γ-Substituted Vinylidene, Chroman-2-ylidene, and Hexahydrochromen-2-ylidene from Ruthenium Allenylidene/Alkenylcarbyne Complexes

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The activation of 1-phenyl-2-propyn-1-ol, 1-(4-methoxyphenyl)-2-propyn-1-ol, and 1-(4-fluorophenyl)-prop-2-yn-1-ol by [Cp*RuCl(dippe)] (dippe = 1,2-bis(diisopropylphosphine)ethane) provides a series of allenylidene derivatives, [Cp*Ru(dippe)(=C=C=CHAr)][BF_4] (Ar = C_6H_5 (**1**), *p*-C_6H_4(OMe) (**2**), *p*-C_6H_4-(F) (**3**)), and the corresponding alkenylcarbyne complexes [Cp*Ru(dippe)(≡C−CH=CHAr)][BF_4]$_2$ (Ar = C_6H_5 (**4**), *p*-C_6H_4(OMe) (**5**), *p*-C_6H_4(F) (**6**)) by allenylidene protonation. The dicationic alkenylcarbyne complexes behave as a carbocationic species able to cause the aromatic electrophilic substitution of 1,3-dimethoxybenzene, furnishing γ-substituted vinylidene complexes [Cp*Ru{=C=CHCHAr(C_6H_3(OMe)$_2$)}-(dippe)][BF_4] (Ar = C_6H_5 (**7**), *p*-C_6H_4(OMe) (**8**), *p*-C_6H_4(F) (**9**)). A series of bicyclic carbene complexes [Cp*Ru(L)(dippe)][BF_4] (L = 7-hydroxy-4-phenylchroman-2-ylidene (**10**), 4-(4-methoxyphenyl)-7-hydroxychroman-2-ylidene (**11**), 4-(4-fluorophenyl)-7-hydroxychroman-2-ylidene (**12**)) are obtained by the direct reaction of resorcinol with alkenylcarbyne complexes. The X-ray structure of **12** shows the formation of a chroman-2-ylidene ligand. The reaction of allenylidene complexes requires the presence of a weak acid (NH_4BF_4) to perform the electrophilic aromatic substitution (step 1) and a strong acid (HBF_4) to induce the intramolecular cyclization (step 2). The γ-substituted vinylidene [Cp*Ru{=C=CHCHPh(C_6H_3(OH)$_2$)}(dippe)][BF_4] (**13**) has been isolated as the intermediate between steps 1 and 2. Similar bicyclic carbon skeletons (hexahydrochromen-2-ylidene, complexes **14b**−**16b**) are obtained by reaction of the allenylidene complexes with cyclohexanedione. In this case, the carbene complexes are in equilibrium with the isomeric γ-substituted vinylidenes **14a**−**16a**. The effect of the presence of electron-donor and electron-withdrawing groups on the allenylidene/alkenylcarbyne substituents is analyzed.

Introduction

The organometallic chemistry of allenylidene complexes, [M]=C=C=CRR′, has been rapidly developed since Selegue's discovery of a general synthetic methodology to allenylidene complexes by activation of propargyl alcohols.[1] A large amount of these cumulene complexes have been characterized with a variety of metallic fragments, showing a remarkable rich chemistry.[2] Owing to the unsaturated character of the cumulated double bonds, allenylidenes are excellent substrates for C−C and C−heteroatom couplings, giving access to a variety of polycyclic carbon skeletons by cycloaddition reactions.[3,4]

Ruthenium allenylidenes constitute the largest group, and they have been studied in depth, particularly those showing an electrophilic reactivity.[5] Electrophilic allenylidenes are cationic complexes that react with nucleophiles through the α- and γ-carbons. This behavior is easily rationalized by the contribution of the propargyl and allenyl resonance forms (Scheme 1).

The electronic and steric properties of the metal fragment have a strong effect on the regioselectivity of the addition. The most electrophilic allenylidenes are very reactive toward weak nucleophiles, giving rise to alkoxycarbene complexes, [Ru]$^+$=C(OR)CH=CRR′, by addition of alcohols to the allenylidene Cα−Cβ double bond.[6] As the steric hindrance and the electron-donating properties of the auxiliary ligands increase, the allenylidene α carbon becomes less reactive.

On the other hand, neutral and some cationic allenylidene complexes bearing bulky electron-donating auxiliary ligands are inert against weak nucleophiles, but they can be protonated at the β carbon to give alkenylcarbyne compounds.[7] Ruthenium alkenylcarbyne species are still very scarce, and the allenylidene reactivity via alkenylcarbyne intermediates remains relatively unknown compared to that of electrophilic allenylidenes. Remarkably, the participation of allenylidene complexes as intermediates in catalytic processes involves electron-rich metal-

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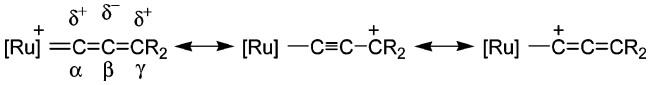
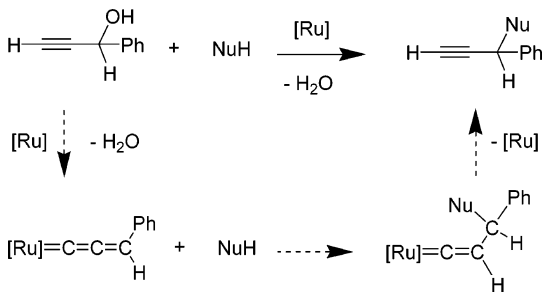
Scheme 1



Scheme 2



lic fragments such as $[(\eta^6\text{-}p\text{-cymene})RuCl(PCy_3)]^+$ [8] and $[Cp^*RuCl(\mu\text{-}SR)_2RuCp^*]^+$.[9]

γ-Substituted vinylidene complexes are key intermediates for the ruthenium-catalyzed propargylic substitution reaction of propargyl alcohols with heteroatom- and carbon-centered nucleophiles.[10] The proposed catalytic cycle involves a nucleophilic addition to the Cβ−Cγ double bond of an allenylidene intermediate, leading to γ-substituted vinylidene complexes, [Ru]═C═CHC(Nu)RR′. This intermediate was not isolated, and surprisingly there is no precedent for a direct and general access to this family of compounds from electrophilic allenylidenes (Scheme 2).

We have recently described a new and alternative approach to γ-substituted vinylidenes via allenylidene/alkenylcarbyne complexes. At difference with electrophilic allenylidenes, the electron-rich $[Cp^*Ru(=C=C=CHPh)(dippe)]^+$ (dippe = 1,2-bis(diisopropylphosphine)ethane) does not react with weak nucleophiles, except those containing acidic protons such as thiophenol, pyrazole, acetylacetone, and related 1,3-dicarbonyl compounds, to give γ-substituted vinylidene complexes. Furthermore, in acidic conditions or by direct reaction with the alkenylcarbyne complex, it is possible to prepare analogous γ-substituted vinylidenes with aprotic nucleophiles such as pyrrole, 2-methylfuran, 2-methylthiophene, acetone, and other simple ketones (Scheme 3).[11,12]

In this paper, we extend our results on the activation of 1-phenyl-2-propyn-1-ol by [Cp*RuCl(dippe)] to the synthesis of new allenylidene and alkenylcarbyne complexes from 1-(4-methoxyphenyl)-2-propyn-1-ol and 1-(4-fluorophenyl)prop-2-yn-1-ol, analyzing the effect of electron-donor and electron-withdrawing groups on the allenylidene substituents. New allenylidene/alkenylcarbyne reactions are reported for the first time: (a) the electrophilic aromatic substitution of 1,3-dimethoxybenzene to obtain γ-substituted vinylidene compounds; (b) the double addition of resorcinol and 1,3-cyclohexanedione to the Cβ−Cγ and Cα−Cβ allenylidene double bonds, furnishing a series of chroman-2-ylidene and hexahydrochromen-2-ylidene derivatives as cycloaddition products. The X-ray structure of a chroman-2-ylidene complex is provided. The isolation and characterization of vinylidene intermediates support the proposed mechanism.

Results and Discussion

Allenylidene synthesis by the standard Selegue methodology is limited by the electronic properties of the particular metallic fragment. Electrophilic precursors tend to directly give alkoxycarbene species without isolation of any intermediate, whereas dehydration is disfavored in the case of electron-rich complexes.[13]

The good electron-releasing capability of the $[Cp^*Ru(dippe)]^+$ fragment has already provided an alternative pathway for the initial alkyne C−H activation, yielding 3-hydroxyalkynyl hydride derivatives, which spontaneously isomerize into 3-hydroxyvinylidene complexes.[14] The subsequent dehydration to allenylidene strongly depends on the allenylidene substituents.

The complex prepared from 1,1-diphenyl-2-propyn-1-ol dehydrates fast and spontaneously, but the resulting allenylidene turned out to be inert against most neutral nucleophilic reagents. With secondary propargyl alcohols such as 1-phenyl-2-propyn-1-ol, a complete dehydration can only be achieved by passing the solution through an acidic alumina column, yielding $[Cp^*Ru(=C=C=CHPh)(dippe)][BF_4]$ (**1**) in pure form. This complex reacts with protic nucleophiles through an alternative pathway involving the initial protonation and the subsequent nucleophilic attack.[11]

This observation encouraged us to test the effect of donor and electron-withdrawing groups at the *para*-position of the allenylidene phenyl substituent, thus modifying and controlling the allenylidene reactivity (Scheme 4).

1-(4-Methoxyphenyl)-2-propyn-1-ol reacts smoothly with the starting complex [Cp*RuCl(dippe)] in the presence of NH_4BF_4 in CH_2Cl_2 to give a dark orange-brown solid in almost quantitative yield. The strong IR absorption at 1920 cm^{-1} clearly indicates the presence of an allenylidene ligand. Signals at δ 287.6, 208.1, and 139.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum and at δ 8.91 ppm in the ^1H NMR spectrum are characteristic for the three allenylidene carbon atoms and the proton at the γ carbon, respectively.

