diffraction experiment on a single crystal of $[Ru(=CHCH=CPh_2)Cl(CO)(P^iPr_3)_2]BF_4$.[8b]

The coordination number 6 for **2** can be achieved by additon of carbon monoxide. Thus, bubbling CO through a hexane solution of **2** results in the formation of the six-coordinate derivative $Ru\{(E)\text{-}CH=CHC(CH_3)=CH_2\}Cl(CO)_2(P^iPr_3)_2$ (**4**), which was isolated as a white solid in 86% yield (eq 3).



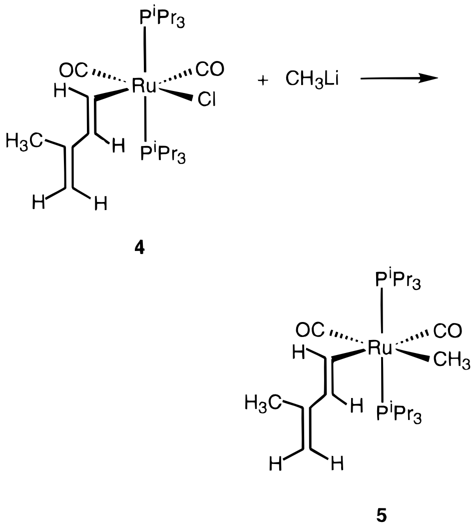
2

(3)

4

Complex **4** is formulated as a *cis*-dicarbonyl derivative on the basis of its IR and $^{13}C\{^1H\}$ NMR spectra. The IR spectrum shows two strong ν(CO) bands at 2000 and 1925 cm^{-1}, a typical pattern for mononuclear *cis*-dicarbonyl complexes. The $^{13}C\{^1H\}$ NMR spectrum supports this proposal, showing two triplets at 198.0 (J_{CP} = 9.0 Hz) and 202.3 (J_{CP} = 11.3 Hz) ppm attributable to the carbonyl ligands. The spectrum also exhibits the expected resonances for the α,β-unsaturated alkenyl ligand. The RuCH= atom gives rise to a triplet at 160.2 ppm, with a C−P coupling constant of 14.3 Hz, while the $C(CH_3)=$, =CH−, $=CH_2$, and CH_3 carbon atoms display singlets at 145.3, 143.1, 108.2, and 19.3 ppm. The CH groups of the phosphine ligands give a virtual triplet at 24.9 ppm (N = 21.0 Hz), which is characteristic of two equivalent phosphine ligands in a *trans* relative position. This is in agreement with the singlet at 36.4 ppm found in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H NMR spectrum shows resonances at 8.08 (d, J_{HH} = 18.3 Hz), 6.49 (d, J_{HH} = 18.3 Hz), 4.92 (s), 4.83 (s), and 2.11 (s) ppm, which were assigned to the RuCH=, =CH−, both $=CH_2$, and CH_3 protons, respectively. The *trans* stereochemistry at the carbon−carbon double bond of the group RuCH=CHR is strongly supported by the proton−proton coupling constant of 18.3 Hz.

Treatment of a toluene solution of **4** with a stoichiometric amount of CH_3Li resulted in the replacement of the Cl^- anion of the starting complex by the methyl group to give $Ru(CH_3)\{(E)\text{-}CH=CHC(CH_3)=CH_2\}(CO)_2(P^iPr_3)_2$ (**5**), which was isolated as a white solid in 80% yield by the addition of methanol, where the complex is stable (eq 4).



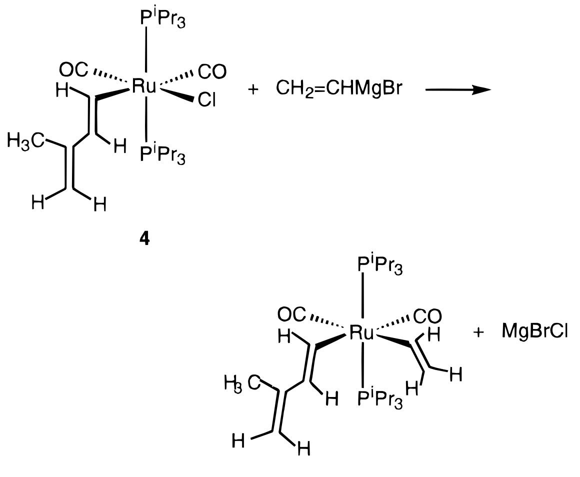
4

(**4**)

5

In agreement with the mutually *cis* disposition of the two carbonyl ligands, the IR spectrum in Nujol shows two ν(CO) absorptions at 1986 and 1920 cm^{-1}, and the $^{13}C\{^1H\}$ NMR spectrum two triplets at 204.4 and 201.4 ppm, with C−P coupling constants of 4.1 and 9.7 Hz, respectively. Furthermore, the spectrum contains four triplets at 161.1 (J_{CP} = 15.2 Hz), 145.2 (J_{CP} = 2.7 Hz), 145.0 (J_{CP} = 4.1 Hz), and −10.4 (J_{CP} = 11.0 Hz), corresponding to the RuCH=, $C(CH_3)=$, =CH−, and $RuCH_3$ carbon atoms, and two singlets at 106.7 and 19.2 ppm due to the $=CH_2$ and $C(CH_3)$ carbon atoms. In the ^1H NMR spectrum, the methyl ligand gives, at 0.18 ppm, a triplet with a P−H coupling constant of 6.3 Hz. The resonances corresponding to the RuCH=CHR group appear at 7.50 (H_α) and 6.99 (H_β) ppm as double triplets with P−H coupling constants of 2.4 and 2.1 Hz, respectively, and a H−H coupling constant of 18.3 Hz, in agreement with the E-stereochemistry around the carbon−carbon double bond. The $^{31}P\{^1H\}$ spectrum agrees well with the mutually *trans* disposition of the phosphine and contains a singlet at 38.0 ppm.

Similarly to the reaction shown in eq 4, the treatment of **4** with $CH_2=CHMgBr$ in toluene leads to $Ru(CH=CH_2)\{(E)\text{-}CH=CHC(CH_3)=CH_2\}(CO)_2(P^iPr_3)_2$ (**6**), which was isolated as a white solid in 75% yield (eq 5).



