Articles

Synthesis of Novel Organometallic Compounds Containing η^1-Carbon Polycyclic Ligands: Condensation of Propargyl Alcohol with the Allenylidene Ligand of $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$

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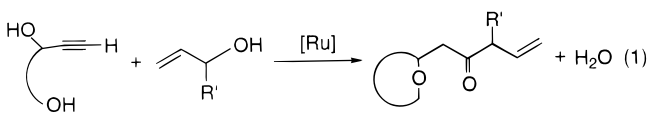
The allenylidene complex $[Ru(\eta^5\text{-}C_5H_5)\{C{=}C{=}CPh_2\}(CO)(PPr^i_3)]BF_4$ (**1**) reacts with propargyl alcohol to give the α,β-unsaturated alkoxycarbene derivative $[Ru(\eta^5\text{-}C_5H_5)\{C(OCH_2C{\equiv}CH)CH{=}CPh_2\}(CO)(PPr^i_3)]BF_4$ (**2**). The structure of **2** was determined by an X-ray investigation, revealing a Ru−C distance of 1.965(4) Å. Treatment of **2** with 1 equiv of Na_2CO_3 affords $[Ru(\eta^5\text{-}C_5H_5)\{9\text{-phenyl-1,3-dihydronaphtho[2,3-}c\text{]-1-furanylidene}\}(CO)(PPr^i_3)]BF_4$ (**3**), which reacts with $NaBH_4$ to give $Ru(\eta^5\text{-}C_5H_5)\{CH_2(1\text{-phenyl-3-hydroxymethyl-2-naphthyl})\}(CO)(PPr^i_3)$ (**4**). The structure of **3** was determined by an X-ray diffraction analysis, revealing a Ru−C bond length of 2.004(2) Å. Treatment of **2** with 3 equiv of $NaOCH_3$ leads to a mixture of compounds containing the racemic form $(Ru_R,C_R;Ru_S,C_S)$-$Ru(\eta^5\text{-}C_5H_5)\{9\text{-phenyl-1,3-dihydronaphtho[2,3-}c\text{]-1-furanyl}\}(CO)(PPr^i_3)$ (**5**) as the main component. This racemic form was obtained as a pure solid by passing the crude products through an Al_2O_3 column using diethyl ether as eluent. The structure of **5** was also determined by an X-ray diffraction analysis. In this case, the investigation reveals a Ru−C distance of 2.203(3) Å. When the crude products were passed through an Al_2O_3 column using a pentane/diethyl ether (5:1) mixture, the epimerization of **5** into $(Ru_R,C_S;Ru_S,C_R)$-$Ru(\eta^5\text{-}C_5H_5)\{9\text{-phenyl-1,3-dihydronaphtho[2,3-}c\text{]-1-furanyl}\}(CO)(PPr^i_3)$ (**6**) was observed. When the above-mentioned chromatography is carried out using an increasing polarity mixture of toluene/diethyl ether (from 10:1 to 1:10) as eluent, the transformation of **5** into its isomer $Ru(\eta^5\text{-}C_5H_5)\{CH_2(1\text{-phenyl-3-carboxa-2-naphthyl})\}(CO)(PPr^i_3)$ (**7**) occurs. The complex $Ru(\eta^5\text{-}C_5H_5)\{9\text{-phenyl-3,3a-dihydronaphtho[2,3-}c\text{]-1-furanyl}\}(CO)(PPr^i_3)$ (**8**) was also synthesized, by passing **2** through an Al_2O_3 column using a tetrahydrofuran/dichloromethane (5:1) mixture as eluent.

Introduction

Transition metal allenylidene complexes ($MC{=}C{=}CR_2$) have attracted a great deal of attention in recent years[1,2] as a new type of organometallic intermediate that may have unusual reactivity in stoichiometric[3] and catalytic[4] processes. Thus, cyclization of diols via transient allenylidene complexes concomitant with the addition of allylic alcohols represents a novel way to build heterocycles (eq 1).[5]



The formation of these heterocycles, which is catalyzed by the fragment $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$, involves the intramolecular addition of the terminal OH group to the $C_\beta-C_\gamma$ double bond of the transient allenylidene and the subsequent nucleophilic addition of the allylic alcohol to the resulting functionalized vinylidene intermediate (Scheme 1). That ring closure of the function-

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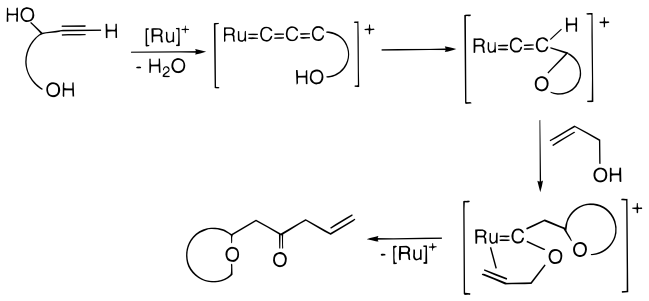
Scheme 1

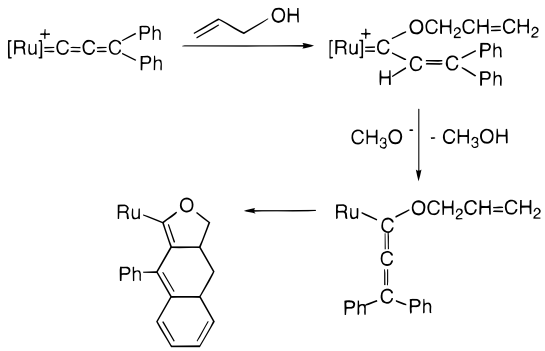


alized allenylidene precedes addition of allyl alcohol is suggested by the total lack of reactivity of the stoichiometrically formed complexes $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CHR)(PPh_3)_2]^+$ with allyl alcohols.[5a] The selectivity observed for the ring closure agrees well with EHT-MO calculations, indicating that the C_α and C_γ atoms of the allenylidene ligands are electrophilic centers, while the C_β atom is nucleophilic.

EHT-MO calculations also indicate that allenylidenes coordinate to metal centers as σ-donor and π-acceptor ligands. The interaction between the HOMO of the allenylidene and the LUMO of the metallic fragment produces a lower charge transfer than the interaction between the HOMO of the metallic fragment and the LUMO of the allenylidene. Then, the π-acceptor component of the metal−allenylidene bond is stronger than the σ-donor one.[6]

As a result of this bonding situation, there are marked differences in reactivity depending on the particular metallic fragment which stabilizes the allenylidene unit. This is nicely illustrated by the behavior of the diphenylallenylidene moiety in the iron triad complexes. The C_3-organic fragment of the osmium complex $Os(\eta^5\text{-}C_5H_5)Cl(C{=}C{=}CPh_2)(PPr^i_3)$ has a marked nucleophilic character, as revealed by its lack of reactivity toward water, alcohols, phosphines, amines, etc. and its reactions with HBF_4 and dimethyl acetylenedicarboxylate, which afford $[Os(\eta^5\text{-}C_5H_5)Cl(CCH{=}CPh_2)(PPr^i_3)]BF_4$ and $Os(\eta^5\text{-}C_5H_5)Cl\{C{=}C(CO_2Me)C(CO_2Me){=}C{=}CPh_2\}(PPr^i_3)$, respectively.[7] In contrast to this complex, the diphenylallenylidene organic moiety stabilized by the metallic fragments $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ [5a] and $[Ru(\eta^5\text{-}C_9H_7)L_2]^+$ (L_2 = 2 PPh_3, dppe, dppm)[8] has a moderated electrophilic character. These complexes do not undergo intermolecular addition of weak nucleophilic reagents (i.e. water and alcohols), and the reactions with strong nucleophiles, such as methoxide, alkyl, and acetylide,

Scheme 2



$[Ru]^+ = [Ru(\eta^5\text{-}C_5H_5)(CO)(PPr^i_3)]^+$

lead to functionalized alkynyl complexes as a result of the regioselective addition of the reagents at the C_γ atom of the diphenylallenylidene group. In this respect, it should be mentioned that, in general, the net charge on the C_α atom is significantly higher than that on the C_γ atom.[6d]

The behavior of these ruthenium compounds is similar to that of other cationic allenylidene complexes of the iron triad stabilized by relatively basic metallic fragments.[1,2,9] Three years ago, interest in the change of properties of the diphenylallenylidene ligand on moving from the more basic metallic fragments led us to prepare the complex $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$ (**1**),[10] where the carbonyl group increases the electrophilicity of the C_3-organic fragment.[11] As a consequence of this increment, complex **1** adds water, methanol, and ethanol at the $C_\alpha{-}C_\beta$ double bond of the allenylidene to afford the corresponding α,β-unsaturated hydroxy- and alkoxycarbene compounds, respectively. By deprotonation the alkoxycarbene complexes give alkoxyallenyl derivatives.[10]

Complex **1** reacts not only with saturated alcohols but also with allyl alcohol without precoordination of the olefinic moiety. The reaction gives rise to the alkoxycarbene derivative $[Ru(\eta^5\text{-}C_5H_5)\{C(OCH_2CH{=}CH_2)CH{=}CPh_2\}(CO)(PPr^i_3)]BF_4$, which by deprotonation at low temperature affords the alkoxyallenyl complex $Ru(\eta^5\text{-}C_5H_5)\{C(OCH_2CH{=}CH_2){=}C{=}CPh_2\}(CO)(PPr^i_3)$. In solution, at room temperature, this compound evolves into the naphtho-furanyl derivative $Ru(\eta^5\text{-}C_5H_5)$(9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-*c*]-1-furanyl)(CO)(PPr^i_3) (Scheme 2) by an intramolecular Diels−Alder reaction, 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 unit acts as dienophile.[12]

As a part of our program directed toward designing new models for homogeneous systems effective in the synthesis of functionalized organic fragments from basic hydrocarbon units, we describe now the cycloaddition products resulting of the condensation of propargyl alcohol with the allenylidene ligand of **1**.