In similar conditions, 1-(4-fluorophenyl)prop-2-yn-1-ol and [Cp*RuCl(dippe)] give rise to a mixture of 3-hydroxyvinylidene and the corresponding allenylidene complexes even after stirring for 5 h at room temperature. The solution must be passed through an acidic alumina column and eluted with methanol to obtain a dark greenish-brown solid after solvent removal. Both the IR band at 1941 cm^{-1} and NMR signals at δ 9.23 ppm, and δ 292.9, 218.6, and 137.4 ppm in the ^1H and $^{13}C\{^1H\}$ spectra, respectively, support the complete generation of an allenylidene complex.

Allenylidene complexes $[Cp^*Ru(=C=C=CHAr)(dippe)][BF_4]$ (Ar = C_6H_5 (**1**), *p*-C_6H_4(OMe) (**2**), *p*-C_6H_4(F) (**3**)) are

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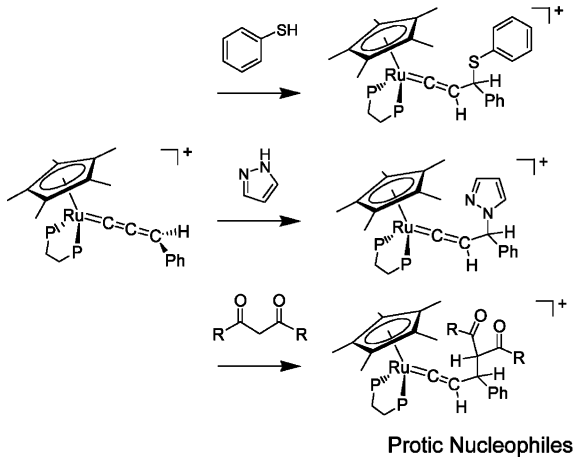
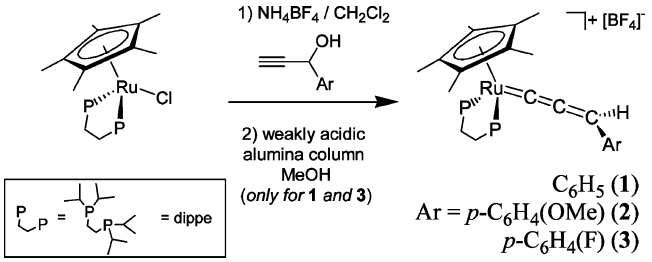
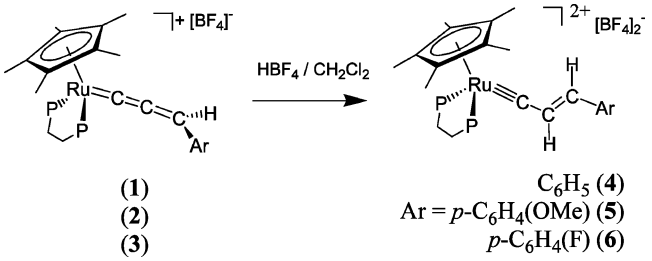
Scheme 3



Scheme 4



Scheme 5



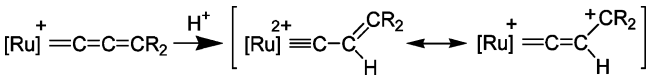
rapidly protonated at the β-carbon atom when treated with an excess of HBF_4 in CH_2Cl_2 solution at room temperature, yielding the corresponding alkenylcarbyne complexes [Cp*Ru(≡CCH═CHAr)(dippe)][BF_4]$_2$ (Ar = C_6H_5 (**4**), *p*-C_6H_4(OMe) (**5**), *p*-C_6H_4(F) (**6**)) as dark red solids, which have been characterized by elemental analysis and IR and NMR spectroscopy (Scheme 5).

The IR spectra of **4**−**6** lack the characteristic allenylidene band. The ^{1}H NMR spectra display a pair of doublets at δ 6.5−6.9 and 8.1−8.4 ppm, attributable to the hydrogens on β and γ carbons. The coupling constants of 15−16 Hz are consistent with a *trans* arrangement around the double bond. The ^{13}C-{^{1}H} NMR spectra show the resonance corresponding to the α-carbon atom of the carbyne ligand at around δ 333 ppm, as a triplet with coupling constants of 12−13 Hz.

These spectroscopic data are in agreement with those shown by [Cp*Ru(≡C−CH═CPh$_2$)(dippe)][$B(Ar_F)_4$]$_2$(Ar_F = $(CF_3)_2C_6H_3$), whose X-ray structure was reported.[11] It is worth mentioning here that the C−C distances within the alkenylcarbyne moiety were identical ($d_{C\alpha C\beta}$ = $d_{C\beta C\gamma}$ = 1.38 Å), showing the high contribution of the vinylidene canonical form and the partial carbocation character of the alkenylcarbyne γ carbon (Scheme 6).

This feature makes the alkenylcarbyne complexes **4**−**6** suitable for promoting the electrophilic aromatic substitution

Scheme 6



of *1,3-dimethoxybenzene* as the activated aromatic compound. In agreement with our previous results, no reaction is observed when allenylidene complexes **1**−**3** are treated with an excess of 1,3-dimethoxybenzene, as expected for an aprotic reagent. However, the corresponding alkenylcarbynes **4**−**6** slowly change color from dark red to light brown when stirred overnight at 40 °C. The reaction of complex **5** (*p*-methoxy-substituted) requires heating at 60 °C during 24 h in order to consume completely the starting alkenylcarbyne complex. After workup, γ-substituted vinylidene complexes [Cp*Ru{═C═CHCHAr(C_6H_3(OMe)$_2$)}-(dippe)][BF_4] (Ar = C_6H_5 (**7**), *p*-C_6H_4(OMe) (**8**), *p*-C_6H_4(F) (**9**)) are isolated as brown solids.

NMR spectra for complexes **7**−**9** are quite distinctive for the family of substituted vinylidene complexes obtained in our laboratory (see Scheme 3). The ^{1}H NMR spectrum shows a pair of coupled doublets corresponding to hydrogens at β- and γ-carbon atoms, at δ 4.69−5.31 ppm. The most characteristic signal in the ^{13}C{^{1}H} NMR spectra is the low-shielded triplet corresponding to the carbenic carbon atom, observed at δ 337−339 ppm. The 1,3-dimethoxyphenyl group is regiospecifically attached to the vinylidene γ carbon through its 4-position, which is the most activated to aromatic electrophilic substitutions with a lesser steric hindrance, as confirmed by ^{1}H and ^{13}C{^{1}H} NMR.

The ^{31}P{^{1}H} NMR spectra show an AB system due to the chiral center at the vinylidene γ carbon, which renders the phosphine groups diastereotopic. Both the chemical shift (at around δ 87−90 ppm) and the $^2J_{PP}$ coupling constant (19 Hz) are characteristic for γ-substituted vinylidene complexes with the [Cp*Ru(dippe)]$^+$ moiety. This effect is also observed for other vinylidene compounds with different metal fragments.[15]

The aryl substituent effect is evidenced in the case of the *p*-methoxy group by the higher thermal activation barrier and longer reaction time required to complete the reaction. This observation matches well with an increased delocalization and stabilization of the alkenylcarbyne γ-carbon partial positive charge along the most electron-rich aryl ring, making the complex less electrophilic (Scheme 8). The rate-determining step

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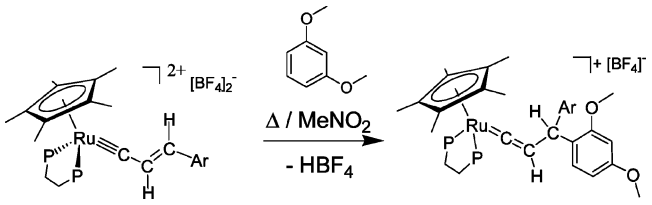
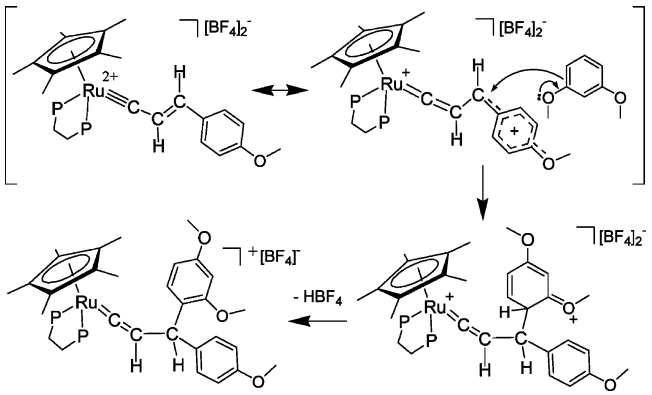
Scheme 7



Scheme 8



for this reaction would be the nucleophilic attack of the aromatic compound to the alkenylcarbyne γ-carbon atom.

We have tested whether the presence of a weak acid such as NH_4BF_4 is able to promote the direct reaction between the allenylidene complex **3** and 1,3-dimethoxybenzene. The reaction was monitored by $^{31}P\{^1H\}$ NMR. After stirring the mixture at 80 °C for 6 days in the presence of NH_4BF_4, 100% of the allenylidene complex was converted into the corresponding γ-substituted vinylidene **9**. It is noteworthy that no reaction is observed in the absence of NH_4BF_4 under the same conditions. This experiment confirms that even weakly acidic conditions activate the allenylidene complex. The allenylidene protonation becomes slower due to the lower proton concentration generated by NH_4BF_4, compared to HBF_4. Small amounts of alkenylcarbyne (not observed by NMR) would react with 1,3-dimethoxybenzene, which finally releases one proton to the medium, thus allowing more alkenylcarbyne formation. The result is an overall slower reaction rate.

This reaction represents, to the best of our knowledge, the first example of an intermolecular electrophilic aromatic substitution with allenylidene complexes[16] and describes for the first time a new type of allenylidene reactivity, which resembles the mechanistic proposal for the catalytic propargylation of aromatic compounds with propargyl alcohols,[10] and it is compatible with the catalytic conditions.

Resorcinol (benzene-1,3-diol) is another arene compound activated toward electrophilic aromatic substitution. The presence of reactive C−H and O−H bonds makes this compound appropriate for a double addition to the unsaturated allenylidene carbon chain. Similarly to 1,3-dimethoxybenzene, allenylidene complexes **1**−**3** do not react directly with resorcinol. However, alkenylcarbyne complexes **4**−**6** undergo a fast transformation, giving rise to a family of bicyclic carbene derivatives with a *neoflavonoid* skeleton derived from 4-phenylcoumarin. It consists of a chromane ring bearing a second aromatic ring in position 4 and the carbene at position 2 (Scheme 9). Again the *p*-methoxy-substituted complex requires more drastic conditions to complete the reaction, probably due to the increased stability of the alkenylcarbyne intermediate.

