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Addition of Ethyl Diazoacetate to the Allenylidene Ligand of $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$: Synthesis of Ruthenium Organometallic Compounds Containing New Cyclic Unsaturated η^1-Carbon Ligands

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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 ethyl diazoacetate to give the cyclic carbene derivative $[Ru(\eta^5\text{-}C_5H_5)\{{=}CCH{=}C(OEt)OC{=}CPh_2\}(CO)(PPr^i_3)]BF_4$ (**2**). The structure of **2** was determined by an X-ray investigation, revealing a Ru−C distance of 2.017(6) Å. Treatment of **2** with sodium methoxide and methyllithium gives rise to the derivatives $Ru(\eta^5\text{-}C_5H_5)\{C{=}CHC(R)(OEt)OC{=}CPh_2\}(CO)(PPr^i_3)$ (R = OMe (**3**), Me (**4**)). When a tetrahydrofuran solution of **3** is passed through an Al_2O_3 column, the lactonyl complex $Ru(\eta^5\text{-}C_5H_5)\{C{=}CHC(O)OC{=}CPh_2\}(CO)(PPr^i_3)$ (**5**) is obtained. Complex **3** reacts with $HBF_4{\cdot}OEt_2$ to regenerate **2** by selective elimination of methanol. The protonation of **4** with $HBF_4{\cdot}OEt_2$ produces the elimination of ethanol and the formation of $[Ru(\eta^5\text{-}C_5H_5)\{{=}CCH{=}C(CH_3)OC{=}CPh_2\}(CO)(PPr^i_3)]BF_4$ (**6**). The structure of **6** was also determined by an X-ray investigation, revealing a Ru−C distance of 2.010(6) Å. The related cyclic carbene compound $[Ru(\eta^5\text{-}C_5H_5)\{{=}CCH{=}C(OH)OC{=}CPh_2\}(CO)(PPr^i_3)]BF_4$ (**7**) has been prepared by reaction of **5** with $HBF_4{\cdot}OEt_2$.

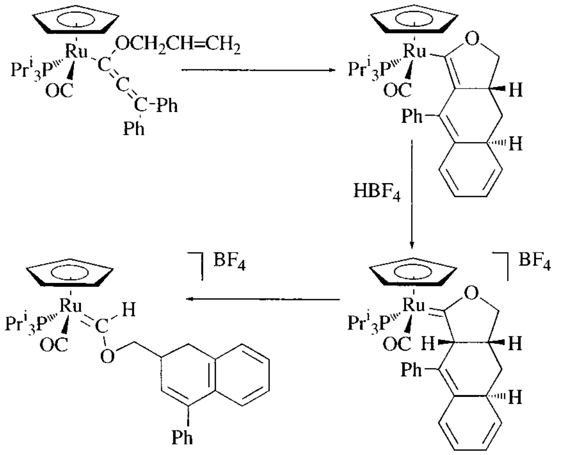
Introduction

We have previously shown that the solvato complex $[Ru(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}OC(CH_3)_2\}(CO)(PPr^i_3)]BF_4$ reacts with 1,1-diphenyl-2-propyn-1-ol to afford the allenylidene derivative $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$, which adds water, alcohols, thiols, and benzophenone imine to afford α,β-unsaturated hydroxycarbene, alkoxycarbene, (alkylthio)carbene, and 2-azaallenyl compounds, respectively. By deprotonation with sodium methoxide, the hydroxycarbene compound gives an acyl derivative, and the alkoxycarbene, (alkylthio)carbene, and 2-azaallenyl complexes yield functionalized allenyl derivatives.[1]

In solution at room temperature, the alkoxyallenyl complex $Ru(\eta^5\text{-}C_5H_5)\{C(OCH_2CH{=}CH_2){=}C{=}CPh_2\}(CO)(PPr^i_3)$ isomerizes into the tricyclic tetraenyl derivative $Ru(\eta^5\text{-}C_5H_5)$(9-phenyl-3,3a,4,4a-tetrahydronaphtho[2,3-c]-1-furanyl)(CO)(PPr^i_3) 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 acts as an inner−outer ring diene and the $CH{=}CH_2$ double bond of the alkoxy fragment acts as a dienophile. By protonation with $HBF_4{\cdot}OEt_2$, this compound gives the tricyclic carbene $[Ru(\eta^5\text{-}C_5H_5)$(9-phenyl-1,3,3a,4,4a,9a-hexahydronaphtho[2,3-c]-1-furanylidene)(CO)$(PPr^i_3)]BF_4$, which in solution at room temperature also isomerizes to afford the acyclic alkoxycarbene $[Ru(\eta^5\text{-}C_5H_5)\{{=}C(OCH_2[1\text{-phenyl-3,4-dihydro-3-naphthyl}])H\}(CO)(PPr^i_3)]BF_4$ (Scheme 1) by a concerted intramolecular hydrogen transfer reaction.[2]

The allenylidene complex $[Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4$ also reacts with acetone in the presence

Scheme 1



[†] Universidad de Zaragoza-CSIC.

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[1] Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423.

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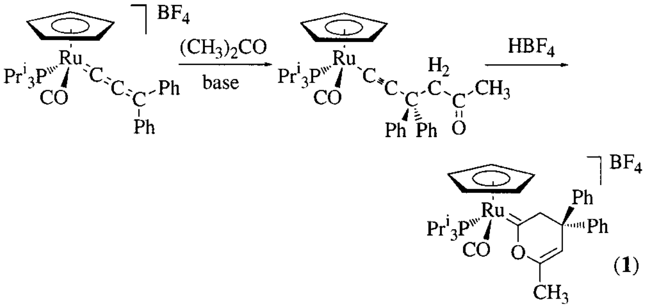
of base. The reaction product is the functionalized alkynyl derivative $Ru(\eta^5\text{-}C_5H_5)\{C\equiv CC(Ph)_2CH_2C(O)CH_3\}(CO)(PPr^i_3)$, which affords the cyclic carbene compound $[Ru(\eta^5\text{-}C_5H_5)\{=CCH_2C(Ph)_2CH=C(CH_3)O\}(CO)(PPr^i_3)]BF_4$ by addition of $HBF_4\cdot OEt_2$ (eq 1).[3]



(**1**)