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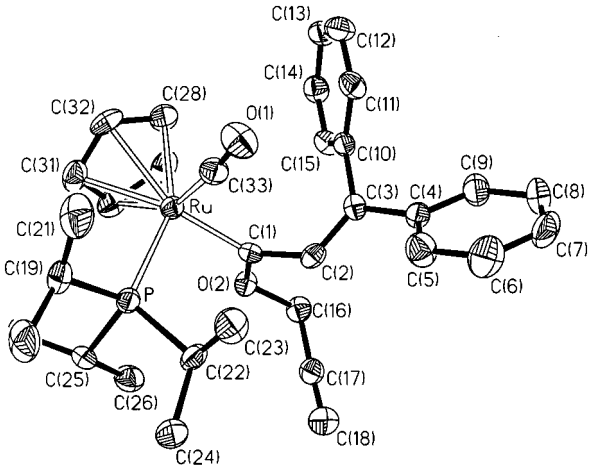
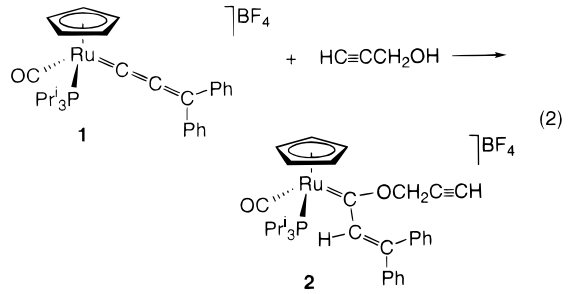


Figure 1. Molecular diagram of the cation of **2**, $[Ru(\eta^5\text{-}C_5H_5)\{C(OCH_2C{\equiv}CH)CH{=}CPh_2\}(CO)(PPr^i_3)]^+$.

Results and Discussion

1. Nucleophilic Addition of Propargyl Alcohol to the Allenylidene Ligand of $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$. The allenylidene ligand of $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$ (**1**) reacts not only with water, methanol, and allyl alcohol but also with propargyl alcohol. After 30 h at 40 °C, the propargyl alcohol solutions of **1** afford the α,β-unsaturated alkoxycarbene derivative $[Ru(\eta^5\text{-}C_5H_5)\{C(OCH_2C{\equiv}CH)CH{=}CPh_2\}(CO)(PPr^i_3)]BF_4$ (**2**) as a result of the addition of the O−H bond of the alcohol to the $C_\alpha-C_\beta$ double bond of the allenylidene unit (eq 2). The selectivity



observed for the addition agrees well with EHT-MO calculations on the model cation $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CH_2)(CO)(PH_3)]^+$, indicating that C_α of the allenylidene is an electrophilic center, while the C_β is nucleophilic.[6d]

Complex **2** was isolated as an orange solid in 88% yield and characterized by MS, elemental analysis, IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and an X-ray crystallographic study. A view of the molecular geometry of the cation of **2** is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The geometry around the ruthenium center of **2** is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The angles formed by the triisopropylphosphine, the carbonyl group, and the carbene ligand are all close to 90°. The most conspicuous features of the structure are, first, the Ru−C(1) bond length (1.965(4) Å), which is consistent with a Ru−C(1) double-bond formulation, and, second, the Ru−C(1)−C(2) (127.0(3)°) and Ru−C(1)−O(2) (116.2(3)°) angles, which clearly indicate sp^2 hybridization for the C(1) carbon atom.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $\{Ru(\eta^5\text{-}C_5H_5)\{C(OCH_2C{\equiv}CH)CH{=}CPh_2\}(CO)(PPr^i_3)\}BF_4$ (2)

Ru−P	2.373(11)	O(1)−C(33)	1.145(5)
Ru−C(28)	3.240(4)	O(2)−C(1)	1.321(4)
Ru−C(29)	2.253(4)	O(2)−C(16)	1.469(4)
Ru−C(30)	2.272(4)	C(1)−C(2)	1.473(5)
Ru−C(31)	2.295(4)	C(2)−C(3)	1.342(5)
Ru−C(32)	2.279(4)	C(3)−C(4)	1.485(5)
Ru−C(1)	1.965(4)	C(3)−C(10)	1.482(5)
Ru−C(33)	1.851(4)	C(16)−C(17)	1.471(6)
		C(17)−C(18)	1.157(6)
P−Ru−G[a]	124.22(14)	C(1)−O(2)−C(16)	121.0(3)
P−Ru−C(1)	92.63(11)	C(1)−C(2)−C(3)	127.6(4)
P−Ru−C(33)	93.72(13)	C(2)−C(3)−C(4)	120.8(4)
G−Ru−C(1)	124.6(2)	C(2)−C(3)−C(10)	121.9(4)
G−Ru−C(33)	121.6(2)	C(4)−C(3)−C(10)	117.3(3)
C(1)−Ru−C(33)	91.1(2)	O(2)−C(1)−C(2)	116.8(3)
Ru−C(33)−O(1)	173.3(4)	O(2)−C(16)−C(17)	110.9(3)
Ru−C(1)−C(2)	127.0(3)	C(16)−C(17)−C(18)	177.8(5)
Ru−C(1)−O(2)	116.2(3)		

[a] G is the centroid of the C(28)−C(32) Cp ligand.

The Ru−C(1) distance is slightly longer than the related bond length in the alkoxycarbene complex $[Ru(\kappa^3\text{-}HBpz_3)\{C(OCH_3)CH_2CO_2CH_3\}(dippe)]BPh_4$ (1.86(2) Å)[13] and in the α,β-unsaturated carbene compound $[RuCl(CHCH{=}CPh_2)(CO)(PPr^i_3)_2]BF_4$ (1.874(3) Å),[14] similar to that found in other cyclopentadienylruthenium carbene complexes such as $[Ru(\eta^5\text{-}C_5H_5)\{C(OCH_3)CH_2CH_3\}(PPh_3)_2]PF_6$ (1.956(6) Å)[15] and $[Ru(\eta^5\text{-}C_5H_5)\{C(OCH_3)CH_2Ph\}(CHIRAPHOS)]PF_6$ (1.93(2) Å)[16] and shorter than the ruthenium−carbon distances in the complexes $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)\{\kappa^1\text{-}OC(CH_3)_2\}(PPr^i_3)_2]BF_4$ (1.967(8) Å),[17] $Ru_3(CO)_{10}(\mu_2\text{-}SMe)(\mu_2\text{-}\eta^2\text{-}NC_6H_4SC)$ (2.075(9) Å),[18] $[\{Ru(\eta^5\text{-}C_5Me_5)(\mu\text{-}SPr^i)\}_2(\mu\text{-}C_{18}H_{15})]BF_4$ (2.04(3) and 1.98(2) Å),[19] and $[\{Ru(\eta^5\text{-}C_5Me_5)(\mu\text{-}SPr^i)\}_2(\mu\text{-}C_{16}H_{18})]OTf$ (2.06(1) and 2.04(1) Å),[20] where a ruthenium−carbon bond between single and double has been proposed.

The bond lengths and angles within the unsaturated η^1-carbon ligand are consistent with the alkenylcarbene proposal. In agreement with the values reported for related compounds,[21] the bond angles around C(2) and C(3) are in the range 117.3(4)−127.6(4)°. Furthermore, C(1) and C(2) are separated by 1.473(5) Å and C(2) and C(3) by 1.342(5) Å. These values agree well with the

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mean values reported for single and double C(sp^2)−C(sp^2) bonds (1.48 and 1.34 Å, respectively)[22] and suggest that there is not delocalization of the π-electron density along the C(1)−C(2)−C(3) chain.

The separation between the oxygen atom O(2) and the C(1) and C(16) atoms reflects the different hybridizations of these carbons. The separation between O(2) and the sp^2 C(1) carbon atom (1.321(4) Å) is about 0.14 Å shorter than that between O(2) and the sp^3 C(16) carbon atom (1.469(4) Å). The C(16)−C(17) bond length (1.471(6) Å) is consistent with a single bond between a sp^3 C and an sp C, whereas the C(17)−C(18) distance (1.157(6) Å) and the C(16)−C(17)−C(18) angle (177.8(5)°) support the alkyne formulation.

In solution, the spectroscopic data of **2** agree well with the structure shown in Figure 1. In the IR spectrum in Nujol, the most noticeable feature is the presence of a ν(C≡C) band at 2126 cm^{-1}. The ^1H NMR spectrum in chloroform-*d* shows the characteristic =CH resonance of the alkenyl unit at 6.59 ppm, which is observed as a singlet, and at 2.75 ppm the ≡CH resonance. The latter appears as a triplet with a *J*(HH) of 2.4 Hz by spin coupling with the OCH_2− group, according to the $^1H-^1H$ COSY NMR spectrum. In the $^{13}C\{^1H\}$ NMR spectrum the resonance corresponding to the Ru=C carbon atom is observed at 305.1 ppm as a broad signal. The resonances due to the C(2), C(3), C(17), and C(18) carbon atoms appear as singlets at 136.0, 137.6, 79.6, and 75.3 ppm, respectively.