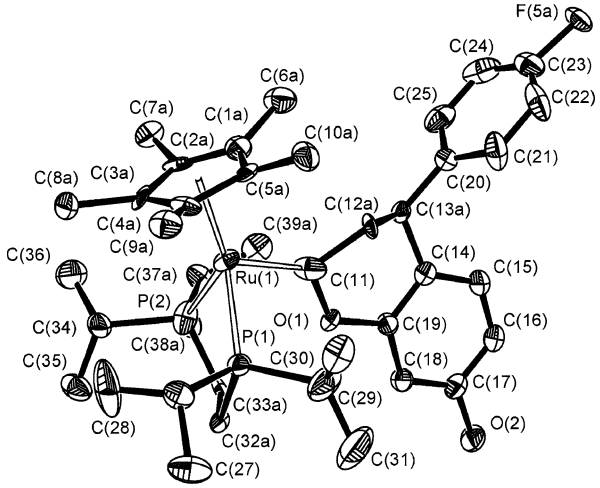


Figure 1. ORTEP view of the cation of the complex [Cp*Ru{=C($C_{14}H_{11}O_2F$)}(dippe)][BF_4] (**12**). Selected bond lengths (Å) and angles (deg): Ru(1)−P(1) 2.3215(17), Ru(1)−P(2) 2.324(2), Ru(1)−C(11) 1.911(7), C(11)−C(12a) 1.575(10), C(12a)−C(13a) 1.540(13), C(13a)−C(14) 1.493(12), C(13a)−C(20) 1.492(11), C(14)−C(19) 1.387(9), C(11)−O(1) 1.358(8), O(1)−C(19) 1.390(7); P(1)−Ru(1)−P(2) 82.41(7), Ru(1)−C(11)−O(1) 124.8(5), Ru(1)−C(11)−C(12a) 126.5(5), C(11)−O(1)−C(19) 124.3(4), O(1)−C(19)−C(14) 122.1(5).

The resulting 7-hydroxy-4-phenylchroman-2-ylidene complexes **10**−**12** have been characterized by elemental analysis, by IR and NMR spectroscopy, and particularly by the X-ray diffraction structure of compound **12**. An ORTEP view of the complex cation **12** is depicted in Figure 1. Selected bond lengths and angles are listed in the Figure 1 caption.The three-legged piano stool geometry around ruthenium is determined by two phosphorus atoms of the chelating diphosphine and the bicyclic carbene ligand. The Ru(1)−C(11) bond length of 1.911(7) Å is slightly longer than the Ru=C distance of a vinylidene complex with the same metal fragment (1.862 Å),[12] but somewhat shorter than that of similar six-membered cyclic oxacarbene complexes such as [CpRu(=C_5H_8O)(dppe)][PF_6] (1.938 Å).[17,18] The chromane ring appears in vertical orientation with the oxygen directed away from the Cp* ligand. The two rings are almost planar, with carbons 11 and 12 twisted out of the plane, in a similar way to the conformation observed in the X-ray structure of 7-hydroxy-4-(4-methoxyphenyl)-3,4-dihydrocoumarin,[19] which shows analogous bond lengths and angles and slightly different torsion angles (C(19)O(1)C(11)C(12a) −16.5(9)°/−22.28°, C(19)C(14)C(13a)C(12a) 42.8(9)°/33.32°, O(1)C(11)C(12a)C-

(16) The formation of $RuCl_2(PPh_3)_2$(3-phenylindenylidene) has been reported to occur by intramolecular electrophilic aromatic substitution from allenylidene/vinylcarbyne complexes: (a) Fürstner, A.; Hill, A. F.; Liebl, M.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1999**, 601. (b) Schanz, H. J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5187. (c) Jafarpour, L.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5416. (d) Harlow, K. J.; Hill, A. F.; Wilton-Ely, J. D. E. T. *J. Chem. Soc., Dalton Trans.* **1999**, 285.

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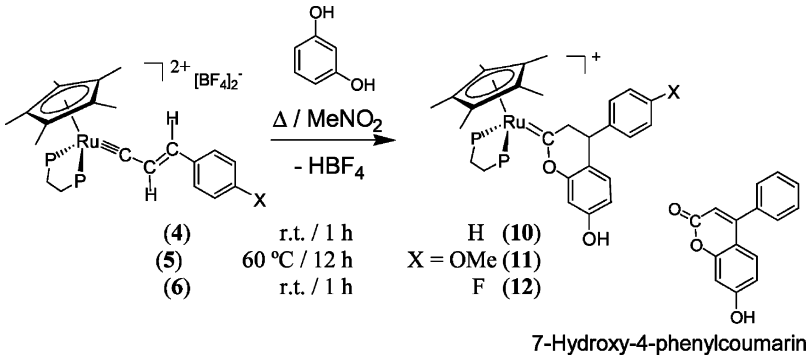
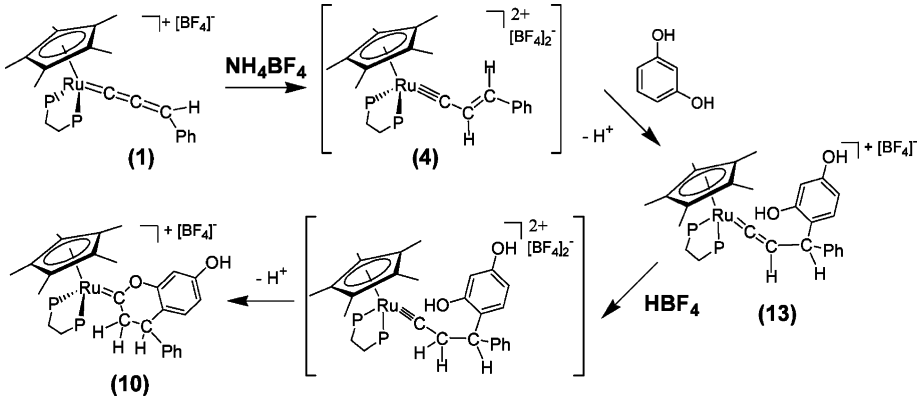
(18) (a) Hansen, H. D.; Nelson, J. H. *Organometallics* **2000**, *19*, 4740. (b) Pavlik, S.; Mereiter, K.; Puchberger, M.; Kirchner, K. *J. Organomet. Chem.* **2005**, *690*, 5497−5507. (c) Kopf, H.; Pietraszuk, C.; Hübner, E.; Burzlaff, N. *Organometallics* **2006**, *25*, 2533.

(19) Rajalakshmi, K.; Jain, N.; Deepthi, S.; Krishnamurthy, H. G.; Pattabhi, V. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, 813.

Scheme 9



Scheme 10



(13a) 57.7(9)°/34.89°), attributable to the steric effect of the $[Cp^*Ru(dippe)]^+$ fragment.

The most characteristic spectroscopic feature of complexes **10**−**12** is the resonance of the carbenic carbon atom, which appears at δ 287−289 ppm in the $^{13}C\{^1H\}$ NMR spectra, shifted to higher field compared to vinylidene α-carbon atoms (337−339 ppm). The adjacent CH_2 group is diastereotopic and shows two signals for the two protons connected to the carbon atom appearing at around δ 60 ppm in the $^{13}C\{^1H\}$ NMR (HSQC bidimensional correlation). The $^{31}P\{^1H\}$ NMR consists of two doublet signals at δ 98−104 ppm.

As mentioned above, the direct reaction between the allenylidene complex **1** and resorcinol failed in the absence of a proton source. In the presence of NH_4BF_4, the reaction takes place by heating at 80 °C during 6 h. Unexpectedly, the isolated brown solid does not correspond to the bicyclic carbene **10**, but to the vinylidene complex $[Cp^*Ru\{=C=CHCHPh(C_6H_3(OH)_2)\}(dippe)][BF_4]$ (**13**). This compound is stable in solution, and it was characterized by NMR spectroscopy. The ^1H and $^{13}C\{^1H\}$ NMR spectra show the characteristic signals for a γ-substituted vinylidene: two doublets at δ 4.87 and 5.23 ppm for protons at β and γ positions, and a low-shielded triplet at 339 ppm for the α-carbon atom, comparing well with NMR data from vinylidene complexes **7**−**9**.

Complex **13** would be the result of the electrophilic aromatic substitution of resorcinol with allenylidene **1** via generation of alkenylcarbyne **4**, as described for the reaction with 1,3-dimethoxybenzene. To check whether this is the actual intermediate in the synthesis of the chromen-2-ylidene species, a CD_3NO_2 solution of complex **13** in a NMR tube has been treated with an excess of HBF_4 at room temperature. An immediate reaction takes place, giving rise to the expected bicyclic carbene **10**, as confirmed by the ^1H and $^{31}P\{^1H\}$ NMR spectra (Scheme 10).

As a conclusion, the reaction proceeds in two steps: first the electrophilic aromatic substitution to give γ-substituted vinylidene species, which requires the presence of a weak acid to generate the electrophilic alkenylcarbyne species *in situ*, and second, the O−H addition to the Cα−Cβ vinylidene double bond under stronger acidic conditions. A hypothetical carbyne formation by vinylidene protonation would explain this requirement and the exceptional reactivity of the vinylidene α carbon, which had never been observed before in similar complexes with the $[Cp^*Ru(dippe)]^+$ fragment.