4

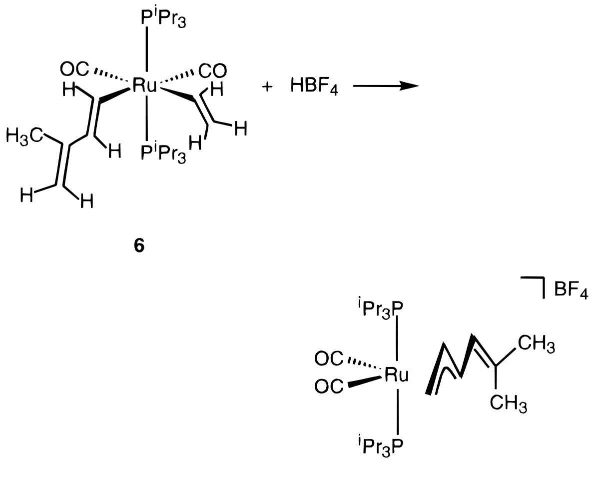
(**5**)

6

As for **5**, the IR spectrum of **6** in Nujol contains two ν(CO) bands, at 1988 and 1925 cm^{-1}. However, in the $^{13}C\{^1H\}$ NMR spectrum the carbonyl ligands are isochronons and give rise at 203.9 ppm to a single triplet with a C−P coupling constant of 9.8 Hz. Furthermore, the spectrum contains four triplets due to the RuCH= and =CHR carbon atoms of the alkenyl ligands at 167.9, 160.8, 145.4, and 127.6 ppm, with C−P coupling constants of 14.7, 15.1, 4.5, and 3.7 Hz, respectively. In the ^1H NMR spectrum, the H_α and H_β protons of the RuCH=CHR group of the α,β-unsaturated alkenyl ligand give rise to double triplets at 7.62 and 6.99 ppm, with P−H coupling constants of 2.5 and 1.8 Hz, respectively, and a H−H coupling constant of 18.6 Hz. The protons of the vinyl ligand display three resonances at 7.82, 6.54, and 6.00 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 35.9 ppm.

Complexes **5** and **6** are stable, and the reductive carbon−carbon coupling between the α,β-unsaturated alkenyl and methyl (**5**) or vinyl (**6**) ligands is not observed even at high temperature (refluxing toluene). This agrees well with previous observations for the compounds $Ru(CH{=}CH_2)\{(E)\text{-}CH{=}CHPh\}(CO)_2(P^iPr_3)_2$,[2] $Ru(CH_3)\{(E)\text{-}CH{=}CHPh\}(CO)_2(P^iPr_3)_2$,[8c] $OsH(CH_3)(CO)_2(P^iPr_3)_2$,[17] and $OsH(CH_2CH{=}CHPh)(CO)_2(P^iPr_3)_2$,[3] which do not evolve either by reductive elimination.

2. Carbon−Carbon Coupling between the Alkenyl Ligands. Although the reductive elimination of 2-methylhexatriene from **6** is not thermally activated, the carbon−carbon coupling between the alkenyl fragments can be carried out in the presence of HBF_4. Thus, the treatment of a diethyl ether solution of **6** with 1.4 equiv of HBF_4 yields, after 20 min at 0 °C, a mixture of products from which the allyl complex $[Ru\{\eta^3\text{-}CH_2CHCH CH{=}C(CH_3)_2\}(CO)_2(P^iPr_3)_2]BF_4$ (**7**) (about 50% yield) was identified by NMR spectroscopy. Complex **7** is formed according to eq 6.



6

(6)

7

In the ^1H NMR spectrum of the mixture, the allyl ligand exhibits two singlets at 1.77 and 1.72 ppm, corresponding to the methyl groups, along with four multiplets at 5.60, 5.27, 4.49, and 3.02 ppm. Furthermore, the ^1H COSY NMR spectrum reveals the presence of a fifth multiplet, which lies under the resonances of the CH−phosphine protons. The P−H and H−H coupling constants within multiplets were inferred from $^1H\{^{31}P\}$ and selective homonuclear $^1H\{^1H\}$ NMR spectra. The value of the H−H coupling constant between the CH_{meso} and the terminal CH_2CHCH*H* protons (11.7 Hz) suggests that these protons are mutually *trans* disposed. The disposition *syn* for the alkenyl group of the allyl ligand appears to be sterically favored, being the usual conformation for allyl ligands in other types of compounds.[18] In the $^{13}C\{^1H\}$ NMR spectrum all carbon atoms of the allyl ligand display singlets between 97.0 and 18.6 ppm, while the carbonyl groups give rise to triplets at 202.6 and 201.0 ppm with P−C coupling constants of 15.1 and 13.2 Hz. For **7**, the $^{31}P\{^1H\}$ NMR spectrum of the mixture shows an AB pattern centered at 41.8 ppm, with a P−P coupling constant of 200.1 Hz, which requires a *trans* disposition of the phosphine ligands.

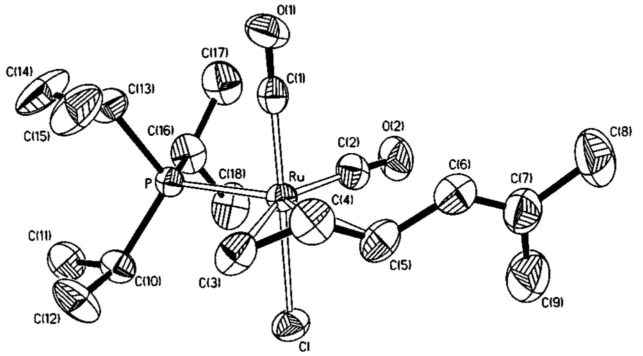
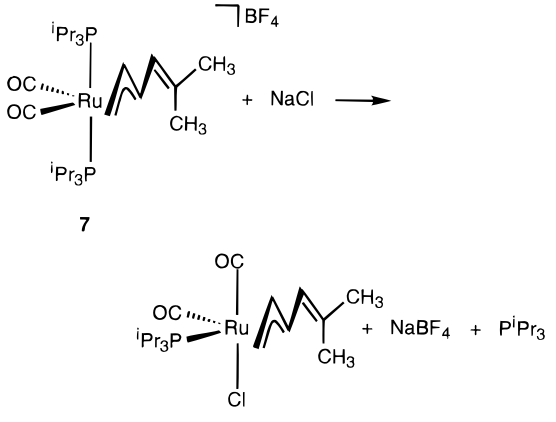


Figure 3. Molecular diagram of complex $Ru\{\eta^3\text{-}CH_2CHCHCH{=}C(CH_3)_2\}Cl(CO)_2(P^iPr_3)$ (**8**).

The full characterization of the allyl ligand was carried out on a monocrystal of the complex $Ru\{\eta^3\text{-}CH_2CHCHCH{=}C(CH_3)_2\}Cl(CO)_2(P^iPr_3)$ (**8**), which is formed according to eq 7, by addition in methanol of an excess of NaCl to the mixture containing **7**. By this procedure complex **8** was obtained as a yellow solid in 75% yield, with regard to the amount of **7** in the mixture.