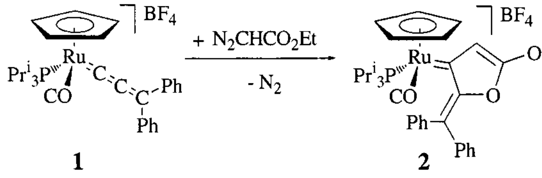
Heteroatom-containing cyclic metal−carbene complexes have been previously prepared via metal ω-haloacyl, carbamoyl, alkoxycarbonyl, or imido intermediates,[4] opening of epoxides by deprotonated Fischer type carbene complexes,[5] activation of homopropargylic alcohols with low-valent d^6 complexes,[6] and direct activation of tetrahydrofuran.[7] Pyranylidene−metal complexes require the initial preparation of propenylidene−metal derivatives or alkynyl−carbene complexes to react with β-dicarbonyl derivatives, acrylates, or enol ethers.[8] α,β-Unsaturated cyclic carbenes have been obtained from a (4-methoxy-2-oxacyclopentylidene)chromium(0) compound via methanol elimination, by addition of alkyl radicals generated from epoxides and $[Cp_2TiCl]_2$,[9] and via direct activation of (*Z*)- and (*E*)-enynols.[10]

As a continuation of our work on the chemical properties of the allenylidene complex $[Ru(\eta^5\text{-}C_5H_5)(C=C=CPh_2)(CO)(PPr^i_3)]BF_4$, we now report the synthesis of new heteroatom-containing cyclic metal carbene compounds which, in contrast to the above, are doubly α,β-unsaturated with endocyclic and exocyclic carbon−carbon double bonds. In addition, we describe the synthesis of the first organometallic compound containing a cyclic ortho ester alkenyl ligand, and a new unsaturated lactonyl ligand.

Results and Discussion

1. Reaction of $[Ru(\eta^5\text{-}C_5H_5)(C=C=CPh_2)(CO)(PPr^i_3)]BF_4$ with Ethyl Diazoacetate.

Treatment of red dichloromethane solutions of $[Ru(\eta^5\text{-}C_5H_5)(C=C=CPh_2)(CO)(PPr^i_3)]BF_4$ (**1**) with 3 equiv of ethyl diazoacetate at 40 °C leads to dark purple solutions, from which the cyclic carbene complex $[Ru(\eta^5\text{-}C_5H_5)\{=CCH=C(OEt)OC=CPh_2\}(CO)(PPr^i_3)]BF_4$ (**2**) is isolated as a result of a 1,3-addition of the organic reagent at the $C_\alpha-C_\beta$ double bond of the allenylidene ligand of **1** (eq 2).



(**2**)

Although the reactivity of transition-metal allenylidene compounds is presently attracting considerable interest,[11] related reactions have not been previously carried out.

Complex **2** was obtained as a dark purple solid in 77% yield and characterized by MS, elemental analysis, IR, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and X-ray diffraction. A view of the molecular geometry is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The geometry around the ruthenium center is close to octahedral with the cyclopentadienyl ligand occupying three sites of a face, and the angles formed by the triisopropylphosphine, the carbonyl group, and the unsaturated η^1-carbon ligand are close to 90°.

The ruthenium and the five atoms of the five-membered ring of the cyclic carbene ligand are almost planar. The deviations from the best plane are 0.050(6) (C(7)), 0.135(6) (C(8)), −0.006(7) (C(9)), 0.064(6) (C(10)), −0.082(5) (O(2)), and −0.0008(6) Å (Ru(1)). The Ru(1)−C(7) distance (2.017(6) Å) is significantly longer than those found in the α,β-unsaturated acyclic carbene complex $[RuCl(=CHCH=CPh)(CO)(PPr^i_3)_2]BF_4$ (1.874(3) Å)[12] and the alkoxycarbene compound $[Ru(\eta^3\text{-}$

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(2) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 2297.

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

(4) (a) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1922. (b) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 3554. (c) Motschi, H.; Angelici, R. J. *Organometallics* **1982**, *1*, 343. (d) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 93.

(5) (a) Casey, C. P.; Brunsvold, W. R.; Scheck, D. M. *Inorg. Chem.* **1977**, *16*, 3059. (b) Lattuada, L.; Licandro, E.; Maiorana, S.; Molinari, H.; Papagni, A. *Organometallics* **1991**, *10*, 807. (c) Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6735.

(6) (a) Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1986**, 514. (b) Dötz, K. H.; Sturm, W.; Alt, H. G. *Organometallics* **1987**, *6*, 1424. (c) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1. (d) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *Organometallics* **1991**, *10*, 2768. (e) Quayle, P.; Rahman, S.; Ward, E. L. M.; Herbert, J. *Tetrahedron Lett.* **1994**, *35*, 3801. (f) Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1996**, 2547. (g) Leung, W. H.; Chan, E. Y. Y.; Williams, I. D.; Wong, W. T. *Organometallics* **1997**, *16*, 3234. (h) Liang, K. W.; Li, W. T.; Peng, S. M.; Wang, S. L.; Liu, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 4404. (i) Bianchini, C.; Marchi, A.; Mantovani, N.; Marvelli, L.; Masi, D.; Peruzzini, M.; Rosi, R. *Eur. J. Inorg. Chem.* **1998**, 211.

(7) (a) Boutry, O.; Gutierrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288. (b) Gutierrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Carmona, E. *J. Am. Chem. Soc.* **1994**, *116*, 791.

(8) (a) Camps, F.; Moreto, J. M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miravitlles, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1560. (b) Juneau, K. N.; Hegedus, L. S.; Roepke, F. W. *J. Am. Chem. Soc.* **1989**, *111*, 4762. (c) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550. (d) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 6419.

(9) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 9855.

(10) Ruiz, N.; Peron, D.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 1095.

(11) For some recent examples see: (a) Touchard, D.; Pirio, N.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 3178. (c) Crochet, P.; Demerseman, B.; Vallejo, M. I.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 5406. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453. (e) Bohanna, C.; Callejas, B.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N.; Valero, C. *Organometallics* **1998**, *17*, 373. (f) Roth, G.; Reindl, D.; Gockel, M.; Troll, C.; Fischer, H. *Organometallics* **1998**, *17*, 1393.

(12) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 4258.

