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Regioselective Addition of Dienes to the C_β−C_γ Double Bond of the Allenylidene Ligand of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$

Miguel Baya, María L. Buil, Miguel A. Esteruelas,* Ana M. López, Enrique Oñate, and J. Ramón Rodríguez

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

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The C_β−C_γ bond of the allenylidene ligand of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ (**1**) adds dienes such as isoprene, cyclopentadiene, and 1,3-cyclohexadiene. The reaction with isoprene selectively affords the disubstituted vinylidene derivative $[Ru(\eta^5\text{-}C_5H_5)(=C=CCH_2C(CH_3)=CHCH_2CPh_2)(CO)(P^iPr_3)]BF_4$ (**2**), whereas in the presence of cyclopentadiene a 1:1 mixture of the diastereomers $Ru_R,C^a{}_S,C^b{}_R(Ru_S,C^a{}_R,C^b{}_S)$-$[Ru(\eta^5\text{-}C_5H_5)(=C=CCPh_2C^aHCH_2C^bHCH=CH)(CO)(P^iPr_3)]BF_4$ (**3**) and $Ru_R,C^a{}_R,C^b{}_S(Ru_S,C^a{}_S,C^b{}_R)$-$[Ru(\eta^5\text{-}C_5H_5)(=C=CCPh_2C^aHCH_2C^bHCH=CH)(CO)(P^iPr_3)]BF_4$ (**4**) is obtained. In contrast to the addition of cyclopentadiene, the reaction with 1,3-cyclohexadiene is diastereoselective and gives only the racemic mixture of one diastereomer: $Ru_R,C^a{}_R,C^b{}_S(Ru_S,C^a{}_S,C^b{}_R)$-$[Ru(\eta^5\text{-}C_5H_5)(=C=CCPh_2C^aHCH_2CH_2C^bHCH=CH)(CO)(P^iPr_3)]BF_4$ (**5**). The structures of **2**, **3**, and **5** have been determined by X-ray diffraction analysis. In the three cases, the geometry around the ruthenium center is close to octahedral, with the cyclopentadienyl ligand occupying one face.

Introduction

The chemistry of transition-metal allenylidene complexes has been the subject of special attention in recent years, due to their potential as organometallic intermediates that may have unusual reactivity in stoichiometric[1] and catalytic reactions.[2]

The reactivity of these types of compounds appears to be marked by the polarization of the three carbon atoms of the unsaturated chain (electrophile−nucleophile−electrophile).[3] Thus, the addition of numerous polar reagents to the cumulene unit has been reported, while there is no precedent for the addition of nonpolar molecules.

The character and the direction of the addition to the C_3 chain of the allenylidene are highly dependent on the electronic nature of the metallic fragment. As a result, the diarylallenylidene complexes of the iron triad have been classified into four groups:[3f] nucleophiles, amphoteres, γ-electrophiles, and α-electrophiles.

The best known α-electrophilic complex is the derivative $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$.[4] The presence of the π-acidic carbonyl group in this complex enhances the reactivity associated with the allenylidene spine, and the complex shows the most versatile behavior in the field.[3e,4,5] This is probably a consequence of the lower energy of the LUMO orbital of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ as compared to the energy of the LUMO orbital of other allenylidene compounds.

In the normal electron demand Diels−Alder reaction, the dominating orbital interaction is HOMO (diene)−LUMO (dienophile). The reactivity of a process of this type depends on the lowest HOMO−LUMO energy separation that can be achieved by reacting partners. Thus, the typical normal Diels−Alder reaction is one

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* To whom correspondence should be addressed. E-mail: maester@posta.unizar.es. Fax: 34 976761187.

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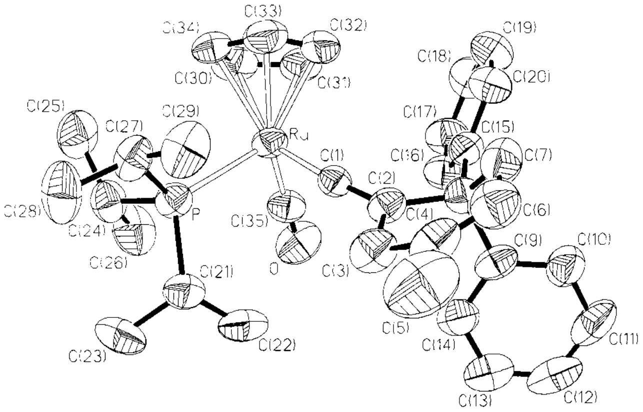


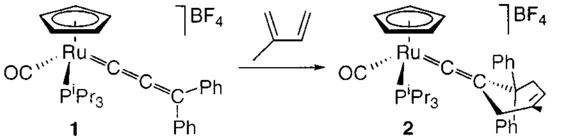
Figure 1. Molecular diagram of the cation of $[Ru(\eta^5\text{-}C_5H_5)(=C=\overline{CCH_2C(CH_3)=CHCH_2CPh_2})(CO)(P^iPr_3)]BF_4$ (**2**). Thermal ellipsoids are shown at 50% probability.

between an electron-rich diene with an electron-deficient dienophile.[6] This prompted us to investigate the reactivity of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ toward dienes such as isoprene, cyclopentadiene, and 1,3-cyclohexadiene.

This paper reports a new reaction in allenylidene chemistry, which is the first addition of nonpolar molecules to the C_3 chain of a transition-metal allenylidene complex, the first intermolecular Diels–Alder reaction involving an allenylidene ligand as dienophile, and a new route for preparing vinylidene derivatives.

Results and Discussion

1. Reaction with Isoprene. Treatment at room temperature of a dichloromethane solution of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ (**1**) with 20 equiv of isoprene leads after 14 days to the vinylidene derivative $[Ru(\eta^5\text{-}C_5H_5)(=C=\overline{CCH_2C(CH_3)=CHCH_2CPh_2})(CO)(P^iPr_3)]BF_4$ (**2**) in 96% yield, according to the ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture (eq 1).



