Cycloaddition between a Transition-Metal Phenylallenylidene Complex and Allyl Alcohol†

Miguel A. Esteruelas,* Angel V. Gómez, Ana M. López, Enrique Oñate, and Natividad Ruiz

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Received February 24, 1998

The allenylidene complex [Ru(η^5-C_5H_5)(C═C═CPh_2)(CO)(P^{i}Pr$_3$)]BF_4 (**1**) reacts with allyl alcohol to give the α,β-unsaturated alkoxycarbene derivative [Ru(η^5-C_5H_5){C(OCH_2-CH═CH_2)CH═CPh_2}(CO)(P^{i}Pr$_3$)]BF_4 (**2**), which affords the alkoxyallenyl compound Ru(η^5-C_5H_5){C(OCH_2CH═CH_2)═C═CPh_2}(CO)(P^{i}Pr$_3$) (**3**) by deprotonation at −78 °C. At room temperature, in solution, complex **3** undergoes an intramolecular Diels−Alder reaction to form the tricyclic tetraenyl complex Ru(η^5-C_5H_5)(9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-*c*]-1-furanyl)(CO)(P^{i}Pr$_3$) (**4**). This isomerization is highly stereospecific due to the chiral nature of **3** and gives a single pair of enantiomers of **4**. For this reaction, first-order constants k_{obs} were obtained in toluene-d_8, which gave activation parameters of $\Delta H^{\ddagger} = 18 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18 \pm 3$ cal K^{-1} mol^{-1}. The structure of **4** was determined by an X-ray investigation, revealing a Ru−C(tricyclic) distance of 2.088(3) Å. Complex **4** reacts with HBF_4 to give the tricyclic carbene compound [Ru(η^5-C_5H_5)(9-phenyl-1,3,3a,4,4a,9a-hexahydronaphtho[2,3-*c*]-1-furanylidene)(CO)(P^{i}Pr$_3$)]BF_4 (**5**). Similarly, the reaction of **4** with DBF_4 affords [Ru(η^5-C_5H_5)(9-phenyl-9a-deutero-1,3,3a,4,4a-pentahydronaphtho[2,3-*c*]-1-furanylidene)-(CO)(P^{i}Pr$_3$)]BF_4 (**5**-d_1). At room temperature with chloroform and tetrahydrofuran as the solvents, complex **5** is unstable and evolves into the cationic acyclic alkoxycarbene derivative [Ru(η^5-C_5H_5){C(OCH_2[1-phenyl-3,4-dihydro-3-naphthyl])H}(CO)(P^{i}Pr$_3$)]$^+$ (**6**), which was isolated as the PF_6 salt by addition of $NaPF_6$. For the isomerization of **5** into **6**, first-order constants k_{obs} were obtained in chloroform-*d*, which gave activation parameters of $\Delta H^{\ddagger} = 20.8 \pm 0.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -10.6 \pm 0.7$ cal K^{-1} mol^{-1}. At room temperature with methanol as the solvent, complex **6** loses the alkoxy group to afford the alcohol 3-hydroxymethyl-1-phenyl-3,4-dihydronaphthalene (**7**) and the organometallic methoxycarbene [Ru(η^5-C_5H_5){C(OCH_3)H}(CO)(P^{i}Pr$_3$)]PF_6 (**8**).

Introduction

The Diels−Alder reaction is one of the most fundamental reactions in synthetic organic chemistry. It is a widely used method for forming carbon−carbon, carbon−heteroatom, and heteroatom−heteroatom bonds. It is a [$_\pi 4_\sigma + {}_\pi 2_\sigma$] cycloaddition in which a conjugated diene compound undergoes a stereospecific addition reaction with another component, called a dienophile. The diene is the 4π component of the reaction, and they may be classified as (i) open ring, (ii) outer ring, (iii) inner−outer ring, (iv) across rings, and (v) inner ring. The dienophile, the 2π reacting partner, is a molecule containing a double or triple bond, which is activated by electron-withdrawing substituents.[1]

The intramolecular version of the Diels−Alder reaction has been used in the total synthesis of natural products.[2] For example, the spontaneous cyclization of an intermediate trienol in the course of the oxidation reaction is the key step in the stereoselective total synthesis of (±)-torreyol.[3] Allenes, acting as dienophiles, have been used to develop a new approach for the synthesis of N-substituted indoles, which are useful intermediates in the synthesis of indol alkaloids.[4]

The formation of carbon−carbon bonds mediated by transition-metal compounds has emerged in its own right over the past few years as an important step in organic synthesis.[5] In this context, allenylidene complexes are attracting considerable interest as precursors

† Dedicated to Prof. Pascual Royo on the occasion of his 60th birthday.

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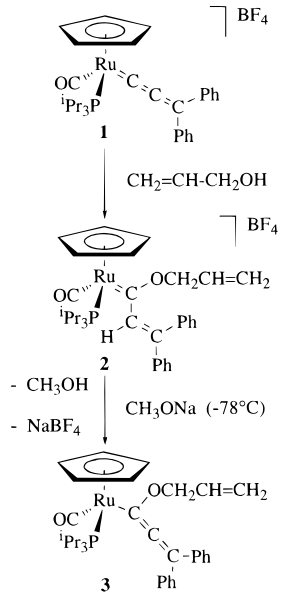
S0276-7333(98)00132-0 CCC: $15.00
Publication on Web 04/30/1998

of new carbon−carbon coupling reactions,[6] in particular, since Selegue reported that propargylic alcohols HCC−CRR′OH could be converted quite smoothly into C=C=CRR′ units in the coordination sphere of an electron-rich transition-metal center by elimination of water.[7] Thus, Werner recently proved that in the series carbene−vinylidene−allenylidene, not only carbene and vinylidene complexes but also allenylidene compounds can be used in metal-assisted C−C bond-forming reactions.[8] In agreement with this, Gimeno et al. have observed that the ruthenium allenylidene derivative $[Ru(\eta^5\text{-}C_9H_7)(C{=}C{=}CPh_2)L_2]PF_6$ (L_2 = 2PPh$_3$, dppm, dppe) underwent regioselective carbon-nucleophilic attacks at C_γ to yield alkynyl derivatives,[9] and Kolobova et al. have shown that the allenylidene ligand of the complex $Mn(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)_2$ can be coupled with *tert*-butylisocyanide to form a cumulenylidene derivative.[10] Fischer et al. have also reported on the formation of binuclear cyclobutenylidene complexes by cycloaddition of the carbon−carbon triple bond of alkynyl complexes to the $C_\alpha-C_\beta$ double bond of allenylidene compounds.[11]

We recently reported that the solvated complex $[Ru(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}OC(CH_3)_2\}(CO)(P^iPr_3)]BF_4$ reacts with 1,1-diphenyl-2-propyn-1-ol to afford the allenylidene derivative $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(P^iPr_3)]BF_4$, which adds water, alcohols, thiols, and benzophenone imine at the $C_\alpha-C_\beta$ double bond of the allenylidene group, to afford diphenyl-α,*β*-unsaturated-hydroxycarbene, -alkoxycarbene, -(alkylthio)carbene, and -2-azaallenyl compounds, respectively. By deprotonation, the hydroxycarbene compounds give acyl derivatives and the alkoxycarbene, (alkylthio)carbene, and 2-azaallenyl complexes yield the corresponding diphenyl−allenyl derivatives.[12]

Although the number and variety of dienes in inter- and intramolecular Diels−Alder reactions is very high, (phenyl)allenes have not been previously used. From the organometallic chemist point of view, this is surprising because transition-metal diphenylallenes, in general, and transition-metal diphenylallenyl complexes, in particular, should be useful inner−outer ring dienes. Our curiosity prompted us to study the reactivity of the diphenylallenylidene complex $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(P^iPr_3)]BF_4$ toward allyl alcohol. In this paper, we report new transition-metal organometallic compounds and new reactions including an intramolecular Diels−Alder reaction on a transition-metal phenylallene complex, where the phenylallene unit acts as an inner−outer ring diene.