We have previously mentioned that similarly to the alkoxy carbene complexes [Ru(η^5-C_5H_5){C(OR)CH=CPh_2}(CO)(PPr^i_3)]BF_4 (R = Me, Et), the treatment of the allyloxycarbene derivative [Ru(η^5-C_5H_5){C(OCH_2-CH=CH_2)CH=CPh_2}(CO)(PPr^i_3)]BF_4 with base produces the deprotonation of the alkenyl unit to give the allenyl complex Ru(η^5-C_5H_5){C($OCH_2CH=CH_2$)=C=CPh_2}(CO)(PPr^i_3), which evolves by a Diels−Alder reaction into a naphtho−furanyl compound. In this case, all attempts to obtain a related allenyl derivative starting from **2** were unsuccessful. Instead, depending upon the reaction conditions, different cycloaddition products were obtained.

2. Reaction of 2 with Na_2CO_3. Treatment at room temperature of a yellow suspension of **2** with 1 equiv of sodium carbonate in tetrahydrofuran affords after 4 h an orange suspension, from which an orange solid was isolated in 30% yield. The remaining yellow solution contains five neutral compounds, as revealed by its $^{31}P\{^1H\}$ NMR spectrum in C_6D_6, which shows five singlets at about 67, 68.5 (two of them), 70, and 72 ppm (vide infra). The orange solid was characterized as the cationic complex [Ru(η^5-C_5H_5)(9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanylidene)(CO)(PPr^i_3)]BF_4 (**3**; eq 3) by elemental analysis, IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and an X-ray crystallographic study. A view of the molecular geometry of the cation of **3** is shown in Figure 2. Selected bond distances and angles are listed in Table 2.

As for **2**, the geometry around the ruthenium center in **3** is close to octahedral with the cyclopentadienyl ligand occupying three sites of a face. The angles formed

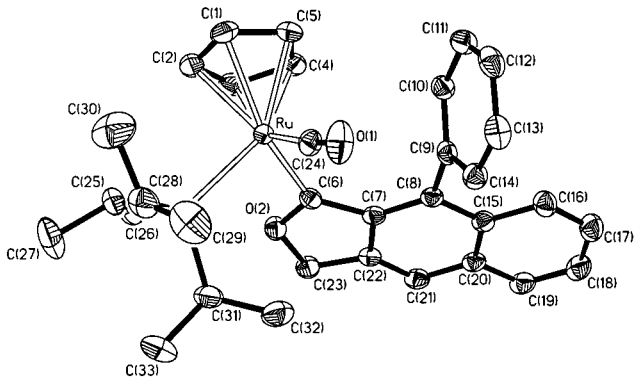
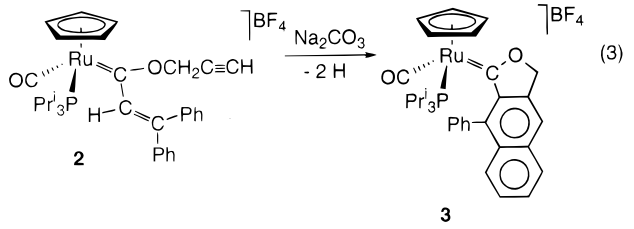


Figure 2. Molecular diagram of the cation of **3**, [Ru(η^5-C_5H_5){9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanylidene}-(CO)(PPr^i_3)]$^+$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex {Ru(η^5-C_5H_5)(9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanylidene)(CO)-(PPr^i_3)}BF_4 (3)

Ru−P	2.3857(6)	O(1)−C(24)	1.146(3)
Ru−C(1)	2.286(2)	O(2)−C(6)	1.323(3)
Ru−C(2)	2.301(2)	O(2)−C(23)	1.465(3)
Ru−C(3)	2.277(3)	C(6)−C(7)	1.482(3)
Ru−C(4)	2.232(2)	C(7)−C(22)	1.424(3)
Ru−C(5)	2.248(2)	C(22)−C(23)	1.480(3)
Ru−C(6)	2.004(2)		
Ru−C(24)	1.850(3)		
P−Ru−G[a]	125.84(8)	O(2)−C(23)−C(22)	102.8(2)
P−Ru−C(6)	91.73(6)	C(6)−C(7)−C(8)	133.0(2)
P−Ru−C(24)	91.31(7)	C(6)−C(7)−C(22)	107.2(2)
G−Ru−C(6)	119.61(10)	C(8)−C(7)−C(22)	119.8(2)
G−Ru−C(24)	123.96(11)	C(6)−O(2)−C(23)	113.9(2)
C(6)−Ru−C(24)	95.86(10)	C(7)−C(22)−C(21)	123.2(2)
Ru−C(24)−O(1)	173.7(2)	C(7)−C(22)−C(23)	108.7(2)
Ru−C(6)−O(2)	112.9(2)	C(21)−C(22)−C(23)	128.1(2)
Ru−C(6)−C(7)	139.0(2)	C(22)−C(23)−O(2)	102.8(2)
O(2)−C(6)−C(7)	107.4(2)		

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



(3)

by the triisopropylphosphine, the carbonyl group, and the cyclic carbene ligand are all close to 90°.

The skeleton of the polycyclic ligand is almost planar, and the maximum deviation (−0.0443(16) Å) is found for the O(2) oxygen atom. The ruthenium atom lies 0.2740(3) Å out from the best plane through the 13 atoms forming the polycyclic skeleton. The Ru−C(6) distance (2.004(2) Å) is about 0.04 Å longer than the Ru−C(1) bond length in **2** and is comparable to the related distance in the cyclic carbene complex [Ru(η^5-C_5H_5){CCH=C(OEt)OC=CPh}(CO)(PPr^i_3)]BF_4 (2.017(6) Å).[3d] The bond angles around C(6), 112.9(2)° (Ru−C(6)−O(2)) and 139.0(2)° (Ru−C(6)−C(7)), support the sp^2 hybridization of this atom. As in **2**, the separation between C(6) and the oxygen atom O(2) (1.323(3) Å) is 0.14 Å shorter than that between O(2) and the sp^3 C(23) carbon atom (1.465(3) Å).

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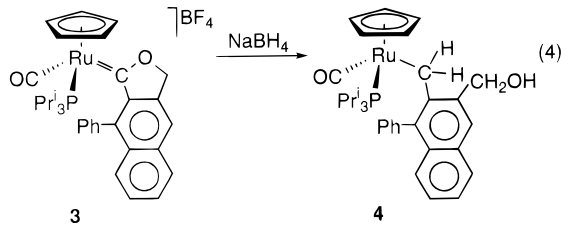
In solution, the spectroscopic data of **3** agree well with the structure shown in Figure 2. In the ^{1}H NMR spectrum in chloroform-*d*, the most noticeable resonances are those corresponding to the OCH_2- protons, which appear at 6.27 and 6.03 ppm as doublets with a *J*(HH) value of 18.9 ppm. The $^{13}C\{^1H\}$ NMR spectrum shows the resonance due to the Ru=C carbon atom at 293.3 ppm as a doublet with a *J*(CP) value of 9.7 Hz.

The formation of **3** involves the loss of two hydrogen atoms, and the formation of two C−C bonds. The formation of one of them takes place by coupling of the terminal C(sp) carbon atom of the propargyloxy unit with an ortho carbon atom of one of the two phenyl groups, whereas the formation of the other is the result of the coupling of the internal C(sp) carbon atom of the propargyloxy fragment with the CH carbon atom of the alkenyl unit.

Although in the five-membered heterocycle the C(6)−O(2) bond is significantly shorter than the O(2)−C(23) bond, the first is more reactive than the second one toward the reduction of **3** with $NaBH_4$. Thus, the treatment at room temperature of tetrahydrofuran suspensions of **3** with 2 equiv of $NaBH_4$ leads to the neutral alkyl compound Ru(η^5-C_5H_5){CH_2(1-phenyl-3-hydroxymethyl-2-naphthyl}(CO)(PPr^i_3) (**4**), which was isolated as a yellow solid in 36% yield, according to eq 4.



3 4 (4)

The presence of a $-CH_2OH$ group in the alkyl ligand of **4** is strongly supported by the IR spectrum of this complex in Nujol, which contains a ν(OH) band at 3572 cm^{-1}. In the ^{1}H NMR spectrum in benzene-d_6, the resonances corresponding to the $-CH_2O-$ group are observed at 5.42 and 5.21 ppm, as complex multiplets, whereas the resonance due to the −OH group appears at 1.42 ppm as a triplet with a *J*(HH) value of 5.4 Hz. In addition, we should mention the resonances corresponding to the $RuCH_2-$ protons, which are observed at 2.78 and 2.42 ppm, as a broad signal and as a broad doublet with a *J*(HP) value of 8.7 Hz, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonance is a doublet with a *J*(CP) value of 8.7 Hz, at −6.7 ppm, which was assigned to the $RuCH_2-$ carbon atom, on the basis of a $^1H-^{13}C$ HETCOR NMR spectrum. In benzene-d_6 as solvent, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 68.5 ppm. This chemical shift is the same as one of the five neutral compounds formed from the reaction of **2** with sodium carbonate, suggesting that during the formation of **3**, a part of this compound decomposes to give **4**.