(1)

A view of the molecular geometry of the cation of **2** is shown in Figure 1. Selected bond distances and angles are listed in Table 1. The geometry around the ruthenium center is close to octahedral, with the cyclopentadienyl ligand occupying a face. The C(1)–Ru–C(35) and P–Ru–C(35) angles are 88.0(2) and 91.75(19)°, respectively. These values agree well with the ideal value of 90°. However the C(1)–Ru–P angle (98.84(16)°) strongly deviates from 90°, suggesting that the triisopropylphosphine and vinylidene ligands experience a large steric hindrance.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $[Ru(\eta^5\text{-}C_5H_5)(=C=\overline{CCH_2C(CH_3)=CHCH_2CPh_2})(CO)(P^iPr_3)]BF_4$ (2)

Ru–C(30)	2.263(6)	C(1)–C(2)	1.297(6)
Ru–C(31)	2.191(6)	C(2)–C(3)	1.537(7)
Ru–C(32)	2.216(6)	C(2)–C(8)	1.542(7)
Ru–C(33)	2.369(6)	C(3)–C(4)	1.506(8)
Ru–C(34)	2.279(5)	C(4)–C(5)	1.484(9)
Ru–P	2.2709(17)	C(4)–C(6)	1.292(6)
Ru–C(1)	1.865(5)	C(6)–C(7)	1.515(8)
Ru–C(35)	1.826(6)	C(7)–C(8)	1.542(7)
		O–C(35)	1.166(6)
M(1)–Ru–P[a]	120.6(2)	Ru–C(1)–C(2)	173.9(5)
M(1)–Ru–C(1)	122.0(3)	C(1)–C(2)–C(3)	117.6(5)
M(1)–Ru–C(35)	127.1(3)	C(1)–C(2)–C(8)	126.9(5)
P–Ru–C(1)	98.84(16)	C(3)–C(4)–C(5)	113.2(7)
P–Ru–C(35)	91.75(19)	C(3)–C(4)–C(6)	127.8(7)
C(1)–Ru–C(35)	88.0(2)	C(4)–C(6)–C(7)	118.1(7)
		Ru–C(35)–O	177.0(6)

[a] M(1) is the midpoint of the C(30)–C(34) Cp ligand.

The vinylidene ligand is bound to the ruthenium in a nearly linear fashion with a Ru–C(1)–C(2) angle of 173.9(5)°. The Ru–C(1) (1.865(5) Å) and C(1)–C(2) (1.297(6) Å) bond lengths compare well with those found in other ruthenium–vinylidene complexes[7] and support the vinylidene formulation. The structural parameters for the sequence C(2)–C(3)–C(4)–C(6)–C(7)–C(8)–C(2) (1.537(7), 1.506(8), 1.292(6), 1.515(8), 1.542(7), and 1.542(7) Å) are in good agreement with the formulation of a C(4)–C(6) unsaturated six-membered cycle.[8]

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **2** are in accordance with the structure shown in Figure 1. In the ^1H NMR spectrum, the olefinic resonance corresponding to the C(6)–H proton appears at 5.56 ppm as a singlet, whereas the $C(3)H_2$ and $C(7)H_2$ groups display AB spin systems defined by δ_A 3.30, δ_B 3.15, $J_{AB} = 18.0$ Hz and δ_A 3.02, δ_B 2.84, $J_{AB} = 18.6$ Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the $Ru-C_\alpha$ resonance appears at 355.8 ppm as a doublet with a C–P coupling constant of 9.3 Hz, whereas the C_β resonance is observed at 129.8 ppm as a singlet. The olefinic carbon atoms C(4) and C(6) of the six-membered cycle give rise to singlets at 130.7 and 120.4 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 80.9 ppm.

Complex **2** is the result of a Diels–Alder addition of an isoprene molecule to the allenylidene ligand of **1**. The addition is regioselective with regard to the dienophile and with regard to the diene; i.e., the reaction is doubly regioselective. Although complex **1** has three double bonds ($Ru-C_\alpha$, $C_\alpha-C_\beta$, and $C_\beta-C_\gamma$), only one of them (the $C_\beta-C_\gamma$ bond) reacts with isoprene. The regioselectivity in the diene is related to the orientation of this molecule in the transition state of the reaction, which could give two isomers: the observed one with the methyl and the vinylidene substituents of the six-

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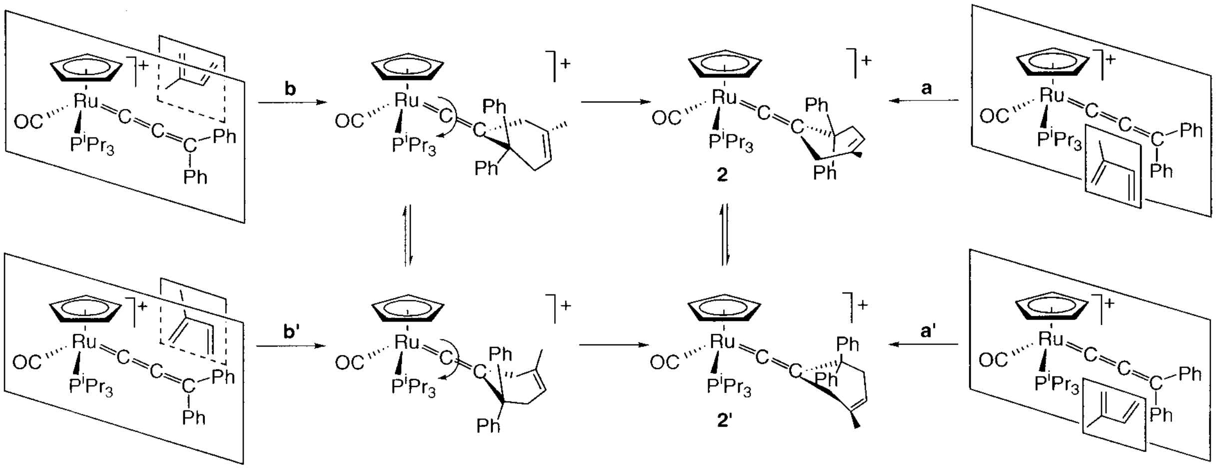
Scheme 1



membered cycle in meta positions and that containing the methyl and the vinylidene substituents in para positions.