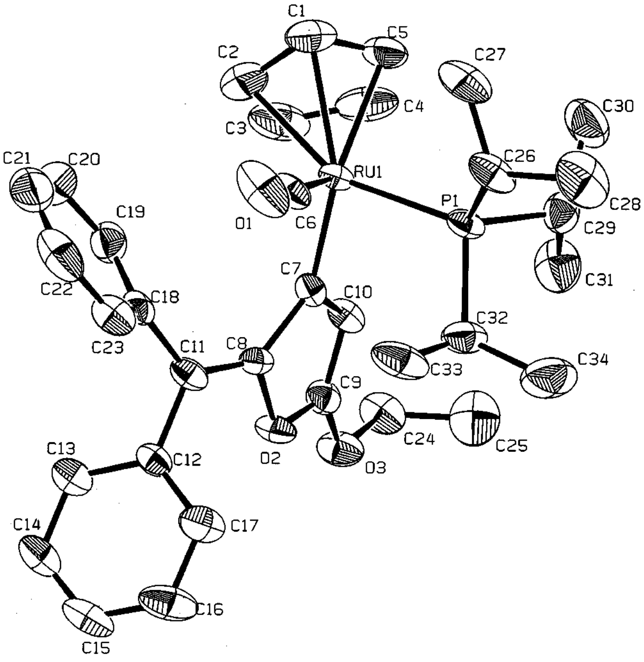


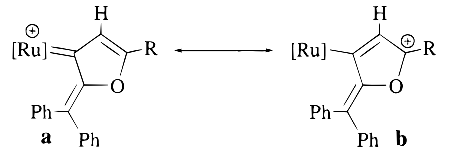
Figure 1. Molecular diagram for $[Ru(\eta^5\text{-}C_5H_5)\{=CCH=C(OEt)OC=CPh_2\}(CO)(PPr^i_3)]BF_4$ (**2**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[Ru(\eta^5\text{-}C_5H_5)\{=CCH=C(OEt)OC=CPh_2\}(CO)(PPr^i_3)]BF_4$ (2)

	Bond Lengths		
Ru−P	2.357(2)	O(2)−C(8)	1.421(7)
Ru−C(1)	2.285(8)	O(2)−C(9)	1.326(7)
Ru−C(2)	2.235(8)	O(3)−C(9)	1.282(8)
Ru−C(3)	2.248(9)	O(3)−C(24)	1.467(8)
Ru−C(4)	2.247(8)	C(7)−C(8)	1.471(8)
Ru−C(5)	2.256(8)	C(7)−C(10)	1.393(8)
Ru−C(6)	1.826(8)	C(8)−C(11)	1.343(9)
Ru−C(7)	2.017(6)	C(9)−C(10)	1.378(8)
O(1)−C(6)	1.165(8)		
	Bond Angles		
P−Ru−C(6)	88.4(2)	C(8)−C(7)−C(10)	102.9(5)
P−Ru−C(7)	91.5(2)	O(2)−C(8)−C(7)	108.7(5)
C(6)−Ru−C(7)	99.1(3)	O(2)−C(8)−C(11)	113.8(5)
C(8)−O(2)−C(9)	104.9(5)	C(7)−C(8)−C(11)	137.0(6)
C(9)−O(3)−C(24)	115.2(5)	O(2)−C(9)−O(3)	113.5(6)
Ru−C(6)−O(1)	170.9(6)	O(2)−C(9)−C(10)	113.0(6)
Ru−C(7)−C(8)	135.7(5)	O(3)−C(9)−C(10)	133.4(6)
Ru−C(7)−C(10)	121.3(4)	C(7)−C(10)−C(9)	109.0(6)

$HBpz_3)\{=C(OMe)CH_2CO_2Me\}(dippe)]BPh_4$ (1.86(2) Å).[13] However, the Ru(1)−C(7) distance is similar to the ruthenium−carbon bond lengths found 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),[14] $Ru_3(CO)_{10}(\mu_2\text{-}SMe)(\mu_2\text{-}\eta^2\text{-}NC_6H_4SC)$ (2.075(9) Å),[15] $[\{Ru(\eta^5\text{-}C_5Me_5)(\mu\text{-}SPr^i)\}_2(\mu\text{-}C_{18}H_{15})]BF_4$ (2.04(3) and 1.98(2) Å),[16] 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),[17] where a ruthenium−carbon bond between single and double has been proposed. Thus, the value of the Ru(1)−C(7) distance suggests that for an adequate description of the bonding situation in **2** a second resonance form such as **b** (Scheme 2) should be considered. This is also supported by the C(7)−C(10) (1.393(8) Å) and C(9)−C(10) (1.378(8) Å) distances, which are between those expected for single and double $C(sp^2)-C(sp^2)$ bonds. In contrast to the C(7)−C(10) and C(9)−C(10) bond lengths, the C(7)−C(8) (1.471(8) Å) and C(8)−C(11) (1.343(9) Å) distances agree well with the mean values reported for single and double $C(sp^2)-C(sp^2)$ bonds (1.48 and 1.34 Å).[12]

Scheme 2



The contribution of the resonance form **b** to the structure of **2** can be also proposed on the basis of the $^{13}C\{^1H\}$ NMR spectrum of this complex, which shows a doublet at 226.2 ppm with a C−P coupling constant of 11.3 Hz. This signal, assigned to C(7), appears about 60 ppm toward a field higher than those reported for the typical C_α resonances of carbene compounds.[18] In the ^1H NMR spectrum of **2**, the most noticeable resonance is a singlet at 7.15 ppm, corresponding to the hydrogen atom bonded to C(10).

As a result of the significant contribution of the resonance form **b** to the structure of **2**, the C(9) atom of the cyclic carbene ligand has a marked electrophilic character. Thus, in tetrahydrofuran as solvent, complex **2** reacts with nucleophiles to give cyclic alkenyl derivatives containing an exocyclic carbon−carbon double bond conjugated with the alkenyl unit. The new ligands result from the addition of nucleophiles at the C(9) atom. The treatment of **2** with sodium methoxide at room temperature gives $Ru(\eta^5\text{-}C_5H_5)\{C=CHC(OMe)(OEt)OC=CPh_2\}(CO)(PPr^i_3)$ (**3**) in 67% yield, while the reaction of **2** with methyllithium at −60 °C affords $Ru(\eta^5\text{-}C_5H_5)\{C=CHC(Me)(OEt)OC=CPh_2\}(CO)(PPr^i_3)$ (**4**) in 56% yield (Scheme 3).

The presence of an ortho ester alkenyl ligand in **3** is strongly supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra. In the ^1H NMR spectrum, the resonance due to the alkenyl $=CH$ proton appears at 5.78 ppm as a singlet, while the OCH_3 resonance is observed at 3.27 ppm, also as a singlet, and the resonances of the OCH_2CH_3 group are observed at 4.03 (CH_2) and 1.23 (CH_3) ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance corresponding to the C_α atom of the alkenyl unit appears at 144.5 ppm as a doublet with a C−P coupling constant of 12.8 Hz, while the resonance due to the C_β atom is observed at 142.3 ppm as a singlet. The ortho ester carbon atom of the cycle gives rise to a singlet at 117.9 ppm. The chemical shift of this resonance agrees well with those observed in molecular ortho esters.[19]

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[13] Jiménez-Tenorio, M. A.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1997**, *16*, 5528.