The formation of **4** is noteworthy. In this context, it should be mentioned that, in general, the treatment of carbene complexes with metal hydrides affords hydride−alkyl derivatives[23] and that the reduction of benzofurans with $NaBH_4$/TFA yields dihydrobenzofurans, without opening of the heterocyclic ring.[24] Even the reduction of 1,3-diphenylbenzo[*c*]furan with sodium leads to 1,3-diphenyldihydrobenzo[*c*]furan. Ring opening of the heterocycle to yield alcohols occurs only in epoxides.[25]

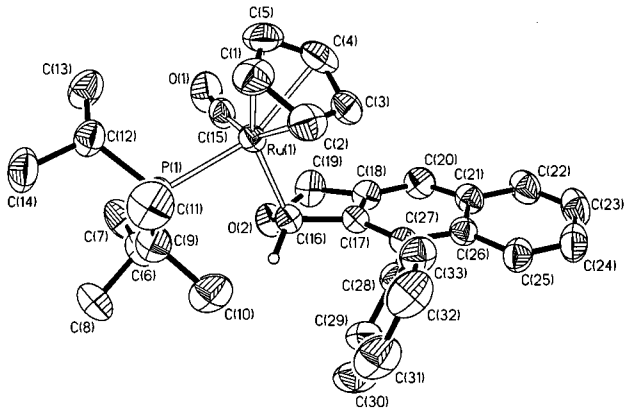
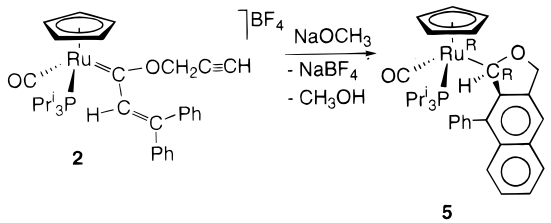


Figure 3. Molecular diagram of the complex Ru(η^5-C_5H_5)-{9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanyl}(CO)(P-Pr^i_3) (**5**).

3. Reaction of 2 with $NaOCH_3$. Treatment at room temperature of a yellow suspension of **2** with 1 equiv of sodium methoxide leads after 3 h to **3** and a mixture of the same neutral compounds as in the case of the reaction with sodium carbonate, according to the $^{31}P-\{^1H\}$ NMR spectrum of the mixture. When the treatment of **2** is carried out with 3 equiv of sodium methoxide, complex **3** disappears and the mixture of neutral products contains, as the main component, a complex displaying a signal at 67.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum.

This complex was obtained as a pure yellow crystalline solid in 53% yield by passing a diethyl ether solution of the mixture through an Al_2O_3 (neutral, activity grade V) column and characterized as a Ru_R,C_R;Ru_S,C_S racemic mixture of the dihydronaphtho−furanyl complex Ru(η^5-C_5H_5)(9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanyl)(CO)(PPr^i_3) (**5**; eq 5) by MS, elemental analysis, IR



2 5 (5)

and ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and an X-ray crystallographic study. A view of the molecular geometry of the Ru_R,C_R enantiomer is shown in Figure 3. Selected bond distances and angles are listed in Table 3.

As for **2** and **3**, the geometry around the ruthenium center in **5** is close to octahedral with the cyclopenta-

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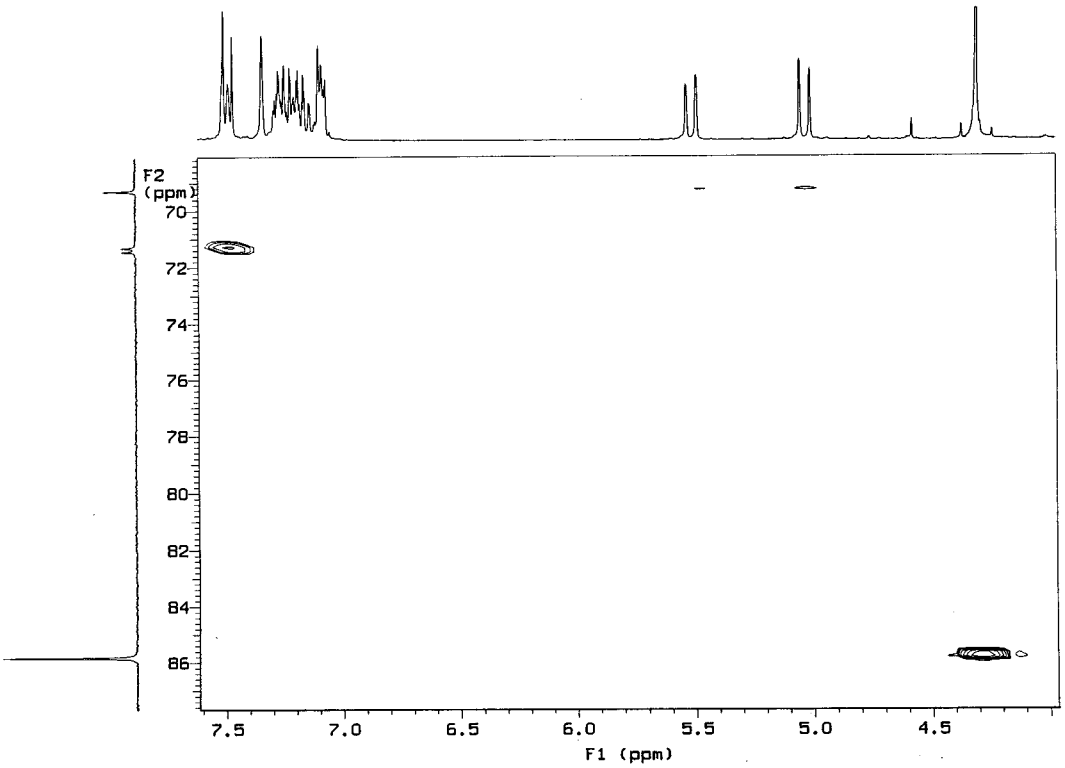

Figure 4. Partial view of the $^1H-^{13}C$ HETCOR NMR spectrum of the complex Ru(η^5-C_5H_5){9-phenyl-1,3-dihydronaphtho-[2,3-*c*]-1-furanyl}(CO)(PPr^i_3) (**5**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Complex Ru(η^5-C_5H_5)(9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanyl)(CO)(PPr^i_3) (5)

Ru(1)−P(1)	2.3434(7)	O(1)−C(15)	1.168(3)
Ru(1)−C(1)	2.284(3)	O(2)−C(16)	1.479(3)
Ru(1)−C(2)	2.285(3)	O(2)−C(19)	1.434(4)
Ru(1)−C(3)	2.274(3)	C(16)−C(17)	1.509(4)
Ru(1)−C(4)	2.260(3)	C(17)−C(18)	1.431(4)
Ru(1)−C(5)	2.283(3)	C(18)−C(19)	1.506(4)
Ru(1)−C(15)	1.836(3)		
Ru(1)−C(16)	2.203(3)		

P(1)−Ru(1)−G[a]	126.97(10)	O(2)−C(16)−C(17)	101.5(2)
P(1)−Ru(1)−C(15)	91.07(8)	O(2)−C(19)−C(18)	104.6(2)
P(1)−Ru(1)−C(16)	89.98(7)	C(16)−C(17)−C(27)	132.2(2)
G−Ru(1)−C(15)	121.2(2)	C(16)−C(17)−C(18)	107.5(2)
G−Ru(1)−C(16)	126.48(13)	C(18)−C(17)−C(27)	120.2(2)
C(15)−Ru(1)−C(16)	90.45(11)	C(16)−O(2)−C(19)	107.3(2)
Ru(1)−C(15)−O(1)	172.0(3)	C(17)−C(18)−C(19)	107.4(2)
Ru(1)−C(16)−C(17)	114.6(2)	C(17)−C(18)−C(20)	121.7(3)
Ru(1)−C(16)−O(2)	112.2(2)	C(19)−C(18)−C(20)	130.9(3)

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

dienyl ligand occupying three sites of a face. The angles formed by the triisopropylphosphine, the carbonyl group, and the heterocyclic ligand are all close to 90°.

The five-membered heterocycle is coordinated to the ruthenium center with a Ru(1)−C(16) bond length of 2.203(3) Å. This value is comparable to the ruthenium−carbon bond lengths reported for the methyl complexes Ru(CH_3){(*E*)-CH=CHPh}(CO)(PPr^i_3)$_2$ (2.205(4) Å),[26] Ru(CH_3)I(η^4-NBD)(dad) (NBD = norbornadiene, dad = glyoxalbis(isopropylimine); 2.222(13) Å),[27] (+)-[Ru(CH_3)(CO)($CNBu^t$)(triphos)]$^+$ (2.209(5) Å),[28] and [*cis*-Ru(CH_3)(PMe_3)$_4$]$_2$Hg (2.205(4) Å).[29]

Both six-membered rings of the dihydronaphtho−furanyl ligand are almost planar, while the five-membered heterocycle adopts an envelope conformation with the O(2) atom out of the plane defined by the other four atoms. In contrast to **3**, the separation between the O(2) atom and the carbon atom bonded to the metal (O(2)−C(16) = 1.479(3) Å) is longer than the separation between O(2) and the other adjacent carbon atom (O(2)−C(19) = 1.434(4) Å).