Scheme 1



Results and Discussion

1. Addition of Allyl Alcohol to the Allenylidene Ligand of $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(P^iPr_3)]BF_4$. Complex $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(P^iPr_3)]BF_4$ (**1**) adds not only water and saturated alcohols, such as methanol and ethanol, at the $C_\alpha-C_\beta$ double bond of the allenylidene group but also unsaturated alcohols, such as allyl alcohol. Thus, at room temperature with allyl alcohol as the solvent, complex **1** evolves to the α,*β*-unsaturated alkoxycarbene derivative $[Ru(\eta^5\text{-}C_5H_5)\{C(OCH_2CH{=}CH_2)CH{=}CPh_2\}(CO)(P^iPr_3)]BF_4$ (**2**, in Scheme 1). These reactions probably require transition states that favor the transfer of the electrophilic OH-hydrogen atom from the alcohols to the C_β atom of the allenylidene by means of an oxygen−C_α interaction. In this context, it should be mentioned that EHT-MO calculations on the model cation $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CH_2)(CO)(PH_3)]^+$ indicate that 23% of the LUMO is located on C_α and 26% of the HOMO on C_β.[13]

Complex **2** was isolated as a yellow solid in 82% yield by addition of diethyl ether. The presence of the unsaturated η^1-carbon ligand in this compound is strongly supported by the ^{1}H and $^{13}C\{^1H\}$ NMR spectra. In the ^{1}H NMR spectrum, the CH proton of the $-CH{=}CPh_2$ unit gives rise to a singlet at 6.58 ppm while the alkoxy group displays a multiplet at 6.01 ($-CH{=}$) ppm, two doublets at 5.41 (J(HH) = 16.5 Hz) and 5.37 (J(HH) = 10.0 Hz) ppm due to the $=CH_2$ protons, and a multiplet at 5.1 ppm corresponding to the $-OCH_2-$ group. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonances appear at 304.0 (br), 136.9 (s), 129.8 (s), 122.7 (s), and 81.1 (s) ppm. Taking into account the $^1H-^{13}C$ HETCOR spectrum, these resonances were assigned to the Ru=C, $-CH{=}CPh_2$, $-CH{=}$, $=CH_2$, and $-OCH_2-$ carbon atoms, respectively.

Treatment of **2** with sodium methoxide in tetrahydrofuran at −78 °C produces the deprotonation of the olefinic group of the alkoxycarbene ligand to give the alkoxyallenyl derivative $Ru(\eta^5\text{-}C_5H_5)\{C(OCH_2\text{-}$

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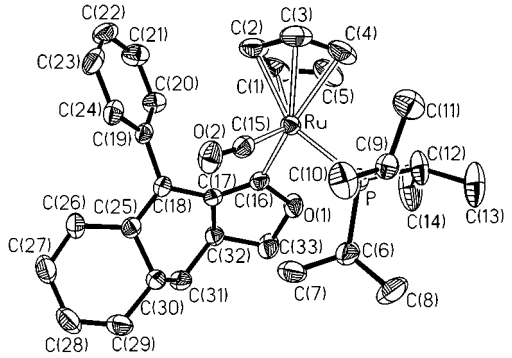


Figure 1. Molecular diagram for Ru(η^5-C_5H_5)(9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-*c*]-1-furanyl)(CO)(P^iPr_3) (**4**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Ru(η^5-C_5H_5)(9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-*c*]-1-furanyl)(CO)(P^iPr_3) (4)

Bond Lengths			
Ru−P	2.355(1)	C(28)−C(29)	1.334(5)
Ru−C(15)	1.858(3)	C(29)−C(30)	1.517(4)
Ru−C(16)	2.088(3)	C(30)−C(31)	1.555(4)
C(16)−C(17)	1.359(4)	C(31)−C(32)	1.561(4)
C(17)−C(18)	1.479(3)	C(32)−C(33)	1.533(4)
C(18)−C(19)	1.500(4)	C(33)−O(1)	1.462(4)
C(18)−C(25)	1.374(4)	O(1)−C(16)	1.424(3)
C(25)−C(26)	1.458(4)	C(25)−C(30)	1.537(4)
C(26)−C(27)	1.350(4)	C(17)−C(32)	1.537(4)
C(27)−C(28)	1.458(5)		
Bond Angles			
P−Ru−C(15)	91.94(9)	C(15)−Ru−C(16)	88.6(2)
P−Ru−C(16)	94.05(8)	C(15)−Ru−G(1)[a]	125.5(2)
P−Ru−G(1)[a]	125.8(2)	C(16)−Ru−G(1)[a]	121.0(2)

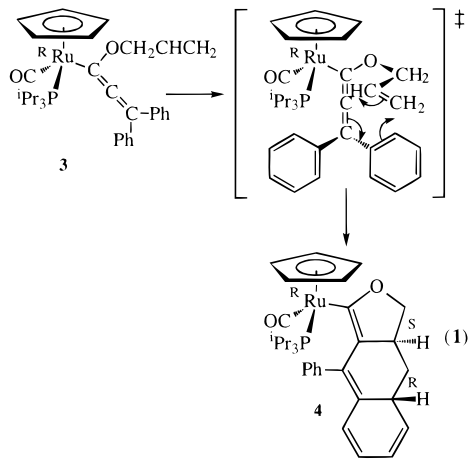
[a] G(1) is the midpoint of the C(1)−C(5) Cp ligand.

$CH{=}CH_2){=}C{=}CPh_2\}(CO)(P^iPr_3)$ (**3**, Scheme 1), which was isolated at −78 °C as a pale yellow solid in 81% yield.

In agreement with the presence of an allenyl ligand in **3**, the IR spectrum of this compound in Nujol shows the characteristic ν(C=C=C) band for this type of ligand[6a] at 1891 cm^{-1} and the $^{13}C\{^1H\}$ NMR spectrum contains a doublet at 136.2 ppm with a C−P coupling constant of 13.8 Hz, which was assigned to the C_α atom, and two singlets at 197.9 and 107.1 ppm corresponding to that C_β and C_γ atoms, respectively. Furthermore the spectrum shows singlets at 135.8, 115.4, and 72.0 ppm due to the $-CH{=}$, $=CH_2$, and $-OCH_2-$ carbon atoms of the alkoxy group, respectively.

Alkoxyallenyl complexes are rare, and the only precedent is the previously mentioned complexes Ru(η^5-C_5H_5)$\{C(OR){=}C{=}CPh_2\}(CO)(P^iPr_3)$ (R = Me, Et), which were prepared in a manner similar to **3**.[12] Attempts to obtain alkoxyallenyl compounds by attack of alkoxy groups at the C_α atom of an allenylidene ligand have been unsuccessful. Thus, Gimeno has found that CH_3O^- is added to the C_γ atom of the allenylidene ligand of the complexes $[Ru(\eta^5\text{-}C_9H_7)(C{=}C{=}CPh_2)L_2]PF_6$ ($L_2 = 2PPh_3$, dppm, dppe).[9b] In agreement with this, we have recently observed that complex **1** and $[Os\{C[C(O)OCH_3]{=}CH_2\}(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2]BF_4$ react with CH_3O^- to give the corresponding γ-functionalized alkynyl complexes Ru(η^5-C_5H_5)$\{C{\equiv}C{-}C(Ph)_2OCH_3\}(CO)(P^iPr_3)$[14] and $[Os\{C[C(O)OCH_3]{=}CH_2\}\{C{\equiv}CC(Ph)_2OCH_3\}(CO)(P^iPr_3)_2$.[15] In addition, it should be mentioned that rhodium-containing γ-functionalized alkynyl groups have been recently prepared by migratory insertion of an allenylidene unit into Rh−OR (R = Ph, CH_3-CO) bonds.[16]

2. Synthesis and Characterization of Ru(η^5-C_5H_5)(9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-*c*]-1-furanyl)(CO)(P^iPr_3) (4). At room temperature, complex **3** evolves, with pentane and toluene as the solvents, into the tricyclic tetraenyl complex **4**, which is a result from two spontaneous carbon−carbon couplings in **3**, the C_β atom of the allenyl unit with the $-CH$ atom of the alkoxy group and, at a time, an *ortho*-carbon atom of one of the two phenyl groups with the $=CH_2$ atom of the alkoxy fragment (eq 1).



Complex **4** was isolated as a yellow solid in 80% yield and characterized by elemental analysis, IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, and an X-ray diffraction study. A view of the molecular geometry is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The geometry around the ruthenium center is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The angles formed by the triisopropylphosphine, carbonyl, and the tetraenyl ligand are all close to 90°. The Ru−C(16) distance (2.088(3) Å) is slightly longer than those found in the alkenyl complexes $Ru(\eta^5\text{-}C_5H_5)\{CC{=}CHCO_2CH_3)OC(O)CH_3\}(PPh_3)$ (2.002(2) Å),[17] $Ru\{C[{=}C(CO_2CH_3)CH{=}CHC(CH_3)_3]C(O)OCH_3\}Cl(CO)(PPh_3)_2$ (2.03(1) Å),[18] $Ru\{(E)\text{-}CH{=}CHC_3H_7\}Cl(CO)(Me_2Hpz)(PPh_3)_2$ (2.05(1) Å),[19] $Ru\{(E)\text{-}CH{=}CHCMe_3\}Cl(CO)(Me_2Hpz)(PPh_3)_2$ (2.063(7) Å),[20] and $[Ru\{(E)\text{-}CH{=}CHCMe_3\}(CO)$-

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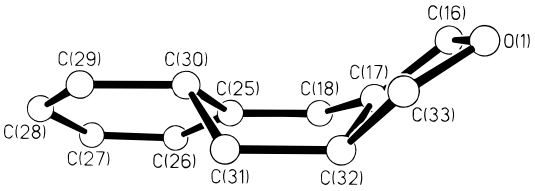

Figure 2. Molecular diagram for the tricyclic ligand of complex **4**.