[14] Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1669.

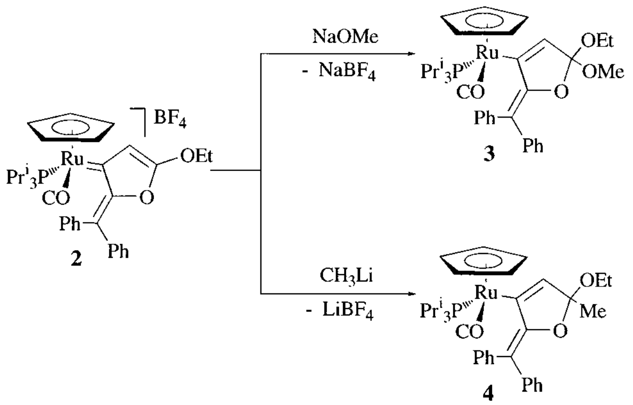
[15] Renouard, C.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1995**, *492*, 179.

[16] Matsuzaka, H.; Hirayama, Y.; Nishio, M.; Mizobe, Y.; Hidai, M. *Organometallics* **1993**, *12*, 36.

[17] Matsuzaka, H.; Takagi, Y.; Hidai, M. *Organometallics* **1994**, *13*, 13.

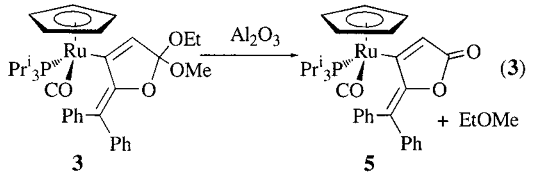
[18] See for example: (a) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100. (c) Wilhelm, T.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001.

Scheme 3



In the ^1H NMR spectrum of **4**, the most noticeable resonances are two singlets at 5.93 and 1.50 ppm corresponding to the alkenyl =C*H* proton and the methyl group. In the $^{13}C\{^1H\}$ NMR spectrum the resonances of the Ru*C*=*C*H unit appear at 150.2 (C_β) and 139.3 (C_α) as doublets with C−P coupling constants of 4.6 and 12.9 Hz, respectively. The *C*OEt carbon gives rise to a singlet at 109.0 ppm, similar to the chemical shift observed for the related carbon atom of **3**.

Complex **3** is isolated at −78 °C by addition of methanol to its tetrahydrofuran solutions, where the complex is stable. When this addition is carried out at room temperature, a mixture of **3** and Ru(η^5-C_5H_5){C=CHC(O)OC=CPh$_2$}(CO)(PPr$^i_3$) (**5**) is obtained. Complex **5** is isolated as a microcrystalline pure yellow solid in 78% yield, by passing a tetrahydrofuran solution of **3** through an Al_2O_3 column. The formation of **5** involves the loss of ethyl methyl ether from **3** (eq 3), in agreement with the trend shown by organic ortho esters to eliminate ethers.[20]



(3)

The most significant spectroscopic feature of **5** is the presence of a ν(CO) band at 1717 cm^{-1} in the IR spectrum, which corresponds to the carbonyl group of the lactonyl ligand. The ^1H NMR spectrum shows the characteristic =C*H* resonance of the alkenyl unit at 6.19 ppm, which is observed as a singlet. In the $^{13}C\{^1H\}$ NMR spectrum the C_α and C_β atoms of the alkenyl unit give rise to a doublet at 178.1 ppm, with a C−P coupling constant of 13.6 Hz and a singlet at 135.4 ppm, respectively.

2. Protonation of 3−5. Treatment at room temperature of the ortho ester alkenyl complex **3** with 1 equiv of $HBF_4{\cdot}OEt_2$ in diethyl ether as solvent regenerates **2**, by selective protonation of the methoxy group of **3**. However, under the same conditions, the treatment of **4** with $HBF_4{\cdot}OEt_2$ leads to [Ru(η^5-C_5H_5){=CCH=C(CH3)OC=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (**6**), by protonation of the ethoxy group of **4** (eq 4). Complex **6** was obtained as a dark green solid in 92% yield.

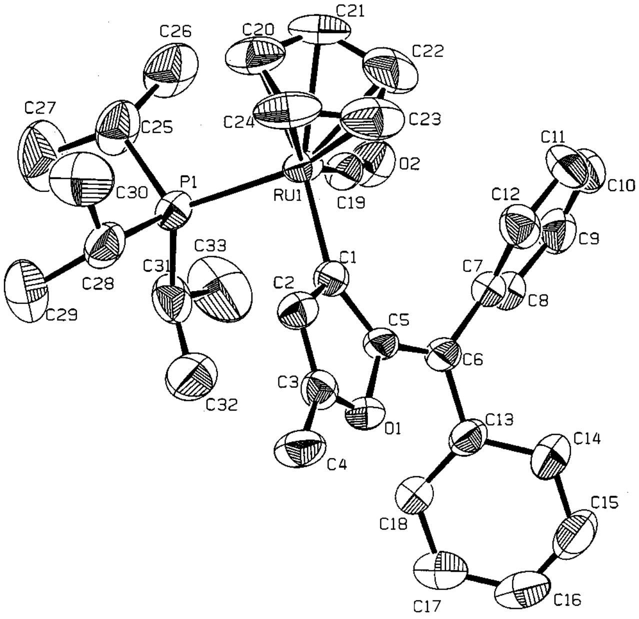
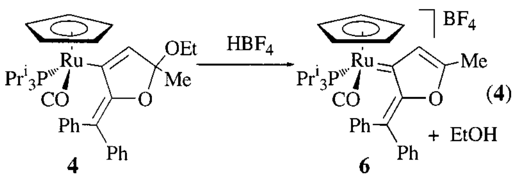


Figure 2. Molecular diagram for [Ru(η^5-C_5H_5){=CCH=C(CH$_3$)OC=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (**6**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex [Ru(η^5-C_5H_5)-{=CCH=C(CH$_3$)OC=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (6)

Bond Lengths			
Ru−P	2.372(2)	O(1)−C(3)	1.353(7)
Ru−C(1)	2.010(6)	O(1)−C(5)	1.437(6)
Ru−C(19)	1.845(7)	O(2)−C(19)	1.145(7)
Ru−C(20)	2.281(7)	C(1)−C(2)	1.409(8)
Ru−C(21)	2.295(7)	C(1)−C(5)	1.464(8)
Ru−C(22)	2.244(7)	C(2)−C(3)	1.360(8)
Ru−C(23)	2.237(8)	C(3)−C(4)	1.468(9)
Ru−C(24)	2.266(7)	C(5)−C(6)	1.349(8)