The phenyl group bonded to the C(27) carbon atom is rotated by 64.4(1)° with regard to the plane defined by the 10 carbon atoms of the naphthyl group. However, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **5** suggest that in solution the phenyl is parallel to the furanyl plane. Figure 4 shows a partial view of the $^1H-^{13}C$ HETCOR NMR spectrum of **5**. In the ^1H part of the spectrum the most noticeable signals are a doublet at 7.50 ppm, with a *J*(HP) value of 10.8 Hz, corresponding to the Ru−CH proton, and two double doublets at 5.53 and 5.05 ppm, with *J*(HH) values of 12.7 and 1.2 and of 12.7 and 0.9 Hz, respectively, due to the OCH_2 protons. In the $^{13}C\{^1H\}$ NMR part of the spectrum, the equivalent carbons are a doublet at 71.3 ppm with a *J*(CP) value of 9.7 Hz for the doublet at 7.50 ppm and a singlet at 69.2 ppm for both double doublets. The above-mentioned chemical shifts are displaced toward lower field with regard to those expected for MCHO and CH_2O groups. In this context, it should be noted that these groups of the five-membered heterocycle lie in the region of a negative shielding contribution produced by the ring current effect of the central ring of the naphthofuranyl ligand. In addition, it should be noted that the resonances of the RuCHO group appear at lower fields that those

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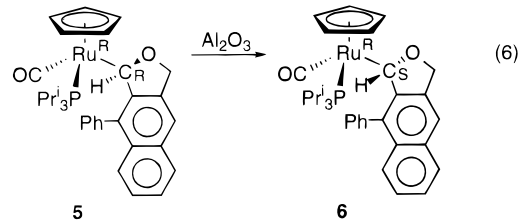
corresponding to the CH_2O group. According to the structure shown in Figure 3, the RuCHO group lies in the region of a positive shielding contribution produced by the ring current effect of the phenyl group, while the CH_2O group is out of this region. This should produce a selective decrease of the effect of the central ring on the RuCHO chemical shifts. Therefore, it is only possible to explain the chemical shifts observed for the RuCHO group by assuming that in solution the disposition of the phenyl group is not that shown in Figure 3, but parallel to the naphtho−furanyl ring. In this way, the RuCHO group would lie in the region of a negative shielding contribution of the phenyl ring, increasing the effect of the naphtho−furanyl ring instead of decreasing it.

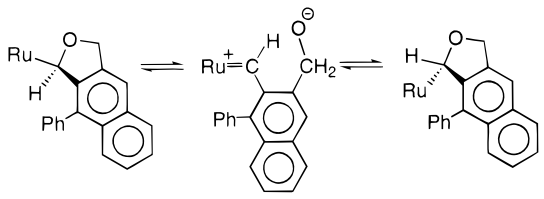
Treatment in a Schlenk tube of a pentane/diethyl ether (5:1) suspension of **5** with Al_2O_3 results in the epimerization of the Ru_R,C_R;Ru_S,C_S racemic mixture (eq 6). The new pair of enantiomers (**6**), which is also



5 6

present as a very minor component in the crude products resulting from the treatment of **2** with sodium carbonate and sodium methoxide ($^{31}P\{^1H\}$ NMR: δ 70.0), is obtained as a pure crystalline solid in 33% yield with regard to **2**, when the crude products resulting from the treatment of **2** with sodium methoxide are purified by column chromatography using a pentane/diethyl ether (5:1) mixture as eluent. The epimerization process could involve the cleavage of the O(2)−C(16) bond of **5** to give the zwitterionic carbene **A** (Scheme 3). Thus, the approach of the oxygen atom over or under the Ru−C double bond should give rise to **5** or **6**.

Scheme 3

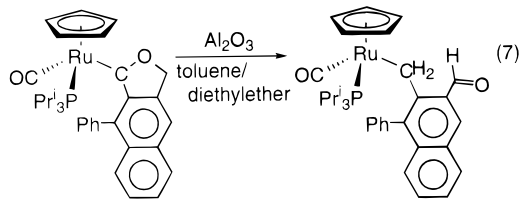


5 A 6

Ru = Ru(η^5-C_5H_5)(CO)(PPr^i_3)

In the ^1H NMR spectrum of **6**, the RuCHO resonance appears at 7.21 ppm, as a doublet with a J(HP) value of 4.5 Hz, whereas the resonances due to the CH_2O group are observed at 4.97 and 4.76 ppm, as doublets with a J(HH) value of 13.2 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the Ru−C carbon atom gives rise to a doublet at 75.9 ppm with a J(CP) value of 8.3 Hz, and the CH_2 carbon atom displays a singlet at 69.0 ppm.

When the purification of the crude products containing **5** as the main component is carried out by column chromatography using an increasing polarity mixture of toluene/diethyl ether (from 10:1 to 1:10) as eluent, a new isomerization of **5** is observed. Under these conditions, the complex Ru(η^5-C_5H_5){CH_2(1-phenyl-3-carboxa-2-naphthyl}(CO)(PPr^i_3) (**7**) is obtained as a yellow solid in 29% yield (eq 7). This isomerization involves a



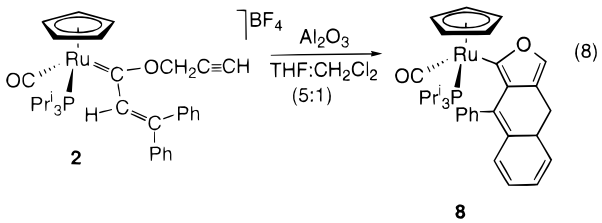
5 7

hydrogen transfer, within the heterocycle of **5**, from C(19) to C(16). The process could proceed via the zwitterionic carbene intermediate **A**. Using a molecular model, it can be observed that in this intermediate the hydrogen transfer from the $-CH_2O^-$ group into the Ru=C carbon atom is highly favored from a geometrical point of view.

The presence of an aldehyde group in the alkyl ligand of **7** is strongly supported by the IR and ^1H and $^{13}C\{^1H\}$ NMR spectra of this compound. The IR spectrum in Nujol contains a ν(C=O) band at 1681 cm^{-1}. In the ^1H NMR spectrum in benzene-d_6 the HCO resonance appears at 11.33 ppm as a singlet. In addition, the spectrum shows at 3.07 ppm a doublet with a J(HH) value of 9.0 Hz and at 2.74 ppm a double doublet with both J(HH) and J(HP) values of 9.0 Hz. Both resonances were assigned to the alkyl protons. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance corresponding to the HCO carbon atom appears at 193.3 ppm as a singlet, whereas that due to the $RuCH_2$ carbon atom is observed at −5.5 ppm as a doublet with a J(CP) value of 9.3 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 68.5 ppm.

This chemical shift is as that of one of the minor components of the initial crude products, suggesting that complex **7** is also formed during the treatment of **2** with bases.

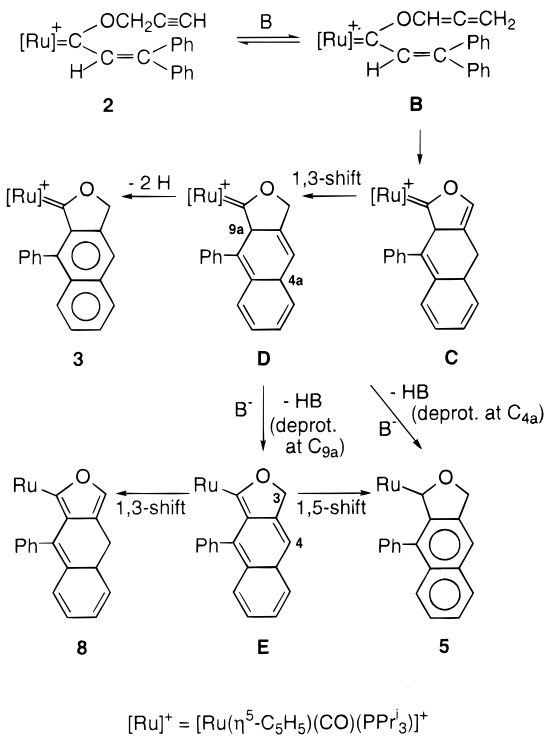
4. Reaction of 2 with Al_2O_3. The complex Ru(η^5-C_5H_5){9-phenyl-3,3a-dihydronaphtho[2,3-*c*]-1-furanyl}-(CO)(PPr^i_3) (**8**), which is another isomer of **5**, can be obtained directly from **2** by passing this complex through an alumina column using a tetrahydrofuran/dichloromethane (5:1) mixture as eluent. By this procedure, complex **8** was obtained as a yellow solid in 38% yield (eq 8).



2 8

The position of the C−C double bond within the unsaturated η^1-carbon ligand of **8** is strongly supported

Scheme 4



by the ^{1}H and ^{13}C{^{1}H} NMR spectra of this compound.[30] The ^{1}H NMR spectrum shows the resonances corresponding to the triisopropylphosphine and cyclopentadienyl ligands, along with eight signals at 7.38, 6.14, 5.89, 5.67, 5.46, 3.40, 2.61, and 2.36 ppm, which according to a ^{1}H−^{1}H COSY NMR spectrum correspond to the H(3), H(8), H(6), H(5), H(7), H(4a), H(4), and H(4′) protons, respectively. In the ^{13}C{^{1}H} NMR spectrum the most noticeable resonances are a doublet at 170.0 ppm with a J(PC) value of 12.4 Hz, assigned to C(1), and three singlets at 138.0, 40.3, and 28.4 ppm, which correspond to the carbon atoms C(3), C(4a), and C(4), respectively, according to the ^{1}H−^{13}C HETCOR NMR spectrum.