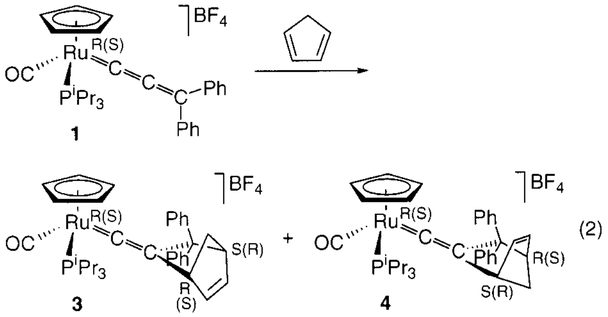
The selectivity in the dienophile appears to be electronic in origin. In this context, it should be mentioned that theoretical calculations on the model complex [Ru(η^5-C$_5$H$_5$)(=C=C=CH$_2$)(CO)(PH$_3$)]$^+$ indicate that the percentage of LUMO orbital on the C$_\gamma$ atom (31%) is higher than that on the C$_\alpha$ atom (23%).[3e] In contrast, the selectivity in the diene appears to be steric in origin. In principle, the orientation of the diene in the transition state of the reaction could be with the substituted double bond on the C$_\beta$ atom of the allenylidene or alternatively opposite to the C$_\gamma$ atom. In the first case, the reaction should give the vinylidene ligand of **2**, while in the second case, the isomer of this vinylidene containing the methyl group and the Ru=C=C= unit of the six-membered ring in para positions should be formed. The first orientation, and therefore the exclusive formation of the vinylidene of **2**, is favored, probably, as a result of the steric hindrance generated by the phenyl groups at the C$_\gamma$ atom.

In addition it should be noted that, as a consequence of the asymmetry of **1**, there are four possible transition states with the substituted double bond of the diene oriented on the C$_\beta$ atom of the allenylidene. They can afford four adducts: two conformers for each of the two possible rotamers. Each one of these species is the result of one of four different approaches of the diene to the dienophile, as is shown in Scheme 1. According to Figure 1, the reaction shown in eq 1 affords only the conformer **2** of the rotamer, containing the phenyl substituents of the six-membered ring toward the carbonyl group.

X-ray diffraction and theoretical studies on M(η^5-C$_5$R$_5$)(=C=C=CR$_2$)L$_2$ complexes indicate that the plane containing the carbon atoms of the C$_3$ unit of the allenylidene and the ipso carbon atoms of its R substituents is almost orthogonal to the ML$_2$ plane.[1,9] Thus, at first glance the formation of **2** should be a result of the approach of the diene to the dienophile in the direction given by the Ru–P bond of **1**, with the methyl group of the diene toward the cyclopentadienyl ligand (via **a** in Scheme 1). Complex **2** could be also the result of the approach of the diene with the methyl group away from the cyclopentadienyl ligand (via **a′**). In this case, the conformer **2′** should be formed, and subsequently it should evolve to **2**.

Using a molecular model, it can be easily established that these approaches are highly handicapped by the isopropyl groups of the phosphine, which protect this face of the allenylidene. Thus, it seems reasonable to assume that the formation of **2** takes place in a two-step process. First, the diene approaches the allenylidene in the direction pointed by the Ru–CO bond of **1**, again with the methyl group of the diene toward the cyclopentadienyl ligand (via **b′**) or away from it (via **b**). These approaches by the CO face afford the rotamers containing the phenyl substituents of the six-membered cycle toward the phosphine ligand. Subsequently, these rotamers rotate around the Ru–vinylidene bond to give **2′** or **2**. The driving force for this rotation must be the large steric hindrance experienced by the phenyl substituents of the six-membered ring of the vinylidene and the isopropyl groups of the phosphine.

2. Reaction with Cyclopentadiene. Treatment of dichloromethane solutions of **1** with 20 equiv of cyclopentadiene under reflux affords after 14 h a 1:1 mixture of the diastereomers Ru$_R$,C$^a{}_S$,C$^b{}_R$(Ru$_S$,C$^a{}_R$,C$^b{}_S$)-[Ru(η^5-C$_5$H$_5$)(=C=CCPh$_2$C^{a}HCH$_2$C^{b}HCH=CH)(CO)(P^{i}Pr$_3$)]BF$_4$ (**3**) and Ru$_R$,C$^a{}_R$,C$^b{}_S$(Ru$_S$,C$^a{}_S$,C$^b{}_R$)-[Ru(η^5-C$_5$H$_5$)(=C=CCPh$_2$C^{a}HCH$_2$C^{b}HCH=CH)(CO)(P^{i}Pr$_3$)]BF$_4$ (**4**) in 87% conversion, according to the ^{1}H and ^{31}P{^{1}H} NMR spectra of the reaction mixture (eq 2).



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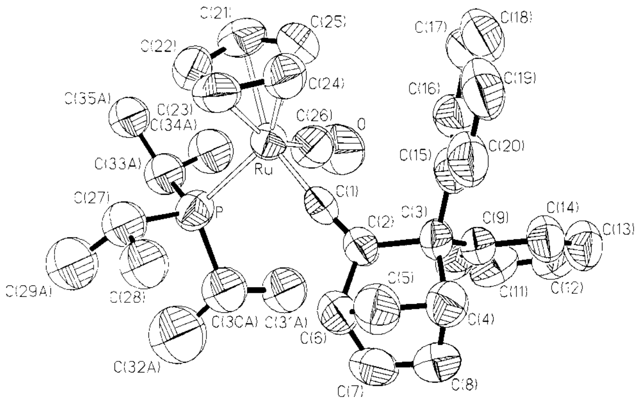


Figure 2. Molecular diagram of the cation of the $Ru_R,C^a{}_S,C^b{}_R$ enantiomer of $[Ru(\eta^5\text{-}C_5H_5)({=}C{=}CCPh_2C^aHCH_2C^bHCH{=}CH)(CO)(P^iPr_3)]BF_4$ (**3**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex $[Ru(\eta^5\text{-}C_5H_5)({=}C{=}CCPh_2C^aHCH_2C^bHCH{=}CH)(CO)(P^iPr_3)]BF_4$ (3)