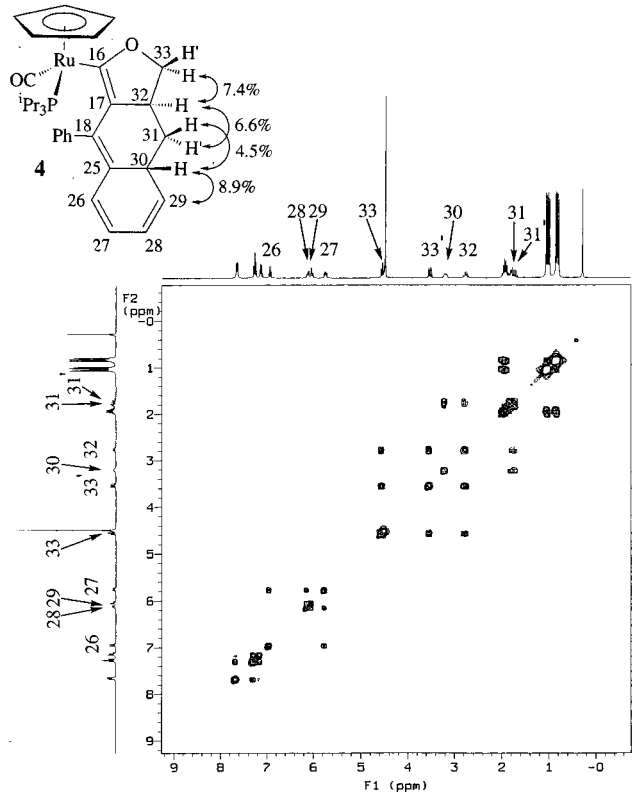

Figure 3. Some selected NOEs and ^{1}H,^{1}H COSY NMR spectra of Ru(η^5-C_5H_5)(9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-*c*]-1-furanyl)(CO)(P^{i}Pr$_3$) (**4**).

{NH=C(Me)(Me$_2$pz}(PPh$_3$)$_2$]PF$_6$ (2.067(8) Å)[21] and is slightly shorter than the Ru−C bond lengths in the complexes Ru(η^5-C_5H_5){C(=CHPh)O^{i}Pr}(CO)(PPh$_3$) (2.103(6) Å),[22] [Ru{C(=CHCO$_2$CH$_3$)CO$_2$CH$_3$}(CO)(NCCH$_3$)$_2$(PPh$_3$)$_2$]ClO$_4$ (2.12(5) Å),[23] and Ru(CH$_3$){(*E*)-CH=CHPh}(CO)$_2$(P^{i}Pr$_3$)$_2$ (2.141(3) Å),[24] where a Ru−C(sp^2) single bond has been also proposed.

Figure 2 shows the skeleton of the tricyclic tetraenyl ligand. The six-membered ring of the corner is almost planar, while the central six-membered ring significantly deviates from planarity, showing a boat conformation. The five-membered heterocycle adopts an envelope conformation with the C(33) atom out from the plane defined by the other four atoms. The structural parameters for the sequence C(16)−C(17)−C(18)−C(25)−C(26)−C(27)−C(28)−C(29) (1.359(4), 1.479(3), 1.374(4), 1.458(4), 1.350(4), 1.458(5), and 1.334(5) Å) strongly

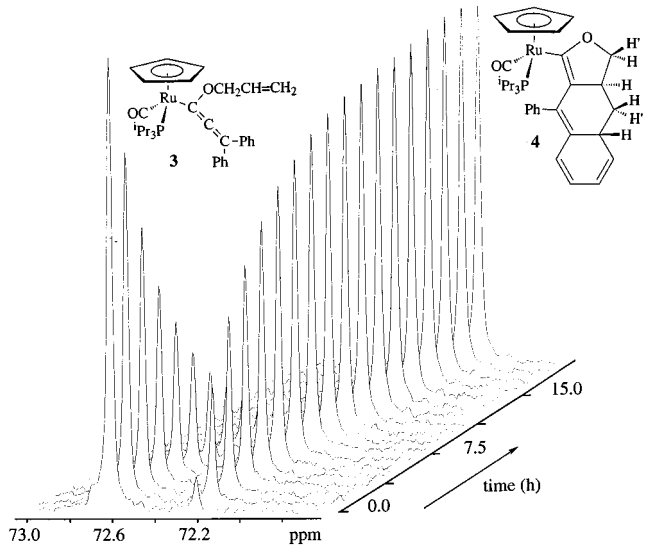

Figure 4. Stacked ^{31}P{^{1}H} NMR spectra illustrating the isomerization of complex **3** to **4** in toluene-d_8 at 293 K.

support the tetraenyl formulation. In this context, it should be mentioned that the distance values for the short−long−short bond sequences are in agreement with those found in the dienyl complex Ru{(*E*)-CH=CH−C(CH$_3$)=CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$ (1.340(4), 1.469(5), and 1.342(5) Å).[25]

In the ^{1}H NMR spectrum, the C*H*− hydrogen atoms of the tricyclic group give rise to resonances at 6.94, 6.11, 6.04, 5.74, 3.20, and 2.76 ppm, which, on the basis of the ^{1}H−^{1}H COSY NMR spectrum shown in Figure 3, were assigned to the hydrogen atoms bonded to the C(26), C(28), C(29), C(27), C(30), and C(32) carbon atoms, respectively. The −CH$_2$− hydrogen atoms display four resonances at 4.54, 3.52, 1.92, and 1.74 ppm. The assignment of these resonances was carried out on the basis of NOE experiments. Irradiation of the resonance at 2.76 ppm gave an increase in the intensities of the signals at 4.54 and 1.74 ppm. From this, we conclude that these resonances correspond to the H(33) and H′(31) hydrogen atoms, respectively (Figure 3). In a further NOE experiment, it was shown that saturation of the resonance at 3.20 ppm increased the intensity of the resonance at 1.92 ppm. In agreement with this, we assign this resonance to the H(31) hydrogen atom.

In the ^{13}C{^{1}H} NMR spectrum, the most noticeable resonance is a doublet at 175.8 ppm, with a C−P coupling constant of 10.5 Hz, which corresponds to the Ru−*C*= carbon atom.

The isomerization of **3** into **4** was followed by ^{31}P{^{1}H} NMR spectroscopy by measuring the disappearance of the P^{i}Pr$_3$ resonance of **3** (δ = 72.6) as a function of time. As shown in Figure 4, the decrease of **3** (with the corresponding increase of **4** (δ = 72.2)) in toluene-d_8 is an exponential function of time, in agreement with a first-order process. The values obtained for the first-order rate constant k_{obs} in the temperature range studied are reported in Table 2. The activation parameters of the reaction were obtained from the Eyring analysis shown in Figure 5, giving values of $\Delta H^{\ddagger} = 18 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18 \pm 3$ cal K^{-1} mol^{-1}. The

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Table 2. Rates of Isomerization of Complex 3 to 4 in Toluene-d_8

temp (K)	k_{obs} (10^5 s^{-1})
293	6.6 ± 0.5
297	9.0 ± 0.6
303	17 ± 2
308	30 ± 2
311	37 ± 3

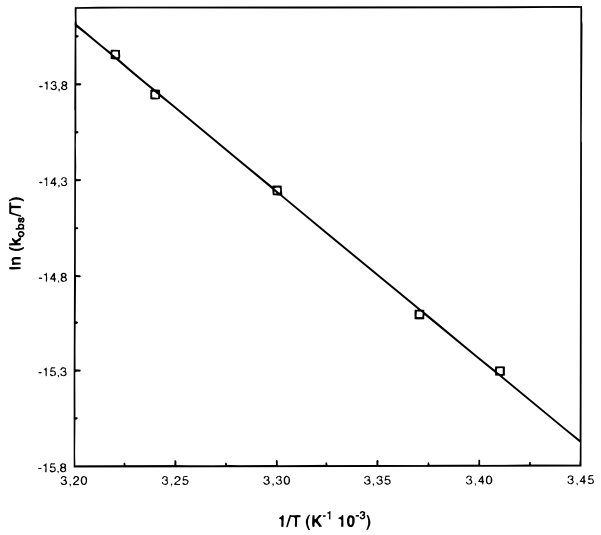


Figure 5. Eyring plot of the first-order rate constants (k_{obs}) for the isomerization of **3** to **4** in toluene-d_8 at 293 K.

large negative value of the activation entropy suggests a concerted mechanism with a geometrically highly oriented transition state. In addition, the stereochemistry observed for the tricyclic ligand (i.e. the relative configurations of the chiral carbons C(30) and C(32)) agrees well with an intramolecular Diels−Alder reaction in **3**, where the $C_\beta-C_\gamma$ double bond and one of the two phenyl groups of the allenyl unit act as an inner−outer ring diene and the $CH{=}CH_2$ double bond of the alkoxy fragment acts as dienophile.