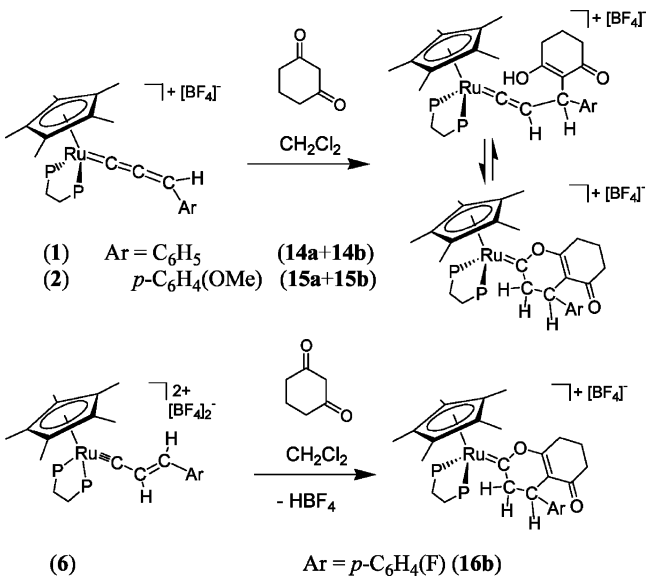
This reaction resembles the catalytic cycloaddition of propargyl alcohols with phenol derivatives, the reaction mechanism of which has not yet been elucidated.[20] The formation of cycloaddition products from *electrophilic allenylidene* complexes such as $[CpRu(P^iPr_3)(CO)(=C=C=CPh_2)][BF_4]$[3] or $[(triphos)Re(CO)_2(=C=C=CPh_2)][OTf]$[4] requires organic molecules containing two nucleophilic heteroatoms. Pyrazole, aminopyridine, mercaptopyridine, thioisonicotinamide, and related species undergo 1,2,3-diheterocyclization reactions involving nucleophilic attack to the allenylidene α and γ carbons and transfer of a proton to the β carbon, through allenyl or alkynyl intermediates. By contrast, the reaction of the allenylidene complex **1** with pyrazole is finished after the first N−H addition, without ulterior cyclization.[11] Other polycyclic ligands are accessible from electrophilic allenylidenes by deprotonation of the corresponding α,β-unsaturated alkoxycarbene after the initial O−H addition to the Cα−Cβ allenylidene double bond.[21]

Cyclohexanedione is a nonaromatic six-membered-ring reagent structurally related to resorcinol and 1,3-dimethoxybenzene, which exists in solution almost exclusively in its tauto-

(20) Nishibayashi, Y.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 7900.

(21) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **2000**, *19*, 4.

Scheme 11



meric enol form 3-hydroxycyclohex-2-enone. Similarly to other 1,3-diketonic compounds, cyclohexanedione is acidic enough to react directly with the allenylidene complexes **1**−**3**. However, at difference with linear 1,3-dicarbonyl compounds (acetylacetone, diethylmalonate, and malononitrile), this cyclic diketone does not afford γ-substituted vinylidene complexes as the only product. Instead, a mixture of two compounds is obtained when reacting with allenylidene complexes **1** and **2** at room temperature. These compounds are not separable and they seem to be in equilibrium. Attempts to obtain only one product by control of the reaction parameters (temperature, reaction time, acidic medium) did not succeed.

The outcome of this novel reactivity can be further rationalized by comparison with our previous results. The NMR spectra have been recorded for the reaction of complex **1** and cyclohexanedione. The $^{31}P\{^1H\}$ NMR shows two pairs of AB systems (four doublets) at δ 86.9 and 87.6 ($^3J_{PP'}$ = 19.3 Hz) and 97.6 and 100.2 ppm ($^3J_{PP'}$ = 15.4 Hz) in 40:60 ratio, respectively. Two triplet resonances at δ 286.5 and 339.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum are assigned to carbene and vinylidene α-carbon atoms, respectively, which is in good agreement with the NMR data of vinylidene **10** (287.0 ppm) and carbene **13** (338.9 ppm). The assignment of signals with the help of COSY and $^1H-^{13}C$ bidimensional correlation (HSQC) is consistent with the existence of a γ-substituted vinylidene [Cp*Ru{=C=CH−CH($C_6H_7O_2$)Ph}(dippe)][BF_4] (**14a**) and a bicyclic carbene [Cp*Ru(L)(dippe)][BF_4] (L = 4-phenyl-5-oxo-hexahydrochromen-2-ylidene, **14b**). Analogous results were obtained from **2**, giving **15a** + **15b** (see Scheme 11).

The enol arrangement of the γ-bonded 2,6-dioxocyclohexyl group in vinylidene complexes **14a** and **15a** is supported by their ^1H NMR spectra, which clearly show an AB system (two doublet signals) for protons at β- and γ-carbon atoms of the vinylidene group, whereas a keto tautomer would exhibit three coupled signals (ABC system) for the three neighboring protons. Thus, the isomeric complexes **14a**,**14b** and **15a**,**15b** can undergo a reversible rearrangement from carbene to vinylidene, establishing the proposed isomerization equilibrium illustrated in Scheme 11.

Acidic medium favors the carbene form. An increase of the amount of the carbene isomer is also observed when starting from allenylidene **3** (*p*-fluoro-substituted). In agreement with these two observations, the reaction between the carbyne complex **6** and cyclohexanedione gave the highest carbene/vinylidene ratio (Scheme 11), obtaining the carbene form in more than 90% ratio. Thus, more accurate NMR data for the bicyclic carbene complex [Cp*Ru(L)(dippe)][BF_4] (L = 4-(4-fluorophenyl)-5-oxo-hexahydrochromen-2-ylidene, **16b**) were recorded.

As in the case of complexes **10**−**12**, the ^1H NMR spectrum shows diastereotopic CH_2 protons at the β position. The $^{31}P\{^1H\}$ NMR exhibits doublets at δ 98.3 and 101.1 ppm. Six signals for quaternary carbons are observed in the $^{13}C\{^1H\}$ NMR, corresponding to the aryl (138.9 and 162.9 ppm), alkenyl (117.5 and 167.4 ppm), carbonyl (199.1 ppm), and carbene (287.6 ppm) groups, in addition to the Cp* ring carbon atom signal (104.2 ppm).

A similar cyclic carbene complex has been reported by Esteruelas et al., obtained from [CpRu(P^iPr_3)(CO)(=C=C=CPh_2)][BF_4] and acetone in two steps.[3,22] At difference with compounds **1**−**3**, this electrophilic allenylidene requires first the generation of the acetonate in the presence of a strong base and then the protonation of the resulting alkynyl intermediate. The reverse mechanism (first protonation then nucleophilic attack), operative for nucleophilic allenylidenes, involves the conjugated pair allenylidene/alkenylcarbyne instead of the classic alkynyl/vinylidene, thus allowing a direct reaction with carbon nucleophiles without the need of a strong base.

The allenylidene + cyclohexanedione reaction rate is not affected by the substituent of the allenylidene aryl group. In all cases the reaction proceeds smoothly at room temperature, suggesting that the carbyne stabilization is not involved in the rate-determining step. Therefore, the allenylidene protonation by the acidic cyclohexanedione generates the alkenylcarbyne/cyclohexanedione enolate pair, which reacts immediately to give the substituted vinylidene complex. The higher nucleophilic character of the enolate species compared to that of activated arenes overcomes the electron density variations induced by the aryl substituents at the electrophilic alkenylcarbyne γ carbon.

As mentioned earlier, γ-substituted vinylidenes are proposed as intermediates in the catalytic propargylic substitution of propargyl alcohols with heterocycles, ketonic compounds, and other C-, N-, P-, and O-nucleophiles.[10] However, these reactions involving allenylidene intermediates had no precedent within the known reactivity of electrophilic allenylidenes. Our recent results provided the first stoichiometric approach to this catalytic reaction, in spite of the obvious differences between the [Cp*Ru(dippe)]$^+$ complexes and the [Cp*RuCl(μ-SR)$_2$RuCp*]$^+$ catalyst.

The correlation between the stoichiometric and catalytic reactivity is further evidenced by the particular behavior of cyclohexanedione (Scheme 12). Whereas linear β-diketones provided γ-substituted vinylidene complexes, cyclohexanedione also yields cyclic carbene compounds. Similarly, the catalytic reaction of propargylic alcohols with 1,3-dicarbonyl compounds affords γ-alkylated products when acyclic β-diketones are employed, whereas 1,3-cyclohexanedione leads to cycloaddition products via initial propargylic alkylation and ulterior intramolecular cyclization.[23]

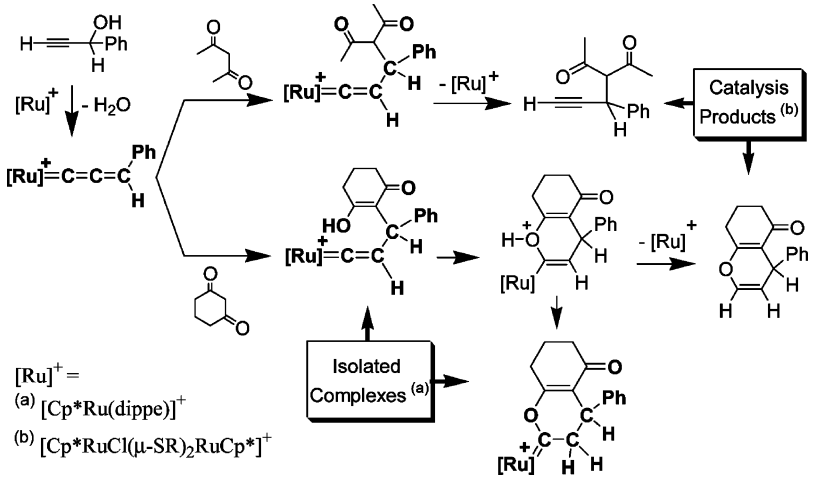
Concluding Remarks

In this paper we have reported a novel reactivity based on the basic character of electron-rich allenylidene complexes and

(22) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826.

(23) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. *J. Org. Chem.* **2004**, *69*, 3408.

Scheme 12



the electrophilic alkenylcarbyne conjugated pair. In contrast to the classical reactivity of electrophilic allenylidene complexes,[2,5] compounds **1**−**3** do not react with nucleophiles unless they contain acidic protons or in the presence of an external proton source. In both cases, the generation of an electrophilic alkenylcarbyne complex seems to be the key step.

X-ray structural data and the chemical behavior of alkenylcarbyne complexes account for the existence of a partial positive charge localized at the γ position, thus generating a stabilized carbocation, which acts as electrophile for the electrophilic aromatic substitution of electron-rich arenes. The presence of electron-releasing groups on the allenylidene aryl substituent contributes to a decrease of the carbocation character, thus slowing the reaction with π-nucleophiles such as resorcinol and 1,3-dimethoxybenzene. Electron-withdrawing groups such as fluoride enhance slightly the allenylidene/carbyne reactivity, but the effect is less marked and essentially equivalent to that of the complex with an unsubstituted phenyl group.