7

8

(7)

A view of the molecular geometry of **8** is shown in Figure 3. Selected bond distances and angles are listed in Table 2.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex $Ru[\eta^3\text{-}CH_2CHCHCH{=}C(CH_3)_2]Cl(CO)_2(P^iPr_3)$ (8)

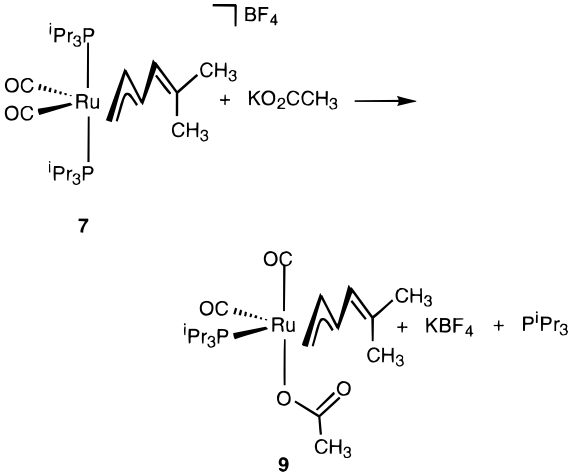
Ru−Cl	2.466(2)	Ru−C(4)	2.231(11)	C(4)−C(5)	1.383(14)
Ru−P	2.398(2)	Ru−C(5)	2.300(8)	C(5)−C(6)	1.463(12)
Ru−C(1)	1.872(7)	C(1)−O(1)	1.109(8)	C(6)−C(7)	1.353(14)
Ru−C(2)	1.918(14)	C(2)−O(2)	1.121(15)	C(7)−C(8)	1.496(13)
Ru−C(3)	2.211(10)	C(3)−C(4)	1.371(15)	C(7)−C(9)	1.470(14)

Cl−Ru−P	88.80(6)	C(2)−Ru−C(4)	123.2(5)
Cl−Ru−C(1)	179.0(2)	C(2)−Ru−C(5)	90.9(4)
Cl−Ru−C(2)	86.5(3)	C(3)−Ru−C(4)	36.0(4)
Cl−Ru−C(3)	86.9(3)	C(3)−Ru−C(5)	65.3(3)
Cl−Ru−C(4)	99.9(3)	C(4)−Ru−C(5)	35.5(3)
Cl−Ru−C(5)	83.9(2)	Ru−C(3)−C(4)	72.9(6)
P−Ru−C(1)	90.2(9)	Ru−C(4)−C(3)	71.2(6)
P−Ru−C(2)	102.1(4)	Ru−C(4)−C(5)	75.0(6)
P−Ru−C(3)	101.0(3)	Ru−C(5)−C(4)	69.5(5)
P−Ru−C(4)	134.2(3)	Ru−C(5)−C(6)	121.7(5)
P−Ru−C(5)	164.7(2)	C(3)−C(4)−C(5)	124(1)
C(1)−Ru−C(2)	93.9(6)	C(4)−C(5)−C(6)	120.5(8)
C(1)−Ru−C(3)	93.2(7)	C(5)−C(6)−C(7)	125.8(8)
C(1)−Ru−C(4)	80.7(4)	C(6)−C(7)−C(8)	120.6(8)
C(1)−Ru−C(5)	97.1(3)	C(6)−C(7)−C(9)	123.5(9)
C(2)−Ru−C(3)	155.8(5)	C(8)−C(7)−C(9)	115.8(8)

The complex is pseudooctahedral with the two carbonyl groups, the chlorine atom, the phosphine ligand, and allyl carbon atoms C(3) and C(5) occupying the six coordination sites. The chlorine atom resides *trans* to one carbonyl ligand (Cl−Ru−C(1) = 179.0(2)°), while the other carbonyl group is *trans* to C(3) (C(2)−Ru−C(3) = 155.8(5)°). The deviation of this angle from the ideal value (180°) results from the small bite angle of the allyl ligand (C(3)−Ru−C(5) = 65.3(3)°). This ligand has a w-shaped *syn* geometry, as has been found previously in related iron,[19] ruthenium[20] and iridium[21] compounds, with torsion angles of 170(1)° and 175(1)° for C(3)−C(4)−C(5)−C(6) and C(4)−C(5)−C(6)−C(7), respectively. Atoms C(3), C(4), C(5), C(6) and C(7) are coplanar. The deviations, with regard to the ruthenium atom, from the best plane are −0.05(1) [C(3)], 0.07(1) [C(4)], 0.029(8) [C(5)], −0.06(1) [C(6)], and −0.002(9) Å [C(7)]. The dihedral angle made by planes C(3)−C(4)−C(5) and C(5)−C(6)−C(7) is 14(1)°. The Ru−C(3) distance (2.211(10) Å) is about 0.09 Å shorter than the Ru−C(5) bond length, possibly due to the different *trans* influence of the carbonyl and phosphine ligands. The carbon−carbon distances within the allylic moiety are 1.371(15) Å for C(3)−C(4) and 1.383(14) Å for C(4)−C(5). Bond C(5)−C(6), which is a carbon−carbon single bond, has a length of 1.463(12) Å. Angle C(4)−C(5)−C(6) (120.5(8)°) is very near the ideal value of 120°, while the angles C(3)−C(4)−C(5) (124(1)°) and C(5)−C(6)−C(7) (125.8(8)°) are somewhat larger.

In the ^1H NMR spectrum, the allyl ligand gives rise to two singlets, at 2.01 and 1.69 ppm, due to the methyl groups and five multiplets at 5.74, 5.36, 4.88, 3.50, and 2.58 ppm corresponding to the four allylic and the olefinic protons. As for **7**, the P−H and H−H coupling constants within multiplets were inferred from $^1H\{^{31}P\}$ and selective homonuclear $^1H\{^1H\}$ NMR spectra. In agreement with the w-shaped *syn* geometry of the ligand, the value of the H−H coupling constant between the CH_{meso} and the terminal $CH_2CHC\mathit{H}$ protons is 11.9 Hz. The $^{13}C\{^1H\}$ NMR spectrum also agrees well with the structure shown in Figure 3. Thus, the signal due to the C(5) carbon atom appears at 84.5 ppm as a doublet with a P−C coupling constant of 17.3 Hz. The other carbon atoms of the allyl display singlets at 16.6 and 16.7 (CH_3), 52.5 [C(3)], 101.8 [C(4)], 126.4 [C(6)], and 135.2 [C(7)]. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 59.4 ppm.

The substitution of one of the two triisopropylphosphine ligands of **7** by acetato, to afford $Ru\{\eta^3\text{-}CH_2CHCHCH{=}C(CH_3)_2\}\{\eta^1\text{-}OC(O)CH_3\}(CO)_2(P^iPr_3)$ (**9**), can be carried out in a manner similar to that previously described for the preparation of **8** (eq 8).



(**8**)

Complex **9** was isolated as a yellow solid in 75% yield and characterized by elemental analysis, IR, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. In agreement with the mutually *cis* disposition of the carbonyl ligands, the IR spectrum shows two $\nu(CO)$ bands in the terminal carbonyl region at 2025 and 1958 cm^{-1}. In addition two $\nu(CO)$ absoptions corresponding to the acetato group are also observed at 1622 and 1320 cm^{-1}. This ligand is formulated as monodentate on the basis of the value calculated for $\Delta\nu$ ($\Delta\nu_{asym} - \Delta\nu_{sym} = 302$ cm^{-1}), which agrees well with those previously reported for related compounds.[22] The structure proposed for **9** in eq 8 is also strongly supported by the $^{13}C\{^1H\}$ NMR spectrum, which contains two doublets at 200.4 ($J_{PC} = 12.1$ Hz) and 199.9 ($J_{PC} = 4.5$ Hz) ppm for the carbonyl ligands and a doublet at 82.5 ($J_{PC} = 17.4$ Hz) ppm for the $CH_2CHC\mathit{H}$ carbon atom of the allyl, which lies *trans* to the phosphine ligand. As for **7** and **8**, from the ^1H NMR spectrum is inferred a value for the H−H coupling constant between the CH_{meso} and $CH_2CHC\mathit{H}$ protons (10.8 Hz), which is in agreement with the proposed w-shaped *syn* geometry. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 59.4 ppm.