The high degree of stereocontrol directed by the ruthenium center in the formation of **4** deserves to be mentioned. In fact, according to the spectroscopic and X-ray diffraction experiments, only one pair of enantiomers is generated of the two possible pairs that could be expected from the concerted mechanism. As illustrated in eq 1, for the *R* enantiomer of **3**, only the enantiomer Ru-*R*, C(30)-*R*, C(32)-*S* of **4** is obtained. This suggests that the dienophile should approach only one of the two phenyl rings, just that which is away from the bulky P^iPr_3 ligand.

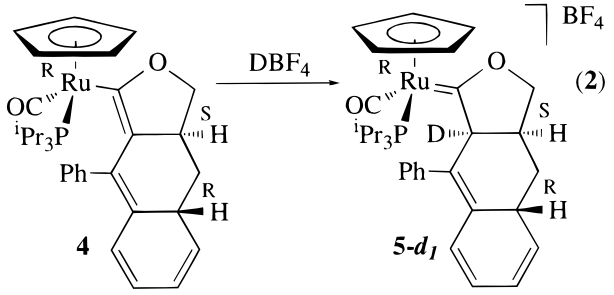
3. Protonation of 4: Preparation of New Cyclic and Acyclic Carbene Derivatives. Treatment of diethyl ether solutions of **4** with 2 equiv of HBF_4 at −78 °C after 3 h leads to the tricyclic carbene derivative [Ru(η^5-C_5H_5)(9-phenyl-1,3,3a,4,4a,9a-hexahydronaphtho[2,3-*c*]-1-furanylidene)(CO)(P^iPr_3)]BF_4 (**5**, in Scheme 2), which is a result of the addition of the proton of the acid to the C(17) atom (C_β-alkenyl carbon atom) of **4**.

Complex **5** was isolated as a white solid in 84% yield and characterized by elemental analysis and IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Figure 6 shows the $^1H-^{13}C$ HETCOR spectrum. The resonances of the ^1H NMR spectrum were assigned on the basis of a $^1H-^1H$ COSY spectrum and NOE experiments. The values of the H−H coupling constants (see Experimental Section) were inferred from selective homonuclear $^1H\{^1H\}$ spectra.

In the ^1H NMR spectrum, the most noticeable resonance is that corresponding to the H(9a) hydrogen atom. It appears at 4.65 ppm as a doublet with a H(9a)−H(3a) coupling constant of 7.8 Hz and shows a positive NOE effect with the resonance due to H(3a), which strongly supports the mutually cis disposition of these atoms. This indicates that the protonation of **4** is also a stereospecific process. Thus, the attack of the proton at the tetraenyl ligand takes place in the direction of the carbonyl group.

In the $^{13}C\{^1H\}$ NMR spectrum, the resonance corresponding to the Ru=*C* (C(1)) carbon atom is observed at 310.4 ppm as a doublet with a C−P coupling constant of 9.2 Hz. The rest of the carbon atoms of the tricyclic ligand give rise to singlets between 139.6 and 28.6 ppm (Figure 6).

Previous studies on alkenyl compounds have identified the localization of electron density at the C_β atom of the alkenyl ligand. The chemical reactivity at this atom is, thus, oriented toward electrophiles.[26] However, the protonation of dienyl complexes occurs at the δ carbon atom of the dienyl ligand, suggesting that in this type of ligands the electron density is located at the C_δ atom.[25,27] The formation of **5** by protonation of **4** suggests that in a tetraenyl ligand the nucleophile center is the C_β atom, as in a simple alkenyl ligand. To confirm this finding and to preclude hypothetical intermediates for the formation of **5**, we carried out the protonation of **4** with DBF_4. Under the same conditions as those previously mentioned for the formation of **5**, we have obtained [Ru(η^5-C_5H_5)(9-phenyl-9a-deutero-1,3,3a,4,4a-pentahydronaphtho[2,3-*c*]-1-furanylidene)(CO)(P^iPr_3)]BF_4 (**5**-d_1, eq 2), which contains the deuterium atom at the C_β carbon atom of the tricyclic carbene ligand. The position of the deuterium atom at the C_β



carbon atom in **5**-d_1 is supported by the ^2H NMR spectrum, which shows a broad singlet at 4.59 ppm. Consequently, the resonance corresponding to H(9a) is absent in the ^1H NMR spectrum of **5**-d_1.

At room temperature with chloroform and tetrahydrofuran as the solvents, complex **5** is unstable and

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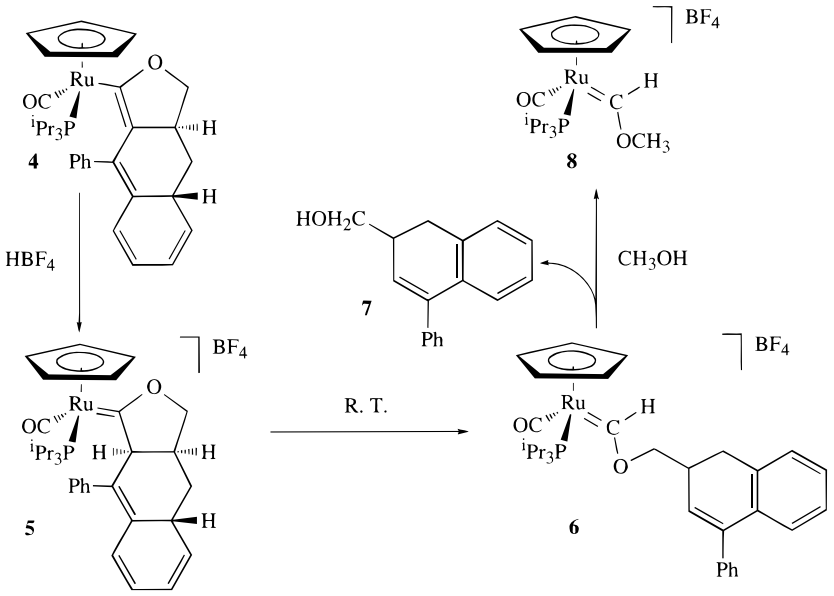
Scheme 2



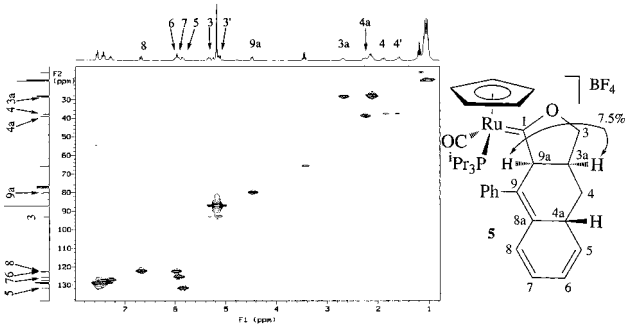


Figure 6. Selected NOE and $^{1}H,^{13}C$ HETCOR NMR spectra of [Ru(η^5-C_5H_5)(9-phenyl-1,3,3a,4,4a,9a-hexahydronaphtho[2,3-*c*]-1-furanylidene)(CO)(P^iPr_3)]BF_4 (**5**).

evolves into the cationic acyclic alkoxycarbene derivative [Ru(η^5-C_5H_5){C(OCH_2[1-phenyl-3,4-dihydro-3-naphthyl])H}(CO)(P^iPr_3)]$^+$ (**6**, Scheme 2) as a result of the intramolecular hydrogen transfer from C(4a) to C(1) with the concomitant aromatization of one of the rings. Complex **6** was isolated as the PF_6 salt in 63% yield by addition of $NaPF_6$ to the tetrahydrofuran solution.

The presence of the alkoxycarbene ligand in this complex is strongly supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra. In the ^1H NMR spectrum, the most noticeable resonance is a singlet at 13.65 ppm, which was assigned to the Ru=C*H* proton, and in the $^{13}C\{^1H\}$ NMR spectrum, a broad resonance at 302.0 ppm corresponding to the Ru=*C* carbon atom is the most prominent.