Ru−C(21)	2.161(6)	C(1)−C(2)	1.286(7)
Ru−C(22)	2.265(6)	C(2)−C(3)	1.550(7)
Ru−C(23)	2.264(6)	C(2)−C(6)	1.542(7)
Ru−C(24)	2.232(6)	C(3)−C(4)	1.572(7)
Ru−C(25)	2.208(6)	C(4)−C(5)	1.542(7)
Ru−P	2.3739(18)	C(4)−C(8)	1.504(8)
Ru−C(1)	1.876(6)	C(5)−C(6)	1.524(8)
Ru−C(26)	1.841(7)	C(6)−C(7)	1.489(9)
		C(7)−C(8)	1.309(7)
		O−C(26)	1.153(6)
M(1)−Ru−P[a]	123.6(2)	C(2)−C(3)−C(4)	98.7(4)
M(1)−Ru−C(1)	121.5(3)	C(2)−C(6)−C(5)	99.5(5)
M(1)−Ru−C(26)	126.7(3)	C(2)−C(6)−C(7)	106.6(6)
P−Ru−C(1)	95.69(16)	C(3)−C(4)−C(5)	103.3(5)
P−Ru−C(26)	89.8(2)	C(3)−C(4)−C(8)	105.3(5)
C(1)−Ru−C(26)	90.1(3)	C(4)−C(5)−C(6)	92.3(5)
Ru−C(1)−C(2)	173.2(5)	C(4)−C(8)−C(7)	109.0(7)
C(1)−C(2)−C(3)	130.6(5)	C(6)−C(7)−C(8)	106.1(7)
C(1)−C(2)−C(6)	122.4(5)	Ru−C(26)−O	178.0(7)

[a] M(1) is the midpoint of the C(21)−C(25) Cp ligand.

Complex **3** was obtained as pure microcrystals formed by a mixture of enantiomers by slow diffusion of diethyl ether into a concentrated solution of the reaction mixture in dichloromethane and characterized by X-ray diffraction analysis. Figure 2 shows a view of the molecular geometry of the cation of **3**. Selected bond distances and angles are listed in Table 2.

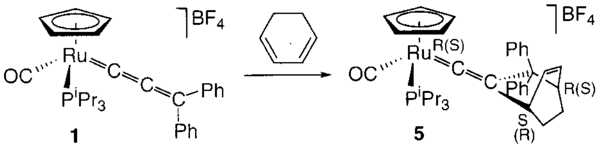
The geometry around the ruthenium atom is like that of **2**: i.e., close to octahedral with the cyclopentadienyl ligand occupying one face. Although the phenyl substituents of the bicycle of the vinylidene are disposed toward the carbonyl group and away from the phosphine, to minimize the steric hindrance between the vinylidene and the phosphine, the C(1)−Ru−P angle (95.69(16)°) deviates from the ideal value of 90°, indicating some residual steric hindrance between these ligands. In agreement with the vinylidene formulation of the unsaturated η^1-carbon ligand, the Ru−C(1) and C(1)−C(2) distances and the Ru−C(1)−C(2) angle are 1.876(7) and 1.286(7) Å and 173.2(5)°, respectively. The value of the C(7)−C(8) bond length, 1.309(7) Å, supports a carbon−carbon double bond between these atoms of the bicycle.

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **3** are in accordance with the structure shown in Figure 2. In the ^1H NMR spectrum, the most noticeable feature is the presence of two olefinic resonances at 5.92 and 6.14 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the $Ru{-}C_\alpha$ resonance appears at 350.5 ppm as a doublet with a C−P coupling constant of 9.6 Hz, whereas the C_β resonance is observed at 131.3 ppm as a singlet. The olefinic carbon atoms of the bicycle give rise to singlets at 140.5 and 134.1 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 79.5 ppm.

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **4** agree well with those of **3**. In the ^1H NMR spectrum, the olefinic resonances are observed at 5.90 and 5.93 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the Ru=C=C unit gives rise to a doublet at 353.8 ppm with a coupling constant of 10.5 Hz and a singlet at 131.9 ppm. The resonances due to the olefinic carbon atoms of the bicycle are observed at 135.5 and 142.1 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 82.0 ppm.

Diastereomers **3** and **4** are the result of regioselective Diels−Alder additions of cyclopentadiene to the $C_\beta{-}C_\gamma$ bond of the allenylidene of **1**, and their formation can be rationalized similarly to the formation of **2** (Scheme 2). The approach of the diene to the allenylidene in the direction pointed by the Ru−CO bond of **1**, with the CH_2 group away from the cyclopentadienyl ligand, followed by the rotation around the Ru−vinylidene bond of the resulting vinylidene intermediate should afford **3**. Diastereomer **4** should be the result of the same approaching process, but with the CH_2 group of the diene toward the cyclopentadienyl ligand of **1**.

3. Reaction with Cyclohexadiene. Treatment of dichloromethane solutions of **1** with 20 equiv of cyclohexadiene under reflux affords after 14 h the racemic mixture of the diastereomer $Ru_R,C^a{}_R,C^b{}_S(Ru_S,C^a{}_S,C^b{}_R)$-$[Ru(\eta^5\text{-}C_5H_5)({=}C{=}CCPh_2C^aHCH_2CH_2C^bHCH{=}CH)(CO)(P^iPr_3)]BF_4$ (**5**) in 85% yield, according to the ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture (eq 3).