The formation of the carbene complex **3** by protonation of the alkenyl compound **2** agrees well with previous observations indicating that in α,β-unsaturated alkenyl ligands the δ-carbon is a nucleophilic center.[4,8b]

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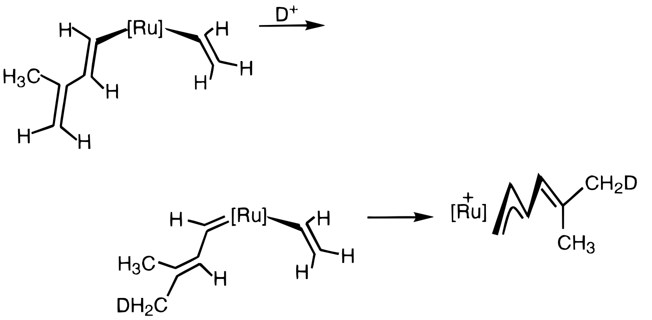
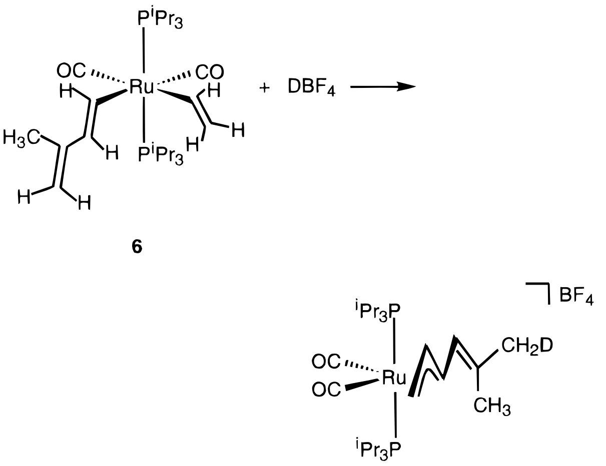
Scheme 2[a]



[a] [Ru] ≡ Ru(CO)$_2$(P^{i}Pr$_3$)$_2$.

In accordance with this, the formation of the α,β-unsaturated allyl ligand of **7**−**9** could be a result of the initial protonation of the alkenyl ligand of **6** and the subsequent vinyl migration from the ruthenium atom to the α-carbon atom of the resulting α,β-unsaturated carbene compound (Scheme 2). Precedents for the alkyl migration from a metal atom to the α-carbon atom of a coordinated carbene ligand are known.[23]

According to Scheme 2, the protonation of **6** with DBF$_4$ should yield an α,β-unsaturated allyl ligand containing a deuterium atom at one of two methyl groups. In fact, the treatment of a diethyl ether solution of **6** with 1 equiv of DBF$_4$ leads to a mixture of products, containing [Ru{η^3-CH$_2$CHCHCH=C(CH$_2$D)CH$_3$}(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**7**-d_1 in eq 9).



6

7-d_1

(**9**)

The presence of a deuterium atom at a methyl group of the α,β-unsaturated allyl ligand is supported by the ^{2}H NMR spectrum of the mixture, which shows a singlet at 1.8 ppm.

Carbene metal complexes, mainly of the Fisher type, are extremely useful in organic synthesis. It is, in particular, the electron deficiency at the α-carbon atom of the carbene ligand which facilitates the attack by nucleophiles, and this promotes the carbon−carbon bond formation.[24] In this context, it should be mentioned that Werner has recently reported the reaction of CH$_2$=CH-MgBr with Ru(η^5-C$_5$H$_5$)Cl(=CR$_2$)(PPh$_3$) to give Ru(η^5-C$_5$H$_5$)(η^3-CH$_2$CHCR$_2$)(PPh$_3$).[25]

Electronic structure and reactivities of organic fragments change, often dramatically, when they coordinate to transition metals to form organometallic complexes. Coordination of [R$_2$C=CH]$^-$ to a transition center transfers the nucleophilicity from the α-carbon atom to the β-carbon atom. Thus, such compounds of electron-donating or electron-rich metals are nucleophilic at the β-carbon atom, and their reactions with electrophiles lead to carbene complexes.[26] According to this, the formation of the α,β-unsaturated ligand by the mechanism shown in Scheme 2 indicates that in **6** the above mentioned electronic transfer is not efficient for the vinyl ligand. A similar situation could be proposed for the alkenyl ligand of the complexes Ru(CH$_3$){(*E*)-CH=CHPh}(CO)$_2$(P^{i}Pr$_3$)$_2$[8c] and Rh(CH=CH$_2$)(C=CH-Ph)(P^{i}Pr$_3$)$_2$.[27]

Concluding Remarks

Although the reductive elimination of 2-methylhexatriene from the complex Ru(CH=CH$_2$){(*E*)-CH=CHC(CH$_3$)=CH$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$ is not thermally activated, this study has revealed that the carbon−carbon coupling of the alkenyl fragments can be carried out in the presence of HBF$_4$. Thus, the protonation of Ru(CH=CH$_2$){(*E*)-CH=CHC(CH$_3$)=CH$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$ with HBF$_4$ leads to [Ru{η^3-CH$_2$CHCHCH=C(CH$_3$)$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$, which reacts with NaCl to afford Ru{η^3-CH$_2$CHCHCH=C(CH$_3$)$_2$}Cl(CO)$_2$(P^{i}Pr$_3$), where the α,β-unsaturated ligand has a w-shape *syn* geometry.

The formation of the α,β-unsaturated allyl ligand involves the electrophilic attack of the proton of the acid to the δ-carbon atom of the α,β-unsaturated alkenyl ligand, and the subsequent vinyl migration from the ruthenium to the α-carbon atom of the resulting α,β-unsaturated carbene ligand. This is a consequence of the high electron density situated on the δ-carbon atom of the α,β-unsaturated alkenyl ligand, as is suggested by the X-ray analysis of complex Ru{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$ and proved by the reaction of this complex with HBF$_4$ to afford [Ru{=CHCH=C(CH$_3$)$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$]BF$_4$. Furthermore, the formation of the allyl ligand suggests that in complex Ru(CH=CH$_2$){(*E*)-CH=CHC(CH$_3$)=CH$_2$}(CO)$_2$(P^{i}Pr$_3$)$_2$ the expected Cα → Cβ electron density transfer is not efficient for the vinyl ligand.

In conclusion, we report the introduction, in a sequential manner, of two alkenyl fragments to a ruthenium atom and the carbon−carbon coupling between these fragments. In addition, we analyze the factors that govern this carbon−carbon coupling.

Experimental Section

General Considerations. All reactions were carried out with rigorous exclusion of air by using Schlenk-tube tech-

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niques. Solvents were dried by known procedures and distilled under argon prior to use.

Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets or NaCl cell windows using a Perkin-Elmer 883 or a Nicolet 550 spectrometer. NMR spectra were recorded on a Varian UNITY 300 or on a Bruker 300 AXR. ^1H NMR spectra were recorded at 299.949 MHz. Chemical shifts are measured relative to the residual ^1H resonance in the deuterated solvent: C_6D_6 (δ 7.15 ppm); $CDCl_3$ (δ 7.24 ppm). $^{13}C\{^1H\}$ NMR spectra were recorded at 75.47 MHz. $^{31}P\{^1H\}$ NMR spectra were recorded at 121.421 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. 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. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. The starting material $RuHCl(CO)(P^iPr_3)_2$ (**1**) was prepared by a published method.[8a]

Preparation of $Ru\{(E)\text{-}CH{=}CHC(CH_3){=}CH_2\}Cl(CO)(P^iPr_3)_2$ (2). A solution of **1** (140 mg, 0.29 mmol) in 10 mL of toluene was treated with 2-methyl-1-buten-3-yne (31 μL, 0.32 mmol). After stirring for 1 h at room temperature, the solvent was removed and the residue was washed repeatedly with cold methanol. It is a violet solid: yield 141 mg (88%). IR (Nujol mull, cm^{-1}): 1908 ν(CO), 1601 and 1549 ν(C=C). Anal. Calcd for $C_{24}H_{49}ClOP_2Ru$: C, 52.21; H, 8.94. Found: C, 52.18; H, 9.19. ^1H NMR (C_6D_6, 293 K): δ 1.18 (dvt, N = 13.2 Hz, J_{HH} = 6.4 Hz, 36H; $PCH(CH_3)_2$), 1.96 (s, 3H; $C(CH_3){=}$), 2.61 (m, 6H; $PCH(CH_3)_2$), 4.70, 4.49 (both s, 2H; $=CH_2$), 6.29 (d, J_{HH} = 12.9 Hz, 1H; =CH−), 8.37 (d, J_{HH} = 12.9 Hz, 1H; RuCH=). $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K): δ 19.7 (s; $PCH(CH_3)_2$), 20.0 (s; $PCH(CH_3)_2$ and $C(CH_3){=}$), 24.6 (vt, N = 19.8 Hz; $PCH(CH_3)_2$), 105.6 (s; $=CH_2$), 138.9 (t, J_{CP} = 5.6 Hz; =CH−), 141.6 (s; $C(CH_3){=}$), 150.2 (t, J_{CP} = 10.3 Hz; RuCH=), 203.6 (t, J_{CP} = 13.3 Hz; CO). $^{31}P\{^1H\}$ NMR (C_6D_6, 293K): δ 38.2 (s).

Preparation of $[Ru({=}CHCH{=}C(CH_3)_2)Cl(CO)(P^iPr_3)_2]BF_4$ (3). A solution of **2** (213 mg, 0.39 mmol) in 15 mL of Et_2O was treated at room temperature dropwise with $HBF_4{\cdot}OEt_2$ (54%) (59 μL, 0.40 mmol). The green-brown precipitate formed was filtered off and washed repeatedly with cold Et_2O and hexane: yield 210 mg (85%). IR (Nujol mull, cm^{-1}) 1975 ν(CO), 1563 ν(C=C), 1050 $\nu(BF_4)$. Anal. Calcd for $C_{24}H_{50}BClF_4OP_2Ru$: C, 45.05; H, 7.88. Found: C, 44.86; H, 7.37. ^1H NMR ($CDCl_3$, 293 K): δ 1.19 (dvt, N = 15.0 Hz, J_{HH} = 7.6 Hz, 18H; $PCH(CH_3)_2$), 1.26 (dvt, N = 14.8 Hz, J_{HH} = 7.3 Hz, 18H; $PCH(CH_3)_2$), 1.99 (s, 6H; CH_3), 2.80 (m, 6H; $PCH(CH_3)_2$), 7.64 (br d, J_{HH} = 11.0 Hz, −CH=), 15.92 (br d, J_{HH} = 11.0 Hz, Ru=CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 240 K): δ 18.9 (s; $PCH(CH_3)_2$), 19.7 (s; $PCH(CH_3)_2$), 22.5 (s; CH_3), 25.2 (vt, N = 22.2 Hz; $PCH(CH_3)_2$), 29.0 (s; CH_3), 146.3 (s; $=C(CH_3)_2$), 167.3 (s; −CH=), 196.2 (t, J_{CP} = 10.6 Hz; CO), 285.3 (br; Ru=CH). $^{31}P\{^1H\}$ NMR (C_6D_6, 240 K): δ 56.8 (s).

Preparation of $Ru\{(E)\text{-}CH{=}CHC(CH_3){=}CH_2\}Cl(CO)_2(P^iPr_3)_2$ (4). Carbon monoxide was bubbled through a solution of **2** (102 mg, 0.19 mmol) in 10 mL of hexane for 2 min at room temperature. The solution was filtered and the solvent was removed. The remaining pale yellow residue was recrystallized from hexane at −78 °C. It is a colorless solid: yield 95 mg (86%). IR (Nujol mull, cm^{-1}): 2000 and 1925 ν(CO), 1600 ν(C=C). Anal. Calcd for $C_{25}H_{49}ClO_2P_2Ru$: C, 44.66; H, 7.25. Found: C, 44.86; H, 7.37. ^1H NMR (C_6D_6, 293 K): δ 1.07 (dvt, N = 12.9 Hz, J_{HH} = 6.0 Hz, 18H; $PCH(CH_3)_2$), 1.30 (dvt, N = 14.0 Hz, J_{HH} = 7.1 Hz, 18H; $PCH(CH_3)_2$), 2.11 (s, 3H; $C(CH_3){=}$), 2.64 (m, 6H; $PCH(CH_3)_2$), 4.92, 4.83 (both s, 2H; $=CH_2$), 6.49 (d, J_{HH} = 18.3 Hz, 1H; =CH−), 8.08 (d, J_{HH} = 18.3 Hz, 1H; RuCH=). $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K): δ 19.2 (s; $PCH(CH_3)_2$), 19.3 (s; $C(CH_3){=}$), 20.3 (s; $PCH(CH_3)_2$), 24.9 (vt, N = 21.0 Hz; $PCH(CH_3)_2$), 108.2 (s; $=CH_2$), 143.1 (s; =CH−), 145.3 (s; $C(CH_3){=}$), 160.2 (t, J_{CP} = 14.3 Hz; RuCH=), 198.0 (t, J_{CP} = 9.0 Hz; CO), 202.3 (t, J_{CP} = 11.3 Hz; CO). $^{31}P\{^1H\}$ NMR (C_6D_6, 293K): δ 36.4 (s).