The isomerization of **5** into **6** was also followed by $^{31}P\{^1H\}$ NMR spectroscopy, by measuring the disappearance of the P^iPr_3 resonance of **5** (δ = 66.9) as a function of time. As shown in Figure 7, the decrease of **5** (with the corresponding increase of **6** (δ = 73.5)) in chloroform is an exponential function of time, in agreement with a first-order process. The values obtained for the first-order rate constant k_{obs} in the temperature range studied are reported in Table 3. The activation parameters of the reaction were obtained from the Eyring analysis shown in Figure 8, giving values of $\Delta H^{\ddagger}$ = 20.8 ± 0.9 kcal mol^{-1} and $\Delta S^{\ddagger} = -10.6 \pm 0.7$ cal K^{-1} mol^{-1}. The large negative value of the activation entropy suggests that, in fact, the hydrogen transfer from C(4a) to C(1) is an intramolecular process, which could proceed by a concerted mechanism with a geometrically highly oriented transition state, as shown in Figure 9.

Table 3. Rates of Isomerization of Complex 5 to 6 in $CDCl_3$

temp (K)	k_{obs} (10^5 s^{-1})
303	3.61 ± 0.08
308	6.0 ± 0.2
313	11.6 ± 0.3
318	16.7 ± 0.4
323	33.9 ± 0.8
328	52 ± 2

At room temperature with methanol as the solvent, complex **6** losses the alkoxy group to afford the alcohol 3-hydroxymethyl-1-phenyl-3,4-dihydronaphthalene (**7**, Scheme 2) and the methoxycarbene derivative [Ru(η^5-C_5H_5){C(OCH_3)H}(CO)(P^iPr_3)]PF_6 (**8**, Scheme 2), which were isolated as white (**7**) and pink (**8**) solids in 81% and 96% yield, respectively.

In the ^1H NMR spectrum of **8**, the methoxycarbene ligand displays a singlet at 11.93 ppm, assigned to the Ru=C*H* proton, and a singlet at 3.45 ppm corresponding to the methoxy group. In the $^{13}C\{^1H\}$ NMR spectrum, the carbene ligand gives rise to a doublet at 299.4 ppm, with a C−P coupling constant of 11.3 Hz, and a singlet at 73.7 ppm, which were assigned to the Ru=*C* and OCH_3 carbon atoms, respectively.

Concluding Remarks

This study has revealed that the allenylidene complex [Ru(η^5-C_5H_5)(C=C=CPh_2)(CO)(P^iPr_3)]BF_4 (**1**) adds allyl alcohol to give the α,β-unsaturated alkoxycarbene [Ru(η^5-C_5H_5){C(OCH_2CH=CH_2)CH=CPh_2}(CO)(P^iPr_3)]BF_4 (**2**), which by deprotonation affords the alkoxyallenyl complex Ru(η^5-C_5H_5){C(OCH_2CH=CH_2)=C=CPh_2}(CO)(P^iPr_3) (**3**).

In solution, complex **3** is stable at low temperature. At room temperature, it evolves into the unprecedented

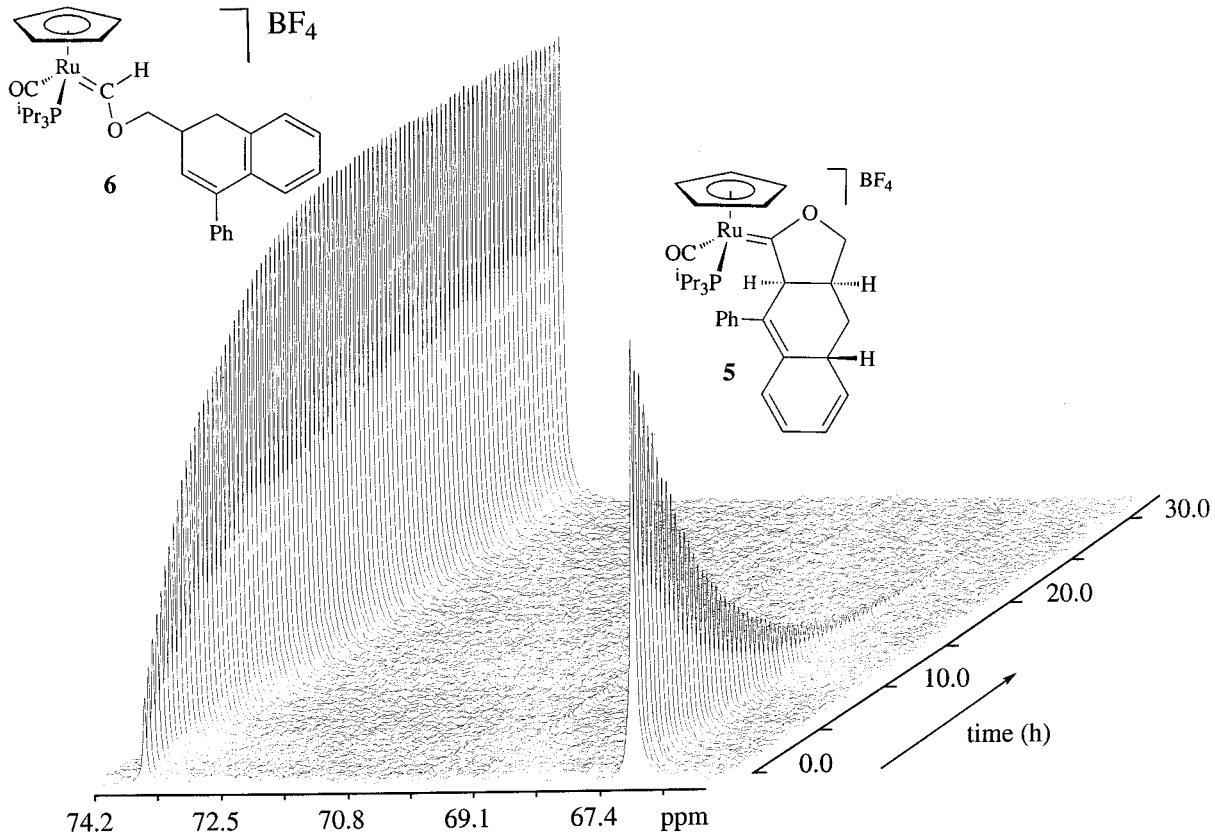


Figure 7. Stacked $^{31}P\{^1H\}$ NMR spectra illustrating the isomerization of complex **5** to **6** in $CDCl_3$ at 303 K.

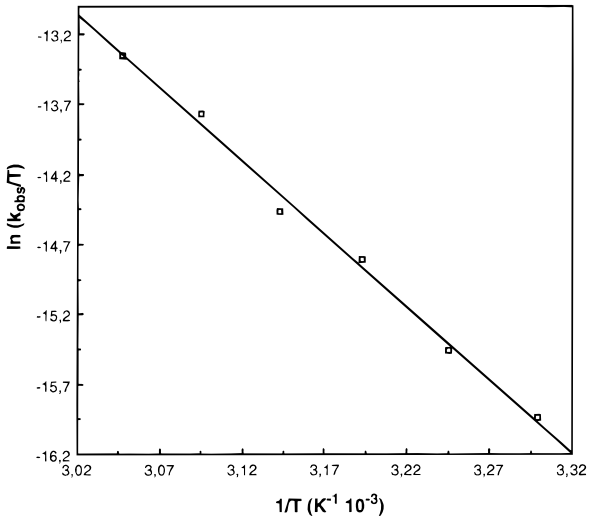
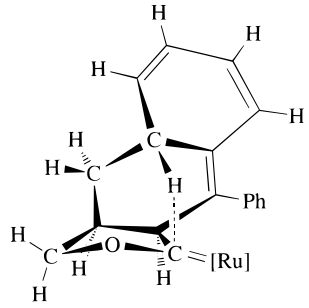


Figure 8. Eyring plot of the first-order rate constants (k_{obs}) for the isomerization of **5** to **6** in $CDCl_3$ at 303 K.

tricyclic tetraenyl derivative Ru(η^5-C_5H_5)(9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-*c*]-1-furanyl)(CO)-(P^iPr_3) (**4**) by an intramolecular Diels−Alder reaction, where the C_β−C_γ double bond and one of the two phenyl groups of the allenyl unit act as an inner−outer ring diene and the CH═CH_2 double bond of the alkoxy fragment acts as a dienophile. The isomerization is highly stereospecific due to the chiral nature of **3**. Thus, the approach of the dienophile to the diene is determined by the *R* or *S* configuration of the metallic center of **3**.

The C_β atom of the tetraenyl ligand of **4** is the nucleophilic center of the molecule. As a consequence, the reaction of **4** with HBF_4 leads to the also unprec-



[Ru] = [Ru(η^5-C_5H_5)(CO)(P^iPr_3)]$^+$

Figure 9. Transition state for the isomerization of **5** to **6**.

edented tricyclic carbene [Ru(η^5-C_5H_5)(9-phenyl-1,3,3a,4,4a,9a-hexahydronaphtho[2,3-*c*]-1-furanylidene)(CO)(P^iPr_3)]BF_4 (**5**) by direct attack of the proton of the acid to the C_β atom of the tetraenyl unit of **4**. The attack is also stereospecific, and the proton makes its entry in the direction pointed by the carbonyl group of **4**.