The ^{31}P{^{1}H} NMR spectrum of **8** in benzene-d_6 shows a singlet at 72.0 ppm. Although this chemical shift seems to indicate that complex **8** is also a minor component of the crude products resulting from the treatment of **2** with sodium carbonate and sodium methoxide, the aromatic character of the six-membered rings of its isomers **5**−**7** suggests that it is not derived from these compounds.

5. Comments on the Formation of Derivatives 3, 5, and 8. The formation of complexes **3**, **5**, and **8** can be rationalized according to Scheme 4. Since the formation of these compounds occurs under basic conditions, and it is well-known that bases catalyze the isomerization of propargylic into allenic moieties,[31] it seems reasonable to propose an alkyne−allene rearrangement to give **B** as the first step of the reaction. This intermediate **B** could evolve via an intramolecular Diels−Alder reaction similar to that previously described for the allyloxyallenyl complex Ru(η^5-C_5H_5){C(OCH$_2$CH=CH$_2$)=C=CPh$_2$}(CO)(PPr$^i_3$) (Scheme 2), where the C_β−C_γ double bond and one of the two phenyl groups of the alkenyl−carbene unit of **B** act as an inner−outer ring diene, while the terminal C−C double bond of the allene moiety should act as a dienophile. Subsequently, a 1,3-hydrogen shift from the CH$_2$ group of the central six-membered ring to the OCH− carbon atom in the resulting intermediate **C** would give **D**. A further step of aromatization[32] of **D** should afford complex **3**.

The formation of complex **5** can be explained as follows. Deprotonation of intermediate **D** at the carbon C_{9a} would give intermediate **E**. Subsequently, a 1,5-hydrogen shift from carbon C_{4a} to C_1 should afford **5**. There is precedent for this hydrogen migration. We have previously shown that the protonation of Ru(η^5-C_5H_5)-{9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-*c*]-1-furanyl}-(CO)(PPr$^i_3$) affords the cation [Ru(η^5-C_5H_5){9-phenyl-1,3,3a,4,4a,9a-hexahydronaphtho[2,3-*c*]-1-furanylidene}-(CO)(PPr$^i_3$)]$^+$, which is stable in solution at low temperature. At room temperature, it 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-Pr$^i_3$) as a result of the intramolecular hydrogen transfer from C_{4a} to C_1.[12] Alternatively, complex **5** could be formed by deprotonation of intermediate **D** at C_{4a} and a hydrogen migration from C_{9a} to C_1.

Complex **8** could be the result of a 1,3-hydrogen migration from C_3 to C_4 on intermediate **E**.

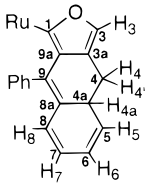
Concluding Remarks

We have previously shown that the allenylidene complex [Ru(η^5-C_5H_5)(C=C=CPh$_2$)(CO)(PPr$^i_3$)]BF$_4$ (**1**) reacts with methanol, ethanol, and allyl alcohol to give the α,β-unsaturated alkoxycarbene derivatives [Ru(η^5-C_5H_5){C(OR)CH=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (R = Me, Et, CH$_2$CH=CH$_2$), which by deprotonation afford the corresponding alkoxy−allenyl compounds. This study has revealed that complex **1** also adds propargyl alcohol. The reaction is similar to those with the above-mentioned alcohols, and the α,β-unsaturated propargyloxycarbene [Ru(η^5-C_5H_5){C(OCH$_2$C≡CH)CH=CPh$_2$}(CO)(PPr$^i_3$)]-BF$_4$ (**2**) is obtained. However, the treatment of **2** with bases does not afford an allenyl derivative but a mixture of six different cycloaddition products. The main component of the mixture depends on the nature of the base used.

In the presence of 1 equiv of sodium carbonate the polycyclic carbene complex [Ru(η^5-C_5H_5){9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanylidene}(CO)(PPr$^i_3$)]BF$_4$ (**3**) is obtained, which by reaction with NaBH$_4$ affords Ru(η^5-C_5H_5){CH$_2$(1-phenyl-3-hydroxymethyl-2-naphthyl)}(CO)(PPr$^i_3$) (**4**).

Treatment of **2** with 3 equiv of sodium methoxide gives rise to the Ru$_R$,C$_R$;Ru$_S$,C$_S$ racemic mixture of the dihydronaphtho−furanyl complex Ru(η^5-C_5H_5){9-phen-

(30)



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(32) (a) March, J. In *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1984; p 1077. (b) Bruce, M. I.; Hinterding, P.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1997**, 715.

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yl-1,3-dihydronaphtho[2,3-*c*]-1-furanyl}(CO)(PPr^i_3) (**5**), which within a chromatography column epimerizes to the corresponding $Ru_R,C_S;Ru_S,C_R$ racemic form (**6**) or is transformed into its isomer Ru(η^5-C_5H_5){CH_2(1-phenyl-3-carboxa-2-naphthyl}(CO)(PPr^i_3) (**7**), depending upon the polarity of the eluent used.

Complex **2** is also deprotonated by Al_2O_3. When this complex is passed through an alumina column using a tetrahydrofuran/dichloromethane (5:1) mixture as eluent, the isomer of **5**, Ru(η^5-C_5H_5){9-phenyl-3,3a-dihydronaphtho[2,3-*c*]-1-furanyl}(CO)(PPr^i_3) (**8**), is formed.

In conclusion, in the presence of bases, the carbene complex **2** evolves into novel organometallic products which are the result of the loss of two (**3**) or one (**5** and **8**) hydrogen atom and the intramolecular formation of two C−C bonds, the terminal C(sp) carbon atom of the propargyl alkoxy unit with an *ortho* carbon atom of one of the two phenyl groups, and the internal C(sp) carbon atom of the propargyloxy fragment with the CH carbon atom of the alkenyl unit.

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)(PPr^i_3)]BF_4 (**1**) was prepared by the published method.[10]

In the NMR spectra, chemical shifts are expressed in ppm downfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, *J*, are given in hertz.

Preparation of [Ru(η^5-C_5H_5){C(OCH_2C≡CH)CH═CPh_2}(CO)(PPr^i_3)]BF_4 (2). A 350 mg portion of **1** was dissolved in 10 mL of propargyl alcohol, and the solution was stirred for 30 h at 40 °C. The color changed from deep red to brown, and the solvent was removed in vacuo. The residue was repeatedly washed, first with diethyl ether and then with a diethyl ether/tetrahydrofuran (1/2) mixture, to afford an orange solid. Yield: 334 mg (88%). Anal. Calcd for $C_{33}H_{40}BF_4O_2PRu$: C, 57.65; H, 5.86. Found: C, 57.24; H, 5.47. IR (Nujol, cm^{-1}): *ν*(≡CH) 3255 (m); *ν*(C≡C) 2126 (w); *ν*(CO) 1973 (s); *ν*(Ph, C═C) 1590, 1570 (both w); *ν*(C−O) 1269, 1174 (s); *ν*(BF_4) 1061 (br). ^1H NMR (300 MHz, 20 °C, $CDCl_3$): *δ* 7.52−7.17 (m, 10H, Ph), 6.59 (s, 1H, HC═), 5.50, 5.12 (both br, OCH_2), 5.01 (s, 5H, Cp), 2.75 (t, 1H, *J*(HH) = 2.4, ≡CH), 2.29 (m, 3H, $PCHCH_3$), 1.27 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 15.3, $PCHCH_3$), 1.22 (dd, 9H, *J*(PH) = 7.2, *J*(PH) = 15.3, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 20 °C, $CDCl_3$): *δ* 65.6 (br). $^{13}C\{^1H\}$ NMR (75.4 MHz, 20 °C, $CDCl_3$, plus HETCOR): *δ* 305.1 (br, Ru═C), 202.8 (d, *J*(PC) = 15.5, CO), 139.7, 137.6 (both s, $C_{ipso-Ph}$ + HC═CPh_2), 136.0 (br s, HC═CPh_2) 131.7, 129.8, 128.8, 128.7, 128.5 (all s, Ph), 89.8 (s, Cp), 79.6 (s, OCH_2C≡CH), 75.3 (s, OCH_2C≡CH), 66.3 (s, OCH_2C≡CH), 29.3 (d, *J*(PC) = 24.2, $PCHCH_3$), 19.8, 19.5 (both s, $PCHCH_3$). MS (FAB^+): *m*/*z* 601 ($[M]^+$).