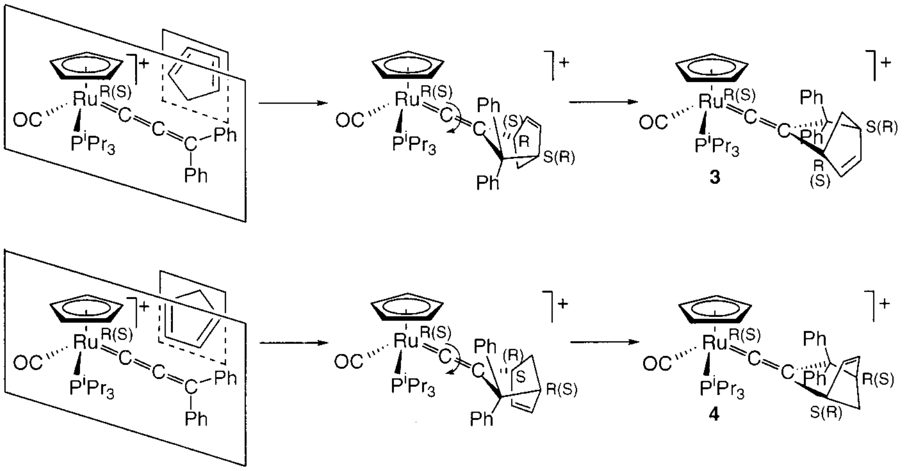
(3)

Complex **5**, like **2** and **3**, was characterized by elemental analysis, IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and an X-ray crystallographic study. A view of the molecular geometry of the cation of **5** is shown in Figure 3. Selected bond distances and angles are listed in Table 3.

Similarly to **2** and **3**, the geometry around the ruthenium atom is close to octahedral with the cyclopentadienyl ligand occupying a face. Also in this case, the phenyl substituents of the bicycle of the vinylidene are disposed toward the carbonyl group and away from the phosphine and despite this, again, the C(1)−Ru−P angle (95.35(15)°) deviates from the ideal value of 90°.

The Ru−C(1) (1.873(5) Å) and C(1)−C(2) (1.293(6) Å) distances and the Ru−C(1)−C(2) (173.9(4)° angle are

Scheme 2



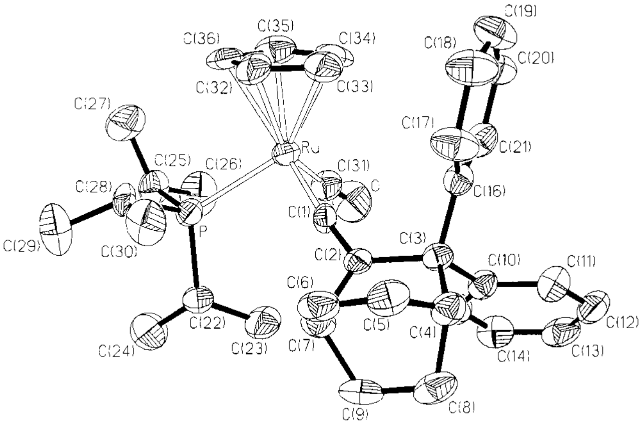


Figure 3. Molecular diagram of the cation of the Ru$_R$,C$^a{}_R$,C$^b{}_S$ enantiomer of [Ru(η^5-C$_5$H$_5$)(=C=CCPh$_2$C^{a}HCH$_2$CH$_2$C^{b}HCH=CH)(CO)(P^{i}Pr$_3$)]BF$_4$ (**5**). Thermal ellipsoids are shown at 50% probability.

statistically identical with the related parameters of **2** and **3**. The value of the C(5)−C(6) bond length, 1.325(7) Å, supports a carbon−carbon double bond between these atoms of the bicycle.

The ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of **5** are consistent with the structure shown in Figure 3. The ^{1}H NMR spectrum shows two olefinic resonances at 6.42 and 6.99 ppm. In the ^{13}C{^{1}H} NMR spectrum, the Ru−C$_\alpha$ resonance appears at 356.8 ppm as a doublet with a C−P coupling constant of 9.3 Hz, whereas the C$_\beta$ resonance is observed at 131.9 ppm as a singlet. The olefinic resonances corresponding to the C(5) and C(6) atoms of the bicycle appear as singlets at 130.6 and 137.5 ppm. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 79.9 ppm.

The formation of **5** can be rationalized according to Scheme 3. Like the reactions shown in eqs 1 and 2, the addition of 1,3-cyclohexadiene to the allenylidene ligand of **1** occurs regioselectively at the C$_\beta$−C$_\gamma$ double bond. The approach of this diene in the direction given by the Ru−CO bond of **1** with the CH$_2$CH$_2$ group toward the cyclopentadienyl ligand, followed by the rotation around the Ru−vinylidene bond of the resulting vinylidene intermediate, should afford **5**. Although we have not found any reason for this fact, it should be noted that the addition of 1,3-cyclohexadiene to the allenylidene of **1** is not only regioselective at the C$_\beta$−C$_\gamma$ bond but also stereoespecific. In contrast to the addition of cyclopentadiene, the addition of 1,3-cyclohexadiene leads to only one diasteromer of the two that are feasible, that related to **4**. At first glance, one could think that the stereoselectivity observed for the reaction shown in eq 3 is a result of a fast isomerization of the diastereomer related to **3** into **5**. However, this does not occur because (i) we have observed that the addition of 1,3-cyclohexadiene to **1** at room temperature also affords **5** selectively and (ii) the isomerization of **3** into **4** is not observed, even after 1 week at 60 °C in chloroform-*d*.

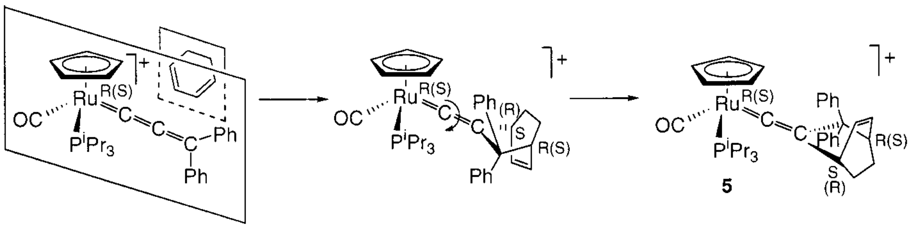
Table 3. Selected Bond Distances (Å) and Angles (deg) for the Complex [Ru(η^5-C$_5$H$_5$)(=C=CCPh$_2$C^{a}HCH$_2$CH$_2$C^{b}HCH=CH)(CO)(P^{i}Pr$_3$)]BF$_4$ (5)