Preparation of $Ru(CH_3)\{(E)\text{-}CH{=}CHC(CH_3){=}CH_2\}(CO)_2(P^iPr_3)_2$ (5). A solution of **4** (60 mg, 0.107 mmol) in 6 mL of toluene was treated with MeLi (0.1 mL, 0.16 mmol), and the mixture was stirred for 20 min at room temperature. The reaction mixture was quickly filtered though Kieselguhr, and the solvent was removed to leave a white residue. Treatment of this residue with methanol gave a white solid, which was washed with methanol and dried in vacuo: yield 46 mg (80%). IR (Nujol mull, cm^{-1}): 1986 and 1920 ν(CO), 1604 and 1542 ν(C=C). Anal. Calcd for $C_{26}H_{52}O_2P_2Ru$: C, 55.79; H, 9.36. Found: C, 55.79; H, 9.28. ^1H NMR (C_6D_6, 293 K): δ 0.18 (t, J_{HP} = 6.3 Hz, 3H; $RuCH_3$), 1.10 (dvt, N =12.6 Hz, J_{HH} = 6.9 Hz, 18H; $PCH(CH_3)_2$), 1.20 (dvt, N =13.3 Hz, J_{HH} = 7.0 Hz, 18H; $PCH(CH_3)_2$), 2.09 (s, 3H; $C(CH_3){=}$), 2.37 (m, 6H; $PCH(CH_3)_2$), 4.82, 4.90 (both s, 1H; $=CH_2$), 6.99 (dt, J_{HH} = 18.3 Hz, J_{HP} = 2.1 Hz, 1H; =CH−), 7.50 (dt, J_{HH} = 18.3 Hz, J_{HP} = 2.4 Hz, 1H; RuCH=). $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K): δ −10.4 (t, J_{CP} = 11.0 Hz; $RuCH_3$), 19.0 (s; $PCH(CH_3)_2$), 19.2 (s; $C(CH_3){=}$), 19.7 (s; $PCH(CH_3)_2$), 25.2 (vt, N = 20.3 Hz; $PCH(CH_3)_2$), 106.7 (s; $=CH_2$), 145.0 (t, J_{CP} = 4.1 Hz; =CH−), 145.2 (t, J_{CP} = 2.7 Hz; $C(CH_3){=}$), 161.1 (t, J_{CP} = 15.2 Hz; RuCH=), 201.4 (t, J_{CP} = 9.7 Hz; CO), 204.4 (t, J_{CP} = 4.1 Hz; CO). $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K): δ 38.0 (s).

Preparation of $Ru(CH{=}CH_2)\{(E)\text{-}CH{=}CHC(CH_3){=}CH_2\}(CO)_2(P^iPr_3)_2$ (6). A solution of **4** (100 mg, 0.18 mmol) in 10 mL of toluene was treated with $CH_2{=}CHMgBr$ (0.2 mL, 0.2 mmol), and the mixture was stirred for 10 min at room temperature. The reaction mixture was quickly filtered through Kieselguhr, and the solvent was removed to leave a white residue. Treatment of this residue with methanol gave a white solid, which was washed with methanol and dried in vacuo: yield 77 mg (75%); IR (Nujol mull, cm^{-1}): 1988 and 1925 ν(CO), 1604, 1557 and 1544 ν(C=C). Anal. Calcd for $C_{27}H_{52}O_2P_2Ru$: C, 56.72; H, 9.16. Found: C, 56.31; H, 8.54. ^1H NMR (C_6D_6, 293 K): δ 1.16 (dvt, N =13.2 Hz, J_{HH} = 6.9 Hz, 36H; $PCH(CH_3)_2$), 2.10 (s, 3H; $C(CH_3){=}$), 2.49 (m, 6H; $PCH(CH_3)_2$), 4.83, 4.90 (both s, 1H; $=CH_2$), 6.00 (ddt, J_{HH} = 19.6 Hz, J_{HH} = 3.1 Hz, J_{HP} = 2.4 Hz, 1H; $=CH_2$), 6.54 (ddt, J_{HH} = 12.0 Hz, J_{HH} = 3.1 Hz, J_{HP} = 2.8 Hz, 1H; $=CH_2$), 6.99 (dt, J_{HH} = 18.6 Hz, J_{HP} = 1.8 Hz, 1H; =CH−), 7.62 (dt, J_{HH} = 18.6 Hz, J_{HP} = 2.5 Hz, 1H; $RuCH{=}CHC(CH_3){=}$), 7.82 (ddt, J_{HH} = 19.6 Hz, J_{HH} = 12.0 Hz, J_{HP} = 2.1 Hz, 1H; $RuCH{=}CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K): δ 19.5 (s; $C(CH_3){=}$), 19.6, 19.7 (both s; $PCH(CH_3)_2$), 26.1 (vt, N = 20.8 Hz; $PCH(CH_3)_2$), 107.2 (s; $=CH_2$), 127.6 (t, J_{CP} = 3.7 Hz; $=CH_2$), 145.4 (t, J_{CP} = 4.5 Hz; =CH−), 145.5 (t, J_{CP} = 3.0 Hz; $C(CH_3){=}$), 160.8 (t, J_{CP} = 15.1 Hz; RuCH=), 167.9 (t, J_{CP} = 14.7 Hz; RuCH=); 203.9 (t, J_{CP} = 9.8 Hz; CO). $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K): δ 35.9 (s).

Reaction of 6 with HBF_4: Formation of $[Ru\{\eta^3\text{-}CH_2CHCHCH{=}C(CH_3)_2\}(CO)_2(P^iPr_3)_2]BF_4$ (7). A solution of **6** (100 mg, 0.17 mmol) in 10 mL of diethyl ether was treated with $HBF_4{\cdot}OEt_2$ (54%) (36 μL, 0.24 mmol). After stirring for 20 min at 0 °C, the solvent was removed and a pale- yellow solid was obtained. It was a mixture of several products, from which the complex $[Ru\{\eta^3\text{-}CH_2CHCHCH{=}C(CH_3)_2\}(CO)_2(P^iPr_3)_2]BF_4$ (**7**) (yield 50%) was identified by IR and NMR spectroscopy. Spectroscopic data for **7**. IR (Nujol mull, cm^{-1}): 2017 and 1964 ν(CO), 1644 ν(C=C). ^1H NMR ($CDCl_3$, 263 K): δ 1.30−1.45 (m, 36H; $PCH(CH_3)_2$), 1.77, 1.72 (both s, 3H; CH_3), 2.50 (m, 7H; $PCH(CH_3)_2$ and $=CH_{2anti}$), 3.02 (dd, $J_{HsynHmeso}$ = 7.1, $J_{HsynHanti}$ = 2.7 Hz; CH_{2syn}), 4.49 (ddd, $J_{HantiHmeso}$ = 11.7 Hz, J_{HH} = 10.5 Hz, J_{HP} = 6.2 Hz, 1H; CH_2CHCH), 5.27 (vtdd, $J_{HmesoHanti}$ = $J_{HmesoHanti}$ = 11.7, $J_{HmesoHsyn}$ = 7.1, J_{HP} = 6.9 Hz, 1H; CH_{meso}), 5.60 (d, J_{HH} = 10.5 Hz, 1H; $(CH_3)_2C{=}CH-$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 263 K): δ 17.6 (d, J_{CP} = 2.9 Hz; $PCH(CH_3)_2$), 18.6 (s; CH_3), 19.2 (d, J_{CP} = 3.2 Hz; $PCH(CH_3)_2$), 19.7 (d, J_{CP} = 7.3 Hz; $PCH(CH_3)_2$), 20.3 (d, J_{CP} = 6.5 Hz; $PCH(CH_3)_2$), 27.3 (d, J_{CP} = 6.5; $PCH(CH_3)_2$), 27.4 (d, J_{CP} = 9.0; Hz, $PCH(CH_3)_2$), 26.4 (s; CH_3), 33.7 (s; CH_2), 76.2 (s; CH_2CHCH), 97.0 (s; CH_{meso},) 122.2 (s; $(CH_3)C{=}CH-$), 139.1 (s; $(CH_3)_2C{=}$), 201.0 (t, J_{CP} =13.2 Hz; CO), 202.6 (t, J_{CP} = 15.1 Hz; CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 263 K): δ AB system (δ_A = 47.6, δ_B = 35.9, J_{AB} = 200.1 Hz).