Bond Angles			
P−Ru−C(1)	90.9(2)	C(1)−C(2)−C(3)	110.9(5)
P−Ru−C(19)	89.9(2)	O(1)−C(3)−C(2)	110.8(5)
C(1)−Ru−C(19)	99.2(2)	O(1)−C(3)−C(4)	117.1(5)
C(3)−O(1)−C(5)	106.5(4)	C(2)−C(3)−C(4)	132.0(6)
Ru−C(1)−C(2)	121.3(4)	O(1)−C(5)−C(1)	107.9(5)
Ru−C(1)−C(5)	135.7(4)	O(1)−C(5)−C(6)	113.8(5)
C(2)−C(1)−C(5)	103.0(5)	C(1)−C(5)−C(6)	138.1(5)



(4)

A view of the molecular geometry of **6** is shown in Figure 2. Selected bond distances and angles are listed in Table 2. As for **2**, the geometry around the ruthenium center is close to octahedral with the cyclopentadienyl ligand occupying three sites of a face, and the angles formed by the triisopropylphosphine, the carbonyl group, and the unsaturated η^1-carbon ligand are close to 90°.

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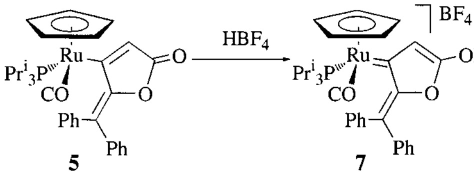
(19) See for example: (a) Dequeker, E.; Compernolle, F.; Toppet, S.; Hoornaert, G. *Tetrahedron* **1995**, *51*, 5877. (b) Li, S.; Dory, Y. L.; Deslongchamps, P. *Tetrahedron* **1996**, *52*, 14841.

(20) De Wolfe, R. H. *Synthesis* **1974**, 153.

In this case, the ruthenium and the five atoms of the five-membered ring of the cyclic carbene ligand are also almost planar. The deviations from the best plane are −0.057(6) (C(1)), −0.079(6) (C(2)), 0.016 (C(3)), −0.098(6) (C(5)), 0.067(4) (O(1)), and 0.0006(5) Å (Ru(1)). Furthermore, the Ru(1)−C(1) (2.010(6) Å), C(1)−C(2) (1.409(8) Å), C(2)−C(3) (1.360(8) Å), C(1)−C(5) (1.464(8) Å), and C(5)−C(6) (1.349(8) Å) distances are statistically identical with the related bond lengths in **2**, suggesting that the resonance form **b** (Scheme 2) also makes a significant contribution to the structure of **6**.

The spectroscopic data for **6** agree well with the structure shown in Figure 2 and with the spectroscopic data found for **2**. Thus, in the ^{1}H NMR spectrum, the resonance due to the hydrogen atom bonded to C(2) appears at 7.65 ppm, as a singlet, and the ^{13}C{^{1}H} NMR spectrum shows at 236.3 ppm a doublet with a C−P coupling constant of 11.0 Hz, corresponding to C(1).

The lactonyl complex **5** also reacts with $\mathrm{HBF_4{\cdot}OEt_2}$. The addition at −60 °C of 4 equiv of $\mathrm{HBF_4{\cdot}OEt_2}$ to dichloromethane solutions of **5** affords $[\mathrm{Ru(\eta^5\text{-}C_5H_5)\{{=}\overline{CCH{=}C(OH)OC}{=}CPh_2\}(CO)(PPr^i_3)]BF_4}$ (**7**), which was isolated as a dark purple solid in 89% yield, by addition of diethyl ether (eq 5).



5   **7**   (**5**)

The IR spectrum of **7** in Nujol shows the ν(OH) absorption at about 3030 cm^{-1}, as a very broad band. In addition two absorptions due to $[\mathrm{BF_4}]^-$ at 1151 and 1130 cm^{-1} are observed. The splitting of the expected T_d symmetry of the $[\mathrm{BF_4}]^-$ group suggests that the anion interacts with the −OH proton of the cyclic carbene ligand. A similar phenomenon has been observed in acyclic hydroxycarbene complexes.[1] In the ^{1}H NMR spectrum the resonance due to the =CH proton of the alkenyl unit of the carbene appears at 6.86 ppm as a singlet. The ^{13}C{^{1}H} NMR spectrum contains a doublet at 210.4 ppm with a C−P coupling constant of 11.9, corresponding to the Ru=C carbon atom, in agreement with the ^{13}C{^{1}H} NMR spectra of **2** and **6**.

Concluding Remarks

This study has revealed that heteroatom-containing cyclic metal−carbene complexes can also be prepared by reaction of transition-metal allenylidene compounds with alkyl diazoacetates. As distinguished from the complexes of this type previously reported, the new derivatives are doubly unsaturated with endocyclic and exocyclic carbon−carbon double bonds.

The X-ray analysis of the structures of the cations $[\mathrm{Ru(\eta^5\text{-}C_5H_5)\{{=}\overline{CCH{=}C(R)OC}{=}CPh_2\}(CO)(PPr^i_3)]^+}$ (R = OEt, Me) suggests that the resonance form $[\mathrm{Ru(\eta^5\text{-}C_5H_5)\{{-}\overline{C{=}CHC^+(R)OC}{=}CPh_2\}(CO)(PPr^i_3)]}$ makes a significant contribution to the structure of these compounds. In agreement with this proposal, the *C*−R carbon atom of the complex $[\mathrm{Ru(\eta^5\text{-}C_5H_5)\{{=}\overline{CCH{=}C(OEt)OC}{=}CPh_2\}(CO)(PPr^i_3)]^+}$ shows a marked electrophilic character, adding nucleophiles. This property is responsible for the formation of $\mathrm{Ru(\eta^5\text{-}C_5H_5)\{\overline{C{=}CHC(OMe)(OEt)OC}{=}CPh_2\}(CO)(PPr^i_3)}$, which, as far as we know, is the first organometallic compound containing an ortho ester alkenyl ligand.