A series of bicyclic carbene complexes have been obtained *directly* by reaction of resorcinol with alkenylcarbyne complexes, and *stepwise* from allenylidene complexes, requiring weak acids to perform the electrophilic aromatic substitution (step 1) and a strong acid to induce the intramolecular cyclization (step 2). The X-ray structure of complex **12** confirms the formation of the bicyclic carbon skeleton. Analogous carbene compounds are obtained by reaction with cyclohexanedione, which seem to be in equilibrium with the isomeric γ-substituted vinylidene bearing the 2,6-dioxocyclohexyl group as the enol tautomer.

These are the first examples of α-carbon reactivity found in the context of vinylidene and allenylidene chemistry with the fragment $[Cp^*Ru(dippe)]^+$, which has been thoroughly studied in our group. The α carbon in this system is usually inaccessible because of the steric hindrance and the effective electronic stabilization. The requirement of strong acid activation could involve the formation of carbyne species *in situ* by vinylidene protonation, which is currently under study.

Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere by following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40−60 °C) were obtained oxygen- and water-free from an Innovative Technology Inc. solvent purification apparatus. Dichloromethane and nitromethane were of anhydrous quality and used as received. All solvents were deoxygenated immediately before use. Propargylic alcohols were prepared by the reaction of the corresponding *p*-substituted benzaldehyde with ethynylmagnesium bromide, except 1-phenyl-2-propyn-1-ol, which is commercially available.

IR spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer. NMR spectra were taken on a Varian Inova 400 MHz or Varian Gemini 300 MHz equipment. Chemical shifts are given in parts per million from $SiMe_4$ (^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). ^1H and $^{13}C\{^1H\}$ NMR signal assignments were confirmed by ^1H-gCOSY, 135-DEPT, and gHSQC($^1H-^{13}C$) experiments. Microanalysis was performed on a LECO CHNS-932 elemental analyzer at the Servicio Central de Ciencia y Tecnología, Universidad de Cádiz.

Preparation of [Cp*Ru(=C=C=CHAr)(dippe)][BF$_4$] (Ar = C$_6$H$_5$ (1), *p*-C$_6$H$_4$(OMe) (2), *p*-C$_6$H$_4$(F) (3)). A 300 mg sample of compound [Cp*RuCl(dippe)] (0.56 mmol) was dissolved in 10 mL of CH_2Cl_2. An excess of NH_4BF_4 (100 mg, 0.91 mmol) and 0.60 mmol of the corresponding propargyl alcohol were added immediately. After stirring for 5 h at room temperature, the solution was passed through an acidic alumina column (activity grade I, height of column 10 cm). The dark brown band collected by elution with MeOH was then taken to dryness under vacuum, giving a dark brown solid. Yields: 345 mg of **1** (89%), 362 mg of **3** (90%). The acidic alumina step is not necessary for the synthesis of allenylidene **2**, and the CH_2Cl_2 solution was directly filtered and dried under vacuum, giving a dark orange solid in almost quantitative yield (400 mg, 98%). Spectroscopic and analytical data for **1** were already reported elsewhere.[12,14]

Complex 2. Anal. Calcd for $C_{34}H_{55}BF_4OP_2Ru$: C, 56.0; H, 7.60. Found: C, 56.1; H, 7.63. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 0.94, 1.10, and 1.21 (m, 24 H, dippe-CH_3), 1.91 (s, 15 H, $C_5(CH_3)_5$), 2.05 and 2.29 (m, 8 H, dippe-CH_2), 3.83 (s, 3 H, OCH_3), 6.90 and 7.70 (both d, 2 H each, $^3J_{HH}$ = 8.3 Hz, $C_6H_4OCH_3$), 8.91 (s, 1 H, Ru=C=C=C*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 161.9 MHz): δ 89.0 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 298 K): δ 11.25 (s, $C_5(CH_3)_5$), 18.13, 18.43, 19.47, and 19.91 (s, dippe-*C*H$_3$), 21.80 and 26.15 (m, dippe-*C*H$_2$), 30.45 (m, dippe-*C*H), 56.06 (s, O*C*H$_3$), 102.6 (s, *C*$_5$(CH$_3$)$_5$), 115.9, 132.4, 136.9, and 163.2 (s, *C*$_6$H$_4$OCH$_3$), 139.2 (s, Ru=C=C=*C*H), 208.1 (t, $^3J_{CP}$ = 2.2 Hz, Ru=C=*C*), 287.6 (t, $^2J_{CP}$ = 17.4 Hz, Ru=*C*). IR (Nujol): ν(C=C=C) 1920 cm^{-1}.

Complex 3. Anal. Calcd for $C_{33}H_{52}BF_5P_2Ru$: C, 55.2; H, 7.30. Found: C, 55.2; H, 7.31. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.03, 1.21, and 1.32 (m, 24 H, dippe-CH_3), 2.03 (s, 15 H, $C_5(CH_3)_5$), 2.15 and 2.39 (m, 8 H, dippe-CH_2), 7.18 (vt, 2 H, $^3J_{HF}$ = $^3J_{HH}$ = 8.6 Hz, *m*-C$_6$H$_4$F), 7.86 (dd, 2 H, $^4J_{HF}$ = 5.7 Hz, $^3J_{HH}$ = 8.5 Hz *o*-C$_6$H$_4$F), 9.23 (s, 1 H, Ru=C=C=C*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, 161.9 MHz): δ 88.8 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2-

Cl_2, 298 K): δ 11.34 (s, $C_5(CH_3)_5$), 18.15, 18.47, 19.54, and 19.93 (s, dippe-CH_3), 21.93 and 26.24 (m, dippe-CH_2), 30.58 (m, dippe-*C*H), 103.4 (s, $C_5(CH_3)_5$), 117.7 (d, $^3J_{CF}$ = 22.7 Hz, *m*-C_6H_4F), 131.9 (d, $^3J_{CF}$ = 8.5 Hz, *o*-C_6H_4F), 137.4 (d, $^5J_{CF}$ = 1.9 Hz, Ru=C=C=*C*H), 139.6 (d, $^4J_{CF}$ = 3.8 Hz, *ipso*-C_6H_4F), 164.6 (d, $^1J_{CF}$ = 256 Hz, *p*-C_6H_4F), 218.6 (s, Ru=C=*C*), 292.9 (t, $^2J_{CP}$ = 17.0 Hz, Ru=*C*). IR (Nujol): ν(C=C=C) 1914.1 cm^{-1}.

Preparation of [Cp*Ru(≡C−CH=CHAr)(dippe)][BF_4]$_2$ (Ar = C_6H_5 (4), *p*-C_6H_4(OMe) (5), *p*-C_6H_4(F) (6)). A 133 mg portion of compound [Cp*RuCl(dippe)] (0.25 mmol) was dissolved in 5 mL of CH_2Cl_2. A slight excess of NH_4BF_4 (40 mg, 0.36 mmol) and 0.33 mmol of the corresponding propargyl alcohol were immediately added, and the solution was stirred at room temperature for 2 h. Addition of 40 μL of HBF_4 (54 wt % solution in Et_2O, 0.30 mmol) rapidly produced a clear color change from brown to dark red. After stirring for 10 min at room temperature the solvent was evaporated under vacuum, and the residue was washed with 2 × 10 mL of Et_2O and dried, giving dark red solid. Yields: 160 mg of **4** (81%), 192 mg of **5** (94%), 181 mg of **6** (90%). Spectroscopic and analytical data for **4** were already reported elsewhere.[11,12]

Complex 5. Anal. Calcd for $C_{34}H_{56}B_2F_8OP_2Ru$: C, 50.0; H, 6.91. Found: C, 49.8; H, 6.90. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.08 and 1.36 (m, 24 H, dippe-CH_3), 2.02 (s, 15 H, $C_5(CH_3)_5$), 2.27 and 2.58 (m, 8 H, dippe-CH_2), 3.90 (s, 3 H, OCH_3), 6.78 (d, 1 H, $^3J_{HH}$ =15.1 Hz, Ru≡C−CH=C*H*), 7.00 and 7.99 (both d, 2 H each, $^3J_{HH}$ = 8.5 Hz, $C_6H_4OCH_3$), 8.18 (d, 1 H, $^3J_{HH}$ = 15.1 Hz, Ru≡C−C*H*=CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K, 161.9 MHz): δ 84.9 (s). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 298 K): δ 11.18 (s, $C_5(CH_3)_5$), 18.33, 18.87, 19.74, and 19.86 (s, dippe-CH_3), 22.85 and 25.23 (m, dippe-CH_2), 33.13 (m, dippe-*C*H), 56.55 (s, O*C*H_3), 108.2 (s, $C_5(CH_3)_5$), 116.4, 125.8, 126.2, and 167.7 (s, $C_6H_4OCH_3$), 166.2 and 170.0 (s, Ru≡C−*C*H=*C*H), 334.6 (t, $^2J_{CP}$ = 13.0 Hz, Ru=*C*). IR (Nujol): ν(Ph) 1590 cm^{-1}.

Complex 6. Anal. Calcd for $C_{33}H_{53}B_2F_9P_2Ru$: C, 49.2; H, 6.63. Found: C, 49.2; H, 6.60. ^{1}H NMR (400 MHz, CD_3NO_2, 298 K): δ 1.21 and 1.49 (m, 24 H, dippe-CH_3), 2.18 (s, 15 H, $C_5(CH_3)_5$), 2.31, 2.58, and 2.81 (m, 8 H, dippe-CH_2), 6.91 (d, 1 H, $^3J_{HH}$ =15.8 Hz, Ru≡C−CH=C*H*), 7.33 (vt, 2 H, $^3J_{HF}$ = $^3J_{HH}$ = 8.8 Hz, *m*-C_6H_4F), 8.01 (dd, 2 H, $^4J_{HF}$ = 5.4 Hz, $^3J_{HH}$ = 8.5 Hz, *o*-C_6H_4F), 8.35 (d, 1 H, $^3J_{HH}$ = 15.8 Hz, Ru≡C−C*H*=CH). ^{31}P{^{1}H} NMR (CD_3NO_2, 298 K, 161.9 MHz): δ 91.5 (s). ^{13}C{^{1}H} NMR (75.4 MHz, CD_3NO_2, 298 K): δ 11.76 (s, $C_5(CH_3)_5$), 18.78, 19.55, 20.38, and 20.50 (s, dippe-CH_3), 24.23 and 26.72 (m, dippe-CH_2), 34.70 (m, dippe-*C*H), 111.2 (s, $C_5(CH_3)_5$), 118.9 (d, $^3J_{CF}$ = 22.8 Hz, *m*-C_6H_4F), 130.5 (d, $^4J_{CF}$ = 2.5 Hz, *ipso*-C_6H_4F), 131.8 (s, Ru≡C−CH=*C*H), 136.3 (d, $^3J_{CF}$ = 10.8 Hz, *o*-C_6H_4F), 165.9 (s, Ru≡C−*C*H), 169.8 (d, $^1J_{CF}$ = 263 Hz, *p*-C_6H_4F), 333.3 (t, $^2J_{CP}$ = 12.9 Hz, Ru=*C*). IR (Nujol): ν(Ph) 1588 cm^{-1}.