In solution, complex **5** is also unstable and evolves into the acyclic alkoxycarbene [Ru(η^5-C_5H_5){C(OCH_2[1-phenyl-3,4-dihydro-3-naphthyl])H}(CO)(P^iPr_3)]$^+$ (**6**) by a concerted intramolecular hydrogen transfer reaction. At room temperature with methanol as the solvent, complex **6** losses the alkoxy group to afford the alcohol 3-hydroxymethyl-1-phenyl-3,4-dihydronaphthalene (**7**) and the methoxycarbene organometallic cation [Ru(η^5-C_5H_5){C(OCH_3)H}(CO)(P^iPr_3)]$^+$ (**8**).

In conclusion, we report a step-by-step study of a new cycloaddition reaction involving a transition-metal phenylallenylidene complex and allyl alcohol, which has usefulness in organic synthesis.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material [Ru(η^5-C_5H_5)(C=C=CPh_2)(CO)(P^iPr_3)]BF_4 (**1**) was prepared by the published method.[12]

NMR spectra were recorded on either a Varian UNITY 300, a Varian GEMINI 2000, or a Bruker 300 ARX spectrometer. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, *J*, are given in hertz. IR spectra were run on a Nicolet 550 spectrophotometer (Nujol mulls on polyethylene sheets or KBr pellets). Elemental analyses were carried out on a Perkin-Elmer 2400 CHNS/O analyzer. MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

Preparation of [Ru(η^5-C_5H_5){C(OCH_2CH=CH_2)-CH=CPh_2}(CO)(P^iPr_3)]BF_4 (2). A 120 mg amount of **1** was dissolved in 5 mL of allyl alcohol, and the solution was stirred for 2 h. The color changed from deep red to deep orange, and the solvent was removed in vacuo. The residue was repeatedly washed with diethyl ether, affording a yellow solid. Yield: 113 mg (86.2%). Anal. Calcd for $C_{33}H_{42}BF_4O_2PRu$: C, 57.48; H, 6.14. Found: C, 57.02; H, 5.98. IR (Nujol, cm^{-1}): ν(CO) 1955 (s); ν(Ph, C=C) 1585, 1564 (both m); ν(C−O) 1262 (s); $\nu(BF_4)$ 1056 (br). ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.5−7.1 (m, 10H, Ph), 6.58 (s, 1H, HC=), 6.01 (m, 1H, OCH_2CH=CH_2), 5.41 (d, 1H, J_{trans} = 16.5, OCH_2CH=C*H*H), 5.37 (d, 1H, J_{cis} = 10.0, OCH_2CH=CH*H*), 5.10 (m, 2H, OCH_2CH=CH_2), 4.97 (s, 5H, Cp), 2.26 (m, 3H, PC*H*CH_3), 1.24 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 15.3, PCHC*H*$_3$), 1.18 (dd, 9H, *J*(PH) = 7.2, *J*(PH) = 16.1, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $CDCl_3$): δ 65.9 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $CDCl_3$, plus HETCOR): δ 304.0 (br, Ru=C), 202.9 (d, *J*(PC) = 15.7, CO), 139.6, 137.7 (both s, $C_{ipso-Ph}$ + HC=*C*Ph_2), 136.9 (br s, H*C*=CPh_2), 131.1, 129.7, 129.6, 128.7, 128.6, 128.4 (all s, Ph), 129.8 (s, OCH_2*C*H=CH_2), 122.7 (s, OCH_2CH=*C*H_2), 89.6 (s, Cp), 81.1 (s, O*C*H_2CH=CH_2), 29.3 (d, *J*(PC) = 24.3, P*C*HCH_3), 19.7, 19.4 (both s, PCH*C*H_3).

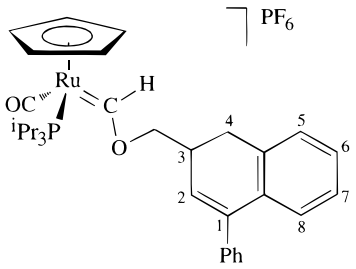
Preparation of Ru(η^5-C_5H_5){C(OCH_2CH=CH_2)=C=CPh_2}(CO)(P^iPr_3) (3). A yellow solution of **2** (200 mg, 0.29 mmol) in 10 mL of THF at −50 °C was treated with sodium methoxide (31.3 mg, 0.58 mmol). The mixture was stirred for 20 min, and the color changed to pale yellow. Solvent was slowly evaporated to dryness. The temperature was decreased to −78 °C, and 15 mL of pentane was carefully added. The suspension was very rapidly filtered to eliminate $NaBF_4$, and the solution recovered at −78 °C. Solvent was slowly evaporated in vacuo to afford a pale yellow solid. Yield: 141 mg (81%). Anal. Calcd for $C_{33}H_{41}O_2PRu$: C, 65.87; H 6.87. Found: C, 65.46; H, 6.91. IR (Nujol, cm^{-1}): ν(CO) 1942 (s); ν(C=C=C) 1891 (w); ν(Ph, C=C) 1643 (w) 1596 (m); ν(C−O) 1030 (s). ^1H NMR (300 MHz, 293 K, C_6D_6): δ 7.71 (m, 4H, Ph), 7.25 (m, 4H, Ph), 7.11 (m, 2H, Ph), 5.94 (dddd, 1H, $J(H_aH_b)$ = $J(H_{a'}H_b)$ = 5.4, J_{trans} = 17.1, J_{cis} = 10.5, $OCH_aH_{a'}CH_b$=CH_cH_d), 5.25 (dddd, 1H, $J(H_aH_d)$ = $J(H_{a'}H_d)$ = $J(H_cH_d)$ = 1.8, J_{trans} = 17.1, $OCH_aH_{a'}CH_b$=CH_cH_d), 5.01 (dddd, 1H, $J(H_aH_c)$ = $J(H_{a'}H_c)$ = $J(H_cH_d)$ = 1.8, J_{cis} = 10.5, $OCH_aH_{a'}CH_b$=CH_cH_d), 4.94 (s, 5H, Cp), 4.37, 4.31 (both dddd, 2H, $J(H_aH_{a'})$ = $J(H_aH_c)$ = $J(H_aH_d)$ = $J(H_{a'}H_c)$ = $J(H_{a'}H_d)$ = 1.8, $J(H_aH_b)$ = $J(H_{a'}H_b)$ = 5.4, $OCH_aH_{a'}CH_b$=CH_cH_d), 1.97 (m, 3H, PC*H*CH_3), 0.96 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 13.5, PCHC*H*$_3$), 0.85 (dd, 9H, *J*(PH) = 7.2, *J*(PH) = 13.2, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 72.6 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 235 K, toluene-d_8, plus apt): δ 207.1 (d, *J*(PC) = 25.8, CO), 197.9 (s, =C=), 141.9, 141.7 (both s, $C_{ipso-Ph}$), 136.2 (d, *J*(PC) = 13.8, Ru−C=), 135.8 (s, OCH_2*C*H=CH_2), 129.1, 129.0, 128,2, 126.0 (all s, Ph), 115.4 (s, OCH_2CH=*C*H_2), 107.1 (s, =*C*Ph_2), 85.8 (s, Cp), 72.0 (s, O*C*H_2CH=CH_2), 27.4 (d, *J*(PC) = 23.0, P*C*HCH_3), 19.7, 19.3 (both s, PCH*C*H_3).