Preparation of Ru{η^3-CH$_2$CHCHCH=C(CH$_3$)$_2$}Cl(CO)$_2$(P^{i}Pr$_3$) (8). A solution of the solid containing **7** (98 mg) was treated with NaCl (20 mg, 0.34 mmol) in 10 mL of methanol. The mixture was stirred for 5 h at room temperature. Then the methanol was removed, and the solid residue was treated with toluene. The toluene suspension was filtered, and the filtrate was concentrated to dryness to afford a pale yellow solid. Recrystallization from pentane at −78 °C gave pale-yellow crystals: yield 25 mg (75% with regard to the amount of **7** in the mixture). IR (Nujol mull, cm^{-1}): 2027 and 1958 ν(CO). Anal. Calcd for C$_{18}$H$_{32}$ClO$_2$PRu: C, 48.26; H, 7.20. Found: C, 48.07; H, 7.54. ^{1}H NMR (C$_6$D$_6$, 293 K): δ 1.02 (dd, $J_{HH} = 14.6$ Hz, $J_{HP} = 7.2$ Hz, 9H; PCH(C*H*$_3$)$_2$), 1.11 (dd, $J_{HH} = 14.3$ Hz, $J_{HP} = 7.0$ Hz, 9H; PCH(C*H*$_3$)$_2$), 1.69, 2.01 (both s, 3H; CH$_3$), 2.37 (m, 3H; PC*H*(CH$_3$)$_2$), 2.58 (d, $J_{H_{anti}H_{meso}} = 12.8$ Hz, 1H; CH$_{2anti}$), 3.50 (d, $J_{H_{syn}H_{meso}} = 7.5$, 1H; CH$_{2syn}$), 4.88 (vddt, $J_{H_{meso}H_{anti}} = 12.8$ Hz, $J_{H_{meso}H_{anti}} = 11.9$ Hz, $J_{H_{meso}H_{syn}} = J_{HP} = 7.5$ Hz, 1H; CH$_{meso}$), 5.36 (ddd, $J_{H_{anti}H_{meso}} = 11.9$, $J_{HH} = 10.3$ Hz, $J_{HP} = 5.7$ Hz, 1H; CH$_2$CHC*H*), 5.74 (d, $J_{HH} = 10.3$ Hz, 1H; (CH$_3$)$_2$C=C*H*−). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): δ 16.6, 16.7 (both s; CH$_3$), 18.9, 19.2 (both s; PCH(*C*H$_3$)$_2$), 25.7 (d, $J_{CP} = 20.4$ Hz; P*C*H(CH$_3$)$_2$), 52.5 (s; CH$_2$), 84.5 (d, $J_{CP} = 17.3$ Hz; CH$_2$CH*C*H−), 101.8 (s; CH$_{meso}$), 126.4 (s; (CH$_3$)$_2$C=*C*H−), 135.2 (s; (CH$_3$)$_2$*C*=), 197.8 (d, $J_{CP} = 11.3$ Hz; CO), 199.9 (d, $J_{CP} = 3.8$ Hz; CO). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 59.4 (s).

Preparation of Ru{η^3-CH$_2$CHCHCH=C(CH$_3$)$_2$)(η^1-OC(O)CH$_3$}(CO)$_2$(P^{i}Pr$_3$) (9). A solution of the solid containing **7** (100 mg) was treated with KO$_2$CCH$_3$ (35 mg, 0.35 mmol) in 10 mL of methanol. The mixture was stirred for 5 h at room temperature, then the methanol was removed, and the residue was treated with toluene. The toluene suspension was filtered, and the filtrate was concentrated to afford a pale yellow solid. Recrystallization from pentane at −78 °C gave pale yellow crystals: yield 27 mg (75% with regard to the amount of **7** in the mixture). IR (Nujol mull, cm^{-1}): 2025 and 1958 ν(CO), 1622 ν(OCO)$_{asym}$, 1320 (OCO)$_{sym}$. Anal. Calcd for C$_{20}$H$_{35}$O$_4$PRu: C, 50.95; H, 7.48. Found: C, 51.09; H, 7.08. ^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.97 (dd, $J_{HH} = 7.1$ Hz, $J_{HP} = 6.8$ Hz, 9H; PCH(C*H*$_3$)$_2$), 1.04 (dd, $J_{HH} = 7.1$ Hz, $J_{HP} = 6.3$ Hz, 9H; PCH(C*H*$_3$)$_2$), 2.02 (m, 3H; PC*H*(CH$_3$)$_2$), 1.70 (s, 3H; CH$_3$), 1.98 (s, 3H; OOCCH$_3$), 2.04 (s, 3H; CH$_3$), 2.19 (d, $J_{H_{anti}H_{meso}} = 12.6$ Hz, 1H; CH$_{2anti}$), 3.46 (d, $J_{H_{syn}H_{meso}} = 7.7$ Hz, 1H; CH$_{2syn}$), 4.16 (ddd, $J_{H_{anti}H_{meso}} = 10.8$ Hz, $J_{HH} = 10.4$ Hz, $J_{HP} = 5.9$ Hz, 1H; CH$_2$CHC*H*$_{anti}$), 4.84 (ddd, $J_{H_{meso}H_{anti}} = 12.6$ Hz, $J_{H_{meso}H_{anti}} = 10.8$ Hz, $J_{H_{meso}H_{syn}} = 7.7$ Hz, 1H; CH$_{meso}$), 5.76 (d, $J_{HH} = 10.4$ Hz, 1H; (CH$_3$)$_2$C=C*H*−). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): δ 19.1, 19.2 (both s; PCH(*C*H$_3$)$_2$), 19.7, 24.0 (both s; CH$_3$), 25.4 (d, $J_{CP} = 19.6$ Hz; P*C*H(CH$_3$)$_2$), 26.2 (s; OOC*C*H$_3$), 52.4 (s; CH$_2$), 82.5 (d, $J_{CP} = 17.4$ Hz; CH$_2$CH*C*H), 102.4 (s; CH$_{meso}$), 126.1 (d, $J_{CP} = 4.5$ Hz; (CH$_3$)$_2$C=*C*H−), 134.5 (d, $J_{CP} = 3.8$ Hz; (CH$_3$)$_2$*C*=), 174.1 (s; OO*C*CH$_3$), 199.9 (d, $J_{CP} = 4.5$ Hz; CO), 200.4 (d, $J_{CP} = 12.1$ Hz; CO). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 59.4 (s).