Preparation of [Cp*Ru{=C=CHCHAr(C_6H_3(OMe)$_2$)}(dippe)][BF_4] (Ar = C_6H_5 (7), *p*-C_6H_4(OMe) (8), *p*-C_6H_4(F) (9)). The first step of the synthesis of compounds **7**−**9** was carried out as described for the preparation of carbyne compound **4**−**6**. The addition of 40 μL of HBF_4 (54 wt % solution in Et_2O, 0.30 mmol) rapidly produced the formation of the carbyne complex *in situ*, shown by the distinctive dark red color. After stirring for 10 min at room temperature the solvent was evaporated under vacuum. The residue was washed with 2 × 10 mL of Et_2O in order to remove the excess acid and then dissolved in 5 mL of nitromethane. An excess of 1,3-dimethoxybenzene (134 μL, 1 mmol) was added and the mixture stirred at 40 °C in CH_2Cl_2 during 12 h (for **7** and **9**) and at 60 °C during 24 h (for **8**). The color changed from dark red to light brown. Then, the solution was filtered and concentrated to less than 1 mL under reduced pressure. Addition of 10 mL of a 1:1 mixture of Et_2O and petroleum ether caused the precipitation of an orange-brown solid, which was filtered, washed with petroleum ether, and dried under vacuum. Recrystallization was carried out by slow ether diffusion into a CH_2Cl_2 solution. Yields: 172 mg of **7** (82%), 184 mg of **8** (85%), 180 mg of **9** (84%). Microanalysis and spectral data are as follows.

Complex 7. Anal. Calcd for $C_{41}H_{63}BF_4O_2P_2Ru$: C, 58.8; H, 7.58. Found: C, 58.7; H, 7.55. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.98−1.28 (m, 24 H, dippe-CH_3), 1.83 (s, 15 H, $C_5(CH_3)_5$), 1.95 and 2.10 (m, 8 H, dippe-CH_2 and C*H*), 3.77 (s, 6 H, OCH_3), 4.69 and 5.17 (both d, 1 H each, $^3J_{HaHb}$ = 11.1 Hz, Ru=C=C*H*^{a}C*H*^{b}), 6.45 (t, 1 H, $^4J_{HH}$ = 2.4 Hz, *m*-C_6H_3(OMe)$_2$), 6.50 (dd, 1 H, $^4J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 8.3 Hz, *m*-C_6H_3(OMe)$_2$), 7.19 (d, 1 H, $^3J_{HH}$ = 8.3 Hz, *o*-C_6H_3(OMe)$_2$), 7.02, 7.14, and 7.23 (m, 5 H, C_6H_5). ^{31}P-{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 87.4 and 87.7 (both d, $^3J_{PP'}$ = 18.8 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 10.78 (s, $C_5(CH_3)_5$), 18.18−21.75 (m, dippe-CH_3), 25.32 and 25.65 (m, dippe-CH_2), 32.38, 32.76, and 33.11 (s, dippe-*C*H), 35.71 (s, *C*HPh), 55.21 and 55.28 (s, O*C*H_3), 102.5 (s, $C_5(CH_3)_5$), 114.4 (s, Ru=C=*C*H), 125.0, 126.7, 128.3, and 144.5 (s, C_6H_5), 98.50, 104.7, 126.1, 127.8, 156.6, and 159.4 (s, $C_6H_3(OCH_3)_2$), 337.5 (t, $^2J_{CP}$ = 14.7 Hz, Ru=*C*). IR (Nujol): ν(C=C) 1640, ν(Ph) 1590 cm^{-1}.

Complex 8. Anal. Calcd for $C_{42}H_{65}BF_4O_3P_2Ru$: C, 58.1; H, 7.55. Found: C, 58.3; H, 7.61. ^{1}H NMR (400 MHz, CD_3NO_2, 298 K): δ 0.85 and 1.05−1.33 (m, 24 H, dippe-CH_3), 1.90 (s, 15 H, $C_5(CH_3)_5$), 2.23, 2.47, and 2.92 (m, 8 H, dippe-CH_2 and C*H*), 3.75, 3.78, and 3.85 (s, 3 H each, OCH_3), 4.92 and 5.28 (both d, 1 H each, $^3J_{HaHb}$ = 11.4 Hz, Ru=C=C*H*^{a}C*H*^{b}), 6.52 (m, 2 H, *m*-C_6H_3-(OMe)$_2$), 6.82 (d, 2 H, $^3J_{HH}$ = 8.5 Hz, *m*-C_6H_4OMe), 7.24 (m, 3 H, *o*-C_6H_3(OMe)$_2$ + *o*-C_6H_4OMe). ^{31}P{^{1}H} NMR (161.9 MHz, CD_3NO_2, 298 K): δ 90.9 and 91.1 (both d, $^3J_{PP'}$ = 19.1 Hz). ^{13}C-{^{1}H} NMR (75.4 MHz, CD_3NO_2, 298 K): δ 11.35 (s, $C_5(CH_3)_5$), 18.58−20.90 (m, dippe-CH_3), 22.58 (m, dippe-CH_2), 26.96, 31.40, and 34.20 (s, dippe-*C*H), 36.37 (s, *C*HPh), 55.92, 56.01, and 56.16 (s, O*C*H_3), 104.1 (s, $C_5(CH_3)_5$), 115.6 (s, Ru=C=*C*H), 114.9, 129.5, 138.9, and 159.5 (s, *p*-C_6H_4OMe), 99.52, 106.1, 127.5, 129.4, 158.3, and 161.1 (s, $C_6H_3(OCH_3)_2$), 339.2 (t, $^2J_{CP}$ = 13.8 Hz, Ru=*C*). IR (Nujol): ν(C=C) 1648 cm^{-1}.

Complex 9. Anal. Calcd for $C_{41}H_{62}BF_5O_2P_2Ru$: C, 57.5; H, 7.30. Found: C, 57.6; H, 7.31. ^{1}H NMR (400 MHz, CD_3NO_2, 298 K): δ 1.11 and 1.27 (m, 24 H, dippe-CH_3), 1.89 (s, 15 H, $C_5(CH_3)_5$), 2.20 (m, 8 H, dippe-CH_2 and C*H*), 3.78 and 3.85 (both s, 3 H each, OCH_3), 4.94 and 5.31 (both d, 1 H each, $^3J_{HaHb}$ = 11.6 Hz, Ru=C=C*H*^{a}C*H*^{b}), 6.53 (m, 2 H, *m*-C_6H_3(OMe)$_2$), 7.00 (vt, 2 H, $^3J_{HF}$ = $^3J_{HH}$ = 8.8 Hz, *m*-C_6H_4F), 7.25 (d, 1 H, $^2J_{HH}$ = 9.1 Hz, *o*-C_6H_3-(OMe)$_2$), 7.35 (dd, 2 H, $^4J_{HF}$ = 5.5 Hz, $^3J_{HH}$ = 8.8 Hz, *o*-C_6H_4F). ^{31}P{^{1}H} NMR (161.9 MHz, CD_3NO_2, 298 K): δ 87.9 and 88.1 (both d, $^3J_{PP'}$ = 19.0 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, CD_3NO_2, 298 K): δ 11.35 (s, $C_5(CH_3)_5$), 18.01−20.81 (m, dippe-CH_3), 22.60 and 26.83 (m, dippe-CH_2), 34.17 (s, dippe-*C*H), 36.54 (s, *C*HPh), 56.07 and 56.18 (s, O*C*H_3), 104.1 (s, $C_5(CH_3)_5$), 115.3 (s, Ru=C=*C*H), 116.1 (d, $^3J_{CF}$ = 21.3 Hz, *m*-C_6H_4F), 130.2 (d, $^3J_{CF}$ = 8.2 Hz, *o*-C_6H_4F), 143.0 (d, $^4J_{CF}$ = 3 Hz, *ipso*-C_6H_4F), 162.6 (d, $^1J_{CF}$ = 242 Hz, *p*-C_6H_4F), 99.56, 106.2, 126.9, 129.4, 158.3, and 161.2 (s, $C_6H_3(OCH_3)_2$), 337.5 (t, $^2J_{CP}$ = 14.7 Hz, Ru=*C*).IR (Nujol): ν(C=C) 1644 cm^{-1}.

Preparation of [Cp*Ru(L)(dippe)][BF_4] (L = 7-hydroxy-4-phenylchroman-2-ylidene (10), 4-(4-methoxyphenyl)-7-hydroxychroman-2-ylidene (11), 4-(4-fluorophenyl)-7-hydroxychroman-2-ylidene (12)). The synthesis of compounds **10**−**12** is carried out similarly to the preparation of compounds **7**−**9**. Addition of an excess of resorcinol (56 mg, 0.50 mmol) to a CH_3NO_2 solution containing the corresponding carbyne complex caused a fast color change from dark red to brown. The solution was stirred for 1 h at room temperature (for **10** and **12**) or overnight at 60 °C (for **11**), then filtered and concentrated to less than 1 mL at reduced pressure. Addition of 10 mL of a 1:1 mixture of Et_2O and petroleum ether caused the precipitation of an orange-brown solid, which was filtered, washed with petroleum ether, and dried under vacuum. Recrystallization of **12** by slow ether diffusion into a CH_2Cl_2 solution gave appropriate monocrystals for X-ray diffraction.

Yields: 184 mg of **10** (91%), 185 mg of **11** (88%), 186 mg of **12** (90%). Microanalysis and spectral data are as follows.