Preparation of Ru(η^5-C_5H_5)(9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-*c*]-1-furanyl)(CO)(P^iPr_3) (4). A solution of **3** (250 mg, 0.63 mmol) in 30 mL of pentane was stirred at room temperature for 20 h, and the color changed from pale yellow to yellow. The solution was concentrated to ca. 2 mL, and a yellow solid precipitated, which was washed with cold pentane. Yield: 200 mg (80%). Anal. Calcd for $C_{33}H_{41}O_2PRu$: C, 65.87; H 6.87. Found: C, 65.63; H, 6.46. IR (Nujol, cm^{-1}): ν(CO) 1935 (vs); ν(C=C, Ph) 1595 (w), 1553 (m), 1521 (s). ^1H NMR (300 MHz, 293 K, C_6D_6, plus COSY, plus NOE): δ 7.65 (m, 2H, Ph), 7.27 (m, 2H, Ph), 7.13 (m, 1H, Ph), 6.94 (dd, 1H, $J(H_{26}H_{27})$ = 9.6, $J(H_{26}H_{28})$ = 0.9, H_{26}), 6.11 (dddd, 1H, $J(H_{28}H_{29})$ = 9.3, $J(H_{27}H_{28})$ = 5.4, $J(H_{28}H_{30})$ = $J(H_{26}H_{28})$ = 0.9, H_{28}), 6.04 (ddd, 1H, $J(H_{28}H_{29})$ = 9.3, $J(H_{29}H_{30})$ = 4.2, $J(H_{27}H_{29})$ = 0.9, H_{29}), 5.74 (dddd, 1H, $J(H_{26}H_{27})$ = 9.6, $J(H_{27}H_{28})$ = 5.4, $J(H_{27}H_{30})$ = 1.5, $J(H_{27}H_{29})$ = 0.9, H_{27}), 4.54 (dd, 1H, $J(H_{33}H_{33'})$ = $J(H_{32}H_{33})$ = 9.0, H_{33}), 4.48 (s, 5H, Cp), 3.52 (dd, 1H, $J(H_{33}H_{33'})$ = 9, $J(H_{32}H_{33'})$ = 12, $H_{33'}$), 3.20 (ddddd, 1H, $J(H_{30}H_{31'})$ = 9.6, $J(H_{30}H_{31})$ = 6.3, $J(H_{29}H_{30})$ = 4.2, $J(H_{27}H_{30})$ = 1.5, $J(H_{28}H_{30})$ = 0.9, H_{30}), 2.76 (dddd, 1H, $J(H_{32}H_{33'})$ = 12, $J(H_{31'}H_{32})$ = 9.6, $J(H_{32}H_{33})$ = 9.0, $J(H_{31}H_{32})$ = 3.6, H_{32}), 1.92 (m, 3H, PC*H*CH_3), 1.81 (ddd, $J(H_{31}H_{31'})$ = 12.6, $J(H_{30}H_{31})$ = 6.3, $J(H_{31}H_{32})$ = 3.6, H_{31}), 1.74 (ddd, $J(H_{31}H_{31'})$ = 12.6, $J(H_{30}H_{31'})$ = $J(H_{31'}H_{32})$ = 9.6, $H_{31'}$), 1.01 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.4, PCHC*H*$_3$), 0.81 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 12.3, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 72.2 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_6, plus DEPT): δ 207.2 (d, *J*(PC) = 18.9, CO), 175.8 (d, *J*(PC) = 10.5, C_{16}), 142.3, 137.2, 133.8, 128.1 (all s, $C_{ipso-Ph}$, C_{17}, C_{18}, C_{25}), 133.0, 131.8, 127.5 (all s, Ph), 126.0, 125.8, 123.4, 119.8 (all s, C_{26}−C_{29}), 85.7 (s, Cp), 78.0 (s, C_{33}), 40.8 (s, C_{31}), 38.4, 36.8 (both s, C_{30}, C_{32}), 27.6 (d, *J*(PC) = 22.1, P*C*HCH_3), 20.7, 19.6 (both s, PCH*C*H_3).

Preparation of [Ru(η^5-C_5H_5)(9-phenyl-1,3,3a,4,4a,9a-hexahydronaphtho[2,3-*c*]-1-furanylidene)(CO)(P^iPr_3)]BF_4 (5). A stirred solution of **4** (200 mg, 0.33 mmol) in 10 mL of diethyl ether at −70 °C was treated with tetrafluoroboric acid (91 μL, 0.66 mmol, 54% in diethyl ether), and the mixture was stirred for 3 h. A white solid precipitated, which was washed with cold diethyl ether. Yield: 192 mg (84%). Anal. Calcd for $C_{33}H_{42}BF_4O_2PRu$: C, 57.48; H, 6.14. Found: C, 57.05; H, 6.08. IR (Nujol, cm^{-1}): ν(CO) 1960 (vs); ν(Ph) 1599 (w); ν(C−O) 1232 (s); $\nu(BF_4)$ 1061 (s). ^1H NMR (300 MHz, 293 K, $CDCl_3$, plus COSY, plus NOE): δ 7.60 (m, 2H, Ph), 7.47 (m, 2H, Ph), 7.31 (m, 1H, Ph), 6.69 (d, 1H, $J(H_8H_7)$ = 9.6, H_8), 5.98 (dd, 1H, $J(H_6H_5)$ = 9.3, $J(H_7H_6)$ = 6.0, H_6), 5.92 (dd, 1H, $J(H_8H_7)$ = 9.6, $J(H_7H_6)$ = 6.0, H_7), 5.79 (dd, 1H, $J(H_6H_5)$ = 9.3, $J(H_5H_{4a})$ = 4.5, H_5), 5.56 (dd, 1H, $J(H_3H_{3'})$ = 9.6, $J(H_{3a}H_3)$ = 7.2, H_3), 5.10 (s, 5H, Cp), 5.08 (dd, 1H, $J(H_3H_{3'})$ = 9.6, $J(H_{3a}H_{3'})$ = 8.1, $H_{3'}$), 4.65 (d, 1H, $J(H_{9a}H_{3a})$ = 7.8, H_{9a}), 2.79 (ddddd, 1H, $J(H_4H_{3a})$ = 1.0, $J(H_{4'}H_{3a})$ = 9.6, $J(H_{3a}H_3)$ = 7.2, $J(H_{3a}H_{3'})$ = 8.1, $J(H_{9a}H_{3a})$ = 7.8, H_{3a}), 2.25 (ddd, 1H, $J(H_5H_{4a})$ = 4.5, $J(H_{4a}H_4)$ = 3.6, $J(H_{4a}H_{4'})$ = 13.2, H_{4a}), 2.19 (m, 3H, PC*H*CH_3), 1.84 (ddd, $J(H_4H_{4'})$ = 13.2, $J(H_{4a}H_4)$ = 3.6, $J(H_4H_{3a})$ = 1.0, H_4), 1.64 (ddd, $J(H_4H_{4'})$ = 13.2, $J(H_{4a}H_{4'})$ = 13.2, $J(H_{4'}H_{3a})$ = 9.6, $H_{4'}$), 1.11 (dd, 9H, *J*(HH) = 7.3, *J*(PH) = 14.7, PCHC*H*$_3$), 1.09 (dd, 9H, *J*(HH) = 7.3, *J*(PH) = 14.1, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $CDCl_3$): δ 66.9 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $CDCl_3$, plus HETCOR): δ 310.4 (d, *J*(PC) = 9.2, C1), 203.4 (d, *J*(PC) = 16.1, CO), 139.6, 139.0, 129.5 (all s, $C_{ipso-Ph}$, C_9, C_{8a}), 131.8 (s, C_5), 129.3, 128.8, 127.6 (all s, Ph), 125.6 (s, C_7), 123.0 (s, C_6), 122.9 (s, C_8), 93.9 (s, C_3), 87.4 (s, Cp), 80.9 (s, C_{9a}), 39.0 (s, C_{4a}), 38.1 (s, C_4), 28.6 (s, C_{3a}), 28.2 (d, *J*(PC) = 23.4, P*C*HCH_3), 19.8 (s, PCH*C*H_3), 19.4 (d, *J*(PC) = 1.8, PCH*C*H_3). MS (FAB^+): *m*/*z* 603 (M^+).

Preparation of [Ru(η^5-C_5H_5)(9-phenyl-9a-deutero-1,3,3a,4,4a-pentahydronaphtho[2,3-*c*]-1-furanylidene)(CO)(P^iPr_3)]BF_4 (5-d_1). The same method as for the preparation of **5** was used but with deuterated tetrafluoroboric acid. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): Absence of the doublet at 4.65 ppm is observed. ^{2}D{^{1}H} NMR (46.07 MHz, 293 K, $CHCl_3$): δ 4.59 (br, D9a).