In agreement with the trend shown by the organic ortho esters to eliminate ethers, this ortho ester alkenyl complex loses ethyl methyl ether, in the presence of $\mathrm{Al_2O_3}$, to afford the lactonyl derivative $\mathrm{Ru(\eta^5\text{-}C_5H_5)\{\overline{C{=}CHC(O)OC}{=}CPh_2\}(CO)(PPr^i_3)}$, which by reaction with $\mathrm{HBF_4{\cdot}OEt_2}$ gives $[\mathrm{Ru(\eta^5\text{-}C_5H_5)\{{=}\overline{CCH{=}C(OH)OC}{=}CPh_2\}(CO)(PPr^i_3)]BF_4}$.

In conclusion, we report a new reaction within the transition-metal allenylidene chemistry, which allows the preparation of organometallic compounds containing new organic fragments, including doubly α,β-unsaturated cyclic carbene, ortho ester alkenyl, and lactonyl ligands.

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 $[\mathrm{Ru(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(PPr^i_3)]BF_4}$ (**1**) was prepared by the published method.[1]

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

Preparation of $[\mathrm{Ru(\eta^5\text{-}C_5H_5)\{{=}\overline{CCH{=}C(OEt)OC}{=}CPh_2\}(CO)(PPr^i_3)]BF_4}$ (2). A solution of **1** (1 g, 1.58 mmol) in 15 mL of dichloromethane was treated with ethyl diazoacetate (500 μL, 4.75 mmol). The temperature was increased to 313 K until evolution of nitrogen ceased, and the color changed from dark red to dark purple. The solution was concentrated to ca. 2 mL, and by slow addition of diethyl ether, a dark purple solid precipitated. Yield: 860 mg (77%). Anal. Calcd for $\mathrm{C_{34}H_{42}BF_4O_3PRu}$: C, 56.91; H, 5.90. Found: C, 56.60; H, 5.95. IR (Nujol, cm^{-1}): ν(CO) 1935 (vs), ν(C=C) 1593 (m), ν(C=C−O) 1544 (vs), $\nu(\mathrm{BF_4})$ 1053 (vs, br). ^{1}H NMR (300 MHz, 293 K, $\mathrm{CDCl_3}$): δ 7.54−7.34 (8H, Ph), 7.15 (s, 1H, RuC=CH), 7.14 (m, 2H, Ph), 5.36 (s, 5H, Cp), 4.67 (dc, 1H, *J*(HH) = 7.2, *J*(HH) = 10.5, OC*H*HCH$_3$), 4.54 (dc, 1H, *J*(HH) = 7.2, *J*(HH) = 10.5, OCH*H*CH$_3$), 2.17 (m, 3H, PC*H*CH$_3$), 1.42 (vt, 3H, *J*(HH) = 7.2, OCH$_2$C*H*$_3$), 1.17 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.1, PCHC*H*$_3$), 1.09 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.4, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, $\mathrm{CDCl_3}$): δ 62.1 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $\mathrm{CDCl_3}$, plus HETCOR): δ 226.2 (d, *J*(PC) = 11.3, Ru=C), 202.8 (d, *J*(PC) = 20.4, CO), 171.6 [s, =*C*(OEt)OC=CPh$_2$], 159.8 [s, =C(OEt)O*C*=CPh$_2$], 149.0 [s, =C(OEt)OC=*C*Ph$_2$], 139.8, 137.7 (both s, C$_{\mathrm{ipso,Ph}}$), 131.9, 131.6, 130.9, 128.2 (all s, Ph), 124.3 (s, CH=), 88.3 (s, Cp), 71.9 (s, OCH$_2$), 27.2 (d, *J*(PC) = 23.4, P*C*HCH$_3$), 19.8, 19.4 (both s, PCH*C*H$_3$), 14.1 (s, CH$_3$). MS (FAB$^+$): *m*/*z* 631 (M$^+$).

Preparation of $\mathrm{Ru(\eta^5\text{-}C_5H_5)\{\overline{C{=}CHC(OMe)(OEt)OC}{=}CPh_2\}(CO)(PPr^i_3)}$ (3). A solution of **2** (390 mg, 0.54 mmol) in 15 mL of tetrahydrofuran was treated with sodium methoxide (59 mg, 1.1 mmol), and the mixture was stirred for 10 min. The color changed from dark purple to orange, and solvent was removed under vacuum. Dichloromethane (10 mL) was added, and the suspension was filtered to eliminate sodium tetrafluoroborate. Solvent was evaporated and the residue was washed with methanol at 198 K to afford a pale yellow solid. Yield: 241 mg (67%). Anal. Calcd for $C_{35}H_{45}O_4PRu$: C, 63.52; H, 6.85. Found: C, 63.11; H, 6.91. IR (Nujol, cm^{-1}): ν(CO) 1933 (vs), ν(C=C–O) 1724 (m). ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 7.58–7.05 (10H, Ph), 5.78 (s, 1H, RuC=CH), 4.75 (s, 5H, Cp), 4.03 (m, 2H, OC*H*$_2$CH$_3$), 3.27 (s, 3H, OCH$_3$), 2.20 (m, 3H, PC*H*CH$_3$), 1.23 (vt, 3H, *J*(HH) = 7.2, OCH$_2$C*H*$_3$), 0.94 (dd, 9H, *J*(HH) = 7.4, *J*(PH) = 15.6, PCHC*H*$_3$), 0.92 (dd, 9H, *J*(HH) = 8.0, *J*(PH) = 15.4, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6): δ 64.3 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6, plus HETCOR): δ 205.8 (d, *J*(PC) = 22.6, CO), 164.6 [s, C(OMe)(OEt)O*C*=CPh$_2$], 145.3 (s, C$_{ipso,Ph}$), 144.5 (d, *J*(PC) = 12.8, RuC=), 142.3 (s, CH=), 131.2, 127.5, 126.2, 125.8 (all s, Ph), 122.3 [s, C(OMe)(OEt)OC=*C*Ph$_2$], 117.9 [s, *C*(OMe)(OEt)OC=CPh$_2$], 86.1 (s, Cp), 58.6 (s, OCH$_2$), 50.5 (s, OCH$_3$), 26.1 (d, *J*(PC) = 22.9, P*C*HCH$_3$), 20.0, 19.8 (both s, PCH*C*H$_3$), 16.2 (s, CH$_3$).