Complex 10. Anal. Calcd for $C_{39}H_{59}BF_4O_2P_2Ru$: C, 57.9; H, 7.34. Found: C, 57.8; H, 7.33. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.94−1.28 (m, 24 H, dippe-CH_3), 1.82 (s, 15 H, $C_5(CH_3)_5$), 1.93, 2.06, 2.52, and 2.68 + 2.16 (m, 8 H, dippe-CH_2 and CH, + dd, 1 H, $^3J_{HaHc}$ = 13.3 Hz, $^2J_{HaHb}$ = 15.7 Hz, CH^aH^{b}CH^{c}Ph), 3.63 (dd, 1 H, $^3J_{HbHc}$ = 3.2 Hz, $^3J_{HaHc}$ = 13.3 Hz, CH^{a}H^{b}CH^cPh), 3.80 (dd, 1 H, $^3J_{HbHc}$ = 3.2 Hz, $^2J_{HaHb}$ = 15.7 Hz, CH^aH^bCH^{c}Ph), 6.47 and 6.58 (both d, 1 H each, $^3J_{HH}$ = 8.6 Hz, C_6H_3OH), 6.84 (s, 1 H, C_6H_3OH), 7.10 and 7.35 (m, 5 H, C_6H_5). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 98.5 and 103.9 (d, $^3J_{PP'}$ = 14.1 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 10.55 (s, $C_5(CH_3)_5$), 18.50−20.87 (m, dippe-CH_3), 25.96−28.95 (m, dippe-CH_2), 31.41 and 32.79 (s, dippe-CH), 37.40 (s, CHPh), 59.70 (s, Ru=C−CH_2), 101.4 (s, $C_5(CH_3)_5$), 128.2, 127.9, 129.0, and 140.1 (s, C_6H_5), 102.8, 112.8, 117.7, 127.5, 151.8, and 157.9 (s, −O−C_6H_3(OH)), 287.0 (t, $^2J_{CP}$ = 13.2 Hz, Ru=C). IR (Nujol): ν(Ph) 1622, ν(OH) 3412 cm^{-1}.

Complex 11. Anal. Calcd for $C_{40}H_{61}BF_4O_3P_2Ru$: C, 57.2; H, 7.32. Found: C, 57.2; H, 7.32. ^{1}H NMR (400 MHz, CD_3NO_2, 298 K): δ 1.05−1.38 (m, 24 H, dippe-CH_3), 1.93 (s, 15 H, $C_5(CH_3)_5$), 2.02−2.67, 2.45, and 2.91 (m, 8 H, dippe-CH_2 and CH, + dd, 1 H, $^3J_{HaHc}$ = 12.9 Hz, $^2J_{HaHb}$ = 15.4 Hz, CH^aH^{b}CH^{c}Ph), 3.82 (dd, 1 H, $^3J_{HaHc}$ = 12.9 Hz, $^3J_{HbHc}$ = 3.8 Hz, CH^{a}H^{b}CH^cPh), 3.83 (s, 3 H, OCH_3), 3.90 (dd, 1 H, $^3J_{HaHb}$ = 15.4 Hz, $^2J_{HbHc}$ = 3.8 Hz, CH^aH^b-CH^{c}Ph), 6.59 (s, 2 H, C_6H_3OH), 6.70 (s, 1 H, C_6H_3OH), 6.96 (d, 2 H, $^3J_{HH}$ = 8.8 Hz, m-C_6H_4(OMe)), 7.17 (d, 2 H, $^3J_{HH}$ = 8.8 Hz, o-C_6H_4(OMe)). ^{31}P{^{1}H} NMR (161.9 MHz, CD_3NO_2, 298 K): δ 102.0 and 106.9 (d, $^3J_{PP'}$ = 15.4 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 11.89 (s, $C_5(CH_3)_5$), 18.55−21.44 (m, dippe-CH_3), 27.51 and 29.15 (m, dippe-CH_2), 30.45 and 33.02 (s, dippe-CH), 37.64 (s, CHPh), 56.03 (s, OCH_3), 60.94 (s, Ru=C−CH_2), 103.3 (s, $C_5(CH_3)_5$), 115.4, 130.6, 133.7, and 160.4 (s, p-C_6H_4-OMe), 103.7, 113.1, 121.7, 129.9, 153.7, and 158.1 (s, −O−C_6H_3-(OH)), 289.3 (t, $^2J_{CP}$ = d 12.8 Hz, Ru=C). IR (Nujol): ν(Ph) 1621, ν(OH) 3398 cm^{-1}.

Complex 12. Anal. Calcd for $C_{39}H_{58}BF_5O_2P_2Ru$: C, 56.6; H, 7.06. Found: C, 56.6; H, 7.06. ^{1}H NMR (400 MHz, CD_3NO_2, 298 K): δ 1.04−1.38 (m, 24 H, dippe-CH_3), 1.92 (s, 15 H, $C_5(CH_3)_5$), 2.01−2.68 and 2.46 (m, 8 H, dippe-CH_2 and CH, + dd, 1 H, $^3J_{HaHc}$ = 13.2 Hz, $^3J_{HaHb}$ = 16.2 Hz, CH^aH^{b}CH^{c}Ph), 3.89 (m, 2 H, CH^aH^bCH^cPh), 6.57 (d, 1 H, $^3J_{HH}$ = 8.5 Hz, C_6H_3OH), 6.60 (dd, 1 H, $^4J_{HH}$ = 2 Hz, $^3J_{HH}$ = 8.5 Hz, C_6H_3OH), 6.74 (d, 1 H, $^4J_{HH}$ = 2 Hz, C_6H_3OH), 7.14 (vt, 2 H, $^3J_{HF}$ = $^3J_{HH}$ = 8.8 Hz, m-C_6H_4F), 7.28 (dd, 2 H, $^4J_{HF}$ = 5.5 Hz, $^3J_{HH}$ = 8.8 Hz, o-C_6H_4F). Note: The ^{1}H NMR signal for $C_6H_3O$$H$ is not observed in CD_3NO_2 or $CDCl_3$, but it appears at δ 8.61 in acetone-d_6 at 298 K. ^{31}P{^{1}H} NMR (161.9 MHz, CD_3NO_2, 298 K): δ 99.1 and 103.9 (d, $^3J_{PP'}$ = 14.8 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 11.87 (s, $C_5(CH_3)_5$), 19.08−21.40 (m, dippe-CH_3), 27.45 and 29.12 (m, dippe-CH_2), 30.28 and 32.79 (s, dippe-CH), 37.76 (s, CHPh), 60.69 (s, Ru=C−CH_2), 103.2 (s, $C_5(CH_3)_5$), 116.8 (d, $^3J_{CF}$ = 21.5 Hz, m-C_6H_4F), 131.4 (d, $^3J_{CF}$ = 8.3 Hz, o-C_6H_4F), 138.0 (d, $^4J_{CF}$ = 2.7 Hz, $ipso$-C_6H_4F), 163.5 (d, $^1J_{CF}$ = 242 Hz, p-C_6H_4F), 103.7, 113.2, 120.9, 129.8, 153.6, and 158.3 (s, −O−C_6H_3(OH)), 288.3 (t, $^2J_{CP}$ = 12.3 Hz, Ru=C). IR (Nujol): ν(OH) 3350 cm^{-1}.

Preparation of [Cp*Ru{=C=CHCHPh(C_6H_3(OH)$_2$)}(dippe)][BF_4] (13). A nitromethane solution of 150 mg of the allenylidene complex **1** (0.21 mmol), resorcinol (56 mg, 0.50 mmol), and NH_4BF_4 (50 mg, 0.45 mmol) was heated at 80 °C during 6 h. Then the solvent was evaporated to less than 1 mL at reduced pressure. Addition of 20 mL of Et_2O caused the precipitation of a brown solid, which was filtered, washed with petroleum ether, and dried under vacuum. Yield: 165 mg (95%). Recrystallization was carried out by slow ether diffusion into a CH_2Cl_2 solution. Analysis and spectral data are as follows.

Complex 13. Anal. Calcd for $C_{39}H_{59}BF_4O_2P_2Ru$: C, 57.9; H, 7.34. Found: C, 57.8; H, 7.33. ^{1}H NMR (400 MHz, CD_3NO_2, 298 K): δ 1.03−1.28 (m, 24 H, dippe-CH_3), 1.89 (s, 15 H, $C_5(CH_3)_5$), 2.00 and 2.30 (m, 8 H, dippe-CH_2 and CH), 4.87 and 5.23 (both d, 1 H each, $^3J_{HaHb}$ = 11.1 Hz, Ru=C=CH^aCH^b), 6.28−6.37 (m, 2 H, m-C_6H_3(OH)$_2$), 7.19 (d, 1 H, $^3J_{HH}$ = 8.3 Hz, o-C_6H_3(OH)$_2$), 7.13 (m, 2 H, p-C_6H_5 + o-C_6H_3(OH)$_2$), 7.25 and 7.31 (m, 4 H, C_6H_5). ^{31}P{^{1}H} NMR (161.9 MHz, CD_3NO_2, 298 K): δ 90.82 (s). ^{13}C{^{1}H} NMR (75.4 MHz, CD_3NO_2, 298 K): δ 11.39 (s, $C_5(CH_3)_5$), 18.98−20.83 (m, dippe-CH_3), 22.49 and 26.92 (m, dippe-CH_2), 33.77 and 34.86 (s, dippe-CH), 37.58 (s, CHPh), 104.1 (s, $C_5(CH_3)_5$), 115.4 (s, Ru=C=CH), 127.6, 128.6, 129.7, and 146.8 (s, C_6H_5), 103.6, 108.6, 124.8, 130.2, 155.2, and 157.5 (s, C_6H_3-(OH)$_2$), 338.9 (t, $^2J_{CP}$ = 14.3 Hz, Ru=C). IR (Nujol): ν(C=C) 1640, ν(Ph) 1590 cm^{-1}.