Preparation of [Ru(η^5-C_5H_5)(9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanylidene)(CO)(PPr^i_3)]BF_4 (3). A yellow suspension of **2** (250 mg, 0.36 mmol) in 10 mL of tetrahydrofuran at room temperature was treated with sodium carbonate (39 mg, 0.36 mmol). The mixture was stirred for 4 h, and the color changed to deep orange. Solvent was evaporated in vacuo, and 10 mL of dichloromethane was added. The mixture was filtered, and the solvent was evaporated. The residue was washed with tetrahydrofuran to afford **3** as an orange solid. Yield: 75 mg (30%). Anal. Calcd for $C_{33}H_{38}BF_4O_2PRu$: C, 57.82; H, 5.59. Found: C, 57.77; H, 5.58. IR (Nujol, cm^{-1}): *ν*(CO) 1964 (vs); *ν*(Ph) 1624 (w); *ν*(BF_4) 1050 (br). ^1H NMR (300 MHz, 20 °C, $CDCl_3$): *δ* 8.20−7.29 (10H, Ar), 6.27 (d, 1H, *J*(HH) = 18.9, C*H*HO), 6.03 (d, 1H, *J*(HH) = 18.2, CH*H*O), 5.15 (s, 5H, Cp), 2.26 (m, 3H, $PCHCH_3$), 1.10 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.7, $PCHCH_3$), 1.05 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.4, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 20 °C, $CDCl_3$): *δ* 69.1 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 20 °C, $CDCl_3$, plus HETCOR): *δ* 293.3 (d, *J*(PC) = 9.7, Ru═C), 202.0 (d, *J*(PC) = 18.4, CO), 146.5, 143.4, 138.1, 136.4, 135.8, 133.9 (all s, C_{ipso}), 132.5, 132.3, 130.6, 129.2, 129.1, 128.8, 128.3, 128.0, 127.3, 120.9 (all a, CH), 87.2 (s, Cp), 86.1 (s, CH_2O), 26.9 (d, *J*(PC) = 23.4, $PCHCH_3$), 19.5 (s, $PCHCH_3$).

Preparation of Ru(η^5-C_5H_5){CH_2(1-phenyl-3-hydroxymethyl-2-naphthyl)}(CO)(PPr^i_3) (4). An orange suspension of **3** (250 mg, 0.36 mmol) in 10 mL of tetrahydrofuran at room temperature was treated with sodium borohydride (27 mg, 0.72 mmol). The mixture was stirred for 5 min to obtain a yellow suspension, which was concentrated to ca. 1 mL and chromatographed on alumina. Tetrahydrofuran eluted a yellow fraction, from which solvent was removed in vacuo. The residue was washed with cold pentane to afford **4** as a yellow solid. Yield: 76 mg (36%). Anal. Calcd for $C_{33}H_{41}O_2PRu$: C, 65.87; H, 6.87. Found: C, 65.58; H, 6.84. IR (Nujol, cm^{-1}): *ν*(OH) 3572 (vs); *ν*(CO) 1887 (vs); *ν*(Ph, C═C) 1619, 1595 (w). ^1H NMR (300 MHz, 20 °C, C_6D_6, plus COSY): *δ* 8.10−7.13 (8H, Ar), 5.42 (m, 1H, C*H*HO), 5.21 (m, 1H, CH*H*O), 4.36 (s, 5H, Cp), 2.78 (br, 1H, Ru−C*H*H), 2.42 (br d, 1H, *J*(PH) = 8.7, Ru−CH*H*), 1.78 (m, 3H, $PCHCH_3$), 1.42 (t, 1H, *J*(HH) = 5.4, OH), 0.85 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 13.8, $PCHCH_3$), 0.72 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 12.3, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 20 °C, C_6D_6): *δ* 68.5 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 20 °C, C_6D_6, plus HETCOR): *δ* 209.8 (br, CO), 152.3, 142.0, 138.9, 133.2, 130.9, 125.2 (all s, C_{ipso}), 132.6, 132.1, 129.1, 128.4, 128.3, 126.5, 126.0, 125.5, 125.2, 123.2 (all s, CH), 86.1 (s, Cp), 64.1 (s, CH_2O), 26.4 (d, *J*(PC) = 21.6, $PCHCH_3$), 19.9, 18.9 (both s, $PCHCH_3$), −6.7 (d, *J*(PC) = 8.7, Ru−CH_2). MS (FAB^+): *m*/*z* 602 ($[M]^+$).

Preparation of ($Ru_R,C_R;Ru_S,C_S$)-Ru(η^5-C_5H_5)(9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanyl)(CO)(PPr^i_3) (5). A yellow suspension of **2** (250 mg, 0.36 mmol) in 10 mL of tetrahydrofuran at −78 °C was treated with sodium methoxide (59 mg, 1.09 mmol). The mixture was stirred for 2 h, while the temperature was slowly increased to 25 °C. The color changed to deep red, and the solvent was evaporated in vacuo. The residue was extracted with 2 mL of diethyl ether and chromatographed on alumina. Diethyl ether eluted a yellow fraction from which solvent was evaporated in vacuo. The residue was washed with cold pentane to afford **5** as a yellow solid. Yield: 116 mg (53%). Anal. Calcd for $C_{33}H_{39}O_2PRu$: C, 66.09; H, 6.55. Found: C, 66.00; H, 6.47. IR (Nujol, cm^{-1}): *ν*(CO) 1913 (vs); *ν*(Ph) 1622 (w). ^1H NMR (300 MHz, 20 °C, C_6D_6): *δ* 7.83−7.67 (2H, Ar), 7.50 (d, 1H, *J*(PH) = 10.8, Ru−CH), 7.52−7.08 (8H, Ar), 5.53 (dd, 1H, *J*(HH) = 12.7, *J*(HH) = 1.2, C*H*HO), 5.05 (dd, 1H, *J*(HH) = 12.7, *J*(HH) = 0.9, CH*H*O), 4.31 (s, 5H, Cp), 1.97 (m, 3H, $PCHCH_3$), 1.01, 0.87 (both dd, 18H, *J*(HH) = 7.2, *J*(PH) = 13.2, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 20 °C, C_6D_6): *δ* 67.3 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 20 °C, C_6D_6, plus HETCOR): *δ* 208.3 (d, *J*(PC) = 21.2, CO), 156.6, 141.6, 140.2, 132.3, 132.2, 125.4 (all s, C_{ipso}), 132.1, 131.7, 129.5, 128.4, 127.8, 127.1, 125.6, 125.5, 124.3, 118.9 (all s, CH), 85.7 (d, *J*(PC) = 0.9, Cp), 71.3 (d, *J*(PC) = 9.7, Ru−CH), 69.2 (s, CH_2O), 27.9 (d, *J*(PC) = 21.2, $PCHCH_3$), 19.8, 19.7 (both s, $PCHCH_3$).

Preparation of ($Ru_R,C_S;Ru_S,C_R$)-Ru(η^5-C_5H_5)(9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanyl)(CO)(PPr^i_3) (6). A yellow suspension of **2** (250 mg, 0.36 mmol) in 10 mL of tetrahydrofuran at −78 °C was treated with sodium methoxide (59 mg, 1.09 mmol). The mixture was stirred for 2 h, while the temperature was slowly increased to 25 °C. The color changed to deep red, and solvent was evaporated in vacuo. The suspension was extracted with 2 mL of dichloromethane and chromatographed on alumina. A pentane/diethyl ether mixture (5:1) eluted a yellow fraction from which solvent was evaporated in vacuo. The residue was washed with pentane at 193 K to afford **6** as a yellow solid. Yield: 73 mg (33%).

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Table 4. Crystal Data and Data Collection and Refinement for {Ru(η^5-C_5H_5){C(OCH$_2$C≡CH)CH=CPh$_2$}(CO)(PPr$^i_3$)}BF_4 (2), {Ru(η^5-C_5H_5)(9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanylidene)(CO)(PPr$^i_3$)}BF_4 (3), and Ru(η^5-C_5H_5)(9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanyl)(CO)(PPr$^i_3$) (5)

	2	3	5
		Crystal Data	
formula	$C_{33}H_{40}BF_4O_2PRu$	$C_{33}H_{38}BF_4O_2PRu$	$C_{33}H_{39}O_2PRu$
mol wt	687.50	685.48	599.68
color and habit	yellow prism	orange prism	yellow prism
symmetry, space group	monoclinic	monoclinic	triclinic, $P\bar{1}$
a, Å	11.121(1)	14.046(1)	9.330(1)
b, Å	22.074(3)	12.430(1)	12.283(1)
c, Å	13.558(2)	17.299(2)	14.073(2)
α, deg	90.0	90.0	80.336(6)
β, deg	103.66(1)	97.36(2)	74.546(6)
γ, deg	90.0	90.0	70.784
V, Å^3	3234.1(9)	2995.4(7)	1462.1(3)
Z	4	4	2
D_{calcd}, g cm^{-3}	1.412	1.520	1.362
		Data Collection and Refinement	
diffractometer	Siemens-STOE AED-2	Siemens-STOE AED-2	Siemens-P4
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
monochromator	graphite oriented	graphite oriented	graphite oriented
μ, mm^{-1}	0.585	0.632	0.618
scan type	*ω*/2*θ*	*ω*/2*θ*	*ω*/2*θ*
2*θ* range, deg	3 ≤ 2*θ* ≤ 50	3 ≤ 2*θ* ≤ 50	3 ≤ 2*θ* ≤ 50
temp, K	200.0(2)	200.0(2)	293.0(2)
no. of data collect	6133 (*h*, −13 to 0; *k*, 0−26; *l*, −15 to +16)	6551 (*h*, −16 to +16; *k*, −24 to +2; *l*, 0−20)	5718 (*h*, −10 to +1; *k*, −14 to +13; *l*, −16 to +16)
no. of unique data	5683 (merging *R* factor 0.0361)	5269 (merging *R* factor 0.0179)	5138 (merging *R* factor 0.0292)
no. of params refined	386	386	335
R1[a] ($F^2 > 2\sigma(F^2)$)	0.0437	0.0282	0.0310
wR2[b] (all data)	0.0792	0.0740	0.0837
S[c] (all data)	1.012	1.068	1.042