Ru−C(32)	2.274(5)	C(2)−C(3)	1.546(6)
Ru−C(33)	2.235(6)	C(2)−C(7)	1.542(6)
Ru−C(34)	2.213(5)	C(3)−C(4)	1.578(6)
Ru−C(35)	2.248(5)	C(4)−C(5)	1.479(8)
Ru−C(36)	2.274(5)	C(4)−C(8)	1.557(8)
Ru−P	2.3799(15)	C(5)−C(6)	1.325(7)
Ru−C(1)	1.873(5)	C(6)−C(7)	1.493(7)
Ru−C(31)	1.856(3)	C(7)−C(9)	1.554(8)
C(1)−C(2)	1.293(6)	C(8)−C(9)	1.519(9)
		O−C(31)	1.150(5)
M(1)−Ru−P[a]	120.9(2)	C(2)−C(7)−C(6)	104.9(5)
M(1)−Ru−C(1)	122.8(2)	C(2)−C(7)−C(9)	108.5(5)
M(1)−Ru−C(31)	124.9(3)	C(3)−C(4)−C(5)	112.1(5)
P−Ru−C(1)	95.35(15)	C(3)−C(4)−C(8)	107.9(5)
P−Ru−C(31)	93.42(18)	C(4)−C(5)−C(6)	116.9(6)
C(1)−Ru−C(31)	91.3(2)	C(4)−C(8)−C(9)	109.6(6)
Ru−C(1)−C(2)	173.9(4)	C(5)−C(6)−C(7)	112.9(6)
C(1)−C(2)−C(3)	126.8(5)	C(6)−C(7)−C(9)	107.8(5)
C(1)−C(2)−C(7)	119.8(5)	C(7)−C(9)−C(8)	109.8(6)
C(2)−C(3)−C(4)	104.0(4)	Ru−C(31)−O	176.1(6)

[a] M(1) is the midpoint of the C(32)−C(36) Cp ligand.

The reactions shown in eqs 1−3 are a novel route to synthesize disubstituted vinylidene complexes. In this context, it should be mentioned that although transition-metal vinylidene compounds are considered the central point of important selective transformations of

Scheme 3



alkynes with atom economy,[10] few disubstituted vinylidene derivatives have been isolated in comparison to the large family of reported monosubstituted vinylidene compounds.[7] The main routes previously described to prepare disubstituted vinylidene complexes involve electrophilic addition to alkynyl precursors,[11] deoxygenation of acylmetal derivatives by treatment with $(CF_3SO_2)_2O$,[12] and rearrangement of alkylidene metallacyclobutene species.[13]

Concluding Remarks

This study proves that transition-metal allenylidene complexes can react not only with polar molecules but also with dienes. The complex $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ reacts with isoprene, cyclopentadiene, and 1,3-cyclohexadiene to afford disubstituted vinylidene derivatives, as a result of the regioselective Diels–Alder addition of the dienes to the C_β–C_γ bond of the allenylidene. The reactions occur under mild conditions and without catalyst.

The addition of isoprene is also regioselective with regard to the diene. Although two isomers could be obtained as a consequence of the possible orientations of the diene in the transition state (the substituted double bond on C_β or C_γ), only that resulting from the approach of the diene with the substituted double bond on C_β is formed.

The reaction with cyclopentadiene affords a mixture of two diastereomers, which arise from the approach of the diene to $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ with the CH_2 group toward the cyclopentadienyl ligand or away from it, respectively. In contrast, the addition of 1,3-cyclohexadiene gives only one diastereomer, indicating that in this case, the reaction is diastereoselective and occurs with specific substrate orientation.

In conclusion, the C_β–C_γ double bond of transition-metal allenylidene complexes can be a useful dienophile in Diels–Alder reactions, under mild conditions. Therefore, this class of compounds should be taken into account as a new type of substrate to obtain novel disubstituted vinylidene ligands.

Experimental Section

All reactions were carried out with rigorous exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The starting material $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ (**1**) was prepared by the published method.[4] In the NMR spectra, chemical shifts are expressed in ppm downfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, *J*, are given in hertz.

Preparation of $[Ru(\eta^5\text{-}C_5H_5)(=C=CCH_2C(CH_3)=CHCH_2CPh_2)(CO)(P^iPr_3)]BF_4$ (2). A solution of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ (**1**; 150 mg, 0.24 mmol) in 15 mL of dichloromethane was treated with isoprene (480 μL, 4.8 mmol). The mixture was stirred at room temperature for 14 days. The solution was filtered through Kieselguhr and evaporated to dryness. According to the ^1H and $^{31}P\{^1H\}$ NMR spectra of the residue, the reaction is almost quantitative (96%). The residue was treated with 10 mL of diethyl ether to obtain a pale pink solid. The solution was decanted, and the solid was washed with diethyl ether and dried in vacuo. The solid was crystallized at room temperature from dichloromethane–diethyl ether to give amber crystals. Yield: 59 mg (35%). Anal. Calcd for $C_{35}H_{44}BF_4OPRu$: C, 60.10; H, 6.34. Found: C, 59.85; H, 6.23. IR (Nujol, cm^{-1}): ν(CO) 1989, ν(C=C) 1667 and 1592, $\nu(BF_4)$ 1052. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.47–7.11 (m, 10H, Ph), 5.56 (s, 1H, =CH), 5.38 (s, 5H, Cp), 3.30 (part A of an AB spin system, *J*(AB) = 18.0, 1H, CH_2), 3.15 (part B of an AB spin system, *J*(AB) = 18.0, 1H, CH_2), 3.02 (part A of an AB spin system, *J*(AB) = 18.6, 1H, CH_2), 2.84 (part B of an AB spin system, *J*(AB) = 18.6, 1H, CH_2), 2.38 (m, 3H, PC*H*CH_3), 1.58 (s, 3H, CH_3), 1.41 and 1.29 (both dd, *J*(HH) = 6.9, *J*(PH) = 13.8, 18H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $CDCl_3$, plus apt): δ 355.8 (d, *J*(CP) = 9.3, Ru=C_α), 199.1 (d, *J*(CP) = 15.2, CO), 145.1, 142.2 (both s, C_{ipso}), 130.7 (s, *C*(CH_3)=), 129.8 (s, Ru=C=C_β), 128.9, 128.4, 128.0, 127.3, 127.0, 126.9, (all s, Ph), 120.4 (s, CH=), 92.1 (s, Cp), 49.9 (s, *C*Ph_2), 36.4 (s, CH_2), 28.4 (d, *J*(CP) = 22.6, P*C*HCH_3), 27.6 (s, CH_2), 22.4 (s, CH_3), 20.6, 19.0 (both s, PCH*C*H_3). $^{31}P\{^1H\}$ NMR (121.421 MHz, 293 K, $CDCl_3$): δ 80.9 (s).