Preparation of [Cp*Ru{=C=CHCH($C_6H_7O_2$)Ar}(dippe)][BF_4] (X = H (14a), OMe (15a)) and [Cp*Ru(L)(dippe)][BF_4] (L = 4-phenyl-5-oxo-hexahydrochromen-2-ylidene (14b), 4-(4-methoxyphenyl)-5-oxo-2,3,4,6,7,8-hexahydrochromen-2-ylidene (15b). A 34 mg amount of 1,3-cyclohexanedione (0.30 mmol) was added to a CH_2Cl_2 solution of the corresponding allenylidene complex (0.25 mmol, 175 mg of **1**/183 mg of **2**) at room temperature. After stirring for 10 min, the color changed from dark to light brown. The mixture was concentrated to less than 1 mL at reduced pressure. Addition of 10 mL of a 1:1 mixture of Et_2O and petroleum ether caused the precipitation of a brown solid, which was filtered, washed with petroleum ether, and dried under vacuum. Yield: 172 mg of **14a** + **14b** (85%) and 175 mg of **15a** + **15b** (83%). Selected spectral data are as follows.

Complexes 14a + 14b. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 0.85−1.38 (m, dippe-CH_3), 1.80 (s, $C_5(CH_3)_5^B$), 1.93 (s, $C_5(CH_3)_5^A$), 1.99 − 2.89 (m, dippe-CH_2 and CH^{A+B} ± $CH_2CH_2CH_2^{A+B}$ + CH^aH^{b}CH^{c}Ph^B), 3.67 (dd, $^2J_{HaHb}$ = 17.6 Hz, $^3J_{HbHc}$ = 3.2 Hz, CH^aH^bCH^{c}Ph^B), 3.83 (br d, $^3J_{HaHc}$ = 8.8 Hz, CH^{a}H^{b}CH^c-Ph^B), 5.24 (d, $^3J_{HH}$ = 11.4 Hz, CH=CHPh^A), 5.37 (d, $^3J_{HH}$ = 11.4 Hz, CH=CHPh^A), 7.06−7.41 (m, $C_6H_5^{A+B}$). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 298 K): δ 86.9 and 87.6 (both d, $^3J_{PP'}$ = 19.3 Hz, **14a**), 97.6 and 100.2 (both d, $^3J_{PP'}$ = 15.4 Hz, **14b**). Ratio: 38:62. ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 298 K): δ 11.18 (s, $C_5(CH_3)_5^A$), 11.73 (s, $C_5(CH_3)_5^B$), 18.30−21.76 (m, dippe-CH_3^{A+B}), 25.33−26.98 (m, dippe-CH_2^{A+B}), 30.43−34.89 (m, dippe-CH + $CH_2CH_2^{A+B}$), 31.53 (s, CHPh^A), 32.29 (s, CHPh^B), 36.82 and 37.10 (s, CH_2-CO^{A+B}), 59.72 (s, Ru=C−CH_2^B), 102.6 (s, $C_5(CH_3)_5^A$), 103.2 (s, $C_5(CH_3)_5^B$), 111.6 (s, Ru=C=CH^A), 116.9 (s, -O−C=C^B), 117.9 (s, −O−C=C^A), 125.9, 127.0, 127.5, 127.6 128.2, 129.1, 141.1, and 145.1 (s, $C_6H_5^{A+B}$), 165.1 (s, −O−C=C^{A+B}), 196.6 (s, C=O^B), 204.4 (s, C=O^A), 286.5 (t, $^2J_{CP}$ = d 11.6 Hz, Ru=C^B), 339.7 (t, $^2J_{CP}$ = 14.6 Hz, Ru=C^A).

Complexes 15a + 15b. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.79−1.28 (m, dippe-CH_3^{A+B}), 1.73 (s, $C_5(CH_3)_5^B$), 1.83 (s, $C_5(CH_3)_5^A$), 1.93−2.85 (m, dippe-CH + dippe-CH_2 + CH_2 + Ru=C−CH^a$H^{b\,A+B}$), 3.55 (dd, $^2J_{HaHb}$ = 17.6 Hz, $^3J_{HaHc}$ = 3.5 Hz, Ru=CCH^aH^{b}CH^{c}Ph^B), 3.66 (br s, Ru=C−CH^{a}H^{b}CH^cPh^B), 3.72 (s, OCH_3^A), 3.74 (s, OCH_3^B), 5.09 and 5.36 (both d, $^3J_{HH}$ = 11.3 Hz, Ru=C=CHCH^A), 6.71 and 7.22 (d, $^3J_{HH}$ = 8.6 Hz, C_6H_4OMe^A), 6.76 and 6.87 (d, $^3J_{HH}$ = 8.6 Hz, C_6H_4OMe^B). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 298 K): δ 86.8 and 87.4 (both d, $^3J_{PP'}$ = 19.3 Hz, **15a**), 97.7 and 100.1 (both d, $^3J_{PP'}$ = 15.4 Hz, **15b**). Ratio: 40:60.

Preparation of [Cp*Ru(L)(dippe)][BF_4] (L = 4-(4-fluorophenyl)-5-oxo-2,3,4,6,7,8-hexahydrochromen-2-ylidene (16b)). A 34 mg sample of 1,3-cyclohexanedione (0.30 mmol) was added to a CH_3NO_2 solution of the alkenylcarbyne complex **6** (0.25 mmol, 200 mg) at room temperature. The color changed immediately from dark red to light brown. After stirring for 10 min, the mixture was concentrated to less than 1 mL at reduced pressure. Addition of 10 mL of a 1:1 mixture of Et_2O and petroleum ether caused the precipitation of a brown solid, which was filtered, washed with

Table 1. Crystal Data and Details of the Structure Determination of Compound 12

crystal data		data collection	
formula	$C_{39}H_{57}BF_5O_2P_2Ru$	temperature [K]	100
fw	826.67	radiation [Å]	0.71073
cryst syst	triclinic	θ min,max [deg]	1.18, 25.05
			h limits −12, 12
space group	$P\bar{1}$	data set	k limits −12, 13
			l limits −20, 20
a, b, c [Å]	10.680(2)		
	10.981(2)	no. of tot, uniq data, R(int)	13 188, 6771, 0.0274
	17.341(4)		
α, β, γ [deg]	93.24(3)		
	92.81(3)	no. of obsd data [$I > 2.0\sigma_I$]	6408
	105.96(3)		
volume [Å^3]	1947.9(7)	refinement	
Z	2	N_{ref}, N_{par}	6771, 547
		R, wR_2[a], S	R_{all} 0.0782
			R_{gt} 0.0737
D_{calc} [g/cm^3]	1.409		wR_{all} 0.1510
			wR_{gt} 0.1483
			S 1.064
μ(Mo Kα) [mm^{-1}]	0.541	max. and av shift/error	0.005, 0.000
F(000)	862	min. and max. resd dens [e Å^{-3}]	−0.939, 1.302
cryst size [mm]	0.39 × 0.30 × 0.22		

[a] $w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 14.0034P]$ where $P = (F_o^2 + 2F_c^2)/3$.

petroleum ether, and dried under vacuum. Small amounts of the isomer **16a** are found in less than 10%. Recrystallization was carried out by slow ether diffusion into a CH_2Cl_2 solution. Yield: 170 mg (82%). Analysis and spectral data are as follows.

Complex 16b. Anal. Calcd for $C_{39}H_{60}BF_5O_2P_2Ru$: C, 56.5; H, 7.29. Found: C, 57.0; H, 7.91. ^{1}H NMR (400 MHz, CD_3NO_2, 298 K): δ 0.89, 1.22, 1.30, and 1.07 (m, 24 H, dippe-CH_3), 1.81 (s, 15 H, $C_5(CH_3)_5$), 1.91 (m, 4 H, dippe-CH), 2.21 (m, 6 H, CH_2 + dippe-CH_2), 2.32−2.50 (m, 3 H, CH_2 + Ru=C−CH^{a}H^b), 2.73 and 2.90 (m, 2 H, CH_2), 3.73−3.83 (m, 2 H, Ru=CCH^{a}H^{b}CHPh), 7.04 (vt, 2 H, $^3J_{HF} = {}^3J_{HH} = 8.7$ Hz, *m*-C_6H_4F), 7.16 (dd, 2 H, $^4J_{HF} = 5.6$ Hz, $^3J_{HH} = 8.7$ Hz, *o*-C_6H_4F). ^{31}P{^{1}H} NMR (161.9 MHz, CD_3NO_2, 298 K): δ 98.3 and 101.1 (both d, $^3J_{PP'} = 15.4$ Hz). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 11.87 (s, $C_5(CH_3)_5$), 18.90−21.80 (m, dippe-CH_3), 27.40 and 27.88 (m, dippe-CH_2), 31.63 and 35.54 (s, dippe-CH), 21.82, 28.46, and 37.65 (s, −$CH_2CH_2CH_2$−), 32.47 (s, CHPh), 60.49 (s, Ru=C−CH_2), 104.2 (s, $C_5(CH_3)_5$), 116.4 (d, $^3J_{CF} = 21.4$ Hz, *m*-C_6H_4F), 117.5 (s, −O−C=C), 130.2 (d, $^3J_{CF} = 8.0$ Hz, *o*-C_6H_4F), 138.9 (d, $^4J_{CF} = 2.9$ Hz, *ipso*-C_6H_4F), 162.9 (d, $^1J_{CF} = 242$ Hz, *p*-C_6H_4F), 167.4(s, −O−C=C), 199.1 (s, C=O), 287.6 (t, $^2J_{CP}$ = d 12.3 Hz, Ru=C).

X-ray Structure Determination. A single crystal of compound **12** was mounted on a glass fiber to carry out the crystallographic study. Crystal data and experimental details are given in Table 1. X-ray diffraction data collection was measured at 100 K on a Bruker Smart APEX CCD three-circle diffractometer using a sealed tube source and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Four sets of frames were recorded over a hemisphere of the reciprocal space by ω scan with $\delta(\omega) = 0.30°$ and exposure of 10 s per frame. Correction for absorption was applied by scans of equivalents using the program SADABS.[24] An insignificant crystal decay correction was also applied. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined on F^2 by full-matrix least-squares procedures using the programs contained in the SHELXTL package.[25] Most of the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were geometrically positioned and isotropically refined using the riding model. In the cation, C_5Me_5 ligand, the ethylene chain, and one isopropyl group in the dippe ligand, the C(12), C(13) atoms and C_6H_4F group were split in two positions, only being refined anisotropically the part with sof > 0.5. The program ORTEP-3[26] was used for plotting.

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Supporting Information Available: CIF file giving crystallographic data for **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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