Preparation of Ru(η^5-C_5H_5){C=CHC(Me)(OEt)OC=CPh$_2$}(CO)(PPr$^i_3$) (4). A solution of **2** (285 mg, 0.40 mmol) in 15 mL of tetrahydrofuran at 213 K was treated with methyllithium (350 μL, 1.6 M in diethyl ether, 0.56 mmol), and immediately, the color changed from dark purple to orange and solvent was removed under vacuum. Toluene (15 mL) was added and the suspension was filtered to eliminate lithium tetrafluoroborate. Solvent was evaporated, and the residue was washed with methanol at 198 K to afford a white solid. Yield: 144 mg (56%). Anal. Calcd for $C_{35}H_{45}O_3PRu$: C, 65.09; H, 7.02. Found: C, 65.25; H, 6.55. IR (Nujol, cm^{-1}): ν(CO) 1932 (vs), ν(C=C–O) 1723 (m), ν(C=C) 1593 (m). ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 7.62–7.04 (10H, Ph), 5.93 (s, 1H, RuC=CH), 4.76 (s, 5H, Cp), 3.73 (dc, 1H, *J*(HH) = 7.2, *J*(HH) = 9.0, OC*H*HCH$_3$), 3.60 (dc, 1H, *J*(HH) = 7.2, *J*(HH) = 9.0, OCH*H*CH$_3$), 2.25 (m, 3H, PC*H*CH$_3$), 1.50 (s, 3H, C(C*H*$_3$)(OEt)), 1.23 (vt, 3H, *J*(HH) = 7.2, OCH$_2$C*H*$_3$), 0.96, (dd, 9H, *J*(HH) = 7.5, *J*(PH) = 13.5, PCHC*H*$_3$), 0.92 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 12.6, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6): δ 64.9 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6, plus DEPT): δ 206.0 (d, *J*(PC) = 23.0, CO), 166.7 [s, C(Me)(OEt)O*C*=CPh$_2$], 150.2 (d, *J*(PC) = 4.6, CH=), 146.0, 143.1 (both s, C$_{ipso,Ph}$), 139.3 (d, *J*(PC) = 12.9, RuC=), 131.6, 127.6, 126.0, 125.5 (all s, Ph), 116.7 [s, C(Me)(OEt)OC=*C*Ph$_2$], 109.0 [s, *C*(Me)(OEt)OC=CPh$_2$], 86.2 (d, *J*(PC) = 1.8, Cp), 58.0 (s, OCH$_2$), 25.8 (d, *J*(PC) = 22.1, P*C*HCH$_3$), 23.1 (s, C(*C*H$_3$)(OEt)OC=CPh$_2$], 20.0, 19.4 (both s, PCH*C*H$_3$), 16.2 (s, OCH$_2$*C*H$_3$). MS (FAB$^+$): *m*/*z* 646 (M$^+$).

Preparation of Ru(η^5-C_5H_5){C=CHC(O)OC=CPh$_2$}(CO)(PPr$^i_3$) (5). Chromatography of **3** (90 mg, 0.14 mmol) on a 10 cm alumina column, using tetrahydrofuran as eluent, afforded a yellow band. Solvent was removed under vacuum, and the residue was washed with diethyl ether, affording **5** as a yellow solid. Yield: 64 mg (78%). Anal. Calcd for $C_{32}H_{37}O_3PRu$: C, 63.88; H, 6.20. Found: C, 63.58; H, 6.15. IR (Nujol, cm^{-1}): ν(CO) 1935 (vs), ν(C=O) 1717 (vs). ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ 7.50–7.06 (10H, Ph), 6.19 (s, 1H, RuC=CH), 4.63 (s, 5H, Cp), 1.85 (m, 3H, PC*H*CH$_3$), 0.75 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 13.1, PCHC*H*$_3$), 0.74 (dd, 9H, *J*(HH) = 7.1, *J*(PH) = 13.1, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6): δ 64.4 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6, plus APT): δ 205.1 (d, *J*(PC) = 22.1, CO), 178.1 (d, *J*(PC) = 13.6, RuC=), 167.6 [s, *C*(O)OC=CPh$_2$], 159.6 [s, C(O)O*C*=CPh$_2$], 143.5, 140.6 (both s, C$_{ipso,Ph}$ + C(O)OC=*C*Ph$_2$), 135.4 (s, CH=), 131.7–127.7 (all s, Ph), 86.5 (s, Cp), 26.5 (d, *J*(PC) = 23.0, P*C*HCH$_3$), 19.6, 19.4 (both s, PCH*C*H$_3$). MS (FAB$^+$): *m*/*z* 602 (M$^+$).

Preparation of [Ru(η^5-C_5H_5){=CCH=C(CH$_3$)OC=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (6).[21] A solution of **4** (55 mg, 0.09 mmol) in 10 mL of diethyl ether was treated with tetrafluoroboric acid (12 μL, 0.09 mmol, 54% in diethyl ether). Immediately, the color changed from pale yellow to green, and a dark green solid precipitated. Yield: 54 mg (92%). IR (Nujol, cm^{-1}): ν(CO) 1946 (vs), ν(C=C–O) 1712 (s), ν(BF$_4$) 1059 (vs, br). ^{1}H NMR (300 MHz, 293 K, CDCl$_3$): δ 7.65 (s, 1H, =CH), 7.61–7.12 (10H, Ph), 5.36 (s, 5H, Cp), 2.33 (s, 3H, C*H*$_3$), 2.12 (m, 3H, PC*H*CH$_3$), 1.12 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.4, PCHC*H*$_3$), 1.04 (dd, 9H, *J*(HH) = 7.2, *J*(PH) = 14.4, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, CDCl$_3$): δ 62.7 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, CDCl$_3$, plus DEPT): δ 236.3 (d, *J*(PC) = 11.0, RuC=), 202.7 (d, *J*(PC) = 19.8, CO), 173.1, 166.1 [both s, =*C*(Me)O*C*=CPh$_2$], 155.6 [s, =C(Me)OC=*C*Ph$_2$], 143.8 (d, *J*(PC) = 2.8, CH=), 140.1, 138.4 (both s, C$_{ipso,Ph}$), 137.8, 133.2, 132.8, 132.1, 129.5, 128.4, 127.6 (all s, Ph), 88.9 (s, Cp), 27.4 (d, *J*(PC) = 24.0, P*C*HCH$_3$), 19.6, 19.4 (both s, PCH*C*H$_3$), 14.4 (s, CH$_3$). MS (FAB$^+$): *m*/*z* 601 (M$^+$).