Preparation of $Ru_R,C^a{}_S,C^b{}_R(Ru_S,C^a{}_R,C^b{}_S)$-$[Ru(\eta^5\text{-}C_5H_5)(=C=CCPh_2C^aHCH_2C^bHCH=CH)(CO)(P^iPr_3)]BF_4$ (3) and $Ru_R,C^a{}_R,C^b{}_S(Ru_S,C^a{}_S,C^b{}_R)[Ru(\eta^5\text{-}C_5H_5)(=C=CCPh_2C^aHCH_2C^b\text{-}HCH=CH)(CO)(P^iPr_3)]BF_4$ (4). A solution of $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]BF_4$ (**1**; 200 mg, 0.32 mmol) in 15 mL of dichloromethane was treated with cyclopentadiene (440 μL, 6.4 mmol). The mixture was stirred at reflux temperature for 14 h. The solution was filtered through Kieselguhr and evaporated to dryness. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the residue show a 87% conversion. The residue was treated with 10 mL of diethyl ether to obtain a pink solid. The solution was decanted, and the solid was washed with diethyl ether and dried in vacuo. The solid obtained was a mixture of the isomers **3** and **4** in a 1:1 molar ratio. Yield: 190 mg (86%). The solid was crystallized at room temperature from dichloromethane–diethyl ether to give orange crystals of complex

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Table 4. Crystallographic Data and Structure Refinement for 2, 3, and 5

	2	**3**	**5**
formula	$C_{35}H_{44}BF_4OPRu$	$C_{35}H_{42}BF_4OPRu$	$C_{36}H_{44}BF_4OPRu$
M_r	699.55	697.54	711.56
space group	triclinic, $P\bar{1}$	orthorhombic, *Pbcn*	monoclinic, $P2_1/n$
a, Å	8.6329(8)	22.3782(15)	9.2125(8)
b, Å	11.9728(11)	15.1047(11)	22.622(2)
c, Å	17.5064(16)	19.8992(14)	16.4397(14)
α, deg	71.808(2)	90	90
β, deg	78.540(2)	90	104.143(2)
γ, deg	78.559(2)	90	90
V, Å^3	1667.1(3)	6726.2(8)	3322.3(5)
Z	2	8	4
ρ_{calcd} (g cm^{-3})	1.394	1.378	1.423
T(K)	296.0(2)	296.0(2)	296.0(2)
μ, mm^{-1}	0.567	0.562	0.570
2θ range data collect (deg)	4−60	4−60	4−60
hkl index ranges	−11 to +11; −16 to +16; −23 to +23	−22 to +30; −19 to +19; −15 to +26	−12 to +11; −29 to +30; −20 to +22
no. of measd rflns	19 754	42 699	29 790
no. of data/params/restraints	7863/400/28	8196/369/35	7974/423/0
$R(F)$ ($F^2 > 2\sigma(F^2)$)[a]	0.0548	0.0547	0.0565
$R_w(F^2)$ (all data)[b]	0.1117[c]	0.1579[c]	0.0871[c]
S [all data][d]	0.753	0.699	0.658

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = (\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2])^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$; $a = 0.0275$ and $b = 0$ for **2**, $a = 0.0758$ and $b = 0$ for **3**, and $a = 0.041$ and $b = 0$ for **5**. [d] $S = [\sum(F_o^2 - F_c^2)^2]/(n - p)$; n = number of reflections, p = number of parameters.

3. Yield of **3**: 89 mg (40%). Anal. Calcd for $C_{35}H_{42}BF_4OPRu$: C, 60.26; H, 6.07. Found: C, 59.93; H, 6.25. IR (Nujol, cm^{-1}): ν(CO) 2024, ν(C=C) 1693 and 1597, ν(BF_4) 1055.

NMR Data for 3. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.36−7.17 (m, 10H, Ph), 6.14 (dd, *J*(HH) = 5.4, *J*(HH) = 3.0, 1H, =CH), 5.92 (dd, *J*(HH) = 5.4, *J*(HH) = 3.1, 1H, =CH), 5.40 (s, 5H, Cp), 4.09 (br, 1H, CH), 3.74 (br, 1H, CH), 2.51 (m, 3H, PC*H*CH$_3$), 1.96 (d, *J*(HH) = 9.6, 1H, CH$_2$), 1.64 (br, 1H, CH$_2$), 1.41 (dd, *J*(HH) = 7.0, *J*(PH) = 15.6, 9H, PCHC*H*$_3$), 1.33 (dd, *J*(HH) = 6.7, *J*(PH) = 12.9, 9H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, CD_2Cl_2, plus apt): δ 350.5 (d, *J*(CP) = 9.6, Ru=C$_\alpha$), 198.7 (d, *J*(CP) = 15.3, CO), 146.9, 146.3 (both s, C$_{ipso}$), 140.5 (s, CH=), 134.1 (s, CH=), 131.3 (s, Ru=C=*C*$_\beta$), 129.7, 128.8, 128.7, 128.5, 128.1, 127.3, 126.9 (all s, Ph), 92.3 (s, Cp), 70.9 (s, *C*Ph$_2$), 55.3 (s, CH), 51.2 (s, CH$_2$), 49.9 (s, CH), 29.1 (d, *J*(CP) = 22.6, P*C*HCH$_3$), 20.7, 19.4 (both s, PCH*C*H). ^{31}P{^{1}H} NMR (121.421 MHz, 293 K, $CDCl_3$): δ 79.5 (s).