Reaction of 6 with DBF$_4$: Formation of [Ru{η^3-CH$_2$CHCHCH=C(CH$_2$D)CH$_3$}(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (7-d_1). A solution of **6** (100 mg, 0.17 mmol) in 10 mL of diethylether was treated with DBF$_4$ (25 μL, 0.17 mmol of HBF$_4$ + 25 μL of D$_2$O). After stirring for 20 min at 0 °C, the solvent was removed and a pale-yellow solid was obtained. It was a mixture of several products, from which complex [Ru{η^3-CH$_2$CHCHCH=C(CH$_2$D)CH$_3$}(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**7**-d_1) was identified by NMR spectroscopy. Spectroscopic data for **7**-d_1 are as follows. ^{1}H NMR (CDCl$_3$, 243 K): δ 1.30−1.45 (m, 36H; PCH(C*H*$_3$)$_2$), 1.77 (br, 2H; CH$_2$D), 1.72 (s, 3H; CH$_3$), 2.50 (m, 7H; PCH(C*H*$_3$)$_2$ and CH$_{2anti}$), 3.02 (dd, $J_{H_{syn}H_{meso}} = 7.1$, $J_{H_{syn}H_{anti}} = 2.7$ Hz; CH$_{2syn}$), 4.49 (ddd, $J_{H_{anti}H_{meso}} = 11.7$ Hz, $J_{HH} = 10.5$ Hz, $J_{HP} = 6.2$ Hz, 1H; CH$_2$CHC*H*), 5.27 (vtdd, $J_{H_{meso}H_{anti}} = J_{H_{meso}H_{anti}} = 11.7$, $J_{H_{meso}H_{syn}} = 7.1$, $J_{HP} = 6.9$ Hz, 1H; CH$_{meso}$), 5.60 (d, $J_{HH} = 10.5$ Hz, 1H; (CH$_3$)$_2$C=C*H*−). ^{31}P{^{1}H} NMR (CDCl$_3$, 263 K): δ AB system ($\delta_A = 47.6$, $\delta_B = 35.9$, $J_{AB} = 200.1$ Hz). ^{2}H NMR (CHCl$_3$, 293 K): δ 1.8 (br; CH$_2$D).

Table 3. Crystal Data and Data Collection and Refinement for Ru{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$ (2) and Ru[η^3-CH$_2$CHCHCH=C(CH$_3$)$_2$]Cl(CO)$_2$(P^{i}Pr$_3$) (8)

	Crystal Data	
formula	C$_{24}$H$_{49}$ClORuP$_2$	C$_{18}$H$_{32}$ClO$_2$RuP
mol wt	552.12	447.95
color and habit	red, prism	yellow, irregular prism
size, mm	0.60 × 0.57 × 0.50	0.25 × 0.34 × 0.47
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	*Pnma* (No. 62)
a, Å	8.7182(7)	20.911(3)
b, Å	12.1936(8)	8.484(1)
c, Å	13.8621(11)	12.127(3)
α, deg	89.825(5)	
β, deg	80.943(9)	
γ, deg	84.865(6)	
V, Å^3	1449.3(2)	2151.4
Z	2	4
D(calcd), g cm^{-3}	1.265	1.383
	Data Collection and Refinement	
diffractometer	4-circle Siemens-STOE AED	
λ(Mo Kα) Å; technique	0.710 73, bisecting geometry	
monochromator	graphite oriented	
μ, mm^{-1}	0.76	0.93
scan type	$\omega/2\theta$	
2θ range, deg	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 50$
temp, K	293	173
no. of data collected	5460	4453
no. of unique data	5131 ($R_{int} = 0.027$)	2033 ($R_{int} = 0.048$)
unique observed data	4677 ($F_o \ge 4.0\sigma(F_o)$)	1598 ($F_o \ge 4.0\sigma(F_o)$)
no. of params refined	264	206
R,[a] R_w[b]	0.0259, 0.0307	
$R(F)$ ($F_o \ge 4.0\sigma(F_o)$),[a] $R_w(F^2)$ (all rflns)[c]		0.0343, 0.0761

[a] $R = (\sum[|F_o| - |F_c|])/\sum F_o$. [b] $R_w = (\sum([|F_o| - |F_c|])w^{1/2})/\sum(|F_o|w^{1/2})$, $w^{-1} = \sigma^2(F_o) + 0.000292F_o^2$. [c] $R_w(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$, $a = 0.0119$, and $b = 1.92$.

X-ray Structure Analysis of Ru{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$ (2). Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of methanol into a concentrated solution of **2** in toluene. A summary of crystal data, intensity collection procedure, and refinement data is reported in Table 3. The prismatic crystal studied was glued onto 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 60 reflections in the range 20° ≤ 2θ ≤ 45°. The 5460 recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no significant variation was observed. Reflections were also corrected for absorption by a semiempirical method (ψ-scan).[28]

The structure was solved by Patterson (Ru atom) and conventional Fourier techniques. 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. Hydrogen atoms were located from difference Fourier maps and included in the refinement riding on carbon atoms with common isotropic thermal parameters. Atomic scattering factors, corrected for anomalous dispersion for Ru, Cl, and P, were taken from ref 29. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weight defined as $w = 1/(\sigma^2(F_o) + 0.000973(F_o)^2)$. Final R and R_w values were 0.0259 and 0.0307. All calculations were performed by use of the SHELXTL-PLUS system of computer programs.[30]

X-ray Structure Analysis of Ru{η^3-CH$_2$CHCHCH=C(CH$_3$)$_2$}Cl(CO)$_2$(P^{i}Pr$_3$) (8). Crystals suitable for an X-ray

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(28) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(29) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(30) Sheldrick, G. M. *SHELXTL PLUS*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

diffraction experiment were obtained from a solution of **8** in methanol at −20 °C. A summary of crystal data, intensity collection procedure, and refinement data is reported in Table 3. The prismatic crystal studied was glued onto a glass fiber with a perfluoropolyetherol (RS-3000) and mounted on a Siemens AED-2 diffractometer at low temperature. Cell constants were obtained from the least-squares fit of the setting angles of 50 reflections in the range 20° ≤ 2θ ≤ 40°. The 4453 recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no significant variation was observed. Reflections were also corrected for absorption by a semiempirical method (ψ-scan).[28]

The systematic absences indicated that the space group of **8** was either *Pnma* or $Pna2_1$. The structure was solved by Patterson (Ru atom) and conventional Fourier techniques in the space group *Pnma*. The use of the centrosymmetric space group requires the inclusion of disorder in the model. Due to orientational disorder, all atoms except the Ru atom had to be split. The two possible orientations of the molecule are related by the mirror plane at $y = {}^1/_4$. Attempts to describe the structure without disorder in the noncentrosymmetric space group $Pna2_1$ were not successful. 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. Hydrogen atoms were calculated ($d_{\mathrm{CH}} = 0.96$ Å) and included in the refinement riding on carbon atoms with common isotropic thermal parameters. Final $R(F)$ ($F_o \geq 4.0\,\sigma(F_o)$) and $R_w(F^2)$ (all reflections) values were 0.0343 and 0.0761. All calculations were performed by use of the SHELX-TL version 5.0 system of computer programs.[31] Atomic scattering factors were implemented by the program.

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Supporting Information Available: Tables of positional and displacement parameters, bond lengths and angles, and full experimental details for the X-ray analyses (26 pages). Ordering information is given on any current masthead page.

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(31) Sheldrick, G. M. *SHELXTL*, v. 5.0; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.