Preparation of Ru[(η^5-C_5H_5){=CCH=C(OH)OC=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (7). A solution of **5** (56 mg, 0.09 mmol) at 213 K in 5 mL of dichloromethane was treated with tetrafluoroboric acid (50 μL, 0.36 mmol, 54% in diethyl ether). The mixture was stirred for 15 min, and the color changed from yellow to purple. Solvent was concentrated to ca. 1 mL, and 10 mL of diethyl ether was very slowly added. A dark purple solid precipitated, which was repeatedly washed with diethyl ether at 213 K. Yield: 57 mg (89%). Anal. Calcd for $C_{32}H_{38}BF_4O_3PRu$: C, 55.70; H, 5.55. Found: C, 55.78; H, 5.16. IR

Table 3. Summary for Crystal Data Collection and Structure Analysis for the Complexes [Ru(η^5-C_5H_5){=CCH=C(OEt)OC=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (2) and [Ru(η^5-C_5H_5){=CCH=C(CH$_3$)OC=CPh$_2$}(CO)(PPr$^i_3$)]BF$_4$ (6)

formula	$C_{34}H_{42}BF_4O_3PRu$	$C_{35}H_{46}BF_4O_3PRu$
fw	717.55	733.59
cryst size (mm)	0.35 × 0.27 × 0.05	0.37 × 0.22 × 0.10
color, shape	deep red, plate	dark green, plate
cell measmts (25 reflns) (deg)	$12.4 \le 2\theta \le 18.3$	$12.4 \le 2\theta \le 15.2$
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
cell params		
a (Å)	10.778(2)	12.236(5)
b (Å)	18.085(4)	14.073(6)
c (Å)	9.325(2)	10.270(7)
α (deg)	99.31(2)	104.15(4)
β (deg)	107.47(2)	100.36(4)
γ (deg)	103.43(2)	80.54(4)
V	1633.0(7)	1673(1)
Z	2	2
ρ_{calcd} (g cm^{-3})	1.459	1.456
λ(Mo Kα) (Å)	0.710 69	0.710 69
μ(Mo Kα) (cm^{-1})	5.72	5.60
F(000)	740	760
abs cor	DIFABS[22]	DIFABS[22]
transmissn factors	0.823–1.416	0.891–1.144
stds: no., interval	3, 100	4, 100
decay (%)	−2.40	−3.30
temp (K)	290(1)	290(1)
scan method	$\omega/2\theta$	ω
scan speed (ω) (deg min^{-1})	4	4
2θ interval (deg)	$5 < 2\theta \le 50$	$5 < 2\theta \le 50.1$
no. of measd rflns	5521	5801
no. of unique rflns	5233 ($R_{int} = 0.044$)	5801 ($R_{int} = 0.137$)
no. of obsd rflns ($I > 3\sigma_I$)	3855	4271
no. of params	397	366
rfln/param ratio	9.71	11.67
refinements	full-matrix ls on *F*	full-matrix ls on *F*
R^a	0.0524	0.055
R_w ($w = \sigma_F^{-2}$)^b	0.0655	0.067
GOF	1.856	2.26
residual peaks (e Å^{-3})	+0.91, −0.84	+1.05, −1.08

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

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[21] All our attempts to achieve a valid elemental analysis determination for complex **6** were unsuccessful. Even when we tried with crystals of the same crop that was used for the X-ray diffraction study, we could not obtain a satisfactory value.

[22] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(Nujol, cm^{-1}): ν(OH) 3030 (br), ν(CO) 1949 (vs), ν(C═C−O) 1717 (s), $\nu(BF_4)$ 1151, 1130 (s). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.46−7.09 (10H, Ph), 6.86 (s, 1H, ═CH), 5.19 (s, 5H, Cp), 2.22 (m, 3H, PC*H*CH_3), 1.14, (dd, 9H, *J*(HH) = 7.5, *J*(PH) = 14.4, PCHCH_3), 1.08 (dd, 9H, *J*(HH) = 6.9, *J*(PH) = 13.8, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $CDCl_3$): δ 63.1 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $CDCl_3$, plus DEPT): δ 210.4 (d, *J*(PC) = 11.9, RuC═), 203.7 (d, *J*(PC) = 20.7, CO), 172.4, 158.6 [both s, ═*C*(OH)O*C*═CPh_2], 143.4 [s, ═C(OH)OC═*C*Ph_2], 140.3, 138.2 (both s, $C_{ipso,Ph}$), 131.6, 130.3, 129.7, 127.9 (all s, Ph), 129.4 (s, CH═), 87.2 (s, Cp), 26.5 (d, *J*(PC) = 23.5, P*C*HCH_3), 19.5, 19.4 (both s, PCHCH_3).

X-ray Structure Analysis of Complexes $[Ru(\eta^5\text{-}C_5H_5)\{=\overline{CCH=C(OEt)OC}=CPh_2\}(CO)(PPr^i_3)]BF_4$ (2) and $[Ru(\eta^5\text{-}C_5H_5)\{=\overline{CCH=C(CH_3)OC}=CPh_2\}(CO)(PPr^i_3)]BF_4$ (6). A deep red crystal of $C_{34}H_{42}BF_4O_3PRu$ (**2**) (0.27 × 0.05 × 0.35 mm) and a dark green crystal of $C_{35}H_{46}BF_4O_3PRu$ (**6**) (0.37 × 0.22 × 0.10 mm) were mounted on glass fibers and transferred to a Rigaku AFC6S diffractometer. Graphite-monochromated Mo Kα radiation was used.

Cell constants were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections (**2** and **6**). The systems were determined to be triclinic, space group $P\bar{1}$. The data were collected using the $\omega/2\theta$ (**2**) and ω (**6**) scan methods. The intensities of 3 standard reflections were measured after every 100 reflections to apply the decay correction. Lorentz−polarization and absorption correction (DIFABS method) were also applied. A summary of experimental details is given in Table 3.

The structures were solved by the Patterson method. All non-hydrogen atoms of **2** and **6** (except the BF_4^- anion of (**6**)) were anisotropically refined on *F* by the full-matrix least-squares method. The tetrafluoroborate anion of **6** was isotropically refined by considering two different orientations, one fluorine in two positions F(4A) and F(4B) with complementary occupations. The hydrogen atoms of **2** and **6** were included in calculated positions and not refined. Sets of 3855 (**2**) and 4271 (**6**) observed reflections ($I > 3\sigma(I)$), with 397 (**2**) and 366 (**6**) variable parameters, were used in the last cycles of refinements. Final values of $R = 0.052$, $R_w = 0.065$ (**2**), and $R = 0.055$, $R_w = 0.067$ (**6**) were obtained. Details of structure solution and refinement can also be found in Table 3. All calculations were carried out using the TEXSAN software package on a VAX 3520 computer at the "Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz".

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Supporting Information Available: Tables of atomic coordinates, anisotropic and isotropic thermal parameters, experimental details of the X-ray study, bond distances and angles, and selected least-squares planes for complexes **2** and **6** (9 pages). Ordering information is given on any current masthead page.

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