NMR Data for 4. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.31−7.07 (m, 10H, Ph), 5.93 (dd, *J*(HH) = 5.7, *J*(HH) = 3.3, 1H, =CH), 5.90 (dd, *J*(HH) = 5.7, *J*(HH) = 3.3, 1H, =CH), 5.77 (s, 5H, Cp), 3.95 (br, 1H, CH), 3.64 (br, 1H, CH), 2.38 (m, 3H, PC*H*CH$_3$), 2.17 (d, *J*(HH) = 9.0, 1H, CH$_2$), 1.80 (d, *J*(HH) = 9.0, 1H, CH$_2$), 1.43−1.18 (m, 18H, PCHC*H*3). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, CD_2Cl_2, plus apt): δ 353.8 (d, *J*(CP) = 10.5, Ru=C$_\alpha$), 199.4 (d, *J*(CP) = 14.8, CO), 147.3, 146.4 (both s, C$_{ipso}$), 142.1 (s, CH=), 135.5 (s, CH=), 131.9 (s, Ru=C=*C*$_\beta$), 129.2, 128.8, 128.7, 128.3, 127.2, 126.9 (all s, Ph), 92.8 (s, Cp), 71.1 (s, *C*Ph$_2$), 55.4 (s, CH), 51.5 (s, CH$_2$), 50.4 (s, CH), 29.7 (d, *J*(CP) = 22.6, P*C*HCH$_3$), 20.8, 19.7 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (121.421 MHz, 293 K, $CDCl_3$): δ 82.0 (s).

Preparation of Ru$_R$,C$^a{}_R$,C$^b{}_S$(Ru$_S$,C$^a{}_S$,C$^b{}_R$)-[Ru(η^5-C$_5$H$_5$)(=C=CCPh$_2$C^{a}HCH$_2$CH$_2$C^{b}HCH=CH)(CO)(P^{i}Pr$_3$)]BF$_4$ (5). To a deep red solution of [Ru(η^5-C$_5$H$_5$)(=C=C=CPh$_2$)(CO)(P^{i}Pr$_3$)]BF$_4$ (**1**; 1000 mg, 1.6 mmol) in 30 mL of dichloromethane was added 1,3-cyclohexadiene (3 mL, 32 mmol). The mixture was stirred at reflux temperature for 14 h. The solution was filtered through Kieselguhr and evaporated to dryness. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the residue show a 85% conversion. The residue was treated with 10 mL of diethyl ether. A pink solid was obtained. The solution was decanted, and the solid was washed with diethyl ether and dried in vacuo. Recrystallization in dichloromethane−diethyl ether gives yellow crystals. Yield: 476 mg (42%). Anal. Calcd for $C_{36}H_{44}BF_4OPRu$: C, 60.76; H, 6.23. Found: C, 60.52; H, 6.02. IR (Nujol, cm^{-1}): ν(CO) 2009, ν(C=C) 1673 and 1597, ν(BF_4) 1049. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.55−7.07 (m, 10H, Ph), 6.99 (t, 1H, *J*(HH) = 7.2, CH=), 6.42 (t, 1H, *J*(HH) = 7.2, CH=), 5.10 (s, 5H, Cp), 3.57 (m, 1H, CH), 3.36 (m, 1H, CH), 2.47 (m, 3H, PC*H*CH$_3$), 1.64 (m, 2H, CH$_2$), 1.43 and 1.35 (both dd, *J*(HH) = 7.2, *J*(PH) = 15.9, 9H, PCHC*H*$_3$), 1.10 (m, 2H, CH$_2$). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, $CDCl_3$, plus apt): δ 356.8 (d, *J*(CP) = 9.3, Ru=C$_\alpha$), 199.1 (d, *J*(CP) = 14.6, CO), 147.6, 146.3 (both s, C$_{ipso}$), 137.5 (s, CH=), 131.9 (s, Ru=C=*C*$_\beta$), 130.6 (s, CH=), 128.8, 128.3, 127.9, 127.1, 126.7 (all s, Ph), 92.5 (s, Cp), 60.6 (s, *C*Ph$_2$), 42.2, 31.4 (both s, CH), 29.0 (d, *J*(CP) = 22.6, P*C*HCH$_3$), 22.5, 21.0 (both s, CH$_2$), 20.6, 19.1 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (121.421, 293 K, $CDCl_3$): δ 79.9 (s).

X-ray Structure Analysis of 2, 3 and 5. Crystals were obtained by slow diffusion of diethyl ether into a solution of the compound in dichloromethane at room temperature. Data were measured on a Bruker Smart APEX CCD diffractometer operating at 50 kV and 40 mA using Mo Kα radiation (λ = 0.71073 Å). Data were collected over the entire sphere by a combination of four sets. Each frame exposure time was 30 s covering 0.3° in ω. Unit cell dimensions were determined by a least-squares fit on the setting angles of 1364 (5° < 2θ < 33°) for **2**, 2766 (5° < 2θ < 35°) for **3**, and 1193 (5° < 2θ < 33°) for **5**. The first 100 frames were collected at the end of the data collection to monitor crystal decay. The absorption correction was made using SADABS.[14] The structure was solved by Patterson and Fourier methods using SHELXS.[14] Full-matrix least-squares refinement was carried out using SHELXL97 minimizing $\sum[w(F_o^2 - F_c^2)^2]$. Weighted *R* factors (R_w) and goodness of fit (*S*) are based on F^2.

In the structure analysis the anomalous thermal parameters observed for several carbon and fluorine atoms revealed the existence of static disorder in the triisopropylphosphine ligand (**3**) and BF_4 anion (**2**, **3** and **5**). A geometrically restrained disorder model was established on the basis of displacement parameters and residual peaks with the splitting of several atoms (see Supporting Information). Hydrogen atoms were

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[14] SHELXTL Software Package, version 6.1; Bruker AXS, Inc., Madison, WI.

included in observed or calculated positions only for nondisordered atoms and were refined as free isotropic atoms (**5**) or with riding positional and displacement parameters (**2**, **3**, and **5**).

Crystallographic data and details of the structure refinement are given in Table 4.

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

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