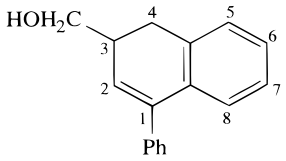
Preparation of [Ru(η^5-C_5H_5){C(OCH$_2$[1-phenyl-3,4-dihydro-3-naphthyl])H}(CO)(P^iPr_3)]PF_6 (6). A solution of **5** (200 mg, 0.29 mmol) in 10 mL of tetrahydrofuran at 50 °C was stirred for 10 h, and the color changed from yellow to orange. Sodium hexafluorophosphate (49 mg, 0.58 mmol) was added, and the mixture was stirred for 30 min. Solvent was evaporated in vacuo, and 10 mL of dichloromethane was added. The mixture was filtered to eliminate excess of sodium hexafluorophosphate and sodium tetrafluoroborate. Solvent was removed in vacuo, and the residue was washed with diethyl ether to afford **6** as a salmon solid. Yield: 137 mg (63%). Anal. Calcd for $C_{33}H_{42}F_6O_2P_2Ru$: C, 53.01; H, 5.66. Found: C, 52.70; H, 5.15. IR (Nujol, cm^{-1}): ν(CO) 1992 (vs);



ν(Ph) 1599 (w); ν(PF_6) 850 (vs). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$, plus COSY): δ 13.65 (s, 1H, Ru=CH), 7.34 (m, 5H, Ar), 7.19 (m, 2H, Ar), 7.12 (m, 1H, Ar), 7.02 (m, 1H, Ar), 5.91 (d, 1H, J(H_2H_3) = 3.6, H_2), 5.54 (s, 5H, Cp), 4.66 (d, 2H, J(HH_3) = 6.6, CH_2O), 3.02 (m, 2H, H_3 + H_4), 2.85 (dd, 1H, J($H_4H_{4'}$) = 16.8, J($H_{4'}H_3$) = 11.7, $H_{4'}$), 2.22 (m, 3H, PC*H*CH_3), 1.22 (dd, 9H, J(HH) = 7.2, J(PH) = 15.0, PCHC*H*$_3$), 1.10 (dd, 9H, J(HH) = 6.9, J(PH) = 15.0, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$): δ 73.5 (s, PCHCH$_3$), −144.4 (sept, J(PF) = 717.0, PF_6). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$, plus HETCOR): δ 302.0 (br, Ru=CH), 201.2 (d, J(PC) = 14.8, CO), 142.0, 139.8, 134.5, 134.1 (all s, $C_{ipso-Ph}$, C_1, C_{4a}, C_{8a}), 129.6, 128.4, 128.2, 127.8, 127.7, 126.7, 125.5 (all s, Ph + C_5−C_8), 125.9 (s, C_2), 90.5 (s, Cp), 89.5 (s, CH_2O), 35.1 (s, C_3), 30.7 (s, C_4), 28.0 (d, J(PC) = 25.3, P*C*HCH$_3$), 19.3, 19.1 (both s, PCH*C*H$_3$). MS (FAB$^+$): *m*/*z* 603 (M$^+$).

Preparation of 3-Hydroxymethyl-1-phenyl-3,4-dihydronaphthalene (7) and [Ru(η^5-C_5H_5){C(OCH$_3$)H}(CO)(P^iPr_3)]PF_6 (8). A solution of **6** (117 mg, 0.16 mmol) in 10 mL of methanol was stirred for 30 min. Solvent was removed in vacuo, and the residue was extracted with diethyl ether, affording a yellow solution and **8** as a salmon solid. Yield: 82 mg (96%). Anal. Calcd for $C_{17}H_{30}F_6O_2P_2Ru$: C, 37.57; H, 5.56. Found: C, 37.83; H, 5.06. IR (Nujol, cm^{-1}): ν(CO) 1986 (vs); ν(PF_6) 850 (vs). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 11.93 (s, 1H, Ru=CH), 4.97 (s, 5H, Cp), 3.45 (s, 3H, OCH_3), 1.94 (m, 3H, PC*H*CH$_3$), 1.01 (dd, 9H, J(HH) = 7.2, J(PH) = 14.7, PCHC*H*$_3$), 0.87 (dd, 9H, J(HH) = 6.6, J(PH) = 15.0, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $CDCl_3$): δ 73.7 (s, PCHCH$_3$), −145.3 (sept, J(PF) = 716.0, PF_6). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$, apt): δ 299.4 (d, J(PC) = 11.3, Ru=C), 202.7 (d, J(PC) = 16.2, CO), 90.2 (s, Cp), 73.7 (s, OCH_3), 27.8 (d, J(PC) = 25.3, P*C*HCH$_3$), 19.3 (s, PCH*C*H$_3$), 18.9 (d, J(PC) = 0.9, PCH*C*H$_3$). MS (FAB$^+$): *m*/*z* 399 (M$^+$).

The yellow solution was concentrated to ca. 1 mL and chromatographed on a 10 cm neutral silica-gel column (eluent, pentane−diethyl ether, 1:1). Solvent was removed in vacuo, and the solid was solved in *n*-pentane and stored at −78 °C to afford **7** as thin white needles. Yield: 30 mg (81%). IR (KBr,



cm^{-1}): ν(OH) 3399 (br); ν(C−O) 1084 (s). ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 7.34−6.93 (m, 9H, Ar), 5.87 (d, 1H, J(H_2H_3) = 3.0, H_2), 3.32 (d, 2H, J(HH_3) = 5.7, CH_2O), 2.69 (d, 2H, J(H_4H_3) = 9.0, H_4) 2.48 (m, 1H, H_3), 1.23 (br s, 1H, OH). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6, plus HETCOR): δ 141.1, 141.0, 136.1, 135.2 (all s, $C_{ipso-Ph}$, C_{4a}, C_{8a}, C_1), 129.2 (s, C_2), 129.1, 128.5, 128.4, 127.6, 127.5, 126.7, 126.1 (all s, C_5−C_8 + Ph), 64.9 (s, CH_2O), 37.6 (s, C_3), 31.3 (s, C_4). MS (FAB$^+$): *m*/*z* 236 (M$^+$).

X-ray Structure Analysis of Ru(η^5-C_5H_5)(9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-*c*]-1-furanyl)(CO)(P^iPr_3) (4). Crystals suitable for the X-ray diffraction study were obtained from a saturated solution of **4** in pentane stored at 4 °C. A summary of crystal data and refinement parameters is reported in Table 4. The yellow, prismatic crystal, of approximate dimensions 0.5 × 0.5 × 0.8 mm, was glued on a glass fiber and mounted on a Siemens-P4 diffractometer. A group of 62 reflections in the range 20° ≤ 2θ ≤ 35 ° were carefully centered at 200 K and used to obtain the unit cell dimensions by least-squares methods. Three standard reflections were monitored at periodic intervals throughout data collection: no significant variations were observed. All data were corrected for absorption using a semiempirical method.[28] The structure was solved by Patterson (Ru atom, SHELXTL-

Table 4. Crystal Data and Data Collection and Refinement for Ru(η^5-C_5H_5)(9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-*c*]-1-furanyl)(CO)(P^iPr_3) (4)

Crystal Data	
formula	$C_{33}H_{41}O_2PRu$
mol wt	601.70
color and habit	yellow, prismatic block
symmetry	triclinic
space group	$P\bar{1}$
a, Å	10.415(3)
b, Å	11.819(4)
c, Å	14.114(5)
α, deg	68.15(2)
β, deg	86.69(2)
γ, deg	69.110(10)
V, Å^3	1500.9(9)
Z	2
D_{calc}, g cm^{-3}	1.331
Data Collection and Refinement	
diffractometer	four-circle Siemens-P4
λ(Mo Kα), Å; technique	0.710 73; bisecting geometry
monochromator	graphite oriented
μ, mm^{-1}	0.60
scan type	$\theta/2\theta$
2θ range, deg	$3 \le 2\theta \le 50$
temp, K	200.0(2)
no.of data collect	7179
no. of unique data	5120 (R_{int} = 0.0495)
no. of params refined	335
R_1[a] ($F^2 > 2\sigma(F^2)$)	0.0297
wR_2[b](all data)	0.0755
S[c] (all data)	1.059

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

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

PLUS[29]) and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL93[30]). Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were located from difference Fourier maps or fixed in idealized positions and refined riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Ru and P, were implemented by the program. The refinement converged to $R_1 = 0.0297$ ($F^2 > 2\sigma(F^2)$) and w$R_2 = 0.0755$ (all data), with weighting parameters $x = 0.0393$ and $y = 0.60$.

Kinetic Analysis. The isomerizations of complexes **3** to **4** and **5** to **6** were followed quantitatively by $^{31}P\{^1H\}$ NMR spectroscopy in toluene-d_8 and $CDCl_3$, respectively. The decrease of the intensity of the signal of P^iPr_3 in complexes **3** and **5** was measured automatically at intervals in a Varian GEMINI 2000 spectrometer. The rate constants and the errors were obtained by fitting the data to an exponential decay function, using the routine programs of the spectrometer. Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained by least-squares fit of the Eyring plot. Error analysis assumed a 6.1% and 2.1% in the rate constants, respectively (the maximum values found in the experimental determinations), and 1 K in the temperature. Errors were computed by published methods.[31]

Acknowledgment. We thank the DGES (Project PB-95-0806, Programa de Promoción General del Conocimiento) for financial support. E.O. thanks the DGA (Diputación General de Aragón) for a grant.

Supporting Information Available: Tables of atomic coordinates, anisotropic and isotropic thermal parameters, experimental details of the X-ray study, bond distances and angles, and selected least-squres planes (13 pages). Ordering information is given on any current masthead page.

OM980132P

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