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $GOF = S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)^2]\}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

Anal. Calcd for $C_{33}H_{39}O_2PRu$: C, 66.09; H, 6.55. Found: C, 65.81; H, 6.80. IR (Nujol, cm^{-1}): *ν*(CO) 1912 (vs); *ν*(Ph) 1626 (w). ^{1}H NMR (300 MHz, 20 °C, C_6D_6): *δ* 7.94−7.72 (2H, Ar), 7.51−7.08 (8H, Ar), 7.21 (d, 1H, *J*(PH) = 4.5, Ru−CH), 4.97, 4.76 (both d, 2H, *J*(HH) = 13.2, CH_2O), 4.60 (s, 5H, Cp), 2.35 (m, 3H, PC*H*CH$_3$), 1.00 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 13.5, PCHC*H*$_3$), 0.97 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 12.3, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 20 °C, C_6D_6): *δ* 70.0 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C, C_6D_6, plus HETCOR): *δ* 205.8 (d, *J*(PC) = 20.7, CO), 155.2, 139.9, 138.6, 133.1, 132.4, 127.9 (all s, C_{ipso}), 130.7, 130.4, 129.7, 128.6, 128.3, 127.8, 125.8, 125.6, 124.3, 118.2 (all s, CH), 85.8 (d, *J*(PC) = 1.4, Cp), 75.9 (d, *J*(PC) = 8.3, Ru−CH), 69.0 (s, CH_2O), 26.3 (d, *J*(PC) = 21.2, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$), 19.3 (d, *J*(PC) = 0.9, PCH*C*H$_3$).

Complex **6** could also be obtained, but not totally pure, by stirring a suspension of **5** and alumina for 3 days. A pentane/diethyl ether mixture (5:1) was used as solvent.

Preparation of Ru(η^5-C_5H_5)[CH$_2$(1-phenyl-3-carboxa-2-naphthyl)](CO)(PPr$^i_3$) (7). A yellow suspension of **2** (250 mg, 0.36 mmol) in 10 mL of tetrahydrofuran at −78 °C was treated with sodium methoxide (59 mg, 1.09 mmol). The mixture was stirred for 2 h, while temperature was slowly increased to 25 °C. The color changed to deep red, and solvent was evaporated in vacuo. The residue was extracted with 2 mL of toluene and chromatographed on alumina. An increasing polarity mixture of toluene/diethyl ether (from 10:1 to 1:10) eluted a yellow fraction from which solvent was evaporated in vacuo. The residue was washed with cold pentane to afford **7** as a yellow solid. Yield: 65 mg (29%). Anal. Calcd for $C_{33}H_{39}O_2PRu$: C, 66.09; H, 6.55. Found: C, 65.93; H, 6.85. IR (Nujol, cm^{-1}): *ν*(CO) 1900 (vs); *ν*(HC=O) 1681 (s); *ν*(Ph, C=C) 1615, 1582 (m). ^{1}H NMR (300 MHz, 20 °C, C_6D_6, plus COSY): *δ* 11.33 (s, 1H, HCO), 8.56−7.02 (8H, Ar), 4.31 (s, 5H, Cp), 3.07 (d, 1H, *J*(HH) = 9.0, Ru−C*H*H), 2.74 (dd, 1H, *J*(HH) = *J*(PH) = 9.0, Ru−CH*H*), 1.74 (m, 3H, PC*H*CH$_3$), 0.81 (dd, 9H, *J*(HH) = 7.5, *J*(PH) = 14.1, PCHC*H*$_3$), 0.68 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 12.6, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 20 °C, C_6D_6): *δ* 68.5 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C, C_6D_6): *δ* 208.8 (br, *J*(PC) = 21.2, CO), 193.3 (s, HCO), 156.0, 140.8, 136.0, 134.2, 133.6, 130.0 (all s, C_{ipso}), 132.4, 131.8, 130.3, 130.1, 129.2, 128.5, 128.2, 126.8, 126.2, 124.3 (all s, CH), 86.3 (s, *J*(PC) = 1.4, Cp), 26.5 (d, *J*(PC) = 22.1, P*C*HCH$_3$), 19.8, 18.9 (both s, PCH*C*H$_3$), −5.5 (d, *J*(PC) = 9.3, Ru−CH).

Complex **7** could also be obtained, but not totally pure, by stirring a suspension of **5** and alumina for 4 days. Pentane was used as solvent.

Preparation of Ru(η^5-C_5H_5)(9-phenyl-3,3a-dihydronaphtho[2,3-*c*]-1-furanyl)(CO)(PPr$^i_3$) (8). 2 (250 mg, 0.36 mmol) was chromatographed on alumina. A tetrahydrofuran/dichloromethane mixture (5:1) eluted a yellow fraction, from which solvent was evaporated in vacuo. The residue was washed with methanol at −78 °C to afford **8** as a yellow solid. Yield: 84 mg (38%). Anal. Calcd for $C_{33}H_{39}O_2PRu$: C, 66.09; H, 6.55. Found: C, 66.04; H, 6.91. IR (Nujol, cm^{-1}): *ν*(CO) 1927 (vs); *ν*(Ph, C=C) 1597, 1525 (both w). ^{1}H NMR (300 MHz, 20 °C, CD_2Cl_2, plus COSY): *δ* 7.38 (d, 1H, *J*(H$_3$H$_{4'}$) = 1.5, H$_3$), 7.37−7.23 (5H, Ph), 6.14 (dd, 1H, *J*(H$_7$H$_8$) = 9.6, *J*(H$_6$H$_8$) = 0.9, H$_8$), 5.89 (dddd, 1H, *J*(H$_5$H$_6$) = 9.6, *J*(H$_7$H$_6$) = 5.7, *J*(H$_{4a}$H$_6$) = 2.4, J(H$_6$H$_8$) = 0.9, H$_6$), 5.67 (ddd, 1H, *J*(H$_5$H$_6$) = 9.6, *J*(H$_{4a}$H$_5$) = 4.5, *J*(H$_7$H$_5$) = 2.1, H$_5$), 5.46 (dddd, 1H, *J*(H$_7$H$_8$) = 9.6, *J*(H$_7$H$_2$) = 5.7, *J*(H$_7$H$_5$) = 2.1, *J*(H$_{4a}$H$_7$) = 1.2, H$_7$), 4.73 (s, 5H, Cp), 3.40 (m, 1H, H$_{4a}$), 2.61 (dd, 1H, *J*(H$_{4'}$H$_4$) = 14.1, *J*(H$_4$H$_{4a}$) = 4.5, H$_4$), 2.36 (ddd, 1H, *J*(H$_{4'}$H$_4$) = 14.1, *J*(H$_{4'}$H$_{4a}$) = 14.1, *J*(H$_3$H$_{4'}$) = 1.5, H$_{4'}$), 2.07 (m, 3H, PC*H*CH$_3$), 1.05 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 12.9, PCHC*H*$_3$), 1.03 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 14.1, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 20 °C, C_6D_6): *δ* 72.0 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C, CD_2Cl_2, plus HETCOR): *δ* 207.3 (d, *J*(PC) = 19.5, CO), 170.0 (d, *J*(PC) = 12.4, C1), 140.8, 137.7, 135.3, 129.8, 121.1 (all s, $C_{ipso-Ph}$, C_{3a}, C_{8a}, C_9, C_{9a}), 132.4, 127.4, 126.3 (all s, Ph), 138.0 (s, C_3), 131.3 (s, C_5), 126.7 (s, C_8), 123.3 (s, C_6), 119.8 (s, C_7), 85.8 (s,

Cp), 40.3 (s, C_{4a}), 28.4 (s, C_4), 27.8 (d, J(PC) = 23.1, P*C*HCH$_3$), 20.3, 19.8 (both s, PCH*C*H$_3$).

X-ray Structure Analysis of {Ru(η^5-C_5H_5){C(OCH$_2$C≡CH)CH=CPh$_2$}(CO)(PPr$^i_3$)}BF$_4$ (2), [Ru(η^5-C_5H_5)(9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanylidene)(CO)(PPr$^i_3$)]-BF$_4$ (3) and (Ru$_R$,C$_R$;Ru$_S$,C$_S$)-Ru(η^5-C_5H_5)(9-phenyl-1,3-dihydronaphtho[2,3-*c*]-1-furanyl)(CO)(PPr$^i_3$) (5). Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of **2** or **3** in dichloromethane or by diffusion of pentane into a concentrated solution of **5** in toluene. A summary of crystal data and refinement parameters is reported in Table 4. Crystals of approximate dimensions 0.40 × 0.23 × 0.15 mm (**2**), 0.40 × 0.32 × 0.29 (**3**), and 0.62 × 0.36 × 0.16 (**5**) were glued on a glass fiber and mounted on a Siemens-STOE (**2** and **3**) or Siemens-P4 (**5**) diffractometer (sealed tube 2.4 kW, λ = 0.710 73 Å). All data were corrected for absorption using a semiempirical method.[33] The structures were solved by Patterson (Ru atoms) and conventional Fourier techniques and refined by full-matrix least squares on F^2 (SHELXL93 (**2** and **3**) and SHELXL97[34] (**5**)). Anistropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms were included in calculated or located positions and refined riding on their respective carbon atoms with a fixed common thermal parameter. Atomic scattering factors, corrected for anomalous dispersion, were implemented by the program. Final convergence parameters are shown in Table 4.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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